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Plenary Lectures

The Never-Ending Story of Fantastic Rings, Loops, and Hoops and Where to Find Them in Melts, Gels, and Nuclei: A Play in Two Acts with Prologue and Epilogue

Michael Rubinstein, Duke University

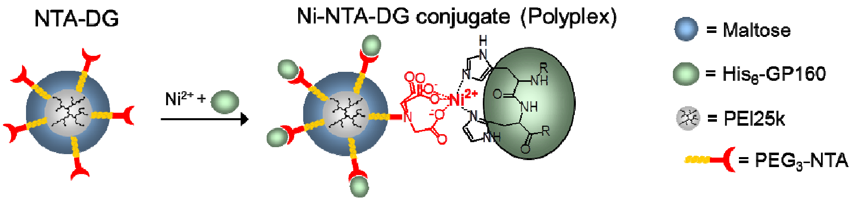
Polymer architecture – linear chains vs star polymer vs rings determines molecular conformations and physical properties of these materials. Topological interactions force non-concatenated cyclic polymers into fractal globular structure with fractal dimension *D=3*. Scaling model of fractal conformations and self-similar dynamics of entangled rings is based on the conjecture that the overlap parameter of loops on all length scales is the same. The predictions of this model are in excellent agreement with computer simulations and experiments. Applications of these ideas to superfast relaxation of polymer melts, superelastic polymer networks, and to chromatin organization in nuclei will be discussed.

Dendritic glycopolymers in bioconjugates, polyplexes and as therapeutics

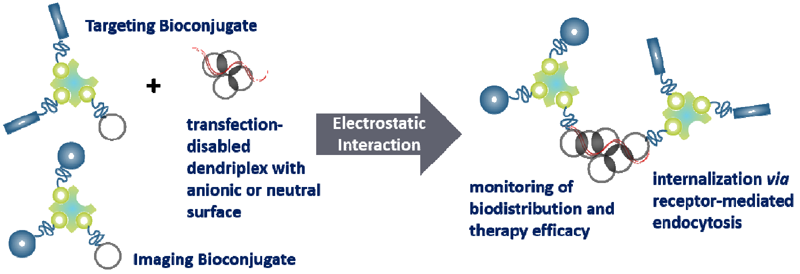
B. Voit*, Dietmar Appelhans

Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany
**voit@ipfdd.de*

The use of glycopolymers is steadily growing up in the field of life sciences and nanotechnology. Especially, the multifunctional features of the sugar moieties in dendritic structures such as non-covalent interactions, molecular recognition, tailoring of biological processes, enhancing biocompatibility and many others are of importance for the development of polymeric therapeutics and in diagnostics.[1] Our main research interest is the fundamental understanding of complexation and stabilization properties of dendritic glycopolymers towards drugs and bio(macro)molecules, the cellular uptake of dendritic glycopolymers, the formation of drug@glycopolymer associates, and their bio-interactions with different biological materials and systems for finally being able to tailoring the biohybrid materials for in-vitro and in-vivo experiments in the field of (bio-)medical applications. Here, we present examples which concern the potential use of dendritic glycopolymers as polymeric therapeutics and as carrier systems, e.g. as non-toxic antiamyloidogenic agents in Alzheimer's disease,[2] treatment of chronic lymphocytic leukemia, ligand-mediated endocytosis, uptake of peptides in immature/mature DC by Ni-NTA-His-tagged conjugation, conjugation in polyplexes with si-RNA for cancer- and immunotherapies, and for diagnostics.



Schematic representation of glycodendrimer-peptides conjugates for immunotherapy[3]



Schematic representation of theragnostic systems based on si-RNA/glycodendrimer polyplexes[4]

Keywords: Dendrimers, glycocpolymers, bioconjugates, therapeutics

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Multi-Colour Synergistic, Antagonistic and Orthogonal Photochemistry for Macromolecular Synthesis

Christopher Barner-Kowollik

Centre for Materials Science, School of Chemistry and Physics, Queensland University of Technology (QUT), 2 George Street, QLD 4000, Brisbane, Australia
Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtzplatz 1, 76344 Eggenstein-Leopoldshafen, Germany
E-mail address: christopher.barnerkowollik@qut.edu.au, christopher.barner-kowollik@kit.edu

The development and understanding of both covalent bond formation as well as dissociation remains a grand challenge in the design of photodynamic material systems. Initially, the lecture will dive into the photophysics of a range of reaction systems devised in our laboratories, exploring how their chemical response varies as a function of varying monochromatic wavelengths, establishing synergistic, antagonistic and orthogonal reactions modes. Surprisingly, the absorption spectrum is a poor indicator for photochemical reactivity, as will be demonstrated by a range of action plots on different reaction systems.

Based on the in-depth insights of our action plot analyses, we will explore how the light-responsive adaptation of polymer materials requires specific wavelengths to induce reversible covalent bond formation and dissociation. Our efforts have been devoted to pioneering a toolbox of photocycloadditions that can be triggered by lower energy visible light, while their cycloreversion functions at the least energetic wavelength, too. The lecture will showcase the latest applications of reversible photochemistry for the generation of light adaptive nano- and micro-structured materials, including examples of out-of-equilibrium photo-dynamic soft matter materials and dual-colour responsive inks for 3D laser lithography. Examples of irreversible photochemical system for wavelength orthogonal materials designed will be additionally highlighted.

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Circular Thermoset Materials:
Merging Academic and Industrial Principles

Filip Du Prez
Ghent University, Ghent, Belgium
filip.duprez@ugent.be; @Filip_Du_Prez

"A European Green Deal: Striving to be the first climate-neutral continent". This highly ambitious target of the European commission is the inspiration of many actual research targets in polymer science. Which solution can we bring as polymer material scientists to answer this prominent environmental challenge and have a direct impact on the role of polymer materials in a circular economy? More specifically, can we find a universal solution for recycling and scalable (re)processing of crosslinked, thermosetting materials? Indeed, thermosets are indispensable for many sustainable applications, but are also one of the most difficult materials to recycle.

Thermoset recycling is one of the holy grails of the plastic industry, which is currently facing increasingly stringent international regulations to stimulate finding solutions towards the sustainable use of plastics. Regarding the lowering of the carbon footprint of polymer materials, many approaches have been proposed and investigated. While many of them deal with the re-use of thermoplastics (PE, PP, PS,…) more and more attention is shifting towards the circularity of thermosets. This class of materials has an annual production of more than 50 million tons but has yet to find its place within a modern circular economy because of the permanently covalent crosslinked nature (e.g. wind blades and tire recycling).

One of the major developments in thermoset research, from an academic perspective, is the incorporation of exchangeable chemical bonds. This concept of so-called covalent adaptable networks (CANs) is a result of the introduction of dynamic covalent bonds within a polymer network, thereby potentially enabling a combination of benefits of the fast processing of thermoplastics and simultaneously the high durability and resistance of thermosets. However, despite the rapid progress made in this field during the last decade, this CAN technology and more specifically so-called vitrimers has not yet been picked up by the large chemical/material industry because of several major limitations. For example, the processing temperatures that would theoretically be required to achieve sufficiently fast processing are beyond the thermal stability limits of most organic materials. This prevents common industrially applied bulk processing techniques such as extrusion or injection moulding.

This presentation will highlight a number of our actual research efforts to overcome remaining limitations for the industrial implementation of this new generation of thermoset materials, mainly based on smart chemical design.[1-7]

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Programming materials with classical conditioning algorithms

O. Ikkala[1*], H. Zhang[1], H. Zeng[2], A. Priimagi[2]

[1]Aalto University, Department of Applied Physics, FI-02150 Espoo, Finland
[2]Tampere University, Faculty of Natural Science and Engineering, FI-33014 Tampere, Finland
[*]olli.ikkala@aalto.fi

In bioinspired, stimulus-responsive, and shape-memory materials there exists an ongoing search for ever more complex functionalities, even towards "life-like" functions [1]. Therein "learning" would probably be among the ultimate desired functions, in its full complexity characteristic to only living matter. Still, we can pose a question, whether one could mimic some limited aspects of learning using artificial functional matter, inspired by selected algorithmic processes known in cognition. Therein, classical (Pavlovian) conditioning is inspiring, as it is among the simplest forms of learning [2]. Here we discuss classical conditioning from behavioral psychology, an elementary form of learning, originally shown by Pavlov in his dog experiments [3]. We demonstrate two soft matter systems where the materials were originally stimuli responsive to allow a desired function only upon heating and not upon light irradiation, but upon simultaneous conditioning by heating and irradiation, they became responsive to specific light irradiation [4-6]. Importantly, to allow Pavlovian conditioning, triggerable memories are invariably needed. In the Pavlovian hydrogel, the response is hydrogel melting and the memory consists of self-assembly of pH-sensitive Au-nanoparticles triggered by merocyanine photoacid [4]. Forgetting is achieved by using competing chemical reactions using systems chemistry, thus erasing nanoparticle assembly, i.e., memory. In splay-aligned liquid crystalline networks the unconditioned response is bending by heating, and the memory is the redistribution by diffusion of light responsive laser dyes upon conditioning [5]. By conditioning, the actuator learns to bend by light irradiation. By selecting the laser dyes, different light conditionings can be engineered. In this talk, the limitations and generalisations are discussed, also to adaptation and sensitization. The most recent findings are shown, related to materials inspired by biological learning. We foresee a wealth of further materials, combinations of stimuli and different memory concepts for classically conditioned functional materials towards mimicking associative learning.

Keywords: material, stimulus-responsive, shape-memory, learning, biological, artificial intelligence

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Innovative Polymers for Next-Generation Batteries

David Mecerreyes[1]

[1]*POLYMAT, University of the Basque Country UPV/EHU, Donostia-San Sebastian, Spain*
david.mecerreyes@ehu.es

Lithium ion batteries are part of our modern life being present in daily used objects such as mobile phones, tablets, computers, watches, sport accessories, electric scooters or cars. The next generation batteries would need the development of innovative polymers that help to improve their performance in terms of power density, cyclability, raw materials availability, low weight, printability, flexibility, sustainability or security.
In this presentation we will show our recent developments in the area of redox polymers and ionic conducting polymer electrolytes.[1-4] This includes the development of innovative binders for electrodes, polymer electrolytes and redox polymer nanoparticles. All these new polymer developments are leading to new battery technologies such as metal-polymer batteries (Li, Na), organic batteries, polymer-air and organic redox-flow batteries which are expected to complement in the future the actual commercial batteries.

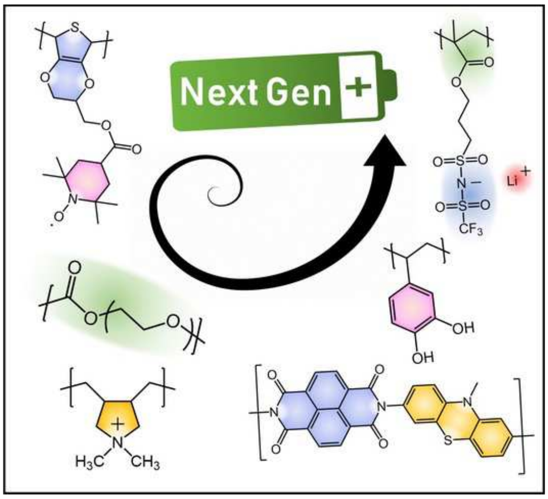

Figure 1: Scheme of polymers that will be discussed for next-gen battery technologies

Keywords: ionic polymers, polymer electrolytes, redox polymers, batteries

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Polymers for Biological and Medical Applications

Enzymatic atom-transfer radical polymerization-induced self-assembly

A. Belluati[1], S. Jimaja[2], N. Bruns[1*]

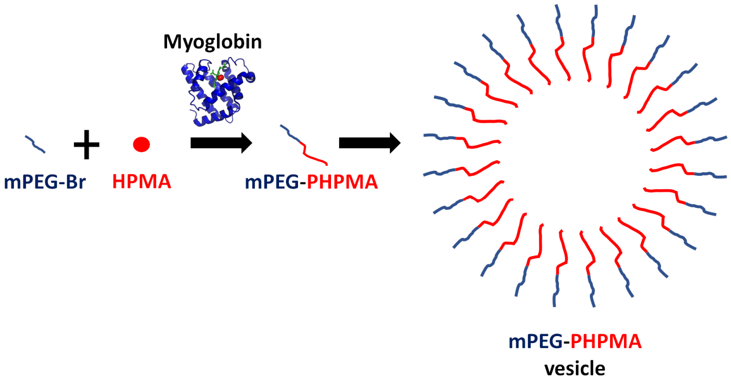
[1] *Technische Universität Darmstadt, Darmstadt, Germany*
[2] *Université de Fribourg, Fribourg, Switzerland*
**nico.bruns@tu-darmstadt.de*

The quest for greener polymer synthesis routes involves nanotechnology too, as the diverse morphologies of polymer nanostructures find extensive applications in (bio)catalysis, gene and drug delivery.[1-2] The chief method to make production of synthetic polymers more sustainable is the use of enzymes as catalysts, and to substitute organic solvents with milder ones. For instance, various acrylate monomers can be polymerized directly in aqueous solution, using common enzymes such as horseradish peroxidase or laccase.[3] This has naturally led to the development of reversible-addition fragmentation chain-transfer (RAFT) processes producing amphiphilic block copolymers that self-assemble into vesicles.[4] However, RAFT requires the use of organic mediators and peroxides, limiting its biocompatibility.

We have thus developed a myoglobin-mediated atom transfer radical polymerization (bioATRP) of 2-hydroxypropyl methacrylate (HPMA) with a monomethyl poly(ethylene glycol) macroinitiator, yielding a mPEG-*b*-PHPMA block copolymer that self-assembles in vesicles as the PHPMA chain is elongated.

Compared to RAFT, ATRPISA requires a simpler reaction mixture, does not rely on the generation of hydrogen peroxide and can be performed in a variety of aqueous media.

The resulting vesicles could be used to encapsulate a variety of macromolecules in a mild and controlled process, allowing the enzymatic generation of stable polymersomes.



Schematic of the ATRPISA reaction, thanks to which myoglobin yields well-defined vesicles.

Keywords: PISA, ATRP, enzymatic polymerization

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DASA-polymer conjugates: synthesis, characterization, and potential applications in medicine

L. F. Boesel*

[1]*Empa, Swiss Federal Laboratories for Materials Science and Technology, St. Gallen, Switzerland*
**luciano.boesel@empa.ch*

Donor-acceptor Stenhouse adducts (DASAs) are a new class of T-type organic photochromic molecules first reported in 2014 that change between an apolar and a highly polar, zwitterionic state. This change is triggered by visible light. DASAs exhibit a range of promising properties such as negative photochromism, visible light activation, and modular synthesis. DASA-materials have been proposed for visible light-controlled drug delivery, colorimetric sensors, fluorescent modulation of dyes, and photoinduced deadhesion of polymers from glass surfaces, among other applications. We have been investigating for years the development, properties, and applications of DASA-polymer conjugates.[1-5]

Initially, we designed a strategy to covalently attach DASAs to polymer matrices. We used a two-step procedure, by first attaching aromatic amine precursors by reaction with the activated ester (pentafluorphenyl acrylate - PFPA) and subsequently reacting the product with activated furan adducts to obtain DASAs attached to the main chain.[1,2] Another strategy involved the initial synthesis of an ene-terminated amine precursor, that was then polymerized or crosslinked with thiol- and ene-terminated monomers bearing multiple functionalities. After crosslinking, DASA was formed by exposing the gel to FA.[3]

We investigated the behavior of DASAs in such matrices and how the matrix properties influence the performance of DASAs. A glassy state hindered DASA photoswitching and, for a given polymer, kinetics sharply increased by increasing the ambient temperature to above the Tg. Independently of the matrix, we have always observed an effect of DASA structure (especially FA type) on the kinetics that mimics the behavior of DASAs in solution.[1-3]

With the use of DASA-polymersomes, we were able to achieve light-controlled delivery and uptake of two model compounds (sodium fluorescein and glucose). [2] Our work also presented other potential applications of DASA-polymer conjugates: light-activated biocatalysis, including wavelength-selective nanoreactors, [2] photochromic resins for 3D-printing, [3] and sensors for volatile amines [4]. In the last case, we took advantage of the spontaneous reaction between FAs and secondary amines and of the increased surface area of electrospun membranes to detect amines at very low concentrations. With an adequate choice of FA type, mesh morphology, and polymer physical properties, we could design a sensor with a limit of detection of only 10 ppb for diethylamine. The sensitivity depended on the amine type (due to the different reactivity of FAs to them). With covalently attached FA, the electrospun sensor was both insensitive to washing (leaching) and non-cytotoxic. It could therefore be used to detect volatile amines arising from food spoilage or bacterial diseases.[4]

Acknowledgments

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Studies on dissolution enhancement and cumulative drug release of polyurethane nanoparticles used as a DNA carrier

Florin Borcan, Roxana Popescu, Nicoleta I. Andreescu, Adela Chirita-Emandi

"Victor Babes" University of Medicine and Pharmacy Timisoara, Romania

Biocompatible and biodegradable copolymers are extensively used in various medical applications, such as implantable devices, drug delivery systems or prostheses [1,2]. We aimed to synthesize different polyurethane nanoparticles and identify methods to improve their dissolution and cumulative drug release. Methods: The synthesis was based on a polyaddition process between polyether-polyester mixtures with different ratios and an aliphatic diisocyanate combined with a simultaneous emulsification using a commercial surfactant. The samples were comparatively characterized using hollow particles and particles loaded with DNA that was extracted from banana fruits. Procedures included: pH, dissolution and Zetasizer measurements, encapsulation efficacy, carrier degradation rate and the release kinetics. Results: Almost neutral acido-basic suspensions were obtained with different aqueous solubility that contain particles with the sizes between 77 and 94 nm, Zeta potentials between +25 and +31 mV. The encapsulation efficacy was more than 81%, while the cumulative release ranged between 40-65% after 20 hours. In conclusion, polyurethane nanoparticles present the advantage of being able to easily balance different properties.

Keywords: drug delivery system, polymer, Zeta potential

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Investigations of Pectin Nanostructures for Enhanced Percutatenous Delivery of Fusidic Acid

Mohammad F. Bostanudin[1*], Mosab Arafat[1], Suk Fei Tan[2]

[1]*College of Pharmacy, Al Ain University, Abu Dhabi 112612, United Arab Emirates*
[2]*School of Pharmacy, Management and Science University, Section 13, 40100 Shah Alam, Selangor, Malaysia*
[*]*Corresponding Author's E-mail address: mohammad.bostanudin@aau.ac.ae*

The name of presenting author should be underlined.Nanostructure-based systems produced from amphiphatically-modified polysaccharides have received a lot of attention owing to their ability to boost active permeation through the skin. Here we present the fabrication of amphiphatically-modified pectin (GBE-PEC) following glycidol butyl ether (GBE) modification (degree of alkylation 18.2 %), which was characterized *via* thermal analysis, spectroscopic, and chromatographic tools and subsequently converted into nanostructures (size 250–290 nm; zeta potential -25 to -34 mV) for the study of their potential in modulating fusidic acid skin permeation. The tightly distributed and spherical nanostructures formed *via* a nanoprecipitation *in situ* cross-linking approach were shown to be stable under pH 4 condition at temperatures of 4 and 25°C. The encapsulated fusidic acid (loading degree 14.9 %) was released from GBE-PEC nanostructures (NS) in a more controlled fashion, with release profiles best characterized by the Higuchi model. Interactions with HaCaT cells *in vitro* demonstrated no apparent cytotoxicity at application relevant conditions, with efficient cellular absorption as evidenced by flow cytometry analysis. Using Franz diffusion cells, the synthesized GBE-PEC NS had a 2-fold greater penetration rate through the Strat-M® membrane than the native pectin NS. Overall, the *in vitro* results demonstrated great potential of GBE-PEC nanostructures for percutaneous delivery, that warrants further exploration.

Keywords: pectin, nanostructures, percutaneous, fusidic acid

The effect of polymer carrier structure on the macromolecular MDR inhibitor activity

A. Braunová[1*], M. Kaňa[2,3], L. Kostka[1], J. Kudláčová[1], M. Šírová[3] and T. Etrych[1]

[1]*Institute of Macromolecular Chemistry, AS CR, Heyrovského nám. 2, 162 06 Prague 6, Czech Republic*
[2]*Department of Otorhinolaryngology and Head and Neck Surgery, First faculty of Medicine, Charles University and University Hospital Motol, V Úvalu 84, 150 06 Prague 5, Czech Republic*
[3]*Institute of Microbiology, AS CR, Vídeňská 1083, 142 20 Prague 4, Czech Republic*

**braunova@imc.cas.cz*

Cancer belongs to the most serious live-threatening human diseases. One of the major problems of current anticancer chemotherapy is the development of multidrug resistance (MDR) after therapeutic use of low-molecular-weight (LMW) cytostatic drugs (doxorubicin etc.). To achieve effective MDR inhibition, and thus improved antitumour therapy, many, especially LMW inhibitors of predominantly ABC transporters (e.g., P-gp) have been studied worldwide. The aim of the present work was the design, synthesis, physico-chemical characterization and biological evaluation of structurally-different types of micellar block copolymers. The copolymers were based on pHPMA copolymer as a water-soluble polymer block and hydrophobic block based on PPO, which is responsible for P-gp inhibition [1]. Here (see Figure 1), we primarily focused on the study of the influence of the detailed copolymer structure on the MDR inhibition ability [2].

In addition, the high molecular weight of the synthesized polymeric inhibitors also plays an important role in utilization of EPR effect as a main mechanism of the passive targeting into solid tumours.

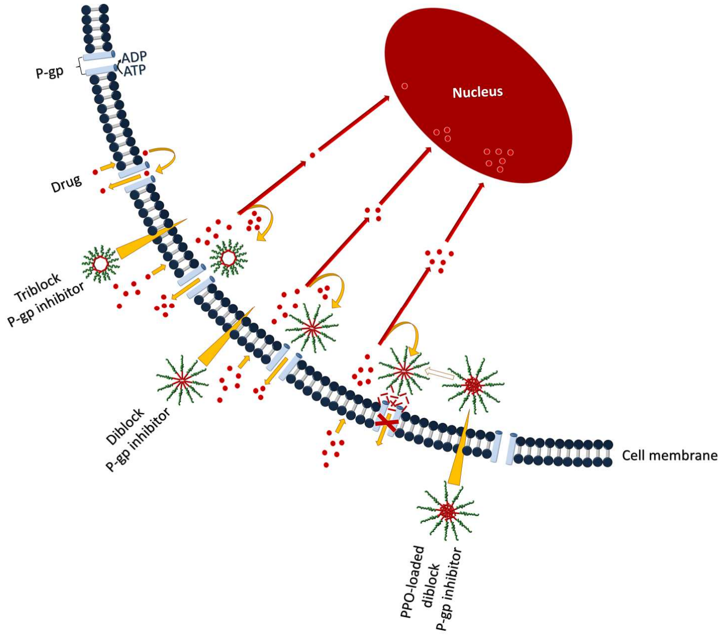

Figure 1 Scheme of expected inhibition mechanisms of synthesized polymeric inhibitors of MDR (P-gp) based on PHPMA-PPO micellar carriers.

Keywords: *N*-(2-hydroxypropyl)methacrylamide (HPMA), poly(propylene glycol) (PPO), multidrug resistance inhibition, P-glycoprotein (P-gp), micellar block copolymer, EPR effect

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Synthesis of peptide nucleic acid based molecularly imprinted polymer microspheres via RAFT polymerization

S. Gaidies[1], Y. Zou[2], H. Zhang[2], O. Brüggemann[1*]

[1]*Institute of Polymer Chemistry and Linz Institute of Technology, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria*
[2] *College of Chemistry, Nankai University, 94 Weijin Road, Nankai District, Tianjin 300071, China*
[*]*oliver.brueggemann@jku.at*

Peptide nucleic acids (PNAs) are synthetic analogues of naturally occurring nucleic acids with a pseudopeptide backbone consisting of N-(2-aminoethyl)glycine units. Due to the high affinity and specificity of PNAs towards Watson-Crick complementary DNA strands, PNAs can perfectly act as structural DNA mimics and have therefore found various applications in biomedicine, such as antisense therapy, gene-detection or drug development [1]. For the intended purpose of gene-detection or sensing of nucleic acid sequences, we prepare molecularly imprinted polymers (MIPs) using specifically synthesized PNAs as templates (Fig. 1). This includes the synthesis of narrowly dispersed core particles via reversible addition-fragmentation chain transfer (RAFT) polymerization [2]. Surface imprinting of the "living" microsphere generates a MIP layer around the core, embedding the PNA template.

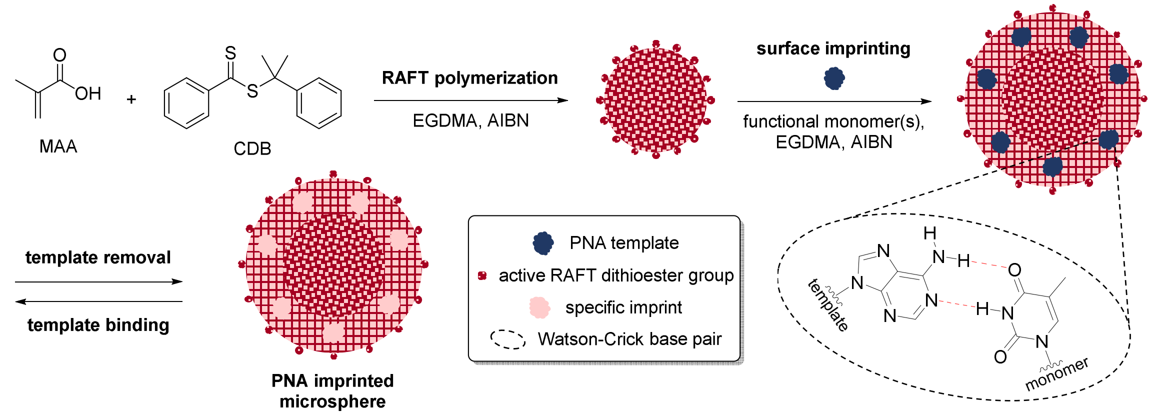

Figure 1. Synthesis of molecularly imprinted microspheres via RAFT polymerization.

Subsequent template removal finally leads to imprinted polymer microspheres with specific PNA binding sites. Since the dithioester groups of the RAFT agent are still active, these imprinted particles can simply be further functionalized for various purposes. Grafting of hydrophilic polymer chains to the particle allows for instance applications in aqueous environments [3].

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Regulated Polyelectrolyte Nanogels for Enzyme Encapsulation and Activation

Ying Cai[1],e.g.† Martien A. Cohen Stuart[1*]

[1]*East China University of Science and Technology, Shanghai 200237*

Polyelectrolyte (PE) nanogels consisting of cross-linked polyelectrolyte networks integrate the advanced features of both nanogels and polyelectrolytes. The soft environment and abundant intrinsic charges are of special interests for enzyme immobilization. However, the crucial factors that regulate enzyme encapsulation and activation remain obscure to date. Herein, we synthesized cationic poly (dimethyl aminoethyl methacrylate), PDMAEMA nanogels with well-defined size and cross-link degree, and fully investigated the effects of different control factors on lipase immobilization. We demonstrate that the cationic PDMAEMA nanogels indeed enable efficient and safe loading of anionic lipase without disturbing their structures. Strong charge interaction achieved by tuning pH and larger particle size are favorable for lipase loading, while the enhanced enzymatic activity demands nanogels with smaller size and moderate cross-link degree. As such, PDMAEMA nanogels with a hydrodynamic radius of 35 nm and 30% cross-linker fraction display the optimal catalytic efficiency, which is 4-fold of that of free lipase. Moreover, the immobilization endows enhanced enzymatic activity in a broad scope of pH, ionic strength, and temperature, demonstrating effective protection and activation of lipase by the designed nanogels. Our study validates the crucial controls of the size and structure of PE nanogels on enzyme encapsulation and activation, and the revealed findings shall be helpful for designing functional PE nanogels and boosting their applications for enzyme immobilization.

Keywords: nanogels, polyelectrolytes, controlled size and cross-link, enzyme immobilization, catalytic activation

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Drug delivery systems based on imino-chitosan nanofibers for burn healing applications

Sandu Cibotaru, Daniela Ailincai, Alexandru Anisiei, Luminita Marin

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

Among the injuries related to human healthcare, the ones caused by burns have a dramatic impact, especially when occur on large skin areas. Even if, the wound itself is not deadly dangerous, due to the skin ability to regenerate, the infections caused by microorganisms which are usually associated with this type of injury can cause serious complications [2]. To prevent them, new bandages with antimicrobial effect, able to protect the wound over its healing process are highly required.

Therefore, in this work we propose the use of chitosan-based nanofibers as starting materials for the obtaining of new bandages as drug delivery systems for the co-delivery of two antimicrobial agents: a physically encapsulated antibiotic with broad spectrum activity and an antifungal one, chemically bonded to the chitosan's backbone [3]. The design of the obtained materials was thought in order to meet the requirements for burn healing applications such as: to be able to ensure the exudate drainage and act as a barrier against bacterial and fungal infections, to be biodegradable, avoiding by this the trauma caused by the debridement process which is characteristic to traditional dressings.

In this sense, the electrospinning technique was used in order to obtain chitosan-based nanofibers, in which the antibiotic was encapsulated by absorption from aqueous or ethanol solution, which were further sealed with the antifungal agent. The obtained bandages were structurally characterized by NMR and FTIR spectroscopy, revealing the drug's presence and also chemical bonding between chitosan and the antifungal agent. POM, SEM and AFM techniques were used to investigate the morphology of the studied bandages, revealing the quite uniform drug's distribution into the nanofibers. The encapsulation degree and the drug release kinetics were investigated by NMR and UV-VIS spectroscopy. The *in vitro* biodegradability of the systems was monitored in the presence of lysozyme, an enzyme associated with burns' exudate. The antimicrobial activity of the obtained bandages was tested *in vitro* revealing a complementary activity of the two biologically active compounds. Moreover, the biocompatibility of the designed systems was evaluated both *in vitro* and *in vivo.* Last but not least, in order to evaluate the efficiency of the formulations on burn injuries, *in vivo* tests on burn mouse model were done, revealing that this new composite fiber design is efficient for non-traumatic healing of burn wounds.

Keywords: Chitosan nanofibers, norfloxacin, burn healing, antimicrobial activity

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Development of antibacterial coatings based on PEG-derived/nanostructured ZnO for titanium prostheses

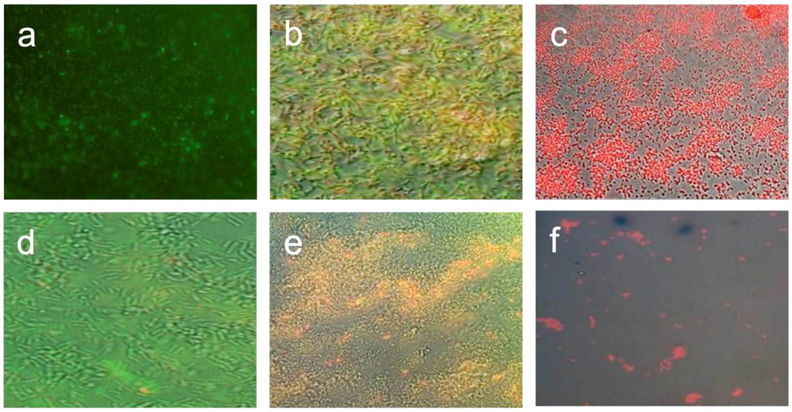
M. Degli Esposti[1,2*], R. Iseppi [3], E.L. Papadopoulou [4],
G. Bolelli [5], D. Morselli [1,2], P. Fabbri [1,2]

[1]*Department of Civil, Chemical, Environmental and Materials Engineering,*
University of Bologna, Bologna, Italy
[2]*Italian Consortium for Science and Technology of Materials INSTM, Firenze, Italy*
[3]*Department of Life Sciences, University of Modena and Reggio Emilia, Modena, Italy*
[4]*Smart Materials Group, Istituto Italiano di Tecnologia, Genova, Italy*
[5]*Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Modena, Italy*
[*]*micaela.degliesposti@unibo.it*

The ageing of the world population has been leading to an overall increase of the medical treatments and healthcare costs and the orthopedic surgeries using artificial titanium implants have become frequent operations with millions of people treated every year. Despite the improvements in the healthcare quality in the last two decades, microbial infections during surgery are still one of the main reasons of implant failure.

Several approaches have been proposed to develop antibacterial titanium implants. Among them, the surface modification with a biocompatible coating containing an active material is the most promising method which allows to envision a straightforward technology transfer from lab to industry.

In this context, the development of a biocompatible nanocomposite obtained by the combination of antimicrobial ZnO nanoparticles (NPs) and a PEG-derived curable resin to obtain sprayable antibacterial coatings to prevent bacterial infections in titanium implants, has been investigated. For this purpose, the optimization of the functionalization, spray-coating and curing procedures of ZnO containing PEG-derivatives has been performed in order to produce homogeneous coatings. After the characterization of the morphological aspects and scratch resistance, the prepared coatings have been studied against different Gram-positive and negative strains in the planktonic state, deriving from both standard collections and nosocomial infections, in order to explore the suitability and reliability of the proposed composite materials and coating method, as potential alternative to the currently used bare inorganic materials. Moreover, the ability to treat biofilm infections has been also evaluated.



Live/dead assay (confocal image, objective 100x) for (a,b,c) *Staphylococcus aureus* ATCC 6538 and (d,e,f) *Pseudomonas aeruginosa* ATCC 9027. Live/dead staining of (a,b) positive control, at 24 h of contact with (b,e) 5% and with (c,f) 20% of ZnO NPs containing PEG-derivative cured resin. Viable cells in green, dead cells in red.

Keywords: antibacterial activity, composite coating, titanium implants, spray-coating, polyethylene glycol, zinc oxide, nosocomial infections, biofilm

End-group modified toughness enhancers for bone replacement materials

B. Dellago[1,2,3*], R. Liska[2,3], S. Baudis[1,2,3]

[1]*Christian Doppler Laboratory for Advanced Polymers for Biomaterials and 3D Printing, Vienna, Austria*
[2]*Institute of Applied Synthetic Chemistry, TU Wien/E163-MC, Vienna, Austria*
[3]Austrian Cluster for Tissue Regeneration
[*]*barbara.dellago@tuwien.ac.at*

High reaction rates and good mechanical properties can be obtained upon photopolymerization of (meth)acrylates, making these monomers promising for producing patient-specific bone replacement materials *via* digital light processing stereolithography. Unfortunately, these compounds may show high irritancy and, in some cases, cytotoxicity. Furthermore, formed upon degradation, poly(acids) can harm the surrounding tissue. As circumvention, vinyl esters combined with thiols are very promising. The thiol-ene polymerization boosters the reactivity and material's impact resistance [1]. Another approach to further increase the toughness of the final scaffold is the incorporation of high molecular weight toughness enhancers into the polymer network. Based on polycaprolactone (PCL) to obtain biodegradability and biocompatibility, these additives exhibit promising results [2].

Herein, a study of the synthesis and characterization of several PCLs modified with different photopolymerizable end-groups is presented. RT-FTIR-photorheology measurements, tensile tests, and dynamic mechanical thermal analysis were conducted to determine their influence on the final polymer network. These toughness enhancer modifications improve reactivity, double bond conversion, and tensile toughness while keeping the glass transition temperature above the body temperature. Specific toughness enhancers can be designed for each application to tune the (thermo)mechanical properties. These results prove the applicability of modified PCL as toughness enhancers in polymer networks for bone replacement materials to treat bone injuries.

Keywords: biomaterials; polyesters; photopolymerization; FT-IR; toughness

Acknowledgments

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Cytocompatible, Soft and Ultrathin Brush Modified Scaffolds with Prolonged Antibacterial Effect to Mitigate Wound Infections

Shaifali Dhingra[1], Vidit Gaur[2], Jayanta Bhattacharya[2], Thomas Loho[3], Sudip Ray[3], Varsha Saini[4], Avinash Bajaj[4], and Sampa Saha[1]*

[1]*Department of Materials Science and Engineering, Indian Institute of Technology Delhi*

[2]*Centre for Biomedical Engineering, Indian Institute of Technology Delhi*

[3]*Department of Chemical and Materials Engineering, The University of Auckland, New Zealand Institute for Minerals to Materials Researc*

[4]*Laboratory of Nanotechnology and Chemical Biology, Regional Centre For Biotechnology*

**Corresponding author: Sampa Saha, Email: ssaha@mse.iitd.ac.in*

Biomedical device or implant associated infections caused by pathogenic bacteria are one of the major leading clinical issues, prevention and/or treatment of which still remain a challenging task. Infection resistant antimicrobial coatings with impressive cytocompatibility offer a step towards addressing this problem. Herein, we report a new strategy for constructing highly antibacterial as well as cytocompatible mixed polymer brushes onto the surface of 3D printed scaffold made of biodegradable tartaric acid based aliphatic polyester blends. The mixed brushes were nothing but a combination of poly(3-dimethyl-(methacryloyloxyethyl) ammonium propane sulfonate) (polyDMAPS) and poly((oligo ethylene glycol) methyl ether methacrylate) (polyPEGMA) with varying chain length (n) of ethylene glycol unit (n= 1, 6, 11, and 21). Both homo and copolymeric brush of polyDMAPS with polyPEGMA exhibited antibacterial efficacy against both gram positive and gram negative pathogens such as *E. coli* (*Escherichia coli*) and *S.aureus* (*Staphylococcus aureus*) because of combined action of bacteriostatic effect originated from strongly hydrated layers present in zwitterionic (polyDMAPS) and hydrophilic (polyPEGMA) copolymer brushes. Interestingly, mixed polymer brush comprising of polyDMAPS and polyPEGMA (ethylene glycol chain unit of 21) at 50/50 ratio provided zero bacterial growth and almost 100% cytocompatibility (tested using L929 mouse fibroblast cells) making the brush modified biodegradable substrate as an excellent choice for infection resistant and cytocompatible surface. An attempt was made to understand their extraordinary performance with the help of contact angle, surface charge analysis and nanoindentation study which revealed the formation of hydrophilic, almost neutral, softest surface (99.99 % reduction in hardness and modulus) after modifying with the mixed brushes. This may completely suppress bacterial adhesion. Animal studies demonstrated that these brush-modified scaffold can mitigate the wound infections. Overall, this study shows that a fascinating combination of infection resistant and cytocompatible surface can be generated onto biodegradable polymeric surface by modulating the surface hardness, flexibility and hydrophilicity by selecting appropriate functionality of the copolymeric brushes grafted onto them, making them an ideal non-leaching, anti-infective, and cytocompatible coatings for biodegradable implant.

Keywords: 3D printed biodegradable implant, copolymer brushes, Surface initiated atom transfer radical polymerization, Antibacterial, Cytocompatibility, Wound infection

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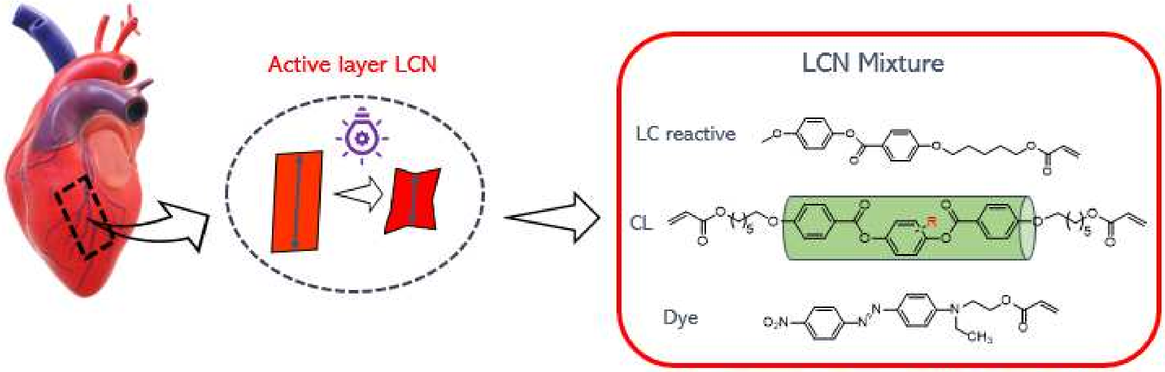
Photo-responsive liquid crystalline networks able to mimic biological muscles

S. Donato[1,2*], D. Martella[1,3], D. S. Wiersma[1,2,3], C. Ferrantini[1,4], L. Sacconi[1,6] and C. Parmeggiani[1,3,5] .

[1] European Laboratory for Non-linear Spectroscopy (LENS), Sesto F.no (FI), Italy;
[2] Department of Physics and Astronomy,Sesto F.no (FI), Italy;
[3] Istituto Nazionale di Ricerca Metrologica (INRIM),Torino (TO), Italy;
[4] Department of Chemistry "Ugo Schiff",Sesto F.no (FI), Italy;
[5] Department of Experimental and Clinical Medicine, Firenze (FI), Italy.
[6] Istituto Nazionale di Ottica, Consiglio Nazionale delle Ricerche, Sesto F.no (FI), Italy

[*] donato@lens.unifi.it

Liquid Crystalline Networks (LCNs) are among the best candidates, within smart materials, for artificial muscles development thanks to their ability to produce mechanical workin response to an external stimulus (light, temperature, etc.) by the production of [1].
In this communication, we will show how is possible the application of these kind of material to build an artificial hearth muscle able to been applied for tissue engineering. Improving the design and synthesis of new molecules we can obtain an enhancement of the material force developed, that for the current mixture is of 70 mN/mm^2 under illumination at a power of 1.5 W/mm^2 [2]. Therefore, a new cross-linker palette possessing bulky substituents (dimethyl,trimethyl, phenyl and tert-butyl) in the aromatic cores have been prepared and used for the preparation of LCNs, as shown in Figure 1. Ideally, the introduction of different substituents will decrease the interactions among a LC molecule and its nearest neighbors thus leading to a reduction in the amount of energy to be supplied to obtain the force development. The modification of the crosslinker was chosen because the crosslinker has the potential to play a major role in influencing the thermal, mechanical and actuation properties of the material. These new active materials, thanks to their stimulability and contractility unlike the currently marketed materials for hearth patches, will be able to revolutionize the treatment of hearth diseases like acute miocardial infraction.



R= methyl, dimethyl, trimethyl, phenyl and tert-butyl

Figure 1: Example of the application of a biomimetic liquid crystalline network for hearth tissue engineering.

Acknowledgments
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Synthesis of *N*-(2-fluoroethyl) acrylamide brushes via surface-initiated atom transfer radical polymerization: Comparison of the antifouling properties to their 2-hydroxyethyl-based counterparts

D.F. Dorado Daza[1*], A. de los Santos Pereira[1], R. Sivkova[1], O. Kopilec[2], R. Poreba[1], J. Svoboda[1],
O. Sedlacek[2], O. Pop-Georgievski[1]

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 16206 Prague, Czech Republic*
[2]*Department of Physical and Macromolecular Chemistry, Charles University, Hlavova 8, 12800 Prague, Czech Republic*
[*]*dfdoradod@gmail.com*

Polymer brushes based on fluorinated monomers are a class of surface-tethered macromolecular architectures that can be potentially used in the design of novel antifouling functional materials and ^{19}F MRI contrast agents [1, 2]. The precise tailoring of the brush thickness and chemical composition can be achieved via "living-like" polymerization methods based on surface-initiated atom transfer radical polymerization (SI-ATRP) [3]. Nevertheless, the polymerization of fluorinated monomers by ATRP could raise several problems, since the monomer can serve as an initiation point during the reaction due to the C—F site [4].

Therefore, we focused on the preparation of a novel polymer brush based on *N*-(2-fluoroethyl) acrylamide (FEAm) and on the comparison of its antifouling properties with the ones of its "classical" hydrophilic monomers counterparts: *N*-(2-hydroxyethyl) acrylamide (HEAm) and 2-hydroxyethyl acrylate (HEA). The corresponding polymer layers were grown from various initiator-modified surfaces via SI-ATRP varying the polarity of polymerization media, the nature of the ligand, the Cu(I)/Cu(II) ratio, the concentration of monomers, and the temperature. We report linear thickness growth kinetics of the polyFEAm, polyHEAm and polyHEA brushes as determined by spectroscopic ellipsometry. Grazing angle attenuated total reflection FTIR (GAATR-FTIR) and X-ray photoelectron (XPS) spectroscopies confirmed the attained chemical composition of the brushes. Analysis of surface-initiated and solution polymerizations showed the absence of any initiation and pointed to the preservation of the C—F side groups. The hydrophilicity of the different polymer brushes was probed via contact angle goniometry. The surface plasmon resonance (SPR) analysis showed that after the modification of the surfaces, the fouling from blood plasma was reduced by more than 95%, thus proving to be outstanding antifouling materials.

Keywords: Polymer brush, surface-initiated atom transfer radical polymerization, antifouling.

Acknowledgments
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Synthesis and characterization of poly(α-amino acid)s based bioinks for 4D bioprinting

J. Dvořáková[1*], A. Golunová[1], V. Proks[1]

[1]*Institute og Macromolecular Chemistry, Prague, Czech Republic*
[*]*dvorakova@imc.cas.cz*

A growing number of scientists are focused on printing 3D objects that are similar to biological tissue, but the construction of complex and functional structures is still a challenge. The revolutionary solution can be found in so-called four-dimensional (4D) bioprinting, in which the factor of post-printing time is integrated with three-dimensional (3D) bioprinting as the fourth dimension[1].

The fast-developing field of 4D bioprinting for tissue engineering is in constant search of new materials for bioinks. These bioinks can be used to fabricate various 3D-designed biologically active structures capable of changing their shapes or functionalities with time when in response to different physical, chemical, or biological stimuli. The crosslinking of the bioink to form a 3D construct should be rapid and durable, that is why the photoinitiated crosslinking is a widely used option.

In this work, we propose fully synthetic and biodegradable bioinks based on poly(α-amino acid)s (PolyAA). The modular chemical structure of polyAA, and adjustable physical parameters in combination with the enzymatical degradation[2] make them a highly potential toolbox for 4D bioprinting that remains undeveloped.

For that, we synthesized the poly[*N*^{5}-(2-hydroxyethyl)-L-glutamine] (PHEG) based polymer precursors able to the photocrosslinking reaction under blue light using tris(bipyridine)ruthenium(II) chloride and ammonium persulfate as the photoinitiaton system. Tyramine or methacrylate functional groups allowing the photocrosslinking of the polymer were introduced via postpolymerization modification of the initial γ-benzyl-L-glutamate residue. Several physicochemical methods (NMR, UV-Vis, GPC) were used to characterize obtained polymers. The addition of the biomimetic functionality of the adhesive RGD peptide sequence was secured by a one-pot reaction in two ways: a) between the polymer precursor and diphenol-peptide during the network formation b) Cu free click chemistry. The efficiency of RGD peptide incorporation was evaluated using NMR analysis and UV/VIS spectroscopy. Moreover, we confirm the printability of PHEG based bioinks on Celink bio X^{TM} bioprinter.

Based on our results we assume that the PHEG based bioinks can become an alternative to commercially used gelatin or alginate-based bioinks.

Keywords: 4D bioprinting, bioinks, poly(α-amino acid)s, biomimetic peptide, blue light

Acknowledgments

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Complex Coacervates between two oppositely charged and intrinsically disordered amphiphilic diblock recombinamers with LCST behavior

J. Fernández*[1], C. Herrero[1],J. Caldevilla[1] ,M. Santos[1], M. Alonso[1], J.C Rodríguez[1]

[1]*BIOFORGE Lab, University of Valladolid, CIBER-BBN, Paseo de Belén 11, 47011 Valladolid (Spain).*
**jfernandez@bioforge.uva.es*

Introduction: Little has been reported on the assembly of recombinant protein complex coacervates, especially when this takes place from intrinsically disordered polypeptides (IDPs) although they are recognized nowadays as playing a key role in the natural processes of self-organization and hierarquical emergence of structure and shape in biological systems [1]. For that purpose, we compare the spinodal decomposition generating self-assembled nano and microstructures of two amphiphilic Elastin-Like Recombinamers with opposite charges in their hydrophilic block and a common neutral and thermally sensitive hydrophobic block. Their mixes at different rates are also studied.

Materials & Methods: The two diblocks were obtained by recombinant DNA technology [2]. Their basic sequences are based on repetitions of consensus motifs found in intrinsically disordered regions of tropoelastin. The two ELRs are dissolved in water at 5ºC, and characterized at physiological temperature by different techniques such as nuclear magnetic resonance (NMR), circular dichroism (CD), differential scanning calorimetry (DSC), dynamic light scattering (DLS) and transmission electron microscopy (TEM).

Results & Discussion: The two separate ELRs are characterized by their soluble and unfolded chains at 5ºC, while at 37ºC they self-assemble hydrophobically into spherical micelles with hydrodynamic diameters between 100 and 200 nm. Then, the two dissolved ELRs are mixed each other and the interaction between them are proved by 1D NMR spectrums and their chemical shifts. Those interactions decrease their inverse transition temperatures and reduce the random coil conformations as the molar ratio converge to equal charge numbers. Contrarily to what happens when they are alone, their mixes generates more complex and bigger self-organizing structures. Thanks to the combination of hydrophobic and ion pairing taking place in those co-coacervates, the formation of worm-like structures of much larger size (hydrodynamic diameter ~ 1 µm) is the predominant morphological even. This is more prominent as the system approaches charge neutralization.

Conclusion: The interplay between hydrophobic and coulomb forces in the mixture of the model amphipilic and thermosensitive IDPs used here conditions the way that those self-organize after spinodal decomposition phase segregation of their water solutions. Contrarily to the simple micellar nanostructures obtained when they are alone, when mixed, worm-like structures of higher complexity and dimensions are found. These results highlight the importance of the interplay between different self-organizing forces as well as the order-disorder balance in the expontaneous emergence of complex hierarchical structures from IDPs. These results provide insights into the understanding the self-organizating nature of biological macromolecules. it is also of interest in the manufacture of supramolecular protein-based materials.

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Molecular Brushes with amphiphilic thermoresponsive side-chains

L. Fietzke[1*], R. Jordan[1]

[1]*Technical University Dresden, Chair of Macromolecular Chemistry, Dresden, Germany*
[*]*laura.fietzke@tu-dresden.de*

Drugs used for cancer treatments often show hydrophobic properties.[1] Therefore, a formulation for use in the human body is essential. Often, excipients, such as poly(ethylene glycol) (PEG)-modified substances Cremophor EL are used.[2,3] However, severe side effects in clinical doses are reported.[4,5] In order to circumvent these side effects, the use of alternative drug delivery systems (DDS) has been investigated. In addition to polymeric micelles introduced by Duncan[6], so-called molecular brushes have advantages over many DDS, such as a high drug load[5] and prolonged blood circulation time due to low renal excretion.[7] The blood retention time is thereby strongly dependent on the architecture of the polymer.[7]
Poly(2-oxazoline)s (POx) offer a versatile system for molecular brushes as the water solubility of the segments can be fine-tuned by variation of the length of the alkyl side chain in the monomer. Additionally, 2-oxazolines with *n-/i-*propyl side chains show thermoresponsive behavior.[8] Therefore, phase behavior of the resulting molecular brushes can be tuned by systematic addition of thermoresponsive segments.
We hereby present the synthesis and systematic investigation of temperature-dependent behavior of molecular brushes from POx in dependence of their architecture.

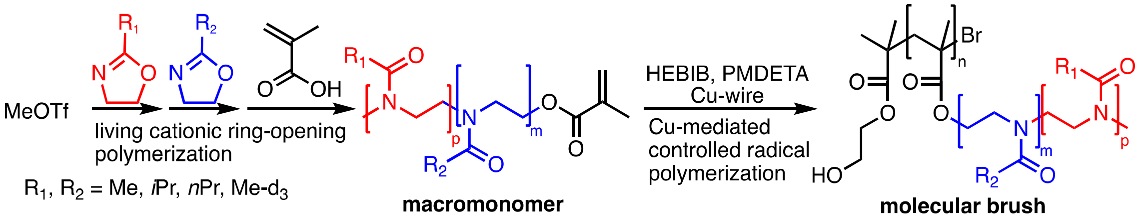

Figure 1: Synthesis scheme of molecular brushes based on POx.

Keywords: molecular brushes, poly(2-oxazoline)s, thermoresponsive behavior

Acknowledgments
This project was funded by the German Research Foundation.

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Glutamic acid based polyesters as promising carriers for drug delivery

N. Fihurka[1*], V. Samaryk[1], S. Varvarenko[1], N. Nosova[1], O. Bordenyuk[1]
[1]*Lviv Polytechnic National University, 12 S.Bandera Str., Lviv, Ukraine*
[*]*figurka.nataliia@gmail.com*

Biodegradable and biocompatible polymer materials with non-toxic degradation products are widely used for different biomedical applications. For this reason polyesters and synthetic approaches to them have been intensively investigated for the last decades. We have developed synthetic approach for polyesters based on the glutamic acid (its N-derivatives) and polyethylene/ polypropylene glycols via Steglich reaction. These polyesters (so-called pseudopoly(amino acid)) possess all advantage of the amino acid properties: biocompatibility, chemical and structural versatility, simple elimination of degradation products via metabolism pathways. On the other hand, the main polymer chain has ester bond instead of amide bond, preventing immune response.

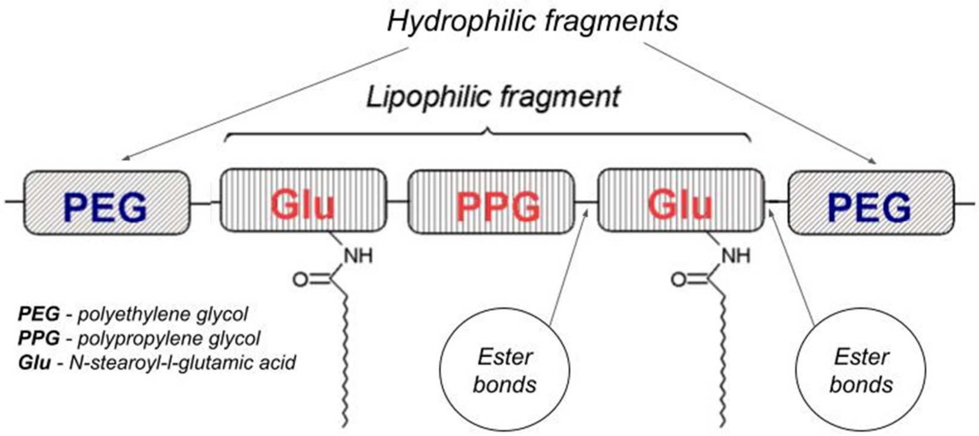

Fig.1. Structure of pseudo-poly(amino acid)s based on glutamic acid and PEG/PPG

As macromolecules of synthesized polyesters are formed of lipophilic and hydrophilic fragments, they possess surface active properties – 1÷2% water dispersions decrease surface tension. Characteristic surface tension isotherms of pseudo-poly(amine acid)s have two inflection points: the first one refers to the critical micelle concentration (CMC1), the second – to the concentration at which structural rearrangement of the dispersed phase takes place (CMC2). This conclusion was confirmed by the dynamic light scattering data.

Dispersed phase particles have complex architecture consisting of lipophilic core and hydrophilic shell. The morphology of particles was studied using methods of small-angle neutron scattering and transmission electron microscopy.

Such particle structure explains their ability to solubilize low-soluble in water organic compounds. In particular, solubilization of toluene and dyes Sudan (III) and Curcumin was studied. It is shown that dispersed phase solubilize 0,5 ÷ 3,0 g of low-soluble compounds per 1 g of polymer in the dispersion depending on the polymer concentration and its composition. Maximal solubilization (up to 1-3,0 grams of dye Sudan III per 1 g of polymer dispersed phase) is observed at concentrations between CMC1 and CMC2. In addition, in vitro cytotoxicity analysis revealed that obtained water dispersions are non-toxic and biocompatible under direct contact with the living cells.

Therefore, synthesized pseudo-poly(amine acid)s can be used to form stable water disperse systems of nano- and microsize for following application as nano- and micro containers for drug delivery.

A comparative study on structure and interaction properties of glycolysed dendrimers and pseudodendrimers

S.Firdaus[1,2*], D. Appelhans[1], B. Voit[1,2], A.Lederer[1,3]
[1]*Leibniz-Institut für Polymerforschung Dresden, Germany*
[2]*Technische Universität Dresden, 01062 Dresden, Germany*
[3]*Stellenbosch University, South Africa*
[*]*firdaus@ipfdd.de*

Dendritic and Pseudo-dendritic [4] structures have a novel type of density distribution and high number of functional groups, making them quite attractive for medical or biological applications. In the present work, three generations of dendritic and pseudo-dendritic structures have been obtained from hyperbranched aliphatic polyester core by modification of a protected AB*2 monomer. The chosen sequence of repeated protection and deprotection steps gave the corresponding dendrimers and pseudo-dendrimers with OH-terminal units. Further modification of all the four generations of dendrimers and pseudo-dendrimers with α-D-Mannose-pentaacetate were performed using copper catalysed "click" reaction, forming glyco-dendrimers and glyco-pseudodendrimers. ^{1}H NMR was used to confirm the degree of branching and the extent of modification in all four generations. The molar mass of each generation was measured by size-exclusion chromatography coupled to static light scattering. Furthermore, the interaction of glyco-pseudodendrimers with amyloid beta 1-40 is investigated using AF4, ThT assay and AFM. A comparative study of their behavior is performed that gives a concise review of their physico-chemical properties and their possible use in various areas of research. [1], [2], [3] Further studies of these dendritic and pseudo-dendritic structures with the amyloid protein residues gives a chance for pioneering investigations in a biological system.

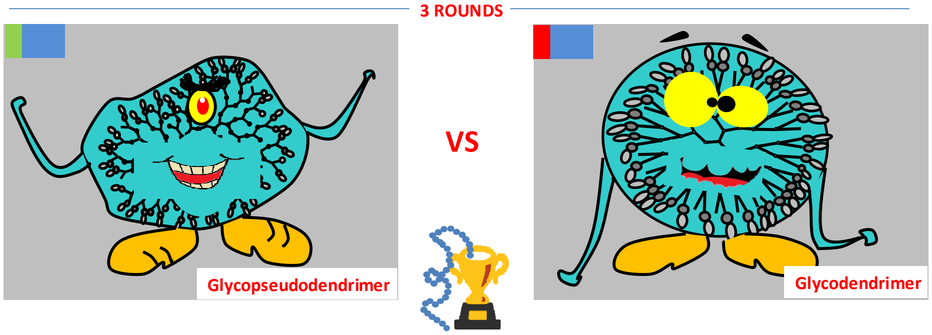

Figure 1. Dendrimers have been used in biomedicine field since a long time. Recently, their cousins the pseudodendrimers joined the field. Let's seen who wins this match. This fight is for amyloid proteins-one of the culprits of Alzheimer's disease. May the best man win.

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Self-reinforcing urethane/urea elastomers as dynamic biomaterials for vascular tissue engineering

M. Fitzka[1,2*], K. Ehrmann[1,2], S. Baudis[1,2,3], R. Liska[1,2]

[1]*Institute of Applied Synthetic Chemistry, TU Wien, Vienna, Austria*
[2]*Austrian Cluster for Tissue Regeneration, Vienna, Austria*
[3]*Christian Doppler Laboratory for Advanced Polymers for Biomaterials and 3D Printing, TU Wien, Vienna, Austria*
**markus.fitzka@tuwien.ac.at*

Thermoplastic urethane/urea elastomers have been increasingly attracting attention as a promising material in vascular tissue engineering of small-diameter blood vessels. This polymer class both meets the demands in mechanical properties of both high tensile strength and flexibility, and provides high versatility through simply exchanging the monomers [1].

Recent achievements in this area have shown even broader applicability of such materials with the introduction of hindered urea bonds (HUB), which give the already versatile material a new dynamic character. This special form of urea bonds is characterized by a reversible covalent binding mechanism, as its destabilization with sterically demanding nitrogen substituents transforms them to be cleavable and healable [2]. Under aqueous conditions at moderate temperatures (*e.g.,* body temperature), a mechanism is proposed to happen, which involves the cleavage of HUBs followed by subsequent partial hydrolysis of freed isocyanates to amines, which can then reform the polymer chains with new irreversible urea bonds. This behavior can therefore lead to changes in the mechanical properties of the polymer even in the final solid form.

Previous research showed the first example of such a material, which could increase its tensile strength after storage under wet conditions (“pre-conditioning”), and the found effect was therefore described by the term “self-reinforcement” [3,4]. In this work, the scope of materials exhibiting this new dynamic behavior was expanded: through the mentioned almost unlimited exchangeability of all monomers in the thermoplastic urethane/urea elastomers and the incorporation of monomers forming hindered urea bonds, a wide range of new polymers were synthesized. Characterization using different (thermo)mechanical tests was then performed to show changes in the material properties before and after pre-conditioning.

Keywords: self-reinforcement, self-reinforcing polymers, polyurethane, polyurea, biodegradable polymers

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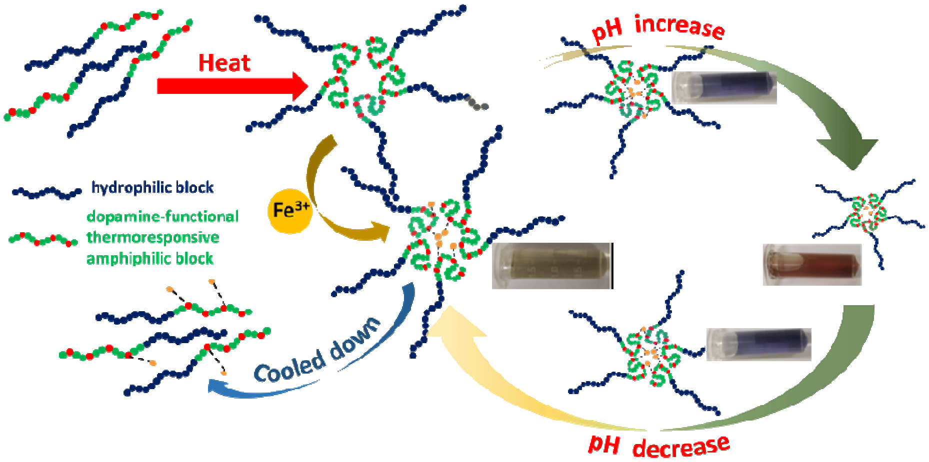
Stimuli-responsive Block Copolymer Micelles Based on Mussel-inspired Supramolecular Crosslinks

Ritabrata Ganguly[a,*], Pabitra Saha[b,c], Sovan Lal Banerjee[a], Andrij Pich[b,c] and Nikhil K. Singha[a]

[a] *Rubber Technology Centre, Indian Institute of Technology Kharagpur, India 721 302*
[b] *Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Germany*
[c] *DWI – Leibniz-Institute for Interactive Materials e.V., Germany*

Amphiphilic di-block copolymers containing dopamine and zwitterions are synthesized via the RAFT polymerization method which undergo temperature-mediated micellization in aqueous media. The presence of catechol moiety in dopamine was exploited to form pH-responsive cross-links with ferric ions (Fe^{3+}) at different pH value . A comprehensive study of the effect of pH as well as temperature on the size and solution behavior of these cross-linked micelles is presented. These micelles crosslinked via metal-catechol coordination bonds could have several important biomedical applications such as degradable scaffolds for payload delivery.[1]



❖ **Increase in pH leads to decrease in micellar size**
❖ **Micelles are pH-reversible in nature**

Keywords: Mussel-mimetic, pH-responsive, temperature-responsive, crosslinked micelles

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Degradable poly(2-oxazoline) analogues from partially oxidized poly(ethylene imine)

N. E. Göppert,[1,2] M. Kleinsteuber,[1,2] M. Dirauf,[1,2] C. Weber,[1,2] U. S. Schubert[1,2]*

[1]*Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstr. 10, 07743 Jena, Germany*
[2]*Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany*
*****ulrich.schubert@uni-jena.de*

A series of degradable poly(2-*n*-alkyl-2-oxazoline-*stat*-glycine)s (dPOx) was synthesized in a modular fashion *via* a straightforward post-polymerization synthesis route comprising the consecutive hydrolysis of poly(2-ethyl-2-oxazoline) (PEtOx) to yield linear poly(ethylene imine), the partial oxidation of the polymer backbone to incorporate statistically distributed glycine moieties, and re-acylation of the secondary amines to re-introduce *N*-acyl ethylene imine repeating units.[1]
The molecular structures were confirmed by analytical techniques such as infrared spectroscopy, size exclusion chromatography (SEC), amino group titration and nuclear magnetic resonance (NMR) spectroscopy. The glycine repeating units enabled a degradation of the polymer backbone under acidic conditions or proteinase K catalysis. The copolymers represent therefore degradable poly(2-*n*-alkyl-2-oxazoline) analogues.

By utilization of an azido-terminated PEtOx as starting material clickable, degradable dPOx were synthesized. They were attached to cyclooctyne functionalized hydrophobic poly(2-*n*-nonyl-2-oxazoline) as well as poly(ε-caprolactone) and poly(lactic acid) blocks *via* strain-promoted azide-alkyne cycloaddition. The successful conjugations were confirmed by in-depth characterization utilizing NMR spectroscopy, SEC and matrix-assisted laser desorption ionization mass spectrometry.
Due to its simplicity and flexibility this SPAAC approach offers numerous possibilities for the design of block copolymers comprising degradable poly(2-oxazoline) segments.

Keywords: Poly(2-oxazoline), degradable polymers, poly(ethylene imine), oxidation, click chemistry

Acknowledgments
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Manufacture of Surgical and Examination Gloves using UV- Techniques by Crosslinking Diene Rubber Latices to Avoid Allergenic Reactions caused by Classic Accelerator Chemicals

Theresa Grabmayer[1], Sandra Schlögl[1], Raimund Schaller[2], Armin Holzner[2], Wolfgang Kern[3]

[1]*Polymer Competence Center Leoben GmbH, Roseggerstraße 12, Leoben 8700, Austria*
[2]*Semperit Technische Produkte GmbH, Triester Bundesstraße 26, Wimpassing 2632, Austria*
[3]*Chair of Chemistry of Polymeric Materials, University of Leoben, Otto Glöckel-Straße 2, Leoben 8700, Austria*

In the generally known dip manufacturing process of carboxylated nitrile butadiene rubber (XNBR) or natural rubber latex (NR) articles, such as medical gloves, conventional sulphur cross-linking is still used as the standard crosslinking process. However, due to the necessary use of accelerator chemicals, allergenic reactions (e.g. skin irritation) often occur among consumers. To reduce the potential allergenic reactions associated with accelerator chemicals, an innovative vulcanization process has been developed based on a UV-initiated thiol crosslinking reaction. The thiol-ene reaction is used to crosslink the polymer chains through covalent bonds between the remaining C=C double bonds of the butadiene units. For improving the mechanical properties of the final products, a dual curing process is applied. This involves the addition of divalent metal oxides (ZnO), which form ionic crosslinking sites with the carboxyl groups of the polymer chains at elevated temperature. The photochemical curing step (thiol-ene reaction) can be carried out both as a pre-vulcanization using a falling film photoreactor and as a post-vulcanization by UV irradiation of dried latex films. The new process enables the production of UV-cured surgical and examination gloves that are characterized by excellent mechanical strength, high ageing resistance and good skin tolerance. Further advantages of the new technology compared to conventional sulphur vulcanization are the low energy consumption and the short vulcanization times.

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Single-Walled Carbon Nanotube Doped Hydrogels for Wound Dressing Applications

Ö. Zeynep Güner Yılmaz[1*], Anıl Yılmaz[1], Serdar Bozoğlu[2], Nilgün Yavuz[2], F. Seniha Güner[1]

[1]Istanbul Technical University, Department of Chemical Engineering, Istanbul
[2]Istanbul Technical University, Energy Institute, Istanbul
[*]*yilmaz.zeynep@itu.edu.tr*

ectin, a natural polymer, is frequently preferred in wound treatment today. Pectin is a material with high water and moisture permeability as well as biocompatible, antibacterial, anti-inflammatory properties. In the presence of divalent cation, it cross-links to form porous structures. Drug release systems can be developed by loading the drug into the porous structure and taking advantage of the high swelling property of the material. [1] Single-walled carbon nanotubes (SWNT) have many uses in the biomedical field, and they are advantageous over other materials with their conductivity, large specific surface area, and chemical stability. However, the cytotoxicity of SWNTs is an obstacle to be overcome in terms of their use in healthcare.[2] In this study, SWNT-doped pectin hydrogels were prepared homogeneously to be used as a wound dressing, and their drug loading and release performances were determined. While preparing the films, calcium chloride was used as a crosslinker and allantoin as an active molecule. The drug loading to the films was carried out using four different ways: In addition to mixing, absorption, and swelling methods, drug loading to the carbon nanotube was also investigated. Furthermore, DSC, TGA, FTIR analysis, surface contact angle measurements were performed for the characterization of the films. According to the obtained data, it was observed that a homogeneous matrix was obtained with the SWNT additive. Moreover, regarding the efficiency of the drug loading method, the study is extended to use coated SWNTs as additives. Thus, the structure of SWNT-doped pectin hydrogels to be used as a drug-releasing wound dressing was optimized in this study.

Keywords: Pectin, Single-Walled Carbon Nanotube, Hydrogel, Wound Dressing

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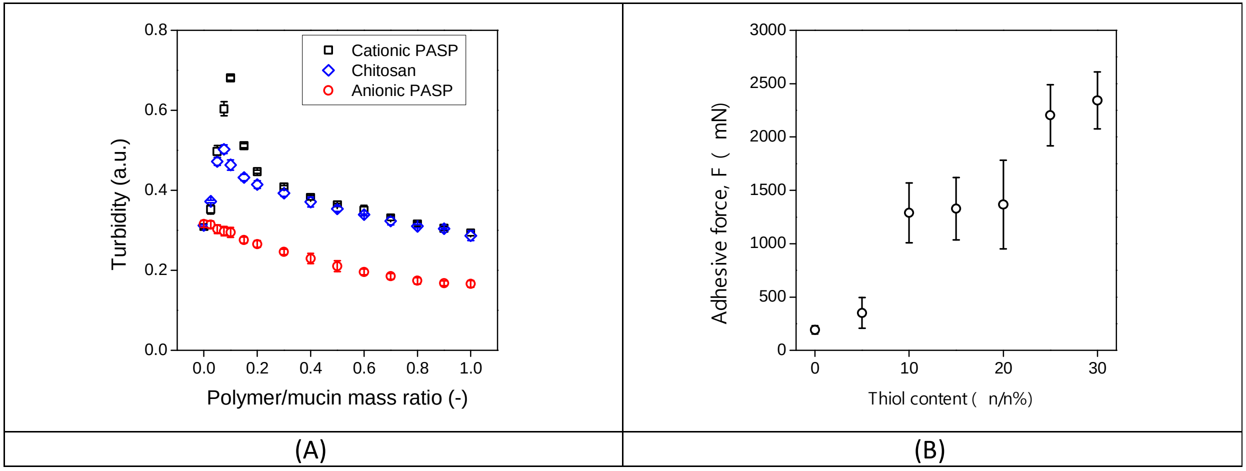
Cationic and thiolated poly(amino acid) derivatives for mucoadhesive drug formulations

B. Gyarmati[1*], B.Á. Szilágyi, A. Mammadova, G. Stankovits, A. Szilágyi

[1]*Department of Physical Chemistry and Materials Science, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary*
**gyarmati.benjamin@vbk.bme.hu*

The efficacy of drug delivery can be largely improved by mucoadhesive dosage forms providing prolonged residence time at the site of action [1]. The adhesion of first generation mucoadhesive polymers such as chitosan is based on their secondary interactions with the mucin, the main macromolecular component of mucosal membranes. Electrostatic interactions play an important role as it was proven with chitosan and we confirmed with the systematic study of poly(aspartic acid) (PASP) derivatives that cationic character enhance interaction with mucin whereas anionic derivatives did not result in mucoadhesion on colloidal scale (Figure 1A) [2]. Second generation mucoadhesive polymers, e.g., thiolated polymers form chemical interactions with mucin. The chemical interaction can increases the strength of mucoadhesion as it was shown for thiolated PASP derivatives (Figure 1B) [3]. To conclude, we expect that the chemical funcationality of PASP derivatives can be optimized for interaction with various mucosal membranes.



(A) (B)

Figure 1. A) Turbidimetric titration of mucin with various polymers; B) Adhesive force of thiolated PASP on porcine conjunctiva at various thiol contents

Acknowledgments

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Water-soluble polymer diblocks with tailored biodegradability designed for advanced drug delivery

M. Hrochová[1], L. Kotrchová[1*], L. Kostka[1], R. Konefal[1], M. Bláhová[1], J.Fang[2], T. Etrych[1]

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic*
[2]*Faculty of Pharmaceutical Sciences, Sojo University, Kumamoto, Japan*

kotrchova@imc.cas.cz

Here, we present synthesis and characterization of new biodegradable polymer drug carriers suitable for drug delivery to solid tumor. To enhance tumor accumulation of polymer carrier, based on EPR effect, as well as the circulation time in the organism, the hydrodynamic volume of the polymer carrier needs to be increased and at the same time polymer excretability from the organism must be ensured. In this regard, renal filtration was recognized as main route for excretion of water-soluble polymer systems, the limit of renal threshold is determined for *N*-(2-hydroxyropyl)methacrylamide-based copolymers as 50 kg/mol. For this reason, we designed new bifunctional chain transfer agents intended for RAFT polymerization of *N*-(2-hydroxyropyl)methacrylamide (HPMA) which allows direct synthesis of diblock copolymers. Employment of novel CTAs enable tailored synthesis of polymer carriers with hydrodynamic volume above the renal threshold, which are designed, due to the hydrolytically cleavable ester bonds, for degradation to fragments excretable through kidneys. This principle is schematically sketched in figure 1.

We synthesized several bifunctional chain transfer agents allowing synthesis of polymeric diblocks with various hydrolytic stability. Finally, four model diblock copolymers with different hydrolytic stability were successfully prepared and their physico-chemical properties including hydrolytic stability were evaluated. Potential applicability of the diblock polymer precursors as drug delivery carriers for treatment of solid tumors was validated by conjugation of drug pirarubicin via pH sensitive hydrazone bond. The biological activity of the polymer-pirarubicin conjugates will be presented.

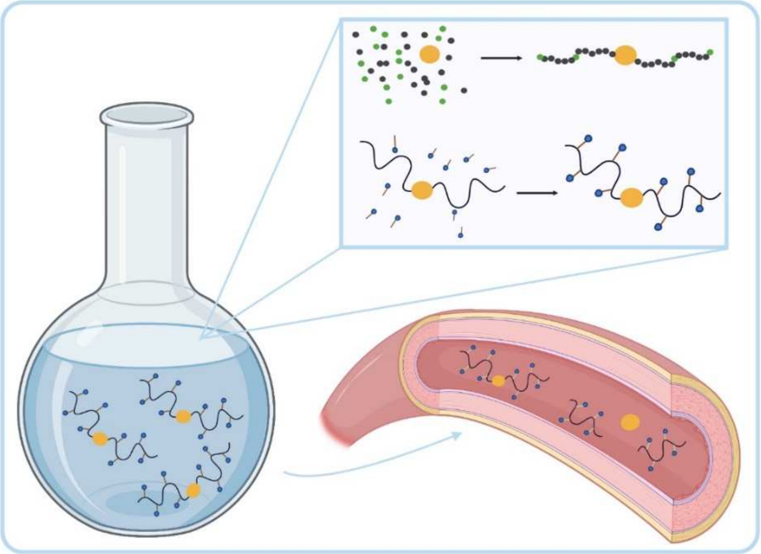

Figure 1: Sketch of diblock synthesis and its degradation in blood vessel

Keywords: HPMA, polymer diblocks, cancer treatment, RAFT agent

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Production of monodisperse and morphologically defined stimuli-responsive polymersomes by microfluidic nanoprecipitation: a step towards drug delivery application

A. Jäger[1*], E. Jäger[1], V. Sincari[1], E. Pavlova[1], K. L. Cavalcante[1], F. C. Giacomelli[2] and M. Hruby[1]

[1]*Institute of Macromolecular Chemistry, Heyrovsky Square 2, 162 06 Prague, Czech Republic*
[2]*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, Brazil*
[*]*alejager@gmail.com*

The engineering of polymersomes (PS) enables encapsulation of hydrophilic molecules within their aqueous lumen making such assemblies very promising platforms for drug delivery.[1] There are several methods described for the preparation of PS such as film rehydration, solvent switch and electroformation.[2] However, most of them are time consuming, difficult to reproduce and polydisperse samples and/or multiple morphologies are usually produced. Recently, microfluidic nanoprecipitation emerges as a promising alternative to control the self-assembly process of amphiphilic block copolymers as it enables the control over supersaturation, concentration and mass transfer allowing the production of monodisperse and morphologically defined nanoparticles. In this work stimuli-responsive amphiphilic block copolymers were tested for the production of the PS using microfluidic nanoprecipitation under various conditions. Dynamic light scattering (DLS) measurements show monodisperse size distribution of Ps with hydrodynamic sizes ranging between 50 to 200 nm depending on the flow rate ratio between the organic solvent and water (Fig. 1a). Small angle X-ray scattering (SAXS) profile (Fig. 1b) and transmission electron microscopy (TEM) of the selected nanoparticles sample produced suggest the presence of monodisperse and morphologically defined population of PS with a diameter around 100 nm (Fig 1c). Fitting of the scarring profile using bilayer form factor (Fig. 1b) suggests that the thickness of the bilayer wall is ~ 15 nm which is in good agreement with TEM. These results demonstrated that microfluidic nanoprecipitation method is a promising alternative on the production of monodisperse and morphologically define PS nanoparticles.

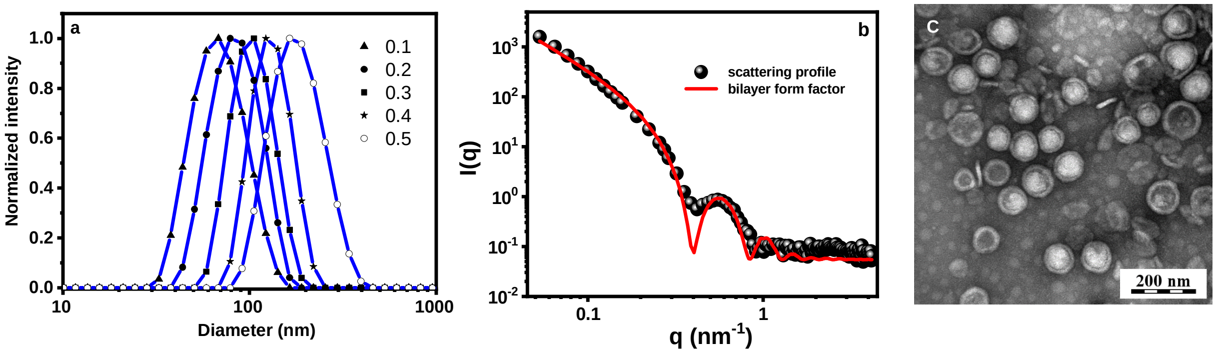

Fig 1. Size distribution in function of the flow rate ratio (a), SAXS profile (b) and TEM image (c) of the of PS nanoparicles prepared at the flow rate ration of 0.4.

Acknowledgments
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Multi Stimuli Responsive Polyphotoacids Based on 1-Pyrenol

Leonid I. Kaberov[1,2*], Maria Sittig[3,4], Benjamin Dietzek[3,4], Felix H. Schacher[1,2]

[1]*Institute of Organic Chemistry and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Jena, Germany*
[2]*Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Jena, Germany*
[3]*Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich Schiller University Jena, Jena, Germany*
[4]*Department of Functional Interfaces, Leibniz Institute of Photonic Technology Jena e.V., Jena, Germany*
[*]*leonid.kaberov@uni-jena.de*

The utilization of the polymeric nanocariers as drug delivery systems often requires their stimuli-responsive association and dissociation. Often the application of only one stimulus could not fulfill the requirements placed on smart polymer materials. Therefore, the focus of plethora of recent studies is to build the materials that able to response at several stimuli.

Recently, several polymeric photoacids containing 1-naphthol were carefully studied in our group.[1,2] The concept of photoacid based on significant drop of pK_a value of such molecules upon irradiation by light of appropriate wavelength – so-called excited-state proton transfer (ESPT). Here, we report on the synthesis and investigation of macromolecular photoacids based on 1-pyrenol. In contrast to naphthols, where the ESPT requires the UV excitation, the pyrenol-based photoacids can be activated by visible light, which is more appropriate for the application on living tissue.

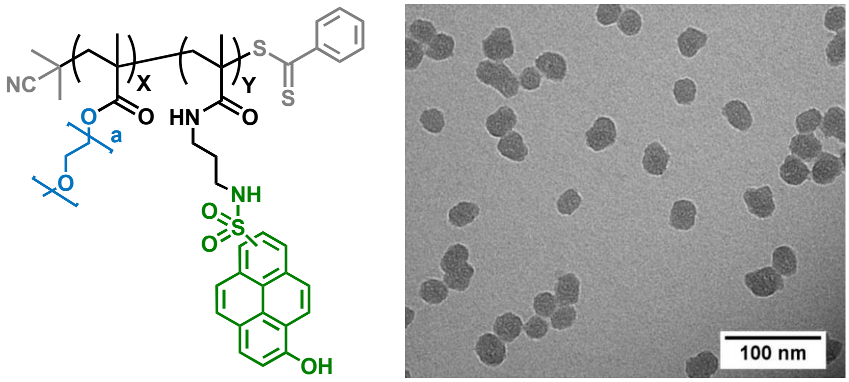

Fig. 1. General structure of pyrenol-based polymeric photoacid (left) and TEM microphotograph of nanoparticles in aqueous solution (right).

Keywords: polymeric photoacid, multi-stimuli responsive, light-responsive, self-assembly

Acknowledgments

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Biological cell killing induced by anisotropic magnetic polymersome rotation under low frequency alternating magnetic field

Diana Kazaryan[1], Sabrina Lacomme[2], Etienne Gontier[2], Ahmed Abdelhamid[3], Loubna Kehal[3], Véronique Gigoux[3], Frédéric Peruch[1*], Olivier Sandre[1*]

[1]Université Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, F-33600, Pessac, France
[2] BIC, UMS 3420, CNRS, INSERM, Univ. Bordeaux, Bordeaux, France
[3] CRCT, UMR1037,Inserm, CNRS, Univ. Paul Sabatier, Toulouse, France
[*]fperuch@enscbp.fr, [*]olivier.sandre@u-bordeaux.fr

Polymeric vesicles containing embedded iron oxide magnetic nanoparticles (MNPs) have been widely studied over the past few years in the field of nanomedicine. This interest is mostly attributed to their potential heating properties under an alternating magnetic field (AMF) for the treatment of cancer through hyperthermia, while their magnetic properties also are being investigated as a possible means to transfer "cargos" to specific locations in the human body by external guidance. On the other hand, polymersomes have been proposed as versatile drug nanocarriers due to their many interesting features, such as long term stability and easily tunable properties[1].

Here, our approach takes into an advantage the magnetic nature of MNPs as well as the plasticity of the polymeric vesicles. MNPs are used to force a morphological change of the polymersomes under a static magnetic field, from spherical vesicles to elongated anisotropic vesicles. This transformation is further locked by crosslinking the membrane, thereby deforming the vesicle permanently.Specifically, iron oxide magnetic nanoparticles are being embedded in the hydrophobic membrane of vesicles through a co-assembly process with amphiphilic copolymers. After verification of the vesicular morphology, an applied static magnetic field forces the MNPs into forming "linear aggregates" in its direction [2]. The allignment of MNPs promotes the extension of the polymersomes into anisotropic vesicles. A controlled cross-linking reaction of the hydrophobic membrane leads to "freezing" the anisotropic morpholgy through the formation of a strong polymeric network. Such"ellipsoidal" polymersomes, are currently tested for their capacity to be used as actioners exerting "mechanical torques"onto cellular membranes after being incubated with pancreatic cancer cells (MIA PaCa-2 cells). A direct and controlled application of a low frequency rotating magnetic field (LF) could prompt these anisotropic polymersomes to rotate around their axis and cause a distortion of cellular membranes, capable of causing cell apoptosis [3].

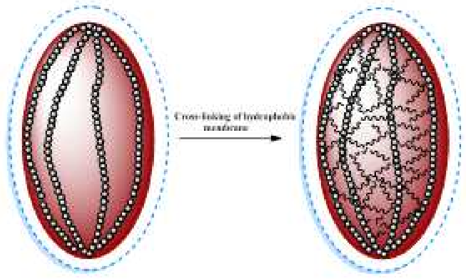

Figure 1: Representation of the cross-linking process under a static magnetic field

Keywords: amphiphilic copolymer,iron oxide nanoparticles,self-assembly, anisotropic vesicles

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Solid amorphous dispersions by hot melt extrusion comprising indomethacin and a new amphiphilic polymer excipient

Larissa Keßler[1]*, Rashmi Mishra[2], Anne Juppo[2], Timo Laaksonen[3], Clare Strachan[2],
Robert Luxenhofer[1]
[1]Department of Chemistry, A.I. Virtasen aukio 1, University of Helsinki, 00014 Helsinki, Finland
[2]Division of Pharmaceutical Chemistry and Technology, University of Helsinki, Viikinkaari 5E, 00014 Helsinki, Finland
[3]Division of Pharmaceutical Biosciences, Faculty of Pharmacy, University of Helsinki, Viikinkaari 5E, 00790 Helsinki, Finland
**larissa.kessler@helsinki.fi*

One main tool for the preparation of amorphous solid dispersions (ASD) for oral dosage forms is hot melt extrusion (HME) of drugs and excipients. The use of excipients in this method is a well-established way to create a polymer matrix, where the drug can be stored in to prevent crystallization, increase the apparent water solubility and to modulate the release rate of the drug. Two well-known and commercially available exipients are poly(vinylpyrrolidone) (PVP) and hydroxypropylmethylcellulose (HPMC). One critical issue of ASDs is a significant patient-to-patient variability, which can be caused by residual micro-crystallinities of the drug.[1] We posit that one approach to overcome this problem could be the use of amphiphilic block copolymers comprising poly(2-oxazoline) and poly(2-oxazine) as new excipient in the HME process, since these are well-established excipients that enable extremely high drug loadings for highly hydrophobic drugs and can retain them in an amorphous state over a long time. In addition to that, intravenous administration in rodents and non-human primates has been shown to be safe, which suggests that oral administration should also be possible.[2]

Here, the preparation and analysis of ASDs using novel polymeric excipients based on amphiphilic ABA triblock copolymers comprising poly(2-oxazoline) and poly(2-oxazine) in different polymer to drug ratios by extrusion are presented. The extrudates were characterized using DSC, PXRD and ssNMR spectroscopy and possible degradation of drug and polymer was investigated by ^{1}H NMR spectroscopy.

The results show the successful formulation of indomethacin into ASD at different drug loading. The solid state characterisation confirmed the amorphous state of both polymer and drug even in high drug concentrations. However, to study the trace crystallinity, new methods need to be established.

Keywords: hot melt extrusion, poly(2-oxazoline), poly(2-oxazine), solid amorphous dispersion

Acknowledgments
The authors would like to thank the Academy of Finland for financial support (Grant No. 337660).

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Recent Progresses in Peptidomimetic Polyethers: A Modular PEGides System Towards Mimicking Mussel and Frog

M. Kim,[1] D. Y. Ryu,[2] D. J. Ahn,[3] B.-S. Kim[1*]

[1]*Department of Chemistry, Yonsei University, Seoul, Republic of Korea*
[2]*School of Chemical and Biomolecular Engineering, Yonsei University, Seoul, Republic of Korea*
[3]*Department of Chemical and Biological Engineering, Korea University, Seoul, Republic of Korea*
[*]*bskim19@yonsei.ac.kr*

Recent advances in synthetic polymer chemistry have allowed the generation of simple, protein-like structures with biological activity from synthetic designer polymers. To mimic the biological functions of the natural proteins, many synthetic approaches have incorporated vinyl monomers bearing the constitutional amino acid residues found in nature. However, since vinyl monomers have an all-carbon backbone, they are structurally rigid and have an intrinsic limitation in aqueous solubility. These factors often pose a challenge for creating systems with full potential to mimic natural polypeptides. Unlike many other existing approaches in the literatures, we present to employ functional polyethers bearing amino acid side chains. Toward this end, we develop a library of a novel class of well-defined, functional epoxide monomers, which are polymerized into functional peptidomimetic polyethers via anionic ring-opening polymerization. The integration of a flexible polyether backbone coupled with amino acid moieties offers several advantages for materials and biomedical fields: (a) functional group availability resulting in improved hydrophilicity in biomimetics, and (b) capability of self-assembly to form hierarchical superstructures. Two specific examples toward mimicking the marine mussel foot proteins[1] and the antimicrobial peptides[2] secreted from frog will be presented with their future biomedical applications.

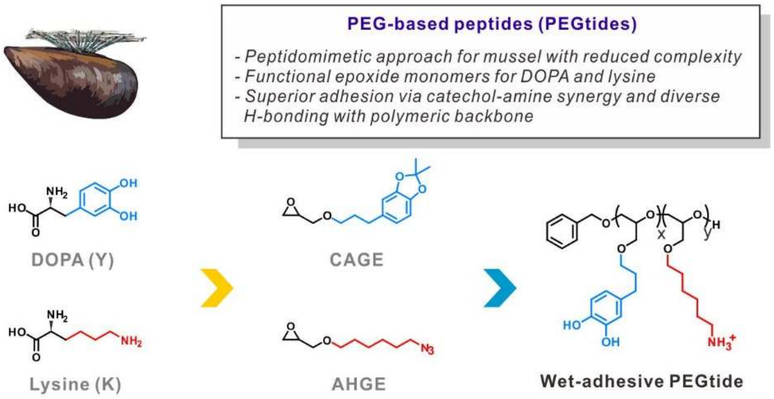

Figure. Schematic representation of the mussel foot protein mimicking PEGtides.

Keywords: Peptidomimetics, Polymer Synthesis, Polyether, Anionic Ring-Opening Polymerization, Functional Epoxide Monomer

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New sulfoxide-containing polymers: From double stimuli responsive materials to nanocarriers for dermal delivery

D. Klinger[1]

[1]*Freie Universität Berlin, Berlin, Germany*
**daniel.klinger@fu-berlin.de*

Sulfoxide-containing polymers are characterized by the outstanding physicochemical properties of the sulfoxide moieties. Their high hydrophilicity can translate into polymers with very low cytotoxicity and excellent biocompatibility. As a result, sulfoxide-based polymers are promising candidates for biomedical applications. However, the potential of this polymer class is limited when hydrophilicity is the only functional feature. To overcome this limitation, we imparted additional functionalities into polymers with sulfoxide side groups. By introducing stimuli-responsive properties and colloidal structures, we have prepared tailor-made sulfoxide-materials to open new areas of applications.

First, we developed a new class of (meth)acrylates with alkyl sulfoxide side groups to realize thermo- and oxidation-responsive homopolymers.[1] The dual-responsive behavior follows a specific design: On one hand, the thermal response can be tuned by varying the sulfoxides' alkyl groups. This balances sulfoxide-water hydrogen bonds and hydrophobic interactions between respective alkyl side chains. On the other hand, partial oxidation of the hydrophilic sulfoxides to more hydrophobic sulfones decreases the polymer's overall hydrophilicity, thus reducing the cloud point temperature (T_{cp}). As a result, these polymers exhibit a dual-responsive behavior and allow accurate adjustment of T_{cp} by post-polymerization oxidation.

Second, new interactions at the bio-interface were assessed through the incorporation of sulfoxide moieties into colloidal systems.[2] Here, we developed soft nanogels as new delivery vehicles to increase dermal bioavailability of therapeutics. Key to adjust the nanogels' interaction with the amphiphilic skin barrier is to mimic the penetration enhancing properties of DMSO. By covalently functionalizing the nanogels' polymer network with such methyl sulfoxide side groups, tailor-made dermal delivery vehicles are developed that can circumvent the skin disrupting properties of the small molecule DMSO.

Overall, our work exemplifies the strong cooperation between the unique properties of the sulfoxide moiety and its structure-property relations in polymers. As a result, a new family of sulfoxide-containing polymers and colloids were developed with potential applications in bionanotechnology.

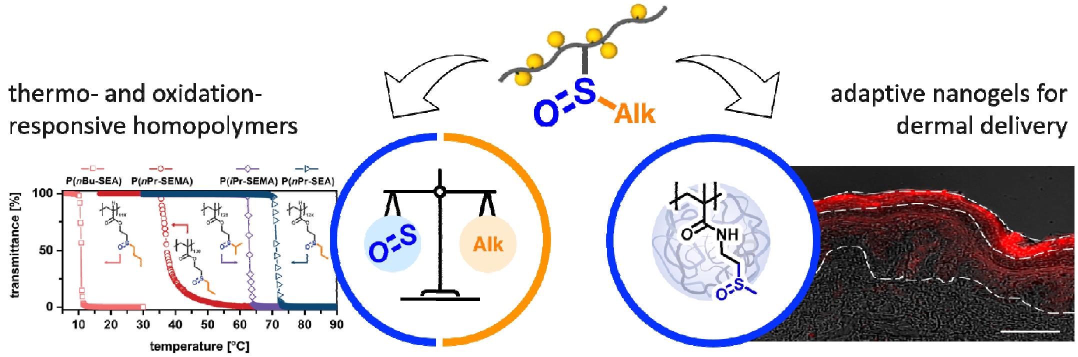

Figure 1. Tailoring the structure of sulfoxide-containing polymers to new applications: double-responsive polymers or dermal delivery vehicles.

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Compartmentalization of multi-enzymatic reactions in microfluidic devices and integration of polymersomes for additional reaction control

A. Koball[1,2*], F. Obst[3], J. Gaitzsch[1], B. Voit[1,2], D. Appelhans[1]
[1] Leibniz-Institut für Polymerforschung Dresden e. V., Dresden, Germany
[2] Technische Universität Dresden, Organische Chemie der Polymere, Dresden, Germany
[3] Technische Universität Dresden, Institut für Halbleiter- und Mikrosystemtechnik, Dresden, Germany
[*]koball@ipfdd.de

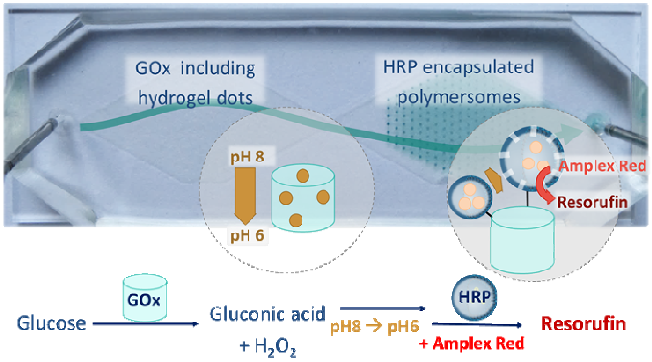

Fig.: Procedure of multi-enzymatic model reaction in microfludic chip

Micro-scaled processing as well as microfluidic components pave the way for research into and utilisation of various biologically active molecules and compartments like body fluids, enzymes and cells. Especially enzymes show great potential as valuable and powerful biocatalysts for chemical conversions of complex substrates covering a wide range of distinct applications ranging from the production of pharmaceuticals to the realization of elegant biosensing concepts. In these processes efficient strategies to avoid cross-inhibition and incompatible steps are necessary for multi-enzymatic and non-linear reactions. An optimal enzyme performance, and consequently high product yields, relies on near-natural reaction conditions and environment, which need to be optimized in labor-intensive step-by-step processes. [1] Compartmentalization in microfluidic systems describe a very promising strategy to overcome these limitations through realizing serial and parallel multi-step enzymatic reactions. We developed a PDMS-based chip structure, consisting of multiple reaction compartments and enzymes encapsulated in hydrogel arrays as well as in immobilized polymersomes for realizing spatial seperation and customization of reaction conditions. [2,3] Due to their stimuli-responsive and switchable membrane, cross-linked and pH sensitive polymersomes were applied as a functional tool to achieve precise reaction control by enabling or restricting substrate diffusion. [4]

We currently facilitate this two-chamber microfluidic chip to run an enzymatic cascade reaction using the classic model enzymes *Glucose Oxidase* (GOx) and *Horseradish Peroxidase* (HRP). For this purpose HRP is entrapped the cross-linked polymersomes, which are opened by the acid produced in the first reaction. Customized hydrogel compositions are applied in each chamber for examining the limitations and opportunities of each system. Thereby we succesfully created a polymersome-controlled pH-responsive enzymatic cascade reaction on the microfluidic reaction chamber.

Keywords: Green Chemistry, Enzyme, Biocatalyst, Microfluidic

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In-depth structural examination of poly(alkylene citrates) towards the structure-property relationship estimation in the perspective of biomedical applicability

F. Koper*[1], , T. Świergosz[1], A. Żaba[1], A. Flis[2], M. Trávníčková[3], L. Bačáková[3], E. Pamuła[2], D. Bogdał[1], W. Kasprzyk[1]

[1]*Faculty of Chemical Engineering and Technology, Cracow University of Technology, Kraków, Poland*
[2]*Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Kraków, Poland*
[3]*Institute of Physiology, CAS, Prague, Czech Republic*
**filip.koper@pk.edu.pl*

Poly(alkylene citrates) (PACs) have grown as one of the most promising alternative biomaterials for vascular tissue engineering in contrary with commonly applied PTFE and PET grafts. PACs are characterized by tunable mechanical and physiochemical properties along with decreased thrombogenicity. PACs also remain a suitable environment for cell adhesion and growth. Moreover, due to the presence of non-substituted carboxyl groups within the polymer network they are suspectible for the introduction of various modificators bringing about novel functionalisation and enlarged applicability.

In the presented work a comprehensive and detailed examination of PACs was performed. The experiments were conducted for discovering the structure-property correlation in PAC polyesthers leading to their application as a vascuar grafts. It was achieved by a novel approach towards the synthesis protocol as well as thorough structural characterisation of PACs. The prepolymers obtained in 1:1 (CA:diol) and 2:3 molar ratio were characterised via NMR, LC-ESI-MS and acid value combined with mechanical and biological evaluation of crosslinked materials from mentioned prepolymers.

The major changes including simplification and strict control applied to the synthesis procedure resulted in improvements in the protocol and in increasement of the reaction yield. Detailed NMR spectra combined with MS and acidity determinations allowed for a thorough understanding of the PAC structure, explanation of chemical nature of the synthesis process and shed a light on the chemistry of the material crosslinking process. The results of mechanical and surface examination confirmed the uniformity of materials obtained and their appropriate properties for applications in tissue engineering of blood vessels. Mechanical and surface examination also emphasized the importance of introduced modifications to the synthesis protocol and exposed several tailorable factors which can be modified for fabrication of materials with desired properties for specific applications. Elaborated analyses of materials fabricated in various times and reaction conditions enabled to estimate of the exact reaction parameters and additionally confirmed the relationship between polycondensation parameters and physiochemical and biological properties of the final polymer materials. All of the performed analyses indicated the undoubted usefulness of PACs in further work on bioresorbable tissue scaffolds.

The final and the most relevant conclusion is the correlation of the acidity, and the molar ratio of reactants with cell viability and proliferation. The results of proliferation studies performed on material extracts indicate the privilege of using a 2:3 molar ratio of reagents than commonly described in the literature 1:1 ratio while maintaining all the properties of the latter. In vitro tests performed in a direct contact with cells show that the final biological output can also be tuned by using diols of a higher number of carbon atoms in the chain.

Acknowledgments

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Synthesis and characterization of amphiphilic, degradable networks based on polyesters and poly(2-isopropenyl-2-oxazoline)

B. Kost, B. Kopka, M. Basko,

[1] *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland*
[*] *Corresponding Author's E-mail address: kost@cbmm.lodz.pl*

Amphiphilic polymer networks which combine the properties of two chemically different polymers in one material are of broad academic and also applications-oriented interest.[1] Due to the specific features, such as the nanophase separated morphology or ability to swell in both aqueous and organic media, this kind of network is broadly explored in various fields including medical, pharmaceutical, and separation science.[2] Our research is aimed at the synthesis of degradable amphiphilic networks containing hydrophilic poly(2-isopropenyl-2-oxazoline) (PiPOx) segments and hydrophobic polyester blocks. To achieve the covalently crosslinked structure the addition reaction proceeding between oxazoline pendant rings and carboxyl functionalized macrocrosslinkers was applied.[3] The proposed synthetic method is facile and can be carried out at simple reaction conditions (insensitive to water or oxygen, without the need for specialized instrumentation). On top of this strategy is a fact, that we have selected building blocks that offer the possibility to construct materials prone to degradation, which is a crucial requirement in modern materials design for a biomedical application, as well as, for everyday use commodity plastics. It can be expected that depending on the composition the obtained materials due to the specific structure may perform multiple functions.

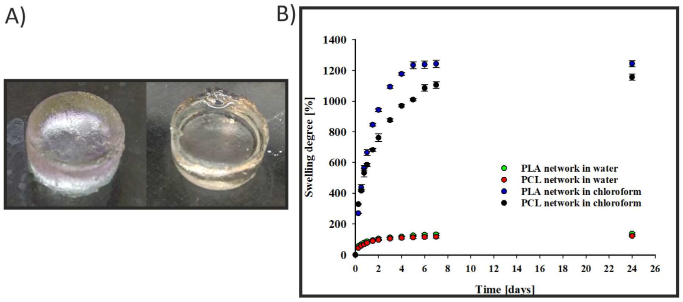

Figure 1. A) Physical appearance of swollen PiPOx/PLA and PiPOx/PCL hydrogels; B) The degree of swelling of PiPOx/PLA network in deionized water and in $CHCl_3$ at room temperature.

In the poster we would like to present an effective formation of PiPOx/polyester networks, that was enabled by the unique reactivity of oxazoline rings at the applied conditions (DMSO, 140°C, 75 min). After the detailed characterization, the capacity of hydrogels to adsorption of Cu^{2+}/Fe^{2+} ions from water was evaluated.

Keywords: networks, hydrogels, degrability, polymer postmodification

Acknowledgments

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Controlling Gene Transfection with Hydrophobic Groups in Guanidinium Containing Terpolymers

M. Kötzsche[1*], C. Cokca[1], F. J. Hack[2], D. Fischer[2], K. Peneva[1]

[1] Institute of Organic and Macromolecular Chemistry, Friedrich Schiller University Jena, Lessingstrasse 8, 07743 Jena, Germany
[2]Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Cauerstr. 4 (Haus 6), 91058 Erlangen, Germany
[*] markus.koetzsche@uni-jena.de

Cationic polymers are suitable carriers for gene delivery mimicking cell-penetrating peptides containing arginine. The positive charge is important for polyplex formation with RNA or DNA and the transfection into cells, but can lead to higher cell toxicity. In our previous study, the incorporation of indole as a hydrophobic moiety into a copolymer of N-(2-hydroxy-propyl) methacrylamide (HPMA) and N-(3-guanidinopropyl) methacrylamide (GPMA) lead to a 200-fold increased transfection efficiency.[1]

To study the impact of the hydrophobic monomer on the cell viability, pDNA complexation and transfection efficiency, *N*-(2-indolethyl)methacrylamide (IEMA), *N*-Phenethylmethacrylamide (PhEMA) or *N*-(4-hydroxyphenethyl)methacrylamide (PhOHEMA) were used as hydrophobic monomer. All three polymers showed similar cell viabilities on L-929 mouse fibroblasts with IC_{50} values around 30 µg mL^{-1} and haemolysis values below 2 % for sheep red blood cells up to 50 µg mL^{-1}. The PhEMA and PhOHEMA containing terpolymers efficiently complexed pDNA for N/P ratios of 2 with polyplexes slightly smaller than 200 nm, while the IEMA containing terpolymer already formed stable polyplexes for a N/P ratio of 1 with 100 nm size. The terpolymer with IEMA showed the highest transfection efficiency achieving half the value of linear polyethyleneimine at N/P ratio of 20. The PhOHEMA containing terpolymer was slightly more efficient compared to the PhEMA terpolymer.[2]

To improve the biocompatibility of the terpolymers, poly(nona(ethylene glycol)methyl ether methacrylate) ($P(MEO_9MA)$) was introduced as a shielding block with 3 to 40 kg mol^{-1} to the HPMA-GPMA-IEMA polymers via a macro-RAFT agent. Except for 3 kg mol^{-1} $P(MEO_9MA)$, the IC_{50} values on L-929 mouse fibroblasts were higher compared to the unshielded polymers and increased with the molecular weight of the $P(MEO_9MA)$ block. A perylene monoimide was incorporated in the $P(MEO_9MA)$ block as fluorescent label and did not affect the cell viability. PEGylation of the terpolymer reduced the pDNA binding efficiency for N/P ratio 1, but the complexation was still efficient for N/P ratio 2 or higher.[3]

Keywords: gene delivery, guanidinium, indole, methacrylamides

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Phosphorus, fluorine and iron containing polymers: biocompatible probes for dual $^1H/^{31}P$ and $^{31}P/^{19}F$ magnetic resonance imaging

Lucie Kracíková[1,2], Natalia Ziółkowska[3], Ladislav Androvič[1], Iveta Klimánková[1], David Červený[3], Martin Vít[3], Petr Pompach[4], Rafał Konefał[1], Olga Janoušková[1], Martin Hrubý[1], Daniel Jirák[3], Richard Laga[1,*]

[1] *Institute of Macromolecular Chemistry, Czech Academy of Sciences Heyrovského nám. 2, Prague, 162 06, Czech Republic*
[2] *Faculty of Chemical Technology, The University of Chemistry and Technology, Prague Technická 5, Prague, 166 28, Czech Republic*
[3] *Institute for Clinical and Experimental Medicine, Vídeňská 1958/9, Prague, 140 21, Czech Republic*
[4] *Institute of Biotechnology, Czech Academy of Sciences, Průmyslová 595, Vestec, 252 50, Czech Republic*
[*] *laga@imc.cas.cz*

Magnetic resonance imaging (MRI) of proton (^1H) or X-nuclei (e.g. ^{31}P, ^{19}F, ^{23}Na, etc.) is an advanced diagnostic technique used in both clinical and experimental medicine to accurately visualize anatomy and physiological processes in living tissue [1, 2]. However, sensitive imaging often requires the administration of an exogenous probe [3, 4]. In this work, we focused on the development of new types of biocompatible polymer and polymer-colloidal probes that can be clearly detected either by ^{31}P MRI or by dual $^1H/^{31}P$ or $^{31}P/^{19}F$ MRI. Specifically, we synthesized and characterized three types of high-molecular-weight probes containing different X-nuclei: (i) hydrophilic phosphorus-containing polymer zwitterion based on *O*-(2-(methacryloyloxy)ethyl) *O*-(2-(trimethylamoniumyl)ethyl) phosphorothioate (TMPC) as a metal-free ^{31}P MRI probe [4]; (ii) water-soluble phosphorus-containing polymer based on 2-methacryloyloxyethyl phosphorylcholine (MPC) coordinated with (a) paramagnetic Fe^{3+} ions or (b) superparamgnetic γ-Fe_2O_3 nanoparticles as dual $^{31}P/^1H$ probes; and (iii) hydrophilic copolymers of phosphorus-containing TMPC monomer with fluorine-containing methacrylamide comonomers bearing (a) 3,5-bis(trifloromethyl)benzylamine or (b) 5-fluorouracil-1-yl acetic acid as dual $^{31}P/^{19}F$ probes. It was shown that all prepared probes possess favorable T_1/T_2 relaxation times at relatively low concentrations and provide a high intensity signal in ^1H, ^{31}P or ^{19}F MRI experiments. In addition, ^{31}P MRI probe (i) underwent structural changes in the presence of reactive oxygen species overproduced in tumors and inflammations and can therefore be used as a sensitive functional ^{31}P MRI sensor of oxidative stress; and $^{31}P/^{19}F$ MRI probe (iii b) containing the cancerostatic drug 5-fluorouracil may serve as an anti-tumor therapeutic.

Keywords: Polymer zwitterions, ^{31}P-MRI, ^{19}F-MRI, MRI probes, polymer theranostics, ROS detection

Acknowledgments

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Antibody-polymer-drug conjugate for treatment of inflammation

J. Kudláčová[1], D. Starenko[1], L. Čtveráčková[1], D. Rubanová[2], E. Randárová[1], L. Kubala[2], T. Etrych[1]*

[1]Institute of Macromolecular *Chemistry CAS, Biomedical Polymers, Prague, Czech Republic*
[2]*Institute of Biophysics CAS, Biophysics of Immune System, Brno, Czech Republic*
*etrych@imc.cas.cz

The inflammatory processes have protective function in body and are important in repair and regeneration. The key roles in proper repair and recovery of homeostasis have immune cells, especially macrophages. However, when their protective role is changed to pathological, the chronic inflammation-related diseases develop [1]. Therefore, the anti-inflammatory therapy is targeted to pro-inflammatory cytokines, such as TNF-α, IL-1 and IL-6 that are produced by macrophages. Glucocorticoids or specific monoclonal antibodies can be administrated for this purpose, since they can decrease an excessive release of pro-inflammatory cytokines. Dexamethasone (DEX) is one of the commonly used glucocorticoid drugs used for treatment of chronic inflammatory diseases. However, the long-term and non-selective drug activity can cause many adverse effect. Therefore, a great effort is being made to minimize its negative side effects by targeted delivery of the drug to the site of inflammation. Application of the polymeric drug delivery systems is one of the actively researched ways of the improvement of inflammatory diseases treatment quality, which enables prolong circulation, optimal distribution and controlled release of the drug. In addition, it was already reported that the coupling of DEX with antibody targeting macrophages increases DEX activity and limits its toxicity [2]. Although antibody-drug conjugate appears to be promising immunosuppressant in the future, there are still some limitations related to higher hydrophobicity with higher drug loading, potential aggregation and increased clearance rates. Therefore, to reduce dose-limitation and overcome the issues associated with decreased physical stability of antibody-drug conjugate, the highly hydrophilic, non-immunogenic, non-toxic polymers based on *N*-(2-hydroxypropyl)methacrylamide (HPMA) backbone were used as carriers of glucocorticoid molecules and subsenquently the polymer drug conjugates were bound to an antibody infliximab (IFX) - chimeric monoclonal antibody, which acts like the inhibitor of TNF-α [3]. For this purpose, the derivative of DEX - dexamethasone 4-(2-oxopropyl)benzoate (DEX-OPB) was synthesized and bound via a pH-sensitive hydrazone bond to semitelechalic HPMA copolymer with terminal maleimide. Subsequently, DEX-OPB containing HPMA copolymers were conjugated with reduced antibody IFX through maleimide thiol reaction. The system was characterized by a number of analytical and biochemical methods. The effect of pH on the rate of release of DEX-OPB from HPMA polymer and the effect of modification of IFX with HPMA polymers on antibody binding activity was studied *in vitro*. The results proved that rapid DEX-OPB release from polymer at lower pH present at the site of inflammation and TNF-α binding activity of IFX in conjugate was maintained. The *in vivo* experiments for determine possible synergistic effect of the drugs are planned in the near future. However, the preliminary *in vitro* results prove the potential of newly prepared polymer system bearing two types of active molecules with different anti-inflammatory mechanism of action in future treatment of inflammatory diseases.

Keywords: HPMA polymer, infliximab, dexamethasone

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Biologically Inspired POSS-based Inks for Bone Grafts

A. Lungu[1*], A. Cernencu[1], A. Dinu[1], S. Dinescu[2], and H. Iovu[1]

[1]Advanced Polymer Materials Group, Faculty of Chemical Engineering and Biotechnologies, University Politehnica of Bucharest (UPB), Romania
[2]Department of Biochemistry and Molecular Biology, University of Bucharest, Romania
[*]adriana.lungu@upb.ro

The combination of different types of nano-fillers into a polymeric matrix used to achieve nanocomposites is a very modern approach and, in the same time, a popular strategy since it favors the interfacial interactions between fillers and the polymer matrix leading to improved properties [1]. Nanocomposite inks are considered also a great promise in 3D (bio)printing to fabricate scaffolds based on polymeric composite materials for various biomedical proposes [2].

The current research study is focused on pursuing the potential in bone tissue engineering of a fascinating combination of two different types of reactive nano-fillers integrated into a hydrophilic polymeric matrix: organic-inorganic nanosized fillers known as polyhedral oligomeric silsesquioxanes (POSS), and nanocellulose (CNF). A mixture of gelatin and pectin was considered as organic matrix for the newly synthesized nanocomposites; both biopolymers were prior functionalized with methacrylate groups to undergo photocrosslinking reaction on exposure to UV light. The so-prepared photocrosslinkable nanocomposites were employed to fabricate cellular constructs through 3D bioprinting using murine osteoblast cells.

The nanocomposite inks synthetized herein have proven suitable rheological and mechanical properties. Furthermore, the *in vitro* cell studies demonstrated the excellent biocompatibility and osteogenic potential of the printed nanocomposite scaffolds (Figure 1). We thus envisioned our hybrid multimaterial scaffolds provide the cells with the optimal environment for tissue regeneration and could be ideal candidates for 3D printing bone grafts.

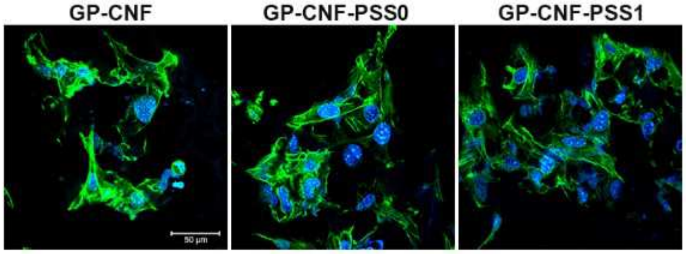

Figure 1: Actin filaments (green) developed by MC3T3-E1 cells after 48 h

Keywords: photocrosslinkable nanocomposites; 3D printing; multimaterial inks

Acknowledgments
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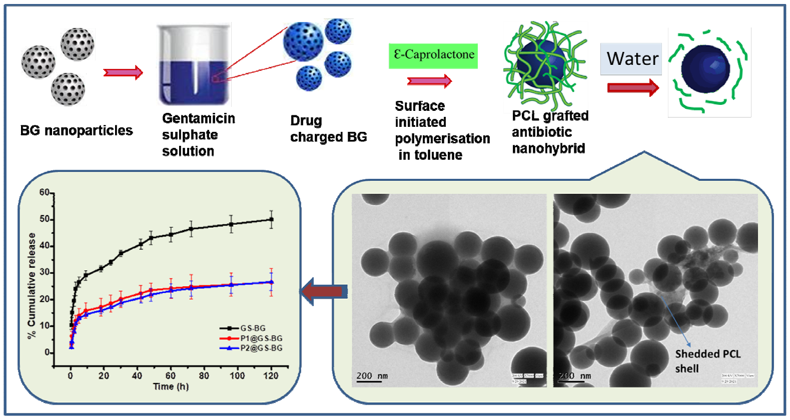
Shell sheddable antibiotic nanohybrid through drug mediated surface initiated polymerization for modulated drug release

L. M. Mukundan[1,2], H. Bora[2], S. Dhara[2] and S. Chattopadhyay[1,*]

[1] *Rubber Technology Center, Indian Institute of Technology Kharagpur, West Bengal, India.*
[2] *School of Medical Science and Technology, Indian Institute of Technology Kharagpur, West Bengal, India.*
[*]*santanuchat71@yahoo.com*

Antibiotic impregnated bioactive therapeutic biomaterials are highly demanding due to the risk of infection associated with musculoskeletal injuries and bone replacement surgeries [1]. In this study, we report the synthesis of antibiotic nanohybrid having an aqueous sensitive sheddable polycaprolactone (PCL) shell grafted over gentamicin sulphate (GS) charged bioactive glass (BG) nanospheres via surface initiated polymerization. This study indeed shows the additional role of GS while it's potential as an initiator for the ring opening polymerization of Ɛ-caprolactone (CL) is investigated choosing 1: 0.175 and 1: 0.53 weight ratio of CL: GS loaded nanoparticles. Synthesized BG nanospheres were characterized to lie in the size range of about 200 -500 nm and a drug encapsulation efficiency of 27.8%. The influence of monomer/ initiator feed ratio on the synthesized PCL was evident in the unbound PCL fractions, suggesting the effective role of GS as initiator. However, in the nanohybrids the percentage grafting and shell thickness were comparable regardless of the quantity of drug loaded particles used. The ^{1}H NMR and MALDI- ToF analysis of the unbound PCL further confirmed the part of GS with the hydroxyl end group served as the surface anchoring group. The successful grafting of PCL was confirmed by FT-IR, TGA, XPS, AFM, contact angle measurements and TEM. The effective shedding of the shell in aqueous environment and the subsequent release of GS was confirmed by the TEM analysis and zeta potential measurements. The release of GS from the nanohybrid in aqueous medium was further quantitatively measured after derivatising using o-phthaldialdehyde. It is found that the PCL sheathing gives a convenient way of controlling the major burst release and adjusting the release rate and duration when compared to the bare drug loaded BG particles. The drug release was modulated with only 15 wt% and 14 wt% release in the nanohybrids in the first 8 h while it is 29 wt% for the unmodified BG nanoparticles. Studies of growth inhibition of *E. coli* and *S. aureus* culture indicated that the GS released from the nanohybrid retained antibacterial activity. Thus the GS initiated polyester functionalization of drug-loaded BG nanoparticles which enables an environment responsive as well as modulated release is considered beneficial for further progresses in drug-loaded scaffolds.



Keywords: Surface initiated polymerization, antibiotic nanohybrid, aqueous responsive, polycaprolactone-bioactive glass nanohybrid, polymer- bioactive glass composite

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Preparation and characterization of functionalized magnetic chitosan nanoparticles for drug delivery to inner ear

Athar Mahdieh[1*]-, Sverre Arne Sande[1], Bo Nyström[1]

[1]*Universty of Oslo, Oslo, Norway*

[*]*athar.mahdieh@farmasi.uio.no*

Hearing impairment is the most prevalent sensory disability affecting over 5% of the world's population, and more than 30% of people over the age of 65, according to statistics in the year 2016 [1]. This disease can be caused by different factors, such as: genetic defects, environmental factors or a combination of both. These factors induce the damage and death of hair cells and neurons in the cochlea, therefore cellular loss and concomitant hearing loss cannot be reversed [2].

Our approach is based on active targeted drug delivery to inner ear which represents an innovative and attractive multidisciplinary method. In fact, the use of nanotechnology for the development of polymeric nanomaterials with predefined characteristics which are capable of being loaded with drugs in order to be transported and released at a desired site, opens multiple perspectives in the field of nanomedicine [3].

In order to increase the effectiveness of the treatment, targeted drug delivery was recently introduced for treating sensorineural hearing deficiencies associated with hair cell pathology. For the first time, we used a dual targeting approach for the treatment of the hearing deficiency and this method was based on the utilization of chitosan as a natural polymer.

We synthesized drug-loaded peptide-functionalized magnetic polymeric nanocarriers with diameters smaller than 200 nm. For this purpose, first, magnetic nanoparticles (MNPs) with a magnetic core diameter around 15 nm were prepared and then coated by macromolecular compounds such as chitosan. Active targeted delivery of nanocarriers to specific inner ear cell populations was achieved by functionalizing the polymeric nanocarriers with specific ligands (peptides).

The size and the morphology of the obtained polymeric nanocarriers was analyzed by DLS, cryo-TEM, FTIR, zeta-potential in the absence and in the presence of the drug. The magnetic properties of the magnetic material and magnetic nanocarriers was obtained by vibrating sample magnetometer at room temperature. Also, physicochemical properties of prepared polymeric nanocarriers were investigated by different analyses.

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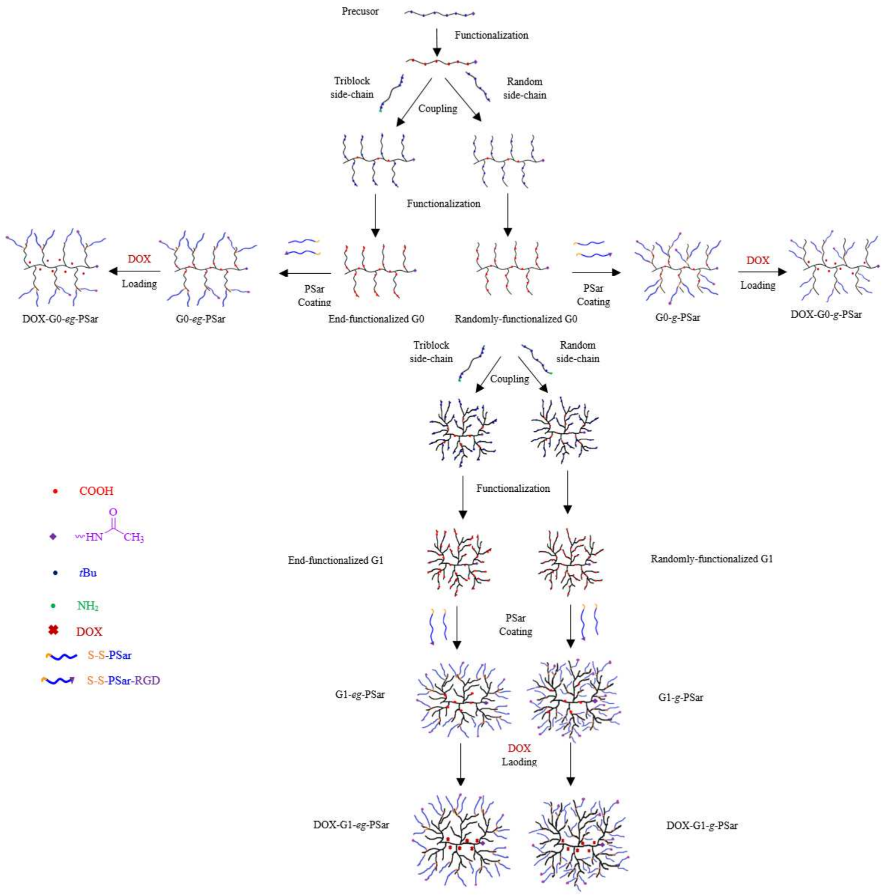
Hybrid Arborescent Polypeptide-Based Unimolecular Micelles

B. Mahi[1], M. Gauthier[2*], N. Hadjichristidis[1*]

[1]Catalysis Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Saudi Arabia.
[2]Department of Chemistry, Institute for Polymer Research, University of Waterloo, Canada
**nikolaos.hadjichristidis@kaust.edu.sa*

This work [1] reports novel hybrid arborescent polypeptides based on poly(γ-benzyl L-glutamate)-*co*-poly(γ-*tert*butyl L-glutamate)-*g*-polysarcosine [P(BG-*co*-Glu(O*t*Bu))-*g*-PSar] (Scheme). Preparative SEC was used to fractionate these complex macromolecular architectures. NMR, Raman spectroscopy, and SEC were used for molecular characterization of all intermediate and final products and DLS, TEM, and AFM for micellar characterization. Doxorubicin was utilized as a chemotherapy model, and loading was achieved successfully by physical entrapment.



Scheme. Synthetic strategy and arechictucture explored in this work.

Keywords: polypeptides, arborescent, unimolecular micelles, drug delivery.

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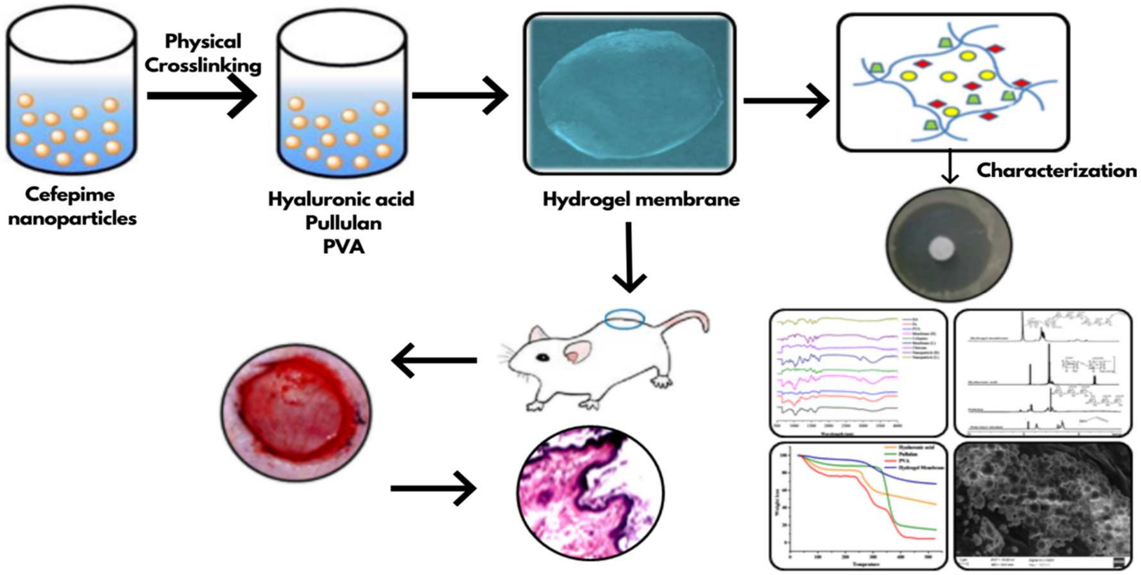
Accelerating wound healing in the elders utilizing hydrogel membranes

Arshad Mahmood[1], Mohammad Sohail[2]

[1]College of Pharmacy, Al Ain University, Abudhabi campus, Abudhabi, UAE.
[2]Department of Pharmacy, COMSATS Institute of Information Technology, Abbottabad 22010, Pakistan
Corresponding Author' email: arshad.mahmood@aau.ac.ae

Deviating from the mainstream wound dressings to the bioactive and biodegradable hydrogel membranes could be a promising approach for wound healing applications. With this thought, the focus of research was to design hydrogel membranes based on hyaluronic acid, pullulan and polyvinyl alcohol and loaded with chitosan-based cefepime nanoparticles for their potential application in cutaneous wound healing. The membrane was appraised using dynamic light scattering, proton nuclear magnetic resonance, fourier transform infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. The outcomes indicated novel crosslinking as well as thermal stability of the fabricated hydrogel membrane. The in-vitro analysis revealed that the promising wound dressing fall in the ideal range with an oxygen permeability between 7 and 14 mg/L, water vapors transmission rate between 2000 and 2500 g/m^2/day. The swelling capacity and surface porosity releases the encapsulated drug (cefepime) in a sustained manner and a total of 88% of the drug release was observed during the study period. Finally, the cefepime encapsulated hydrogel membrane demonstrated a higher inhibition zone against Staphylococcus aureus, Pseudomonas aeruginosa, and Escherichia coli and excisional rat model exhibit prompt recovery rate. Based on the outcomes, it can be stated that the newly developed hydrogel membrane loaded with cefepime nanoparticles for topical application is a promising approach in wound healing acceleration in elderly since they have impaired wound healing.

Keywords: Controlled Drug Delivery; Biomaterials; Hydrogel Membranes; Nanoparticles; Wound Healing



In-depth investigation on drug release of solid lipid nanoparticles for the treatment of malaria

N. Makarova [1,2,*], Z. Viktor [1,3], A. Lederer [1,3], C. Tzachev [4, 5], S. Gaydarova [4, 5]

[1] *Leibniz-Institut für Polymerforschung, Center Macromolecular Structure Analysis, Dresden, Germany*
[2] *Technical University Dresden, Dresden, Germany*
[3] *Stellenbosh University, Department of Chemistry and Polymer Science, Stellenbosh, South Africa*
[4] *Sofia University, Sofia, Bulgaria*
[5] *Lead Biotherapeutics LTD*
**natalia.makarova@mailbox.tu-dresden.de*

Malaria is a global threat that causes millions of deaths each year. It is particularly a huge problem in developing countries where malaria continues to spread, placing millions of lives at risk. For this reason, there is a continuous need for advanced malaria treatment [1]. To address this problem is needed to develop new strategies to improve not only the treatment of malaria but sustainability as well. Solid lipid nanoparticles (SLN) are well established as advanced drug delivery systems which are distinct with their safety, enzyme degradation to nontoxic metabolites, unimpeded travel through cell membranes, and other biological barriers [2]. The particles can be customized to deliver an encapsulated drug to the delivery site and degrade and release the drug. To ensure that the particle performs its specific function, the particle's size, surface properties, and drug release properties need to be controlled and modified. Therefore, in-depth characterization of the nanoparticles is a crucial component.

In this work, novel solid lipid nanoparticles (SLNs) encapsulated with an antimalarial drug were investigated. The bulk characterization of the SLNs, with regards to size distribution, temperature, and time stability was performed by dynamic light scattering (DLS) and an advanced separation via Asymmetrical Flow Field-Flow Fractionation (AF4). With the aid of microscopy analysis information on the size and surface of the SLNs was acquired. Using ultraviolet-visible (UV-Vis) spectroscopy and fluorescence spectroscopy, in-depth studies on drug release of the SLNs were performed [3], [4]. The study is focused on determining the encapsulation efficiency of the SLN, quantification of the antimalaria drug release, and the degradation of the SLNs in the presence of enzymes.

Keywords: malaria, characterization techniques, drug-delivery, fluorescence, DLS, UV, AF4, microscopy, spectroscopy

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Control over hydrolitic degradation of thiolated cationic polyaspartamides

Aysel Mammadova[1*], András Szilágyi[1], Benjámin Gyarmati[1]

[1]*Department of Physical Chemistry and Materials Science, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary*
[*]*aysel.mammadova@edu.bme.hu*

Macromolecular drug carriers must meet various requirements including long circulation time in the blood stream and the ability to degrade to non-toxic monomers after reaching the target cell. Here, we designed *in situ* gelling cationic poly(amino acid) derivatives which can be used to bind negatively charged phosphodiester backbones of DNA or mucous membrane of epithelial cells [1].To investigate the effect of side groups on the hydrolyitc stability of these polymers, we synthesized thiolated polyaspartamides with various cationic groups such as N,N- dimethyl-2-aminoethyl (DME) and N,N-dimethyl-3-aminopropyl (DMP) groups and neutral 2-hydroxyethyl (HE) side groups. The stabiliy of polyaspartamides depended strongly on composition and non-enzymatic degradation was observed for certain derivatives. Polymers with high DMP and HE content were more stable against hydrolytic degradation in physiological and endosomal pH than derivatives with high DME content which degraded at pH=7.4 within one day due to breakage of polymer main-chain structure confirmed by size exclusion chromatography. The rate of degradation could be controlled by the composition of the polymers. Linear thiolated polyaspartamides could be converted to disulfide cross-linked hydrogels regardless of the type of side groups. Rheological characterization indicated that disulphide cross-linked polyaspartamide hydrogels with high DME content possess a weaker gel structure compared to hydrogels with high DMP and HE content [2]. Hemolysis assay confirmed that polyaspartamides having cationic groups in large concentration cause membrane disruption to some extent, while the replacement of cationic groups to neutral ones partly or completely reduce the hemolytic effect. It can be concluded that hydrolytic degradation and stability of linear polyaspartamides and their hydrogels can be easily controlled by the chemical composition and the pH and the degradation rate can be tuned to the needs of application [3].

Acknowledgments

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New multifunctional formulations based on imino-chitosan hydrogels

M.M. Iftime[*], L. Marin

"Petru Poni" Institute of Macromolecular Chemistry of Romanian Academy, Iasi, Romania
[*]*e-mail: ciobanum@icmpp.ro*

Chitosan-based hydrogels have been exploited for a great realm of applications of modern interest, due to their versatile properties: they are biodegradable, biocompatible, non-toxic and have the ability to swell and absorb various active compounds [1]. In line with this, a promising route towards hydrogels with controlled properties was developed within our laboratory, based on the chemical crosslinking of chitosan with different naturally-derived monoaldehydes [2]. By this procedure, novel hydrogels with properties tailored for specified applications were synthesized, by varying the chosen aldehydes as well as the reaction parameters [3, 4].

Scheme 1. Synthesis of the chitosan-based formulations

Thus, the purpose of this paper is the obtaining and characterization of new hydrogels, in relationship with their ability to act as matrix to encapsulate different bioactive compounds (urea or diclofenac sodium salt) to be applied in medicine and agriculture, respectively. The hydrogels were synthetized by the condensation reaction of chitosan with salicylaldehyde, in different ratio of the reagents, in order to adjust the intrinsic properties for the specified fields [2, 3]. They were completely characterized by NMR, FTIR, WRXD, SEM and POM, proving that the chitosan's hydrogelation is a result of both imination and self-ordering processes. The obtained hydrogels have superporous morphology, thixotropic and self-healing properties, as well as high swelling ability. Further, the developed chitosan-based hydrogels were used as a matrix of new delivery systems by *in situ* hydrogelation of chitosan and salicylaldehyde in the presence of the active compound (urea and DCF sodium salt), with various encapsulation degrees. After assessing the success of the encapsulation by corresponding techniques, an important evaluated property was the release kinetics, revealing a sustained release during 35 days in water the case of urea, and 10 days in PBS in the case of DCF. The formulations designed as soil conditioners, showed ability to retain water and improving the nitrogen in soil, demonstrating promising results. The formulations designed as drug delivery systems exhibited biodegradability, biocompatibility, swelling ability and release of DCF in a controlled manner. Considering all these results, the studied hydrogels are considered excellent candidates to be further exploited as matrices for the encapsulation of various active ingredients towards formulations for applications that dictate the quality of everyday's life.

Acknowledgments

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Ureido-polycarbonates with UCST-type thermoresponse in aqueous solution

J. Martín[1], L. Oriol[1], M. Piñol[1], M. Arruebo[2], V. Sebastián[2]

[1]*Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Departamento de Química Orgánica, C/ Pedro Cerbuna 12, 50009, Zaragoza, Spain.*
[2]*Instituto de Nanociencia y Materiales de Aragón (INMA), Universidad de Zaragoza, Departamento de Ingeniería Química, Campus Río Ebro-Edificio I+D, C/ Poeta Mariano Esquillor s/n, 50018, Zaragoza, Spain.*
**martinj@unizar.es*

Thermoresponsive polymers have extensively been applied in several biological fields such as controlled drug delivery. However, nanocarriers based on polymers exhibiting upper critical solution temperature (UCST) in water, which show separation phase below transition temperature T_{cp}, are scarce [1]. In addition, most of them are composed of vinyl copolymers that are non-biodegradable or turn into toxic compound *in vivo*. Hence, the development of degradable and biocompatible UCST nanocarriers is desired for biomedical application [2].

Herein, we report the synthesis of new degradable homopolycarbonates and amphiphilic block copolymers formed by a hydrophilic monomethyl poly(ethylene glycol) (PEG) block and a polycarbonate block derived from 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) and functionalized with pendant ureido groups (Figure 1). The thermoresponsive behaviour has been studied in aqueous solution.

The homopolycarbonate P(MPCU) exhibited UCST properties at high temperatures. However, the decrease of number of ureido units in P(MACU) resulted in the disappearance of UCST transition (Figure 2).

The block copolymers PEG-*b*-P(MPCU) and PEG-*b*-P(MACU) were able to self-assembly into micelles in water at room temperature. The increase of temperature above 45°C entailed a growth of the micelles size due to the swelling.

Therefore, the thermoresponse of these polymers and self-assembly properties make them attractive materials for the preparation of nanocarriers with a drug release triggered by temperature as stimulus.

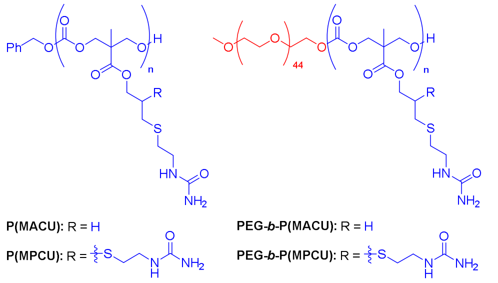

Figure 1. Homopolycarbonates P(MACU) and P(MPCU) and amphiphilic block copolymers PEG-*b*-P(MACU) and PEG-*b*-P(MPCU) synthesised

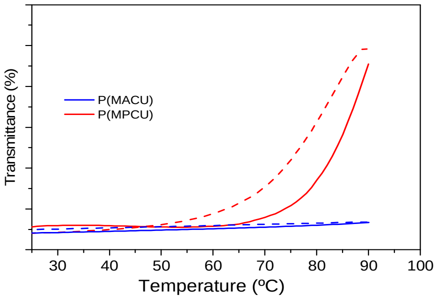

Figure 2. Transmittance curves of P(MACU) and P(MPCU) at 0.3 mg/mL in water (dashed curves are cooling process and solid curves are heating process)

Keywords: UCST, ureido polymers, polycarbonates, block copolymers, nanocarriers

Acknowledgments

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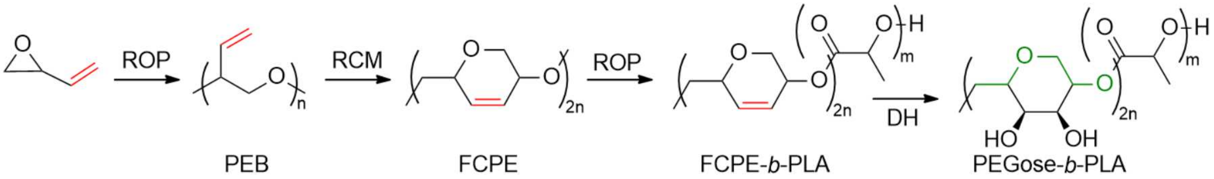
PEGose-*b*-PLA nanoparticles for drug delivery

Jean-Baptiste Masclef[1], E. Acs[1], J. Köhnke[1], J. Prunet[1]*, B.V.K.J. Schmidt[1]*

[1]*School of Chemistry, University of Glasgow, Joseph Black Building, G12 8QQ, Glasgow, UK*
**Joelle.Prunet@glasgow.ac.uk, Bernhard.Schmidt@glasgow.ac.uk*

Developing PEG alternatives for medical applications is becoming an urgent matter. It has been reported that in 2016, 70% of patients possessed anti-PEG antibodies prior to any treatment, thus limiting the efficiency of PEGylated drugs or nanocarriers[1]. Polysaccharide mimics could be great PEG substitutes, combining the innocuity of natural polysaccharides while having a well-defined mass and structure. To this end, our group developed a stereocontrolled synthesis of an amylose-like polymer coined PEGose[2]. More recently, we developed a new synthesis of PEGose-*b*-PLA block copolymers with well-defined molar masses in the range of 4.0 to 11.0 kDa.



Scheme 1. Synthesis of PEGose-*b*-PLA: ring-opening polymerization of butadiene monoxide, followed by ring-closing metathesis, ring-opening polymerization of D,L-lactide and dihydroxylation

These copolymers self-assembled in water into nanoparticles with an average diameter of 150-200 nm and a low polydispersity. The unique structure of PEGose led to complex aggregates that differ from traditional polymeric micelles or vesicles. These nanoparticles were able to encapsulate both hydrophilic and hydrophobic compounds, with an encapsulation efficiency of 68% and 52% for rhodamine B and nile red respectively. The release was substained and could be tuned by changing the PEGose/PLA length ratio. *In vitro* biological tests revealed that nanoparticles were not cytotoxic and were able to cross the cell membrane for potential intracellular drug delivery. Interestingly, the nanoparticles exhibited an outstanding stability, resisting harsh conditions such as low pH, high temperature, high bile salts concentration or digestive enzymes.

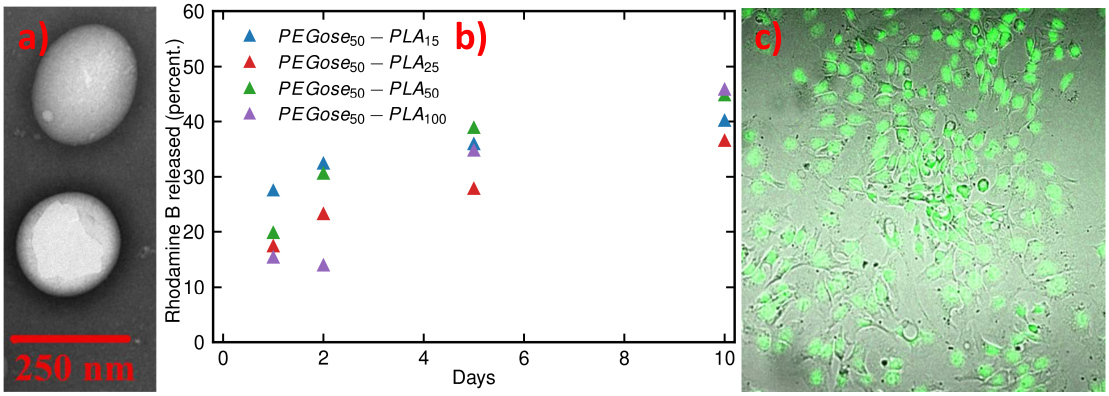


Figure 1. a) TEM image of PEGose-PLA nanoparticles b) Amount of rhodamine B released over days by PEGose-PLA nanoparticles c) Confocal microscope image of cells incubated with fluorescent PEGose-PLA nanoparticles

These combined results suggest that the presented nanoparticles could be potent alternatives to PEG based nanocarriers. Moreover, due to their increased stability, PEGose-*b*-PLA nanoparticles could also deliver drugs in harsh environments such as the gastrointestinal tract, where typical liposomes/polymersomes usually fail[3].

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Adsorbable and salt responsive polymer brushes with switchable antibacterial and antifouling properties

R. Methling[1], A. Jagic[2], M. Müller[2], H. Schönherr[2*], D. Kuckling[1**]

[1]*Paderborn University, Paderborn, Germany*
[2]*University of Siegen, Siegen, Germany*
[*]*schoenherr@chemie.uni-siegen.de*
[**]*dirk.kuckling@uni-paderborn.de*

The prevention of bacterial adhesion and biofilm formation has gathered widespread interest, particularly in connection with biomedical applications. Naturally, implants are exposed to human tissue and body fluids rich in proteins, which provides optimal conditions for bacterial growth and development of robust biofilms that are challenging to eradicate. Endosseous implants are frequently used in dental medicine, however, patients are still suffering from complications due to bacterial infections.[1] As dental implants are usually made up of titanium alloy, there have been many attempts to overcome the insufficient intrinsic antibacterial properties of the metal, for example via surface contact-killing mediated by antibacterial polymers. To address this, polycations can be used, which interact with the negatively charged cell membrane leading to bacterial membrane disruption and therefore to cell death.[2] However, as dead material accumulates on the polymer, the bactericidal moieties are screened and the surface loses its desired antimicrobial and antifouling properties.[3]

We developed a multifunctional triblock copolymer as a coating for metallic substrates to overcome this drawback. The antibacterial properties of this copolymer are afforded by a polycationic block based on ammonium moieties. In order to remove dead bacteria and residual biomass, the pronounced polarity of zwitterionic moieties is exploited by preventing the nonspecific adhesion of biomolecules via a pronounced hydration shell that is formed, whereby an easy cleaning process is facilitated.[4] Polycations and polyzwitterions show opposing behavior in aqueous solution with respect to ionic strength (polyelectrolytic effect and anti-polyelectrolytic effect). Thus, the salt concentration of the supernatant solution can be used to switch between antibacterial and antifouling activity.

A connective block between the charged strands anchors the polymer to titanium surfaces via phosphonic acid groups. This allows the coating of arbitrarily shaped titanium implants through a “grafting to” approach. Thus, we synthesized and characterized polymer brushes with unique surface properties that mediate both antibacterial and antifouling activities on coated titanium. This work may pave the way to new efficient strategies to sustainably prevent dental implant associated bacterial infections.

Keywords: Salt-responsive polymer, antimicrobial polymer, polymer brushes, polyelectrolyte, polyzwitterion

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Structure-Property Investigation of Diels-Alder Polymer Networks

G. Misiakos[1], Sandra Van Vlierberghe[1]

Polymer Chemistry and Biomaterials Group (PBM), Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium
**Georgios.misiakos@ugent.be*

Diels-Alder (DA) polymer networks have attracted attention in recent years due to their potential for bridging the gap between thermoplastics and thermosets[1]. Diels-Alder adducts are cleaved at elevated temperatures; Breaking these covalent bonds transforms the mechanical properties of the material, allowing it to be (re)processed. This has shown great promise in fused deposition modeling (FDM) since it can adress one of the greatest drawbacks of the widely adopted AM technique being mechanical anisotropy[2]. While cooling down after printing new DA bonds can be formed between layers[3] whereas covalent interlayer bonding is not possible with current FDM materials. By using the well established furan-maleimide as a DA pair, there are different approaches to the architecture of these polymer networks i.e. furan groups can be incorporated into the polymer backbone or as pendand groups in this work (Fig. 1).

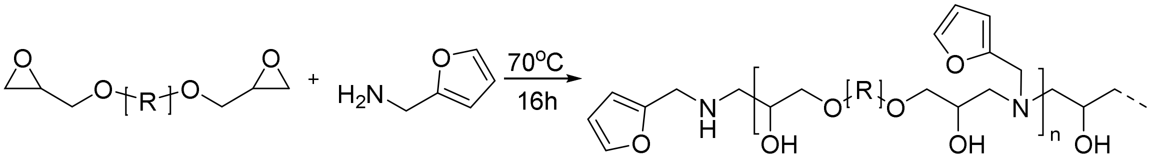

Figure 1: Ring-opening polymerization reaction to create a vaersatile backbone with furan pendant groups

By mixing bismaleimide (BM) crosslinkers in different proportions to the furan groups present, materials with a range of structures and properties can be made. The mechanical properties of the resulting materials depend on the flexibility and length of the repeating unit and of the bismaleimide. A proof of concept demonstration can be seen in Fig. 3 where two polymers (building blocks in Fig .2) are crosslinked with similar proportions of the same BM. The increased length of the repeating unit of PGDE results in a less densly crosslinked network giving rise to a completely different mechanical property profile. Ongoing research on a variety of building blocks is currently ongoing to produce a library of materials that will be evaluated for their mechanical properties, biocompatibility and 3D printing potential.

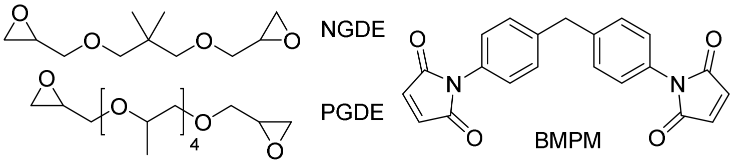

Figure 2: Compounds used in proof of concept.

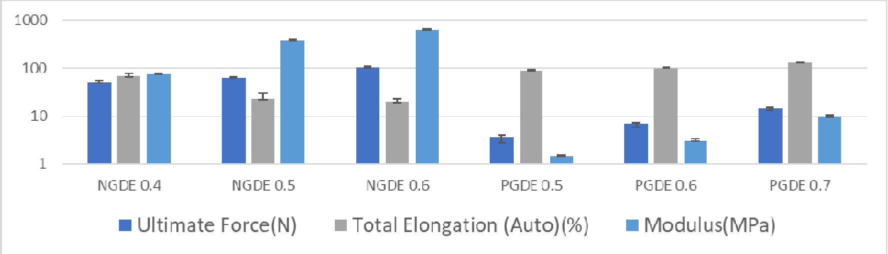

Figure 3: Tensile property comparison between NGDE and PGDE with different (0.4-0.7) furan/maleimide ratios of BMPM

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Poly(2-oxazoline) based micelles as drug delivery systems

P. A. Naumann[1*], *R. Jordan*[1]
[1]*Technical University, Dresden*
Paul_Alexander.Naumann@tu-dresden.de

Most hydrophobic drugs are limited in their application due to low bioavailability, fast blood clearance or loss of their activity and gain of toxic side effects due to first-pass metabolization in the liver.[1,2]

Amphiphilic triblockcopolymers of 2-oxazolines show promising features like stealth properties and a prolonging of blood circulation time like the well-known and often used polyethylenglycole.[3] Furthermore studies on the encapsulation of hydrophobic drugs in micelles of poly-(2-oxazoline)s (POx) reported high loading capacities and good biocompatibility.[4]

Triblock copolymers featuring an A-B-A-type structure with hydrophilic poly-2-methyl-2-oxazoline as A-part and varying hydrophobic B-blocks were synthesized. For the core, monomers with different alkyl side chain lengths like 2-butyl-, 2-heptyl-, 2-nonyl-2-oxazoline as well as the aromatic 2-phenyl-2-oxazoline were used.

Furthermore, the hydrophobic antitumor agent paclitaxel, the antimalarial artemisinin and curcumin were used to study the ability of the synthesized polymers to formulate drugs in aqueous solution. The encapsulation was realized via thin film method and analysis proceeded via HPLC measurements.

In this work it is shown that the use of two different drugs in the same formulation is beneficial in regards of the maximal achievable loading capacity. Through the coformulation of paclitaxel and artemisinin even higher loading capacities for poly-2-oxazolines than already reported could be achieved.[5]

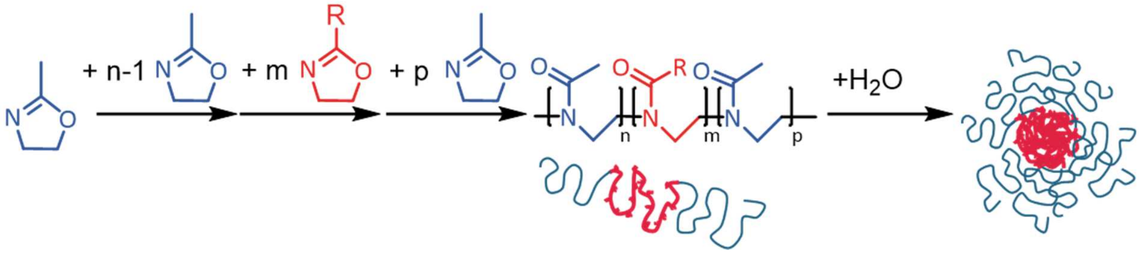

Figure 1: Scheme for the formation of POx-micelles in aqueous medium

Keywords: Poly(2-oxazoline)s, Drug delivery, Antitumor, Anti-malaria, Solubilization, Micelles

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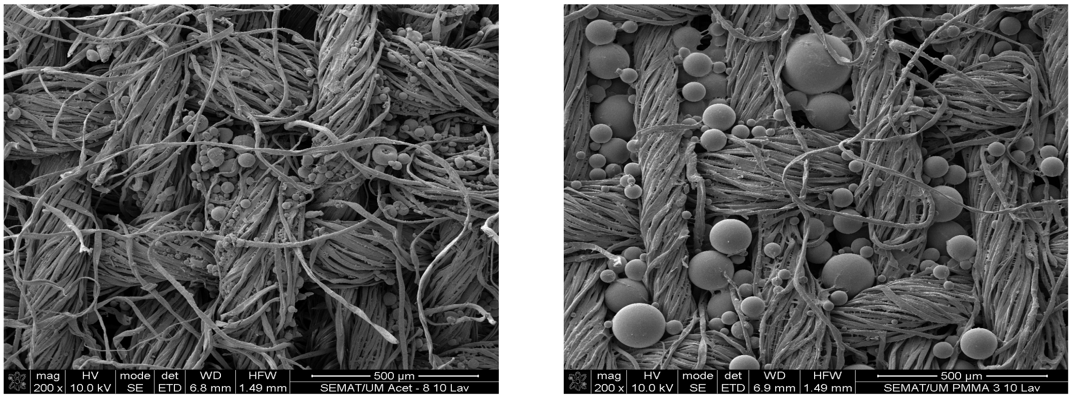
Functionalization of woven fabrics for antimicrobial capability using microcapsules with essential oils

T. Nicolau[1,2*], J.F. Parente[2], V.I. Sousa[2], J. Padrão[1], C.J. Tavares[2], A. Zille[1]

[1]2C2T – Centre for Textile Science and Technology, University of Minho, Guimarães, Portugal
[2]Centre of Physics of the Universities of Minho and Porto, Guimarães, Portugal
[*]tali_nicolau@hotmail.com

The functionalization of textiles encompasses multiple objectives, such as the attribution of perfumes, dyes, antimicrobials, some medicines, softeners, moisturizers, flame retardants, insect repellents, and phase-change materials. Among these objectives, antimicrobial capability is crucial for industrial applications. Antimicrobial capacity guarantees that microorganisms will not thrive in textiles, allowing users a safer use of these products in different scenarios. This research evaluates fabrics' antimicrobial capability of cotton fabric by applying microcapsules containing essential oils. The used microcapsules combined a poly(methyl methacrylate) (PMMA) shell with lavender oil in the core or a cellulose acetate shell with a eucalyptus oil core. The nanoparticles were applied using the screen printing technique in a 100 % cotton fabric. Subsequently, a fastness to washing test (ISO 105-C06:2010) was performed up to ten times. These washing cycles simulate real-life domestic applications. This cleaning simulation helped define whether the microcapsules would be washed away from the textiles. Then, we collected samples without washing, or after five and ten rounds, which were analyzed by scanning electron microscope (SEM). For biological indicators, we performed the antimicrobial test using *Staphylococcus aureus* and *Escherichia coli*. The bacteria concentration (CFU/mL) was analyzed in contact with the fabric test (AATCC TM100-TM 100). Antibacterial properties of the fabric was analyzed for all microcapsules combinations. The better results were obtained for the Gram-negative bacterium displayed the better even after ten washing rounds (5.23 – 7.23 log-reduction). Moreover, SEM images displayed for both microcapsule combinations a high concentration of microcapsules even after ten washing cycles (Figure 1). Collected results indicate controlled release, meaning that as the washing cycles occurred, the essential oils were released. Finally, these promising results stimulate the application of this method for functionalizing textile products and the application of microcapsules with essential oils for antimicrobial capability.

Keywords: microcapsules, essential oils, antibacterial capability, woven fabrics



(a) **(b)**

Figure 1 – SEM images after ten washing cycles. (a) cellulose acetate microcapsules. (b) PMMA microcapsules.

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Self-assembly of oleyl-hyaluronan derivative controls its drug carrier performance

F. Ondreáš[1, 2*], J. Sita[1, 2], M. Čepa[1], V. Velebný[1]

[1]*Contipro a.s., Dolní Dobrouč, Česká republika*
[2]*Central European Institute of Technology, Brno University of Technology, Brno, Česká republika*
**Frantisek.Ondreas@contipro.com*

The hydrophobically modified hyaluronan (HA) derivatives can serve as effective and biocompatible drug carriers [1, 2]. Amphiphilic polysaccharides can self-assemble into supramolecular structures with with a hydrophilic shell and one or more hydrophobic domains. The nanostructure of such polymeric carriers can control active compound loading capacity, targeted delivery, controled release, and skin penetration. Therefore, the understanding of the self-assembly process is crucial for the design of their properties.

Investigated oleyl derivate of HA (oleyl-HA) is a polyelectrolyte with an amphiphilic character given by hydrophobic oleyl grafts with the degree of substitution of 6.8 % at the C6 position on the 18 kDa HA backbone. Oleyl-HA derivatives self-associated spontaneously into stable aggregates, which were observed below critical aggregation concentration (CAC) evaluated from conventional methods. These results were explained as the structural reorganization of aggregates' nanostructure rather than aggregates formation. Structural reorganization towards well-developed hydrophobic domains correlated well with the concentration dependence of curcumin loading capacity, which decreased significantly below CAC. Rheological characterization revealed pronounced hydrophobic interactions at a critical concentration.

The cations in phosphate-buffered saline (PBS) screened the negative charges of carboxylic groups in the oleyl-HA backbone and increased significantly chain flexibility. It led to the pronounced change in aggregates' structure. The large aggregates with a diameter of roughly 500 nm with multiple hydrophobic domains were observed in water while small aggregates with a diameter of approximately 25 nm with one hydrophobic domain and core-shell structure were determined in PBS (**Figure 1**). This dramatic structural change led to the pronounced increase of functional properties in PBS. The loading capacity of curcumin increased by 260 %, and skin penetration was significantly more effective in PBS. The acquired correlation between physicochemical behavior, the nanostructure of self-assembled aggregates, and their functional properties provides valuable knowledge for the development of HA-based carriers of active compounds.

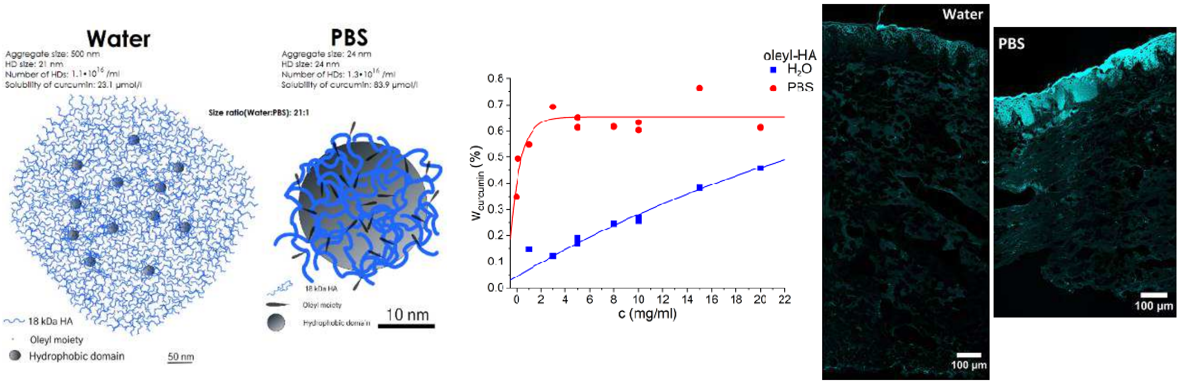

Figure 1: Structure and properties (curcumin loading capacity and skin penetration) of oleyl-HA carriers in H_2O and PBS [2].

Keywords: hyaluronan, amphiphilic derivative, self-assembly, drug carrier, structure-property function.

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Graphene oxide composites for antitumor applications

J. Pérez Quiñones[1]*, C. Roschger[2], A. Zierer[2], O. Brüggemann[1]

[1]*Kepler University Linz, Institute of Polymer Chemistry, Altenberger Straße 69, 4040 Linz, Austria.*
[2]*Johannes Kepler University Linz, Kepler University Hospital GmBH, Department for Cardiac-, Vascular- and Thoracic Surgery, Altenberger Straße 69, 4040 Linz and Krankenhaustraße 9, 4020 Linz, Austria.*
* *javier.perez_quinones@jku.at*

Camptothecin (CPT) is an anticancer drug with high antitumor activity against different cancers and hepatitis C virus [1]. However, CPT is halted of anticancer therapy due to its poor aqueous solubility, high toxicity and limited stability at physiological conditions. On the other hand, graphene oxide (GO) composites with different polymers (e.g. chitosan, PEG, hyaluronic acid) are proposed in biomedicine for tissue engineering and different applications. Therefore, in this work is proposed the preparation of GO composites with glycol chitosan (GC), silk fibroin (SF), and other polymers for the controlled release of CPT as antitumor candidates.

GO particles of about 240 nm were prepared from commercial graphite 325 mesh using a modified Hummer method. These particles were functionalized as –CH_2COOH terminated for sequential reaction with CPT glycinate and the different polymers (glycol chitosan, silk fibroin, MeO-PEG5000, etc) via carbodiimide. The GO-CPT-polymer composites were purified using dialysis and thoroughly characterized with FT-IR, UV, DLS, DSC, TGA and fluorimetric methods.

Sustained CPT release was observed over 1 week.

GO-CPT-polymer composites exerted good cytotoxicity to MCF-7 cancer cells, whereas blank GO-polymer composites appeared no toxic to MCF-7 cancer cells and some non-cancer cell lines.

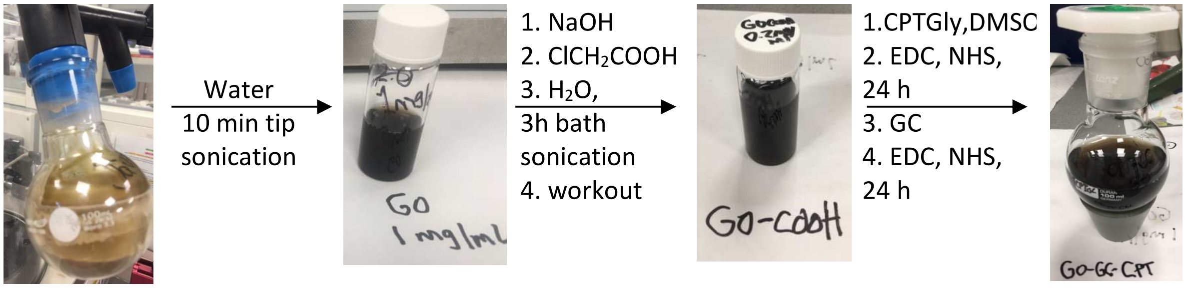

Figure 1. Preparation of GO-CPT-polymer composites.

Table 1. Zeta potential (ζ)values of GO derivatives in bi-distilled water at 25 °C.

	ζ (mV)
GO	**-27 ± 1 mV**
GO-CH_2COOH	**-26.3 ± 0.3 mV**
GO-GC-CPT	**13.0 ± 0.2 mV**

Keywords: graphene oxide, nanoparticles, camptothecin, controlled release, antitumor activity

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Polymerization-Induced Self-Assembly (PISA) for in situ drug encapsulation or drug conjugation in cancer application

Hien Phan,[a] Mélissande Cossutta,[b] Claire Houppe,[b] Clémence Le Cœur,[a] Sylvain Prevost,[c] Ilaria Cascone,[b,d] José Courty,[b,d] Jacques Penelle,[a] Benoit Couturaud*[a]

[a] Univ Paris Est Créteil, CNRS, Institut de Chimie et des Matériaux Paris-Est (ICMPE), UMR 7182, 2 rue Henri Dunant, 94320 Thiais, France. E-mail: couturaud@icmpe.cnrs.fr
[b] INSERM, U955, Immunoregulation and Biotherapy, F-94000, Créteil, France
[c] Institut Laue-Langevin, 71 Avenue des Martyrs, 38042 Grenoble, France
[d] AP-HP, Groupe hospitalo-universitaire Chenevier Mondor, Centre d'investigation clinique Biothérapie, F-94010 Créteil, France
**Email: couturaud@icmpe.cnrs.fr*

Hypothesis

We describe the possibility of using the same block copolymer carriers prepared by PISA for *in situ* drug encapsulation or drug conjugation.

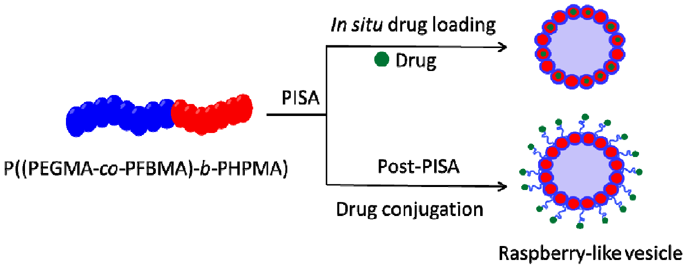
Experiments

Block copolymers containing poly((ethylene glycol) methacrylate)-*co*-poly(pentafluorophenyl methacrylate)-*b*-poly(hydroxypropyl methacrylate) (P((PEGMA-*co*-PFBMA)-*b*-PHPMA)) were synthesized at 10 wt% using PISA. The first approach involved *in situ* Doxorubicin (DOX) loading during PISA, while the second exhibited surface functionalization of PISA-made vesicles with dual drug therapies, N-acetyl cysteine (NAC) and DOX using *para*-fluoro-thiol reaction (PFTR) and carbodiimide chemistry, respectively. Cytotoxicity, cell uptake, and cell apoptosis were assessed on MDA-MB-231 cell lines.

Findings

P((PEGMA-*co*-PFBMA)-*b*-PHPMA) nanocarriers were prepared, showing size and shape transformations from spheres, cylinders to raspberry-forming vesicles. DOX was readily loaded into NPs during PISA with relatively high encapsulation efficiency of 70 %, whereas the plain PISA-made vesicles could be functionalized with NAC and DOX at high yields. DOX-free NPs showed biocompatibility, whilst DOX-conjugated NPs imparted a concentration-dependent cytotoxicity, as well as an enhanced cell uptake compared to free DOX. The results demonstrated that the same PISA-derived self-assemblies enabled either *in situ* drug encapsulation, or post-polymerization surface engineering with useful functionalities upon tuning the macro-CTA block, thus holding promises for future drug delivery and biomedical applications.

Keywords: polymerization-induced self-assembly (PISA), block copolymers, drug-loaded nanoparticles, polymer-drug conjugates.



Graphical Abstract: PISA-prepared Block copolymer for *in situ* drug loading and post-PISA drug functionalization

HPMA based copolymer conjugates with octahedral molybdenum clusters for photodynamic therapy

R. Pola[1*], M.R. Tavares[1], T. Etrych[1], K. Kirakci[2], K. Lang[2], J. Zelenka[3], T. Ruml[3]

[1]*Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Prague, Czech Republic*
[2]*Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Řež, Czech Republic*
[3]*Department of Biochemistry and Microbiology, University of Chemistry and Technology, Prague, Czech Republic*
[*]*pola@imc.cas.cz*

Photodynamic therapy (PDT) represents a promising modality for the cancer treatment. In this work, we prepared biocompatible core-shell nanoparticles (NPs) for induced photodynamic therapy containing octahedral molybdenum clusters (OMC) compounds which behave as radiosensitizers. OMC have red luminescence, which is quenched by oxygen to produce singlet oxygen in high quantum yields. However, most of these compounds reported so far show a limited solubility in water and underwent hydrolysis connected with aggregation, sedimentation, and diminishing luminescence and singlet oxygen-sensitizing properties. This behavior prevented the investigation of their photophysical properties as well as *in vitro* biological activities in aqueous media. Aiming to overcome these shortcomings and thus open the possibilities for their real clinical application, these clusters were coated using biocompatible hydrophilic *N*-(2-hydroxypropyl)methacrylamide copolymers, therefore improving their water solubility and protecting them from aggregation. Moreover, luminescence properties and the quantum yields of singlet oxygen of these nanoparticles remained unchanged. The polymer layer ensures a prolonged circulation, negligible interaction with serum proteins and next possible advantage is their specific targeting to tumor cells.

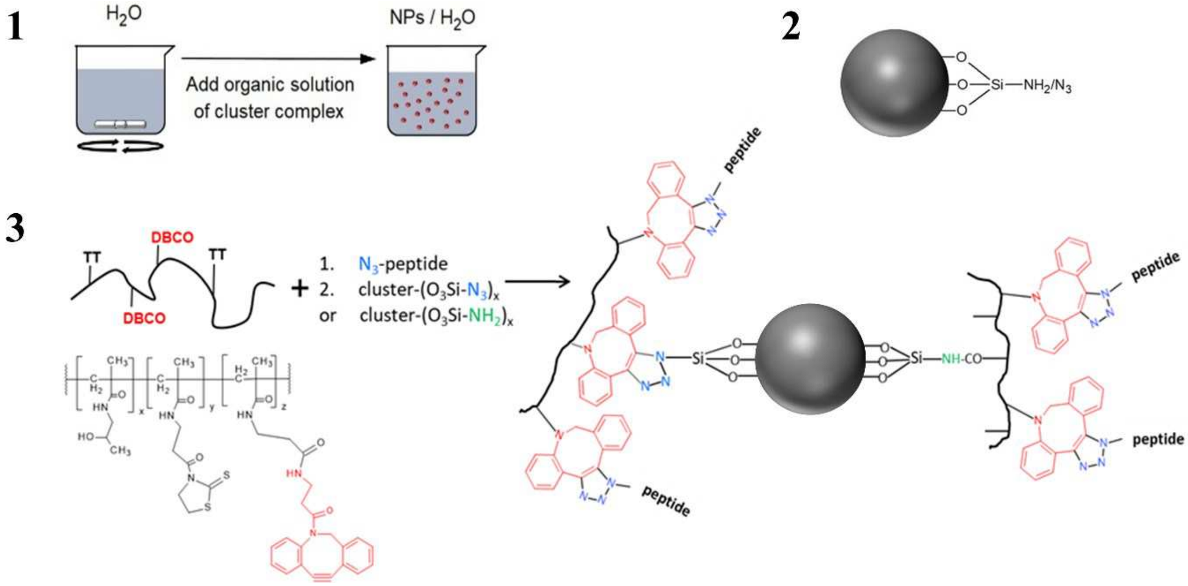


Figure 1. Strategy for the preparation of the core-shell nanoparticles: 1. Nanoprecipitation. 2. Their functionalization with organosilane. 3. Reaction of polymer precursor with azide-peptide and coating of Mo6 complex using either click chemistry or aminolytic reaction.

Keywords: HPMA conjugates; photodynamic therapy; octahedral molybdenum clusters; radiosensitizer; tumor treatment.

Acknowledgments
Financial support for this work is gratefully acknowledged from the Grant Agency of the Czech Academy of Sciences (grant No. 21-11688S).

Highly water-soluble polymer drug carriers intended for cancer treatment

S. Pytlíková[1]*, Jun Fang[2], P. Chytil[1], L. Čtveráčková[1], M. Filipová[1], T. Etrych[1]

[1]*Institute of Macromolecular Chemistry of the Czech Academy of Sciences*
Heyrovského nám. 1888, Prague 6, 162 00, Czech Republic
[2] *Faculty of Pharmaceutical Sciences, Sojo University, Kumamoto 860-0082, Japan*
**pytlikova@imc.cas.cz*

One of the main limitations of numerous low molecular weight cytostatic drugs is their non-specific biodistribution causing several adverse effects on healthy part of the organism during cancer treatment. This phenomenon together with fast blood clearance and frequently observed biotransformation results in low efficacy of classic anti-cancer drugs and necessity of repeated drug administration.

A way how to achieve enhanced therapeutic effect of classic cancerostatics is the use of biocompatible polymer carriers of these drugs. The passive tumor accumulation of polymer-drug conjugates in solid tumors based on the enhanced permeability and retention (EPR) effect increase theatment efficacy and avoid adverse effects. In recent decades, polymer carriers based on copolymers of *N*-(2-hydroxypropyl) methacrylamide (HPMA) were introduced as efficient drug carriers intended for delivery and controlled release of anticancer drugs in tumor tissue.[1] The basic prerequisite for high biocompatibility is the excellent non-fouling properties of the polymeric materials used. In the case of highly hydrophobic drugs, HPMA copolymers are no longer a suitable choice and the need for new highly hydrophilic and non-fouling polymers is obvious.

In this work we focused on the development of extremely water soluble polymer carriers based on *N*-(1,3-dihydroxypropyl) methacrylamide (DHPMA).[2] Employment of free radical polymerization (FRP) enabled the polymer and copolymer syntheses, however disperity ($Đ$) reached value close 2. Therefore, controlled radical reversible addition chain transfer (RAFT) polymerization was used instead to prepare polymers with defined molecular weight (M_w from 30 000 to 50 000 g/mol) and low dispersity ($Đ$ about 1.1). Prepared DHPMA copolymers were fully not cytotoxic when performed on various cell lines even at high concentrations. Moreover, the biodistribution experiment proved that the carrier do not significantly accumulate in healthy tissues.

Further on, we designed and prepared conjugates of DHPMA and HPMA copolymers with a model anticancer drug pirarubicin bound by pH-sensitive hydrazone bond (M_w 40 000 g/mol). Cytotoxicity tests of polymer conjugates proved negligible toxicity without any significant differences between used polymer carriers. Importantly, *in vivo* experiments on mice showed that DHPMA polymer conjugates, both prepared using either FRP, or RAFT polymerization, suppressed tumor growth more efficiently in comparison with appropriate HPMA polymer conjugates. Considering observed results, we are convinced that novel highly hydrophilic polymer-drug conjugates have a great potential as efficient drug delivery vectors.

Keywords: targeted drug delivery, polymer carriers, cancer treatment

Acknowledgments
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Ionic combisomes: A new class of biomimetic vesicles to fuse with life

Jonas Quandt,[1,2] Anna M. Wagner,[1,2] Dominik Söder,[1,2] Manuela Garay-Sarmiento,[1,2] Anton Joseph,[1,2] Vladislav S. Petrovskii,[3] Lena Witzdam,[1,2] Thomas Hammoor,[2] Philipp Steitz,[2] Tamás Haraszti,[1] Igor I. Potemkin,[1,3] Nina Yu. Kostina,[1,2] Andreas Herrmann[1,2] and Cesar Rodriguez-Emmenegger[1,4]*

[1] *DWI – Leibniz Institute for Interactive Materials, Aachen, Germany*
[2] *Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany*
[3] *Lomonosov Moscow State University, Moscow, Russian Federation*
[4] *Institute for Bioengineering of Catalonia (IBEC), Barcelona, Spain*
*****rodriguez@dwi.rwth-aachen.de*

The fabrication of biomembranes that closely replicate the properties and dynamic functions of natural cell membranes is a major challenge in the development of synthetic cells and their applications. Herein, we introduce a new concept for fully synthetic cell membranes based on a new family of amphiphilic comb polymers which self-assemble into vesicles, termed ionic combisomes (i-combisomes). These combs consist of a polyzwitterionic backbone to which lipid-like hydrophobic tails were linked by electrostatic interactions. Using a combination of molecular simulations, optical, electron, and force microscopies, we screened the self-assembly of a library of combs with tailored structural variations to unravel the structure–property relationship. We discovered that a high density of hydrophobic tails drives the formation of the membrane's core and forces the hydrophilic backbone into a rod conformation with nematic-like ordering confined to the water-bilayer interface. This specific molecular organization led to membranes that combine the biomimetic thickness, lateral mobility, and flexibility of liposomes with the stability of classic polymersomes. Such high mimicry of biophysical properties and the ability to locally remodel the molecular topology of their components allows them to harbor functional components of natural membranes and to fuse with living bacteria to "hijack" their periphery. This offers a powerful set of tools for designing the chemical and biological composition of the i-combisome membrane, providing a platform for fundamental studies, equipping synthetic cells with advanced functions and (bio)technological applications that go beyond biological limits.

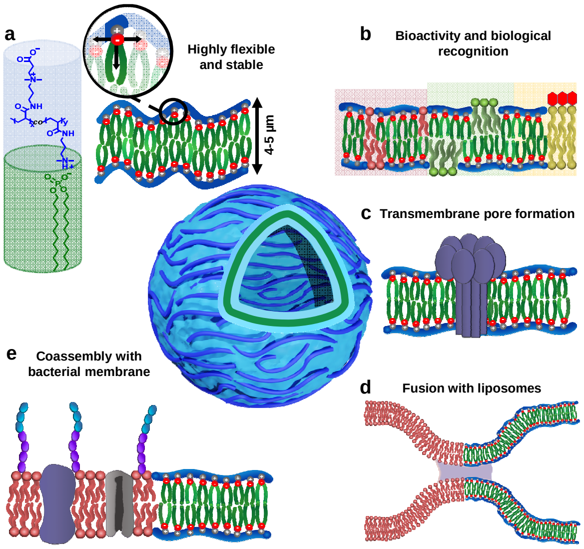

Figure 1. i-Combisomes concept: iCPs self-assembled into biomimetic giant unilamellar vesicles where the backbone is a rod confined at the water interface. (a) The chemical structure of iCP. In water, the iCPs form bilayers with biomimetic thickness and high flexibility. (b) Biofunctionalization with lipids and generation of raft-like domains. (c) Pore formation by pore-forming peptides. (d) Facile fusion with liposomes. (e) Formation of hybrid protocells by fusion with living bacteria.

Acknowledgments

European Commission EVPRO grant 814495-2; Deutsche Forschungsgemeinschaft (DFG) within the SFB 985.

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Poly(trimethylene carbonate-*co*-valerolactone) copolymers: promising materials for delivery of cancer therapeutics

L. Reinišová[1*], S. Hermanová[1], M. Reiniš[2], J. Brožek[1]

[1] *Department of Polymers, Faculty of Chemical Technology, University of Chemistry and Technology, Prague, Technická 5, 16628 Prague, Czech Republic*
[2] *Laboratory of Immunological and Tumour Models, Institute of Molecular Genetics of the Czech Academy of Sciences, Vídeňská 1083, 142 20 Prague, Czech Republic*
[*] *Lucie.Reinisova@vscht.cz*

Aliphatic poly(ester-carbonates) are promising materials in electronic and biomedical applications due to their tailorable properties, biocompatibility, and lower environmental impact. They can be synthesized via metal-free organocatalytic ring-opening copolymerization (ROCOP)[1] and their monomers can be obtained from biomass.[2] Furthermore, aliphatic poly(ester-carbonates) based on lactones and cyclic carbonates are a rising alternative to poly(lactide-*co*-glycolide) due to absence of *p*H lowering degradation products, which can present an issue in certain bioapplications. Most attention is given to their use in neuroregeneration, where they have shown high promise, while there are limited reports on their utilization in cancer therapy.[3] In this work, we analyzed the potential of poly(trimethylene carbonate-*co*-δ-valerolactone) (P(TMC-*co*-VL)) copolymers as materials for preparation of lipid-polymer hybrid nanoparticle systems (LPHN) for delivering cancer therapeutics. First, copolymers with various comonomer ratios were synthesized via ROCOP using 1,5,7-triazabicyclo[4.4.0]dec-5-ene as a catalyst and benzyl alcohol as an initiator. The copolymers were then used for preparation of LPHN via modified nanoprecipitation method with phospholipid-PEG conjugates as lipid shell materials. Doxorubicin (DOX) was chosen as a representative chemotherapeutic compound and superparamagnetic iron oxide nanoparticles (SPIONs) were selected as support therapeutics for repolarization of tumor-associated macrophages. The LPHN had diameters under 200 nm and PdI ≤ 0.2. DOX-loaded systems exhibited cytotoxicity towards a mouse tumor cell-line comparable to free DOX, while SPION-loaded systems displayed magnetic properties, which can be utilized for precision targeting towards solid tumors. Overall, P(TMC-*co*-VL) copolymers exhibited highly promising properties for applications in cancer therapy.

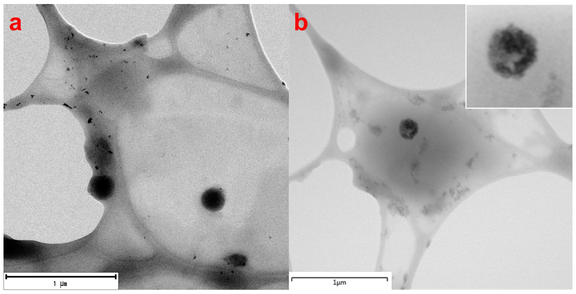

Figure 1 TEM images of P(TMC-*co*-VL) LPHNs with encapsulated SPIONs; a) nanoparticle cluster, b) nanoparticle with magnification.

Keywords: poly(ester-carbonates), organocatalysis, drug delivery, chemotherapy

Acknowledgments
This work was supported from the grant of Specific university research – grant No A2_FCHT_2021_085.

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Development of electrospun mats based on hydrophobic hydroxypropyl cellulose esters

Sofia Saraiva[1*], Patrícia Pereira[1,2], C.T. Paula[1], R. C. Rebelo[1], Jorge F.J. Coelho[1], Arménio C. Serra[1], Ana C. Fonseca[1]

[1] *CEMMPRE, Department of Chemical Engineering, University of Coimbra, Rua Sílvio Lima-Pólo II, 3030-790 Coimbra, Portugal*

[2] *IPN, Instituto Pedro Nunes, Associação para a Inovação e Desenvolvimento em Ciência e Tecnologia, Rua Pedro Nunes, 3030-199 Coimbra, Portugal*

[*]*sofiateixeira19@gmail.com*

Introduction: Electrospinning allows the preparation of mats with high porosity and surface area, suitable and controllable mechanical properties, and adaptive morphologies. These properties make electrospun mats highly desirable materials for biomedical applications, especially wound dressings. Both synthetic and natural polymers have been used to produce electrospun mats. Natural polymers can be considered as obvious candidates for the production of such mats due to their recognized biocompatibility. However, natural polymers are completely or partially insoluble in the most common low boiling point organic solvents used in electrospinning. Hydroxypropyl cellulose (HPC), a FDA approved cellulose derivative, is an exception, as it can be dissolved in some organic solvents [1]. However, it is not easily electrospun and it is highly susceptible to moisture absorption, which affects its mechanical properties, and ultimately leads to its dissolution. To avoid this, HPC is electrospun together with hydrophobic polymers, or it is previously modified and subjected to a crosslinking step after electrospinning [2], to obtain a mat with enhanced properties, especially in terms of resistance to moist environments. In this work, hydroxypropyl cellulose esters (HPCE) with long aliphatic chains were prepared and innovatively used in electrospinning to obtain hydroxypropyl cellulose (HPC)-based mats with enhanced resistance to moist environments. The mats are easy to obtain and do not require post-treatment (e.g. cross-linking) to overcome the premature loss of properties of cellulose-based materials when in contact with moisture[1].

Materials and methods: HPCE were obtained by the esterification of HPC with stearoyl chloride in mild conditions, for 24h. The electrospinning solutions were prepared with a final HPCE concentration of 35% (w/v). The solvent used was $CHCl_3$ containing 10% (v/v) DMF. The optimized electrospinning conditions were 15 kV, 1.5 ml/hr, with a collector distance of 10 cm, and a humidity around 40%.

Results: HPCE with two different degrees of substitution (DS) were successfully synthesized. The HPCE-based electrospun mats exhibited a highly porous structure that was almost free of defects. They exhibited a swelling capacity of over 115%. In vitro hydrolytic degradation tests demonstrated the high structural integrity of the mats (< 5% weight loss) over a 30-day period. The in vitro cytotoxicity tests showed that the mats of HPCE were cytocompatible and promoted the adhesion, proliferation and spreading of NIH3T3 fibroblast cells.

Conclusion: Electrospun mats of HPCE were successfully fabricated for the first time. The swelling ability of the mats was dependent on DS and showed resistance to humid environments, even without post-treatment. The HPCE showed no deleterious effect on NIH3T3 fibroblast cells. These data suggest that the HPCE mats could be interesting materials for wound dressings as well as for other tissue engineering applications.

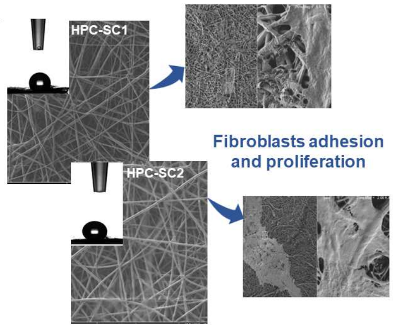

Fig.1. Characterization of the mats obtained using HPC esters

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Bioactive polyurethanes: goals and methods of creation

Yu. Savelyev, L.Robota, O.Gonchar, L.Markovska, O.Akhranovych*

Institute of Macromolecular Chemistry, NAS of the Ukraine, Kyiv, Ukraine
* *elena_akh@ukr.net*

The use of polymers as carriers of biologically active substances (BAS) and/or modifiers allows to create fundamentally new BAS with a prolonged biological effect and differing in the type of polymer-BAS bond.
Created polyurethanes (PU): ***a)*** linear PU with immobilized biologically active (metal)-organic compounds as extenders and/or blockers of the macro chain, including by transforming the existing end group; ***b)*** aqueous PU-dispersions based on ionomeric PUs (IPUs) with immobilized (in)organic compounds as macro chain extenders and salt-forming agents; ***c)*** linear PU containing nanoparticles [Ag, Cu]; ***d)*** polyurethane-polyacrylates obtained by the emulsion method using as an emulsifier ionomeric PU, immobilized BAS as a macro chain extender; ***e)*** polyurethane foams with immobilized (in)organic compounds and BAS of natural origin - essential oils.
By structural modification, using PU, obtained: i) bactericidal - active against the main pathogens of nosocomial infections (*Staph.aureus, E. coli Klebsiella pn., Pseud. Aerug., Proteus vulgaris*) - biologically active protective coatings and ***ii)*** fungicidal - active in relation to *Aspergillis oryzae (Ahlburg) Cohn, Aspergillis niger van Tieghem, Aspergillis niger van Tieghem, Aspergillis terreus Thom, Chaetomium varioti Bainier, Penicillium funiculosum Thom, Penicillium chrysogenum Thom, Penicillium cyclopium Westling, Trichoderma viride Pers. ex Fr.* PUs are able to inhibit the growth of microorganisms on their surface for up to 3-6 days and, thus, prevent infection of the environment with spores of pathogenic microorganisms. To solve the urgent problem of combating a complex of pathogenic microorganisms in urological practice used a complex silver ion, in the technology of functional IPU created aqueous polyurethane dispersions (APD) with antimicrobial and antifungal properties against *gram-positive* and *gram-negative* bacteria for use in mold and mildew, in particular, to protect clothing, bedding, and dressings.
In order to create biologically active water-emulsion coatings for the protection of interior surfaces in medical institutions, emulsion polymethyl methacrylate was obtained using synthesized biologically active IPU as an emulsifier. Aqueous polymer emulsions show antimicrobial activity against pathogens of nosocomial infections (*Staph. Aureus, E. coli, Candida*), guarantee prolonged sterility of the indoor atmosphere.
By transforming the terminal hydrazide group of UDMH-based polyurethanes into hydrazine-type structures by reacting with alkylhalides and arylsulfochlorides, polymers with fungicidal properties against molds and yeasts were obtained: *Aspergillis oryzae (Ahlburg) Cohn, A.niger van Tieghem, A.terreus Thom, Chaetomium varioti Bainier, Penicillium funiculosum Thom, P.chrysogenum Thom, P.cyclopium Westling, Trichoderma viride Pers. ex Fr., Candida albicans, C. tropicalis, C. krusei, C. parapsilosis, C. guilliermondii.*
Biologically active thermoplastic PUs nanocomposites with in situ polycondensation with silver and copper content from 15 to 667 ppm, as well as PUs nanocomposites with their joint content, have been developed. PUs are characterized by a complex of bioactivity - bactericidal and fungicidal properties, as well as biocompatibility.
A range of polyurethane foam materials with a complex of step-by-step input properties has been developed: prolonged action bactericidal action against *E. coli ATC 25922, E.coli 150, Klebsiella pneumon 6447, S. aureus 180, Pseudomonas aeruginosa 8180, Proteus mirabilis F – 403, Proteus mirabilis 6054, Pr.vulgaris 8718;* self-adhesive properties; local anesthetic action. PUFs are characterized by high hydrophilicity and lack of toxic effects.

Keywords: polyurethanes, aqueous PU-dispersions, polyurethane-polyacrylates, polyurethane foams, bactericidal and fungicidal properties, antimicrobial activity.

Formulation of new Antibiotics in Poly(2-oxazoline)-based Micelles

Martin Schmidt[1*], Rainer Jordan[1]

[1]*Technische Universität Dresden, Chair of Macromolecular Chemistry, Dresden, Germany*
[*]*Martin.Schmidt9@tu-dresden.de*

Resistant bacteria pose a challenge to the healthcare system. Polycyclic polyprenylated acylphloroglucinols (PPAPs) are a class of natural compounds with promising antibiotic properties against such germs *in vitro*.[1] The practical application of these novel antibiotics *in vivo* is however limited by their low water solubility. Drug transport systems are of interest to solve solubility problems, but also to modify the biodistribution of drugs. One possible example are drug loaded micelles. The encapsulation process is based on the self-assembly of amphiphilic molecules and the hydrophobic drug in water. This simple method of formulation is especially interesting since it does not require chemical modification of the drug.[2]

Poly(2-oxazoline)s (POx) are a versatile polymer class, well suited for drug delivery purposes. They are synthesized in the living cationic ring-opening polymerization of 2-substituted-2-oxazolines. The living character of this polymerization enables the synthesis of well-defined block-copolymers through sequential monomer addition. In an A-B-A triblock copolymer, comprised of hydrophilic 2-methyl-2-oxazoline (A) and a hydrophobic 2-substituted-oxazoline (B), the middle block B can be varied to formulate different drugs.[3]

The aim of this work was to formulate PPAPs in POx-based micelles (figure 1). To this end, two different PPAPs, as well as multiple POx species where synthesized. The hydrophobic middle block B was systematically changed and the formulated concentration was evaluated by high performance liquid chromatography. Both water insoluble PPAPs were successfully formulated in POx-based micelles and dissolved to more than 5 g/l in water. This corresponds to loading capacities (mass of formulated drug divided by total mass of the drug transport system) of over 30 % and might offer a chance for their intravenous application.

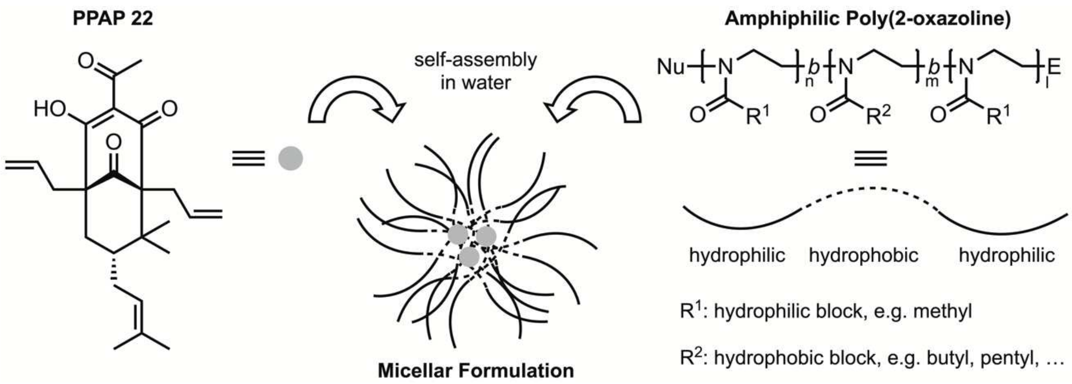

***Figure 1:** Polycyclic polyprenylated acylphloroglucinol 22 (PPAP 22)[1] is formulated in micelles formed by amphiphilic poly(2-oxazoline)s.*

Keywords: Poly(2-oxazoline), Polycyclic Polyprenylated Acylphloroglucinol, Antibiotic, Micelle, Formulation

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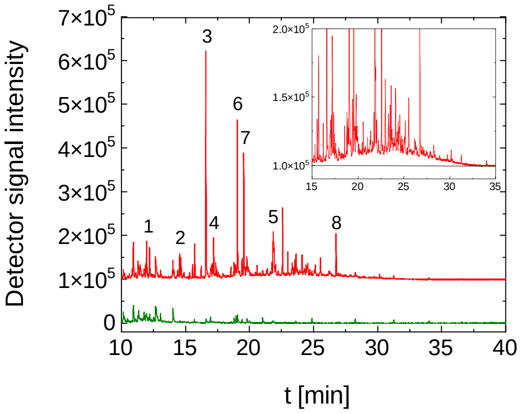
New methods for purification of water-soluble polymers and monomers: how to get rid of hydrophobic contaminants

M. Sedlák*, D. Rak

Institute of Experimental Physics, Slovak Academy of Sciences, Košice, Slovakia
**marsed@saske.sk*

Water-soluble polymers are commonly purified by methods such as dialysis and ultrafiltration, in which low molecular mass contaminants are removed via a passage through a membrane with pores large enough for contaminants and small enough to prevent the passage of polymers. In every case, contaminants must be water-soluble in order to be able to be removed from a polymer solution in this way. Hydrophobic contaminants therefore represent a problem. We will introduce in this presentation new methods of purification of water-soluble polymers and monomers from hydrophobic contaminants, which are subject of granted and pending patents [1-3] and are based on interesting physico-chemical research results [4]. These methods are cost-effective and enabling purification to high degrees of purity (below 1 ppm). The source of hydrophobic contaminants in water-soluble polymers is predominantly the monomer, but also other compounds such as monomer stabilizers, initiators, quenchers, and emulsifiers in emulsion polymerizations. A secondary contamination due to manufacturing processes and storage is also possible. If one takes common monomer purity ≥ 99%, then the contaminants content is ~ 10g/kg (grams, not micrograms or milligrams!). In practice, only a fraction of this amount represents hydrophobic contaminants, nevertheless their content is anyway substantial. We have studied in detail [4] behavior of hydrophobic contaminants in water-soluble compounds upon dissolving in water. At concentrations which correspond to real situations in practice, hydrophobic contaminants neither molecularly solubilize nor macrophase separate, but instead undergo mesoscopic solubilization [4]. The whole volume of solution is homogeneously filled with nanoparticles or nanodroplets comprising hydrophobic contaminants. A detailed knowledge of these nanoobjects, their occurrence, stability over time, mechanical strength, and shape stability enables us to eliminate hydrophobic contaminants by filtering out mesoscopic objects, based on a proper choice of filter pore sizes and filtration pressures [1,2]. In the case of purification of polymers instead of monomers, situation is slightly different in that the hydrophobic contaminants tend to adhere to polymer chains. It was found [3] that upon ionization of chains, hydrophobic contaminants are expelled to bulk water where they are forced to self-assembly into mesoscopic nanoobjects. Given the properties and importantly also the size of these nanoobjects (larger than the size of most polymer chains), it is possible to separate hydrophobic contaminants from polymers by filtration with a proper choice of pore sizes and filtration pressures.



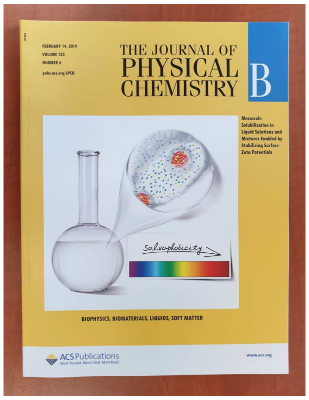


Fig. 1. GC-MS HS-SPME elugrams obtained on aqueous solution of sodium polymethacrylate before filtration (red) and after filtration (green). Elugrams are vertically shifted for the sake of clarity. 1–dodecane, 2–tridecane, 3–bifenyl, 4–tetradecane, 5–hexadecane, 6–dodecanol, 7–2-tridecanone 8–isopropyl tetradecanoate. The inset indicates a large number of hydrophobic contaminants which elute simultaneously.

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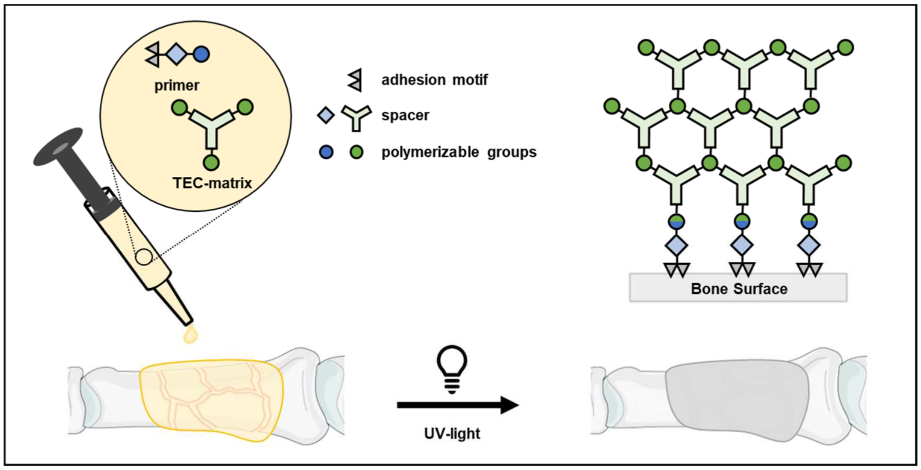
One-Step Photopolymerizable Adhesives for Bone Fracture Fixation

P. Steinbauer[1,2,3], L. Sinawehl[1,2,3*], R. Liska[2,3], S. Baudis[1,2,3]

[1]*Christian Doppler Laboratory for Advanced Polymers for Biomaterials and 3D Printing, Vienna, Austria*
[2]*Institute of Applied Synthetic Chemistry, TU Wien/E163-MC, Vienna, Austria*
[3]Austrian Cluster for Tissue Regeneration
[*]*lisa.sinawehl@tuwien.ac.at*

For the treatment of complicated bone traumata, such as comminuted fractures, conventional means of fracture fixation (*i.e.* plates, screws or casts) cannot be used or result in severe bone loss. In such cases, biocompatible bone adhesives are needed, comprising advantages such as shorter operation times, homogeneous force distribution and no need for revision surgeries [1]. Despite three decades of research, no surgically realizable bone glue has been identified, due to high requirements such as biocompatibility, sufficient bonding strength and ease of usage [2]. In this work, we present the first-known bone adhesive system, based on thiol-ene “click” chemistry (TEC), which is curable by UV-light in a fast one-step process applicable in surgeries. Inspired by self-etching dental adhesives, the one-step formulations are comprised of matrix monomers, thiols and adhesive molecules, so-called primers. These newly synthesized primer molecules contain adhesion motifs with high binding affinity to bone and implants, and polymerizable groups for matrix incorporation [3]. By selecting ene moieties with different reactivity towards the thiol component, improved primer incorporation into the polymer network and a 1-step process were achieved. Results show, that this easily applicable system exhibits exceptional shear bond strength on bone and implant surfaces, which is significantly higher compared to commercial bone glues currently reviewed by the FDA. First *ex-vivo* indentation tests were highly promising and *in-vitro* biocompatibility was confirmed. Hence this adhesive system combines practicability and applicability and paves the way towards future fracture treatment.



Schematic principle of the 1-step bone adhesive system.

Acknowledgments

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PMMA microcapsules for elimination of SARS-CoV-2

Vânia I. Sousa[1], Joana F. Parente[1], Juliana F. Marques[1,2], Carla Calçada[3,4], Maria I. Veiga[3,4], Aldo Costa[2], Nuno S. Osório[3,4], Carlos J. Tavares[1*],

[1]Centre of Physics of the Minho and Porto Universities, Campus of Azurém, 4804-533 Guimarães, Portugal
[2]Interhigiene - Indústria De Produtos De Higiene Lda., Rua General Humberto Delgado, nº 588 4765-546 Serzedelo (Guimarães), Portugal
[3]Life and Health Sciences Research Institute (ICVS), School of Medicine, University of Minho, Campus Gualtar, 4710-057 Braga, Portugal
[4]ICVS/3Bs—PT Government Associate Laboratory, 4806-909 Guimarães, Portugal
**ctavares@fisica.uminho.pt*

The emergence of SARS-CoV-2 virus has become a serious threat to public health and frequent surface disinfection begun to play a key role in controlling COVID-19. Disinfection products available on the market are effective in a very short space of time, due to their high rate of evaporation, corrosivity and immediate action, implying frequent applications on surfaces to be disinfected [1]. Therefore, the market need to develop new materials that maximize the action of these disinfecting agents, in order to prolong the sterilization time and reduce the frequency of their application [2]. Microencapsulation appears as an alternative to overcome this limitation, providing stability to the active agents of disinfectants, allowing the safe transport of this type of substances, which are normally extremely volatile [3]. Hydrogen peroxide (H_2O_2) is highly used in disinfectant products due to its bactericidal, sporicidal, fungicidal potencial and the ability of eliminate viruses that includes SARS-CoV-2. However, the synthesis of microcapsules filled with aqueous compounds, such as H_2O_2, is under explored [4]. Polymethylmethacrylate (PMMA) microcapsules were developed with encapsulated H_2O_2, used as active agent for elimination of SARS-CoV-2 virus. Morphological and thermal analysis showed that PMMA-H_2O_2 microcapsules have a spherical shape and a smooth structure with low porosity and high thermal stability. Non-fabric substrates functionalized with PMMA-H_2O_2 microcapsules were tested by a highly sensitive and specific polymerase chain reaction (PCR)-based detection method to evaluate its efficacy in SARS-CoV-2 elimination by measuring its nucleic acid quantity. The highest percentage of viral nucleic acidelimination was obtained when exposing the viral sample for 1h to PMMA-H_2O_2 microcapsules, resulting in an elimination >97% of the coronavirus. Hence, it is demonstrated that this microcapsule system is efficient for SARS-CoV-2 elimination and inherent surface disinfection.

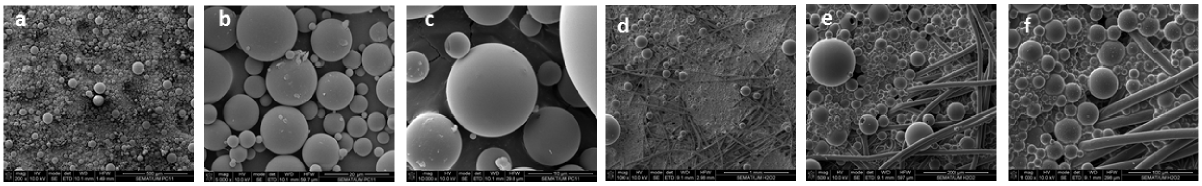

Figure 1 - Scanning electron microscopy micrographs of PMMA-H_2O_2 microcapsules with magnification of (a) 200x, (b) 5,000x and (c) 10,000x; non-woven fabric samples with PMMA-H_2O_2 microcapsules with magnification of (d) 100x, (e) 500x and (f) 1,000x.

Keywords: SARS-CoV-2, COVID-19, microcapsules, microencapsulation, controlled release, disinfection

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Material interaction between amphiphilic carriers and free chains of hyaluronic acid in solutions designed for electrospinning

K. Skuhrovcová[1,2*], A. Kotzianová[1], Z. Hrubá[1], O. Židek[1], F. Ondreáš[1], V. Velebný[1]

[1]*Contipro a.s., Dolní Dobrouč 401, Dolní Dobrouč 561 02, Czech Republic*
[2]*Centre of Polymer Systems, Tomas Bata University in Zlin, Třída Tomáše Bati 5678, 760 01 Zlín, Czech Republic*
**Kristyna.Skuhrovcova@contipro.com*

Electrospinning is a technologically simple process, but to produce samples without defects, it is necessary to find suitable parameters as well as the best composition of polymer solutions. Usually, synthetic and/or natural polymers are used along with various additives, which could be biologically active. Moreover, these additives could be electrospun encapsulated in a secondary carrier such as nanoparticles or amphiphilic aggregates. This encapsulation could bring a lot of benefits (e.g., higher encapsulation efficacy, more efficient transdermal penetration), but it also complicates the parameterization of the solution. Carrier systems are sensitive to ambient pH, concentration and environmental viscosity. [1] Usually, the secondary carriers are prepared separately/externally and added to the dissolved polymer (mostly in lyophilized form). We focused on the "*in situ*" preparation of aggregates in one solution with spinning polymers, so the aggregate doesn´t undergo a double state change to dry form. In this work, material interactions between the secondary carriers and free dissolved polymers were experimentally investigated when combining the common composition of a spinning solution based on hyaluronic acid (HA) and synthetic polyethylene oxide (PEO)[2] with amphiphilic aggregates of modified hyaluronan, which have the ability to incorporate a specific hydrophobic active substance into their inner structure. It was verified that even polymers of the same nature have a non-binding material interaction, which is influenced especially by three parameters: the concentration of free HA chains in solution, its molecular weight and the ratio between free HA and PEO. This interaction is manifested by a significant change in the size and shape permanence of the secondary carrier particles. It has been shown that a suitable combination of these parameters can create a stable formulation, which minimizes the effect of this interaction and at the same time creates a suitable water-based solution for electrospinning. Stabilization of the solution also should reflect the stability of aggregates during spinning process and afterwards in dry form. Degree of interaction and its development were investigated primarily by confocal fluorescence microscopy using fluorescent dyes and rheological measurements. [3]

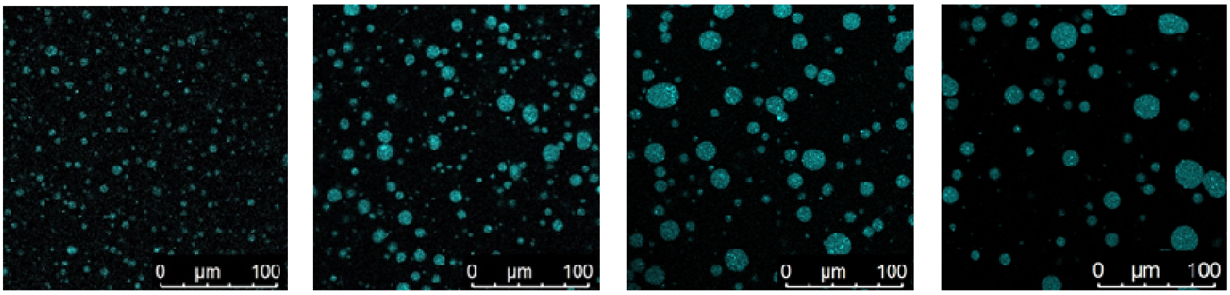

Fig.1 Diameter differences of amphiphilic nanoparticles with increasing amount of HA and decreasing amount of PEO in solution (→)

Keywords: hyaluronic acid, amphiphilic particles, nanofibers, incorporation, material interaction

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Mucin-containing physically cross-linked PVA hydrogel for in vitro testing of mucoadhesion

Gergely Stankovits[1*], Benjámin Gyarmati[1] and András Szilágyi[1]

[1]*Department of Physical Chemistry and Materials Science, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary*
E-mail: stankovits.gergely@vbk.bme.hu

Mucoadhesive drug delivery systems are capable to adhere to the surface of mucosa membranes and provide a prolonged drug release bypassing the first pass metabolism [1]. The strength of adhesion is conventionally determined by tensile tests on animal tissues. However, the preparation and storage of animal mucosa samples are difficult and the reproducibility of measurements is not always satisfactory [2]. Here we describe the preparation of a semi-synthetic mucosa-mimetic material, which can be produced easily by the physical cross-linking of polyvinyl alcohol (PVA) containing the mucin protein (Mucin/PVA), which is the main compomonent of the mucus covering the mucosal membranes [3]. The hydrogel was characterized by ATR-FTIR, SEM and oscillatory rheology. Tensile test was used to determine the strength of adhesion using polymer tablets made of positively charged chitosan, negatively charged poly(acrylic acid) (PAA) and neutral hydroxypropylmethylcellulose (HPMC). Zeta potential of the polymers used and that of mucin are shown in Figure 1A. Chitosan as a positively charged polymer showed enhanced adhesion on Mucin/PVA substrate compared to mucin-free PVA (Figure 1B) showing the determining role of electrostatic interactions in mucoadhesion.

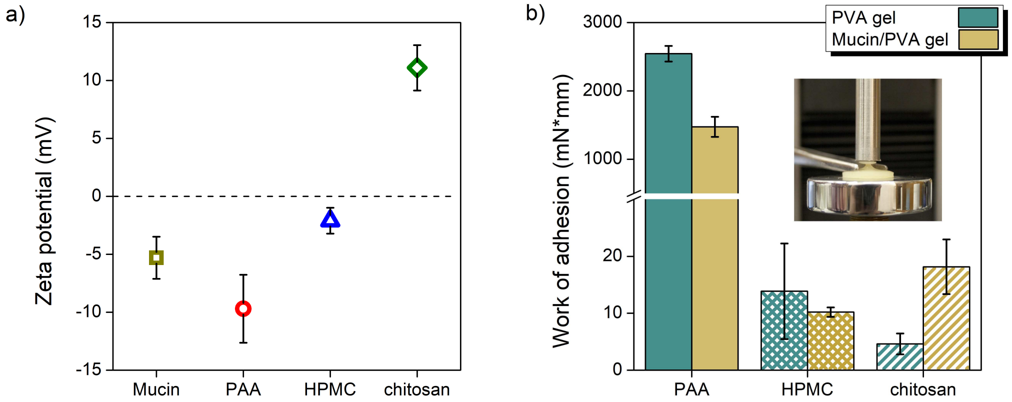

Figure 1 (a) Zeta potential of mucin dispersion and polymer solutions (b) adhesion measurements with polymer tablets comparing Mucin/PVA and mucin-free PVA hydrogel substrate

Keywords: poly(vinyl alcohol), freezing–thawing gelation, mucosa mimetic material

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Polylactide-based nanofibrous membrane as a substrate for cultivation and transplantation of retinal pigment epithelial cells

H. Studenovská[1], J. Nováčková[1], L. Machová[1], O. Janoušková[2], M. A. Thottappali[1], V. Proks[1]

[1]Institute of Macromolecular Chemistry, Academy of Sciences of the CR, Prague 6, Czech Republic
[2]University of J.E.Purkyně, Ústí nad Labem, Czech Republic
**studenovska@imc.cas.cz*

The transplantation of retinal pigment epithelial (RPE) cells via nanofibrous membrane could be a promising therapeutic option for the treatment of an age-related macular degeneration or other degenerative retinal disorders. In this work, we compare two conventional culturing membranes for retinal tissue engineering made either from polyethylene terephthalate (PET, track-etched, thickness 10 µm, pore density 1×10^{8} cm^{-2}) or polyimide (PI, track-etched, thickness 7 µm, pore density $2{,}2\times10^{7}$ cm^{-2}) with cell carrier based on 400-nm-thick poly(L-lactide-DL-lactide) fibres (thickness 4 µm, porosity 80%). Nanofibrous membranes were prepared by electrospinning that easily allowed an embedding of a supporting frame. Such a frame enables not only handling without irreversible folding of carrier and keeping a side-orientation of the sample while seeded with cells, but also to regain membrane's flat shape when inserted into the subretinal space during surgery. ARPE-19 cells were seeded onto PET, PI and nanofibrous membranes. Viability of ARPE-19 cells was monitored in different stages of sample preparation. After cutting of samples from inserts by punch there was no significant difference in viability of ARPE-19 cells in all membranes. To keep sterility of samples, a femtosecond laser to cut the samples was applied. PET and PI membranes were impossible to cut by laser. In nanofibrous membranes viability of cells after laser cutting was similar to those after using a punch. Thus, a femtosecond laser proved as a powerful tool in preparation of samples for retinal tissue engineering in sterile conditions. Viability of ARPE-19 cells in nanofibrous membranes were tested also after loading to the surgical injector with a flat loading tube. Loss of cells during loading is as low as 15%. The presented ultrathin, highly porous, and surgically convenient cell carriers have key characteristics in order to improve the integration and the functionality of transplanted RPE cells.

Keywords: nanofibrous membrane, PDLLA, RPE cells

Acknowledgments
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Synthesis and study of PLA/- and PLGA/poly(ethylene adipate) copolymers for the preparation of sustained release spray-dried microparticles

E. Christodoulou, A. Zamboulis, Z. Terzopoulou*, D. Bikiaris

Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece
terzoe@gmail.com

Biobased and biodegradable aliphatic polyesters, such as poly(lactic acid) (PLA), poly(lactic-co-glycolic acid) (PLGA), poly(ε-caprolactone) (PCL), poly(alkylene succinate)s, polyglycerol hyperbranched polyesters etc. serve as excellent candidates for a broad range of applications (biomedical, pharmaceutical, agricultural and industrial). Recent strategies for the development of drug delivery systems suggest the use of such polymers, which present great potential for the effective delivery of a broad range of active ingredients. PLA and PLGA, the polymers of interest here, are commercially available, FDA-approved, bio-based synthetic polymers, widely used in biomedical applications due to their biocompatibility, biodegradability and excellent properties. Further tuning of these properties can been achieved, by the synthesis of either polymer nanocomposites or copolyesters, using biobased comonomers. In this sense, poly(ethylene adipate) (PEAd), a biodegradable linear, aliphatic, non-toxic polyester, originating from adipic acid and ethylene glycol, can be employed to produce copolymers with enhanced biodegradation rates and new attractive properties.

The present work describes the synthesis of PLA/PEAd and PLGA/PEAd copolymers (of 90/10 and 75/25 weight ratios), through a reactive melt-mixing (RMM) method, namely a melt transesterification-induced intermolecular chain exchange reaction. The newly produced aliphatic polyesters were characterized by a combination of techniques (NMR and FT-IR spectroscopy, X-ray diffraction, calorimetry, polarized optical microscopy etc.). They were then used to prepare microparticles for sustained release drug delivery applications using spray-drying.

Acknowledgments

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Mechanistic insights in controlling host-guest (de)complexation by thermoresponsive polymer phase transitions

Hui Guo[1,2]*, Gaëlle Le Fer[3], Thi Nga Tran[2], Aurélie Malfait[3], Dominique Hourdet[2], Alba Marcellan[2], François Stoffelbach[4*], Joël Lyskawa[3], Richard Hoogenboom[5] and Patrice Woisel[3]*

[1] School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai 519082, China

[2] Soft Matter Sciences and Engineering, ESPCI Paris, PSL University, Sorbonne University, CNRS, F-75005 Paris, France

[3] Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France

[4] Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, UMR 8232, Equipe Chimie des Polymères F-75252 Paris Cedex 05, France

[5] Supramolecular Chemistry Group, Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281 S4-bis, 9000 Ghent, Belgium

*Corresponding Authors: guoh37@mail.sysu.edu.cn, francois.stoffelbach@sorbonne-universite.fr, patrice.woisel@centralelille.fr

The combination of (thermo)responsive polymers with supramolecular chemistry, recently allowed the development of adaptative materials based on the reversible regulation of host-guest complexation. [1] The properties of these artificial systems rely on their synthetic design, which implies a perfect understanding of the mechanisms triggering the thermo-induced decomplexation. [2] Nevertheless, the origin of this phenomenon is still unclear. To investigate the effect of phase separation mechanism on the host-guest (de)complexation behavior, different naphthalene-functionalized (guest) thermoresponsive polymers, including lower critical solution temperature (LCST) and upper critical solution temperature (UCST) polymers, were prepared. The host-guest complexation of the polymers with cyclobis(paraquat-*p*-phenylene) (Blue Box) was investigated in water at different temperatures. Host-guest complexation was lost upon heating-induced hydrophobic phase separation of LCST-polymers, in contrast, the host-guest complex was retained upon cooling-induced hydrogen bond-driven phase separation of a UCST polymer. This comparative analysis showed that the mechanism behind the thermoresponsive polymer phase separation is the key factor that dominates the host-guest (de)complexation.

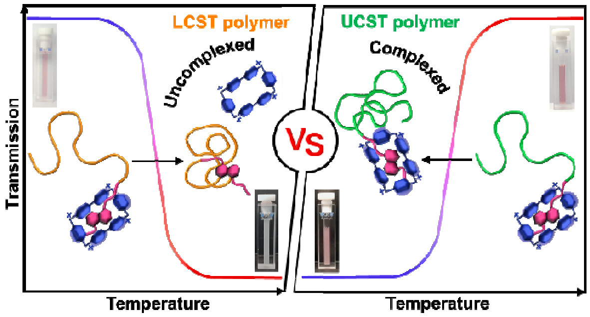

Figure 1. The host-guest decomplexation due to the LCST thermoresponsive polymer phase separation (left) and the retention of host-guest complexes durig phase separation of UCST polymer (right)

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The new generation dental composites with reduced polymerization shrinkage

Monika Topa-Skwarczyńska[1*], Joanna Ortyl[1,2,3]

[1]Cracow University of Technology, Faculty of Chemical Engineering and Technology,
Laboratory of Photochemistry and Optical Spectroscopy,
Warszawska 24 St. 31-155 Cracow, Poland,
[2]Photo HiTech Ltd., Bobrzyńskiego 14, 30-348 Kraków, Poland
[3]Photo4Chem sp. z o.o.., Lea 114, 30-133 Kraków, Poland
[*]*Corresponding Author's:* monika.topa@doktorant.pk.edu.pl

The most commonly used photo-cured dental materials are dimethacrylic compounds, which guarantee the production of high crosslinking networks. Nevertheless, these monomers have significant polymerization shrinkage, which is not decent in the dentist. [1-2] It is well known that cationic monomers have a very low polymerization shrinkage. Therefore, in our work, we believed that the use of photocurable systems containing more than one type of monomer with different polymerization mechanisms is an interesting alternative for conventional free-radical cross-linking dimethacrylates organic matrix. Dual cure formulations based on a combination of cationic monomer and free-radical-type monomer can form interpenetrating networks to adjust the photopolymerization rate and cross-linking density suitable and; therefore, control the final properties for dental applications.

The main advantage of these IPNs is that they combine the properties of the two kinds of the polymer network. The photocured, interpenetrating polymer networks seem to be a promising way to obtain photocurable polymeric materials characterized by improved properties, such as high-damping effect, lower shrinkage upon photopolymerization and better adhesion properties.

On the other hand, the commonly used photoinitiating system for the radical photopolymerization process is the system based on camphorquinone/aromatic amine. In the step of generating radicals in the photolysis process, amine interacted with the excited camphorquinone molecule. This process involves the transfer of the electron from the amine to the ketone, followed by the abstraction of the proton. The radicals initiating the polymerization process are mainly radicals formed from amines. The basic problem of this system is the fact that too high a concentration of camphorquinone in dental composites may generate a yellow colour. Such discolouration can influence the aesthetics and quality of the final product. In addition, amines are cytotoxic and genotoxic factors. [3-5]

In this work, we present new initiating systems dedicated to simultaneous radical and cationic photopolymerization processes. Spectroscopic investigations including absorbance and photolysis measurements were performed. The kinetics of the photopolymerisation process were studied using Real-Time FT-IR and Photo-DSC techniques. Rheological measurements were also performed using a Modular Compact Rheometer MCR302e to determine, among others, polymerisation shrinkage.

Acknowledgments

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Poly(glycerol methacrylate)-coated upconverting nanoparticles synthesized by miniemulsion polymerization

T. Vasylyshyn*, V. Patsula, D. Horák

Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 162 06 Prague 6, Czech Republic (www.imc.cas.cz)
*vasylyshyn@imc.cas.cz

Lanthanide-doped upconverting nanoparticles (UCNPs) are a new class of light-emitting materials possessing unique ability to convert near-infrared light into visible one using anti-Stokes shift. UCNPs can be used in bioimaging and photodynamic therapy of cancer. However, the application of neat UCNPs in biomedicine is limited due to their aggregation and leakage of lanthanide and fluoride ions resulting from particle degradation in buffers and biological fluids. This decreases the luminescence of the particles and increases their toxicity. Thus, the development of surface-modified UCNPs with excellent colloidal and chemical stability is crucial for use of these materials in different theranostic applications.

The aim of this work was to prepare poly(glycerol methacrylate)-coated UCNPs via miniemulsion reversible addition-fragmentation transfer (RAFT) polymerization. To achieve this, the uniform UCNPs were prepared and functionalized with hydrophobic penta(methyl ethylene glycol) phosphate methacrylate (SIPOMER) to reduce the ion leakage and allow particle participation in the miniemulsion polymerization (Figure 1 a, b). Then, the poly(glycidyl methacrylate)-coated multicore UCNPs were synthesized via miniemulsion RAFT polymerization (Figure 1 c, d). As a surfactant and chain transfer agent, pre-synthesized poly(glycerol methacrylate)-based macroRAFT was used. The amount of polymer on the particle surface and the particle size were controlled by adjusting synthesis parameters. The hydrophobic poly(glycidyl methacrylate) shell is suitable for the incorporation of theranostic agents including drugs and photosensitizers and it can be further transformed in hydrophilic shell by hydrolysis.

The synthesized surface-modified multicore-shell UCNPs with diameters up to 500 nm were characterized by dynamic light scattering and transmission and scanning electron microscopy. The presence of polymer layer on the surface was confirmed by IR and fluorescent emission spectroscopy and thermogravimetric analysis.

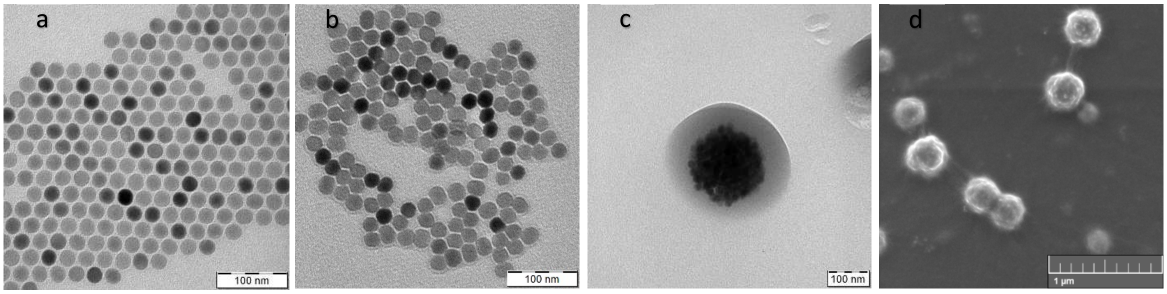

Figure 1. TEM micrographs of (a) neat UCNPs, (b) SIPOMER-stabilized UCNPs, and (c) poly(glycidyl methacrylate)-coated UCNPs. (d) SEM micrograph of (c).

Keywords: lanthanide-based upconverting nanoparticles, miniemulsion polymerization, RAFT

Acknowledgments

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Engineering nanogels for drug delivery to pathogenic *Aspergillus fumigatus*

T. Vogel[1*], Y. Yu[2], A. Beilhack[2], J. Groll[1], K. Albrecht[1]

[1]Department of Functional Materials in Medicine and Dentistry, University of Würzburg,
Pleicherwall 2, 97070 Würzbur
[2]Department of Medicine II, Center for Experimental Molecular Medicine, Würzburg University Hospital,
Zinklesweg 10, 97078 Würzburg, German
[*]theresa.vogel@fmz.uni-wuerzburg.de

The opportunistic mold *Aspergillus fumigatus* is one of the main fungal pathogens causing invasive infections in immunocompromised humans. Unfortunately, conventional antifungal agents are associated with low therapeutic efficacy and/or severe side effects.[1] A promising alternative treatment approach is nanoparticle-based antifungal therapy. It leads to increased drug bioavailability and reduced toxicity, both boosting treatment efficacy.[2] We previously showed that poly(glycidol)-(PG)-based nanogels have great potential when being used as vehicle for antifungals but need improvement when being co-incubated with fungus in the presence of serum.[3] In this study the nanogels were modified to increase their affinity towards the positively charged cell wall of fungal hyphae by tuning their surface charge to more negative values. To form nanogels PG was modified with thiol groups as cross-linking moieties. Thiolated PG was synthesized via a three-step procedure beginning with an anionic ring opening polymerization followed by STEGLICH esterification for introduction of thiol groups. PG-based nanogels were prepared using an inverse nanoprecipitation technique as described before.[3] The polymer was precipitated in acetone succeeded by oxidation leading to formation of hydrogel nanoparticles. To modify the nanogel surface charge an additional quenching step was introduced after oxidation. To analyze the influence of a more negative surface charge on the interaction between *Aspergillus fumigatus* hyphae and nanogels, co-incubation was carried out in *Aspergillus* minimal medium (AMM) and silkworm (*Bombyx mori*) hemolymph, respectively, the latter was used as a pre-screening step prior to *in vivo* screening in this invertebrate animal model. In conclusion it can be stated that nanogel preparation and the modification to a more negative surface charge were successful. *In vitro* studies demonstrated that modified nanogels show increased interaction with fungal hyphae compared to unmodified particles when co-incubated in AMM. The co-incubation in hemolymph did not show a significant improvement of interaction. These results encourage future studies to further improve the interaction of nanogels with fungus in hemolymph as well as the functionalization of particles with different targeting moieties and loading with antifungal agents.

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Grafting-To vs. Grafting-From: The Influence of Methodological Approach to the Antifouling Brushes of poly[*N*-(2-Hydroxypropyl) Methacrylamide]

Y. M. Wang[1, 2*], A. Kálosi[3, 4], Y. Halahovets[4], J. Slabý[5], J. Homola[5], J. Svoboda[1], I. Romanenko[1, 2], A. de los Santos Pereira[1], O. Pop-Georgievski[1]

[1]Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 16206 Prague, Czech Republic
[2]Department of Physical and Macromolecular Chemistry, Charles University, Hlavova 8, 12800 Prague, Czech Republic
[3]Centre for Advanced Material Application, Slovak Academy of Sciences, Dúbravská cesta 9, 84511 Bratislava, Slovakia
[4]Department of Multilayers and Nanostructures, Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 84511 Bratislava, Slovakia
[5]Institute of Photonics and Electronics, Czech Academy of Sciences, Chaberská 1014/57, 18251 Prague, Czech Republic
[*]presenting authour: wang@imc.cas.cz

Antifouling polymer brushes are widely utilized in biomedical applications to supress non-specific interactions with biological fluids.[1] They consist of surface-tethered polymer chains and are commonly formed when the chains are grafted "to" (GT) a surface by chemisorption or grafted "from" (GF) a surface in a surface-initiated polymerization. Although the antifouling polymer brushes have been studied for the last few decades, the relationship between the used grafting method and the ability of the polymer brush to resist fouling has not been established yet. In this study, we investigate physical and antifouling properties of poly[*N*-(2-hydroxypropyl) methacrylamide] (poly(HPMA)) brushes synthesized by GT and GF methods using reversible addition-fragmentation chain-transfer (RAFT) polymerization. The chemical structure of the polymer layers was confirmed via FTIR spectroscopy and X-ray photoelectron spectroscopy and the polymer chain parameters were determined by in situ and ex situ variable angle spectroscopic ellipsometry. Specifically, we compare the fouling resistance of polymer brushes prepared by both methods with identical molar mass of the grafted polymer chains, as confirmed by size exclusion chromatography equipped with multiple angle laser light scattering (MALLS-SEC) and atomic force spectroscopy-based single-molecule force spectroscopy (AFM-SMFS).[2] While both types of poly(HPMA) brushes are shown to substantially reduce fouling from blood plasma, the GF polymer brushes suppress fouling by 15 fold better than the GT polymer brushes. The observed difference in the antifouling performance is related to the difference in grafting densities which were influenced by the selected grafting method. In this study, we experimentally demonstrated that the GF method leads to the highest grafting density, more pronounced brush character and in turn to best antifouling properties out of the three presented methods. This study highlights the importance of the used grafting method for achieving high antifouling performance.

Acknowledgments

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Poly(2-oxazoline)-PLGA nanoparticles for cancer vaccination

Ana I. Matos,[1,2] Erik Wegener,[3] Theresa Vogel,[3] Helena F. Florindo,[1] Rainer Jordan,[3*]

[1] Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Lisbon, Portugal
[2] Instituto de Medicina Molecular (IMM), Faculdade de Medicina, Universidade de Lisboa, Lisbon, Portugal
[3] Chair of Macromolecular Chemistry, Faculty Chemistry and Food Chemistry, School of Science, Technische Universität Dresden, Dresden, Germany
**rainer.jordan@tu-dresden.de*

Poly(2-oxazoline)s (POx) are flexible pseudo-peptides that can be tailored to various applications such as excipient for various drugs, carrier in tissue engineering or surface modification.[1] Individual end-groups can be easily introduced by the living cationic ring-opening polymerization. Further, an amphiphilic contrast can be introduced.

Herein, we employ an amphiphilic POx diblock-copolymer and its conjugates to coat biodegradable poly(lactide-co-glycolide) (PLGA) nanoparticles (NPs).[2] Using a double emulsion process, PLGA-NPs are formed and subsequently coated by POx through hydrophobic interaction of PLGA and the lipophilic block of the amphiphilic POx. These POx-PLGA-NPs are loaded with antigens and siRNA for combination therapy. In in vitro experiments, the system did not influence dendritic cell viability. Upon in vivo administration, the labeled NPs are captured by circulating dendritic cells.

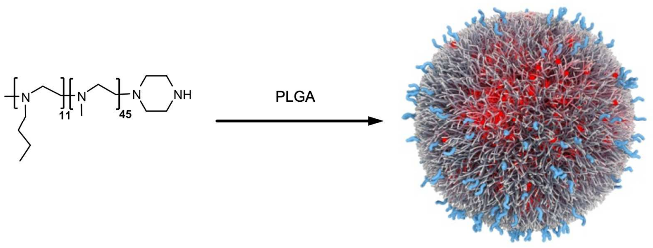

Fig. 1: Schematic representation of poly(2-oxazoline) coated PLGA-NPs.

Keywords: polyoxazoline, PLGA, nanoparticle

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[1] Lorson, T.; Lübtow, M. M. et al. Poly(2-oxazoline)s based biomaterials: A comprehensive and critical update. *Biomaterials* **2018**, *178*, 204-280.
[2] Silva, J. M.; Videira, M. et al. Immune system targeting by biodegradable nanoparticles for cancer vaccines *J. Contr. Rel.* **2013**, *2*, 179-199.

Poly(glycerol pimelate), a hyperbranched polyester for ocular drug delivery

Eirini Nakiou[1], Alexandra Zamboulis[1] and Dimitrios Bikiaris[1]*
[1]*Laboratory of Polymer Chemistry & Technology, Department of Chemistry, Aristotle University of Thessaloniki, Greece*
*dbic@chem.auth.gr

Aliphatic polyesters are widely used for biomedical and pharmaceutical applications due to their convenient biodegradability and low-cost production. Besides linear polyesters, star and hyperbranched polyesters based on glycerol and ω-fatty diacids have recently gained considerable interest for the development of novel biodegradable and biocompatible materials. Pimelic acid is a seven-carbon aliphatic dicarboxylic acid with the chemical formula $HOOC(CH_2)_5COOH$, that similarly to glycerol is regarded as a safe material according to the US Food and Drug Administration (FDA) [1].

Ocular drug delivery is one of the most challenging tasks faced by pharmaceutical researchers due to the numerous protective barriers of the eye, which must be by-passed without causing tissue damage or discomfort [2]. In this context, we have investigated the synthesis of poly(glycerol pimelate) (PGP) as a promising candidate for ocular biocompatible materials. The synthesis and characterization of PGP polyesters will be reported in this work. The synthesis of PGP was performed in two stages: (a) a polycondensation leading to the pre-polymer (oligoesters) and (b) thermal crosslinking. The effect of reaction parameters (molar ratio of the reactants, reaction time and temperature (160 - 180 °C)) on the properties of the PGP pre-polymers was studied. Crosslinking was further carried out at 120 °C under vacuum for 24 - 48 h to obtain the final elastomeric products. Pre-polymers and final polymers were characterized by infra-red and nuclear magnetic spectroscopies, differential scanning calorimetry and X-ray diffraction. The optimal polyesters were further used as contact lenses for the delivery of the ophthalmic drug liftegrast for the dry eye disease treatment.

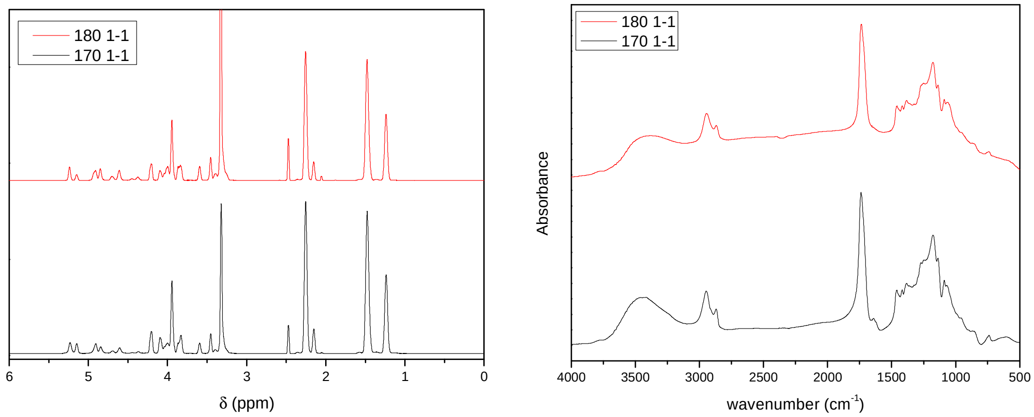

Figure 1.^{1}H NMR and IR spectra of two PGP pre-polymers.

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Novel Tetrazole-decorated Polymers via Sequential Post-Polymerization Modification Reactions

Meryem S. Akdemir[1], Phillip Werner[1], Daniel Döpping[2], Patrick Theato[1,2*] and Hatice Mutlu[1*]

[1] Soft Matter Synthesis Laboratory, Institute for Biological Interfaces 3 (IBG 3), Hermann-von-Helmholtz-Platz 1, D-76344, Eggenstein-Leopoldshafen, Germany

[2] Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Engesserstr. 18, D-76131, Karlsruhe, Germany

patrick.theato@kit.edu, hatice.mutlu@kit.edu

Over the years, nitrogen-rich functional groups such as tetrazole and its derivatives have been found increasing interest in small molecule chemistry.[1] While triazole containing polymers are rather popular, nitrogen-rich polymers containing tetrazole functional groups are rather limited.[2] Nevertheless, there is an ever-increasing interest in polymers containing a large amount of nitrogen for potential biomedical applications, because of their broad range of biological properties, such as being antibacterial, anticancer and anti-inflammatory.[3] On this premise, we report a novel sequential post-polymerization modification route for the synthesis of 1,5-disubstituted-1H-tetrazoles (1,5-DS-Ts) decorated polymers from easy accessible functionalized poly(2-hydroxyethyl methacrylate) (PHEMA). Accordingly, the hydroxyl functionality of PHEMA, which in turn was obtained by the reversible addition−fragmentation chain-transfer (RAFT) polymerization, has been modified to furnish aldehyde functionalized polymers. Subsequently, the Ugi-Azide four-multicomponent reaction (UA-4MCR), which allows the construction of the targeted tetrazole-containing functional units, has being applied as an efficient post-polymerization modification. Last but not at least, special interest was devoted to the investigation of the thermal and physical properties of the synthesized polymers, to reveal their potential in biomedical applications ranging from biomaterials to other research areas.

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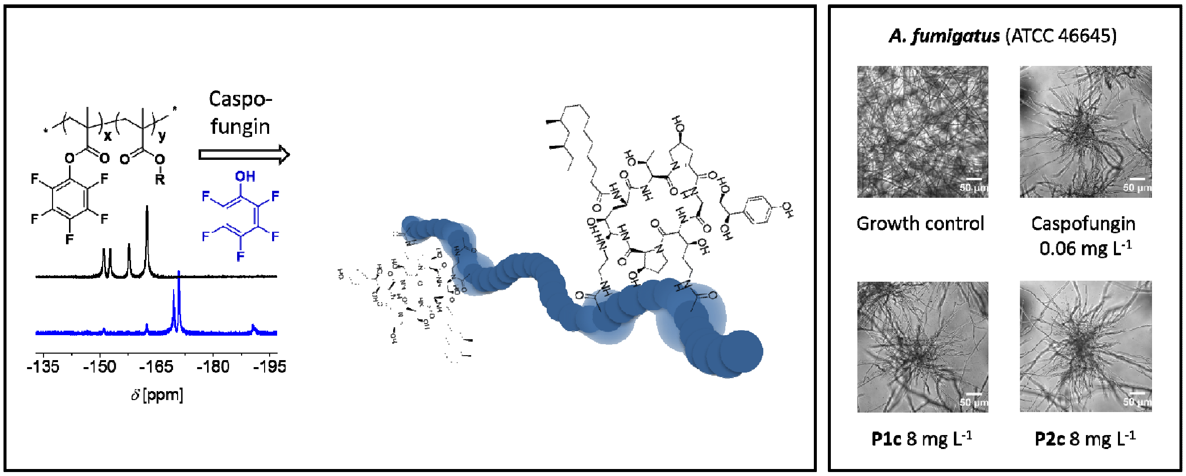
Polymer-drug conjugates for antimicrobial therapy

Julien Alex,[1,3] Katherine González,[2] Christine Weber,[1,3] Thorsten Heinekamp,[2] Thomas Orasch,[2] Carlos Guerrero-Sanchez,[1,3]* Ulrich S. Schubert,[1,3]* Axel A. Brakhage[2]*

[1]Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstr. 10, 07743 Jena, Germany
[2]Department of Molecular and Applied Microbiology, Leibniz Institute for Natural Product Research and Infection Biology-Hans Knöll Institute (HKI), Beutenbergstr. 11a, 07745 Jena, Germany
[3]Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany
*carlos.guerrero.sanchez@uni-jena.de, *ulrich.schubert@uni-jena.de, *axel.brakhage@leibniz-hki.de

Inhalation of spores (conidia) of the most important airborne human pathogenic fungi *Aspergillus fumigatus* culminate with phagocytosis of conidia by alveolar macrophages in the lung. However, this pathogen has evolved strategies to survive inside the immune cells, and cause invasive aspergillosis in immunocompromised patients.[1] Thus, polymer-drug conjugates based on the clinically used antifungal caspofungin were synthesized to fight persistent intracellular conidia. Here, we describe the synthesis of hydrophilic poly(poly(ethylene glycol) methyl ether methacrylate) (PmPEGMA) and hydrophobic poly(methyl methacrylate) (PMMA) caspofungin conjugates by a post polymerization modification of copolymers containing 10 mol% pentafluorophenyl methacrylate (PFPMA). The coupling of caspofungin was confirmed and quantified in detail by combination of ^{1}H-, ^{19}F- and diffusion ordered nuclear magnetic resonance spectroscopy, UV-Vis spectroscopy and size exclusion chromatography.



Schematic representation of the synthesis of polymer-drug conjugates and susceptibility testing against one strain of the human pathogenic fungus *A. fumigatus*.

Both polymer-drug conjugates revealed activity against important human-pathogenic fungi, *i.e.*, two strains of *Aspergillus fumigatus* and one strain of *Candida albicans*. RAW 264.7 macrophages as well as HeLa cells remained unaffected at these concentrations.[2]

Acknowledgement: This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – project number 316213987 – SFB1278 (projects B02, Z01).

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Synthesis of hybrid polymer brush via combination of surface initiated ring-opening metathesis polymerization and thiol-ene click reaction and its use in dna hybridization

E. Altay Ozturk[1*], M. S. Eroglu[2,3], T. Caykara[1]

[1]*Department of Chemistry, Faculty of Science, Gazi University, Besevler, 06500 Ankara, Turkey*
[2]*Department of Chemical Engineering, Faculty of Engineering, Marmara University, Kadikoy, 34722 Istanbul, Turkey*
[3]*Chemistry Group Laboratories, TUBITAK-UME, PO Box 54, 41471 Gebze, Kocaeli, Turkey*

[*]*esraaltayy@gmail.com*

In recent years, surface-initiated forms of controlled polymerization methods such as nitroxide-mediated polymerization (NMP)[1], atom transfer radical polymer polymerization (ATRP)[2] reversible addition-fragmentation chain transfer (RAFT) polymerization[3] and ring opening metathesis polymerization (ROMP)[4] have been used to provide good versatility and functional group compatibility.

In this study, well-defined hyaluronated poly(exo-7-oxabicyclo[2.2.1]hept-5-en-2,3-dicarboxylic anhydride) [poly(EHDA)-HA] brushes on the hydroxyl terminated silicon (Si-OH) surface were prepared through the combination of surface-initiated ring-opening metathesis polymerization (ROMP) and thiol-ene click reaction. This process was realized in successive four steps: (i) formation of self-assembled monolayer of (3-aminopropyl)triethoxysilane on the Si-OH surface (Si-APTES), (ii) bonding of EHDA monomer to the Si-APTES surface, (iii) synthesis of poly(EHDA) brushes via surface-initiated ROMP and (iv) coupling of thiolated hyaluronic acid (Th-HA) to poly(EHDA) chains via thiol-ene click reaction. Surface wettability, surface morphology and chemical compositions of poly(EHDA)-HA brushes were characterized by contact angle measurements, atomic force, microscopy and X-ray photoelectron spectroscopy, respectively. Grafting density (σ, chains nm-2) and average distance between grafting points (D, nm) of the poly(EHDA) brushes were measured to be 0,50 chains nm-2 and 1,65 nm, independent of the [catalyst]/[monomer] ratios, which indicated that high grafting was created on the silicon substrate. However, low amounts of HA molecules were bonded to poly(EHDA) chains due to the high volume of Th-HA chains creating some steric hindrances.The biocompatibility of the brushes was determined by (3- (4,5-dimethylthiazol-2-yl) -2,5-diphenyl tetrazolium bromide) (MTT) cytotoxicity test. First, single stranded RNA molecules were attached to the poly(EHDA)-HA brushes, then hybridized with conjugated DNA probe and the surface was examined by Fluorescence Spectrum and Laser Scanning Confocal Microscope. As a result, the biocompatible property of poly(EHDA)-HA brushes could be useful a candidate for making advanced biological devices to control the behavior of biomolecules on surfaces.

Keywords: Exo-7-Oxabicyclo[2.2.1] Hept-5-en-2,3-Dicarboxylic Anhyride, Surface Initiated Ring-Opening Metathesis Polymerization (ROMP), Thiol-Ene Click Reaction, Grafting Density, DNA Hybridization

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Biopolymer-based hydrogel coatings: enhancement of biomaterials performance by the controlled release of bioactive agents

J. Andrade del Olmo[1,2*], J. M. Alonso[1], V. Sáez Martínez[1], R. Pérez González[1], J. L. Vilas-Vilela[2,3] and L. Pérez-Álvarez[2,3].

[1]*i+Med S. Coop. Technology Park of Álava, Albert Einstein St., 15, 01510 Vitoria-Gasteiz, Álava, Spain.*
[2]*Macromolecular Chemistry Research Group (LABQUIMAC), Physical Chemistry Department, Faculty of Science and Technolofy, University of the Basque Country, 48940 Leioa, Spain.*
[3]*BCMaterials, Basque Center for Materials, Applications and Nanostructures, University of the Basque Country, 48940 Leioa, Spain.*
[*]*jandrade@imasmed.com*

The development of implantable medical devices with improved bioactivity has been a great concern for biomedical community, whih can be achived by biocompatible biopolymer-based hydrogel coatings, mainly that ones based on hyaluronic acid and chitosan. [1] In fact, they own a potential ability to release in a controlled space-time manner to the therapeutic target specific low- to high-doses of bioactive agents (drugs, proteins, peptides, growth factors, nanoparticles or nucleic acids). This way, highly stable hydrogel-based coatings developed onto the surface of biomaterials could provide combinations of outstanding bioactive properties: antibacterial, anti-inflammatory, self-healing, wound healing, bone-tissue engineering, and osseointegration, among others. [2] In summary, the development of such improved version of biomaterials with privileged pharmacokinetic profiles, personalized therapies, reduced side effects, and increased therapeutic efficacy could posess a bright and promising future in biomedical field improving patients quality life.

Figure 1. Bioactive properties provided by the sustained release of bioactive agents from biopolymer-based hydrogel coatings.

Keywords: Biomaterials, biopolymers, hydrogels, coatings, sustained release, bioactive agents.

Acknowledgments

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Biomaterials based on imino-quaternary ammonium salts of chitosan; synthesis and characterization

B.I. Andreica*, I. Rosca, L. Marin

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania
**andreica.bianca@icmpp.ro*

Development of biomaterials based on chitosan is an active research field, due to its remarkable biological properties and, moreover, it represents a sustainable choice due to its natural origin. Over the last few decades, significant attention has been given to biomaterials based on water soluble chitosan derivatives, considered well-suited for biomedical and cosmetic applications. As an example, quaternary ammonium salts of chitosan keep the promise for real life applications in a large realm of biomedical fields, such as antimicrobial products, gene therapy, drug delivery, wound healing, tissue engineering and cosmetics [1]. Our last researches, focused on the development of chitosan-based hydrogels, revealed a friendly crosslinking route consisting in the condensation reaction with monoaldehydes, *via* imination and self-assembling of the newly formed imine units into crosslinking clusters. It was proved that this method is a valuable choice to generate hydrogels with tailored properties, further exploited for targeted applications [2, 3]. In this framework, this study presents the synthesis and characterization of hydrogels based on *N*-(2-hydroxy)propyl-3-trimethyl ammonium chitosan chloride (HTCC), crosslinked with salicylaldehyde, designed for biomedical applications. A series of 15 hydrogels was prepared by condensation reaction in water, in different molar ratios of amine aldehyde functionalities, between 1/1 and 15/1 (Figure 1a).

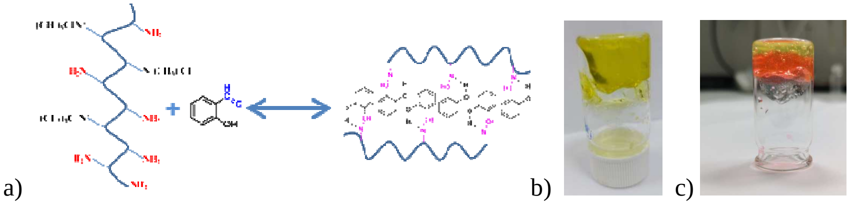

Figure 1. a) Imination process between HTCC and salicylaldehyde; b) Inverted tube test; c) Self-healing ability

All the hydrogels passed the inverted tube test (Figure 1b), while the hydrogelation mechanism was established to be a consequence of both imination, proved by FTIR and NMR spectroscopy, and self-assembling into a three-dimensional network of the imino-HTCC derivatives, revealed by WXRD and POM techniques. The obtained dried materials exhibited a porous morphology determined by SEM, they were able to rehydrate in the form of hydrogel in less than an hour, and had superabsorbent properties, reaching a mass equilibrium swelling of 190 in 4 hours. The ability of the hydrogels to self-heal was demonstrated by complementary techniques (Figure 1c). Moreover, the xerogels/hydrogels presented a dissolution rate in aqueous medium, controlled by the crosslinking density and the medium pH, and biodegradation in soil, the longest time extent needed for the degradation was 5 days, for the hydrogel with the highest crosslinking density. They proved good *in vitro* antimicrobial properties and *in vivo* biocompatibility on mice. All these properties recommend these hydrogels for wound healing applications.

Acknowledgments

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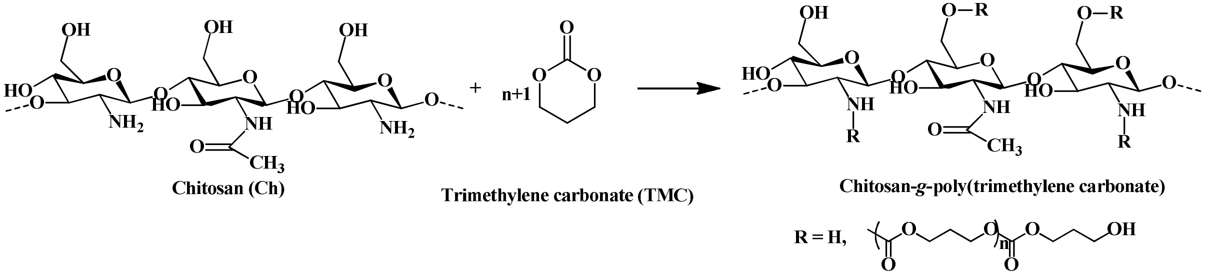
Synthesis of chitosan based derivatives with improved solubility in water, towards biomaterials' design

B. I. Andreica*, D. Ailincai, L. Marin

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania
**andreica.bianca@icmpp.ro*

Keywords: chitosan, trimethylene carbonate, water solubility, ring-opening polymerization

During the last decades, tremendous awareness regarding the suitability of using naturally-derived polymer for diversified applications in life is increasing. Particular attention was given to chitosan, due to its remarkble properites: biodegradability, biocompatibility, nontoxicity and antimicrobial activity [1]. However, the applicability of chitosan in biomedical field is still limited, due to its main drawback, the lack of solubility in physiological pH. In this line of thought, the objective of this study was the synthesis and characterization of novel chitosan derivatives, by ring-opening polymerization (ROP) technique of a 6-membered cyclic carbonate, using chitosan as an initiator. The reaction was conducted using different molar ratios between chitosan and monomer, in melt bulk or in heterogeneous system, in presence of a swelling agent for chitosan [2].



Scheme 1. Synthetic pathway for obtaining of the chitosan derivatives

The novel synthesised amphiphilic derivatives were characterized from the structural point of view, using NMR and FTIR spectroscopy. The supramolecular changes induced by grafting the side chains on the chitosan backbones, along with the morphology of the films casted from solution, were investigated using POM and AFM techniques.

The solubility of the chitosan grafted copolymers was evaluated by varying different parameters, including the solvent, pH and temperature. The derivatives with a substitution degree around 5%, and a polymerization degree of the poly(trimethylene carbonate) of 7 presented the property of being soluble in water and DMSO. The improvement in solubility lead to an increase in the degradation rate, in the presence of lysozime, in buffer solution. The solubility had a possitive effect on biocompatibility of the chitosan derivatives, increasing with 30% in comparison with chitosan solutions with the same concentration, this being only the first step for the upcoming research.

Acknowledgments

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE2020-2717, within PNCDI III, no. PCE 2/2021.

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Odorless polymeric hydroperoxides as part of redox initiator systems in dental materials

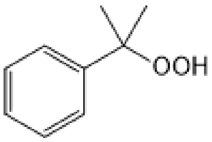
J. Angermann[1*], Y. Catel[1], P. Fässler[1], T. Schnur[1], S. Monge[2], P. Morandi[2], J. Robin[2]

[1]*Ivoclar Vivadent AG, Schaan, Principality of Liechtenstein*
[2]*Université de Montpellier, Montpellier, France*
[*]*joerg.angermann@ivoclar.com*

Self-curing materials are widely used in clinical dentistry, e.g. in composites for direct restorations or in cements to fix indirect restorations, like crowns or bridges. In addition to the monomer matrix (usually a mixture of methacrylates), the filler system (e.g. milled glasses, highly dispersed silica) and additives (e.g. pigments, stabilisers), these materials also contain an initiator system to start the radical polymerization and lead to materials with high mechanical strength.[1] Polymerization of self-curing materials is often initiated by redox initiator systems, like hydroperoxide/ thiourea systems.

Cumene hydroperoxide **1** is one of the most commonly used oxidizer in such systems due to its high radical generation ability. It is known as a very efficient oxidant in such systems, on the other hand, it has a very strong unpleasant odor and shows unfavorable toxicological properties which complicates its application in dental materials.

One way to circumvent these problems could be polymers bearing hydroperoxy groups. We investigated a number of such polymers and found telomers with the general structure **2** to be the one with the most promising effect.



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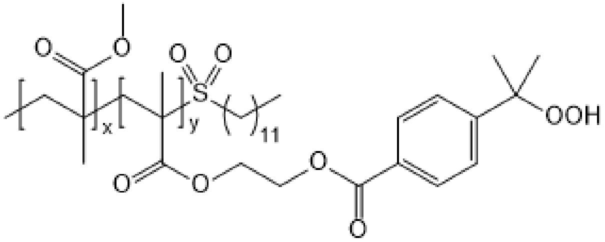

2

Telomers **2** were synthesized in a multistep synthesis which includes among others the preparation of a methacrylate monomer bearing the cumyl unit, its co-telomerization with methyl methacrylate in various ratios to obtain a statistical copolymer and hydroperoxydation of the cumyl unit in the side chains as the final step.

Physical properties and spectroscopic characteristics of the synthesized monomer and the telomers were determined. The synthesized telomers were used in model formulations to investigate their influence on polymerization behavior as well as selected mechanical properties of the cured materials. Results were compared with those of materials with conventional redox systems. Finally, the toxicological properties of **2** were determined.

Keywords: redox-initiated polymerization, telomerization, hydroperoxide, dental material

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Electrospinning of chitosan/quaternary salts of chitosan nanofibers for biomedical application

A. Anisiei[1*], B.-I. Andreica[1], L. Marin[1]

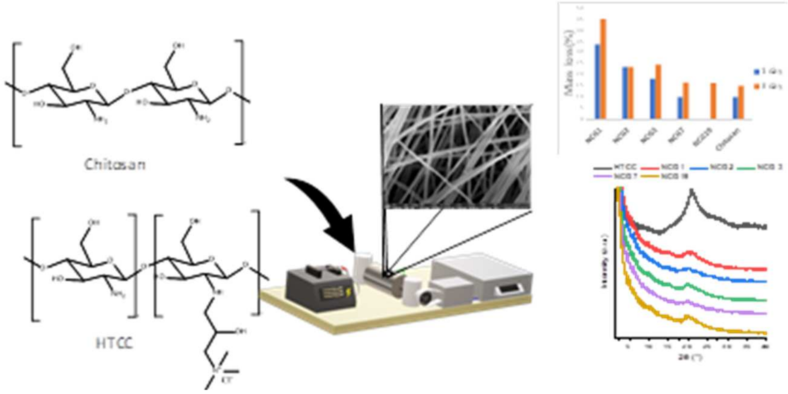
[1]" *Petru Poni" Institute of Macromolecular Chemistry, Iasi*

Chitosan (Ch) is a biocompatible, biodegradable polysaccharide produced by deacetylation of chitin, an abundant polymer obtained from renewable sources like exoskeletons of insects and fungi. The materials obtained from chitosan can have many bioactive properties derived from it, including antimicrobial, hemostatic, spermicidal, CNS depressant, anti-tumor effect, and so on. Even that statement sounds opportunistic, a major drawback for applications of this polymer is its insolubility in aqueous solutions with a pH above 6, which hinders both the preparation and bioapplication of materials based on it [1]. The modification of the chitosan to give water-soluble quaterinzed chitosan derivatives (QC) is a good opportunity to avoid the low solubility and to take advantage of enhanced antimicrobial, antioxidant, and mucoadhesive properties [2].

In this line of thought, we prepared Ch/QC nanofibers by electrospinning different ratios of Ch/QC, from 95/5 to 50/50, with a low content of PEO of 10% that was later removed by washing with dried EtOH.

The obtained materials presented a semicrystalline fibrillar morphology with fibers around 200 nm and a strong birefringence. The fibers presented a rapid swelling and their solubility was strongly influenced by the Ch/QC ratios, being proportional to the increase of QC content and dilution rate. They were biodegradable in PBS of physiological pH in the presence of lysozyme, showing that the degradation rate is accelerated by the dissolution of QC.

The *in vitro* biocompatibility test showed relative good viability for all samples, inversely proportional with the quantity of QC. Neverthless, the *in vivo* test on mice didn`t show any clinical changes. The antimicrobial activity assay was realized to complete testing the properties needed to use the material in wound healing. The results showed that the material work as an antibacterial/antifungal physical barrier. All these promising results recommend Ch/QC fibers for use in resorbable wound bandages.



Keywords: Chitosan, quaternary salts of chitosan, electrospinning, nanofibers, wound healing.

Acknowledgments

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Imination of chitosan fibers towards potential antimicrobial wound dressings

A. Anisiei, I. Rosca, A.-I. Sandu, A. Bele, L. Marin
"Petru Poni" Institute of Macromolecular Chemistry
**anisiei.alexandru@icmpp.ro*

The study aimed to prepare and to characterize chitosan nanofibers with enhanced antimicrobial activity for wound dressing application. To this end, chitosan nanofibers were obtained by electrospinning a mixture of chitosan and PEO in concentrated acetic acid at room temperature, followed by PEO removing to obtain neat chitosan nanofibers [1]. In order to improve the antimicrobial activity of chitosan, the fibers were functionalized by imination with 2-formylphenilboronic acid, in a heterogeneous system in different reaction conditions [2]. The FTIR and ^{1}H-NMR spectroscopy were used to confirm the successful imination of the fibers, and the conversion degree of the amine groups of chitosan into imine units. The functionalized fibers were characterized in terms of morphology, crystallinity, porosity, and intermolecular forces by POM, SEM, water vapor sorption, and TGA. To quantify their potential for wound healing application, the obtained fibers were subjected to different tests: swelling in both water and PBS, biodegradation in media mimiking wound exudate, antimicrobial activity, in vitro cytocompatibility on normal human fibroblasts, and bioadhesivity. The results indicated that the functionalization of chitosan with 2-formylphenylboronic acid led to biomaterials with (i) ability to swell and thus to drain the wound exudate favoring a moist medium proper for healing (ii) biocompatibility and bioadhesivity beneficial for tissue repair; (iii) antimicrobial activity beneficial for preventing the wound infection in the first stages of healing (iv) biodegradation rate fitting well the wound healing period, pointing for avoiding of traumatic debridement. All these results encourage further investigations in order to develop a marketable product. Moreover, the paper brings to researchers' attention the imination of chitosan fibers as a reliable method towards improving specific properties.

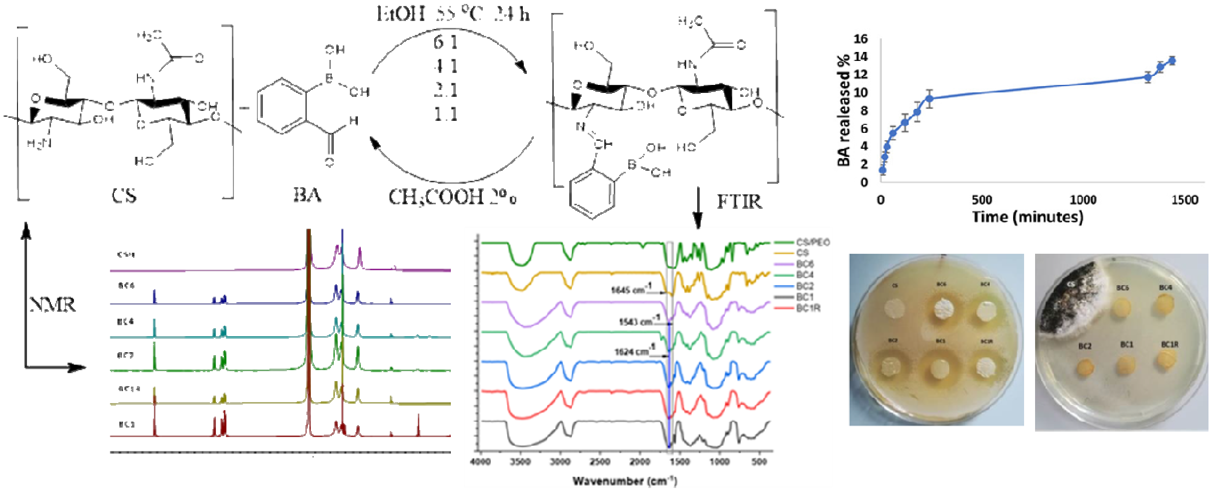

Figure 1. NMR and FTIR spectra of the functionalized nanofibers, the in vitro release of aldehyde and antimicrobial tests

Keywords: chitosan, nanofibers, wound dressing, imine, antimicrobial, biocompatible, biodegradable

Acknowledgments

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Biomedical textile converted to a thermosensitive sensor and SERS device

Sonia Lanzalaco[1,2]*, Júlia Mingot[1,2], Carlos Alemán[1,2], Elaine Armelin[1,2]*

[1] *IMEM-BRT – Innovation in Materials and Molecular Engineering-Biomedical Regenerative Therapies, Dpt. of Chemical Engineering, Universitat Politècnica de Catalunya (UPC), C/ d'Eduard Maristany, 10-14, Building I, 2nd floor, 08019 - Barcelona (Spain).*
[2] *Barcelona Research Centre for Multiscale Science and Engineering, Universitat Politècnica de Catalunya (UPC), C/ d'Eduard Maristany, 10-14, Building I, basement, 08019 - Barcelona (Spain).*
**Corresponding Authors: elaine.armelin@upc.edu, sonia.lanzalaco@upc.edu*

Nowadays, the detection and control of inflammatory processes caused by plastic implants (surgical meshes, sutures, surgical staples, plastic stents, etc.) is unfeasible with clinical detection standards. When such problems appear, the patients are usually post-intervened. In this sense, the development of non-invasive or semi-invasive tools for infection detection can play an important role in the future. Thermo-sensitive mesh material based on commercial biomedical textiles was successfully produced and reported in our previous works.[1-3] The innovative device composed by a coating of poly(*N*-isopropylacrylamide) (PNIPAAm), covalently bonded to polypropylene (PP) yarns, and biomarker-targeting surface-enhanced Raman scattering (SERS) nanoparticles (NPs), strategically attached to the plastic surface, has the potential to improve such detection by using, for example, a miniaturized, non-contact, opto-electro-mechanical Raman probe as that described by Garai *et al*.[4] The authors used SERS NPs flavors for rapid circumferential scanning of topologically complex surfaces, such as colon and esophagus, and were able to produce quantitative images of the relative concentrations of SERS NPs that were present.

In this work, for first time, a successful methodology to convert a PP mesh complex structure into a thermosensitive and SERS responsive surface, by combining surface functionalization with AuNPs/Raman reporter (RaR) and a coating of PNIPAAm hydrogel is described. AuNPs/RaR molecules were properly adhered to the PP fibres and were stable even after several washing steps. After graft copolymerization of PNIPAAm-co-MBA hydrogel above PP@AuNPs/RaR fibres, a positive SERS response was obtained due to the synergist effect of the thermosensitive hydrogel (i.e. collapse under heating) together with the presence of the Au metal particles, which helps to dissipate local heat increase accused by the IR irradiation source (785 nm). The thermosensitive response of the new bilayer material under controlled temperature ramp was monitored in a humidity-controlled chamber by using an infrared camera.

Therefore, by tuning the plasmonic coupling of Au/RaR NPs and their homogenous distribution over the PP yarns (good surface coverage), it was possible to modulate the SERS performance for the ultrasensitive detection of RaR molecules and to evaluate the thermal behaviour of the sample under successive heating-cooling cycles.

Keywords: *poly(N-isopropylacrylamide), thermosensitive hydrogels; gold nanoparticles, SERS spectroscopy*

Acknowledgments
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Tough double network hydrogels for 3d printing and tissue regeneration

Mariana Arreguín Campos[1,2*], Mahsa Ebrahimi[1,2], Matt Baker[2], Prof. Louis M Pitet[1]

[1]*Institute for Materials Research (IMO) and Advanced Functional Polymers (AFP) Group, Hasselt University, Hasselt, Belgium*
[2]*MERLN Institute for Technology-Inspired Regenerative Medicine, Maastricht University, Netherlands*
[*]*mariana.arreguincampos@uhasselt.be*

As humans, injuries, diseases, and congenital malformations have always been part of our lives. Despite significant progress, pharmaceutical treatments often have limited efficacy. It is here where regenerative medicine and tissue engineering emerge, trying to provide solutions for treating severe injuries, where the body's response is not sufficient to restore comprehensive functionality. Nevertheless, mimicking native tissue is a formidable task.

Hydrogels are hydrophilic materials that can take up to thousands of times their dry weight in water. Due to their soft consistency and permeability to small molecules, hydrogels are attractive materials for regenerating tissue. Even though hydrogels are already being used in applications such as contact lenses, drug delivery, and wound dressing, the challenge of achieving mechanical integrity while incorporating other complex characteristics, and maintaining biocompatibility, still remains.

Double network hydrogels (DN hydrogels) are systems consisting of a combination of two different hydrogels. The contrasting properties of the two networks provide the material with exceptional mechanical properties. For instance, DN hydrogels have demonstrated mechanical properties comparable to the strength and toughness of cartilage.[1] Despite the success in developing hydrogels with high mechanical performance, fabricating double network hydrogels that can be processed into complex three-dimensional (3D) structures continues to represent a challenge. Synthesizing DN hydrogels typically requires multiple steps, contrasting with the "one-pot" setup used for most injection/3D printing techniques. We tackle the problem with orthogonal crosslinking chemistry in two compatible networks. We employ both thiol-ene crosslinking and reversible ionic bonding (Figure 1). Thus, the selective reactivity of the two networks will potentially allow the formation of a double network hydrogel in a one-pot manner, which can further translate into the fabrication of complex 3D structures for the tailored treatment of various ailments.

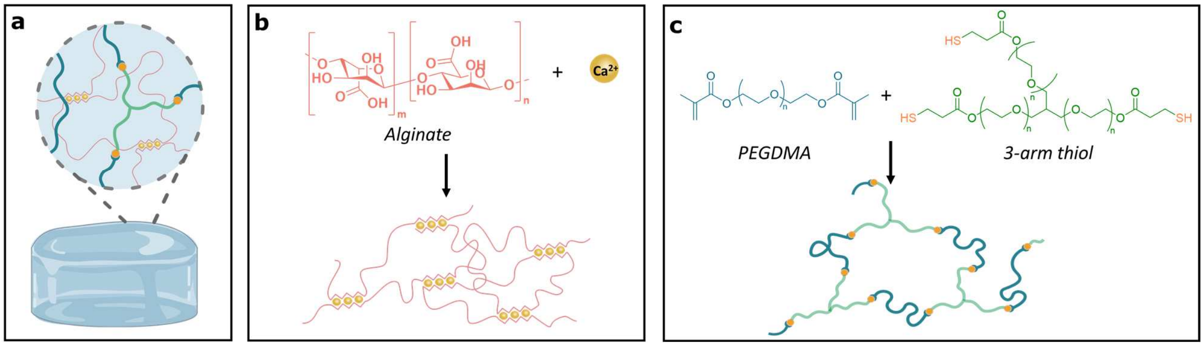

Figure 1. (a) Representation of a DN hydrogel from the two orthogonal networks; (b) first network: ionically crosslinked alginate; (b) second network: thiol-ene crosslinked PEO

Keywords: hydrogels, tissue regeneration, 3D-printing, DN-hydrogels

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Optimization of oil-in-water cosmetic formulation with bacterial Extracellular Polysaccharide FucopoL: bio-physical evaluation, rheological and texture assessments

S. Baptista[1,2,3], F. Freitas[1,2]

[1] Associate Laboratory i4HB - Institute for Health and Bioeconomy, School of Science and Technology, NOVA University Lisbon, Caparica, Portugal;
[2] UCIBIO – Applied Molecular Biosciences Unit, Department of Chemistry, School of Science and Technology, NOVA University Lisbon, 2819-516 Caparica, Portugal
[3] 73100, Lda. Edifício Arcis, Rua Ivone Silva, 6, 4º piso, 1050-124 Lisboa, Portugal

The cosmetic industry has been increasing its interest in designing and launching polysaccharides as natural rheological modifiers to create novel emulsion systems with improved stability and functionality of skin-care products [1]. Oil-in-water (O/W) emulsions for cosmetic use are complex multiple-phase systems, which may contain several interacting emulsifiers, fatty acids, vitamins, and other excipients. In this study, cosmetic formulations with improved properties were developed based on the natural anionic polysaccharide FucoPol as multifunctional emulsifier [2–4], antioxidant [5], and photoprotective agent [6]. Microscopic analysis, physicochemical properties, physical stability, rheological and texture analysis of FucoPol-based emulsions demonstrated the biopolymer's suitability for preparing O/W emulsions possessing appropriate characteristics for the development of improved skin-care products.

Keywords: FucoPol; Cosmetic O/W emulsions; emulsion stability; rheology; texture analysis

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Novel hydrophilic cryogels as potential 3D cell culture materials: Synthesis and characterization of lucosyl methacrylamide based polymer scaffolds

F. Behrendt[1,2*], D. Pretzel[1,2,3], Z. Cseresnyes[4], Leon Lange[1], N. Fritz[1,2], M. Kleinsteuber[1,2], T. Wloka[1,2], M. Gottschaldt[1,2], U. S. Schubert[1,2,3*]

[1]Laboratory for Organic Chemistry and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Jena, Germany
[2]Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Jena, Germany
[3]Abbe Center of Photonics (ACP), Jena, Germany
[4]Applied Systems Biology, Leibniz Institute for Natural Product Research and Infection Biology, Hans Knöll Institute (HKI), Jena, Germany
[*]florian.behrendt@uni-jena.de, ulrich.schubert@uni-jena.de

Cryogels represent a promising class of porous polymeric materials consisting of an interconnected macropore network. Depending on the material attributes such as biocompatibility, specific mechanical properties and certain chemical properties, *e.g.*, hydrophilicity[1], cryogels mimic natural habitats of microorganisms and could be used as novel 3D (cell) culture models. Poly(2-ethyl oxazoline)s (PEtOx) are known to be water soluble and biocompatible polymers with the ability to vary both their α- and ω-end group. In contrary to commercially available *N*,*N*-methylenebisacrylamide, acrylate endcapped difunctional PEtOx cross-linking agents allow the preparation of flexible polymer networks due to extended chain-to-chain distances with an increased hydrophilicity.[2] In this study, a library of hydrophilic cryogels have been prepared based on bisacrylamide and tailor-made PEtOx diacrylate cross-linking agents. The incorporation of different amounts of glucosyl methacrylamide into the gel network was proven by solid-state NMR and FTIR spectroscopy. Additionally, scanning electron microscopy imaging was applied to observe the morphology and to calculate the pore sizes using an automated image analysis approach. L929 cells were seeded onto cryogel slices to investigate their potential as novel 3D cell culture models and their cytocompatibility.

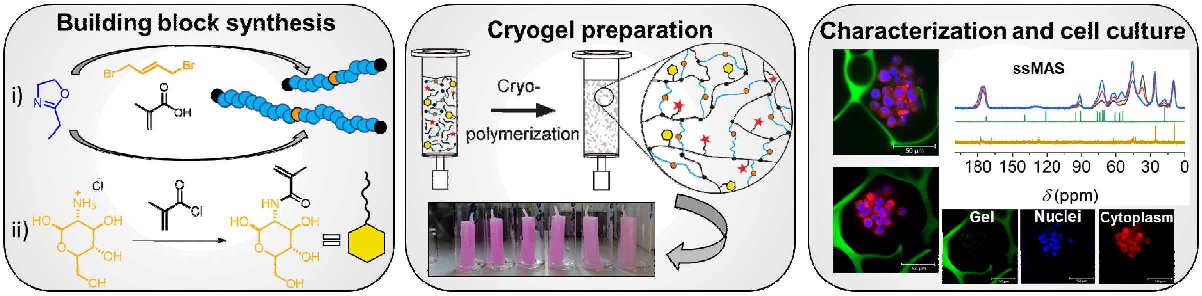

Figure 1: Workflow for the preparation of hydrophilic cryogels and their characterization prior to cell culture studies with L929 cells.

Keywords: Cryogels, 3D culture, glucosyl methacrylamide, poly(2-ethyl-2-oxazoline) diacrylates

Acknowledgements
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ROS/light degradable poly(urethane-urea) hydrogels films

C. T. B. Paula[1*], Patrícia Pereira[1,2], Jorge F.J. Coelho[1], Ana C. Fonseca[1], Arménio C. Serra[1]

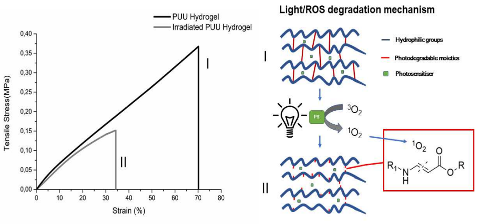
[1] *CEMMPRE, Department of Chemical Engineering, University of Coimbra, Rua Sílvio Lima-Pólo II, 3030-790 Coimbra, Portugal*
[2] *IPN, Instituto Pedro Nunes, Associação para a Inovação e Desenvolvimento em Ciência e Tecnologia, Rua Pedro Nunes, 3030-199 Coimbra, Portugal*
**ctadeu@eq.uc.pt*

Introduction: Hydrogels are materials with outstanding potential for biomedical applications. [1] They are characterized by unique versatility and favorable chemical properties that can be easily modulated by rational selection of their components. The ability to develop hydrogels that can respond to external stimuli broadens the range of applications. Among the polymers used to prepare hydrogels, polyurethane (PU) and polyurethane-urea (PUU) are some of the most cited examples. [2] In this work, new PUU/light-reactive hydrogel films are proposed. With a strategy inspired by photodynamic therapy (PDT), these films were prepared using polyethylene glycol (PEG) as the main component and contain a ROS -sensitive β-aminoacrylate bond. [3] The hydrogel films were characterized in terms of their mechanical and thermal properties, swelling ability, and in vitro cytocompatibility.

Materials and Methods: The synthesis of the precursors bearing the β-aminoacrylate linkage was performed by a two-step reaction: a Fisher esterification of PEG with propiolic acid followed by the amino-yne "click" reaction with diethanolamine (DEA). Using these telechelic precursors, PUU hydrogel films were prepared with hexamethylene diisocyanate (HDI). Chlorin e6 (Ce6) was added to the films to induce the photoresponsive ability.

Results and Discussion: The precursors were fully characterized by ATR-FTIR and ^{1}H NMR. The presence of both urethane and urea bands in hydrogel was confirmed by ATR-FTIR. The hydrogels were able to swell up to 180% of their dry weight. The PUU hydrogel films presented good mechanical properties with a tensile strength maximum (σ_{max}) between 0.5 and 1.3 MPa.

To induce a light-dependent degradation process, [3] Ce6 was incorporated into the films and they were irradiated for different periods of time. The mechanical properties of the hydrogels decreased significantly after irradiation (Fig.1). The in vitro cytotoxicity of the PUU hydrogel films proved that these platforms were not cytotoxic to HEK293T cells.



Loss of mechanical properties after irradiation.

Fig.1 Light/ROS degradation mechanism.

Conclusion: PUU hydrogels with interesting mechanical properties, good water uptake and low cytotoxicity were successfully prepared by a straightforward method. More importantly, the hydrogel films exhibited a light-degradable profile through an innovative ROS-mediated cleavage process, as indicated by the loss of mechanical properties.

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Keywords: Hydrogel; Films; Polyurethane-urea; Light; Singlet Oxygen

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Postmodification of poly(2-isopropenyl-2-oxazoline) by carboxyl-functionalized polymers

M. Basko, B. Kost, B. Kopka

[1] *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland*
**Corresponding Author's E-mail address: baskomeg@cbmm.lodz.pl*

Poly(2-isopropenyl-2-oxazoline) (PiPOx) is a relatively new, less-explored hydrophilic polymer that can perform functions similar as poly(ethylene oxide) (often used as the standard hydrophilic-building block in hydrogels), but additionally has the unique advantage of having reactive side functional groups in the polymer chain, that allows further transformations[1]. PiPOx chain modification through pendant oxazoline rings was already demonstrated at relatively simple systems, using selected low-molecular-weight compounds containing carboxyl, thiol, or amine functional groups, as a means to develop smart responsive copolymers or networks[2]. Our research aims at further extending this approach by employing carboxyl-terminated polymers to tailor the final structure and properties of the resulting polymeric materials[3]. The use of monofunctional polyesters potentially opens the way to the graft copolymers synthesis (Fig. 1A). A unique combination of PiPOx and macro-crosslinkers based on di-carboxyl-functionalized polyesters is proposed to access novel (bio)degradable amphiphilic networks/hydrogels (Fig. 1B).

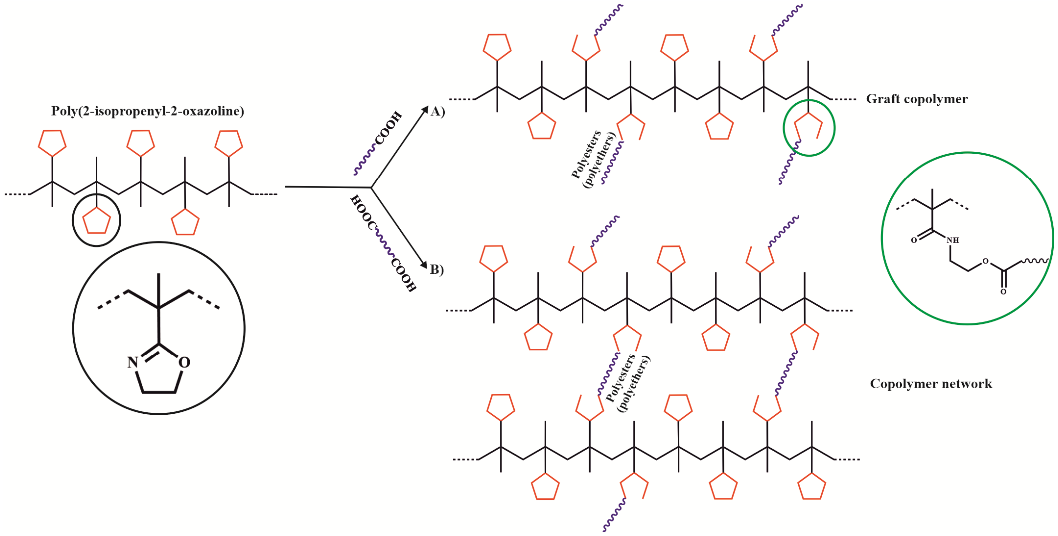

Figure 1. Synthesis of graft copolymers (A) and copolymer networks (B) by postmodification of poly(2-isopropenyl-2-oxazoline) with carboxyl-functionalized polymers.

It should be stressed, the presented synthetic method is relatively facile, free from toxic catalysts and by-products, thus well suited for the biomaterials preparation.

Keywords: networks, hydrogels, grafted copolymers, degrability, polymer postmodification

Acknowledgments

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In situ reinforcing polymers as high performance biomaterials

K. Ehrmann,[1,3] M. Fitzka,[1,3] O. Berk,[1,2,3] R. Liska,[1,3] S. Baudis[1,2,3*]

[1]*Institute of Applied Synthetic Chemistry, TU Wien, Vienna, Austria*
[2]*Christian Doppler Laboratory for Advanced Polymers for Biomaterials and 3D Printing, TU Wien, Vienna, Austria*
[3]*Austrian Cluster for Tissue Regeneration, Vienna, Austria*
[*]*stefan.baudis@tuwien.ac.at*

The processing window of high performance polymers is a crucial bottle neck in technology, including scaffolds for regenerative medicine. Here, often unfavorable compromises between the processability and the final material properties have to be made.[1] The excellent properties of high performance polymers – either thermoplasts or thermosets (and their precursors) – rely on physical interaction between the polymer chains and hence also contribute to high viscosity and low- or even non-solubility of the polymers to be processed. Recently, we discovered self-reinforcing polyurethane ureas (srPUUs), which transform *in situ* just by storing them in aqueous media at moderate temperatures (*e.g.*, body temperature), referred to as pre-conditioning, forming polymeric materials of increased strength, extensibility, and toughness.[2] This process relies on the dynamic nature of hindered urea bonds (HUBs) [3]; In aqueous media, we propose that these bonds transform to non-hindered urea bonds by a concerted sequence of chemical conversions, including the dynamic opening of HUBs, the partial hydrolysis of formed isocyanates, and the reaction of resulting amines with residual isocyanate to form the final urea connections. In this study, we systematically investigated the behavior of different srPUUs by variation of the components – macrodiol, isocyanate and HUB – and characterization of their properties before and after pre-conditioning.
This new type of polymers are promising material candidates for electrospun vascular grafts.[4]

Keywords: self-reinforcing polymers, polyurethanes, polyureas, biodegradable polymers

Acknowledgments

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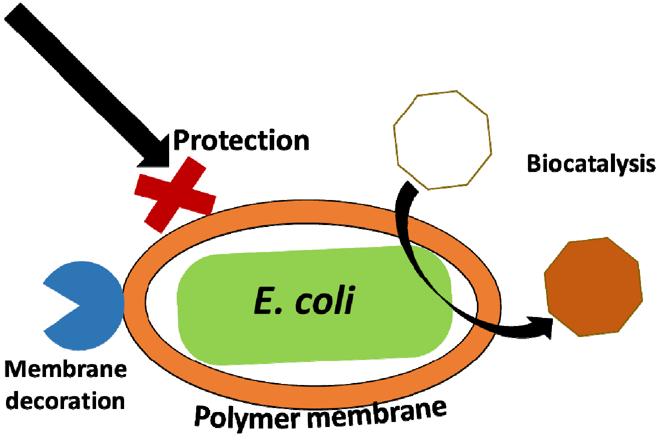
Armoured bacteria: single-cell polymer coatings protect and endow *E. coli* with novel functionalities

A. Belluati[1], N. Bruns[1*]

[1] *Technische Universität Darmstadt, Darmstadt, Germany*
**nico.bruns@tu-darmstadt.de*

In nature, layers of various biomaterials protect cell membranes: the outer membrane of Gram-negative bacteria, the diverse cell walls of bacteria, plants and fungis, up to the use of biomineralized shells. These casings are necessary against physical and chemical agents, enzymes and predators, and such principle has been adapted to cell-mimics as well, providing protection from harsh environments.[1] The microencapsulation of cells is a mature subject, however it is mainly focused on encapsulating more than a single cell, which decreases the surface/volume ratio and increases the overall size, a drawback in many biomedical applications, with single-cell encapsulation usually relying on the formation of cross-linked microgels or nanodeposition of coating molecules.[2-3] With a simple and robust co-extrusion protocol[4] with a commercial block copolymer (Pluronic® L-121), we produced block copolymer-enwrapped *E. coli*, which could withstand a variety of harsh shocks, *e.g.* temperature, pressure, osmolarity and chemical agents. This bio-similar additional membrane helped the bacteria resist against enzymatic digestion and could degrade toxic compounds.

Moreover, the membrane acted as a new region for surface modification, allowing us to decorate the bacteria with several molecules, for instance α-amylase, endowing them with the ability to digest starch, and lysozyme, creating self-predatory bacteria, requiring nothing but a simple co-extrusion step.



The diverse benefits of a Pluronic® membrane enwrapping the bacterium

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Structure and shape control in polymer nanostructures for biomedical applications

F. V. Gruschwitz[1], T. Klein[1], E. Gardey[2], A. Stallmach[2], J. C. Brendel[1*]

[1]*Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University, Jena, Germany*
[2]*Department of Internal Medicine IV, Jena University Hospital, Jena, Germany*
[*]*Corresponding Author's E-mail address: johannes.brendel@uni-jena.de*

One dimensional (1D) structures are ubiquitous in nature. Structures, such as the cytoskeleton or the extracelluar matrix, rely heavily on self-assembly processes based on supramolecular interactions which enable the dynamic formation of large and well-defined structures from macromlecular building blocks. Of course, material scientist have tried to mimic these structures Considering polymer chemistry, the self-assembly of amphiphilic block copolymers has undoubtedly attracted most of the attention.[1]
A precise control of structure formation and their stability in different biological media however remains a challenge, in particular, if 1D or fibrous shapes are considered. However, their large surface area and high aspect ratio offer unique advantages in cellular interaction and tissue penetration, as for example demonstrated in the interaction with inflamed areas in inflammatory bowel diseases (IBD).[2] Our research effort, therefore, focuses on the development of polymeric materials, which are capable of forming strong unidirectional hydrogen bonds to create bottlebrush-like assemblies.[3] Depending on the strength of interaction, the formation of one-dimensional aggregates can be enforced in water (Figure 1) resulting in kinetically trapped fibers, which can be tuned in their length by the assembly pathway.[4] Overall, this merging of supramolecular and polymer chemistry promises exciting new avenues towards functional and hierarchically ordered materials for various application.

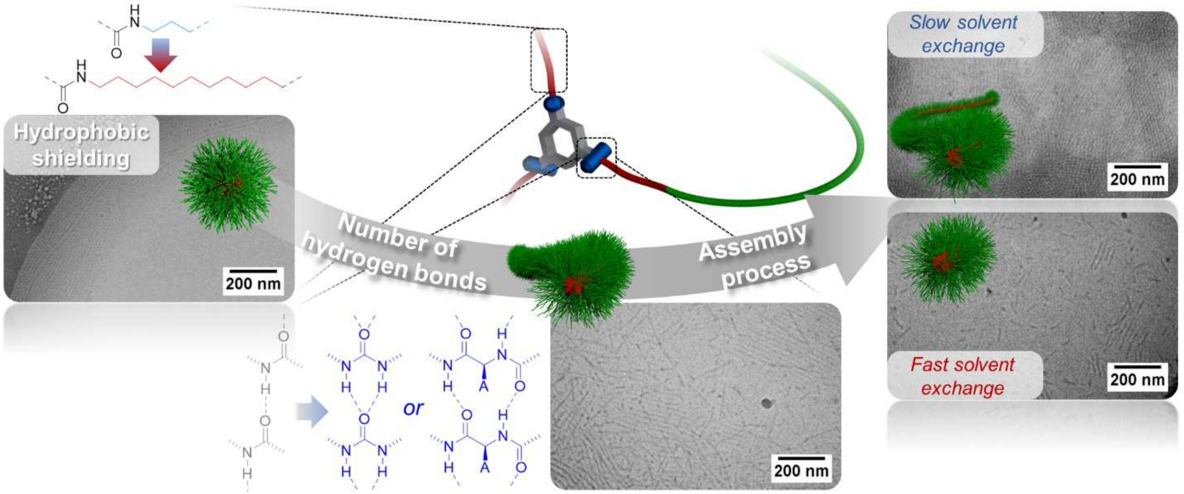

Figure 1. Schematic overview of key steps to create supramolecular fibers from polymer building blocks: hydrophobic shielding as prerequisite for assembly in water (left), sufficient number of hydrogen bonds to enforce 1D-structure (bottom), and kinetic control of their length (right).

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Lauroyl Hyaluronan: a Versatile Biopolymer for Medical Applications

J. Chmelař*, L. Bardoňová, L. Horáčková, A. Kotzianová, J. Kubíčková, J. Mrázek, K. Skuhrovcová, M. Hermannová, V. Velebný

Contipro a.s., Dolní Dobrouč, Czech Republic
**chmelar@contipro.cz*

Hyaluronan (HA) is an anionic linear polysaccharide that is a natural constituent of the human body and is present, e.g., in the extracellular matrix, synovial fluid, skin, and cartilage. It plays an important role in processes such as lubrication, tissue hydration, and wound healing. Due to its advantageous properties and inherent biocompatibility, HA is frequently used in medicine. However, HA is highly hydrophilic and readily dissolves in water, which complicates its use in applications requiring insolubility or prolonged residence time at the site of application. Several strategies can be used to overcome the solubility of HA, including ionic cross-linking, covalent cross-linking, and the modification of HA with hydrophobic side groups.

In this contribution, we present lauroyl modified hyaluronan (LAU-HA) as a versatile biopolymer suitable for application in medicine. The hydrophobic modification of HA by lauroyl side-chains provides insolubility in aqueous environments due to hydrophobic interactions (physical cross-linking) [1] and also affects the rate of enzymatic degradation. This enables long-term application compared to unmodified HA.

LAU-HA can be processed into self-supporting films [2], nanofibers [3], non-woven textiles, or „endless" fibres, which can be further processed into threads and textiles (EP2925916B1). LAU-HA can be dissolved in water-alcohol mixtures, i.e., it is not necessary to use hazardous (toxic) solvents. Advantageously, the properties of LAU-HA forms can be tuned by the degree of HA modification, ranging from gel-like behaviour to tough and elastic insoluble materials. With increasing lauroyl content, the material becomes more hydrophobic and exhibits lower swelling and improved mechanical properties. The degree of modification also influences enzymatic degradation, the rate of which decreases with increasing lauroyl content due to the lower swelling and the reduced susceptibility of acyl-modified HA to enzymatic degradation [5]. However, in clinical applications, degradation will also depend on the site of application due to varying local conditions (fluid volume, enzyme concentration, presence of biomolecules, etc.).

With respect to medical applications, it is important that the materials generally have good mechanical properties in the solid-state, enabling convenient handling and application. The safety of LAU-HA forms was tested extensively both *in-vitro* (cytotoxicity, skin sensitization, skin irritation) and *in-vivo* (intraperitoneal, topical, and oral cavity application) with good results. We also demonstrated that drugs (e.g., antiseptics) can be incorporated into LAU-HA forms and studied the drug release under various conditions [3,4]. The amphiphilic character of LAU-HA proved to be advantageous as it enabled to incorporate both hydrophilic and hydrophobic drugs. Examples of specific applications are wound dressings for the protection and moist healing of topical wounds and dental applications (WO2021148066A1). To summarize, LAU-HA is a safe and versatile biopolymer that can be processed into various application forms with a broad range of properties and has clear potential in the field of medicine.

Keywords: lauroyl hyaluronan, film, nanofiber, microfiber, thread, textile, medical device.

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Advanced glycopolymers as potent inhibitors of galectin-induced tumor progression

P. Chytil[1*], M. R. Tavares[1], M. Filipová[1], V. Křen[2], P. Bojarová[2], T. Etrych[1]

[1]Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Heyrovského nám. 2, 162 06 Prague 6, Czech Republic
[2]Institute of Microbiology of the Czech Academy of Sciences, Vídeňská 1083, 142 20 Prague 4, Czech Republic
**chytil@imc.cas.cz*

The overexpression of galectins is known to be associated with several life-threatening disorders, namely neoplastic diseases. In tumorigenesis, galectins participate in cellular adhesion, invasion, angiogenesis, and metastatic processes. Most studies focus on the two most common galectin-1 and galectin-3, which are prospective targets for therapeutical applications. Human galectin-1 and galectin-3 have shown affinity to ligands based on *N*-acetyllactosamine. Moreover, multivalent presentation these ligands often increases the affinity by several orders of magnitude via the cluster glycoside effect.[1]

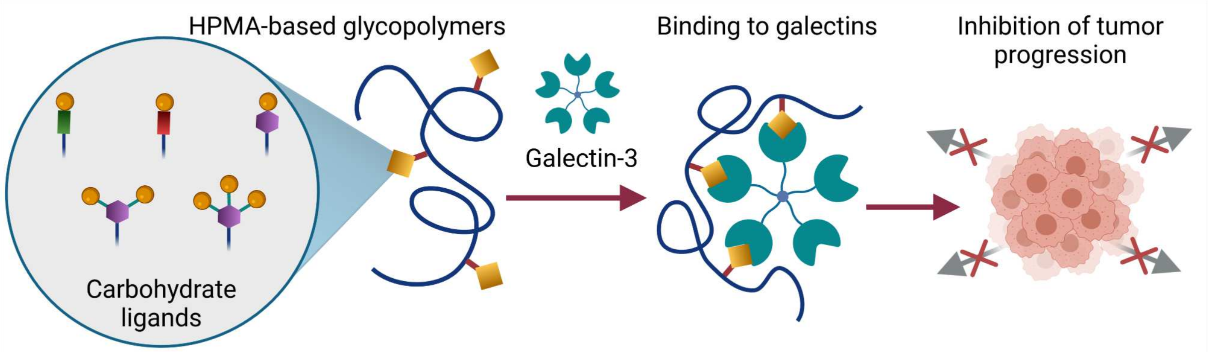

Figure 1 Schematic representation of binding to galectins resulting in the inhibition of galectin-induced processes.

This study presents the synthesis and characterization of various glycopolymers based on water-soluble *N*-(2-hydroxypropyl) methacrylamide (HPMA) copolymers, which are known for their biocompatibility, lack of any toxicity or immunogenicity.[2] Glycopolymers, prepared using controlled radical reversible addition−fragmentation chain-transfer (RAFT) polymerization, differed in the structure and content of carbohydrate ligands, namely *N*-acetylated lactosamines or their glycomimetics. Moreover, carbohydrate ligands were presented by several spacers statistically distributed along the polymer backbone. Besides monovalent linkers, also bi- or trivalent branched linkers we employed to enhance the clustering of carbohydrate ligands. We evaluated the structure-activity relationship of glycopolymers concerning their binding affinity to galectins. By tuning of the glycopolymers' structure, namely ligands' type, content and type of presentation on the polymer carrier, we were able to selectively target and inhibit galectin and, moreover, discriminate between galectin-1 and -3. Thus, we believe HPMA based glycopolymers are attractive as effective drug-free nanomedicines supporting targeted tumor treatment (See Figure 1).[3-5]

Keywords: polymer carriers, HPMA copolymers, galectins, cancer treatment

Acknowledgments

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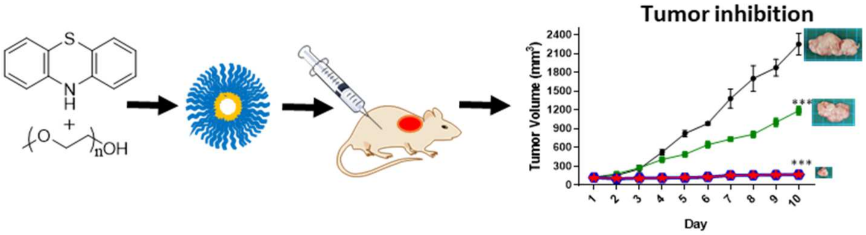
PEGylated phenothiazine derivatives with potent antitumor activity

S. Cibotaru[1], V. Nastasa[2], A. I. Sandu[1], A. C. Bostanaru[2], M. Mares[2], L. Marin[1]

[1] *Petru Poni” Institute of Macromolecular Chemistry of Romanian Academy, Iasi, Romania*
[2] *"Ion Ionescu de la Brad" University of Life Sciences, Iasi, Romania*
* *cibotaru.sandu@icmpp.ro*

Despite decades of basic and clinical research and trials of promising new therapies, cancer remains a major cause of mortality. Acording to the World Health Organization (WHO), in 2020, the estimated number of people with cancer was about 19 milions, and the percentage of mortality was about 50 %. Besides, cancer is an economical burden, the cost of cancer on the public health being calculated at more 70 billion of euro per year [1]. In this light, the development of new efficient antitumor drugs is of utmost importance. Among anticancer potent compounds, phenothiazine based derivatives proved a promising potential, but their low solubility in bio-dispersants limit their application [2,3]. To overcome this issue, the goal of this study was to synthesise new water soluble phenothiazine derivatives with antitumor properties. To this end, PEGylated phenothiazine derivatives were obtained by coupling a poly(ethylene glycol) chain to the nitrogen atom of the phenothiazine *via* three different linking groups: ether, ester and amide. Their structure was confirmed by FTIR and NMR spectroscopy, and their ability to self-assemble into an aqueous medium was investigated by DLS and UV-vis techniques, and also by fluorescence spectroscopy, SEM, AFM, POM and UV light microscopy [4]. The biocompatibility and antitumor potential of the new synthetised compounds was assesed (i) *in vitro* on normal human dermal fibroblasts and five human cancer cell lines: cervical carcinoma; malignant melanoma; osteosarcoma, breast and liver cancer, and (ii) *in vivo* on mice by determining LD50 and monitoing the tumor growth. The compounds proved biocompatibility on normal cells and a concentration dependent cytotoxicity against cancer cell lines, the diminishing of LD50 compared to pristine phenothiazine and high tumor inhibition (92%) [4]. Investigation of potential antitumor mechanism indicated the binding of PEG to phenothiazine *via* ester linkage as driving force the inhibition of cancer cell proliferation. All these findings recommend the PEGylated phenothiazine derivatives as a valuable workbench for a next generation of antitumor drugs.



Keywords: Phenothiazine, Poly(ethylene glycol), Tumour growth inhibition.

Acknowledgments

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PEO/PEDOT:PSS humidity sensors: application in breath monitoring

Edilene Assunção da Silva[1]*, Caroline Duc[1]*, Natalie Redon[1], Félix Sene[1] and Jean-Luc Wojkiewicz[1]

[1] *IMT Nord Europe, Centre for Energy and Environment, Douai, France*
**edilene.dasilva@imt-nord-europe.fr*

Breath monitoring constitutes a promising non-invasive tool for the diagnostics of several diseases. For instance, we have e-nose devices that work as an array of sensing units with distinct chemical compositions and electrical responses to a certain compound of interest [1]. However, humidity is a factor that can greatly affect the e-noses response toward the gases that are present in the human breath which can compromise its analysis [2]. Therefore, a humidity sensor is an important array component for a device which is dedicated to such medical applications. Herein, we assembled a matrix of polyethylene oxide (PEO) with 10%wt of conductive poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) doped with etylene glycol to design a humidity chemiresistor-based sensor. At first, we drop-casted the aqueous solution from this blend to observe its response and selectivity toward humidity. Later on, due to its promising primary results, we decided to print a sensor from the PEO/PEDOT:PSS solution aiming the industrial applicability and the enhancement of the sensor performance. Thus, for the humidity tests, multisensor cards were put inside an exposure chamber and the humidity around the sensors was varied using mass flow controllers. Then, we measured the resistance changes according to the variations in the environment. From the dropcast results, we have found out that the sensors show high sensibility, repeatability, and selectivity in relation to VOCs present in breath, response/recovery times within the range of the organic-based chemiresistive sensors. Moreover, their performance is not compromised by the temperature and, it responds even faster than the reference commercial sensor. The printed sensor, at its turn, in addition to the features of the casted one revealed an even stronger sensibility (up to toward humidity which can be attributed to the tuning of the morphology promoted by this technique. Which allowed more sites available to interact with the water molecules and it opens the way to industry application, since it constitutes an upscaling method.

Keywords: humidity sensor; organic polymer composite; breath monitoring; chemiresistor; printed sensor

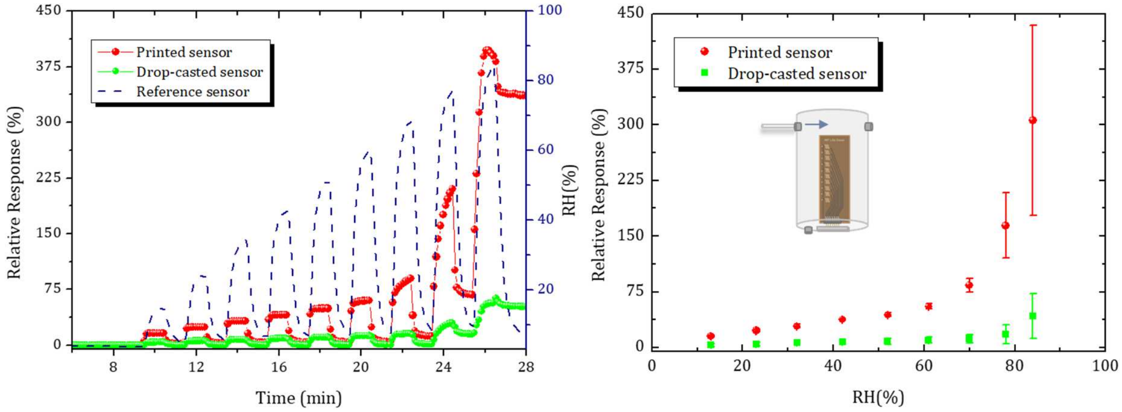

Figure 1 – a) Calibration curves of the reference commercial sensor and, of the PEO/PEDOT:PSS printed and drop-casted sensors, b) relative resistances of mixed polymer sensors versus relative humidity during the humidifying scan,

Acknowledgments

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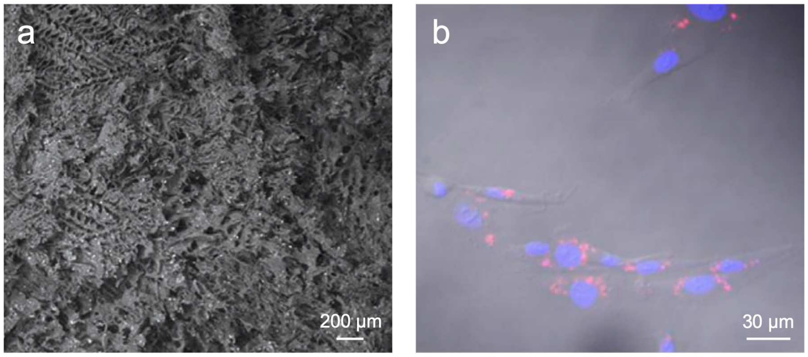
Highly porous bioactive filler/biopolymer scaffolds designed for bone regeneration

M. Degli Esposti[1,2*], D. Morselli[1,2], F. Zamparini[3], M.G. Gandolfi[3], C. Prati[3], P. Fabbri[1,2]

[1]*Department of Civil, Chemical, Environmental and Materials Engineering,*
University of Bologna, Bologna, Italy
[2]*Italian Consortium for Science and Technology of Materials INSTM, Firenze, Italy*
[3]*Department of Biomedical and Neuromotor Sciences, University of Bologna, Bologna, Italy*
[*]*micaela.degliesposti@unibo.it*

The prolonged life expectancy has led to a rapid increase of musculoskeletal pathologies in the last decades and the fabrication of a suitable scaffold material, able to support the regeneration of damaged or lost bone tissue, is one of the major challenges. Nanocomposite biomaterials, that are the result of the combination of biocompatible and bioresorbable polymers with bioactive fillers, are an efficient strategy to mimic the complex structure and biological functions of natural bone and to stimulate specific response at molecular level.
Poly(lactic acid) (PLA), poly(caprolactone) (PCL) and poly(3-hydroxybutyrate) (PHB) have been used to prepare highly porous scaffolds by Thermally Induced Phase Separation (TIPS) technique, whereas the bioactivity has been introduced through the incorporation of bioactive hydroxyapatite (HA), calcium silicate (CaSi) and dicalcium phosphate (DCPD). The inorganic particles have been also generated in the PHB-based materials using an innovative filler *in situ* synthesis, and the properties of the composite scaffolds have been then compared to scaffolds obtained by conventional mechanical dispersion of *ex situ* synthesized mineral particles.
Morphological analyses revealed highly porous structures with interconnected pores. Notwithstanding the extremely high level of open porosity reached during the fabrication of the scaffolds (up to 95%), compression mechanical properties remained at appropriate levels to ensure a proper handling and use of the scaffolds. The mineral-doped compositions showed apatite forming ability and were able to release biologically relevant ions (OH and Ca), creating the conditions of a bone forming osteoblastic microenvironment. Cell viability and proliferation tests revealed the total lack of cytotoxicity and highlighted the suitability of the proposed scaffolds to sustain cell adhesion and proliferation. In addition, the composites were able to promote osteogenic differentiation as supported by the evaluation of early osteogenic markers and/or specific gene expression patterns also mediated by the internalization of exosome vesicles derived from mesenchymal stem cells. PCL an PLA compositions were also tested for gene expression for angiogenic differentiation revealing their potential to induce the formation of new microvessels.



PLA-10CaSi-10DCPD as represedntative: (a) cross-section ESEM micrograph; (b) confocal image showing exosomes present inside the cytoplasmatic region of hAD-MSCs at 24 h after seeding (exosomes in red, nuclei in blue).

Keywords: biomimetic scaffolds, bioactive fillers, biopolymers, bone tissue regeneration, biocompatibility, vasculatization, exosome vescicles

Rapid Detection of SARS-CoV-2 Antigens and Antibodies Using OFET Biosensors Based on a Soft and Stretchable Semiconducting Polymer

K. Ditte[1,2], T. A. Nguyen Le[3,4], O. Ditzer[1,2], D. I. Sandoval Bojorquez[3], S. Chae[1], M. Bachmann[3,4], L. Baraban[3*], F. Lissel[1,2*]

[1]*Leibniz Institute of Polymer Research Dresden e.V., Dresden, Germany*
[2]*Faculty of Chemistry and Food Chemistry, Dresden Technical University, Dresden, Germany*
[3]Institute of Radiopharmaceutical Cancer Research, Helmholtz-Zentrum Dresden-Rossendorf*, Dresden, Germany*
[4]*Faculty of Medicine Carl Gustav Carus, Dresden Technical University, Dresden, Germany*
[*]*lissel@ipfdd.de, l.baraban@hzdr.de*

In the midst of the COVID-19 pandemic, adaptive solutions are needed to allow us to make fast decisions and take effective sanitation measures, e.g., the fast screening of large groups. Although being reliable, most of the existing SARS-CoV-2 detection methods lack the ability of being integrated into garments to be used on demand. Here, recently we presented[1] - at proof-of-concept level - an OFET biosensor platform for the detection of SARS-CoV-2 antigen and anti-SARS-CoV-2 antibodies (S1 Abs) on the basis of our previously reported soft and stretchable triblock copolymer (TBC) as an active layer.[2] The biosensor was produced by functionalizing a TBC film either with the S1 Abs or the receptor-binding domain (RBD) of the S1 protein, targeting CoV-2-specific RBDs and anti-S1 Abs, respectively. The obtained sensing platform is easy to realize due to the straightforward, solution-based fabrication of the TBC film and the utilization of the reliable physical adsorption technique for biomolecule immobilization. The device demonstrates a high sensitivity and low limit of detection (LOD) for S1 Abs and RBD detection respectively. The TBC used as active layer is soft, has a low modulus of 24 MPa, and can be stretched up to 90% with no crack formation of the film. With proper transfer to a stretchable-flexible substrate, the presented concept offers the possibility to realize stretchable biosensors, which might allow the fabrication of wearable platforms for on-the-fly detection of biomoecules to aid reducing - and eventually stopping - the spread of COVID-19 and future pandemics.

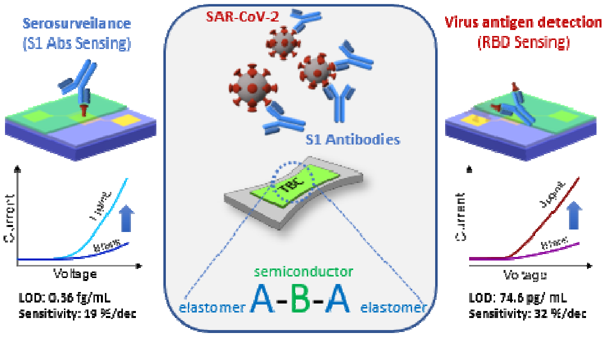


Figure 1: Schematic of the conceptual design of the biosensor for S1 Abs sensing (left) and RBD sensing (right).

Keywords: organic field-effect transistor, biosensor, block copolymers, semiconducting polymers, SARS-CoV-2 antigen sensor, SARS-CoV-2 antibody sensor

Acknowledgments

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Tumor-targeted polymer therapeutics for navigated surgery, photodynamic therapy and tumor imaging

R. Pola[1], M. R. Tavares[1], P. Chytil, Jun Fang,[2] Jean-Luc Coll,[3] M. Šubr[1], M. Filipová[1], T. Etrych[1*]

[1]*Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Heyrovského nám. 2, 162 06 Prague 6, Czech Republic*
[2] *Faculty of Pharmaceutical Sciences, Sojo University, Kumamoto, Japan*
[3] *Institute for Advanced Biosciences, Grenoble Alpes University, Grenoble, France*
**etrych@imc.cas.cz*

In the past several decades, nanosized drug delivery systems with various targeting functions and controlled drug release capabilities inside targeted tissues or cells have been intensively studied. Understanding their pharmacokinetic properties is crucial for the successful transition of this research into clinical practice[1] .

Among others, fluorescence imaging has become one of the most commonly used imaging tools in pre-clinical research. Moreover, theranostics, which links therapy and diagnostics, are widely studied for the disease treatment and the generation of diagnostic information using one multi-functional system. Recently, photodynamic therapy (PDT) has arised as a smart approach which employs the light irradiation to activate photosensitizers in situ after the selective tumor accumulation. Here, the exogenous light stimulus induces the formation of cytotoxic oxygen free radicals, i.e., singlet oxygen species ($^1O_2$), resulting in the cell death.

In this work, polymer platform suitable for efficient stimuli-sensitive therapeutics, diagnostics and even theranostics based on water-soluble and amphiphilic polymer conjugates is presented. Synthetic nanocarriers based on methacrylamide-based copolymers are highly attractive for *in vivo* application as they are fully biocompatible, water soluble and non-toxic biomaterials with tailored physico-chemical properties for application in medicine. Their favorable pharmacokinetics altogether with Enhanced Permeability and Retention effect-driven tumor accumulation enable a higher uptake in solid tumors with an enhanced therapeutic outcome. The set of polymer biomaterials differing in their inner structure, molecular weight and functionality was designed, synthesized and evaluated for their therapeutic, diagnostic and even theranostic properties. The presented work will comprise the synthetic strategy of polymer materials and their utilization as the carrier of the therapeutically or/and diagnostically active molecules. Within this aproach selected photosensitizers were used for the development of tumor-targeted theranostics for both efficient tumor imaging and PDT. Their physico-chemical, *in vitro*, and *in vivo* behavior were investigated and the results indicate that the attachment of the hydrophobic photosensitizer molecule results in the formation of micelles, which protects the active molecules during its transport. The cytotoxicity of developed polymer nanomedicines was remarkably increased when light was irradiated and they showed high tumor targeted accumulation based on the EPR effect, therefore these polymer systems are promising candidates for tumor diagnostics and treatment.

Keywords: polymer carriers, photodynamic therapy, navigate surgery, cancer treatment

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Biomimetic polymer vesicles through asymmetric and chiral amphiphlic block-copolymers

R. Wehr[1], D. Daubian[1], D. Fotiadis[2], W. Meier[1], J. Gaitzsch[1,3*]

[1]*University of Basel, Mattenstrasse 24 – BPR 1096, 4058 Basel, Switzerland*
[2] *University of Bern, Bühlstrasse 28 , 3012 Bern, Switzerland*
[3]*Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany*
[*]*gaitzsch@ipfdd.de*

The self-assembly of amphipilic block-copolymers into polymer vesicles, or polymersomes, has already proven to be of great asset for potential applications in drug delivery. Efforts to biomimic natural vesicles have underlined these potentials even further. Despite all of these advantages, a number of challenges, especially in biomimicry, still remain open.

Natural vesicles, for example, have distinct differences between their inner and outer surface (i.e. asymmetric membranes) also to ensure that transmembrane transporters are inserted correctly. We have shown that the formation of polymersomes with asymmetric membranes can be achieved well by using ABC triblock copolymers. In adjusting the hydrophilic-to-hydrophobic balance, different self-assemblies like multi-core-micelles and multi-core vesicles could be achieved as well. [1] Once the asymmetric membrane is there, it can also host functional directional transmembrane proteins. In our case the light-activated proton pump proteorhodopsin was used to form a pH gradient in the presence of light. The gradient equillibrated in the dark and could be achieved reversibly over various cycles. (Figure 1a) [2]

Another key aspect of natural membranes is their chirality. All natural compounds are usually either D- or L- derivatives, while synthetic polymers mostly have no defined chirality in their backbone. We managed to synthesise the fully chiral (i.e. isotactic), yet non-crystalline block-copolymer poly(butylene oxide)-*block*-poly(glycidol) (PBO-PG) in an all-S and an all-R configuration. A full characterisation of the small and giant polymersomes from 100 nm to 40 µm gave a much-needed insight into the interconnection of polymer tacticity and vesicle properties. (Figure 1b) [3]

Altogether our works have shown that fine-tuning the chemistry of the amphiphilic block-copolymers forming the vesicles, can open a new range of biomimetic synethetic vesicles.

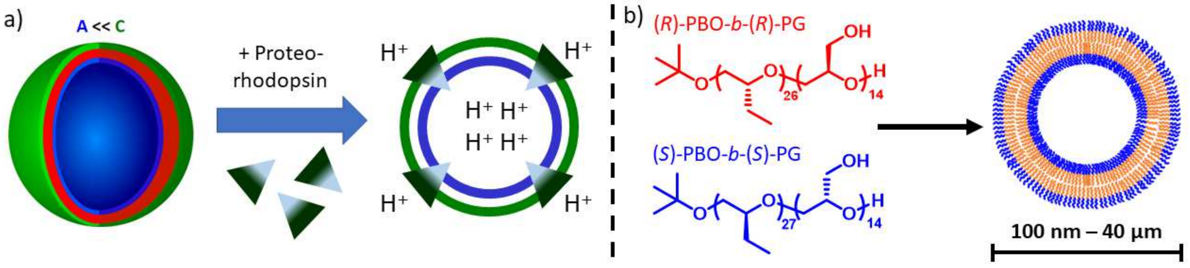

Figure 1: a) An asymmetric polymersome forms, when A is shorter than C in an ABC triblock copolymer. The asymmetric vesicle then allows for the direction insertion of the transmembrane protein proteorhodopsin (triangle symbols), which can then generate a pH gradient. b) Fully chiral PBO-PG block-copolymers self-assemble into polymersomes of 100 nm to 40 µm and can then be characterised in detail.

Keywords: Polymersomes, Asymmetric membranes, Proteorhodopsin, Membrane Proteins, Chirality

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Activation via photo-degradation and functionalization of light responsive hydrogels

T. N. Gevrek *[1], A. Turanli[1], N. Demirbilek[2]

[1]*Gebze Technical University, Department of Chemistry, Kocaeli, Turkey*
[2]*Gebze Technical University, Institute of Biotechnology, Kocaeli, Turkey*
[*]*tcivan@gtu.edu.tr*

Photosensitive hydrogels undergo physical and/or chemical changes due to light-dependent transformations of the functional groups in their structures when exposed to light at the appropriate wavelength[1]. The development of photosensitive materials is very advantageous since light is non-invasive, does not require contact with the material and has low thermal effect. In photosensitive hydrogels photochromic unit captures the optical signal and converts it into a chemical signal via a photoreaction (isomerization, cleavage/cleavage or dimerization, etc.). Thus, photosensitive hydrogels can expand, contract, degrade or gain functionality under ultraviolet (UV) or visible light[2]. Azobenzene, spiropyran, spiroxaless, cinnamic ester that reacts [2+2] under light, coumarin and diarylethene groups are used in photosensitive materials researches[1]. The most commonly used light sensitive group in research is the orthonitrobenzyl (ONB) group, with its high sensitivity and acceptable UV wavelength requirement for biological applications (365 nm)[3-4] After exposure to UV light, the ONB group decomposes forming a nitrosobenzaldehyde (or nitrosoketone) and a carboxylic acid (or alcohol) [5].

In this study, novel hydrogels containing ONB group were prepared by reaction of orthonitro benzyl containing monomer with a hydrophilic co-monomer. Chemical characterization of hydrogels was performed using fourier transform infrared spectroscopy. Water absorption capacities, surface morphology and thermal stability of hydrogels were investigated. When exposed to UV irradiation, the cross-linking density of these hydrogels decreases and also they gain amine reactive property due to newly formed nitrosobenzaldehyde units. The functionalizability of the hydrogels was demonstrated by attachment of the amine containing small molecules and biomolecules.

Keywords: functional hydrogels, photo-labile units, photo-degradation, photo-activation, orthonitrobenzyl

Acknowledgments
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Influence of accelerated aging on the rheological properties and structure of irradiation sterilized low-density polyethylene

B. Günther[1,2]*, S. Mörl[1], J. Kaschta[2], D.W. Schubert[2]

[1]*B. Braun Melsungen AG, Melsungen, Germany*
[2] *Institute of Polymer Materials, University Erlangen-Nuremberg, 91058 Erlangen, Germany*
**bjoern.guenther@bbraun.com*

With a 44.5 % market share, ionizing radiation is the most commonly used sterilization method besides ethylene oxide sterilization for single-use medical devices. [1] It is well known that radiation can induce significant chain scission and crosslinking in polymers. [2–4] Nevertheless, the impact of different radiation doses in combination with aging on the properties of the polymers is mostly unknown and of high interest in the medical technology industry. [5,6] This study investigates the impact of gamma radiation on four different commercially available, medical-grade low-density polyethylenes in combination with accelerated aging. [7] Rheological, as well as structural analyses regarding gelation, molar mass, and crystallinity, have been carried out. It could be demonstrated that increasing the radiation dose results in significant crosslinking and an increase in viscosity of the different LDPE. Aging on the other hand leads to a pronounced reduction in viscosity and an increased crystallinity with time, which was attributed to a chain scission during aging. Furthermore, it has been observed that depending on the radiation dose the stated effects are most pronounced after longer aging times (>100 d).

Keywords: low density polyethylene, gamma sterilization, artificial ageing, rheology

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Amphiphilic block statistical copolymer nanoparticles for targeting inflammation by RAFT PISA

S. A. Harrison[1*], and S. G. Spain[1]

[1]*University of Sheffield, Sheffield, United Kingdom*
[*]*Sharrison6@sheffield.ac.uk*

The body defends itself against threats from foreign invading cells by using reactive oxygen species (ROS) to attack and destroy them: this is called inflammation. ROS can also attack the body itself in auto-immune diseases such as rheumatoid arthritis (RA) and multiple sclerosis (MS).[1,2] RA affects the joints in the body which causes pain and can lead to loss of mobility. MS damages the myelin sheath on nerves in the central nervous system (CNS) which can lead to physical disability. Both diseases cannot be cured but are treated with disease modifying drugs, which aim to alleviate symptoms. The drugs used are non-targeted and can cause serious side-effects.[3,4] Polymeric nanoparticles, such as Doxil, can be used for drug delivery. Doxil is a pegylated liposome loaded with doxorubicin which improves circulation time and reduces cardiotoxicity compared to the free drug. However, there are issues with accumulation in the hands and feet giving rise to hand-foot syndrome.[5] Targeted drugs affect only the areas of need, meaning doses can be lowered and the risk of side-effects reduced.[6] Using an oxidation responsive group within a polymeric nanoparticle system would allow for drug targeting at specific sites of inflammation and includes the benefits of longer circulation time and reduced side-effects.

In this work 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl methacrylate (OxM2), a boron-based oxidation responsive monomer, is polymerised statistically with 2-hydroxypropyl methacrylate (HPMA) in different ratios to form the hydrophobic component of diblock coploymer nanoparticles via reversible addition−fragmentation chain transfer (RAFT) polymerisation. A poly(glycerol monomethacrylate) macro chain transfer agent is used as the hydrophilic component in this polymerization-induced self-assembly (PISA) system. $p[GMA_{51}\text{-}b\text{-}(HPMA_x\text{-}s\text{-}OxM2_y)]$ nanoparticles exhibit an oxidation response when exposed to hydrogen peroxide at 37 °C due to OxM2 transitioning from hydrophobic to hydrophilic, thus changing the packing parameter which affects the size of the nanoparticles. The oxidation responsive behaviour has been monitored over time using NMR, DLS, and TEM showing decreasing particle size over time and increasing free aromatic species from OxM2 degradation. No response is seen in the absence of hydrogen peroxide at 37 °C. It is expected that order-order/order-disorder transitions can be found for this system allowing for a range of delivery modes. Future work will look at drug loading/release capabilities of the nanoparticles and cell cytotoxicity studies.

Keywords: Inflammatory diseases, drug-delivery, RAFT, PISA, nanoparticles, oxidation-responsive

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Supercritical CO_2 blown poly(ε-caprolactone) covalent adaptable networks as smart materials for biomedical applications.

Maxime Houbben[1], Christine Jérôme[1]

[1]*Center for Education and Research on Macromolecules (CERM), University of Liege (ULiege), CESAM-RU, Sart Tilman, Building B6a, B-4000 Liege, Belgium*

Foams are versatile materials encountered in our daily life for a wide variety of uses such as cushioning, thermal and acoustic insulation or medical applications. The combination of the mixed properties between a continuous matrix and gas cells and the diversity of pore structures represents a powerful tool for the design of new materials. Among the different polymer foam fabrication processes, the use of supercritical CO_2 has been one of the most investigated in the past decade[1]. It is especially interesting when biomedical applications are foreseen since CO_2 is non-toxic and avoid VOCs emission. Nevertheless, the design of crosslinked polymer foams with low density still remains a challenge. Various crosslinking processes mainly based on heating, irradiation with the addition of an external agent have been applied after foaming but remain difficult to perform due to mass transfer issues of the crosslinking agent. When crosslinking occurs before foaming, it dramatically limits the material expansion.

In order to overcome these drawbacks, the present work aims taking advantage of the thermoreversible Diels-Alder cycloaddition to elaborate foams of poly(ε-caprolactone) (PCL) covalent networks. Based on this reaction, we considered to induce cross-linking after the foam expansion by playing on the thermal equilibrium of the thermoreversible Diels-Alder cycloaddition. Therefore, low molar mass star-shape PCL[2] end-capped by furan or maleimide were impregnated with CO_2 under supercritical conditions and then foamed under appropriate control of the pressure and temperature. The resulting foam possesses a much higher volume expansion than a sample fully crosslinked before foaming in the same conditions, thanks to the low crosslinking ratio during foaming. These foams exhibit also improved thermal stability thanks to the chemical crosslinking as compared to non-crosslinked PCL foams. Interestingly, these foams possess shape memory properties due to the semi-crystallinity of the PCL. Thermal stability and shape memory properties were evaluated by dynamic mechanical analysis in both tensile and compression testing with controlled force mode, stress and temperature ramps. Since significant maleimide/furan adduct cycloreversion can be achieved at high temperature, system reversibility and recyclability have also been attested.

This foaming process proves itself very interesting by the formation of highly physically expanded and recyclable crosslinked foams from a non-initially foamable material. These innovative shape memory PCL-CAN foams are attractive candidates as self-deploying implants for vessels occlusion, as it is shown by dynamic mechanical analysis and illustrated by mechanical occlusion of a large simulated vessel.

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Formulation of glyco-nanostructures via polymerization induced self-assembly in aqueous dispersion

D. Ikkene,[1] J. L. Six [1] and K. Ferji[1]

[1]*Laboratoire de Chimie Physique Macromoléculaire, Université de Lorraine, Nancy, France*
djallal.ikkene@univ-lorraine.fr

Abstract: Soft nanostructures obtained by self-assembly of amphiphilic copolymers (ACP) are of great relevance for nanomedicine, where they can be used as Drug Delivery Systems (DDSs). Among these DDSs, polymersomes (vesicles) are under intense scrutiny because they allow simultaneous encapsulation of hydrophobic and hydrophilic drugs.[1] Amphiphilic glycopolymers (AGPs), amphiphilic copolymers associating hydrophilic polysaccharides and hydrophobic synthetic polymers, are a potential alternative for the formulation of DDSs, thanks to the high biodegradability, non-toxicity and biocompatibility of polysaccharides. However, primitive morphologies (spherical micelles and core/shell nanoparticles) have been frequently reported in the literature using AGPs. This can be explained by the difficulty to induce the self-assembly of AGPs by conventional techniques (nanoprecipitation and solvent emulsion-evaporation).

This talk will demonstrate the ability of the emerging methodology called "Polymerization Induced Self-Assembly" (PISA) to produce efficiently vesicular or cylindrical morphology nanostructures based on polysaccharide in aqueous dispersion. A water-soluble monomer (2-hydroxypropylmethacrylate, HPMA), forming a hydrophobic polymer (PHPMA), is polymerized from a water-soluble macromolecular Chain Transfer Agent based on dextran (DexCTA).[2] Photomediated Reversible Addition-Fragmentation chain Transfer (Photo-RAFT) was employed to extend hydrophobic PHPMA grafts from DexCTA to produce Dex-g^N-PHPMA$_x$ glycopolymers, where N and X are respectively the number and the degree of polymerization of PHPMA grafts. When the PHPMA grafts reach a critical size, the glycopolymers become amphiphilic and self-assemble *in-situ* to form glyco-nanostructures.[3] Advanced characterization techniques including light scattering (DLS/SLS), small-angle X-ray scattering, transmission electron microscopy and atomic force microscopy have been employed to highlight the influence of the experimental conditions (solid concentration and temperature) and the structural parameters of the glycopolymers (length and number of PHPMA graft) on the morphology of the nanostructures. On the one hand, our results revealed that Dex-g-PHPMA could self-assemble into various morphologies, including spheres, worm-like micelles, unilamellar and multicompartment vesicles.[3] On the other hand, we demonstrated that the radius and the membrane thickness of the produced unilamellar vesicles can be tuned with the length of the PHPMA graft.[4]

Keywords: PISA, Polysaccharide, Vesicles, Light scattering, Nanomedicine

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Tumor microenvironment-specific stimuli-responsive nanomedicines for anticancer therapy

E. Jäger[1*], A. Jäger[1], M. Hrubý

[1]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,*
Heyrovsky Sq. 2, 162 06 Prague, Czech Republic
[*]*jager@imc.cas.cz*

Systemic use of chemotherapeutic agents is often accompanied with severe side effects, mostly related to lack of cellular and tissue selectivity of these drugs for tumors over healthy tissue.[1] Over the past years breakthroughs have been made in the development of advanced drug delivery systems with the aim to obtain precision medicine to fight cancer. A strategy that has successfully been applied is to use the chemistry of the tumor microenvironment to induce the more specific release of therapeutic cargo at the site of the tumor.[2] Herein, several polymer nanomedicines (polymer-drug conjugates, polymer nanoparticles – polymersomes)[3-5] were designed to display tunable oxidative triggered degradation in the presence of physiologically relevant reactive oxygen species (ROS)-concentrations or low pH, as well as multiresponsive systems able to respond to multiple different chemical triggers. The chemical approaches, polymers' characterization, there in vitro degradation and their potential application is demonstrated in in vitro and in in vivo models. The most optimal nanomedicines outperformed frequently used chemotherapeutics such as doxorubicin and paclitaxel/docetaxel in terms of tumor growth inhibition and survival, shedding light on chemical requirements for successful cancer nanomedicine.

Keywords: nanomedicines, stimuli-responsive materials, chemotherapy, drug-delivery

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Reversible Protein Capture and Release by Redox-Responsive Hydrogel in Microfluidics

Chen Jiao[1,2], Jens Gaitzsch[1*], Brigitte Voit[1,2*]

[1]*Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany*
[2] *Lehrstuhl Organische Chemie der Polymere, Technische Universität Dresden, 01062, Dresden, Germany*
*voit@ipfdd.de; gaitzsch@ipfdd.de

Stimuli-responsive hydrogels have a wide range of potential applications in microfluidics, which has drawn great attention. In order to fabricate the next generation of microfluidic devices, we have integrated double cross-linked redox-responsive hydrogels.[1,2] Our device is based on a poly(*N*-isopropylacrylamide) (PNiPAAm) hydrogel with a permanent cross-linker (*N,N'*-methylenebisacrylamide, BIS) and a reversible cross-linker (*N,N'*-bis(acryloyl)cystamine, BAC). An array of hydrogel dots was integrated into a microfluidic chamber through photopolymerization (Figure 1). Cleavage and re-formation of disulfide bonds introduced by BAC changed the cross-linking densities of the hydrogel dots, making them swell or shrink.[3] Rheological measurements allowed for selecting hydrogels that withstand long-term shear forces present in microfluidic devices. Once implemented, the thiol-disulfide exchange allowed the hydrogel dots to successfully capture and release the protein bovine serum albumin (BSA). BSA was labelled with rhodamine B and functionalized with 2-(2-pyridyldithio)-ethylamine (PDA) to introduce the disulfide bonds. The reversible capture and release of the protein reached an efficiency up to 84% in release rate and could be repeated over 3 cycles within the microfluidic device. These results demonstrate that our redox-responsive hydrogel dots enable the dynamic capturing and release of various different functionalized molecules and have a great potential to be integrated into a lab-on-a-chip device for detection and/or drug delivery.

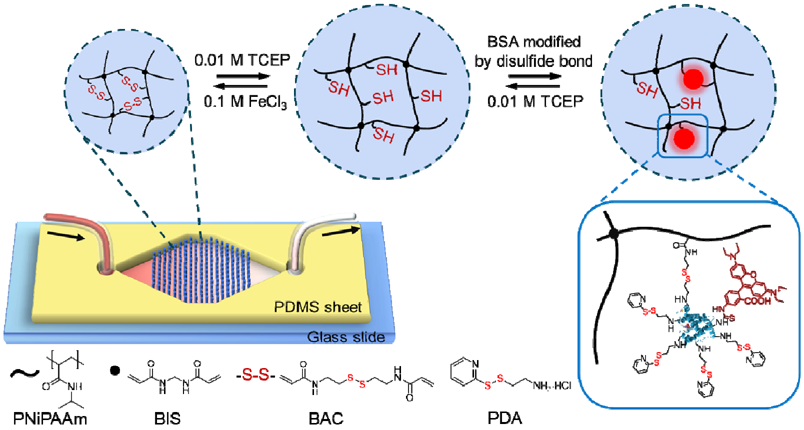

Figure 1. Schematic drawing of the microfluidic chip design and the reversible redox-responsive property of double cross-linked PNiPAAm hydrogel dots permanently cross-linked by BIS and reversibly cross-linked by the disulfide bonds of BAC.

Keywords: microfluidics; disulfide bonds; redox-responsive; hydrogels; protein capture and release; swelling behaviors; mechanical properties

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Poly(alkylene citrate)-based fluorescent polymers with antioxidative properties as a versatile platform for tissue engineering

W. Kasprzyk*[1], F. Koper[1], T. Świergosz[1], A. Flis[2], E. Pamuła[2], S. Bednarz[1], D. Bogdał[1], M. Trávníčková[3], L. Bačáková[3], H. Beneš[4], O. Pop-Georgievski[4], L. Kobera[4]

[1]*Faculty of Chemical Engineering and Technology, Cracow University of Technology, Kraków, Poland*
[2]*Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Kraków, Poland*
[3]*Institute of Physiology, CAS, Prague, Czech Republic*
[4]*Institute of Macromolecular Chemistry, CAS, Prague, Czech Republic*
**wiktor.kasprzyk@pk.edu.pl*

Nowadays synthetic grafts prepared from PET or ePTFE are materials of choice in the treatment of vascular diseases. On the other hand biodegradable aliphatic polyesters have been proven to be an alternative in regenerative medicine related applications. Among many aliphatic polyesters, poly(alkylene citrates) (PACs) have grown as one of the most promising alternative biomaterials for vascular tissue engineering. PACs are susceptible to modification facilitating the introduction of additional functionalities and broadening the spectrum of their possible applications. In addition, cell proliferation studies indicated their remarkable biocompatibility and absence of cytotoxicity, with a significant decrease in thrombogenicity [1].

In this contribution, we will highlight our recent progress in the preparation of novel antioxidant and fluorescent materials for vascular tissue engineering by modifying PAC materials with glutathione (GSH). The research hypothesis for this project assumes that GSH can react with citrate moieties present in the bulk and surface layers of PAC materials to form esters, amides and derivatives of ring-fused 2-pyridones [2, 3]. Therefore, the above modification ensures that both luminescence and antioxidant properties are imparted to the material in one step.

The succesfull incorporation of aforementioned properties has been confirmed with several techniques including solution and solid state NMR, XPS, contact angle, spectrofluorimetry and DPPH assay. The chemical structure and optical properties of fluorescent 2-pyridone derivative formulating *in situ* in the course of PAC modification were characterized using NMR, HR-LC-MS and optical spectroscopy analyses [4]. For biological activity studies, cell adhesion, viability and proliferation in the extracts and in direct contact with materials were studied under oxidative stress conditions. In order to interpret the biological results correctly it was necessary to evaluate the influence of the carboxyl groups content within the unmodified PAC materials on cell viability and proliferation. The latter was achieved by comparison of biological response of PAC materials obtained at two different molar ratios of citric acid to diol used during synthesis (2:3 and 1:1) [5, 6].

Those results: (i) showed the privilege of using a 2:3 molar ratio of reagents over commonly described 1:1 ratio and (ii) indicated that the improved antioxidative properties of the GSH-modified PAC materials originate from the presence of reduced form of GSH in its chemical structure. The developed PAC materials might be useful in reduction of post-implantation oxidative stress, preventing excessed neointima growth as well as in bioimaging and visualizing of implant degradation.

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Enhanced interchain interactions for fine-tuning bioprintability of hydrogels and their use of tissue engineering scaffold

B. Köksal[1*], U.H.Yıldız[1]

[1]*Izmir Institute of Technology, Izmir, Turkey*
[*]busrayildiz@iyte.edu.tr, hakanyildiz@iyte.edu.tr

The bioprinting of hydrogels are becoming attractive alternative in tissue engineering applications since they exhibit good mechanical properties, biocompatibility as well as tunable porosity that provide matter transfer in complex tissue models with specified geometry, functions and properties. The bioprinting of gelatin-based hydrogels are one of the most studied hydrogel based ink (1-5) yet needs chemical modifications to increase printability, and integrity. It is possible to increase printability and integrity of gelatin via addition of photocurable groups into gelatin backbone. The photocurable groups on gelatin can increase chemical gelation extent and overall integrity. We here describe a new synthetic route for gelatin-based photocurable hydrogels with fast gelation by chemical modification of gelatin by 2-isocyanatoethyl methacrylate (NCO-Gel) and allyl isocyanate (Allyl-Gel). The photochemical gelation kinetics is monitored by Dynamic Light Scattering (DLS) to analyze microrheological properties and results shows that methacrylate and isocyanate groups decreases gelatin time to 5 seconds in 5% NCO-Gel. Theoretical calculations based on interaction between amino acids on polymer backbone reveals that NCO-Gel hydrogel 560 meV whereas GelMA has 210 meV. The increased interaction energy proves that 2-isocyanatoethyl methacrylate group on NCO-Gel organizes hydrogen bonding pairs and enhanced interactions nearly three folds as compared to the commonly used methacrylic anhydride. Together with DLS analysis, theoretical results clarify assembly of macromolecular chains to gets gelation faster (6). Moreovwe we have shown that gelation time of the hydrogels can be tuned by combining NCO-Gel and Allyl-Gel in specified compositions. Morphological and nanomechanical analysis via Atomic Force Microscopy (AFM) shows that NCO-Gel has deafer slope on Force-Distance curve explaining stiffer nature of NCO-Gel hydrogels than GelMA hydrogels (6). These new crosslinker molecules exhibit extremely fast gelling process onset of bioprinting process. The printability of gelatin-based bioink is increased using novel hydrogels of NCO-Gel and Allyl-Gel. As an ongoing work we have employled melt electrowriting (MEW) method to fabricate tissue scaffolds with exact shapes and properties. The scaffolds modified with gelatin or NCO-Gel polymer to increase biocompatibility have been studied to confirm promising potential of NCO-gel in various bio-printing modalities.

Keywords: Hydrogel, Biomaterials, Gelatin, Bioprinting, Melt electrowriting, AFM, PCL

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Thermoresponsive Triblock Copolymers: Widely Applicable ^{19}F MRI Tracers

Kristyna Kolouchova[1*], Ondřej Groborz,[2,3,4] Miroslav Šlouf,[2] Vít Herynek,[5] Laurence Parmentier,[1] David Babuka,[2] Ondrej Sedlacek,[3] Martin Hruby,[2] Richard Hoogenboom,[1] Sandra Van Vlierberghe[1*]

[1]Department of Organic and Macromolecular Chemistry, Centre of Macromolecular Chemistry, Ghent University, Krijgslaan 281-S4, 9000 Ghent, Belgium
[2]Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského sq. 2, Prague 6, 162 06, Czech Republic
[3]Institute of Biophysics and Informatics, Charles University, First Faculty of Medicine, Salmovská 1, 12000 Prague 2, Czech Republic
[4]Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo sq. 2, Prague 6, 160 00
[5]Center for Advanced Preclinical Imaging, First Faculty of Medicine, Charles University, Salmovská 1, 120 00 Prague 2, Czech Republic
**Corresponding author, email: Sandra.VanVlierberghe@UGent.be, Kristyna.Kolouchova@UGent.be*

Magnetic resonance imaging (^{1}H MRI) is a commonly used diagnostic tool that provides high-resolution morphological and anatomical information on soft tissues, with no limitations regarding sample penetration and, hence, has found an irreplaceable role in medicine.[1] Nevertheless, some anatomical structures or pathologies can be difficult to observe with standard ^{1}H MRI techniques, due to a lack of contrast with surrounding tissues. Its potential can be improved by introducing an MRI tracer. The most promising tracers are ^{19}F-based compounds, due to their high sensitivity, biocompatibility, negligible biological background along with the possibility of measuring ^{19}F in commonly used ^{1}H MRI devices. In our study, we prepared a wide spectrum of thermoresponsive triblock copolymers as ^{19}F MRI tracers. These ABA triblock copolymers are able to form nano-particles in diluted aqueous solutions and which enable transition into a physically cross-linked hydrogel upon increasing the polymer concentration. Thermoresponsive hydrogels are useful for tissue engineering applications, while the nano-particles can be used as drug delivery systems as well as for cell/tissue labelling. In general, we created therapeutic and diagnostic (theranostic) tracers enabling straightforward synthesis while serving a multitude of applications. The polymers are based on biocompatible poly[*N*-(2,2-difluoroethylacrylamide)] (PDFEA) and poly(ethyleneglycol) (PEG) polymers, of which the potential was already shown in our previous studies.[2–5]

Keywords: Physically crosslinked hydrogels, ABA copolymers, ^{19}F MRI

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In-depth structural examination of poly(alkylene citrates) towards the structure-property relationship estimation in the perspective of biomedical applicability

F. Koper*[1], T. Świergosz[1], A. Żaba[1], A. Flis[2], M. Trávníčková[3], L. Bačáková[3], E. Pamuła[2], D. Bogdał[1], W. Kasprzyk[1]

[1]*Faculty of Chemical Engineering and Technology, Cracow University of Technology, Kraków, Poland*
[2]*Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Kraków, Poland*
[3]*Institute of Physiology, CAS, Prague, Czech Republic*
**filip.koper@pk.edu.pl*

Poly(alkylene citrates) (PACs) have grown as one of the most promising alternative biomaterials for vascular tissue engineering in contrary with commonly applied PTFE and PET grafts. PACs are characterized by tunable mechanical and physiochemical properties along with decreased thrombogenicity. PACs also remain a suitable environment for cell adhesion and growth. Moreover, due to the presence of non-substituted carboxyl groups within the polymer network they are suspectible for the introduction of various modificators bringing about novel functionalisation and enlarged applicability.

In the presented work a comprehensive and detailed examination of PACs was performed. The experiments were conducted for discovering the structure-property correlation in PAC polyesthers leading to their application as a vascuar grafts. It was achieved by a novel approach towards the synthesis protocol as well as thorough structural characterisation of PACs. The prepolymers obtained in 1:1 (CA:diol) and 2:3 molar ratio were characterised via NMR, LC-ESI-MS and acid value combined with mechanical and biological evaluation of crosslinked materials from mentioned prepolymers.

The major changes including simplification and strict control applied to the synthesis procedure resulted in improvements in the protocol and in increasement of the reaction yield. Detailed NMR spectra combined with MS and acidity determinations allowed for a thorough understanding of the PAC structure, explanation of chemical nature of the synthesis process and shed a light on the chemistry of the material crosslinking process. The results of mechanical and surface examination confirmed the uniformity of materials obtained and their appropriate properties for applications in tissue engineering of blood vessels. Mechanical and surface examination also emphasized the importance of introduced modifications to the synthesis protocol and exposed several tailorable factors which can be modified for fabrication of materials with desired properties for specific applications. Elaborated analyses of materials fabricated in various times and reaction conditions enabled to estimate of the exact reaction parameters and additionally confirmed the relationship between polycondensation parameters and physiochemical and biological properties of the final polymer materials. All of the performed analyses indicated the undoubted usefulness of PACs in further work on bioresorbable tissue scaffolds.

The final and the most relevant conclusion is the correlation of the acidity, and the molar ratio of reactants with cell viability and proliferation. The results of proliferation studies performed on material extracts indicate the privilege of using a 2:3 molar ratio of reagents than commonly described in the literature 1:1 ratio while maintaining all the properties of the latter. In vitro tests performed in a direct contact with cells show that the final biological output can also be tuned by using diols of a higher number of carbon atoms in the chain.

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MULTIARM POLYMER CARRIERS FOR DRUG DELIVERY

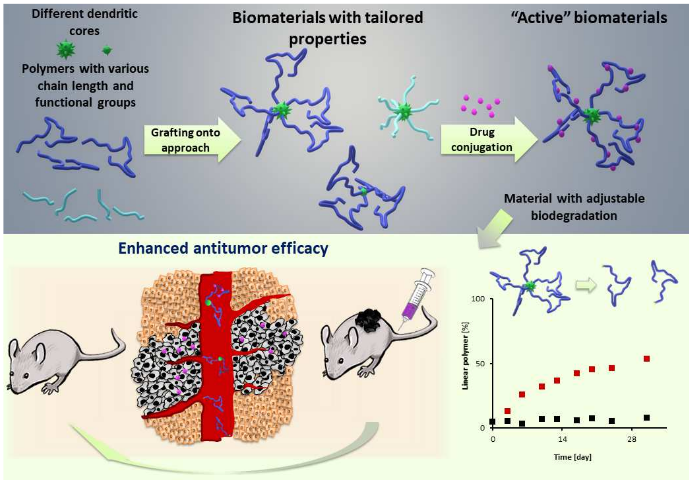
L. Kostka[1*], L. Kotrchová[1], V. Šubr[1], W. Cai[2], M. Šírová[3], T. Etrych[1]

[1]*Institute of Macromolecular Chemistry CAS, Department of Biomedical Polymers*
Prague, Czech Republic
[2]*University of Wisconsin-Madison, Madison, WI, United States*
[3]*Institute of Microbiology CAS, Laboratory of Tumour Immunology, Prague , Czech Republic*
[*]*kostka@imc.cas.cz*

The copolymers based on N-(2-hydroxypropyl)methacrylamide (HPMA) represent one of the most intensively studied synthetic carriers. It was shown that the conjugates based on HPMA copolymers containing cytostatics, e.g. doxorubicin, pirarubicin or docetaxel bound via pH sensitive hydrazone bond are highly potent drug-delivery systems for cancer treatment. The accumulation of water-soluble polymer carriers in tumor tissue is molecular-weight dependent. Nevertheless, not only the size, but also the shape of polymer carriers is crucial for their biological behavior, thus star-like architectures of HPMA copolymers with different molecular weight were designed and synthesized.

Generally, excretion of polymer carriers through renal filtration is limited by its molar mass, i.e. for HPMA copolymers the limit 50 kg/mol was estimated.[1] For high-molecular weight polymer carriers, their degradation to products with molecular weight bellow the renal threshold is necessary to facilitate their removal from the body. Therefore, we focused on design and synthesis of high-molecular HPMA structure with various biodegradable “cores”.

Cytostatic drug doxorubicin was attached to these carriers via pH-sensitive hydrazone bond and activity of these conjugates was tested *in vitro* and *in vivo*. We successfully tested accumulation of the released drug for various star-like polymer conjugates. Various polymer carriers without attached drug were also traced in the organism via positron emission tomography. An *in vivo* antitumor study was performed where these new conjugates showed higher efficacy than the first generation of carriers, even at very low drug doses.[2]



Schematic description of presented system

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Magnetically-guided biodegradable microrods in inhalation medicine

M. Nikolaou[1], K. Avraam[1], A. Kolokithas-Ntoukas[2], A. Bakandritsos[3], 4, F. Lizal[5], O. Misik[5], M. Maly[5], J. Jedelsky[5], I. Savva[6], F. Balanean[7], T. Krasia-Christoforou[1]*

[1] *University of Cyprus, Department of Mechanical and Manufacturing Engineering, Nicosia, Cyprus*
[2] *University of Patras, Department of Pharmacy, Patras, Greece*
[3] *Palacký University, Regional Centre of Advanced Technologies and Materials, CATRIN, Olomouc, Czech Republic*
[4] *Nanotechnology Centre, CEET, VŠB–Technical University of Ostrava, Ostrava-Poruba, Czech Republic*
[5] *Brno University of Technology, Faculty of Mechanical Engineering, Energy Institute, Brno, Czech Republic*
[6] *Romanian Academy – Timisoara Branch, Center for Fundamental and Advanced Technical Research, Laboratory of Magnetic Fluids, Timisoara, Romania*

**Corresponding Author's E-mail address: krasia@ucy.ac.cy*

Anisotropically-shaped pulmonary drug delivery systems such as microrods attract considerable attention in inhalation medicine since their geometry allows them to travel deeper into the lung airways, thus enabling the efficient accumulation of therapeutic compounds at the point of interest with minimized transport losses.

The present study focuses on the fabrication and characterization of superparamagnetic, biodegradable drug-loaded electrospun microrods [1]. Such airborne magnetoactive microrods consisting of poly(L-lactide) (PLLA), polyethylene oxide (PEO) and pre-fabricated, oleic acid-coated magnetite nanoparticles ($OA\cdot Fe_3O_4$) provide the possibility of reducing transport losses and enhancing the targeted delivery of encapsulated therapeutic molecules to lower airways by their manipulation with DC magnetic field. Moreover, magnetic hyperthermia studies were carried out demonstrating their heating ability under an AC magnetic field [1].

Keywords: electrospinning, pulmonary drug delivery, magnetic hyperthermia, magnetic guidance.

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Poly(2-isopropenyl-2-oxazoline) conjugates with non-steroid anti-inflammatory drugs for sustained drug release

M. Majerčíková[1], E. Paulovičová[2], M. Faktorová[1], J. Markuš[3], S. Letašiová[3], Z. Kroneková[1]*, J. Kronek[1]*

[1]Department for Biomaterials Research, Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia
[2]Institute of Chemistry of the Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia
[3] MatTek In Vitro Life Science Laboratories, Mlynske Nivy 73, 821 05 Bratislava, Slovak Republic
*juraj.kronek@savba.sk, zuzana.kronekova@savba.sk

Poly(2-isopropenyl-2-oxazoline) (PIPOx) represents an universal platform for the preparation of biomaterials for various biomedical applications. Pendant 2-oxazoline groups allow to introduce in post-polymerization modifications different moieties such as hydrophobic groups, fluorencent labels or prepare biocompatible hydrogels. [1,2] PIPOx was tradionally prepared by free-radical polymerizations resulting to poor control of molar mass and dispersity. Recently we published synthesis of PIPOx by aqueous ATRP polymerization, that enables to prepare polymers with low dispersity and wide range of molar masses. [3] Moreover, we have demonstrated the high biocompatibility and immunomodulation activity of PIPOx providing possibility of various biomedical applications, especially as drug delivery systems. [4,5]

In this work, we focused on the preparation of PIPOx conjugates with various non-steroid antiinflammatory drugs. We have selected derivatives containing free carboxylic groups, namely ibuprofen, aspirin, and indomethacin. Prepared drug conjugates contained from 1 to 10 mol. % depending on drug used. Release profiles of aspirin and ibuprofen at 37°C and at different pH were monitored using HPLC with UV detection. We found that the rate of drug release was increasing with increasing pH.

In vitro cytotoxicity and anti-inflammatory properties of PIPOx and prepared drug conjugates were studied by both, MTT and ELISA assays, using EpiDerm^{TM} 3D tissue culture. We demonstrated that we can control the molar ratio of a conjugated drug and the rate of release is dependent on pH.

Keywords: drug conjugate**,** drug release, poly(2-oxazoline)

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PAMAM dendrimer-based star copolymers as structurally tunable nanocarriers for HIV-1 peptide vaccine delivery

G. Mužíková[1], L. Kracíková[1], L. Androvič[1], Geoffrey M. Lynn[2], Yaling Zhu[2], E. Tihlaříková[3], V. Neděla[3], R. Laga[1,*]

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 162 06 Prague, Czech Republic*
[2]*Vaccitech North America, 855 N. Wolfe St. Suite 102, Baltimore, MD 21205, USA*
[3]*Institute of Scientific Instruments, Czech Academy of Sciences, Královopolská 147, 612 64 Brno, Czech Republic*
[*]*laga@imc.cas.cz*

Peptide-based immunogens derived from the virus binding sites are considered safe and customized alternative to traditional whole-cell vaccines, however their small size gives them poor pharmacokinetic and immunological properties[1]. Conjugation of peptide immunogens to a nanoparticle carrier appers to be an effective solution eliminating these shortcomings as it can provide immunogens with improved avidity and longer persistence in the body, both leading to the induction of a stronger and longer-lastinge immune response[2]. High-molecular-weight star copolymers represent an advanced class of nanoparticle vaccine delivery platform that are distinguished by tunable structural properties, high immunogen-loading capacity and unique rheological properties[3]. In this work, we designed, synthesized and characterized a library of star copolymers consisting of hydrophilic bio-compatible poly[*N*-(2-hydroxypropyl)methacrylamide] (PHPMA) arms extending from a poly(amidoamine) (PAMAM) dendrimer core. Multiple copies of glycopeptide immunogens (Man9V3) derived from the HIV-1 binging site were covalently conjugated to the terminus of the PHPMA chains. The relationship between the structural properties of the nanocarrier (dendrimer core generation, polymer arm length, number of attached polymer arms) and the immunological properties (antibody and T cell immune response) of their conjugates with immunogen were studied in detail in mouse models.

Keywords: Star polymers, nanocarriers, peptide antiges, vaccine delivery, HIV-1 vaccines

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Controlled growth factor delivery using in situ crosslinked hydrogel via visible light-induced reaction

Hyun Jong Lee*

[1]*Department of Chemical and Biological Engineering, Gachon University, Republic of Korea*
**hjlee2@gachon.ac.kr*

Hyaluronic acid (HA) has been applied as a biomaterial for injectable dermal filler due to its unique viscoelastic property. Although HA derivatives are promising dermal filler materials, poor durability by degradation is the limitation of HA dermal filler. The chemical crosslinking of HA hydrogel is necessary to restrain the degradation rate. In a previous study, we fabricated an injectable in situ HA hydrogel containing a basic fibroblast growth factor that was crosslinked via a visible light-induced thiol-ene reaction. However, the release profile of the growth factor was much faster than HA hydrogel degradation, so most growth factors were released within 2 days. Here, we introduced functional groups to epidermal growth factor (EGF) to prolong the release periods. Acrylate groups were conjugated through N-hydroxysuccinimide (NHS) ester chemistry. We investigated the bioactivity, encapsulation efficiency, release rate, and proliferative effect on cells.

HA hydrogels were created by a thiol-ene reaction with RFP. An alkyl sulfide bond between thiolated HA (SH-HA) and methacrylated HA (MA-HA) was formed with initiation by RFP under blue light (BL) exposure. RFP was used as the photoinitiator and activated by BL.

The molecular weight differences of the reaction products of conjugated EGFs were measured by MALDI-TOF. The acrylate and PEG-acrylate groups were successively introduced to EGFs. As a result, the molecular weights of EGFs were increased, and these are consistent with the molecular weight increases that would be expected by the addition of one, two, or three functional groups.

The bioactivity of conjugated EGFs was evaluated by MTT assay. Acrylate-EGF and acrylate-PEG-EGF were added to the cell culture media, and the MTT absorbances were compared to the effect of normal EGF. All conjugated EGFs showed similar levels with the normal EGF in the MTT assay.

The release profile of conjugated EGF were measured after encapsulated in the thiol-ene crosslinked HA hydrogel. The acrylate group conjugation retarded the EGF releases compared to the normal EGF. Also, the long-term effect of growth factors were showed when the EGFs were incorporated in HA hydrogel after acrylate group conjugation.

HA-based hydrogels are versatile in therapeutic applications, and in situ visible light-induced thiol-ene reactions can extend the applications of HA hydrogels to injectable systems and on-site crosslinking. The introduction of functional group to growth factor provides more controlled release system.

Keywords: Hyaluronic acid, thiol-ene reaction, photo-crosslinking, hydrogel

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The impact of anionic polymers on gene delivery: how composition and assembly help evading the toxicity-efficiency dilemma

F. Richter[1], K. Leer[1], L. Martin[1], P. Mapfumo[1], J. I. Solomun[1], M. T. Kuchenbrod[1], S. Hoeppener[1,2], J. C. Brendel[1,2] and A. Traeger[1,2*]

[1]*Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University, Jena, Germany*
[2]*Jena Center for Soft Matter (JCSM), Friedrich Schiller University, Jena, Germany*
[*]*anja.traeger@uni-jena.de*

The research on non-viral nanocarriers for the delivery of genetic material showed great progress in the last decades and climaxed in the development of safe and effective vaccines. Polymer-based cationic nanocarrier systems have the ability to bind and transport genetic material into cells besides possessing great flexibility and stability. However, widespread use *in vivo* is limited by the residual positive charges of the polymers, which can lead to undesirable side effects, such as clearance.[1]

To increase the biocompatibility and reduce unwanted immune effects, the cationic polymers of the nanocarrier systems are coated with stealth polymers such as poly(4-acryloylmorpholine) (PNAM) or anionic polymers such as poly(acrylic acid) (PAA). In this work all polymer compositions and architectures were synthesized by reversible addition-fragmentation chain-transfer (RAFT) polymerization. The diblock copolymer poly[(*n*-butyl acrylate)-*b*-(2-(dimethylamino)ethyl acrylamide)] (P(*n*BA-*b*-DMAEAm)) was assembled into cationic micelles and coated with different shielding polymers, namely, PAA, PNAM or the block copolymer P(NAM-*b*-AA). These coated micelles were compared to a triblock terpolymer micelle containing PAA as the middle block.

Shielding with the hydrophilic and anionic block copolymer P(NAM-*b*-AA) showed the highest impact on cell viability, almost completely eliminating cytotoxic effects and maintaining moderate transfection efficiency. Coating with the stealth homopolymer PNAM revealed no improvement in toxicity and transfection efficiency compared to the naked cationic micelle, pointing out the requirement of anionic charges for shielding. In fact, the combination of PAA and the cationic micelle demonstrated low cytotoxicty while maintaining high transfection efficiency. The best ratio of viability and transfection efficiency was observed for the triblock terpolymer micelle containing PAA as the middle block.[2]

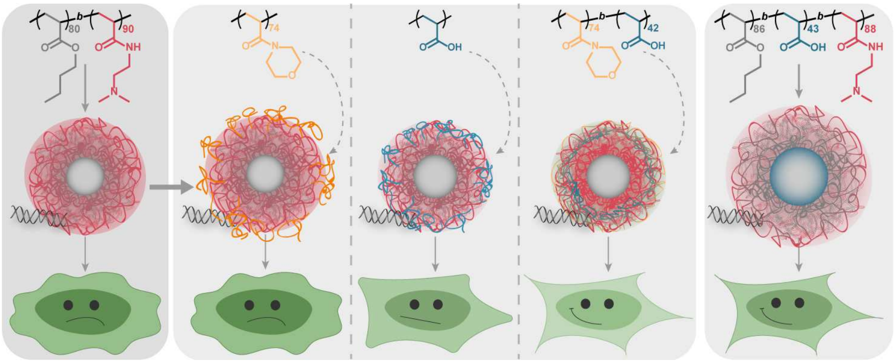

Figure 1: Shielding of the catonic micelle with PNAM, PAA and P(NAM-*b*-AA) and comparison to the triblock terpolymer micelle.

Keywords: Gene delivery, Cationic polymer, Micelle, Transfection, Anionic polymer, Shielding

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Responsive coacervate pDNA carriers for gene therapy

R. Lewis[1*], B. Klemm[1], A. Muralidharan[1], P. Boukany[1], R. Eelkema[1]

[1]*Dept. Chemical Engineering, Delft University of Technology, Delft, the Netherlands*
[*]*R.W.Lewis@tudelft.nl*

Gene therapy holds great promise as a treatment for genetic diseases such as cancer, cardiovascular disease, cystic fibrosis and arthritis. These treatments require a vector to transport nucleic acid cargo into the intracellular milieu, and in the case of DNA, the nucleus. Cationic polymers can electrostatically bind to negatively charged nucleic acids, resulting in the formation of nanoparticle complexes.[1] An excess of cationic charge is typically used to achieve sufficient DNA packaging and cellular entry, however this can increase cytotoxicity and limit complex dissociation once inside the cell, resulting in poor transcription efficiency. This has motivated the development of charge-reversing cationic polymers which are able to transition from cationic to neutral or negative charge, often in response to intracellular signals such as ATP, H_2O_2, and esterases.[2]

We have recently developed a chemical reaction network (CRN) which enables controlled cationization of poly(vinylpyridine) (PVP) by successive additions of an allyl acetate (ionization), and thiol or amine nucleophiles (deionization).[3, 4] Importantly, we found that the de-ioniziation reaction is significantly faster for thiols compared to primary amines. We therefore hypothesised that the cationized PVP could be applied as a two-stage charge reversing polymer (**Figure 1**). The first stage would occur extracellularly, where a relatively high concentration of free amino acids (~3 mM in human blood plasma) could be exploited to slowly reduce cationic charge, leading to reduced cytotoxicity. Once inside the cell, the second stage can begin where an elevated concentration of the thiol glutathione (GSH, 1 – 10 mM in cytosol and 2 - 20 µM extracellularly), could be used to rapidly trigger an accelerated decationization and intracellular release of pDNA for transfection.

We synthesised a range of allyl acetate cationized PVP polymers of various archictures and molecular weights by RAFT polymerisation. We then studied the decationization of their pDNA coacervate complexes in model intracellular and extracellular conditions, demonstrating accelerated release in intracellular conditions. We will present the latest data for the cellular internalisation and transfection of these complexes and compare them to non-charge reversing controls.

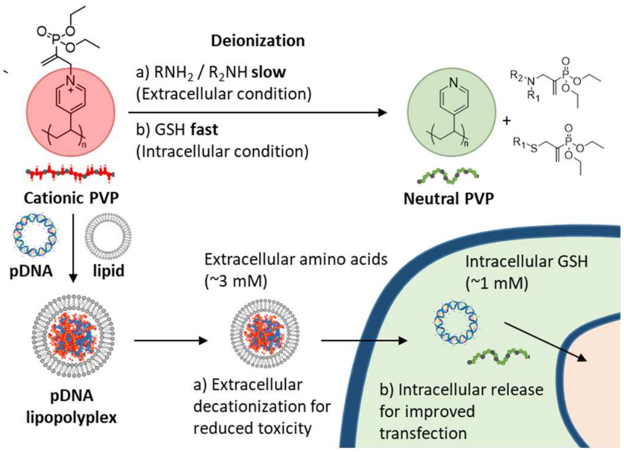

Figure 1. Scheme showing two-stage charge reversing cationic polyvinylpyridine (PVP) and its application to pDNA transfection. Addition of amines (slow) or thiols (fast) initiates deionziation of the cationic PVP. When the cationic PVP is combined with pDNA and lipids, a pDNA lipopolyplex responsive to both extracellular amino acids and intracellular GSH is formed.

Keywords: Coacervation, transfection, responsive

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Polymeric drug delivery system with dexamethason for the treatment of rheumatoid arthritis

A. Libánská[1*], E. Randárová[1], G. Renault[2], D. Rubanová[3], L. A. Cerezo[4], D. Scherman[5], T.Etrych[1]

[1]*Institute of Macromolecular chemistry CAS, Prague, Czech Republic*
[2]*Institute Cochin - INSERM U1016, Paris, France*
[3]*Institute of Biophysics CAS, Brno, Czech Republic*
[4]*Institute of rheumatology, Prague, Czech Republic*
[5]*CNRS UMR8258 – U1267 Inserm Paris, France*
[*]*libanska@imc.cas.cz*

In recent years nanomedicines for various severe diseases have been developed in order to enhance the therapeutic outcome and decrease the side effects of the conventional drugs, e.g. in therapy of chronic inflammatory diseases, especially rheumatoid arthritis. The standard treatment often includes long-term administration of glucocorticoids, e.g. dexamethasone. As an immunosuppressant, it brings several severe side effects[1] and heart disease risks[2].

In this work, we developed the drug delivery systems based on biocompatible *N*-(2-hydroxypropyl methacrylamide) (HPMA)[3] copolymers bearing the anti-inflammatory drug dexamethasone. These copolymers serve as efficient and safe drug carriers capable of passive targeting to inflamed joints which is attributed to the vasodilatation of the blood vessels nearby the affected site. The dexamethasone is bound via a pH-sensitive hydrazone bond preventing its release at the physiological pH of the blood. The drug release occurs mostly at acidic pHs which are present in the inflammation. Moreover, due special linkers between the polymer platform and the drug we can tune drug release rates from rapid to sustained release. The physicochemical properties were established in detail, and the superior anti-inflammatory biological properties compared to free dexamethasone were proved in vitro (e.g. synovial fibroblasts from patients) and in vivo (murine model of adjuvant-induced arthritis and collagen II-induced arthritis). Based on the results we strongly believe that our polymer conjugates have a great potential in the treatment of rheumatoid arthritis and other joint inflammation-related diseases.

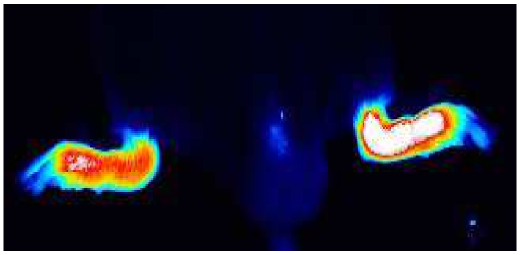

Figure: Accumulation of the drug delivery systems in the arthritic paws of the mouse.

Keywords: nanomaterials, drug delivery, HPMA, linear copolymer, rheumatoid athritis, dexamethasone

Acknowledgments
This work was supported by the Ministry of Health of the Czech Republic (project NU20-08-00255) and by Czech Science Foundation (grant 19-00956Y).

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Towards the design of emulsion-templated T-responsive polymer capsules for protein release

Lucas Sixdenier[1], Christophe Tribet[1], Emmanuelle Marie[1]

[1] PASTEUR, Département de chimie, École normale supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France
E-mail: emmanuelle.marie@ens.fr

The on-demand release of pre-encapsulated bioactive molecules is increasingly required to precisely probe and unveil complex interactions in living matter, such as cell intercommunications. Responsive capsular systems that can burst under remote stimulation are promising systems for a spatiotemporally precise control of molecular cues delivery. If polymers are generally good candidates for the design of rigid capsules, responsive polymers often suffer from complex synthesis, tedious protocols for capsule formation and sometimes slow release kinetics under stimulation.

To circumvent these issues, we propose here a new strategy based on interfacial complexation. To optimize the physico-chemistry of this system, we first focused on the well-known poly(N-isopropylacrylamide) (PNIPAM), a model thermoresponsive water-soluble polymer exhibiting a conformational transition from a hydrophilic soluble state at low temperature to a hydrophobic insoluble state at high temperature. A water-in-(perfluocarbon oil) emulsion was used as a template to form polymer shell walls at the water/oil interface, confining the aqueous content in a spherical capsule precursor. For that, PNIPAM chains are grafted on a poly(L-lysine) (PLL) cationic backbone that adsorbs at the water/oil interface via ionic interactions with an anionic surfactant present in the oil phase [1]. Results show evidences for (i) the formation of a shell wall of PLL-PNIPAM copolymer at the water/oil interface, (ii) the transition of interfacial PNIPAM chains under temperature changes, (iii) accumulation of polymer material at the interface upon T-switch.[2] This strategy was then applied to UCST type polymer, thereby leading to capsules that dissolve upon T increase, which, to the best of our knowledge, has not been reported before.

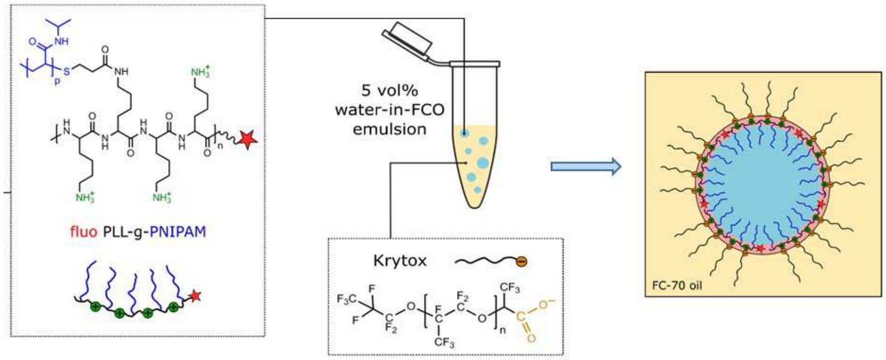

Figure 1. *Strategy for the design of light-responsive polymer capsules templated in a water-in-oil inverse emulsion.*

Keywords: polymer capsules, W/O emulsion, thermoresponsive polymer, interfacial complexation.

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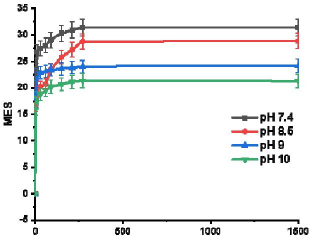
Biodegradable chitosan based nanofibers with broad spectrum antimicrobial activity for wound healing applications

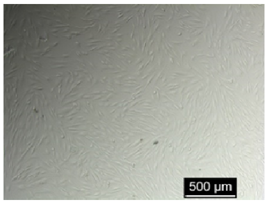
L. Marin[1], D. Ailincai[1], S. Cibotaru[1], A. Anisiei[1], I. Rosca[1], L. Mititelu-Tartau[2]

[1]*Institute of Macromolecular Chemistry, Iasi, Romania*
[2]*"Gr. T. Popa" University of Medicine and Pharmacy, Iasi, Romania*
[*]*lmarin@icmpp.ro*

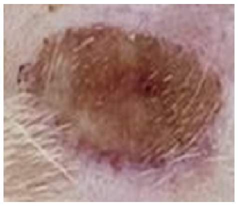
Wound healing is a frequent skin trauma which severely impacts the public health. As an example, every day over 30000 people worldwide suffers severe burns which require medical attention [1]. Among them, the invasive infection is responsible for 51% of the burn deaths, especially in low- and middle-income countries with a deficient care system. This social and economic context guided considerable efforts to the development of efficient approaches for wound healing. In this light, the aim of the study was to design new multifunctional biomaterials targeted to fulfil the main requirements of an ideal wound dressing. Thus, microporous neat chitosan fibers (pore size up to 2 nm) were prepared by electrospinning [2], loaded with a broad spectrum antibiotic and further sealed with an antifungal agent *via* reversible imination reaction. The as obtained fibers showed rapid swelling, biodegradation in medium mimicking the wound exudate, strong antimicrobial activity against gram positive andd gram negative bacteria, and fungal strains, *in vitro* cytocompatibility on normal human fibroblasts and *in vivo* biocompatibility on rats. Furthermore, *in vivo* tests on burn model in rats exhibited the wound healing during the fiber biodegradation (Figure 1). All these results indicated that the fiber preparation procedure yilded biomaterials suitable for a smooth wound healing, circumventing the traumatic debridement.



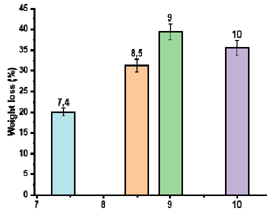
Fast swelling



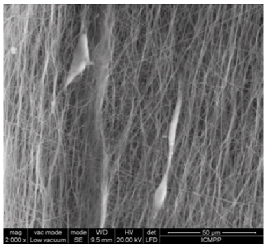
Biocompatibility on NHDF cells



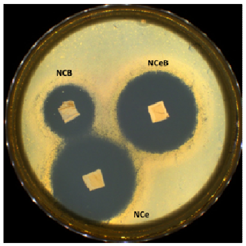
In vivo wound healing



Biodegradation controlled by pH



Bioadhesivity



Antimicrobial activity

Figure 1. The image of the designed fibers and their representative properties

Acknowledgments

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Cell instructive polymers based on liquid crystals

D. Martella[1,2*], M. Rojas,[1] D. S. Wiersma,[1,2,3] C. Parmeggiani[1,2,4]

[1] *European Laboratory for Non Linear Spectroscopy, Sesto Fiorentino, Italy*
[2] *Istituto Nazionale di Ricerca Metrologica (INRiM), Torino, Italy*
[3] *Department of Physics and Astronomy, Università di Firenze, Sesto Fiorentino, Italy*
[4] *Department of Chemistry "Ugo Schiff", Università di Firenze, Sesto Fiorentino, Italy.*
[*]*martella@lens.unifi.it*

Control of the collective cells organization and their correct differentiation are key steps to reproduce biological tissues *in vitro*. So far, many attempts to prepare polymeric scaffolds that mimic the biological environment have been done, trying to reproduce the mechanical properties or the extracellular matrix composition and topography. To date, cell differentiation protocols required scaffolds bearing micro/nanometric features or stimulated ones (by mechanical stretching or electric field). However, the complexity of these methodology strongly limits their wide application.

A completelty different approach, described in this communication, for the alignment and differentiation of several cell lines, exploit Liquid Crystalline (LC) polymers. Materials with anisotropic molecular structure and tunable rigidity have been prepared by photopolymerization of acrylate-based LCs and tested as support for cell growth (from human fibroblasts, C2C12 myoblasts and cardiomyocytes). We demonstrated LC polymers to present several advantages with respect to commercial scaffolds such as and improved adult-like dimensions and a more mature cell function of human induced pluripotent stem cell-derived cardiomyocytes (hiPSC-CMs) in a shorter time. [1] Furthermore, LC organization is able to drive specific cells arrangements during fibroblast and myoblast cultures, as shown in Figure 1. Cell alignment was found to follow the nematic director thus demonstrating for the first time as the LC order inside the material can be translated to a living organism. [2] At the end, myotube maturation has been investigated with electrophysiological studies demonstrating as muscular fibres cultured on our LCs present better functional features with respect of those obtained on standard supports. [3]

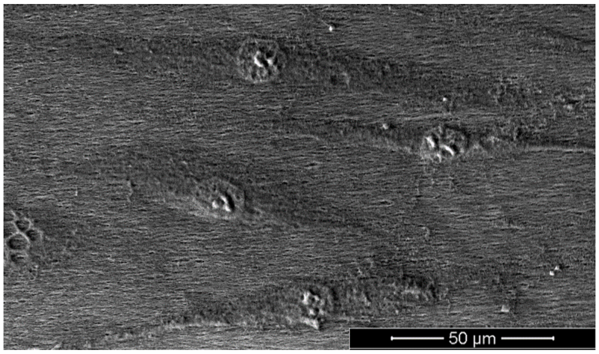

Figure 1: SEM images of aligned fibroblast on a LC scaffold

Keywords: Cell scaffolds, Liquid Crystalline Networks, Biomaterials

Acknowledgments

The research leading to these results has received funding from MUR under the FISR program, project FISR2019_00320 Leonardo.

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Fine-tuning endcap chemistry of AUP-based hydrogels for effective exudate management

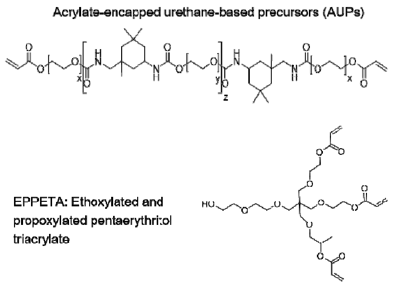
M. Minsart[1], N. Deroose[1], L. Parmentier[1], S. Van Vlierberghe[1], A. Mignon[1,2], P. Dubruel[1,*]

[1]*Polymer Chemistry & Biomaterials Research Group, Centre of Macromolecular Chemistry (CMaC), Ghent University, Belgium.* *Peter.Dubruel@UGent.be

[2]*Biomaterials and Tissue Engineering, Department of Materials Engineering, KU Leuven, Belgium*

Wound exudate is beneficial in several ways. It can facilitate autolytic debridement, prevents wound dehydration and helps wound re-epithelialization. However, exudate can also be harmful for the patient as it provides an excellent environment for bacterial infection, can lead to maceration and even cause malodor. Effective exudate management is therefore crucial[1]. To date, a wide range of wound dressings is commercially available with hydrogel-based dressings being the most relevant for exuding wounds due to their strong exudate uptake capacity. Nevertheless, most commercial dressings with moderate to high exudate uptake capacities are typically mechanically weaker and/or require the use of a secondary dressing[2].

Our research therefore focuses on the development of a novel hydrogel-based wound dressing combining tunable mechanical strength and high exudate absorption capacity. Different acrylate-endcapped urethane-based precursor (AUP)[3] materials with varying poly(ethylene glycol) backbone molar masses (10 and 20 kg/mol) and endcap chemistries were succesfully synthesized in toluene (^{1}H-NMR), subsequently processed into UV-cured hydrogel sheets (Figure 1) and electrospun fibers and were benchmarked against several commercial wound dressings. The AUP materials showed high gel fractions (> 90%) together with high swelling degrees in H_2O, PBS and simulated wound fluid (SWF) (12.7 – 19.6 g/g), as well as varying mechanical properties (e.g. Young's modulus: 0.026 – 0.061 MPa). The AUP materials had significantly ($p <$ 0.05) higher swelling degrees than tested commercial dressings (Hydrosorb, Kaltostat and Mepilex Ag), while also being mechanically resistant. The elasticity of the synthesized materials led to an increased resistance against fatigue. The di- and hexa-acrylated AUPs showed excellent *in vitro* biocompatibility against human foreskin fibroblasts (HFF), evidenced by indirect MTS assays and live/dead cell assays. Due to the close mimic between the morphology of the native extracellular matrix (ECM) and electrospun nanofibers, electrospinning was chosen as processing technique to fabricate different prototype wound dressings from the synthesized AUP materials and homogeneous fibers could be easily obtained. It can thus be concluded that the AUP materials hold great promise for wound healing application.



Hydrogel sheets	Backbone molar mass (g/mol)	Endcap agent
AUP10kDA	10 000	Bisomer PEA-6
AUP10kHA	10 000	EPPETA
AUP20kDA	20 000	Bisomer PEA-6
AUP20kHA	20 000	EPPETA

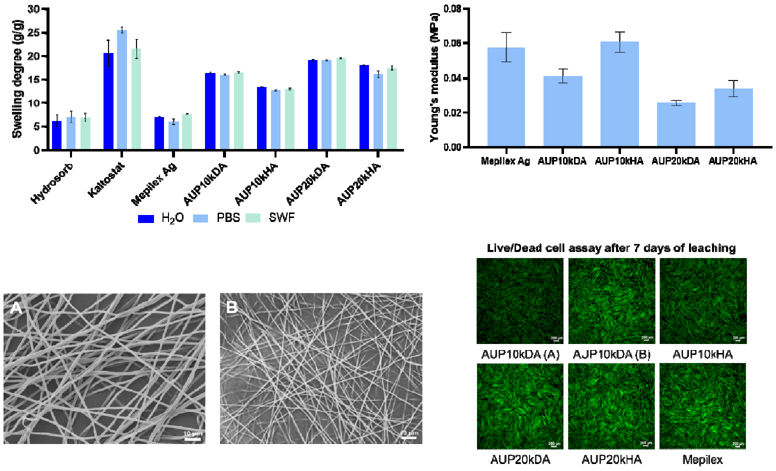


Figure 1: (top left) Chemical structure of AUPs. (top middle) Swelling degree of the materials in different media.(top right) Young's moduli of the swollen materials. (below) Light and scanning electron microscopy visualization of electrospun fibers and results of the indirect cell assay.

Keywords: burn wounds, hydrogels, electrospinning, biocompatibility, benchmarking

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Using Melt Electrowriting to Prepare Highly Porous Microfiber Scaffolds of Amorphous Solid Dispersions of Indomethacin

Zeynab Mirzaei[1*], Juliane C. Kade[2], Larissa Keßler[1] , Robert Luxenhofer[1,2]

[1]*Department of Chemistry, A.I. Virtasen aukio 1, University of Helsinki, 00014 Helsinki, Finland*
[2]*Polymer Functional Materials, Chair for Advanced Materials Synthesis, Institute or Functional Materials and Biofabrication, Department of Chemistry and Pharmacy, Julius-Maximilians-University Würzburg, Würzburg, Germany*
[*]*zeynab.mirzaei@helsinki.fi*

Melt electrowriting (MEW) is a high resolution additive manufacturing technology electrostatically drawing polymer melts out of a syringe onto a computer-controlled collector. This enables accurate microfiber placement and producion of unique printing patterns, as well as highly porous microfiber scaffolds, which can be used in biomedical applications, including drug delivery[1]. Indomethacin (IND) is a non-selective and nonsteroidal anti-inflammatory drug to manage pain. Sublingual delivery of IND offers various advantages, such as minimized contact with the gastrointestinal tract mucosa to overcome IND side-effects and the fast absorption by the veins located in the mouth floor[2]. Combining sublingual route with a highly porous and biodegradable IND-loaded MEW scaffolds with small thickness of 400-500 µm can allow fast distribution of IND through the bloodstream. For rapid dissolution and potential supersaturation, an amorphous solid dispersion should be favorable.

Residual micro-crystallinities of the drug can cause problems such as recrystallization instead of dissolution resuling in patient-to-patient variability. This should be addressed by suitable excipients. Here, a poly(2-oxazoline) based amphiphilic triblock copolymer is introduced as a new excipient to disperse IND in solid amorphous state using hot melt extrusion (HME) of drugs and excipients, suitable for oral dosage[3].

The objective of the study is to prepare melt electrowritten highly porous IND-loaded scaffolds and to investigate the stability, amorphicity and release rate of the drug.

First, different polymer:drug ratios up to 2:1 were prepared by using hot melt extrusion and the extrudates subsequently subjected to MEW. The final drug-loaded microfiber scaffolds were characterized using SEM, DSC, XRD, and UV spectrophotometry to assess the morphology, porosity and degradation of the scaffolds and stability, crystallinity and degradation of drug and polymer.

The results illustrate no degradation of the polymer and drug during and after HME and MEW, even in high drug concentrations and the dispersions were found to be completely amorphous. To conclude, we report the first water soluble melt electrowritten IND-loaded microfiber scaffolds comprising poly(2-oxazoline) and poly(2-oxazine) with different dosages of drug which can potentially be used for sublingual and fast delivery of indomethacin.

Keywords: melt electrowriting, amphiphilic block copolymer, poly(2-oxazoline), drug formulation, indomethacin.

Acknowledgments

The authors would like to thank the Academy of Finland for financial support (Grant No. 337660).

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Stimuli-responsive polymeric vesicles as therapeutic nanoreactors

S. Moreno[1*], K. Fishna, X. Xu, C. Effenberg[1], S. Boye1, B. Voit[1,2], D. Appelhans[1]

[1] *Leibniz-Institut für Polymerforschung Dresden e. V., 01069 Dresden, Germany*
[2] *Technische Universität Dresden, 01062 Dresden, Germany*
[*]moreno@ipfdd.de

In the field of next-generation therapeutics and synthetic biology, the development of multiresponsive particles that allow cascade reactions or therapeutic actions in a local space have gained a huge interest providing a selective spatial control. For instance, smart polymeric vesicles (polymersomes) have gained a huge interest in this field due to high stability, adaptable physiochemical properties, easy surface modification, asymmetric functionalization and adjustable membrane permeability using different stimuli.[1, 2]

This contribution will focus on the use of therapeutic enzymes as cargo and the fabrication and characterization of different enzyme loaded crosslinked polymersomes. Using all of them, three major issues will be addressed: (i) different possibilities of enzyme loading into the nanocontainer depending on the enzyme and its application; (ii) a deep validation of the molecular parameters of these biohybrids using a combination of sophisticated caracterization methods; (iii) to study the protective capacity of these nanocontainers in different simulated body fluids as a function of enzyme location.[3, 4] Moreover, among the broad variety of stimuli-responsive mechanisms, especially redox-reactions comprising the addition of oxidizing/reducing agents or by applying electrical potentials are much less investigated. Theforore, taking it a step further, pH and redox (ferrocene units) responsive polymersomes will be shown. These polymersomes exhibit peroxidase-like activity, host-guest interaction using β-cyclodextrin (β-CD) and agent as H_2O_2 can be used to trigger the release of loaded cargo.

All these preliminary studies show a very promising synthetic platform for designing dual-functional therapeutic nanocontainers, but in addition, the redox capability and the subsequent docking process could smooth the way for the functionalization of electrodes and their use as biosensors.

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3D Printed hyaluronic acid and photocrosslinkable chitosan hydrogels with self-healing properties

Sheila Maiz-Fernandez[1,3], Leyre Pérez-Álvarez[1,3], Antonio Veloso-Fernández[1], Leire Ruiz-Rubio[1,3], José Manuel Laza[1], Caterina Lopes[1], Isabel Moreno[2], José Luis Vilas Vilela[1,3]

[1] Macromolecular Chemistry Group, Department of Physical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, 48940 Leioa (Spain).
[2]Macromolecular Chemistry Group, Department of Organic and Inorganic, Faculty of Science and Technology, University of the Basque Country UPV/EHU, 48940 Leioa (Spain)
[3] Basque Center for Materials, Applications and Nanostructures, Martina Casiano Building, UPV/EHU Science Park, 48940 Leioa (Spain).
**leyre.perez@ehu.eus*

Biocompatible and biodegradable hydrogels with biomimetic properties, such as self-repairing capability, are increasingly interesting for biomedical applications, in particular when they can be printed in three dimensional structures as personalized implantable devices in tissue regeneration or drug delivery processes. [1] Photocrosslinkable chitosan and hyaluronic acid (HA) offer the possibility to develop double crosslinked hydrogels thanks to the covalent network formed by the photopolymerization of methacrylated chitosan (CHIMe) and the physical network based on the electrostatic interactions between two polysaccharides promoting a robust self-healing behaviour. In this context, herein is presented the development of biocompatible, biodegradable, photocrosslinkable *in situ* forming and self-healable hydrogels based on these polysaccharides. So far, few studies have investigated the properties of the direct mixture of chitosan and hyaluronic acid, that highlights the interest on studied system. [2] Besides, the characterization of these hydrogels shown tailored swelling, mechanical and rheological properties according to polysaccharides relative content. The biodegradation and self-healing ability of the hydrogels were investigated together with their potential as bioinks for 3D printing. Clear evidences were found that fast photopolymerization of CHIMe/HA solutions leads to 3D printable hydrogels with tuneable physico-chemical properties, suitable for advanced biomedical and tissue engineering applications.

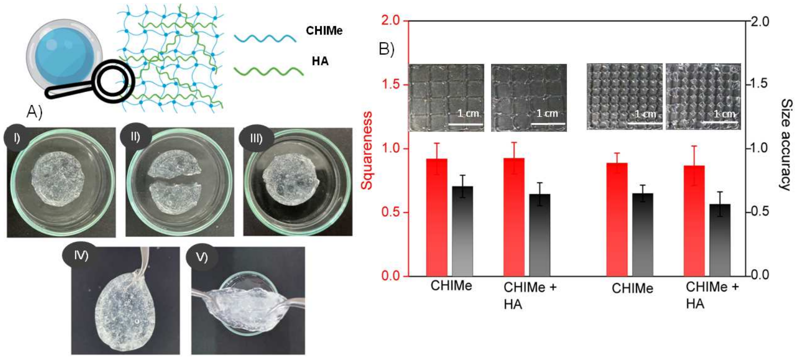

Figure 1. a) Self-healing process of hydrogels CHIMe:HA, and b) Comparison of the printing quality of printed 4x4 and 8x8 square scaffolds.

Acknowledgments

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The effect of polysaccharides and magnetite on the physico-chemical properties of polyurethane composites for biomedical applications

N. Paprota, P. Szatkowski, M. Szlachta, W. Piekarczyk, K. Pielichowska*

AGH University of Science and Technology, Faculty of Materials Science and Ceramics,
Department of Biomaterials and Composites, al. Mickiewicza 30, 30-059 Kraków, Poland
Corresponding Author's E-mail address: kingapie@agh.edu.pl

One of the most popular applications of polyurethanes (PU) in medicine are implants and prostheses. Polyurethanes can be obtained from a variety of available monomers and chain extenders/crosslinkers that give opportunities to change selected properties of PU-based biomaterials, such as biodegradability, mechanical properties, phase separation and cellular structure [1, 2]. To improve PU biocompatibility and stiffness, polysaccharides can be applied as crosslinkers [3]. On the other hand, magnetic particles like magnetite can used in tissue regeneration and hyperthermia treatment of tumour [4,5]. It was revealed that externally applied magnetic field promotes bone-implant integration, increases bone density and calcium content, and accelerates healing of bone fractures [6].

In this work PUs were crosslinked using selected polysaccharides and additionally modified with hydroxyapatite (HAp), a phase change material (PCM), and magnetite to form potential scaffolds for bone tissue regeneration. PUs were synthesized using both one-step and prepolymer methods. The synthesis of PUs was carried out using poly(ε-caprolactone) diol (PCL) and poly(ethylene glycol) (PEG) with average molar mass 2000 as soft segments, and 4,4'-methylenediphenyl diisocyanate (MDI). Various molar ratios of polysaccharide and 1,5-pentanediol (PDO) as crosslinker/chain extender were applied, and the effects of incorporating different amounts of magnetite, as well as the role of PDO to polysaccharide ratio, were studied. The prepared PUs were investigated using Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetry (TG), and dynamic mechanical analysis (DMA) methods. Scanning electron microscopy (SEM)/energy-dispersive X-ray spectroscopy (EDX) analysis and preliminary bioactivity assessment were also performed. It was revealed that both PCM and magnetite enhanced thermal stability and in vitro chemical stability. The addition of magnetic particles did not cause significant changes in the properties of the obtained materials. The tested materials have the potential to be used to fill or replace bone defects in orthopedics, where they can undergo hyperthermia treatment.

Keywords: polyurethanes, polysaccharides, magnetite, bone scaffolds, biomaterials, orthopedics

Acknowledgments

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Poly(Thioether Phenyl Acrylate) Block Copolymer Micelles Show Exclusively ROS-triggered Breakdown

I. Piergentili[1], P. R. Bouwmans[1], L. Reinalda[1], R. W. Lewis[1] and R. Eelkema[1*]

[1] *Department of Chemical Engineering, Delft University of Technology, Delft, The Netherlands*
[*]*r.eelkema@tudelft.nl*

Polymers that are susceptible to stimuli from a tumour environment are of great interest as platform for the development of disease-targeted drug carriers. In certain tumor and diseased tissues, reactive oxygen species (ROS), such as H_2O_2, are produced in higher concentrations than in healthy cells.[1] Drug delivery and release systems that respond selectively to the presence of ROS while maintaining their stability in "healthy" biological conditions, have great potential as on-site therapeutics.

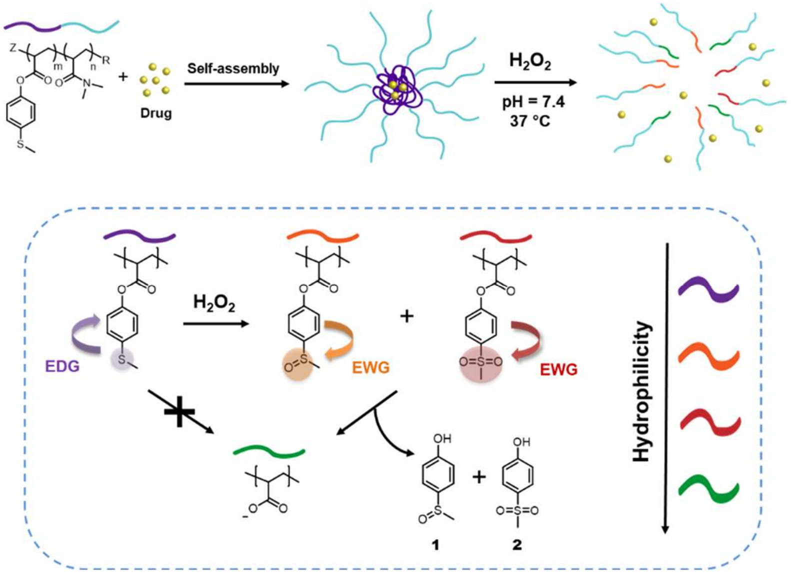

Figure 1. General concept: drug release from ROS-responsive micelles, triggered by the hydrolytic cleavage of ester bonds through switching from electron donating (EDG) thioether group to electron withdrawing (EWG) sulfoxide **1** and sulfone **2** upon oxidation by H_2O_2.

This work presents a ROS-responsive logic gate cascade mechanism based on 4-(methylthio) phenyl ester. Here, the oxidation of the thioether to the corresponding sulfoxide/sulfone triggers the hydrolysis of the proximal ester (Figure 1).[2] 4-(methylthio) phenyl acrylate was used as hydrophobic monomer and N,N-dimethylacrylamide as hydrophilic monomer to synthesize two block copolymers *via* light-initiated RAFT polymerization.[3] In aqueous environment, both polymers form micelles with a diameter between 30 and 50 nm, ideal size for nanotherapeutics.[4] The micelles show great stability for days in physiological (pH = 7.4, 37°C) and mildly acid (pH=5.0 and pH=6.0, 37°C) conditions in oxidant-free environment. In contrast, micellar disassembly is found on a timescale of days in the presence of 2 mM H_2O_2 and within hours at higher concentrations of H_2O_2 (60 – 600 mM). When H_2O_2 is added, the thioether oxidation leads to ester hydrolysis, unmasking a hydrophilic acrylate anion block and causing the disassembly of the micelles. This ROS-triggered degradation mechanism is particularly interesting since promotes controlled and sustained drug release.[5]

Keywords: block copolymers, controlled release, logic gates, micelles, reactive oxygen species, responsive materials

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Biofunctional polymer brush coatings at the nanoscale

I. Romanenko[1,2], A. Cernescu[3], R. Sivkova[1], J. Svoboda[1], Y. M. Wang[1,2], W. T. Hsu[1], V. Proks[1], A. de los Santos Pereira[1], Ognen Pop Georgievski[1,*]

[1] Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 16206 Prague, Czech Republic
[2] Department of Physical and Macromolecular Chemistry, Charles University, Hlavova 8, 12800 Prague, Czech Republic
[3] Neaspec – attocube systems AG, Eglfinger Weg 2, D-85540 Munich-Haar, Germany

[*]*georgievski@imc.cas.cz*

Antifouling polymer layers containing extracellular matrix-derived peptide motifs offer promising new options for biomimetic surface engineering [1]. In this contribution, we report the design of antifouling polymer brushes bearing biofunctional peptide motifs for tissue regeneration applications. We utilize grafting-to and grafting-from synthesis methods for attaining the polymer brush conformation, and further functionalize the brushes with various biomimetic peptide sequences, such as RGD and TYRAY. The characterization of obtained systems goes beyond the state-of-the art findings based on far-field analytical techniques for proving the brush character of the synthesized polymer structures, their antifouling character and the biofunctionality induced by the presence of various peptide motifs. By utilizing mid-infrared nanoscopy methods of scattering-type scanning near-field optical microscopy (s-SNOM) and near-field infrared spectroscopy (nano-FTIR) we unravel the conformation and orientation of the individual polymer chains constituting the polymer brush films [2] and directly determine the distribution of bifunctional peptides with a nanoscale resolution. We foresee that measurements under controlled temperature, humidity, or in liquids will give further physicochemical insight into bioactivity of these polymer brushes architectures [2, 3].

Keywords: biofunctional polymer brushes, surface initiated polymerization, sSNOM, nanoFTIR, nanoscopy

Acknowledgments

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Controlled Polymerization of Antifouling Poly(*N*-(2-hydroxypropyl)methacrylamide) Poly(HPMA) Brushes from Silicon and PDMS Surfaces *via* Interface-Mediated RAFT Polymerization Technique

Manisha Singh[1], Alessandro Jäger[1], Eliezer Jäger[1], Mareike Müller[2], Ognen Pop-Georgievski[1], Melanie Lammert-Baumgartner[2], Holger Schönherr[2] and Rafal Poreba[1*]

[1] Institute of Macromolecular Chemistry Czech Academy of Sciences
Heyrovsky sq. 2, Prague 162 06, Czech Republic
[2] Physical Chemistry I and Research Center of Micro and Nanochemistry and Engineering (Cμ)
University of Siegen Adolf-Reichwein-Str. 2, 57076 Siegen, Germany
[*] poreba@imc.cas.cz

Densely-packed polymer brushes are frequently utilized to prevent fouling caused by non-specific adsorption of proteins and other biomolecules and can also help to reduce or completely prevent cell or bacteria adhesion. From the application point of view, protein fouling is a highly undesired event when taking place on surfaces of biomedical devices, leading to adverse complications, such as thrombosis, infection and pathogenic calcification.[1] In this context, polymer brushes have been successfully applied to reduce non-specific protein adsorption in implants, to avoid disturbing background signals in affinity biosensors or to modify urinary catheters in order to prevent bacterial adhesion.[2]

Reversible deactivation radical polymerization techniques (RDRP) have become a method of choice for surface modification with polymer brushes. Among the RDRP methods, the reversible addition-fragmentation chain transfer (RAFT) technique has emerged as one of the most powerful tools for polymer brush synthesis, particularly due to its relatively high tolerance to residual oxygen levels, the wide variety of polymerizable vinyl monomers, its experimental simplicity, and renunciation of metal catalysts.

Polydimethylsiloxane (PDMS) represents one of the most widely used silicon-based materials used in blood contacting devices, such as catheters, blood oxygenators, and prosthetic heart valves, but also urinary catheters. However, due to non-polar nature of PDMS, its surface is highly susceptible to protein adsorption. Currently several surface modification strategies are being used to decrease non-specific protein adsorption and bacteria adhesion to PDMS surfaces. Among them, surface modification with poly(ethylene glycol)-based brushes have been the most widely utilized. However, PEG-based polymers are highly susceptible to metal ion oxidation, which leads to polymer degradation and in consequence to increased protein fouling.

In this contribution, we present a facile strategy for the synthesis of antifouling poly(*N*-(2-hydroxypropyl)methacrylamide) (poly(HPMA)) brushes from silicon and PDMS surfaces *via* interface-mediated RAFT technique in a well-controlled fashion. This has been achieved by immobilizing the CTA, 4-(3-(triethoxysilyl)propylcarbamoyl)-2-cyanobutan-2-ylbenzodi-thioate via its R-group onto the surfaces and using cyano-4-[(ethylsulfanylthiocarbonyl)sulfanyl]-4-methylbutanoic acid as the sacrificial CTA. The evaluation of the feasibility of the developed methodology for the modification of PDMS surface and the impact of the presence of poly(HPMA) brushes on the adhesion of eukaryotic cells derived from connective tissue as well as medically relevant bacterial pathogens will be presented.

Acknowledgments

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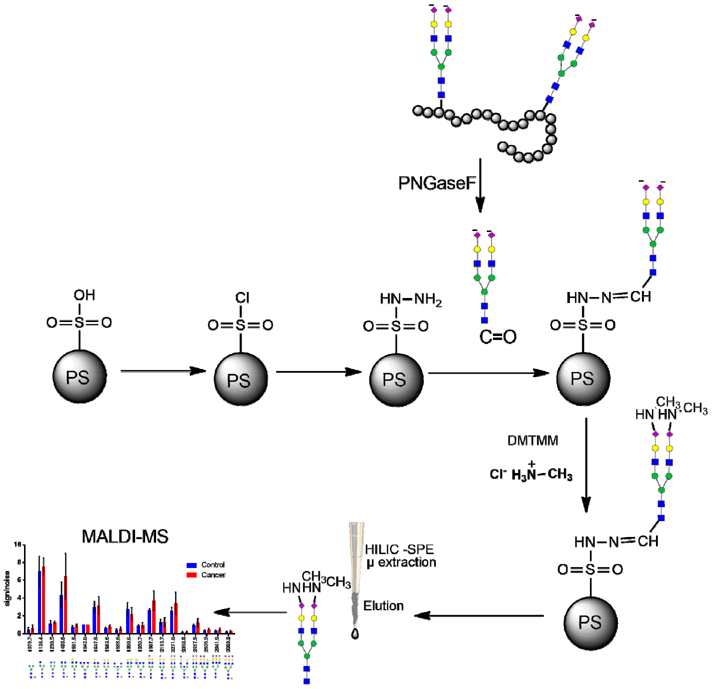
Glycan capture and release using reversible hydrazone polymer based solid phase extraction

D. Ret[1*], D. Köpplinger[1], A. Gentile[1,2], A. Ammaturo[1], E. Untersmayr[2], S. Knaus[1]

[1]*Research Unit Macromolecular Chemistry, Institute of Applied Synthetic Chemistry, TU Wien, 1060 Vienna, Austria*
[2] *Institute of Pathophysiology and Allergy Research, Center for Pathophysiology, Infectiology and Immunology, Medical University of Vienna, 1090 Vienna, Austria*
[*]*davide.ret@tuwien.ac.at*

Glycans are key components in most biological and pathological processes including: recognition, inflammation, cytotoxicity, cancer, autoimmune diseases, viral infections, bacterial infections are some examples. Characterization of body fluids glycans with matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) in positive-ion mode needs a derivatization step to stabilize and neutralize the negative charge on sialic acids, a class of acid sugars attached to the end of glycoproteins, glycolipids or gangliosides. Hydrazide beads to capture reducing end free glycans are a powerful and efficient method for purify glycans from complex matrix. The capture-release method simplifies the glycan preparation, producing pure samples.



Schematic preparation of functional resin synthesis and glycan purification

Hydrazide functionalized beads are synthetized starting from polystyrene(PS). PS beads are sulfonated, afterwards chlorosulfonated with chlorosulfonic acid and then converted into PS sulfonyl hydrazide by reaction with an excess of hydrazine. Hydrazide activated PS beads can be produced in large amount, high yield and allow an easy and fast purification of free reducing end glycans from complex samples mixture for spectrometry analysis.

Keywords: Glycans, solid phase extraction, hydrazone

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Cyclic acetals as photopolymerizable precursors for degradable biomaterials

A. Ricke[1*], B. Dellago[1,2], K. Ehrmann[1], R. Liska[1], and S. Baudis[1,2]

[1]*Institute of Applied Synthetic Chemistry, TU Wien, Austria & Austrian Cluster for Tissue Regeneration*
[2]*Christian Doppler Laboratory for Advanced Polymers for Biomaterials and 3D Printing, TU Wien, Austria*
[*]*alexander.ricke@tuwien.ac.at*

Aging societies combined with the growing trend of minimally invasive surgeries increase the demand for medicinal graft materials applicable for tissue engineering (TE) [1]. Most materials currently used in TE are based on ester polymer backbones *e.g.* poly(hydroxy acids) like poly(ε-caprolactone) (PCL) [2]. Those materials can have limiting factors for applications. For example, esters degrade slowly under acid conditions and cause a lowering of the surrounding tissue´s pH, which can lead to inflammatory reactions. This makes them less suitable candidates for bone grafts [3]. Thus, novel biodegradable materials are needed, and acetals as degradable moieties can be the answer to tackle the limitations of esters. Within this work, the (thermo-)mechanical properties of cyclic acetal photopolymer precursors are determined by RT-FTNIR-photorheology, DMTA, and tensile testing. The influence of the thiols TMPMP, PETMP, and diPETMP, which have an increasing thiol functionality, was studied in thiol-ene systems to photopolymerize biobased, biocompatible, and biodegradable cyclic acetals. The most promising systems implemented were selected and *in vitro* degradation studies at physiological pH levels were carried out on a molecular level *via* NMR analysis. Additionally, swelling and degradation rates of the bulk photopolymer networks were determined, synthesized acetals degrade 80 to 200 times faster compared to similar esters. The developed materials can be cured under mild, physiological conditions and are thus generally applicable as tissue grafts or bone replacement materials.

Keywords: Photoprecursors, Photopolymers, Acetal, Biocompatibility

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Cancer biomarker sensor based on a hydrogel containing water soluble pillar[5]arene

M. Rodin[1], R. Probst[1], D. Kuckling[1*]

[1] *Paderborn University, Paderborn, Germany*
[*] *dirk.kuckling@uni-paderborn.de*

Pillar[n]arenes (P[n]A) are one of the newest classes of macrocyclic compounds, discovered in 2008. [1] Due to their prominent ability to form host-guest complexes as well as the possibility to tune it by introducing various rim substituents different P[n]A derivatives were utilized in such systems as catalysts, absorbents, and sensors. The latter is especially promising for biomedical applications of P[n]As due to their affinity to aminoalkanes [2], such as spermine (SP) and spermidine (SD) that were shown to be prostate cancer biomarkers [3]. The detection of biomarkers can be clue to make cancer diagnostics possible on early stages [4]. In the current work a chip sensor towards SP and SD was developed based on a hydrogel with water soluble P[5]A (WSPA) attached onto the pendant groups of the polymer. Due to a higher affinity of the analyte to WSPA, the host molecules detach from the polymer chains, which leads to a drop in the polarity of the system, thus to the decrease in swelling degree, which can be detected using surface plasmon resonance (SPR).

WSPA decaammonium (decacarboxylato)pillar[5]arene was synthesized according to the literature procedure [5]. Binding affinity of the WSPA towards aminohexanol (AH) and SP was compared using different techniques.

Dimethyl acrylamide (DMAAm) was copolymerized with 4,4-dimethyl-2-vinylazlactone (VDMA, "click"-modifiable moiety) using RAFT technique to obtain the copolymer P0 (50 kDa, 10% VDMA units). P0 was modified simultaneously with a photo-crosslinkable moiety *N*-(3,4-dimethylmaleimido)ethyl amine (DMIEA) and AH (DMAAm:DMIEA:AH = 18:1:1) to obtain a guest terpolymer GP. Complex formation between WSPA and GP in water was proved by NMR by the upfield shift and significant broadening of the CH_2-OH methylene peak of the AH moieties, which returned to its initial position in the presence of SP.

The solution of GP (10 wt.% in $CHCl_3$) was spin-coated onto a quartz wafer with a deposited gold layer (modified with an adhesion promoter *S*-(*N*-(3,4-dimethyl maleimido)propyl) ethanethioate) and after the solvent evaporation the chip was irradiated with UV-light (252 mW/cm^2; 90 s). The thickness of the photo-crosslinked gel layer was determined by SPR. The chip was then immersed in deionized water and measured in the flow cell in the swollen state and in the presence of SP and SD. The dependence of the layer thickness on the analyte concentration was determined.

Keywords: cancer biomarker, hydrogel sensor, pillar[n]arenes, surface plasmon resonance.

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Tumor-targeted HPMA-based nanomedicines for photodynamic therapy and tumor imaging

Marina Rodrigues Tavares[1*], Vladimír Šubr[1], Jun Fang[2], Tomáš Etrych[1]

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic*
[2]*Faculty of Pharmaceutical Sciences, Sojo University, Kumamoto, Japan*
[*]*tavares@imc.cas.cz*

Photodynamic therapy (PDT) has arised as a smart approach which employs the light irradiation as external stimuli to activate compounds called photosensitizers (PSs), such as pyropheophorbide-a (PyF).[1] Nanocarriers based on *N*-(2-hydroxypropyl)methacrylamide (HPMA) copolymers are attractive for *in vivo* application as they are fully biocompatible, water soluble and non-toxic. Their favorable pharmacokinetics allows a higher accumulation in solid tumors, thus improving the outcome of the cancer therapy.[2,3] This study involves the synthesis and detailed characterization of HPMA-based nanomedicines carrying PyF, affording well-defined polymer-based tumor-targeted theranostics. PyF derivatives were covalently attached to HPMA copolymers, which were previously synthesized by the controlled radical reversible addition fragmentation chain transfer (RAFT) polymerization. The hydrophobic character of the photosensitizer resulted in self-assembly of the nanomedicines into micelles and the use of HPMA carriers allowed the solubilization of PyF, longer circulation time, and a selective tumor accumulation by the Enhanced Permeability and Retention (EPR) effect. Light irradiation was employed to induce the formation of cytotoxic reactive oxygen species (ROS), i.e., singlet oxygen ($^1O_2$), resulting in a remarkably increased cytotoxicity even when low doses were administered,[1] therefore these conjugates are promising candidates for the targeted PDT and tumor diagnostics (Figure 1).

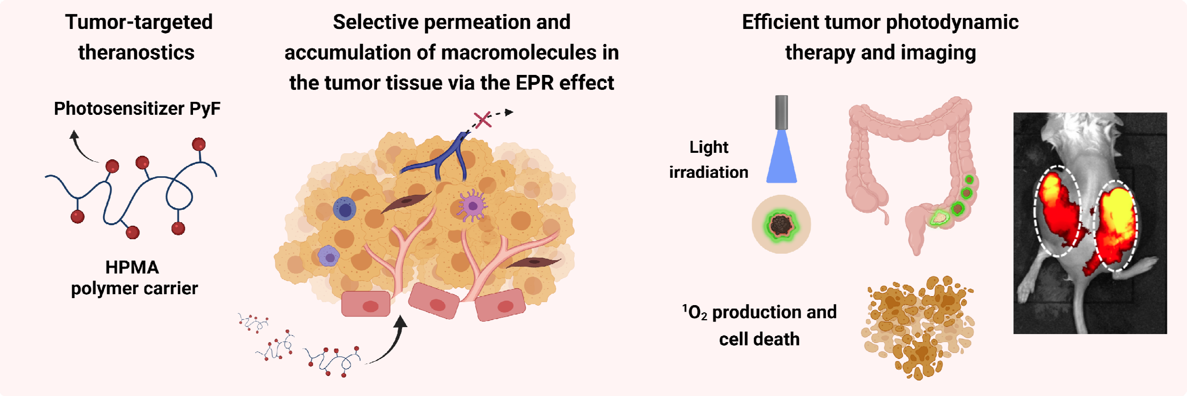

Figure 1. Schematic representation of tumor-targeted HPMA-based nanomedicines for PDT and tumor imaging. Created with Biorender.com.

Keywords: Photodynamic therapy, Tumor imaging, HPMA copolymers, theranostics, nanomedicines

Acknowledgments

We gratefully acknowledge the support from the Grant Agency of the Czech Academy of Sciences (grant No. 21-11688S).

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Increasing the Stability of Anti-microbial Peptides with Different PEGylation Designs and Its Effect on *in vitro* Evaluation

Seray Sahsuvar[1], Ozge Can[2], Ozgül Gok[2*]

[1]Acibadem Mehmet Ali Aydinlar University, Health Sciences Institute, Department of Medical Biotechnology, Istanbul, Turkey
[2]Acibadem Mehmet Ali Aydinlar University, Engineering Faculty , Department of Medical Engineering, Istanbul, Turkey
ozgul.gok@acibadem.edu.tr

The main reason why many antibiotics have not shown sufficient effectiveness against infections in recent years is that the bacteria causing the infection have developed resistance to the antibiotic treatments used [1]. One way to avoid this situation is the development of new antibiotics, and in this context, special peptide sequences consisting of 9-13 amino acids were developed in our research laboratory. In this research study, it is aimed to covalently conjugate anti-microbial peptides (AMPs) to linear PEG chains with different architecture to provide both improved stability and prolonged circulation time along with increased water solubility in the body [2]. Within the scope of this project, polymer-peptide conjugates containing both single and double peptide molecules were synthesized and purified.

Synthesis of peptide sequences: Cystine modification (C-TN6 and TN6-C) was made to the TN6 peptide during synthesis, from the N-terminus and C-terminus to two combinations, respectively. These peptide sequences were synthesized in the peptide synthesis device and purified using the HPLC method.

Synthesis of polymer-peptide conjugates: Polymer-peptide conjugates, amine functional PEG molecule from one end and cystine modified peptide sequences from one end, were prepared using different hetero-functional intermediate linker molecules. Mal-PEG8-NHS ester was used for mono-PEGylated peptides (PEG-Pep), while Bis-Mal-Lysine-PEG4-acid interlinker molecules were used for multivalent conjugates (PEG-Pep2). On the other hand, for bivalent PEG–peptide conjugates (Pep-PEG-Pep), firstly, 6-maleimido hexanoic acid was used to give maleimide functionality to the polymer ends and then peptide conjugation was performed. Characterized by 1HNMR and FT-IR spectroscopies using HPLC and LC-MS/MS.

***in vitro* experiments:** MIC (Minimal Inhibition Concentration) study was performed on S.aureus, P.aeruginosa, E.coli, C.albicans bacterial strains of polymer-peptide conjugates whose anti-microbial activities were investigated (Table 1). The cytotoxicity of the prepared conjugates was investigated in 3T3 fibroblast and HaCaT keratinocyte cells using MTT cell viability kit. The most recent hemolytic activities were also checked. It is among the data obtained that these conjugates are not cytotoxic and do not significantly affect cell viability (>50%) up to at least 4 times the MIC values.

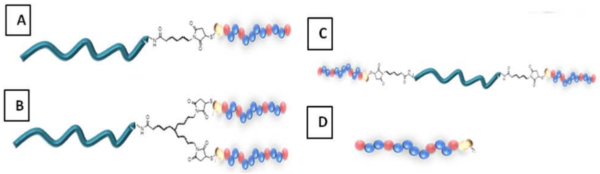

Figure 1: Schematic representation of polymer-peptide conjugates. (a) PEG-Pep, (b) PEG-Pep2, (c) Pep-PEG-Pep, (d) Peptide

Table 1. MIC (µg/ml) values of conjugates.

No	Conjugate Type	Thiolated Peptide	S.aureus	E.coli	P.aureginosa	C.albicans
1	PEG-Pep	C-TN6	64	64	128	32
2		TN6-C	16	16	128	32
3	PEG-Pep2	C-TN6	128	128	256	128
4		TN6-C	64	128	256	64
5	Pep-PEG-Pep	C-TN6	4	4	32	8
6		TN6-C	32	64	128	16
7	Pep	TN6	1	1	4	1

Acknowledgments

This study was supported by Acıbadem Mehmet Ali Aydınlar University Scientific Research Commission (ABAPKO Project No: 2019/04-08) and Tubitak (Project No: 217S060).

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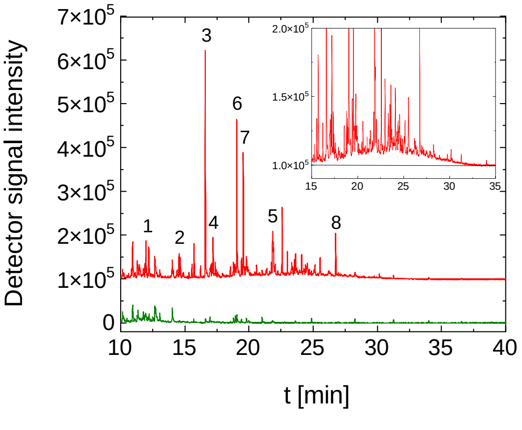
Towards (ultra)pure water-soluble polymers: how to get rid of hydrophobic contaminants

M. Sedlák[*], D. Rak

Institute of Experimental Physics, Slovak Academy of Sciences, Košice, Slovakia, [*]marsed@saske.sk

Water-soluble polymers are commonly purified by methods such as dialysis and ultrafiltration, in which low molecular mass contaminants are removed via a passage through a membrane with pores large enough for contaminants and small enough to prevent the passage of polymers. In every case, contaminants must be water-soluble in order to be able to be removed from a polymer solution in this way. Hydrophobic contaminants therefore represent a problem. We will introduce in this presentation new methods of purification of water-soluble polymers and monomers from hydrophobic contaminants, which are subject of granted and pending patents [1-3] and are based on interesting physico-chemical research results [4]. These methods are cost-effective and enabling purification to high degrees of purity (below 1 ppm). The source of hydrophobic contaminants in water-soluble polymers is predominantly the monomer, but also other compounds such as monomer stabilizers, initiators, quenchers, and emulsifiers in emulsion polymerizations. A secondary contamination due to manufacturing processes and storage is also possible. If one takes common monomer purity ≥ 99%, then the contaminants content is ~ 10g/kg (grams, not micrograms or milligrams!). In practice, only a fraction of this amount represents hydrophobic contaminants, nevertheless their content is anyway substantial. We have studied in detail [4] behavior of hydrophobic contaminants in water-soluble compounds upon dissolving in water. At concentrations which correspond to real situations in practice, hydrophobic contaminants neither molecularly solubilize nor macrophase separate, but instead undergo mesoscopic solubilization [4]. The whole volume of solution is homogeneously filled with nanoparticles or nanodroplets comprising hydrophobic contaminants. A detailed knowledge of these nanoobjects, their occurrence, stability over time, mechanical strength, and shape stability enables us to eliminate hydrophobic contaminants by filtering out mesoscopic objects, based on a proper choice of filter pore sizes and filtration pressures [1,2]. In the case of purification of polymers instead of monomers, situation is slightly different in that the hydrophobic contaminants tend to adhere to polymer chains. It was found [3] that upon ionization of chains, hydrophobic contaminants are expelled to bulk water where they are forced to self-assembly into mesoscopic nanoobjects. Given the properties and importantly also the size of these nanoobjects (larger than the size of most polymer chains), it is possible to separate hydrophobic contaminants from polymers by filtration with a proper choice of pore sizes and filtration pressures.



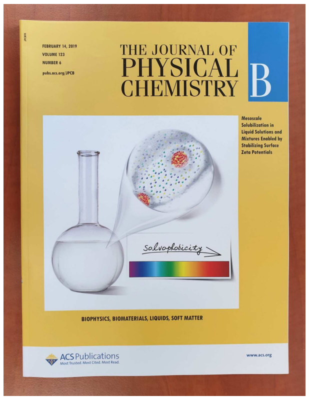


Fig. 1. GC-MS HS-SPME elugrams obtained on aqueous solution of sodium polymethacrylate before filtration (red) and after filtration (green). Elugrams are vertically shifted for the sake of clarity. 1–dodecane, 2–tridecane, 3–bifenyl, 4–tetradecane, 5–hexadecane, 6–dodecanol, 7–2-tridecanone 8–isopropyl tetradecanoate. The inset indicates a large number of hydrophobic contaminants which elute simultaneously.

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Preparation and characterization of chitosan thin films for the modification of surfaces and their application in bacterial adhesion

C. Garreau[1], M. Diallo[1], S. Trombotto[1], T. Delair[1], G. Sudre[1*]

[1]*Univ Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, F-69622 Villeurbanne Cédex, France*
[*]*guillaume.sudre@univ-lyon1.fr*

Chitosan is the only naturally occuring cationic copolymer belonging to the class of polysaccharides. It is industrially obtained by partial deacetylation of chitin, which is generally extracted from shrimp shells or squid pens. Chitosan is composed of D-glucosamine (GlcN) and N-acetyl-D-glucosamine (GlcNAc) units linked by β-(1→4) glycosidic bonds. [1] Because of its biocompatibility, biodegradability and non-toxicity, this polysaccharide has received considerable attention for biomedical applications, *e.g.* for the preparation and the formulation of biologically compatible *in vivo* and *ex vivo* materials. [2]

It has also been shown that surfaces covered with chitosan can modulate bacteria adhesion. [3] We have further demonstrated that the chemical parameters of chitosan are key to control the physiological response of the bacteria. [4, 5] Indeed, depending on the degree of N-acetylation (DA), these surfaces can allow the immobilization of bacteria (Fig. 1) without destroying them or altering their reproduction. This property of chitosan could be helpful for the modification of surfaces for the development of new techniques in fast diagnosis. The aim of this study is to evaluate the physicochemical properties (thickness, wettability, surface energy, film morphology) and the biological responses of various surfaces modified with different chitosans. To this end, we have prepared a library of chitosans of various molar masses and DA, which have been dissolved in mild acidic conditions to form thin solid films by spin-coating. We also have developped a method to graft chitosan thin films onto surfaces to improve their stability. We seek to understand the effect of some molecular parameters of chitosan on the bacteria adhesion and to correlate the physicochemical properties of chitosan films to the adhesion response of bacteria.

Figure 1. Growth of *Escherichia coli* on chitosan grafted films (left: DA = 21%, right: DA = 35%); the time of growth is indicated in minutes.

Keywords: chitosan, thin film, grafting, surface characterization, bacterial adhesion.

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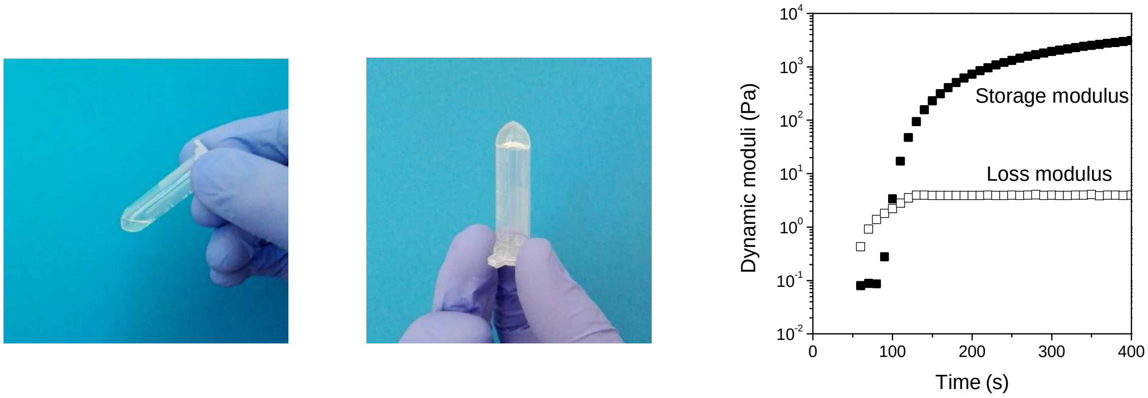
In situ gellable thiolated and thiol-protected poly(aspartic acid) derivatives for drug delivery

B. Gyarmati, B. Á. Szilágyi, A. Mammadova, A. Szilágyi[*]

Department of Physical Chemistry and Materials Science, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary

The bioavailability of liquid drug formulations can be improved by using *in situ* gelling mucoadhesive polymers [1]. In our work, a biocompatible synthetic poly(amino acid), poly(aspartic acid), was chosen as the backbone of a thiolated and S-protected, bioadhesive polymer [2]. Thiolated poly(aspartic acid)s were prepared by reacting polysuccinimide with cysteamine, whereas S-protected polymers were synthesized by attaching 6-mercaptonicotinic acid onto the thiolated derivatives. Aqueous solutions of the two types of polymers could be converted into hydrogel without any external agent as a result of intermolecular disulfide formation. The gelation time and the mechanical properties were controlled by the composition. Interestingly, the aqueous stability and degradation of the hydrogels strongly depended on free thiol content. *In vitro* safety of the polymers was confirmed by several tests: free radicle damage assay (lipid peroxidation), metabolism enzyme assays (CYP450 inhibition), hemolysis assay (red blood cell lysis), and cellular toxicity (cytotoxic effect). Compared to a liquid formulation, the cohesive hydrogel matrix ensured the sustained release of the encapsulated antibiotic, ofloxacin. In the continuation of the work, the bioadhesion of the hydrogels is to be investigated.



(A) (B) (C)

Figure 1. (A) The low-viscosity solution of thiolated and thiol-protected PASP derivatives is converted to (B) hydrogel. (C) Time-dependent change of dynamic moduli during gelation.

Acknowledgments

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The interplay of polymer matrix and microbial cells in living materials

H. Priks, T. Tamm
[1]*Institute of Technology, University of Tartu, Tartu, Estonia*

Recent advances in additive manufacturing have enabled the three-dimensional (3D) printing of polymer materials with embedded microbial cells, creating living materials. Such advanced materials allowing metabolic activity of the cells ladden therein are expected to find applications in various fields of biomedicine, in form of drug delivery or tissue engineering, and biotechnology in form of production platforms or screening tools. Naturally, to successfully employ such complex systems, an in-depth understanding of the multiple aspects governing the performance of both the cells and the surrounding material are needed in the rare interwoven field of materials science and biology. Here, we present an approach to analyze the interplay of the cells via their phenotype and the performance of the polymer matrix in a system where the budding yeast *Saccharomyces cerevisiae* is embedded in hydrogels of three different photo-crosslinkable triblock copolymers (Figure 1) of F127-bis-urethane methacrylate, F127-dimethacrylate, and poly(alkyl glycidyl ether)-dimethacrylate. The hydrophilic poly(ethylene oxide) (A) blocks were arranged with hydrophobic (B) poly(propylene oxide) blocks in ABA formation and with poly(alkyl glycidyl ether) blocks in BAB formation. The normal or reverse flower micelles can further be crosslinked by means of photo-initiated polymerization during or after the 3D-printing to form stable structures of the living materials. Moreover, we have shown that the method and materials can be applied for multiple kingdoms, either separately or in consortia, as shown by the examples of yeasts, bacteria and algae [1].

Optical and scanning electron microscopy characterization have shown the stability of the materials under physiological conditions, while the yeast colonies demonstrated clear differences in their interactions with the matrix materials [2]. Depending on the composition and structure of the hydrogel matrix, the size of the embedded cells was reduced compared to that of suspension cells. Certain effects could be distinguished on immobilization patterns, colony growth, and colony coatings. In particular, the storage moduli of the polymers forming the hydrgels could be linked to the cell size redution. On the other hand, the cells also impacted the matrix with composition-dependent degradation patterns of the polymers, linked to the cells residing in the living materials. The carbamate bonds of one of the polymers involved directly showed suitability for scenarios where biodegradable materials are needed, for long-term stability other polymers can and must be selected. Future perspective of the materials will be discussed in the presentation.

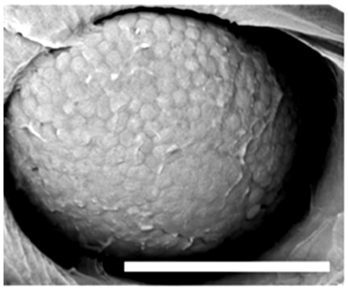

Figure 1. A yeast colony inside a F127-BUM hydrogel, SEM micorgraph (30 μm scale bar).

Keywords: living materials, 3D printing, triblock copolymers

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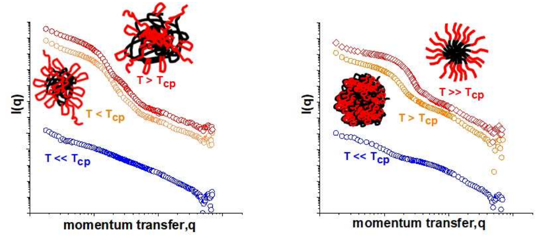
Hydration and nanoscale aqueous morphologies in thermoresponsive double hydrophilic block copolymers with drug encapsulation potential

A. Vagias[1*], A. Papagiannopoulos[2], L. P. Kreuzer[1,3], D. Giaouzi[2], S. Busch[4],
S. Pispas[2], P. Müller-Buschbaum[1,3]

[1]Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstr. 1, 85748 Garching, Germany
[2]Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 11635 Athens, Greece
[3] Physik-Department, Lehrstuhl für Funktionelle Materialien, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany
[4]German Engineering Materials Science Centre (GEMS) at Heinz Maier-Leibnitz Zentrum (MLZ), Helmholtz-Zentrum Hereon, Lichtenbergstr. 1, 85748 Garching, Germany
[*]apostolos.vagias@frm2.tum.de

By synergy of Fourier transform infrared (FTIR) spectroscopy and small angle neutron scattering (SANS) experiments, we obtain a thorough understanding of the nanoscale aqueous assemblies of novel thermoresponsive and double hydrophilic poly(N-isopropylacrylamide)-*block*-poly(oligo ethylene glycol methyl ether acrylate) (PNIPAM-*b*-POEGA) copolymers. [1] The purely hydrophilic POEGA block maintains the stealth properties like PEO, [2] but adopts a more complex comb-shaped topology. Assemblies of this diblock copolymer have succeeded in encapsulating the hydrophobic drug indomethacin. [3] We focus on the influence of temperature as external stimulus and block length asymmetry, in order to broaden our understanding of the self-assembly of the drug delivery scaffolds. We resolve differences in morphologies (Fig.1) and molecular hydration characteristics in assemblies of symmetric and asymmetric PNIPAM-*b*-POEGA diblock copolymers. [1] Upon heating, block-length dependent nanostructural transformations from hierarchical assemblies to more well-defined spherical morphologies are evidenced by SANS. Differences in the strength and/or amount of hydrogen bonding and hydrophobic interactions lead to distinct morphological transformations expressed by variations in cluster compactness and hydration. The methyl side group hydration, as evidenced by FTIR, sensitively depends on the PNIPAM block length. The understanding of these assemblies allows to optimize these scaffolds for drug encapsulation protocols.



PNIPAM$_{19}$-*b*-POEGA$_{10}$ PNIPAM$_{9}$-*b*-POEGA$_{9}$

Figure 1. Schematic of SANS intensity curves for (left) asymmetric and (right) symmetric PNIPAM-*b*-POEGA solutions in D_2O at different temperatures (T) below and above the nominal cloud point (T_{cp}), as well as the associated nanoscale assemblies. Adapted from [1].

Keywords: thermoresponsive polymers, double hydrophilic block copolymer, block length, SANS, FTIR

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3D printing ancient biopolymer and nanomaterials for ideal biological scaffold to provide structural support and the ability to change as the functional requirements of the target tissue change

C. De Maria,[1] I. Chiesa,[1] D. Morselli,[2,3] M. R. Ceccarini,[4] M. Degli Esposti,[2,3] P. Fabbri,[2,3] A. Morabito,[6,7] T. Beccari,[4] L. Valentini*[3,5]

[1]Department of Ingegneria dell'Informazione and Research Center E. Piaggio, University of Pisa, Largo Lucio Lazzarino 1, 56122 Pisa, Italy
[2]Department of Civil Chemical, Environmental and Materials Engineering (DICAM), Università di Bologna, Via Terracini 28, Bologna 40131, Italy
[3]Italian Consortium for Science and Technology of Materials (INSTM), Via Giusti 9, 50121 Firenze, Italy
[4]Department of Pharmaceutical Sciences, University of Perugia, 06123 Perugia, Italy
[5]Dipartimento di Ingegneria Civile e Ambientale, Università degli Studi di Perugia, Strada di Pentima 4, 05100, Terni, Italy
[6]Department of Pediatric Surgery, Meyer Children's Hospital, Viale Pieraccini 24, 50139 Firenze, Italy
[7]Dipartimento Neuroscienze, Psicologia, Area del Farmaco e della Salute del Bambino NEUROFARBA, Università degli Studi di Firenze, Viale Pieraccini 6, 50121 Firenze, Italy
**luca.valentini@unipg.it*

Regenerative Medicine is a branch of medicine that aims to regenerate tissues and organs dealing with creating biological scaffolds. The ideal biological scaffold would provide structural support appropriate for the tissue of interest, an adhesion surface that maintains phenotypic cues suited to the tissue and the ability to change as the functional requirements of the target tissue change [1-2]. The scaffold should allow cell seeding and proliferation. This work is part of a much larger research project that aims to create scaffolds that can be used clinically and are therefore able to provide support for cell seeding and proliferation, making tissue reproduction possible *in vivo*.

We introduced the use of two materials in the creation of scaffolds: silk fibroin and nanomaterials (graphene), two materials capable of improving the electro-bio-mechanical properties of the scaffold.

We then combined these materials in different compositions and studied their adhesive characteristics and properties, cell growth support and 3D printability, in order to demonstrate their potential use in the field of bioadhesives and of cellularized and implantable 3D printed scaffolds.

Keywords: biocomposites, biodegradable devices, biomimetic scaffolds, nanostructured materials, 3D printing

Acknowledgments

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Fluorinated Diselenide Nanoparticles as Radiosensitizers for Cancer Treatment

M. Vetrik [1,2], J. Kucka[1], L. Kobera[1], R. Konefal[1], V. Lobaz[1], E. Pavlova[1], M. Bajecny[3], T. Heizer[3], J. Brus[1],L. Sefc[3], G. Pratx[2], M. Hruby[1]

[1]Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Prague, Czech Republic
[2]Stanford University, Stanford School of Medicine, Stanford, California, USA
[3]Center for Advanced Preclinical Imaging (CAPI), First Faculty of Medicine, Charles University, Prague, Czech Republic

Radiation resistance of cancer cells represents one of the major challenges in cancer treatment. The novel self-assembled alkylfluoralkylated diselenide nanoparticles (fluorosomes) based on seleno L-cystine ($17FSe_2$) possess redox-active properties (**Figure 1**). They autocatalytically decompose hydrogen peroxide (H_2O_2) and oxidize the intracellular glutathione (GSH) needed for the regulation of cellular oxidative stress. Diselenides under the presence of H_2O_2 generate seleninic acid responsible for additional autocatalytic processes resulting in additional cellular oxidative stress. An increase in H_2O_2 was elicited artificially by gamma radiation treatment with ^{60}Co source. Alkylfluoroalkylated diselenide nanoparticles showed a significant cytotoxic and radiosensitizing effect on cancer cells. The EL-4 tumor-bearing C56BL/6 mice treated with $17FSe_2$ followed by fractionated radiation treatment (4x 2Gy) completely suppressed tumor growth. Our results suggest that described diselenide system behaves as a potent radiosensitizer agent targeting tumor growth and preventing tumor recurrence.

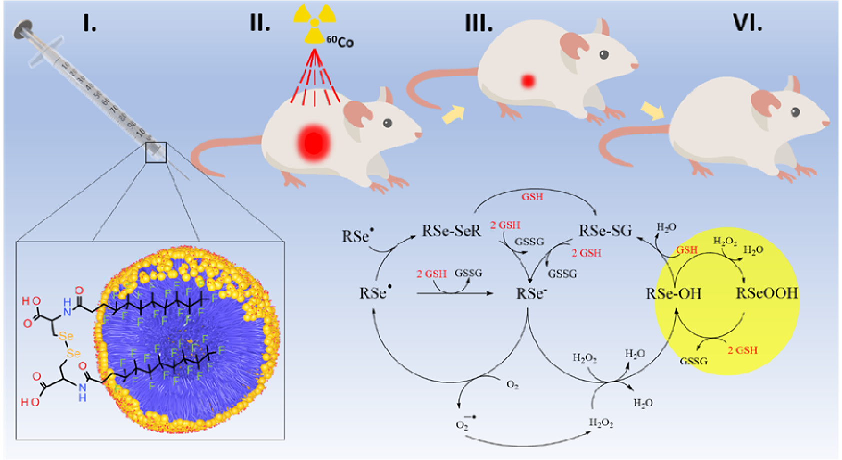

Figure 1. Structure, scheme of the cancer treatment and mechanism of action using alkylfluoralkylated diselenide nanoparticles.

Acknowledgments

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Preparation and Complex Characterization of Drug-Loaded Sericin Nanocarriers for the Management of Brain Tumors

C. Zaharia[1], I.C. Radu[1], M. Teodorescu[1], B. Galateanu[2], M.I. Necolau[1], A. Hudita[2], E. Vasile[3], C. Stavarache[1]

[1]*University Politehnica of Bucharest, Advanced Polymer Materials Group, Bucharest, Romania*
[2]*University of Bucharest, Department of Biochemistry and Molecular Biology, Bucharest, Romania*
[3]*University Politehnica of Bucharest, Bucharest, Romania*
**Corresponding Author's E-mail address: zaharia.catalin@gmail.com*

Keywords: sericin, atom-transfer radical polymerization, nanoprecipitation, glioblastoma

Introduction: Tumors of the central nervous system are the most common solid malignancies in adults and second most common malignancy overall in children [1]. Among them, Glioblastoma remains one of the most lethal cancers in humans with a median survival after maximal therapy of less than two years after first diagnosis. Despite improvements in the past few decades with intraoperative surgical techniques, chemotherapy, and radiation therapy, predictable curative treatment for glioblastoma is not fully developed. However, the chemotherapy is rapid growing to oppose this lethal disease. Various types of active agents (drugs, analogues, genes, etc.) and delivery methods are continuously tested to reveal their benefits. Polymeric nanocarriers are suitable hosts for the active delivery of biological agents based on their size, size distribution and surface chemistry. Modern polymeric nanocarriers can be designed and developed by combining protein engineering tool with top techniques of polymer growth. Therefore, living/controlled radical polymerization is a powerful tool able to shape new polymeric nanocarriers based on proteins.

Experimental: New polymeric nanocarriers have been developed based on the grafting functionalization of silk sericin with synthetic side chains (Poly(2-dimethylamino ethyl methacrylate)). Silk sericin had a macroinitiator role while the synthetic chains generate the side chains such as a brush-like structure. The sericin was firstly modified with an alkyl halogen to provide the growing sites for the poly(2 dimethylamino ethyl methacrylate) chains. In this respect, atom transfer radical polimerization (ATRP) was employed. The polymerization technique is able to control the growth of the side chains resulting in a brush-like stucture. Furthermore, the grafted sericin was used to prepare small size polymeric nanocarriers by nanoprecipitation. In this regard, solutions of grafted silk sericin were precipited into a non-solvent to generate self-assembled polymeric structures. Drug loading (ganciclovir, ribavirin) and release tests were performed by drug dissolution into the grafted silk sericin media followed by the self-assembling step. The morphological investigation is a key procedure to reveal the nanocarriers' size, size distribuion and shape as important charactistics. These important features and differences between the nanocarriers generated by the two synthesis conditions were shown through SEM and DLS. These nanocarriers were further tested for their *in vitro* biocompatibility and cytotoxic potential effect on human glioblastoma cells cultured in a modern microfluidic device. The biological investigations performed in this view highlighted the cells viability and proliferation potential under the treatment of the cells with pristine nanocarriers, drug-loaded nanocarriers as compared with a reference treated with the simple drug and also with an untreated sample. These investigations were done using fluorescence microscopy and spectrophotometric assays such as MTT and LDH activity measurements. **Results and discussion:** Nanoparticles had narrow size distribution with low size and significant differences considering the synthesis conditions. The drug release tests revealed an expected behavior considering the pH conditions. The biological assesment revealed that the pristine nanocarriers did not display cytotoxic effects on the cells, while the drug loaded delivery systems exerted similar toxic effects as the drugs alone. **Conclusions:** In conclusion, we reported here the development of new protein-based nanocarriers able to deliver various drugs with potential benefits for the central nervous system cancer management (glioblastoma). The nanocarriers were successfully investigated in terms of morphology, size distribution, drug release behavior and biological assesment. ***Acknowledgements:*** *"This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2020-1448, within PNCDI III".* **References:** [1] Miller, K.D.; Ostrom, Q.T.; Kruchko, C.; Patil, N.; Tihan, T.; Cioffi, G.; Fuchs, H.E.; Waite, K.A.; Jemal, A.; Siegel, R.L.; Barnholtz-Sloan, J.S. Brain and other central nervous system tumor statistics, *CA: A Cancer Journal for Clinicians* **202**1, *71(5)*, 381-406.

Patterned polymer brushes by two-photon-initiated raft polymerization

S. Helfert[1,6], T. Zandrini[3,6], A. Rohatschek[2,4,6], M. Rufin[4,6]; P. Machata[5], A. Zahoranová[1,2,6*], O. G. Andriotis[4,6], Ph. J. Thurner[4,6], A. Ovsianikov[3,6,] R. Liska[1,6,] S. Baudis[1,2,6*]

[1] Institute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9/163MC, Vienna 1060, Austria
[2] Christian Doppler Laboratory for Advanced Polymers for Biomaterials and 3D Printing
[3] Institute of Materials Science and Technology, TU Wien, Getreidemarkt 9/308, Vienna 1060, Austria
[4] Institute of Lightweight Design and Structural Biomechanics, TU Wien, 1060 Vienna, Austria
[5] Department of Composite Materials, Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 84541, Bratislava, Slovakia
[6] Austrian Cluster for Tissue Regeneration, Vienna, Austria

Photopatterned polymer brushes enable tailoring surface properties on demand, which is especially important for biosensors, substrates for tissue engineering, implants with microelectronic active parts, or microfluidic devices.[1] Direct laser writing technique represents a convenient method to prepare photomask-free micropatterned surfaces. However, conventional one-photon photopolymerization process limits the achievable pattern resolution. In this work, we address this drawback by employing two-photon absorption process for the preparation of photopatterned polymer brushes. Multi-photon grafting of small functional molecules is already known as a powerfull technique to alter polymer surface properties.[2,3] Here, we prepared surface-attached polymer brushes via two-photon-initiated reversible addition-fragmentation chain transfer (2PRAFT) polymerization.

For the preparation of polymer brushes, we selected hydrophilic and biocompatible monomer N-acryloylmorpholine (NAM). The model silicon wafers were covalently modified with RAFT agent 4-cyano-4-(((dodecylthio)carbonothioyl)thio)pentanoic acid (CDTPA) by two-step procedure. Prior 2PRAFT surface patterning, the formulation composition was optimized in one-photon photopolymerization process, employing effective photoinitiator Ivocerin. The effect of the irradiation time and the ratio NAM:CDTPA on the dry polymer brush thickness was evaluated, with the maximum achieved thickness 10.4 ± 1.5 nm. The chemical composition of resulting polymer brushes was confirmed by X-ray photoelectron spectroscopy.

Further, we studied the possibility of patterned brush formation via 2PRAFT. To achieve this goal, we used (2E,6E)-2,6-bis(4-(dimethylamino)benzylidene)-4-methylcyclohexanone (M2CMK) as already established photoinitiator for 2P fabrication. The model substrates used in this case were glass slides, to enable 2P irradiation. We incorporated two different fluorescent co-monomers, namely fluorescein-o-acrylate and Nile Blue acrylamide, which allows us to examine the printed structures via laser scanning fluorescence microscopy. Indeed, we confirmed the formation of well-defined printed patterns down to 5 µm size formed by means of 2PRAFT. The thickness of patterned polymer brushes was further examined via atomic force microscopy measurement. We showed here that 2PRAFT is a versatile method of surface patterning. This method has a future potential in use especially for modification of non-flat geometries, such as microfluidic channels.

Acknowledgments

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Polycaprolactone/Graphene oxide scaffolds with surface porosity and gelatin-coating for tissue regeneration applications

C. Loyo[1], H. Palza[2], C. García-Herrera[3] and P.A. Zapata[1*]
[1]*Departamento de Ciencias del Ambiente, Facultad de Química y Biología, Universidad de Santiago de Chile (USACH), Grupo Polímeros, Santiago, Chile.*
[2]*Departamento de Ingeniería Química, Biotecnología y Materiales, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Beauchef 851, Casilla 277, Santiago, Chile.*
[3] *Laboratorio de Biomateriales y Biomecánica, Departamento de Ingeniería Mecánica, Universidad de Santiago de Chile, Santiago, Chile*
[*]*paula.zapata@usach.cl*

Tissue engineering (T.I.) aims to construct functional structures that restore, maintain or improve damaged tissues or entire organs by designing 3D porous scaffolds that stimulate the regeneration of human tissues [1]. Synthetic and natural biodegradable polymers are the primary materials used to manufacture scaffolds due to their versatility and high compatibility. Polycaprolactone (PCL) is a synthetic polymer that stands out for its good mechanical properties, further approved by the Food and Drug Administration (FDA) for manufacturing biomaterials. However, it has a high biodegradability time and low bioactivity due to its hydrophobic nature [2]. One strategy for improving the bioactivity of these synthetic polymers is to include nanomaterials and natural polymers, alongside changing the surface topography. The goal of this contribution is to add graphene oxide (GO), which contains oxygenated functional groups that improve cell adhesion and proliferation, and a gelatin coating, into PCL scaffolds to improve its wettability and biodegradability. The scaffolds were prepared by electrospinning with a porous surface morphology obtained by the non-solvent induced phase separation (NIPS) method to obtain a larger surface area and similar structure to the extracellular matrix (ECM). After gelatin coating, 189% and 115% increased water absorption was obtained for non-porous and porous scaffolds, respectively, after immersing the scaffolds during 24 hours. Indeed, when 2% GO was incorporated into coated scaffolds, water absorption increased by 175% and 167% for non-porous and porous-coated scaffolds compared with non-porous and porous scaffolds without GO, respectively. Scaffolds with surface pores increased biodegradability after 60 days in SBF solution by 13% and 29% for uncoated and gelatin-coated scaffolds, respectively. In addition, 2% of GO increased the biodegradability of porous scaffolds by 27% and 161% for uncoated and gelatin-coated scaffolds, respectively. However, the presence of pores mainly affected mechanical properties, decreasing ultimate tensile stress by 48% and 50% for PCL and PCL/2%GO scaffolds, respectively. Bioactivity analysis showed spherical minerals deposited on the porous gelatin-coated scaffolds corresponding to hydroxyapatite crystals. Gelatin can induce calcium phosphate formation due to interactions between -COO- anions found in the gelatin structure with Ca^{2+} cations present in the simulated body fluid solution [3]. In conclusion, gelatin-coated PCL/GO scaffolds with surface porosity are promising materials for tissue regeneration applications.

Keywords: Scaffolds, Polycaprolactone, Gelatin.

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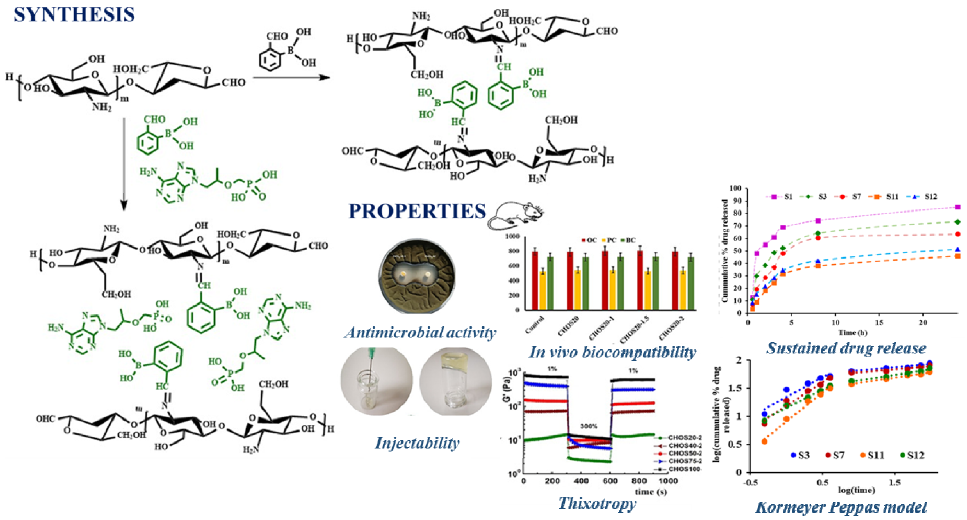
Antifungal biocompatible hydrogels as matrix for antiviral drug release

Daniela Ailincai, Luminita Marin

[1]*Petru Poni Institute of Macromolecular Chemistry, Iasi, Romania*
**ailincai.daniela@icmpp.ro*

One of the most widespread sexually transmitted infections worldwide is Human immunodeficiency virus (HIV), having negative impact from multiple points of view - economic, biomedical and social, being the main cause of discriminatory atitudes towards people suffering from it. Even if, in the last years HIV doesn't represent a death cause by itself, by weakening the immune system of the host, it creates an appropriate background for virulent microorganisms infections, which may lead in the worst cases to death. Among these microorganisms, *Candida* species are the most opportunistic ones in immunocompromised patients, creting severe complications. Therefore, the development of systems with a paliative effect for the infected patients and with strong antimicrobial activity is a hot topic in research.

In this light, the present study had as objective the obtaining of new hydrogels able to deliver both antifungal and antiviral bioactive compounds [1]. The systems are obtained by the imination reaction of chitooligosaccharides with different polymerization degrees with 2-formylphenylboronic acid, a monoaldehyde known for its antifungal activity. Drug's encapsulation occured simultaneously with imination in order to asure its homogenous distribution into the polymeric matrix. The matrix and the drug delivery systems were characterized from the structural, morphological, supramolecular points of view, while their properties regarding bioapplication were also investigated: enzymatic degradability, thixotropy, antifungal activity and *in vivo* biocompatibility on mice. Further, drug release kinetics was monitored from the formulations by UV-VIS technique while the obtained data were fitted on different mathematical models, in order to establish the parameters which influence the release of the encapsulated drug.



The investigated samples presented high porosity and high swelling ability, high degradation rates in the presence of lysosime, strong antimicrobial properties and *in vivo* biocompatibility. Moreover, due to the strong interactions established between the drug and the matrix, the systems released the encapsulated drug in a sustained manner, proving that this systems can be of real help for the treatment of HIV and HIV associated co-infections.

Acknowledgments

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Electrochemical Activation for Sensing of 3D-Printed Poly(lactic Acid) Using Low-Pressure Plasma

Adrián Fontana-Escartín,[1,2] Sonia Lanzalaco,[1,*] Maria del M. Pérez-Madrigal,[1] Oscar Bertran[2] and Carlos Alemán[1,3,*]

[1] Departament d'Enginyeria Química and Barcelona Research Center in Multiscale Science and Engineering, EEBE, Universitat Politècnica de Catalunya, C/ Eduard Maristany, 10-14, 08019, Barcelona, Spain
[2] Departament de Física EETAC, Universitat Politècnica de Catalunya, c/ Esteve Terrades, 7, 08860, Castelldefels, Spain
[3] Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute of Science and Technology, Baldiri Reixac 10-12, 08028 Barcelona Spain
[*] *carlos.aleman@upc.edu*

Plasma irradiation treatment consists on the interaction of a mixture of electrons, ions, radicals and neutral species, which can possess a massive internal energy, with a surface for cleaning, activation or etching. The plasma is generated when enough energy is provided to gas molecules, ionizing the system and affecting its electrical properties. Within the context of polymer materials, plasma processing has been widely used for, among others, polymerizing gaseous monomers, promoting the grafting of (nano) microstructured polymers, cleaning and etching surfaces, sterilizing and disinfecting, and functionalizing surfaces.

Among the different applications of polymers processed with plasma technologies, the fabrication of advanced biomedical sensors is gaining attention.[1] In recent studies we reported a procedure to transform recycled polyethylene into an electrochemically responsive material by applying atmospheric (*i.e.* air-open) corona discharge plasma.[2,3] Herein, we significantly improve our technology to fabricate electrochemical sensors using exclusively insulating plastics considering the following changes: 1) replacing the air corona discharge plasma by a plasma in a chamber that allows to control both the feeding gases and the pressure; and 2) introducing additive manufacturing (*i.e.* 3D printing) for the processing of the plastic samples. Poly(lactic acid) (PLA), an insulating biopolymer that has a substantial potential in biomedical applications, has been chosen for this purpose. Specifically, 3D printed PLA samples has been subjected to N_2, O_2 and air low-pressure plasma treatment. After compare the chemical structure, morphology, electrochemical response and biocompatibility of the modified materials, their potential as electrochemical sensor has been evaluated by detecting the electrocatalytic oxidation of dopamine.

Acknowledgments

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Glycyrrhizin-based hydrogels accelerate cutaneous wound healing

S. Alexandris[1*], M. Mees[2], W. Thielemans[2]

[1]Soft Matter, Rheology and Technology (SMaRT) Chemical Engineering Department - KU Leuven Celestijnenlaan 200J (NanoCentre), 3001 Leuven, Belgium
[2]Renewable Materials and Nanotechnology Research Group, Department of Chemical Engineering, KU Leuven, Campus KULAK Kortrijk, Etienne Sabbelaan 53, B-8500, Kortrij, Belgium

Efficient wound healing is crucial for mammalian survival however this process is severely hampered in patients suffering from diabetes. A frequent comorbidity in diabetics is foot ulcer development, resulting in chronic wounds that are difficult to treat. Here, we demonstrate that a hydrogel constituted uniquely by glycyrrhizin [1,2,3] and water accelerates cutaneous wound regeneration in normoglycemic and diabetic mice. By varying the concentration of glycyrrhizin in water, the rheological properties of the hydrogels can easily be modified, enabling customized wound care. We show that based on the glycyrrhizin concentration, these hydrogels have different effects on wound healing kinetics of the skin. In a pig model of cutaneous injury, glycyrrhizin-based hydrogel outperforms a standard-of-care hydrogel for wound treatment.

Keywords: hydrogel, wound healing, rheology

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Supramolecular water soluble self-assembled nucleobase copolymers: new synthetic platforms towards biomimetic materials

L. Arsenie[1], V. Ladmiral[1], M. Semsarilar[2], A. Geneste[1], B. Prelot[1], S. Catrouillet[1,*]

[1]*ICGM, University of Montpellier, ENSCM, CNRS, Montpellier, France*
[2]*IEM, University of Montpellier, ENSCM, CNRS, Montpellier, France*
[*]*sylvain.catrouillet@umontpellier.fr*

Two-strand DNA structure is a result of self-assembly via H-bonds between complementary nucleobases (e.g. adenine with thymine). Inspired by this biological feature, the development of supramolecular architectures from self-assembled nucleobase-containing copolymers attracted a major interest in the last few years. Similarly to DNA, the self-assembly of nucleobase copolymers occurs via H-bonds and hydrophobic interactions.[1] However, the self-assembly of nucleobase copolymer systems faces two significant challenges: low water solubility of the copolymers, and difficult control of the system dynamics (e. g. association/dissociation constants, strength of H-bond, other interactions between nucleobases, etc.). The water insolubility is a serious issue that limits the use of these self-assembled systems in biology (e. g. in cellular transfection, drug delivery, etc.).[2] A control over the dynamic of the self-assembly process is the first step to understand why a specific copolymer structure self-assembles into a particular morphology with a certain size. In addition, controlling the system dynamics should be the key to determine the distribution of unimers in the self-assembly. Understanding the system dynamics is instrumental to better characterize and predict the supramolecular H-bond interactions between nucleobases and their influence on the self-assembly. [3]

Our study aims at answering theses two major problematics (e. g. water solubility and system dynamics). The variation of hydrophobic/hydrophilic balance could overcome these issues by a fine design of the macromolecular structure of the starting nucleobase copolymers. A range of methacrylate copolymers bearing uracil or adenine as nucleobases were synthesized. The variation of the degree of polymerization and of the nucleobase density led to structures with high water solubility. Then, the selected polymer structures containing complementary nucleobases were mixed in water, and the properties of the resulting self-assemblies were studied.

This talk will be divided in two parts. First, the physico-chemical characterization (SLS, DLS, TEM) of the self-assembled nucleobase copolymers in water will be presented, and the effect of the polymer structure on the self-assembled morphologies will be underlined. Second, preliminary investigations on the dynamics of selected self-assembled systems will be discussed, with a focus on the H-bond interactions between complementary nucleobases.

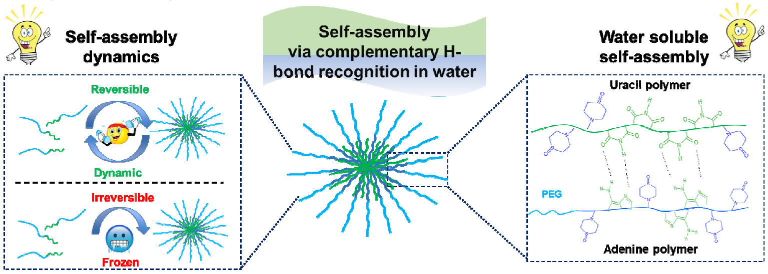

Fig. 1. Self-assembled nucleobase copolymers

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Development of advanced synthetic photocrosslinkable bioinks for 4D bioprinting

Anna Golunova[1*], Jana Dvořáková[1], Nadiia Velychkivska[1], Aneta Dydowiczová[1], Vladimír Proks[1]

[1]*Institute of Macromolecular Chemistry, Prague, Czech Republic*
**golunova@imc.cas.cz*

The fast-developing field of 4D bioprinting for tissue engineering is in constant search of new materials for bioinks. Bioinks are crucial for bioprinting. The ideal bioink should combine specific mechanical, chemical, and biological properties to secure 3D bioprinting in presence of cells, as well as their adhesion and proliferation. [1] Moreover, the material should be biodegradable and promote the formation of the desired tissue upon the application of the 4th dimension of time.

To fulfill these requirements we propose to use synthetic biodegradable polymer bioinks based on poly(α-amino acid)s. This exceptional material combines the perks of controlled biodegradability, versatile structure, and stable hydrogel formation. [2] Therefore they offer an interesting alternative to commercial bioinks based on gelatin, collagen or alginate.

The crosslinking of the bioink to form a 3D construct should be rapid and durable. To secure that we have chosen photocrosslinking initiated with a system of tris(bipyridine)ruthenium(II) chloride and ammonium persulfate under blue light. Synthesized polymer precursor contained tyramine groups to secure the photocrosslinking reaction via photoinitiated nature-like [3] diphenol bond formation.

The key point for the bioink is the ability to communicate with cells. That is why the presence of bioactive motifs such as cell adhesion peptide sequences is highly required. Here we propose one-pot peptide incorporation with simultaneous gel formation via photocrosslinking which was possible due to the use of the unique branched dihydroxyphenyl peptide. The in-house synthesized peptide can form a diphenol bond with polymer and this approach allows better control over the peptide concentration in the gel.

Synthesized polymer precursor was analyzed with several physicochemical methods (NMR, UV-Vis, GPC) to confirm the structure and showed the shear-thinning behavior required for bioinks. Hydrogels obtained from the polymer precursor were characterized with gel yields and swelling capacity. Moreover, the mechanical properties of hydrogels were tested and were shown to be similar to the ones of the gels formed of commercially available Gel-Ma. Besides, *in vitro* experiments confirmed that obtained hydrogels were noncytotoxic for rat mesenchymal stem cells and human embryonic lung fibroblasts.

Keywords: 4D bioprinting, bioinks, biomimetic peptide, photoinitiation

Acknowledgments
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Poly(2-alkyl-2-oxazoline) as Precursor for Monoplasmidic Vectors for Gene Delivery Application

G. Delecourt[1], L. Plet[1], V. Bennevault[1, 2], C. Huin[1, 2], T. Montier[3], G. Tresset[4], P. Midoux[5], P. Guégan[1*]

[1] *LCP-IPCM Sorbonne Université, Paris, Franc*
[2]Université d'Evry, Evry, France
[3]Université de Bretagne Occidentale, Brest, France
[4]LPS, Université Paris-Saclay, Saclay, France
[5]Centre de Biophysique Molécularie, Orléans, France
[*]*philippe.guegan@sorbonne-universite.fr*

Linear polyethylene imine (lPEI) has been demonstrated to be an efficient polynucleotide vector for gene delivery application[1]. Hydrolysis of poly(2-alkyl-2-oxazoline) (POx) is the standart way to obtain the LPEI. Synthesis of cyclic POx to generate cyclic PEI is a way to reduce the high toxicity of lPEI[2], demonstrating the positive effect of varrying the lPEI architecture on the gene delivery application. Various groups have recently investigated the synthesis of well-defined star poly(2-alkyl-2-oxazoline), including ourself, opening the opportunity to develop star-shaped PEI[3]. We synthesized new initiators having 3 to 6 initiating functions able to polymerize 2-ethyl and 2-methyl-2-oxazoline. Characterization of the star polymers revealed the presence of the expected structures whatever the number of arms of the stars. Basic and acidic hydrolysis of the star-Pox was then conducted to provide a library of star PEI with various numbers of arms and various molar masses. Formation of nanoparticles between these polymers and a plasmid encoding for the luciferase was investigated. 100 nm scale nanoparticles were obtained for typical plasmid concentrations for *in vitro* tests. High transfection on HEPG2, A549, HeLA and C2C12 cells was obtained, with a reduced cyctotoxicity compared to commercial references. Based on the viral technology, a ten times increase of plasmid concentration is suitable for *in vivo* transfection essays. Precipitations of the PEI-based vectors formulations are observed at these concentrations, that has hampered the development of *in vivo* essays with such technology. A formulation of the nanoparticles one by one has then been designed to circumvent the precipitation of the particles whatever the plasmid concentration, and monoplasmidic nanoparticles at the 100 nm scale at high concentration could be obtained. New formulations of PEI-based vectors with various architectures and molar masses have been injected in the tail vein of mices. The vectors efficiency was then measured as a function of time by bioluminescence and a nanoparticle structure-*in vivo* transfection properties have been drawn for further therapies development.

Keywords: Poly(2-alkyl-2-oxazoline), Star polymers, Gene transfer

Acknowledgments

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How to activate drugs, proteins and genes by ultrasound employing principles of polymer-mechanochemistry

A. Herrmann[1,2*]

[1]*DWI – Leibniz Institute for Interactive Materials, Aachen, Germany*
[2] *RWTH Aachen University, Aachen, Germany*
[*]*herrmann@dwi.rwth-aachen.de*

The field of optogenetics has enabled the fundamental understanding of neural circuits and disorders.[1,2] However, current optogenetic techniques require invasive surgical procedures to deliver light to target cells due to the low penetration depth of light into tissue. Therefore, ultrasound (US) was used as alternative trigger since US can deeply penetrate tissue with high spatiotemporal control. Our group develops general molecular technologies based on nucleic acid aptamers and mechanochemistry to control the activity of proteins and drugs (Fig. 1) by US.[3,4] Therefore, we produce high molecular weight polynucleic acids by rolling circle amplification or transcription that encode multiple aptamer binding sites for proteins or drugs. Once these loaded nucleic acid carriers are subjected to ultrasonication, covalent and non-covalent bond cleavage occurs by collapse of US-induced cavitation bubbles leading to activation of protein or drug cargoes. Similarly, we liberate small bioactive trigger molecules by US that initiate gene expression involving riboswitches relying on modified tRNA scaffolds.[5] A particular emphasis is paid to reducing US energies to make these sonogenetic and sonopharmacological systems compatible with living matter.[3]

Keywords: polymer-mechanochemistry, sonogenetics, sonopharmacology, drug delivery

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In Situ Thiol-ene Click Reactions To Ensure Strong Adhesion of Polymers to Mucosal Surfaces

V.V. Khutoryanskiy

[1]*Reading School of Pharmacy, University of Reading, Reading, United Kingdom*

Drug delivery via mucosal surfaces offers a number of advantages including improved drug bioavailability and possibility of targeting particular organs [1]. Water-soluble and water-swellable polymers have been traditionally used to develop mucoadhesive dosage forms, capable of adhering to mucosal surfaces, resulting in better retention on the mucosa and hence facilitated drug absorption [2]. These are usually considered as mucoadhesives of first generation and their adhesion to mucosa is due to physical interactions such as electrostatic attraction, hydrogen bonding, hydrophobic effects as well as formation of interpenetration layer with the mucus gel. Thiolated polymers have been introduced as mucoadhesives of second generation because of their capability to form covalent S-S bonds with mucins [3]. For the last 5 years, we have been working on the design of several new classes of mucoadhesives of second generation by introducing unsaturated functional groups into water-soluble polymers or nano-/micro- gels and particles. These functional groups include maleimide, acryloyl and methacryloyl. Polymers functionalised with these groups exhibited strong mucoadhesive properties and potential to retain on mucosal tissues due to in situ thiol-ene click reactions occuring between their macromolecules and thiol groups present in mucins. This communication will consider our advances in the synthesis of these polymers and nanomaterials, including maleimide-functionalised nanogels [4] and nanoparticles [5], acryloylated nanogels [6] and Eudragit® EPO [7], methacryloylated chitosan [8], gellan gum [9] and poly(2-ethyl-2-oxazoline) [10]. The application of these novel polymeric systems in transmucosal drug delivery to the eye, nose and urinary bladder will be discussed. The advantages of the polymers bearing reactive unsaturated groups (maleimide, acryloyl and methacryloyl) over thiolated polymers will be highlighted.

Keywords: mucoadhesion, thiol-ene click, drug delivery

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Expanding the Scope of Surface-Initiated Polymerization

H.-A. Klok*

Ecole Polytechnique Fédérale de Lausanne (EPFL)
Institut des Matériaux, Laboratoire des Polymères
Station 12, CH-1015, Lausanne (Switzerland)
* *harm-anton.klok@epfl.ch*

Surface-initiated polymerization reactions provide access to chain-end tethered polymer brushes. In particular controlled radical polymerization reactions have proven an extremely powerful tool to generate polymer brush films from a broad range of monomers. Such polymer brushes have attracted interest, for example, as nonfouling biointerfaces or as boundary lubricants. The vast majority of polymer brushes is produced from surfaces that present covalently tethered polymerization initiators using copper catalyzed atom transfer radical polymerization reactions with (meth)acrylate-based monomers.

This presentation will give an overview of examples of recent work from our laboratory in which we have tried to expand the scope of surface-initiated polymerization reactions. Work that will be covered will include the use of supramolecular interactions to grown non-covalently tethered polymer brushes, the use of light-mediated controlled radical polymerizations to facilitate access to brushes generated from "unconventional" monomers as well as polymer brush films that can be produced from very large substrates with extraordinary control over polymer architecture, and synthetic strategies that provide access to all-carbon based polymer brush films.

Introducing thiol-ene polymerisations into emulsion templating: new possibilities in biomedical applications

Peter Krajnc*, Viola Hobiger, Stanko Kramer

PolyOrgLab, Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova ulica 17, 2000 Maribor, Slovenia
**peter.krajnc@um.si*

PolyHIPEs are hierarchically porous polymers exhibiting macropores generated by the droplets of the templating high internal phase emulsions while a second level of pores are connecting the macropores. Meso and micropores can be introduced either via porogenic solvent inclusion or via a post polymerisation hypercrosslinking process. Tipically, a water-in-oil emulsion is used and a free radical polymerisation mechanism is applied resulting in porous polymers with a low degree of control over architecture and mechanical properties. Moreover, biodegradability is usually not achieved. The introduction of multifunctional thiols enables the preparation of porous networks via the thiol-ene polymerisation mechanism and thus offering possibilities for more control over polymer architecture, degradability and mechanical properties. Furthermore, use of photo initiation improves the pore size control and adds the possibilities of combining emulsion templating with additive manufacturing technologies, fused- bead templating and the use of multiple emulsions thus widening the spectrum of tailored materials preparation. Thiol-ene polymerisation in combination with emulsion templating will be demonstrated and new materials thus prepared discussed in the view of biomedical applications.

Keywords: polyHIPE, thiol-ene polymerisations, emulsion templating

Thermogelling hydrogel blends for improved 3D printing with excellent shape fidelity

C. Hu[1], Z. Mirzaei[2], L. Hahn[1], R. Luxenhofer[1,2*]

[1]*Functional Polymer Materials, Chair for Advanced Materials Synthesis, Institute for Functional Materials and Biofabrication, Department of Chemistry and Pharmacy, Julius-Maximilians-University Würzburg, Röntgenring 11, 97070 Würzburg, Germany*
[2] *Soft Matter Chemistry, Department of Chemistry and Helsinki Institute of Sustainability Science, Faculty of Science, University of Helsinki, PB 55, 00014 Helsinki, Finland*
[*]*robert.luxenhofer@helsinki.fi*

We have previously discovered a diblock copolymer, which, when dissolved in aqueous media, forms a thermogelling and highly shear-thinning hydrogel [1].This hydrogel shows excellent cytocompatibility and could be used for 3D printing with live mammalian cells (fibroblast) with high cell viability. However, while this hydrogel could be 3D printed, shape-fidelity and long term stability was not satisfactory. Addition of laponite XLG could be shown to significantly improve this [2]. Further, the hydrogel could be blended with a monomer (N,N-dimethlyacrylamide) allowing for post-printing curing to create a interpenetration network, greatly improving the mechanical properties. Notable, extremely high extensibility of the resulting hydrogels was achieved [3]. Also, blending with alginate was investigated. After printing, the alginate could be crosslinked by simple addition of Ca^{2+} containing solutions, which at the same time, washes out the thermogelling polymer. The entire process, mixing, printing, crosslinking and washing was found to be highly cytocompatible [4]. Moreover, the hydrogel could also be mixed with PEG-diacrylate, which could be cured using two-photon polymerization, allowing freefrom laser writing and creation of microscopically small topologically connected 3D "chain-mail" like hydrogel. Such structure are of interest for advanced cell culture and tissue engineering [5]. Currently, we are exploring the potential of hydrogel blends further by using other biobased bioinks and could already increase their printability drastically. We believe our approach can be generalized rather broadly and will boost the potential of many biobased bioinks in biofabrication.

Keywords: additive manufacturing, rheology, shear-thinning

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Repairing ruptured deep flexor tendons, using a tubular polymer-based electrospun construct with a controlled anti-adhesion and anti-inflammation potential

Nele Pien[1,2], Ian Peeters[3], Liesbet Deconinck[1], Lana Van Damme[1], Lieven De Wilde[3], Sandra Van Vlierberghe[1], Peter Dubruel[1], Arn Mignon[1,4*]

[1]*Polymer Chemistry & Biomaterials Research Group, Centre of Macromolecular Chemistry (CMaC), Ghent University, Belgium*
[2]*Laboratory for Biomaterials and Bioengineering, Department of Min-Met-Materials Engineering & Regenerative Medicine, Laval University Canada*
[3]*Faculty of Medicine and Health Sciences, Department of Human Structure and Repair, Ghent University Hospital, Belgium*
[4]*Biomaterials and Tissue Engineering, Department of Materials Engineering, KU Leuven, Belgium*
[*]*Arn.Mignon@KULeuven.be*

Tendons are indispensable parts of the human body. By connecting muscle to bone, they provide strength and stability, withstand tension and release stored energy. Current treatment methods of hand tendon traumas have several shortcomings, including an insufficient mechanical strength, possible adhesion reactions with surrounding tissue and inflammation issues. The current research has the aim to counter both the mechanical and biological problems. To achieve this, a reinforced, multi-layered tubular polymeric construct has been electrospun (Figure 1, middle) composed of: an inner electrospun polymer layer containing an anti-inflammatory component, a middle layer with a braided monofilament as a reinforcement layer and an outer electrospun polymer layer containing an anti-adhesion component. As polymer material, a novel acrylate endcapped urethane-based poly(ε-caprolactone) precursor (AUP) has been developed which was benchmarked against commercially available poly(ε-caprolactone) (PCL). After proving the successfulness of the AUP synthesis (^{1}H-NMR), the materials together with the anti-adhesion (HA) and anti-inflammatory (Naproxen) compounds have been electrospun on a tubular collector, whereby PCL clearly led to thicker fibers (8.77 ± 1.88 µm) than the blend of AUP and PCL (4.30 ± 0.41 µm). The constructs proved to remain stable for > 9 weeks, which is the period that a lesioned tendon needs to pass to an advanced healing stage [1]. *In vitro* assays showed that incorporation of the bio-active components was successful and not-cytotoxic for human fibroblasts. These tests also indicated that HA induced a burst release in the PCL constructs, while a prolonged release was observed in the stronger and denser network of AUP/PCL. The mono-layered constructs were insufficiently strong (< 4 MPa) for the intended application. Introduction of an intermediate braided monofilament layer, between the electrospun layers led to strengths of 8.56 ± 1.92 MPa as shown by *ex vivo* sheep tendon tensile tests (Figure 1, left) [2]. These multilayered AUP/PCL electrospun constructs represent a very promising mechanical and biological solution to repair deep flexor tendons. The final constructs have also been used in an *in vivo* study on 40 rabbits (Figure 1, right) [3].

Figure 1: (left) *ex vivo* sheep tendon tensile tests, (middle): electrospun, multi-layered tubular polymeric construct, (right) *in vivo* study on rabbits

Keywords: tendon repair, polymer synthesis, electrospinning, *ex vivo*, *in vitro*, *in vivo*

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Unveiling and Exploiting Thermally-Triggered Changes in Hydration State in LCST Polymer Brushes for Biomedical Applications

H. Schönherr,[1]* H. Choi,[1] M. Greiter,[1] A. Schulte,[1] D. Wesner,[1] J. Schumacher,[1] S.I. Druzhinin[1]

[1] *University of Siegen, Physical Chemistry I and Research Center of Micro- and Nanochemistry and (Bio)Technology) (Cμ), 57076 Siegen, Germany*
* *E-mail: schoenherr@chemie.uni-siegen.de*

Stimulus-responsive polymers have been reported to afford essential functionality in various architectures and devices, not limited to biomedical applications. By exploiting the transition at the lower critical solution temperature (LCST), changes in important interfacial properties may be triggered. These include among others pronounced changes in swelling as well as mechanical and adhesive properties, and a more gradual change in wettability. In our contribution ultrathin polymer coatings of thermoresponsive poly(di(ethylene glycol) methyl ether methacrylate (PDEGMA) brushes are introduced as powerful platforms for culturing and selective purification of e.g. human induced pluripotent stem cells (iPS) from differentiated cells [1] and for the implementation of a triggered antibiotic release function in titanium-based implants afforded via the intelligent polymer brush coating [2]. In particular, the results of recent studies aimed at (*i*) broadening the scope of the cell release platforms to a broad range of substrates and (*ii*) obtaining a deeper understanding of the property changes associated to the transition at the LCST will be elucidated. This insight is afforded by time-resolved fluorescence microscopy analyses of the tracer dye Nile red, which serves as a local nanoprobe for the hydration state of the brushes, and atomic force microscopy (AFM) nanoindentation analyses performed *in situ* at various temperatures across the LCST. Similarly the temperature-dependent release of the fluorescent antibiotic levofloxacin from PDEGMA brushes was analyzed quantitatively, revealing a hitherto unreported 3 stage release behavior over more than of 4 orders of magnitude in time from 30 s until 174 h. This complex behavior observed indicates the presence of distinct environments within the brush layer.

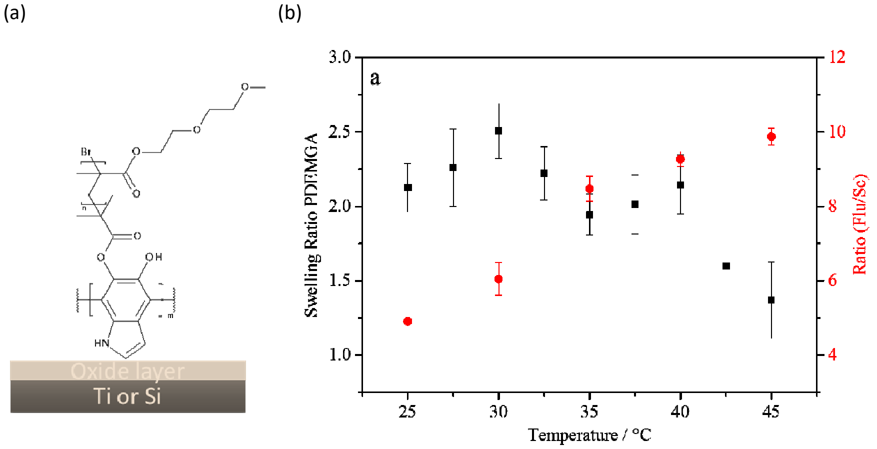

Figure 1. (a) Schematic structure of PDEGMA brushes polymerized from a polydopamine layer on oxidic substrates. (b) Comparative plot of swelling ratio and fluorescence intensity of Nile red revealing the changes of brush hydration associated to the transition at the LCST.

Acknowledgments

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New thermoplastic elastomer triblock copolymer of PLLA for cardiovascular tissue engineering: Annealing as efficient tool to tailor the solid-state properties

G. Guidotti[1], M. Soccio[1*], M. Gazzano[2], L. Fusaro[3], F. Boccafoschi[4], A. Munari[1], N. Lotti[1]

[1]Civil, Chemical, Environmental and Materials Engineering Dept., University of Bologna, Via Terracini 28, 40131, Bologna, Italy
[2]Organic Synthesys and Photoreactivity Institute, CNR,Via Gobetti 101, 40129, Bologna, Italy
[3]Tissuegraft s.r.l., Via Solaroli 17, 28100, Novara, Italy
[4]Department of Health Sciences, University of Piemonte Orientale "Amedeo Avogadro", Via Solaroli, 17, 28100, Novara, Italy

**m.soccio@unibo.it*

Tissue engineering is a frontier biomedical research with infinite potential to replace damaged human tissue and its functionality by proper engineered supports. Synthetic polymers, such as polylactic acid (PLA), are particularly suitable for the realization of these matrices. Even if widely used in this field [1], PLA is too rigid and brittle for cardiovascular tissue regeneration. Copolymerization represents a very effcient tool to modulate and improve the properties of a homopolymer, without detriment of those already satisfactory.

In this study, a new -ABA- triblock copolyester, being A the hard segment and B the soft one, was successfully synthesized by ring opening polymerization of L-lactide using as initiator a hydroxyl terminated random copolymer of poly(butylene succinate) (PBS). To increase the final polymer molecular weight, thus ensuring both good processability and mechanical properties, chain extension reaction has been performed with hexamethylene diisocyanate (HDI) as chain extender. All the synthetic steps have been carried out in solvent-free conditions. Specifically, the hard A block consists of L-lactic acid sequences (LLA), whereas the soft B one is an aliphatic biodegradable and biocompatible random copolyester of poly(butylene succinate) containing PEG-like moiety (Figure 1). The so-obtained material was firstly characterized by the molecular point of view and then, prior to further characterization, subjected to two different annealing treatments. Annealing revealed to be an efficient tool to control the kind and amount of crystalline phase developed by the material, as confirmed by WAXS structural analysis, and to tailor the mechanical properties towards those of thermoplastic elastomers. Thermal treatment was found to affect also the mechanism of polymer degradation under physiological conditions. Last, but not least, in order to explore the possible use of such new PLLA-based copolymer in vascular tissue engineering, preliminary biocompatibility tests using endothelial cells were carried out.

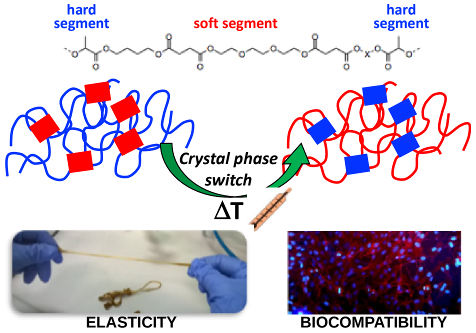

Figure 1. Schematic representation of chemical architecture, thermal treatment, elastic and biocompatible character of the ABA-triblock copolymer.

Keywords: Poly-L-lactic acid, Triethylene glycol, Triblock copolymers, Thermal annealing, Tissue engineering, Biocompatibility

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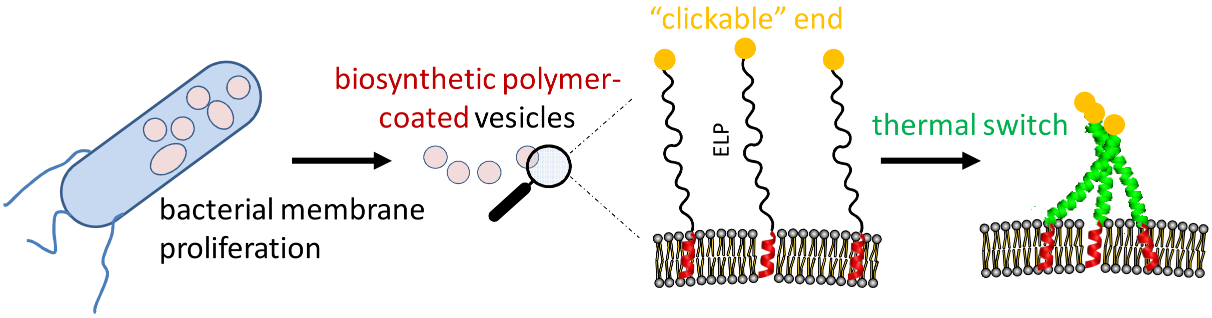
Bioengineered temperature-responsive polymer capsules: Bacterial proteolipidic assemblies with a switchable polymer corona.

J. Royes[1], P. Talbot,[2] B. Miroux[2], C. Tribet [1*]

[1]*Ecole Normale Superieure Paris, PSL University, Sorbonne Univ., CNRS, Paris France*
[2]*CNRS UMR7099, Institut de Biologie Physico-Chimique, Université de Paris, France*
[*]*christophe.tribet@ens.psl.eu*

As a possible eco-friendly alternative to chemical synthesis, "microbial factories" have become a promising tool to replace "in glassware" synthesis. As regard material and polymers, biopoly(esters) are now prepared at industrial scale, and polypeptides such as the temperature-responsive elastin-like polymers (ELP) are considered as promising functional products. We propose to use bacteria to shape capsules that are densily covered by ELPs and easy to post-modify/graft with other chains of interest.

We characterized genetically-encoded, ELP-coated liposomes, similar to polymer-decorated liposomes used in drug-delivery systems and cosmetics, though they contained a significantly higher protein density (up to 5:1 polymer:lipid wt/wt ratio). We induced membrane proliferations by overexpression of a protein scaffold derived from the b subunit of ATP synthase.[1] Mild extraction procedures (aqueous enzymolysis, low mechanical shear) yielded an homogenous population of capsules (size distribution and composition were characterized by particle tracking, DLS, fluorescence). The response of capsules to temperature, was studied by circular dichroism and light scattering. We assessed the high density and controlled orientation (outer corona) of the ELP strands and their chemical post-modifications via thiol-ene "click" by attaching either fluorescent probes or poly(N-isopropylacrylamide). Our first results suggest that bioengineering offers a vast diversity of combinations to design compact coatings of macromolecules onto lipid compartments.(2)



Keywords: stimuli-responsive, vesicles, Elastin-like block copolymers

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Oil-core nanocapsules based on amphiphilic polyelectrolytes as drug carriers and water-dispersable nanoreactors

S. Zapotoczny*

[1] *Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Krakow, Poland*
* *s.zapotoczny@uj.edu.pl*

Realization of (bio)chemical processes in confined and isolated environments is a challenge accomplished in complex natural systems like animal/plant cells. The production of synthetic water-dispersible nanoreactors would allow for carrying out efficient and selective chemical reactions in a biomimetic approach. Polymeric micro- and nanosystems with core-shell structure may serve not only as efficient containers of hydrophobic and lipophilic substrates but can be also navigable for reloading of a cargo using external stimuli or merge in controlled conditions to efficiently mix such delivered reagents.

In this work, core-shell nanocapsules based on amphiphilic polyelectrolytes, both synthetic and natural, are presented. [1-5] Such systems were formed and loaded in a simple sonication procedure leading to stable aqueous dispersions. The capsules can be e.g. navigated using magnetic field (encapsulated magnetic nanoparticles), efficiently internalized by cells (hyaluronic acid shell), and can be also used as mergeable reactors (oppositely charged shells). Such capsules are going to be shown as versatile platforms for delivering hydrophobic compounds and as nanoreactors for controlled reactions of hydrophobic reagents in aqueous media.

Keywords: nanocapsules, amphiphilic polyelectrolytes, core-shell systems

Acknowledgments
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Molecularly imprinted photonic polymers inspired by chameleon skin for biosensing and wound healing monitoring

A. Estrada[1], Y. Salinas[1], H.-R. Lin[2], O. Brüggemann[1*]

[1]*Institute of Polymer Chemistry and Linz Institute of Technology, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria*
[2]*Department of Chemical and Materials Engineering, Southern Taiwan University of Science and Technology, Nan-Tai St. No.01, 710 Tainan, Taiwan*
[*]*oliver.brueggemann@jku.at*

Inspired by the nanostructures found in chameleon skin [1], we were aiming on the development of an easily readable colour-changing biosensing polymeric material being able to, e.g., monitor the development of wounds. For this purpose, we synthesised molecularly imprinted polymers (MIPs) to detect collagen as an exemplary marker of the wound healing process, with ordered crystalline arrays to reflect a visual signal. In a first step, silica nanoparticles (SiNPs) with an immobilized short peptide as an epitope of collagen acting as template were arranged in highly ordered photonic structures [2] which in turn reflects a specific wavelength. Then, the SiNPs matrix was infiltrated with a solution of methacrylic acid as functional monomer (MA) and ethylene glycol dimethacrylate (EGDMA) as crosslinker which were finally photo-polymerized leading to MIP shells around the SiNPs. To leave specific recognition sites, the SiNPs and the peptide-template were fully removed by etching with hydrofluoric acid (Fig. 1).

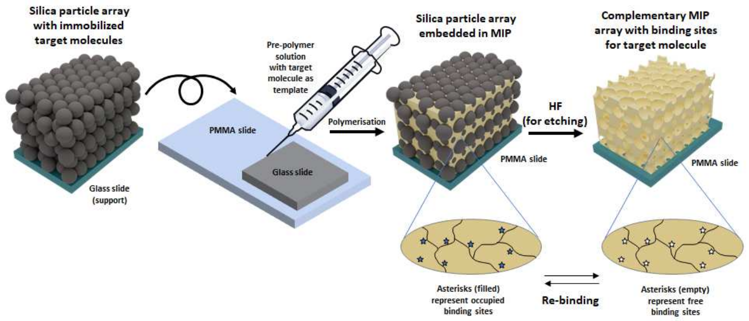

Figure 1. Procedure of synthesizing molecularly imprinted photonic polymers using target molecules immobilized on silica particle arrays.

This approach was optimized under different preparative conditions. The effect of the functional monomers on the nanoparticles arrangement was also investigated as well as their impact on the reflected wavelength and by consequence on the visual colour-change of the material. This approach shall allow obtaining a promising biosensing material that is convenient for the detection of biomolecules by an easily naked-eye readable colour-changing signal upon binding (Fig. 2).

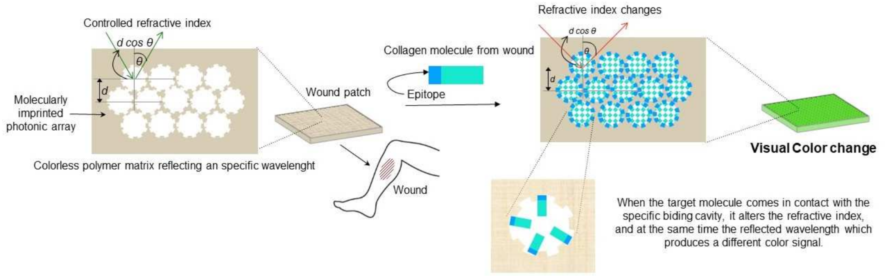

Figure 2. Proposed approach of the visual colour change produced by a change in reflected wavelength upon selective binding of the protein.

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Tailoring the Sol-Gel Transition of ThermoGels based on Block Copolymers and their Mixtures

Anna P. Constantinou, Qian Li, Bailin Feng, Lezhi Wang, Birsen Somuncuoğlu, Amy Tall, Nikitas Provatakis, Theoni K. Georgiou*

[1] *Department of Materials, Imperial College London, Exhibition Road, SW7 2AZ*
* *t.georgiou@imperial.ac.uk*

Thermoresponsive polymers that form gels upon increasing the temperature, i.e. thermogels like Pluronic® F127 (Fig. 1), are an exciting class of smart materials that find applications in drug delivery, tissue engineering and 3-D printing.[1,2] For these applications to be utilised the gelation point, i.e. the temperature that the gel is formed has to be controlled.[3] Our group have performed many systematic studies to identify key criteria that affect the gelation temperature and the critical gelation concentration. Here we will give an oveview of our studies that includes how the chemistry, molar mass, composition but also the position of the monomers within the polymer chain affect the thermogelling properties.[4-10] Futhermore, mixtures of these polymers are also examined to identify further ways that both the gelation temperature and critical gelation concentration can be tailored.[11]

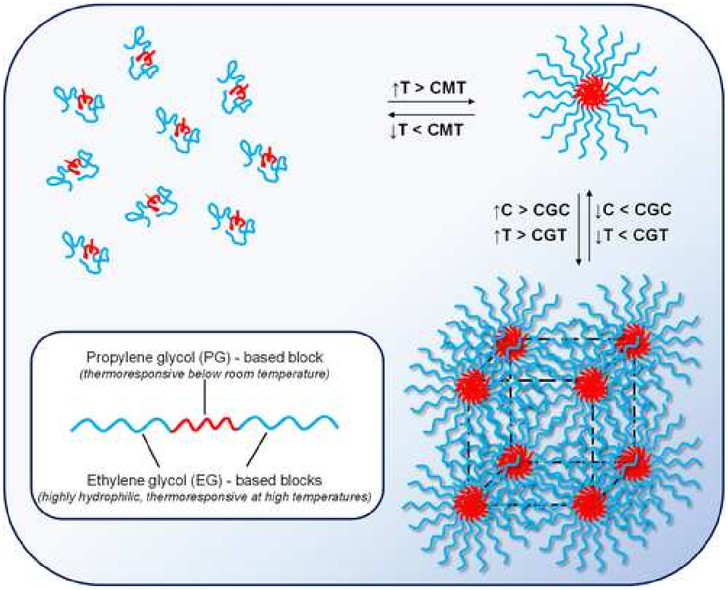

Figure 1. Thermoreversible micellisation and gelation of poloxamers in aqueous solutions. The black dotted lines in the gel structure are for guidance only. CMT, CGC and CGT stand for critical micellisation concentration, critical gelation concentration and critical gelation temperature, respectively.[2]

The text should be 11-point Calibri in the single-column format in A4 paper with margins 2cm on all sides.
Keep the layout of the text as simple as possible.
The maximum length of the abstract is one page A4.
Figures and tables can be embedded in this section. Caption (Calibri, 8 pt., Bold) should be given below the figures & above the tables.
The file must be saved in the format MS Office Word (doc, docx, **NOT pdf**).
The name of presenting author should be underlined.

Keywords: thermoresponsive polymers, block copolymers, thermogels, sol gel transition, lower critical solution temperature (LCST).

Acknowledgments

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Hydrogel-based Chemical and Biochemical Sensors

G. Gerlach[1]

[1]*Institute of Solid-State Electronics, Dresden, Germany*

Hydrogels are cross-linked polymer networks able to absorb or to release large amounts of water [1]. This ability is caused by hydrophilic functional groups attached to the polymer backbone. At the same time, due to the cross-links between the polymer`s network chains, hydrogels show an extremely high resistance to dissolution. The mechanical properties of hydrogels are characterized by a pronounced elastic modulus accompanied by a considerably smaller viscous modulus. The latter part can significantly influence repeatability and long-term behavior since it might cause relaxation and creep.

The water uptake is associated with a considerable volume change. In doing so, hydrogels show remarkable properties: (i) The strong volume change can be excited by a large spectrum of different physical (e.g. temperature, electrical voltage, magnetic field) and (bio-) chemical factors (e.g. pH value, solvent concentration) [2]. (ii) This swelling process is reversible. (iii) The energy density of hydrogels is very high what easily enables miniaturization.

All these properties make hydrogels a promising candidate for being used in sensors and actuators and allow their integration into microsystems. Hence, hydrogel-based microsystems enable novel sensor solutions in microsystem technology with a high potential for miniaturization and cost-effective fabrication, in particular by using silicon-based MEMS technologies.

The property of hydrogels that the volume or other material parameters change depending on external variables can be easily exploited for chemical or biochemical sensors. This can be done simply by coupling the hydrogel to a corresponding transducer which converts the change in hydrogel properties into an electrical signal. Hydrogels can be specially tailored so that they are sensitive to a particular measurand. The transducer can then be exploited as a platform technology serving as a family of sensors for a variety of (bio-)chemical species. Examples are the measurement of the swelling pressure by means of pressure or optical sensors. In addition to this advantage, there are a number of further advantages: (iv) Unlike electrochemical sensors, no counter and reference electrodes are required, which are often the source of long-term instabilities. (v) When measuring the swelling pressure, the separation between electronic components and the chemical part can easily be achieved. (vi) MEMS-based sensors are miniaturized and cost-efficient.

However, in addition to good sensitivity, chemical sensors should also exhibit high selectivity, good long-term stability and short response times. The talk will present promising sensor concepts that are being worked on at the Institute for Solod-State Electronics[3]. In addition, the approaches with which high selectivity, fast sensor response and good long-term stability can be achieved are considered. On the one hand, this concerns measures that can be achieved with the hydrogel itself, but also measures that can be realized by technical approaches like the force (pressure) compensation method [4].

Keywords: hydrogels, chemical sensors, biochemical sensors, sensitivity, selectivity, long-term stability

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Nanostructured Polymers, Composites, Blends, and Soft Matter

Contribution of Polymer Chemistry to the Design of Functional Porous Polymers

Daniel Grande

Univ Paris Est Creteil, CNRS, Institut de Chimie et des Matériaux Paris-Est (ICMPE), 2 rue Henri Dunant, 94320 Thiais, France
daniel.grande@cnrs.fr

Over the last decade, the generation of organic porous (nano)materials with tunable pore sizes and desired functionalities has been the subject of increasing attention in materials science. Interest in such porous frameworks originates from the large variety of sustainable applications in which they are involved, *e.g.* monoliths for advanced chromatographic techniques, nanofiltration membranes, high specific area catalytic supports, as well as 3-D scaffolds for tissue engineering [1-4].
This lecture examines the scope and limitations of three different approaches toward porous polymers with controlled porosity and functionality at different length scales. The first approach relies on the synthesis of diblock copolymers with functional groups at the junction between both blocks, followed by their macroscopic orientation, and the subsequent selective removal of the sacrificial minority block to afford ordered nanoporous materials with channels lined with chemically accessible functionalities (*e.g.*, COOH, SO_3H, SH, COH) [1]. The second strategy entails the preparation of functional doubly porous polymer networks through the use two distinct types of porogen templates, namely a macroporogen in combination with a nanoporogen. To generate the macroporosity, either NaCl particles or fused PMMA beads or Nylon® threads are used, while the lower porosity level is obtained by using a porogenic solvent [2,3]. Finally, 3-D macroporous scaffolds based on biodegradable polyesters have been engineered by electrospinning to generate nanofibrous biomaterials as tissue engineering scaffolds or wound dressings. The potentialities afforded by these approaches will be addressed, and some typical applications of the resulting porous materials will be illustrated [4,5].

Keywords: porous materials, functional polymers, diblock copolymers, polymer networks, electrospun fibers

Acknowledgments
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Polymer Conetworks as a Novel Nanostructured Material Platform with Unexpected Unique Properties

Béla Iván[1]*, Csaba Fodor[1], Tímea Stumphauser[1], György Kasza[1], Gergely Kali[1], Péter Mezey[1], Szabolcs Pásztor[1], Bálint Becsei[1], Attila Domján[1], Ralf Thomann[2], Yi Thomann[2], Rolf Mülhaupt[2]

[1]*Polymer Chemistry Research Group, Institute of Materials and Environmental Chemistry,*
Research Centre for Natural Sciences, H-1117 Budapest, Magyar tudosok krt. 2, Hungary

[2]*Freiburg Material Research Center, Institute for Macromolecular Chemistry and Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), University of Freiburg, Stefan Meier Str. 31, D-79104 Freiburg, Germany*
**E-mail: ivan.bela@ttk.hu*

Polymer conetworks, especially amphiphilic conetworks (APCNs) with a variety of high value-added opportunities, consisting of covalently bonded, otherwise immiscible hydrophilic and hydrophobic polymer chains, belong to a new class of rapidly emerging nanostructured materials (see e.g. Refs. 1-10). The synthesis of polymer conetworks with immiscible polymer components is quite challenging, and several successful synthetic routes have recently been developed by us to obtain desired conetworks. Unique bicontinuous (cocontinuous) nanophase separated morphology exists in APCNs with domain sizes in the range of 2-30 nm in a broad composition window. In addition, the glass transition temperatures of the crosslinked chains follow the Fox-Flory relationship by the unprecedented scissors effect of the macromolecular crosslinkers in conetworks [1,9,10]. These novel nanophasic materials have a variety of high value-added potential applications from intelligent drug delivery to antibacterial biomaterials, organic-inorganic nanohybrids by applying one of the nanophases as nanoreactor, nanocatalysis, photonics, environment protection related materials, sensors, ion conducting conetworks for batteries and specialty poly(ionic liquid) conetwork gels as specialty, selective superabsorbents for organic solvents etc.

Figure 1. Schematic structure of an amphiphilic conetwork (APCN) and an AFM image of the bicontinuous nanophasic morphology (image size: 250x250 nm).

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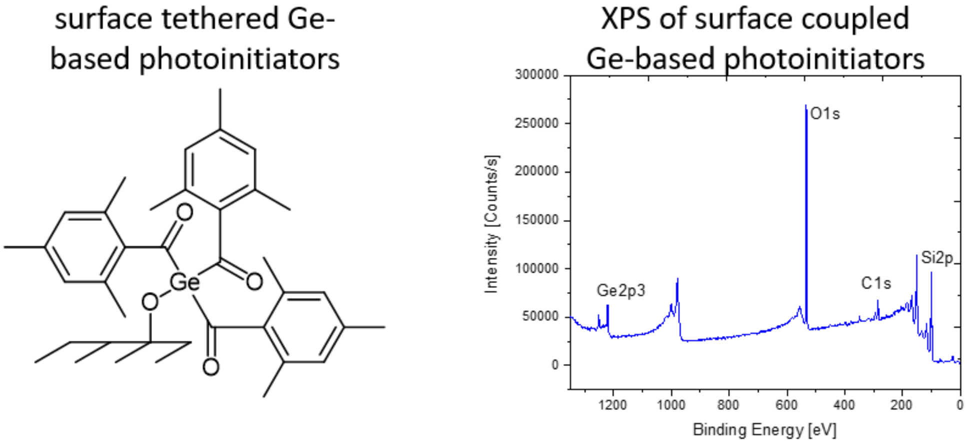
Photoreactive surfaces and particles: Immobilized bisacylphosphinoxides and acylgermanes as photoinitiating systems

Wolfgang Kern [1,2]*, Matthias Müller [1], Christine Bandl [1], Micheal Haas [3], Manfred Drusgala [3]

[1] Chair in Chemistry of Polymeric Materials, University of Leoben, Otto Glöckel-Straße 2, A-8700 Leoben
[2] Polymer Competence Center Leoben GmbH, Roseggerstraße 12, A-8700 Leoben
[3] Institute of Inorganic Chemistry, Graz University of Technology, A-8010 Graz
** E-mail: wolfgang.kern@unileoben.ac.at*

Immobilized photoinitiators are an interesting approach in surface photochemistry, providing polymerization initiating species which are employed for surface functionalization and the fabrication of nanostructured materials. Typically, photoinitiators are coupled to inorganic surfaces via trialkoxysilyl or thiol anchoring units. Photosensitive molecular layers at surfaces can be utilized to adjust properties such as polarity, chemical reactivity, and optical properties upon light induced irradiation. Moreover, light induced transformations (e.g., isomerizations) are useful to confer new properties on surfaces. In combination with lithographic patterning, 2D structures can be generated.
Besides planar surfaces, also inorganic particles can be functionalized towards photoreactivity. Selected examples encompass (i) the addition of photoreactive fillers based on silica nanoparticles modified with Norrish type I photoinitiators (e.g., tri(alkoxy)silyl functionalized acylphosphine oxides) to acrylate and thiol-ene resins as low-migration photoinitiators [1], and (ii) the generation of inorganic protection layers on inert polymer films and fibers (e.g., PE and PET) by attachment of azidophenyl functionalized silica particles [2].
Recent results on a new class of photoinitiators based on acylgermanes are presented. Group-14 based photoinitiators, in particular triacylhalogermanes (X = Br and I), were prepared and equipped with different coupling units. These reactive groups were then attached to inorganic surfaces such as pre-activated silicon and inorganic particles. The light sensitive surfaces were then used for surface initiated polymerization of, e.g., styrene and acrylic monomers. Both surface composition and reactivity were studied, using FT-IR and XPS spectroscopy as well as optical techniques and atomic force microscopy.

The high potential and suitable applications of this promising class of photoinitiators are highlighted.


surface tethered Ge-based photoinitiators

XPS of surface coupled Ge-based photoinitiators

Figure 1: Schematic representation of a surface coupled Ge-based photoinitiator (left), and XPS survey spectrum of a modified surface (right)

Acknowledgments

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Unconventional Microdomains of Block Copolymers

Sukwon Kang, Hyeongkeon Yoon, and Jin Kon Kim*

National Creative Research Initiative Center for Smart Block Copolymers, Department of Chemical Engineering, Pohang University of Science and Technology, 77 Cheongam-Ro, Nam-Gu, Pohang, Gyeongbuk 37673, South Korea.
E-mail: jkkim@postech.ac.kr

The microdomains obtained by block copolymer (BCP) self-assembly are mainly decided by the volume fraction of one block. For instance, the lamellar microdomains are expected for symmetric volume fractions, whereas spherical microdomains are obtained for highly asymmetric volume fraction. Thus, it is very difficult to obtain lamellar microdomains at highly asymmetric volume fraction. In addition, cylindrical or spherical microdomains are not expected at symmetric volume fraction.

We obtained highly asymmetric lamellar morphologies by the use of binary blends of block copolymers [polystyrene-*b*-poly(2-vinyl pyridine) copolymer (PS-*b*-P2VP) and PS-*b*-poly(4-hydroxystyrene) copolymer (PS-*b*-PHS)] where P2VP and PHS are capable of the hydrogen bonding. We obtained the asymmetric lamellar microdomains having lamellar width ratio of 4:1. [1} This ratio was even increased up to 6:1 with increasing the degree of hydrogen bonding. [2]

We investigated morphology transitions of linear tetrablock copolymers of polystyrene-*block*-polyisoprene-block-polystyrene-block-polyisoprene ($S_1I_1S_2I_2$) by varying volume fraction of PI_1 block (f_{PI1}), while maintaining the symmetric volume fraction of total PS blocks and PI blocks ($f_{PS1}+f_{PS2}$: $f_{PI1}+f_{PI2} \approx 1:1$). An interesting sequence of morphology transitions was observed as f_{PI1} was increased: lamellae (L) → asymmetric lamellae (aL) → hexagonally packed PI-cylinders (C_{PI}) → double gyroid with PI-network domains (G_{PI}) → short-period lamellae (sL). Thus, we found cylindrical and gyroid morphologies at symmetric volume fraction. [3}

Finally, by chaning the architecture of BCP, we demonstrate inverted cylinders where cylindrical volume is as large as 71%.[4}

Keywords: Block Copolymer, Self-Assembly, Inverted Cylinders

Acknowledgments

This work was supported by the National Creative Research Initiative Program, the National Research Foundation of Korea (2013R1A3A2042196)

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Seeded Polymerization in Ellipsoidal Block Copolymer Nanoparticles: Controlling Shape, Morphology, and Chemical Functionality

D. Klinger[1]

[1]*Freie Universität Berlin, Berlin, Germany*
**daniel.klinger@fu-berlin.de*

Shape anisotropic particles show unique packing behavior, rheological properties, and interactions with biological systems. Combining such non-spherical colloids with internal nanostructures and patterned surface chemistries would considerably increase their functionality and open new advanced applications in biology, photonics, and catalysis.

A promising method to access such multifunctional nanoparticles is the evaporation-induced phase-separation of block copolymers (BCPs).[1-3] To adjust shape and morphology, post-assembly treatments are of high interest since they circumvent laborious optimization of phase separation conditions. While solvent vapor annealing or the addition of reactive small molecules are promising approaches, they are still limited in their versatility. These strategies often address the problem of morphological control and chemical functionality individually. As a result, efficiently introducing multifunctionality after particle preparation is still challenging.

In addressing this challenge, we have developed a new strategy to control overall shape, internal morphology, and chemical functionalization simultaneously. Key to the versatility is a seeded polymerization in striped ellipsoidal PS-b-P2VP nanoparticles. In this method, the addition of styrene-based monomers to pre-formed BCP particles results in the selective swelling of the PS domains. Subsequent polymerization in these swollen domains selectively increases the PS lamellae thickness. This creates a new asymmetric lamellar morphology, which is not accessible through established assembly methods for asymmetric BCPs. In addition, this structure translates to particle elongation, i.e., a strong increase of the aspect ratio. By using a reactive styrene-based monomer, the selective functionalization of the PS domains can be achieved concurrently.

Overall, our simple and versatile method represents a new synthetic tool to access a wide variety of multifunctional BCP colloids from a single batch of pre-formed particles.

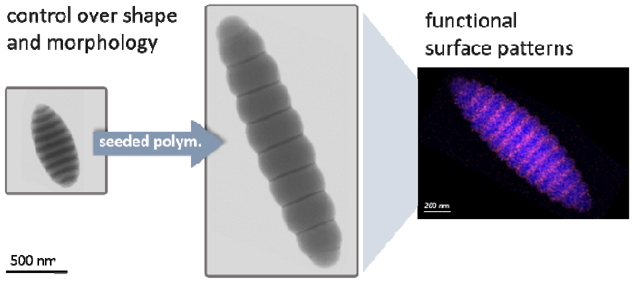

Figure 1. Seeded polymerization in BCP nanoparticles enables control over shape, morphology, and surface functionality.

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Hybrid Nanomaterials in Polymeric Composites and Solar Cells

M. Omastová[1*], A. Stepura[1], Y. Soyka[1], M. Mičušík[1], P. Siffalovič[2], E. Majkova[2], D. Zeleniakiene[3], A. Aniskevich[4]

[1] *Polymer Institute SAS, Dúbravská cesta 9, 845 41 Bratislava, Slovakia*
[2] *Institute of Physics SAS, Dúbravská cesta 9, 845 11 Bratislava, Slovakia*
[3] *Kaunas University of Technology, Studentu Str. 56, 51424 Kaunas, Lithuania*
[4] *University of Latvia, Jelgavas Str. 3, LV-1004 Riga, Latvia*
**Corresponding Author's E-mail address: maria.omastova@savba.sk*

Hybrid nanomaterials usually contain two or more different components, typically inorganic and organic components. In the last decade, new functional nanostructured materials based on graphene, graphene oxide and carbon nanotubes (CNTs) have been developed with promising electrical, mechanical and thermal properties. The fast-growing family of 2D nanomaterials are MXenes. Different MXenes are prepared from different MAX phases of the formula $M_{n+1}AX_n$, where M is the most common transition metal, A is an element of the 13 or 14 group of the periodic table, X is usually C and/or N [1]. This combination used in polymeric composites provides interesting 3D structures and properties, which is why they have been intensively studied in recent years [2,3].

In our study, hybrids were created by combining 2D nanosheets with zero-dimensional nanoparticles such as quantum dots or 1D nanoparticles such as CNTs. Due to the metallic conductivity, high mechanical strength and hydrophilic character of MXenes, they are regarded as one of the most promising materials for supercapacitor electrodes or in solar cells. We studied the incorporation of MXene and perovskite quantum dots (PQDs) monolayer at the charge transfer layer/perovskite active layer interface in planar direct and inverted perovskite solar cells (PSC) as a direct application of newly prepared hybrids.

Composites, where poly(methyl methacrylate)- PMMA was used as matrix and MXenes and CNTs as conducting fillers, were prepared and studied in the next step. The range of fillers in PMMA/CNT, PMMA/MXenes and PMMA/MXenes/CNTs composites varied from 0.5 to 10 wt.%. Composites were prepared by solvent casting method. The higher the MXene amount, the higher the final conductivity of polymeric composites, but the highest conductivity value was about 10^{-5} S/cm. Much higher conductivity was achieved for composites with hybrid 2D and 1D nanofillers. PMMA/2.5% MXene/3% CNTs reached a conductivity of about 30 S/cm. Synergistic 1D-2D nanostructures are the reason for better electrical properties compared to composites containing only 2D or 1D fillers.

Incorporating MXenes or hybrid 2D and 1D nanofillers into polymeric matrices will result in a number of advanced applications, such as lightweight and flexible electromagnetic interference (EMI) shielding materials, damage-tolerant in-situ sensors, components of structural composites with additional functionalities (e.g. de-icing, electrostatic discharge) and many others.

Keywords: 2D Nanoparticles, MXenes, carbon nanotubes, polymeric composites, solar cells

Acknowledgments

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Multifunctional Elastomer/Graphene Nanocomposites

Bernhard Schartel, A. Battig, M. Böhning, D. Frasca, D. Schulze, B. Strommer, W. Tabaka, V. Wachtendorf

[1]*Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany, bernhard.schartel@bam.de*

A few layer/multilayer graphene (MLG) with a specific surface area of BET=250 m^2/g is proposed as an efficient multifunctional nanofiller for rubbers. The preparation method, i.e., ultrasonically-assisted solution mixing of master batches followed by two-roll milling, strongly influences the dispersion in the elastomeric matrix and is fundamental for the final properties. When homogenously dispersed, single stacks of only approximately 10 graphene sheets, with an aspect ratio of 34, work at low loadings, enabling the replacement of large amounts of carbon black (CB), an increase in efficiency, and a reduction in filler load. The appropriate preparation yielded nanocomposites in which just 3 phr are sufficient to significantly improve the rheological, curing, gas barrier properties, electrical and thermal conductivity, as well as mechanical properties of different rubbers, as shown for chlorine-Isobutylene-Isoprene rubber (CIIR), nitrile-butadiene rubber (NBR), natural rubber (NR), and styrene-butadiene rubber (SBR).[1-4] 3 phr of MLG tripled the Young's modulus of CIIR, an effect equivalent to 20 phr of CB. The stronger interactions between MLG and NR or SBR also resulted in a reduction in the elongation at break by 20% and 50%, respectively, while the same parameter was hardly changed for CIIR/MLG and NBR/MLG. CIIR/MLG and NBR/MLG were stiffer but just as defomable than CIIR and NBR. The strong reinforcing effect of 3 phr MLG was confirmed by the increase of greater than 10 Shore A in hardness. MLG reduces gas permeability, increases thermal and electrical conductivities, and retards flammability, the latter shown by the reduction in heat release rate in the cone calorimeter. We investigated MLG also as a synergist for reducing the aluminium trihydrate loading in flame retardant hydrogenated acrylonitrile-butadiene (HNBR), polybutadiene chloroprene (BR/CR), and chlorosulfonated polyethylene rubber(CSM).[5-7] The higher the nanofiller concentration is, the greater the improvement in the properties. For instance, the permeability decreased by 30% at 3 phr of MLG, 50% at 5 phr and 60% at 10 phr, respectively. Moreover, the MLG nanocomposites improve stability of mechanical properties against the effects of weathering. In key experiments an increase in UV-absorption and a pronounced radical scavenging were proved as stabilizing mechanisms. In a nutshell, MLG is an efficient multifunctional nanofiller ready to be used for innovative rubber development.

Acknowledgments

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Synthesis of Emulsion-Templated Polymers: Hierarchical Porosities, Tough Hydrogels, and Encapsulation

Michael S. Silverstein*

Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel
**michaels@technion.ac.il*

PolyHIPEs have traditionally been hydrophobic polymers with highly interconnected macroporous structures synthesized via free radical polymerization (FRP) within water-in-oil (w/o) high internal phase emulsions (HIPEs), emulsions containing more than 74% individually dispersed droplets in the internal phase. Emulsion templating now extends far beyond those systems and encompasses a wide variety of synthesis chemistries (including controlled radical polymerizations and step growth polymerizations (SGP)) and a wide variety of emulsions (including oil-in-water (o/w) and oil-in-oil). Recent advances in several very different polyHIPE systems will be discussed. For adsorption applications, a variety of approaches have been used to generate polyHIPEs with hierarchical porosities, porosities that combine polyHIPE macroporosity with mesoporosity and/or microporosity. For absorption applications, tough hydrogel polyHIPEs have been synthesized within o/w HIPEs using a variety of monomers. Truly closed-cell polyHIPEs were used to encapsulate aqueous solutions, melts of inorganic salts, and organic liquids.

Keywords: emulsion-templating, polymerization mechanisms, hierarchical porosity, hydrogels, encapsulation

Polymers for Advanced Membrane Separations in Organic Solvents

Gyorgy Szekely*

King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia
**gyorgy.szekely@kaust.edu.sa*

Improving the chemical resistance of membranes without sacrificing their molecular sieving performance is highly challenging. Crosslinking of polymer membranes induces changes in both membrane stability and separation performance. Numerous membrane-crosslinking methods have been developed with the aim to obtain improved membranes, in particular for the use under harsh conditions such as certain organic solvents. However, none of these methods systemically investigated the stereochemical effects of the crosslinker in the pursuit of better stability and performance. Herein, we address this knowledge gap by presenting a systematic investigation of the stereochemistry of crosslinkers [1]. Crosslinkers were carefully selected based on the stereochemical position of the two benzyl bromide functional groups, separated by distances of 4.3, 8.2, 8.5, and 12.4 Å and significant effects arising from crosslinking on membrane physical properties, morphology, and OSN performance were investigated.

Moreover, a novel scalable methodology was developed for fabricating solvent-resistant nanofiltration membranes based on metal–polymer coordination (MPC) through a facile yet highly effective method. The controlled deposition of copper(I) iodide enabled the fine-tuning of the molecular sieving performance of MPC membranes by altering both their chemistry and morphology. Reversible crosslinking using difunctional acids were also achieved [2], and the obtained membranes exhibited excellent organic solvent nanofiltration performance.

Poly(ether-ether-ketone) has received increased attention due to its high thermal and chemical stability, and high performance in various applications. However, it suffers from a semi-crystalline morphology, low fractional free volume, and poor processability, requiring the use of harsh acidic solvents, which leads to undesired sulfonation. Therefore, three intrinsically microporous poly(ether-ether-ketones) (iPEEKs), incorporating spirobisindane, Tröger's base, and triptycene contorted structures, were developed for organic solvent nanofiltration [3]. Molecular dynamics simulations have assisted the molecular engineering of the polymers and the understanding of the improved membrane performance through the binding energies between solvents and polymers. Application of the design principles of polymers of intrinsic microporosity has led to a paradigm shift with a notable enhancement in both the polymer properties and the subsequently fabricated nanofiltration membranes' performance. The iPEEKs showed excellent solution processability, a high surface area of 205–250 $m^2\ g^{-1}$, and excellent thermal stability. Mechanically flexible nanofiltration membranes were prepared from *N*-methyl-2-pyrrolidone dope solution at iPEEK concentrations of 19–35 wt%. The molecular weight cutoff of the membranes was fine-tuned in the range of 450–845 g mol^{-1} displaying 2–6 fold higher permeance (3.57–11.09 L $m^{-2}\ h^{-1}\ bar^{-1}$) than previous reports. The long-term stabilities were demonstrated by a 7 day continuous cross-flow filtration.

Keywords: crosslinking, polybenzimidazole, polymers of intrinsic microporosity, metal–organic frameworks

Acknowledgments
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Polypyrrole cryogels, aerogels and carbogels: preparation and applications

P. Bober*, K. A. Milakin, I. M. Minisy, S. Gupta

Institute of Macromolecular Chemistry, Czech Academy of Sciences, 162 06, Prague 6, Czech Republic
**bober@imc.cas.cz*

Polypyrrole (PPy) is one of the most studied conducting polymers, due to its unique physico-chemical properties and realatively easy way of preparation with low cost [1]. However, conventional synthesis of PPy leads to the formation of insoluble powder, which limits its application potential. To overcome this problem, three-dimensional and porous PPy cryogel (Figure 1) can be prepared by facile one-step procedure [2-4]. Additionally, they can be freeze-dried to obtain aerogels and then futher carbonization in inert atmosphere leads to the formation of nitrogen-containing carbogels [5]. In the presented studies, pyrrole monomer was oxidized with iron(III) chloride in the presence of gelatin in frozen reaction mixture. The influence of various concentrations of gelatin on the resulting properties of PPy cryogel/aerogel was investigated by SEM, specific surface area, electrical conductivity and mechanical properties measurements [2]. The applications of such three-dimensional conducting polymeric or carbonaceous networks in medicine, wastewater purification and energy-storage devices have been evaluated.

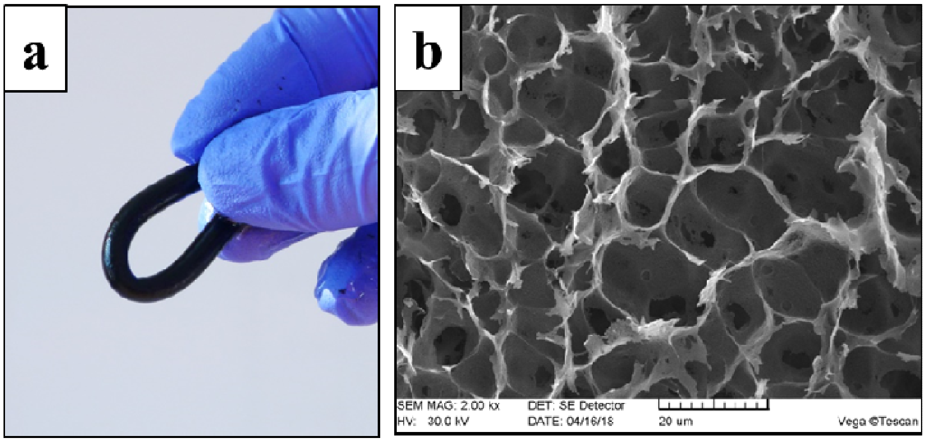

Figure 1. Polypyrrole/gelatin cryogel (a) and illustration of macroporous morphology of corresponding aerogel (b).

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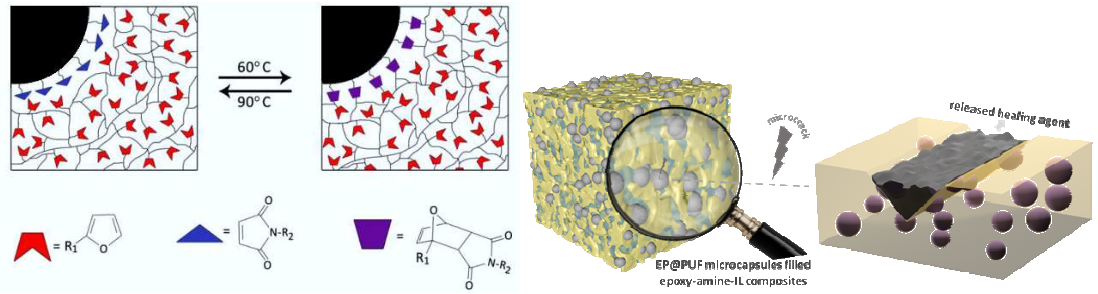
How to repair thermosetting based composites?

T.Shi, W. Zhang, J.Duchet-Rumeau, S.Livi, J.F. Gérard

Univ Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, F-69621 Villeurbanne Cédex, France

Composite materials constitute a new type of waste source since these materials have appeared in many industrial applications with relatively long life spans such as structural composites for aeronautics, the naval sector, sports and now for energy with wind turbines. The self-healing of composite materials can be an alternative to the recycling for which few industrial solutions are proposed fot thermosetting matrices. Design polymer composite for having the ability to heal the cracks and to prolong the life time is a real challenge. Two main routes to achieve self-healing into composite can be considered as shown in Figure 1 : i) intrinsic self-healing based on introduction of reversible bonding and ii) extrinsic self-healing based on microcapsules containing monomer as healing agent [1]. This talk will describe the two pathways of self-healing used for repairing the carbon fiber/epoxy matrix composite. The first route will describe the effect of reversible bonds introduced in the interphase of carbon fiber reinforced composite in order to generate an ability of interfacial self-healing that will be evaluated by single fiber micro-droplet pull-out testing. Thermally reversible diels-alder adducts were generated between maleimide groups grafted onto carbon fibers surface and furan groups within the epoxy-amine matrix [2]. The second route is the embedding of microcapsules into epoxy matrix which are previously filled with liquid healing agent [3]. Different types of microcapsules were synthesised and characterized, either with a silica shell via sol-gel process and a core filled with a ionic liquid, or with a poly(urea-formaldehyde) (PUF) shell containing an epoxy resin able to be a healing agent in presence of ionic liquid. The effect of the presence of the self-healing agent on the epoxy-amine network will be studied as well as its reactivity in the self-healing process. The thermal and mechanical properties as well as self-healing ability of these matrices for composites will be discussed.



Route#1- *Route#2*

Figure 1-Two pathways of self-healing into composite : 1) via reversible bonding generated in a critical place*, i.e.* interface; 2) via microcapsules within the matrix

Keywords: Self-healing, encapsulation, ionic liquid, epoxy matrix, reversible bonding

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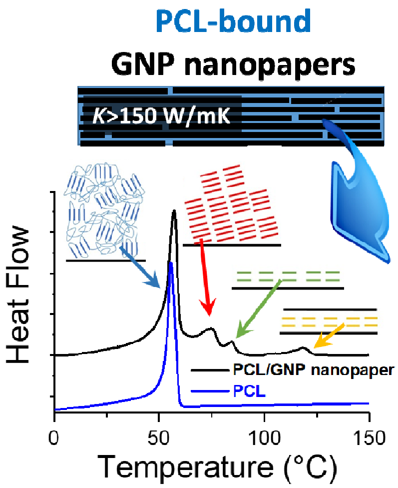
Polycaprolactone adsorption and nucleation onto graphite nanoplates for highly flexible, thermally conductive and thermomechanically stiff nanopapers

K. Li[1], D. Battegazzore[2], R. A. Pérez-Camargo[3], G. Liu[3,4], O. Monticelli[1], A. J. Müller*[5,6], A. Fina*[2]
[1] *Dipartimento di Chimica e Chimica Industriale, Università di Genova, Genova, Italy*
[2] *Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Alessandria, Italy*
[3] *Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China*
[4] *University of Chinese Academy of Sciences, Beijing, China*
[5]*POLYMAT and Department of Polymers and Advanced Materials: Physics, Chemistry and Technology, Faculty of Chemistry, University of the Basque Country UPV/EHU, San Sebastián, Spain*
[6] *IKERBASQUE, Basque Foundation for Science, Bilbao , Spain*
**Corresponding authors: alejandrojesus.muller@ehu.es; alberto.fina@polito.it*

Nanopapers based on graphene and related materials, such as reduced graphene oxide and graphite nanoplates (GNP), have been widely investigated and applied as flexible heat spreaders[1-2]. To overcome typical brittleness of those materials, polycaprolactone (PCL) was exploited as a polymer binder to enhance resistance and flexibility of GNP nanopapers, while maintaining high thermal conductivity (*K*)[3]. Excellent PCL adhesion and strong nucleation of the surface of GNP flakes were found to affect thermomechanical properties of nanopapers. In particular, different crystalline populations were observed for PCL within the nanopaper and investigated in detail via differential scanning calorimetry advanced techniques and X-ray diffraction. Co-existence of different crystalline population was demonstrated, including 1) conventional un-oriented PCL crystals, 2) oriented PCL crystals obtained as a consequence of the strong nucleation effect, and 3) highly stable PCL fractions explained by the formation of crystalline pre-freezing layers, the latter having melting temperatures well above the equilibrium melting temperature for pristine PCL. The presence of high thermal stability crystals, strongly bound to GNP flakes, coexisting with the highly flexible amorphous fraction, provides a solution for the strengthening and toughening of GNP nanopapers. Thermomechanical properties of PCL-bound GNP nanopapers was investigated both on heating ramp and creep tests at high temperatures, demonstrating superior stiffness up to far above the melting temperature of pristine PCL. Furthermore, a thermal conductivity up to 190 W/mK was obtained for PCL/GNP nanopapers, representing an alternative to traditional metals in terms of heat dissipation, while guaranteeing lightweight and flexibility, which cannot be obtained metals or ceramics. Besides the present application to thermally efficient nanopapers, the formation of polymer crystals stable above the equilibrium melting temperature may be exploited in the self-assembly of highly ordered nanostructures based on graphene and related materials.



Keywords: Polycaprolactone /graphite nanoplates nanopapers, oriented polycaprolactone, pre-freezing effect, thermomechanical properties, thermal conductivity, graphene-related materials

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Polypropylene-boron nitride composite fibers: effect of the elongational flow on mechanical properties and thermal conductivity

R. Arrigo[1*], A. Frache[1], G. Malucelli[1]

[1]*Department of Applied Science and Technology, Polytechnic of Turin, Alessandria, Italy*
[*]*rossella.arrigo@polito.it*

Nowadays, due to the rapid development in integration and miniaturization of electronic devices, high performance thermally conductive materials are required for thermal management. Polymers are broadly employed in advanced technological applications, ranging from organic electronic to wereable computing devices, owing to their unique properties such as low cost, lightweight and easy processing. However, their low thermal conductivity limits their exploitation in several functional applications [1]. The formulation of polymer-based composites containing thermally conductive fillers such as boron nitride (BN) may offer a solution to this drawback; unfortunately, adequate values of thermal conductivity are usually obtained through the incorporation of high amounts (about 50 wt.%) of fillers, which causes a significant modification of the matrix rheological behavior, hence compromising its processability. Furthermore, high filler loadings usually induce particle agglomeration phenomena, thus worsening the polymer mechanical properties. In this work, an easy and industrially viable method to obtain polypropylene (PP)-based composites containing high loadings of BN (namely up to 30 wt.%) with enhanced thermal conductivity and mechanical properties is proposed. In particular, PP+BN composites obtained through melt compounding in a twin-screw extruder were subjected to uniaxial elongational flow at the exit of the extruder, aiming at exploiting the well-documented ability of the elongational flow in preventing the formation of filler agglomerates and in inducing some preferential orientation of the embedded particles along the flow direction [2]. The results of the mechanical characterization showed that the elastic modulus and the tensile strength of the composite fibers progressively increase with increasing the BN loading and the draw ratio (DR), highlighting the beneficial effect of the application of the elongational flow. Furthermore, SEM observations confirmed the achievement of a more homogeneous morphology for the composites fibers, with the disappearance of BN agglomerates observed in the as-extruded composites and some preferential orientation of the embedded fillers along the flow direction. Finally, PP+BN composites subjected to elongational flow exhibited enhanced thermal conductivity as compared to their isotropic as-extruded counterparts, paving the way to the exploitation of these materials for future applications requiring effective thermal management.

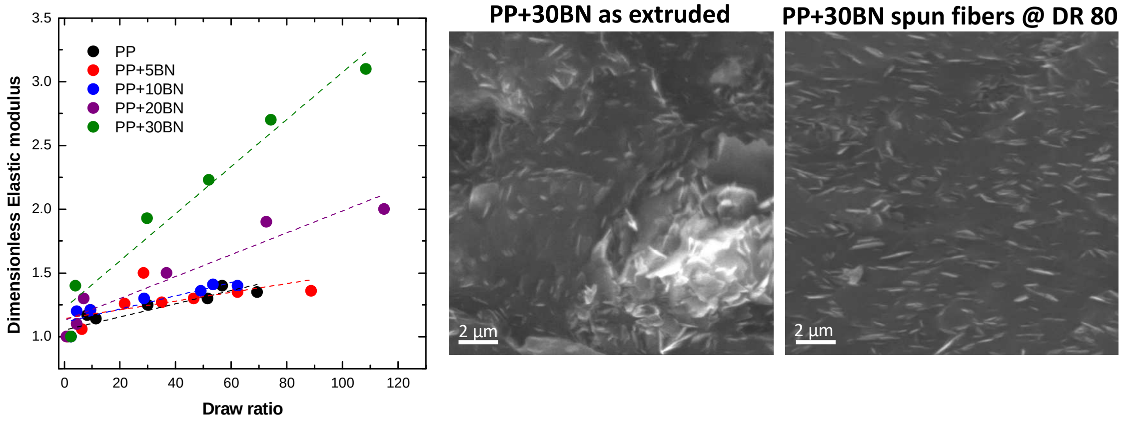

Figure 1. Dimensionless Elastic Modulus as a function of DR for unfilled PP and BN-containing composites and representative SEM micrographs of as-extruded and spun PP+30BN system.

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Precise telechelic bottlebrush polymers for soft materials

V. Asadi[1], X. Li[1,2], Dr. F. S. Ruggeri[1,2], Prof. J. van der Gucht[1], Dr. T. E. Kodger[1*]

[1]*Physical Chemistry and Soft Matter, Wageningen University & Research, The Netherlands*
[2]*Laboratory of Organic Chemistry, Wageningen University & Research, The Netherlands*
[*]*thomas.kodger@wur.nl*

Designing soft materials with controllable stiffness is an emerging topic in materials science to address the high demand in applications requiring low moduli such as medical implants, tissue engineering, soft robotics, and wearable electronics. In this context, linear-bottlebrush-linear (LBBL) triblock copolymers are topologically-tunable elastic materials showing the ability to replicate most of soft tissue mechanics, for example, the strain-stiffening response [1]. Utilizing bottlebrush molecules instead of linear chains as building blocks enables lower moduli than the limit dictated by entanglements as topological constraints in conventional elastomers. However, the synthesis of LBBL copolymers in a controlled and consistent way remains challenging. In this study, a new synthetic methodology is presented to synthesize LBBL polystyrene-b-polydimethylsiloxane-b-polystyrene (PS-PDMS-PS) triblock copolymer via the “grafting onto” approach where the precursors are individually synthesized through living anionic polymerization and a selective coupling reaction. In this approach, polystyrene-b-polymethylvinylsiloxane (PS-PMVS) diblock copolymer with a low polydispersity index couples with another living PS block to form PS-PMVS-PS triblock copolymer followed by grafting of separately prepared monohydride-terminated PDMS chains with controllable grafting density through a hydrosilylation reaction confirmed by high resolution Atomic Force Microscopy (AFM). In addition to fully tunable architectural parameters, an important novel feature of this synthesis method is the ability to accurately quantify the composition of bottlebrush chains; the precise knowledge of the composition is crucial for correlating microstructure to mechanical properties. Moreover, employing a “grafting onto” approach can allow for multiple bottlebrush topologies with identical backbone to minimize the batch-to-batch variation, hence improves consistency in the mechanical properties. Additionally, this approach lacks permanent crosslinks between bottlebrushes as the elasticity emanates from the microphase separated high Tg PS domains that could dissociate at high temperature. Thus these soft LBBL elastomers experience a temperature triggered solid-to-liquid transition which makes them functional candidates for 3D printing of soft and strain-stiffening tissue scaffolds [2].

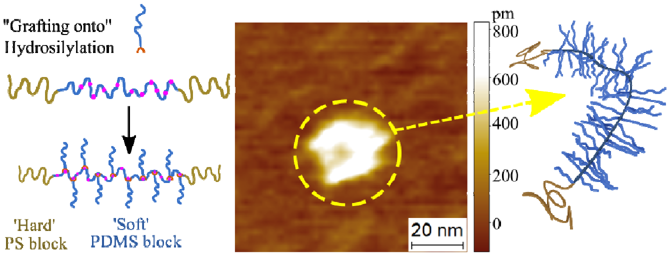

Figure 1: Grafting onto approach for synthesis of LBBL PS-PDMS-PS triblock copolymer and the captured high resolution AFM image of it on mica substarte

Keywords: Thermoplastic elastomer, Anionic polymerization, Copolymer, Topology, Elasticity

Acknowledgments

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Surfactant-mediated co-existence of Single-Walled Carbon Nanotubes Networks and Cellulose Nanocrystals mesophases

David Attia [1], Evgenee Yekymov [1], Yulia Shmidov [1], Yael Levi-Kalisman [2], Orit Mendelson [3], Ronit Bitton [1,4] and Rachel Yerushalmi-Rozen [1,4] *

[1]*Department of Chemical Engineering, Ben-Gurion University of the Negev, 84105 Beer-Sheva, Israel.*
[2]*The Center for Nanoscience and Nanotechnology, and The Institute of Life Sciences, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel.*
[3]*Department of Chemistry, Nuclear Research Center-Negev, Beer-Sheva 84190, Israel*
[4]*The Ilse Katz Institute for Nanoscience and Technology, Ben-Gurion University of the Negev, 84105 Beer-Sheva, Israel.*
**Correspondence: rachely@bgu.ac.il*

Hybrids comprising cellulose nanocrystals (CNCs) and percolated networks of single-walled carbon nanotubes (SWNTs) may serve for casting of hybrid materials with improved optical, mechanical, electrical, and thermal properties. However, CNCs-dispersed SWNTs are depleted from the chiral nematic (N*) phase and enrich the isotropic phase. Herein, we report that SWNTs dispersed by non-ionic surfactant or triblock copolymers are incorporated within the surfactant-mediated CNCs mesophases. Small Angle X-ray measurements indicate that the nanostructure of the hybrid phases is only slightly modified by the presence of the surfactants, and the chiral nature of the *N** phase is preserved. Cryo-TEM and Raman spectroscopy show that SWNTs networks with typical mesh size from hundreds of nanometers to microns distribute equally between the two phases. We suggest that the adsorption of the surfactants or polymers mediates the interfacial interaction between the CNCs and SWNTs, enhancing the formation of co-existing meso-structures in the hybrids phases.

Keywords: CNCs, CNTs, Chiral-nematic phase.

Block Copolymers in 3D Confinement: Janus Nano Cups

Suna Azhdari,[1] Deniz Coban, [1] Manuel P. Trömer[1] Giada Quintieri,-[1] André H. Gröschel*[1,2]

[1] *Physical Chemistry, University of Muenster, Corrensstr. 28/30, 48149 Muenster*

[2] *Center for Soft Nanoscience, University of Muenster, Busso-Peus-Str. 10*

Block copolymer nanoparticles with complex surface outstanding morphologies are in high demand as non-trivial soft matter due to their exclusive physical properties.[1] In comparison to topologies such as spheres, vesicles and cylinders,[2] the precise formation of patchy polymeric cups with defined surface structure are still rare. Geometrically controlled anisotropic Janus nanoparticles (JNP) have gained considerable interest in the polymer science community. However, currently only a few controlled bottom-up synthesis routes are known that enable JNPs synthesis with high selectivity towards the desired geometries.[3] In the present work, we aim to achieve cup-shaped JNPs and the control of their size and curvature. First, several ABC triblock terpolymers consisting of polystyrene-*b*-polybutadiene-*b*-poly (tert-butyl methacrylate) (SBT) are emulsified in conjunction with high-molecular poly (methyl methacrylate) (PMMA) in varying blending ratios through a SPG membrane, followed by evaporation-induced confinement assembly (EICA) process. This led to the formation of two hemispherical particles, with PMMA forming a hemisphere on its own and SBT instead, arranging in a concentric lamella-lamella morphology. In the second step, the PB microdomain is crosslinked with OsO_4, and the PMMA hemisphere is subsequently removed by washing with THF, whereby dispersed cup shaped JNPs are obtained. The curvature of the JNPs is controlled by the blending ratio of PMMA, as its content increases the more the curvature is decreasing, going from hemispheres to cups to disk like particles. By removing the PMMA phase with THF and redispersing the SBT tulip bulb phase, it is possible to produce Janus nano cups in high yield. Further, the PT nanodomain is hydrolyzed, in order to produce negative charges, that can be paired with cationic species, *e.g.* Au NPs, in order to prove the Janus character. Due to the particular shape, the Janus nano-cups may find application in biotechnology and nanomedicine, as well as templating of inorganic materials and to perform as cargo in biotechnology and nanomedicine due to their cup-like shape.

Keywords: Janus Nano Cups, Blends and Soft Matter, Template, Cargo

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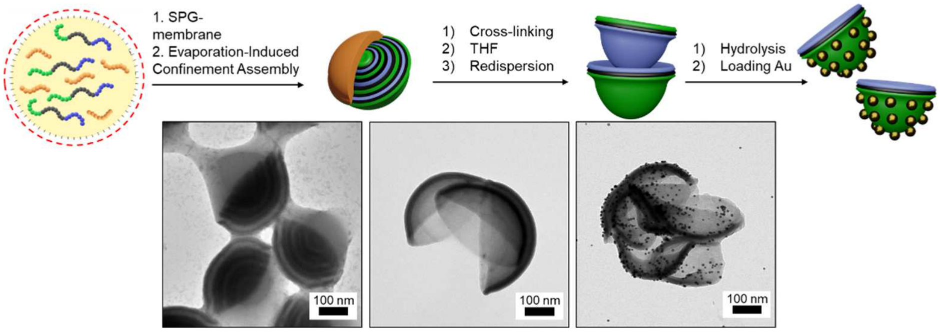

Cyclic Polyethylene Glycol as Nanoparticle Surface Ligand

F. Barroso-Bujans[1,2,3*]

[1]*Donostia International Physics Center (DIPC), 20018 San Sebastián, Spain*
[2]*Materials Physics Center, 20018 San Sebastián, Spain*
[3]*IKERBASQUE - Basque Foundation for Science, E-48013 Bilbao, Spain*
[*]*fbarroso@dipc.org*

Cyclic polymers behave dramatically different than linear polymers due to the lack of end groups and smaller coil dimensions. We demonstrate that cyclic polyethylene glycol (PEG) can be used as an alternative of classical linear PEG ligands for gold nanoparticle (AuNP) stabilization. To this aim, we first introduced a synthetic approach to synthesize cyclic PEG chemically attachable to gold surfaces [1] and then, we evaluated the colloidal stability of AuNP grafted with cyclic PEG [2]. Our results showed that cyclic PEG brushes presented more extended conformations than their linear counterparts. Such structural effect and the reduced footprint diameter in cyclic brushes helped to explain the distinct response of AuNPs to ionic strength and temperature, respectively, compared to linear analogues.

Our latest studies on the colloidal stability of AuNPs modified with cyclic PEG were performed in ethanol [3], a solvent where neat PEG exhibit a non-conventional upper critical solution temperature. We observed that linear PEG brushes cause the precipitation of AuNPs (13 nm diameter) in hours without altering their surface plasmon resonance in a non-conventional temperature-reversible process. However, when the polymer brush topology is cyclic the precipitation is avoided while providing a very high colloidal stability to AuNPs in ethanol at -25 ºC for months. We postulated a mechanism where a fast reversible collapse of chain brushes leads to a state that is favorable for the interpenetration of linear chains and precipitation of AuNPs in a slow process, but which is not favorable for the interpenetration of cyclic polymer brushes. Our results evidence that the topology of PEG brushes plays an important role on the colloidal stability of AuNPs.

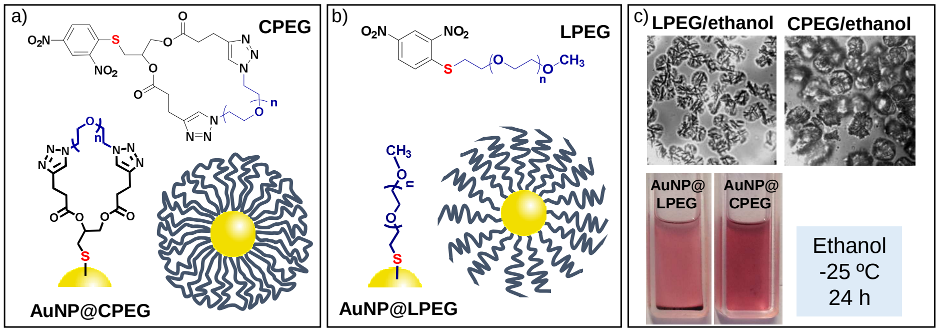

Figure 1: Gold nanoparticles stabilized with PEG of different topologies. Structure of a) cyclic PEG (CPEG) and b) linear PEG (LPEG) with protected thiol groups. c) Optical microscopy of neat polymers in ethanol at -10 ºC and pictures of AuNPs modified with CPEG and LPEG in ethanol, stored at -25 ºC overnight.

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Ionic liquid-modified LDH: multifunctional additives for biodegradable polyester composites

Sonia Bujok[1], Magdalena Konefal[1], Jakub Peter[1], Ewa Pavlova[1], Petra Ecorchard[2], Hynek Beneš[1,]*

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 162 06 Prague 6, Czech Republic*
[2]*Institute of Inorganic Chemistry, Czech Academy of Sciences, Husinec-Řež 1001, 25068 Řež, Czech Republic*
**benesh@imc.cas.cz*

Layered double hydroxides (LDH), also known as hydrotalcite-like compounds or anionic nanoclays, have two-dimensional structures represented by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2](A^{n-})_{x/n}\cdot zH_2O$, where M^{2+}, M^{3+} and A^{n-} stand for divalent metal cation, trivalent metal cation and interlayer anion, respectively, and x is the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$ [1]. The unique LDH ability to regenerate the layered structure after calcination enables the design and fabrication of novel composite materials with various intercalated functional guest anions. The immobilized active species demonstrate enhanced catalytic activity, selectivity, stability and recyclability compared to their homogeneous analogues.

We have recently demonstrated that ionic liquids (ILs) with highly variable chemical structures can be advantageously used for efficient LDH modification. The prepared IL-functionalized LDH exhibited multifunctional roles in biodegradable polyester nanocomposites. First, they exhibit catalytic/initiating effect (4.6-fold increase of the reaction rate) of microwave-assisted ring opening polymerization (ROP) of cyclic esters [2]. Second, they improved gas/water vapor barrier properties of aliphatic (polycaprolactone, PCL) [3] and aliphatic/aromatic (polybutylene adipate-co-terephthalate, PBAT) [4] polyesters. Finally, they increase the rate of biodegradation and at the same time cause bactericidal effect against food-born pathogenic bacterium *E. coli* of the polycaprolactone (PCL)-based films [5].

In this contribution, we demonstrate how i) LDH structure (MgAl, ZnAl and CaAl LDH), ii) synthetic pathway of IL-modified LDH (direct co-precipitation in the presence of IL vs. two-step synthesis with anion exchange) and iii) different type of IL-anion will affect preparation and final properties of polyester nanocomposites. Our findings show a novel environmental-friendly and solvent-free synthetic route of organometallic catalyst-free polyester nanocomposites, which can be considered as functional biodegradable materials in various perspective applications, e.g. active bio-packaging of foods.

Acknowledgments

Financial support of the Czech Science Foundation (project 22-05244S) is gratefully appreciated.

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Multifunctional EPDM/paraffin foams coupling shape memory behavior and TES properties

M. Bianchi*, F. Valentini, G. Fredi, A. Dorigato and A. Pegoretti

Department of Industrial Engineering and INSTM Unit, University of Trento, Trento, Italy
**marica.bianchi@unitn.it*

Nowadays ethylene propylene diene monomer (EPDM) foams are widely employed for thermal and acoustic insulation in residential and non-residential buildings [1]. However, their installation in confined spaces is often complicated, and the capability of EPDM foams to exhibit a shape memory behavior could be thus desirable to overcome such limitation [2]. In the literature, several works have demonstrated that blending elastomeric matrices with paraffin, a well-known phase change material (PCM), could be an interesting method to obtain shape memory polymers with a tunable switching temperature [3,4]. In order to improve the applicability of elastomeric insulating panels in the building sector, EPDM foams filled with a paraffin wax, having a melting temperature of 70 °C, were produced and characterized from a microstructural and thermo-mechanical point of view. Samples were prepared by melt compounding and hot pressing, and the PCM content in the foams was varied between 0 and 60 wt% (with respect to the EPDM compound). The results of the shape memory tests evidenced the crucial role played by the PCM in providing excellent shape fixability for the expanded rubber. It was found that even a limited amount of paraffin was able to raise the strain fixity parameter to a value higher than 80%. On the other hand, a slower recovery process was highlighted with increasing PCM content. Consequently, a compromise between a fast recovery and an optimum shape fixability should be determined. Differential scanning calorimetry (DSC) demonstrated that the EPDM/paraffin foams were endowed with noticeable thermal energy storage properties, especially at higher PCM contents (up to 145 J/g with a paraffin amount of 60 wt%). These results made EPDM foams potentially easier to be installed and interesting to be used for thermal management applications.

Keywords: EPDM rubber, polymer foams, shape memory polymers, thermal energy storage.

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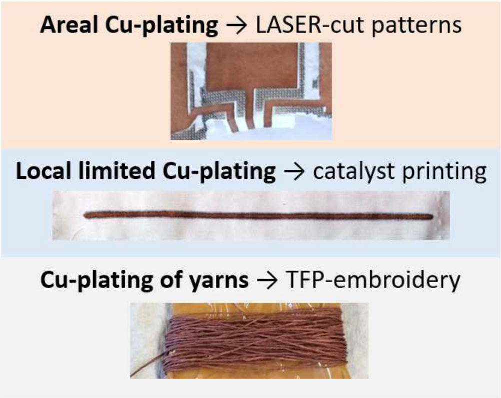
Multi-Layer Conductive Structures by Metal Coatings on Polymers – Functional Ageing of Metal-Polymer Hybrids

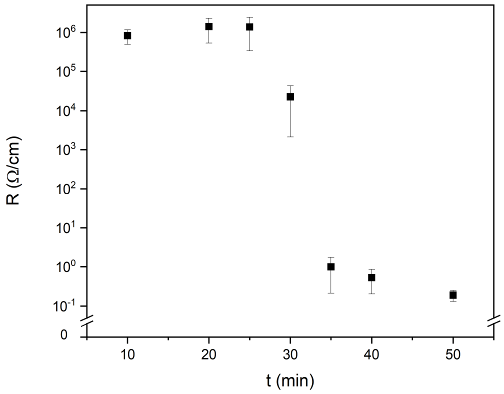
Christian Biermaier,[1]* Carolin Gleißner,[1] Thomas Bechtold,[1] Tung Pham[1]

[1] *Research Institute for Textile Chemistry and Textile Physics, University of Innsbruck, Hoechsterstraße 73, A 6850 Dornbirn, Austria; *e-mail: christian.biermaier@uibk.ac.at*

Conductive textiles are often based on multiphase material structures. While the textile substrate consists of classical polymers like cellulose or PA 66, conductivity is introduced by carbon derivatives, intrinsically conductive polymers or metals, etc. One simple approach to generate such hybrid structures utilises the direct electroless copper deposition (ECD) principle, requiring no electrical current or continuous conductivity in advance [1]. Metal particle or metal precursor seeding provides an initial catalyst for starting the self-catalytic ECD [2]. In our approach, we utilise citrate to bind silver(I)-ions to the textile surface. The silver citrate is precipitated directly on the textiles surface. Thermal treatment in air decomposes the silver citrate to silver metal and oxidises the silver metal immediately to silver oxide. The ECD-solution then reduces the silver oxide to silver metal, which initiates the copper deposition. This technique simplifies the course of preparation by far with respect to costs and environment [3]. Applying our method, we are able to copper-plate entire fabrics, conductive lines on fabrics and yarns (scheme 1).



Scheme 2: application variety for ECD according to the silver citrate method.



Scheme 1: time resolved course of the electrical resistance during ECD.

From the material point of view, the ECD increases the dimension of the initial catalyst metal particles. During the course of reaction, the contact of the particle forms a conductive percolation path that results in a fast drop of the electrical resistance (scheme 2). This percolation threshold plays an important role for the mechanical behaviour and for ageing effects. Abrasion, aqueous dissolution and hot air oxidation are descriptive examples for the loss of conductive material following a similar course. Also cyclic stretching causes statistically distributed interruptions, e.g. cracks. These cause temporary or permanent loss of percolation and change the properties of conductive lines and conductive areas. Additionally to single ageing events, we constructed a roll based machine wash simulator to study cumulative effects of chemical and mechanical ageing.

Keywords: metal polymer hybrid, conductive textiles, electroless copper deposition, functional ageing

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Elastomers filled with polymer-grafted silica nanoparticles: material synthesis and characterization

Maxime Blanchard[1,2]*, Trang N.T. Phan[2], Marine Bonnevide[1], Nicolas Malicki[1], Marc Couty[1], Didier Gigmes[2]

[1]Manufacture Française des Pneumatiques MICHELIN, Site de Ladoux, 23 place des Carmes Déchaux, F-63 040, Clermont-Ferrand, Cedex 9,France

[2]Aix Marseille University, CNRS, Institut de Chimie Radicalaire, avenue Escadrille Normandie Niemen, F-13 397, Marseille, Cedex 20, France

Innovation in tyre industry remains a constant challenge for the development of high-performance and fuel-efficient nanocomposite materials. In this context, understanding the phenomena that rule nanocharges spatial dispersion in elastomeric matrices is crucial to optimize material mechanical properties. Previous works showed that polymer-grafted nanoparticles self-assemble to anisotropic superstructures once dispersed in the corresponding polymeric matrix [1]. It has been established that parameters such as ratio of the graft to matrix chain lengths and grafting density can impact these superstructures [2]. In this project, we aim at synthesising and analysing elastomer-based nanocomposites, easily transposable to standard tyre formulations, to understand if new parameters such as nanoparticle loading, nature and amount of plasticizers and nanocomposite shaping method can also influence nanoparticle self-assembly process.

In this communication, we will first present the strategy developed by our team for the synthesis of Polyisoprene (PI), Polybutadiene (PB) and Styrene-Butadiene Rubber (SBR) – grafted silica nanoparticles by Surface-Initiated Nitroxyde-Mediated Polymerization (SI-NMP) [3]. Then, we will share our characterization results of elastomer-silica nanocomposites obtained by Small-angle X-ray Scattering (SAXS) and Cryogenic Transmission Electron Microscopy (Cryo-TEM).

Keywords: Polymer Nanocomposite, Elastomers, Silica nanoparticles, Surface-Initiated Nitroxyde-Mediated Polymerization (SI-NMP)

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Unprecedented polylactide-based copolymer matrix composites by Resin Transfer Molding

*B. Miranda-Campos, G. Stoclet, S. Bourbigot, G. Fontaine, F. Bonnet**

Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations,
F-59000 Lille, France
* *fanny.bonnet@univ-lille.fr*

Composite materials display many advantages over traditional materials, whether in terms of lightness or mechanical and chemical resistance. The development of composites meets the requirements of industrial markets for applications in the fields of transport and construction, as well as sports and leisure. In a context of sustainable development, a growing number of works relate to the production of composites with bio-based matrices [1] including polylactide (PLA), which has become a major actor in the market which could in the long term serve as an alternative to petroleum-based polyolefins.[2]

Among the various composites production processes, Resin Transfer Molding (RTM) is a specific process which relies on the injection, into a mold containing fibers, of a monomer and a catalyst in order to carry out the polymerization of the matrix *in situ*. The major advantage over conventional melt processes is the possibility of reaching a high amount of fibers while improving their wetting by the matrix. While a wide selection of thermosetting matrix resins are available on the market for RTM process, there are only a few commercial resins for thermoplastic matrices.[3]

Although work has been carried out in RTM with ε-caprolactone,[4] composites with a polylactide matrix via this process had never been described, due to the lock linked to the solid state of the monomer at room temperature (initiation of polymerization before injection into the mold during the melting phase in the presence of the catalyst). Recent work carried out at UMET made it possible to obtain the first prototypes of PLLA/glass fiber composites with different reinforcement rates.[5] We present here current work aimed at strengthening the mechanical properties of the PLLA matrix, and in particular its elongation at break, by producing a novel family of composites with PLLA-based copolymer matrices, by copolymerization of L-LA with other cyclic esters.

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Hard-Templating of Nanoporous Poly(melamine-*co*-formaldehyde) Particles and Application in Water Treatment

Konstantin B. L. Borchert[1], Christine Steinbach[1], Berthold Reis[1], Niklas Gerlach[1], Simona Schwarz[1], Dana Schwarz[1]

[1] *Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany*
[*] *borchert@ipfdd.de*

The applicability of highly porous and cross-linked polymers is constantly expanding due to their exceptional properties such as high thermal stability, good pH resistivity, and high specific surface area. Poly(melamine-*co*-formaldehyde) (PMF) shows remarkable surface properties, as it consists of aromatic structures and a high amount of nitrogen functionalities. It has been investigated for several applications as CO_2 capture [1], catalysis [2,3], and adsorption of various pollutants [4]. The before-mentioned applications are demanding in terms of an appropriate surface morphology, as the specific surface area and the pore structure are the limiting factors for diffusion and surface interactions. However, as PMF is not exhibiting any intrinsic porosity, a hard-templating approach was used for the generation of pores. PMF-SiO_2 hybrid particles were obtained by a dispersion polymerization with SiO_2 nanospheres in water. Subsequent etching with aqueous NaOH solution resulted in PMF particles with defined mesopores and specific surface areas up to 400 m²/g. The obtained particles were analyzed by electron microscopy (i.e. SEM and TEM), and N_2 sorption (BET), among other methods. In batch adsorption experiments, the removal of oxyanions such as sulfate and phosphate ions [5] with exceptional adsorption capacities was successfully proven. The respective mechanisms of adsorption was analyzed to gain knowledge about potential selectivity in adsorption onto the PMF-SiO_2 hybrid and highly porous PMF particles.

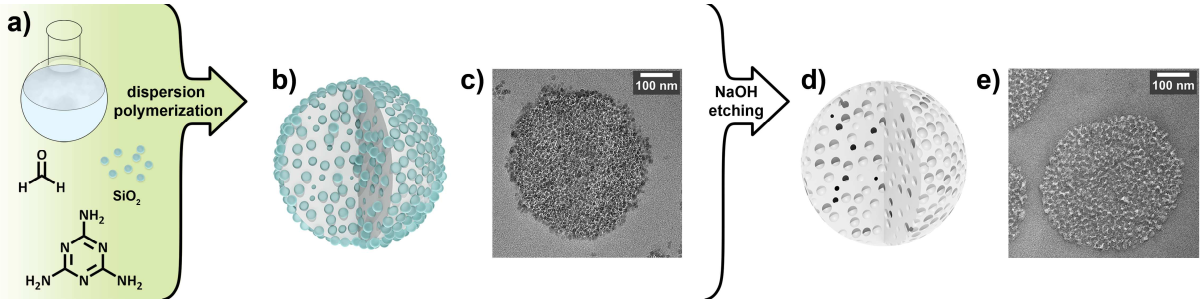

Figure 1. a) Educts for the synthesis of b) the PMF-SiO_2 hybrid and d) the mesoporous PMF particles. c) and e) are showing transmission electron microscope (TEM) images from thin sections of embedded PMF-SiO_2 hybrid particles (c) and the mesoporous PMF particles after template removal (e), respectively.

Keywords: poly(melamine-*co*-formaldehyde), hard templating, nanostructured particles, adsorption.

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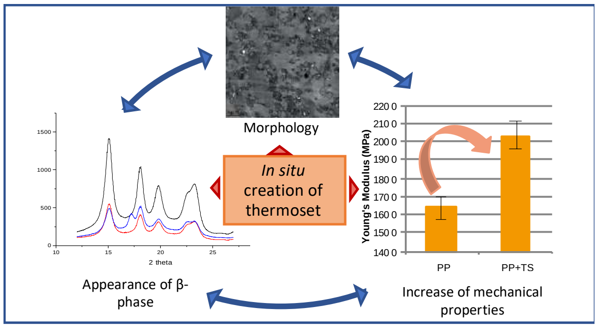
Impact of the In Situ Creation of an Epoxy Based Thermosetting Minor Phase on the Physical Properties of a PP Based Blend

L. Barroso Gago[1], Mathilde Auclerc[1], Karim Delage[1], Nicolas Garois[2], Philippe Cassagnau[1], Véronique Bounor-Legaré[1]*
[1]*Univ Lyon, Université Lyon1, CNRS UMR 5223, Ingénierie des Matériaux Polymères, F-69622, LYON, France ;*
[2]*Hutchinson, Centre de Recherche, Rue Gustave Nourry - B.P. 31, 45120, Chalette-sur-Loing, France*
**bounor@univ-lyon1.fr*

Polypropylene (PP) is a widely known and used polymer, and its production represents 20% of the total production of plastic in Europe in 2016. Its use covers almost all types of industries, from food packaging to automotive parts and bank notes. PP is an attractive polymer due to its low cost, high macromolecular diversity, low density, and inertness to other chemicals. It has a fairly good mechanical strength at room temperature and becomes brittle at low temperature since its glass transition is around 0 °C. To benefit the qualities of PP and to replace expensive polymers, physical and chemical modifications are required in order to reinforce PP. In the present study, we choose to *in situ* create a reinforcing thermosetting phase [1-3]. The epoxy based thermosetting chemistry was scrutinized and the relation with the morphology and the mechanical properties was established. The role of polypropylene grafted maleic anhydride (PP-g-MA) on the size of the dispersed domains was classically and clearly evidenced. The evolution of the PP crystallinity by wide angle X-ray scattering analysis (WAXS) was studied and allowed to explain some mechanicals properties modifications.



Keywords: Epoxy based thermoset, Reactive extrusion, PP blend

Acknowledgments

The authors are grateful to the joint laboratory IMP/HUTCHINSON for the financial support.

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Impact of the In Situ Creation of an Epoxy Based Thermosetting Minor Phase on the Physical Properties of a PP Based Blend*, Industrial and Engineering Chemistry Research*, **2021**,60(515), 5421-5431

Polymeric Biomimetic Multicompartment Vesicles by Microfluidics

T. Ivanov[1], S. Cao[1], S. Jiang[2], K. Landfester[1], L. Caire da Silva[1*],

[1] *Max Planck Institute for Polymer Research, Mainz, Germany*
[2]*Ocean University of China, Qingdao, China*
[*]*silva@mpip-mainz.mpg.de*

Biomimetic multicompartment vesicles (BMVs) are artificial systems that mimic the architecture of eukaryotic cells. BMVs consist of synthetic sub-compartments encapsulated within a larger compartment (> 1 µm in diameter) that serves as a host. [1] In this way, a multicompartmental structure is created that, like in cells, enables the organization of chemical reactions and other processes with high spatiotemporal control. BMVs allow the construction of sophisticated systems with cell-like properties, including multifunctional drug delivery vehicles and biochemical microreactors.[2] Vesicles made of amphiphilic block copolymers have demonstrated superior mechanical properties and unmatched chemical versatility compared to lipids, making them excellent materials for engineering robust BMVs with tunable properties. However, few methods exist for producing well-defined polymeric BMVs.

In this presentation, we will describe the preparation of polymeric BMVs using a microfluidic approach that does not require the use of additives or harmful organic solvents. By using a combination of low molecular weight block copolymers and amphiphilic oil phases, we were able to produce micron-sized polymer vesicles with controllable membrane permeability, narrow size distribution, and high throughput. These well-defined microcompartments were used to construct BMV systems with different functions determined by the encapsulation of active components. In the first example, we will describe a hybrid microreactor constructed via the precise encapsulation of enzyme-containing silica nanoreactors that served as internal organelles. [3] We will also discuss the construction of adaptive microreactors with sub-compartments made of coacervates droplets that can be formed and dissolved in a stimuli-responsive manner. The combination of precise microfluidic methods with robust polymeric compartmentalization offers a powerful platform for the construction of multi-functional BMVs.

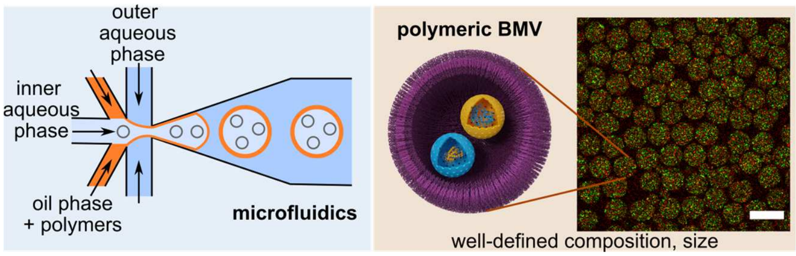

Figure 1. Production of polymeric multicompartment vesicles by microfluidics. Scale bar: 100 µm. Adapted from reference 3.

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Polymer/Graphene oxide nanocomposites: Altering the interfacial interactions by tuning the degree of oxidation of GO

K. Chrissopoulou[1,*], I. Karnis[1,2], F. Krasanakis[1], A. N. Rissanou[1,3] and K. Karatasos[4]

[1]*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion Crete, Greece*
[2]*Department of Chemistry, University of Crete, Heraklion Crete, Greece*
[3]*Institute of Applied and Computational Mathematics, Foundation for Research and Technology-Hellas, Heraklion Crete, Greece*
[4]*Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece*
[*]*kiki@iesl.forth.gr*

Polymer nanohybrids with enhanced properties can be developed via the addition of nanosized additives to a polymeric matrix. In this work, nanohybrids of hyperbranched polymers of different generations and graphene oxide (GO) of varying degree of oxidation are developed to investigate the effect of the different hydrophilicity of the filler on the final structure and properties of the nanohybrids. Additives with different degree of oxidation were attained by altering either the reaction time or the amount of the oxidation medium during the oxidation reaction of graphite. The obtained GOs were characterized with X-Ray Diffraction (XRD) and X-Ray Photoelectron Spectroscopy (XPS) and their degree of oxidation was found to depend strongly on the amount of oxidant but not on the oxidation time. All GOs were consequently mixed with the Hyperbranched Polymers (HBPs) to form nanocomposites. A plethora of experimental techniques was utilized to investigate the hybrids structure (Figure 1), morphology as well as their thermal and rheological properties. Molecular Dynamics simulations were utilized to predict and interpret the behavior of both the GO additives and the nanocomposites and to assist in correlating the obtained structure with the observed properties.

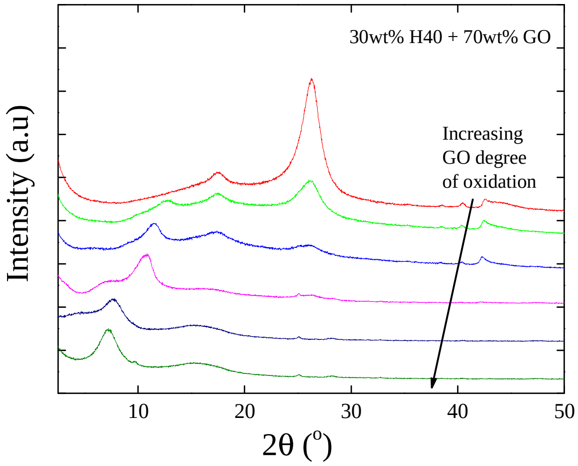

Figure 1: X-ray diffraction measurements of nanohybrids composed by hyperbranched polymer H40 and graphene oxides of varying dergee of oxidation

Keywords: Polymer nanocomposites, graphene oxide, hyperbranched polymers, degree of oxidation, interfacial interactions

Acknowledgments
This research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning 2014-2020» in the context of the project "Polymer / graphene derivatives nanocomposites: Influence of the interfacial interactions on the polymer structure and properties (POLYGRAPH)." (MIS 5050562).

Supramolecular Janus Nanocylinders: breaking symmetry through the assembling units

S. Han,[1,2] T. Choisnet,[1,3] D. Yilmaz,[2] S. Kalem,[1,2] F. Niepceron,[1] L. Bouteiller,[2] S. Pensec,[2] J. Rieger,[2] F. Stoffelbach,[2] D. Canevet,[3] M. Sallé,[3] JM. Guigner,[4] J. Jestin,[5] C. Lorthioir,[6] P. Woisel,[7] E. Nicol[1] and O. Colombani[1,*]

[1] *Institut des Molécules et Matériaux du Mans (IMMM), UMR 6283 CNRS Le Mans Université, France*

[2] *Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, UMR 8232, Equipe Chimie des Polymères, 75252 Paris, France.*

[3] *Univ Angers, CNRS, MOLTECH-Anjou, SFR MATRIX, Angers F-49000, France*

[4] *Sorbonne Université, CNRS, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, UMR 7590-IRD-MNHN, 75252 Paris, France.*

[5] *Laboratoire Léon Brillouin, UMR12 CEA-CNRS, Bât. 563, CEA Saclay, 91191 Gif-sur-Yvette, France.*

[6] *Sorbonne Université, CNRS, Laboratoire de Chimie de la Matière Condensée de Paris, UMR 7574, 75252 Paris, France.*

[7] *Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, France*

[*] olivier.colombani@univ-lemans.fr

Janus particles are characterized by two sides with different chemistries and are the subject of intense current interest[1] with applications ranging from optics, magnetism, catalysis, and surface nanopatterning to interface stabilization. Many strategies exist to prepare micrometric spherical Janus particles,[2] but the design of Janus NanoCylinders (JNC) remains an extremely difficult challenge because of their nanometric dimensions and anisotropic character. Müller et al.[3] and Perrier et al.[4] both proposed a strategy relying on the incompatibility between two polymer arms to force their phase segregation into either sides of supramolecular nanocylinders, resulting in a Janus topology. These strategies are however polymer dependent and not efficient with weakly incompatible polymer arms.[5]

Here we propose a versatile strategy where the Janus character can be achieved independtly of the compatibility of the polymer arms by using two polymers functionalized with non symmetrical hydrogen bonding units.[6] The directional and strong assembly of the hydrogen bonds drives the formation of supramolecular nanocylinders, while their non symmetrical design forces the two polymer arms on each side of the nanocylinder, resulting in a Janus character even for compatible arms (Figure 1). The approach proved successful and versatile: it worked with two alternative pairs of assembling units and both in organic and aqueous medium. JNC prepared with this strategy were shown to be excellent emulsion stabilizers, which represents only one of the many potential applications of these complex nanoparticles.

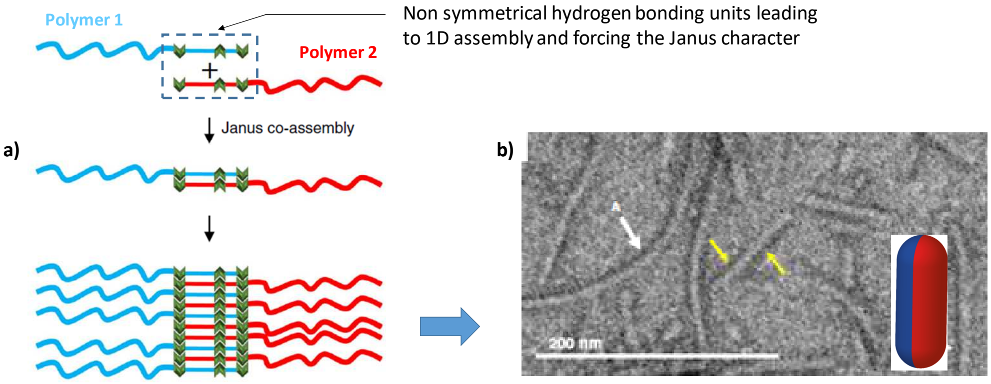

Figure 1. a) Concept: two polymers functionnalized with different and non-symmetrical hydrogen bonding units co-assemble into JNC obseved by b) TEM after selective matching of one of the arms.

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Development of multifunctional bioactive polysaccharide-based composite hydrogels by a dual ice-templating strategy

M. V. Dinu*, I.E. Raschip, C.-A. Ghiorghita, M.M. Lazar, I.V. Platon

“Petru Poni” Institute of Macromolecular Chemistry, Department of Functional Polymers, Grigore Ghica Voda Alley 41A, Iasi 700487, Romania
Corresponding Author’s E-mail address: vdinu@icmpp.ro

The encapsulation or entrapment of bioactive compounds (polyphenols, essential oils) into polymer matrices based on natural macromolecules [1] is a promising approach to: (i) prevent the oxidation and volatilization, (ii) enhance the stability and water solubility, (iii) prolong the shelf-life, (iv) increase the bioavailability and efficacy, and (v) enable the controlled release of bioactive compunds. These attractive features promoted use to explore the entrappment of *Thymus vulgaris* essential oils (EO) [2], grape pomace extracts [3], or spruce bark extracts within physically or chemically cross-linked sponge-like architecture of polysaccharide-based cryogels (Figure 1) by a dual ice-templating assembly strategy, and to investigate the properties of the new biomaterials.

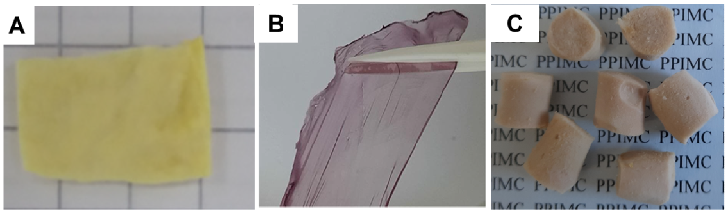

Figure 1. Optical images of composite hydrogels: (A) chitosan-containing EOs, (B) xanthan-entrapping grape pomace extracts, and (C) dextran-enriched with spruce bark extracts.

The embedment of EOs within the chitosan/dextrin matrices generated porous films with an increased elasticity that allows their fast shape recovery after full compression. In addition, the encapsulation of bioactive compounds endows the bio-based films with both antioxidant and antifungal properties, showing a radical scavenging activity of 65% and a zone inhibition diameter of 40 mm for *Candida parapsilosis* fungi [2]. On the other hand, the ice-templated xanthan gum/polyvinyl alcohol (XG/PVA) cryogel networks containing hydro-alcoholic extracts from Merlot pomace had superior antibacterial activity toward Gram-negative bacteria (*Escherichia coli* and *Salmonella typhymurium*) and a Gram-positive bacterium (*Listeria monocytogenes*) compared to the XG/PVA cryogel without the extracts [3]. The stabilization of spruce bark extracts within porous chemically cross-linked dextran hydrogels has been also demonstrated. In conclusion, our results recommend the entrapment of bioactive compounds into bio-based cryogel carriers as a straightforward approach to provide ‘green’ polysaccharide-based films having both improved physicochemical properties and remarkable antioxidant and antimicrobial activities.

Keywords: bioactive compounds, polysaccharides, cryogels, stabilization

Acknowledgments *This work was supported by the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, projects PN-III-P4-ID-PCE-2020-0296 and PN-III-P4-PCE-2021-1132*.

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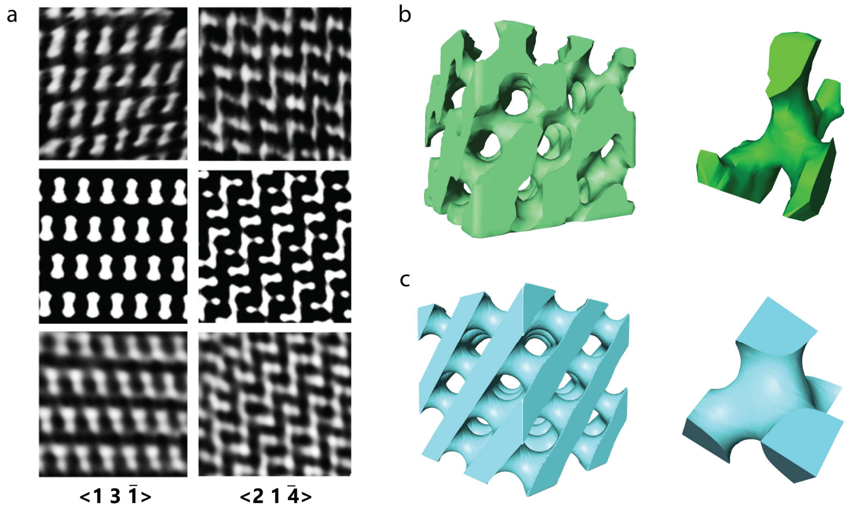
Discovery of single diamond networks in block copolymer films by nanotomography

K. Djeghdi[1], K. Godlewska[1], D. Karpov[2], J. Llandro[3], B.D. Wilts[4], U. Wiesner[5], U. Steiner[1], I. Gunkel[1*]

[1]*Adolphe Merkle Institute, Fribourg, Switzerland*
[2]*Paul Scherrer Institut, Villigen, Switzerland*
[3] *Tohoku University, Sendai 980-85, Japan*
[4] *University of Salzburg, Salzburg, Austria*
[5] *University of Cornell, Ithaca (NY), USA*
[*]*ilja.gunkel@unifr.ch*

Driven by the incompatibility between different blocks, block copolymers self-assemble into a wide range of morphologies, from simple lamellae, spheres and cylinders to more complex triply periodic bicontinuous structures [1]. While the general phase behavior of block copolymers is very well understood, both theoretically and experimentally, allowing for tuning the morphology and structural dimensions, some morphologies remain elusive. The single diamond phase (space group *Fd-3m*) for instance, has never been achieved experimentally despite theoretical predictions [2]. This phase, which is ubiquitous in nature, is of particular interest in the field of photonics, where it is known as the "champion" structure with the largest known photonic bandgap [3]. Here we present the first truly polymeric self-assembled diamond and show that triblock terpolymers can self-assemble into single diamonds in films upon slow solvent evaporation. The morphology was identified and characterized using state-of-the-art tomography techniques (FIB-SEM Slice-and-View and X-ray Ptychography) with unprecedented resolution. Not only does this finding hold great promise for future photonic applications, we also believe that recent improvements in the tomography techniques employed here will enable the precise characterization of three-dimensional nanostructured matter, potentially enabling the identification of other new phases.



a) Two sets of matching cross-sections with the indicated <hkl> Miller indices, from top to bottom: FIB-SEM dataset – computed levelset single diamond – X-ray ptychography dataset, b) subset V = $(145\ \text{nm})^3$ and single node extracted from the experimental FIB-SEM tomogram compared to c) a computed levelset single diamond.

Keywords: Block copolymer self-assembly, single-diamond morphology, ptychography, FIB-SEM

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Alginate-based micelles for nanomedicine: a self-assembly study

M. Fauquignon[1], A. Solberg[2], C. Schatz[1,*], B. Christensen[2,*]

[1]*Laboratoire de Chimie des Polymères Organiques (UMR UBdx, CNRS et Bdx INP), Pessac, France*
[2]*NOBIPOL, Department of Biotechnology and Food Science, NTN, Trondheim, Norway*
[*] *martin.fauquignon@enscbp.fr*

Alginates comprise a family of polysaccharides isolated from brown seaweeds and some bacterial species. They are made up of 1,4-linked β-D-mannuronate (M) and its C-5 epimer, 1,4-linked α-L-guluronate (G), forming a M- and G-blocks sequence interspaced by polyalternating MG-blocks. G-blocks are responsible for the gel forming properties of alginate in the presence of calcium. The specific and strong cooperative interactions between two or more G-blocks and some divalent cations are described by the classical egg-box model[1]. Alginate have been explored for biomedical applications, mainly for their gelation properties. However, the preparation of alginate nanoparticles with a narrow size distribution and high stability remains a challenge. Recently, the use of specific linkers to prepare diblock polysaccharides has been reported[2]. By using this approach, alginate-based diblock polysaccharides were synthesized by coupling a homopolymeric guluronate block (G) to dextran (Dex). It was possible to trigger the self-assembly of the oliguluronate-*b*-dextran by adding calcium ions[3].

In this work, we present an in-depth study of the stimuli-induced self-assembled morphologies obtained with G-*b*-Dex diblocks in the presence of calcium, strontium and barium ions. Time-resolved dynamic light scattering (DLS) and small angle neutron scattering (SANS) were used to study the formation of the nanoparticles during the dialysis of G-*b*-Dex against $CaCl_2$, $BaCl_2$, and $BaCl_2$ solutions. The kinetics of micellization and micelle sizes correlated well with the affinity of alginate for the different cations. Eventually, we obtained small, stable and monodisperse micelles (radius < 10 nm). These nanoparticles are considered as promising vehicles for several medical applications due to their small size, stability and the loading of different ions in the micellar core (*e.g.* radionuclides, contrasting agents, catalysts, *etc.*).

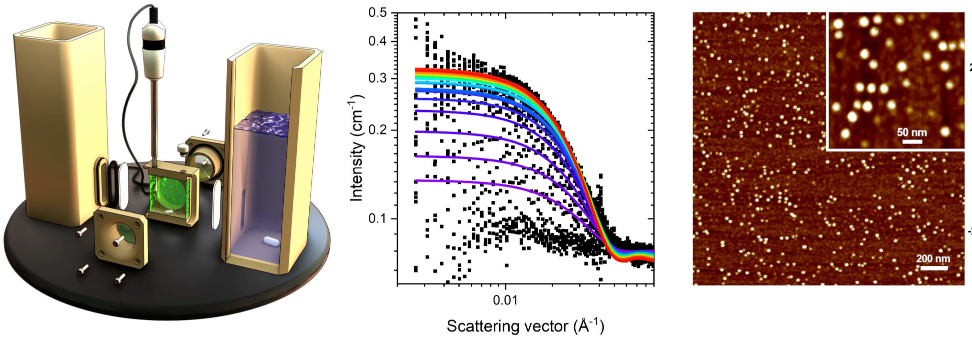

Figure 1- Oligoguluronate-*block*-dextran self-assembly by dialysis against a calcium solution. Left: dedicated dialysis cell allowing in situ neutron and light scattering analysis. Middle: SANS curves obtained during the dialysis process. Right: AFM pictures showing the micelle structures formed.

Keywords: alginate, nanoparticle, micelle, self-assembly, dialysis

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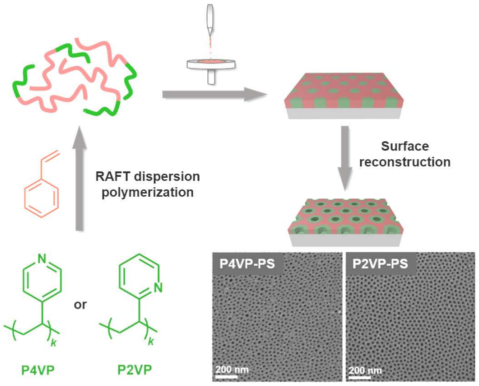
Well-defined block copolymers via RAFT aqueous-alcoholic dispersion polymerization. Synthesis and isoporous thin films.

Katharina Nieswandt,[1] Prokopios Georgopanos[1,*] and Volker Abetz[1,2]
[1]*Helmholtz-Zentrum Hereon, Institute of Membrane Research, Geesthacht, Germany*
[2]*Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany*
[*]*prokopios.georgopanos@hereon.de*

Reversible addition-fragmentation chain transfer (RAFT) dispersion or emulsion polymerization has drawn a lot of interest in the last decades. [1] RAFT polymerization is not only a fascinating way for the synthesis of tailor-made polymers but also provides the opportunity for the synthesis of block copolymers with combinations of monomers that were not easily polymerizable by other methods. [2] In this presentation, the synthesis, the characterization of polyvinylpyridine-polystyrene (PVP-b-PS) diblock copolymers via reversible addition-fragmentation chain transfer (RAFT) dispersion polymerization and the isoporous thin-film formation is presented (Figure 1). A series of poly(4-vinylpyridine) (P4VP) and poly(2-vinylpyridine) (P2VP) homopolymers were prepared by RAFT bulk polymerization at 80 °C using either a carboxylic acid functionalized trithiocarbonate or a non-functionalized trithiocarbonate RAFT agent. The P4VP and P2VP macroRAFT agents acted as stabilizers in the subsequent RAFT-mediated polymerization-induced self-assembly (PISA), when they were chain extended via RAFT aqueous-alcoholic dispersion polymerization of styrene at 70 °C. High styrene conversions between 86–99% were achieved, leading to a series of well-defined, high molecular weight PVP-b-PS diblock copolymers with narrow molecular weight distributions as confirmed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and gel permeation chromatography (GPC). The bulk and surface morphologies of the diblock copolymers were investigated via transmission electron microscopy (TEM), atomic force microscopy (AFM), and scanning electron microscopy (SEM). The solution-cast and spin-coated thin films of the PVP-b-PS diblock copolymers exhibited microphase-separated structures with spherical or cylindrical order according to their compositions. Spin-coated PVP-b-PS diblock copolymer films with weight fractions of the minority PVP block ranging from 17–24% were converted into porous surfaces by a controlled alignment and swelling strategy, exploiting the distinct solvent selectivities for the individual blocks. [3]



Figures 1: Synthesis and isoporous thin-film formation of PVP-b-PS block copolymers. [3]

Keywords: RAFT polymerization, block copolymers, isoporous thin films

Acknowledgments
Funding for the Helmholtz Association via the HRSF-0075 project is gratefully acknowledged.

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Strengthening Polymer Interfaces by Grafting Acrylates on PA66

Carolin Gleißner[1*], Thomas Bechtold[1], Tung Pham[1]

[1]*Research Institute of Textile Chemistry and Textile Physics, Leopold-Franzens University Innsbruck, Dornbirn, Austria*
[*]*carolin.gleissner@uibk.ac.at*

High-performance polymer fibres have a wide range of application due to their excellent mechanical and chemical properties. They are used in the automotive and aerospace, the personal protection equipment, the medical, or smart textiles sector, often in the form of composites and hybrids. However, by creating hybrids, interface stability problems are commonly observed. Therefore, activation, functionalization or modification techniques of fabric surfaces are needed to overcome the interface stability problem by changing the surface chemistry and/or topography while not altering the bulk properties negatively. Several studies on surface modification of fabrics exist that use a broad variety of principles via wet chemical, physical, or gas phase treatments [1].

In contrast to degradative surface modification techniques such as hydrolysis, oxidation, plasma treatment, or ozone treatment, the formation of adhesion promotion layer presents a non ablative surface treatment. The aim is to introduce defined chemical functionalities with defined chemical interface reactions.

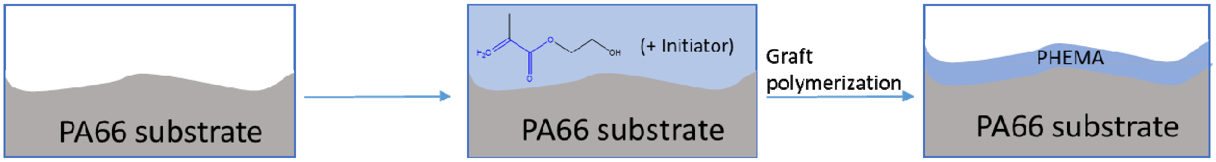

Figure 1: Scheme for the preparation of a PA66-graft-polyacrylate.

The study focusses on the development of the grafting process of acrylates such as hydroxyethylmethacrylate, short HEMA, on polyamide 66 substrates. HEMA finds application in several fields due to its easy synthesis and polymerization. It provides a vinylgroup that is radically polymerizable and polar oxygen containing groups promoting the wetting behaviour of the coated surfaces [2].

The grafting process involves plasma polymerization via atmospheric pressure plasma with the optional use of initiators. The grafted polyamide substrates are analysed via fourier-transform infrared spectroscopy, wettability tests, microscopy, and mechanical tests. In addition, the impact of the grafting on a subsequent metallization with copper is investigated [3].

Keywords: Hydroxyethyl methacrylate, Grafting, Functionlization

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Nanostructured actuators based on block copolymers with ionic liquids

Aynur Guliyeva,[1*] Hélène Pung,[1] Anatoli Serghei,[2] Matthieu Gervais,[1] Cyrille Sollogoub,[1] and Sébastien Roland[1]

[1]*Laboratoire PIMM, Arts et Metiers Institute of Technology, CNRS, Cnam, HESAM Universite,75013 Paris, France*

[2]*Laboratoire Ingenierie des Matériaux Polymères, UMR CNRS 5223, Université Lyon 1, 15 Bd. A. Latarjet, 69621 Villeurbanne, France*

[*]*E-mail address: aynur.guliyeva@ensam.eu*

Block copolymers (BCPs) self-assembly leads to plenty of promising applications from nanoporous membranes to nanoelectronic devices. Thus, improving the ordering of BCP is crucial to optimize its performance in different applications. Adding ionic liquids (ILs) to BCPs leads to realize fast ordering because of its plasticization effect, increases the χ parameter of BCP, and influences the center-to-center distance by swelling the IL-containing phase. This type of blends also allows for obtaining a solid conductive materials from non conductive BCPs for applications in several areas, such as in the manufacturing of polymer electrolytes for batteries, membranes, fuel cells, actuators, photonics, etc. with the need to produce a material that is not only conductive but also solid.[1, 2, 3] Indeed, the conductivity is necessarily associated with molecular mobility, which reduces the mechanical properties of the final material. Then, the use of ABA triblock copolymers, which ensures both mechanical strength and ionic conductivity by selectively incorporating ILs within nanostructured morphologies of triblock copolymers, appears obvious. In this study, we developed ionic polymer actuators of nanostructured commercial BCPs, which could be used to achieve a fast response time under low-voltage operating conditions.

In this presentation, firstly we will present the effect of ILs additives on the self-assembly process of ABA type triblock copolymers with an elastomeric central B block and rigid end A blocks which are well-known commercially available thermoplastic elastomers (TPEs). Two different compositions of the same polymer were tested with and without ILs additives and were characterized by different technics to analyze final morphologies (see Fig 1). The key point of the study is to obtain well-ordered morphology after the solvent casting of the film by adding ILs without any thermal annealing from initially non-ordered ABA polymer. To our knowledge, in most of the studies, researchers applied a solvent vapor annealing step or thermal heating after film casting to increase the mobility of polymer chains to obtain targeted nanostructure. Secondly, the actuating test of the final material based on BCPs and ILs mixtures will also be presented. The effect of different parameters on the actuating process, such as the applied voltage value, IL percentage in the mixture and morphology type of BCP were studied. The main goal of the second part is to understand the relation between the tortuosity of different morphologies and ionic conduction path, which is crucial for actuators. These type of actuators with their flexibility, ease in manufacturing, low cost and lightweight are promising candidates, which are capable of large displacement under low operation voltages of only a few volts for the application in the domain of soft robotics and biomedicin.

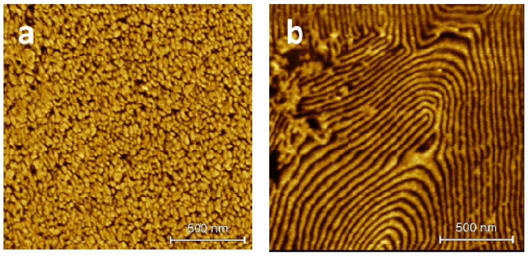

Fig. 1: AFM phase images (2 x 2 µm) for Poly(methyl methacrylate-*b*-butyl acrylate-*b*-methyl methacrylate) (PMMA-PBA-PMMA) block copolymer blended with ionic liquids (ILs) over different weight concentrations ϕ_{IL}: (a) 0% (b) 33%. Scale bars = 500 nm

Keywords: Block copolymer, self-assembly, ionic liquids, rapid annealing

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Robust, stretchable, and self-healable hierarchically structured supramolecular elastomers for soft robots

Gurunathan Thangavel, Matthew Wei Ming Tan, Pooi See Lee*

School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798
**Correspondence and requests for materials should be addressed to P. S. Lee* (e-mail: pslee@ntu.edu.sg)

Soft electronics and actuators are in increasing demand due to their softness, inherently safe, and adapt well to unstructured environments. However, current methods for prototyping soft actuators remain cumbersome and struggle to achieve a combination of excellent actuating performance and robust mechanical strength. This creates a need for high stretchable and soft functional elastomeric materials with good resilient and regenerative properties. In this work, we show a unique multi-functional supramolecular polyurethane elastomer for soft robotics with robust circuitry that is self-healing, absorbing energy without fractures, reconfigurable, and ultimately good toughness. Through an easy condensation reaction, the system explored incorporates dynamic and reversible hierarchical bonds within polyurethane chains, namely urethane, urea, ureido-4[1H]-pyrimidinone (UPy) and carboxyl bonds, which is particularly interesting to trigger a controlled self-healing efficiency and toughness simultaneously. We further found that they were able to tune the healing efficiency by introducing organic polar solvents during the healing process. This can be attributed to the solvent's act as a temporary plasticizer and a de-crosslinking agent that allows greater chain entanglements. The healed elastomer displayed exceptional mechanical properties of elongation at break of 1865%, tensile strength of 5.57 MPa and toughness of 41.74 MJ m^{-3} within 12 hours. Proving to be one of the first healed polymers that realized both high tensile strengths and elongations simultaneously. Furthermore, the dielectric elastomer actuation (DEA) delivers higher actuator performance and achieves significant recovery of its actuator performance in terms of area strains after self-healing. Ultimately this is explained by hydrogen bond moieties are polar in nature, contributing to the high dielectric permittivity of the film.

Aqueous Dispersions of Polypropylene and Polyethylene: Toward Reference Materials for Nanoplastics Characterization

J. Hildebrandt[1*], A. Thünemann[1]

[1]*Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany*
[*]*jana.hildebrandt@bam.de*

Plastic debris in micron and nanometer scale pollutes the nature all over the world. The potential dangers of these pollutants remain unpredictable. While risk assessment studies on microplastics are already popular, nanoplastic has not yet reached the same focus of investigation. The reason for this difference is simple: There is a "methodological gap" in the analytics of plastic particles with a diameter smaller than 1 µm. Submicron and nanoplastic particles are currently not detectable in environmental matrices. Therefore, it is important for researchers to have a well-characterized nanoplastic material, that serves as a reference for nanoplastics found in nature.

Our aim was to synthesize nanoplastics made from the most common used plastics such as polypropylene (PP) and polyethylene (PE). We found an easy way to form nanoparticles consisting of PP and PE (nano-PP/PE), adapting and improving the method presented for polystyrene (PS).[1] Nano-PP/PE was formed via a top-down method where the polymer was dispersed to acetone and then transferred to water. No additional surfactant is needed to obtain a dispersion which is stable for more than 35 weeks.

The success of forming nanoplastics and their size was detected via scattering methods, predominantly dynamic light scattering (DLS). The chemical analysis of the nanoplastics was performed via Fourier Transform Infrared spectroscopy. To examine the good stability of the nanoparticles, zeta potential measurements were performed, which revealed zeta potentials of -30 to -40 mV.

Table 1: Radii of gyration R_g, hydrodynamic radii R_h and PDI for particles made of PP and PE. The radii R were calculated for a spherical particle.

	SLS results		**DLS results**	
	R_g	R	R_h	**PDI**
PP particles	52 mn	67 nm	68 nm	0.09
PE particles	49 nm	63 nm	63 nm	0.14

The presented preparation method leads to a PP or PE dispersion, that contains only slightly different particle sizes, even when repeated several times. This method is therefore well suited for the production of reference material, as which we propose our prepared particles, based on a homogeneity study, that we performed, following the ISO Guide 35[2] for reference materials.

Keywords: nanoplastics, polyethylene, polypropylene, reference material

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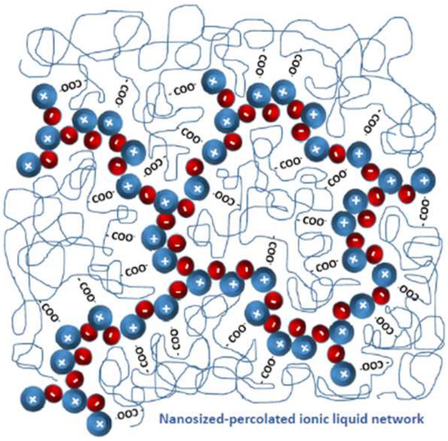
Lionomers: New materials based on the combination of IL and polymers

Liutong HOU, Sebastien Livi*, Jean-François Gérard, Jannick Duchet-Rumeau

Univ Lyon, INSA Lyon, CNRS, IMP UMR 5223, F-69621, Villeurbanne, France
**Corresponding Author's E-mail address: sebastien.livi@insa-lyon.fr*



Ionomer is ragarded as macromolecule containing one kind of ionic/ionisable groups that are composed of the acid anions (like carboxylic and phosphoric acids) and metal salts (like Zn^{2+} and Na^{+})[1-4]. The formation of complex aggregate nodes and their ability to physically cross-link play the dominant role on the microstructure and the properties of such materials. The phase separation phenomena causes physical gelation due to the ionic interaction, which may result in siginificant reforcement on thermal-mechanical, physical and rheological properties, and sometimes produce thermoplastic properties to the ionomers. In this present, lionomer as new generation of ionomer is designed (right side) by combining polypropylene grafted maleic anhydride (PPgMA) and the phosphonium-based ionic liquids (PhILs). Thanks to excellent characteristics of ILs and their limitless anion-cation combinations, the physicochemical interactions can be tuned for designing a new microstructure with relevant functional properties. Firstly, two kinds of lionomers have been obtained by introducing tributyl (ethyl) phosphonium diethyl phosphate (IL-DEP) and tetradecyl (trihexyl) phosphonium bis(2,4,4-trimethylpentyl) phosphinate (IL-TMP) into the precursor-PPgMA matrix. The ionic interactions between PhILs and grafted groups have been proved by ATR-FTIR, and are highlighted with the increase of PhILs content. The interaction limits the movement ability of polypropylene chains and leads to the increase of melting viscosity. The rheological properties are also very sensitive to these ionic interactions. This continuum of interactions COO^{-}/P^{+} is all the more promoted than cation is less sterically hindered and can ionically interact with carboxylic anions. Thus, PhILs owning a lowly hindered cation (IL-DEP) increases the melting viscosity of PPgMA by near four times, meanwhile increases the modulus and strain break which is not the case with a strongly hindered cation. Furthermore, this intimate interaction between cation and COO^{-} is also evidenced by the increase of mechanical relaxation temperature with IL-DEP, *i.e.* increase of 17°C with 10wt% IL-DEP due to the fomation of ionic mulpiles/clusters in rigid amorphous fraction (RAF) region. The morphology in relation with mechanical property was systematically investigated by exploring the effect of MA content, PhILs concentration and the nature of ionic liquid.

Keywords: ionic liquid, maleic anhydride grafted polypropylene, lionomers, ionic interactions

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Transient networks of hydrophobically associating multiblock copolymers in aqueous solution: micellar network topology, elasticity and relaxation dynamics

A. Huysecom[1], W. Thielemans[2], R. Cardinaels[1], P. Moldenaers[1*]

[1] *Soft Matter, Rheology and Technology, Department of Chemical Engineering,*
KU Leuven, Leuven, Belgium
[2] *Sustainable Materials lab, Department of Chemical Engineering,*
KU Leuven Kulak, Kortrijk, Belgium
**paula.moldenaers@kuleuven.be*

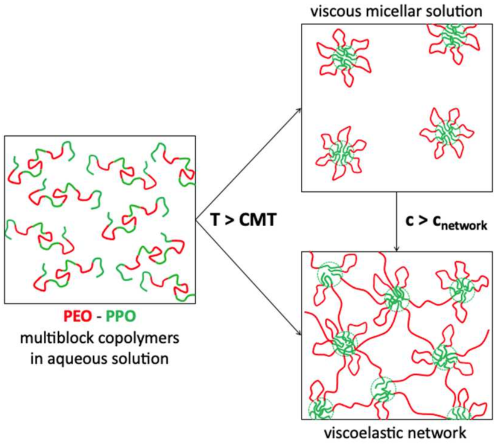

Fig. 1 Schematic representation of PEO-PPO multiblock copolymers in aqueous solution. Formation of micellar assemblies above the Critical Micelle Concentration (CMT) and formation of bridges between micellar cores above the critical network concentration ($c_{network}$).

Hydrophobically associating block copolymers contain hydrophobic blocks which spontaneously self-assemble in micellar aggregates when brought into aqueous media. At sufficiently high concentrations, hydrophilic blocks capped by two hydrophobic blocks have the potential to bridge two nearby hydrophobic cores, instead of looping back to the same core. The formation of such bridges transforms the material from a viscous solution of isolated micelles into a viscoelastic 3D micellar network with dynamic crosslinks (see Fig. 1). Whereas most studies use telechelic triblock copolymers bearing their hydrophobic blocks as end groups, our study focuses on alternating PEO-PPO multiblock copolymers having multiple hydrophobic PPO blocks distributed along the chain. One copolymer chain thus has the potential to form multiple hydrophilic bridges between different micellar nodes. This significantly increases the possible chain configurations of a copolymer in the micellar network and mandates a novel approach as compared to telechelic triblock copolymers. In this contribution we adopt a combinatorics approach to extend and generalize the mechano-statistical transient network model originally developed by Annable for telechelic triblock copolymers [1,2] to more general alternating multiblock copolymers. Based on our model, we can predict the concentration dependent rheological properties of transient networks formed by multiblock copolymers, using knowledge of the transient network microstructure. For this purpose, dynamic and static light scattering have been combined with small-angle X-ray scattering (SAXS) to detect concentration dependent microscopic changes in the micellar assemblies and overall network topology. Using information about the spatial distribution of the micellar nodes, as inferred from SAXS, our model allows to unravel how these microstructural changes translate to macroscopic behavior. Interestingly, the model predictions of elasticity as a function of concentration show excellent agreement with experimental rheological data. The evolution of the high-frequency plateau modulus and hence the elasticity can be linked to a change in the network topology from loop-dominated with low-functional crosslinking nodes at low concentrations to bridge-dominated with highly functional crosslinking nodes at more elevated concentrations. A thorough understanding of the network topology and its effect on the rheological properties of the network will pave the way for the development of transient networks with designed elasticity and relaxation dynamics.

Keywords: multiblock copolymer, hydrophobic association, transient network model

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Large-scale ordered block copolymer gyroid films by solvent evaporation annealing

R. Iseli[1*], D. Abdelrahman, B. Wilts, U. Steiner, I. Gunkel

[1]*Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland*
[*]*rene.iseli@unifr.ch*

The numerous morphologies achievable with block copolymer self-assembly open many doors for the creation of new materials, whereas the gyroid lattice especially is a highly suitable candidate for the production of metamaterials[2,3]. Applications which rely on metamaterials need relatively large-scaled, homogeneous patches of such. This is possible using solvent vapor annealing techniques, where polymer chains of already dried films are mobilized through infiltration of solvent vapor. Subsequent swelling of the film allows reorganization of the polymer chains and enhance the order in the film. However, it requires often long waiting time, loses efficiency going towards thicker films and is not reliably producing large homogeneous areas.
Here I introduce the manipulation of the "Solvent Evaporation Annealing" (SEA)[4] procedure, allowing annealing in optimized speed and reliable generation of large-scale order in block copolymer gyroid films.

The key point is to slow down annealing during the beginning of microphase separation. As this minimizes the nucleation rate and promotes growth of domains. Dissolving the polymer in a volatile and nonvolatile solvent mixture separates the self-assembly into two evaporation steps, where first order organization is achieved with the evaporation of the volatile component during spin coating up to the nucleation point. The slow evaporation of the nonvolatile component then causes the slowdown of the mentioned above. Reliably getting domains up to the size of 0.5 mm^2 is a huge improvement compared to previously documented domain sizes and a step further towards the application of metamaterials. Thanks to the birefringent nature of our block copolymer (PS-*b*-PI-*b*-PEO), the polarization and size characterization of single domains can be performed using cross polarization light microscopy. Structural analysis and surface characterization are further carried out on SEM and FIB-SEM microscopy.

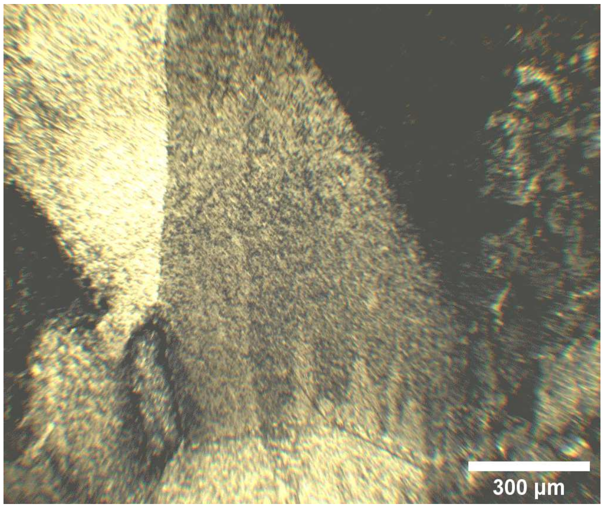

Fig. 1 Large-scale homogeneous block copolymer gyroid domain viewed under cross polarization light microscopy.

Keywords: block copolymer, gyroid, self-assembly, additive solvent, large-scale order

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Controlled dispersion of (chemically modified) halloysite nanotubes in LLDPE/EVA blend

E. Jasinski[1*], E. Beyou[1], V. Bounor-Legaré[1], A. Taguet[2]

[1]*Univ Lyon, UCBL, CNRS, IMP UMR 5223, F-69622, Villeurbanne, France*
[2]*Polymers, Composites and Hybrids (PCH), IMT Mines Ales, Ales, France*
[*]*euphrasie.jasinski@univ-lyon1.fr*

The dispersion and localization of fillers in a polymer blend (either in the matrix, in the dispersed phase, or at the interface) may affect some macroscopic material properties such as fire and mechanical properties. A way to improve the dispersion and control the localization of the fillers into a polymer blend is to use a compatibilizer [1] and/or to chemically modify their surface to increase their affinity with one of the phases of the polymer blend. Another method to selectively disperse fillers is to vary the sequence of mixing during the process [2].

In the frame of our study, we dealt with halloysite nanotubes which is a mineral from the kaolinite group with a chemical composition based on $Al_2Si_2O_5(OH)_4.nH_2O$ and a polymer blend composed of linear low-density polyethylene (LLDPE) and ethylene-vinyl-acetate copolymer (EVA). HNTs are inexpensive, non-toxic, and naturally available fillers which makes them attractive. Without any modification, HNTs are localized in the EVA phase and poorly dispersed. Nevertheless, the presence of silanol groups on their external surface allowed us to functionalized them with different silanes (mechanism in Figure 1). Moreover, the presence of aluminol groups on their internal surface permit to selectively graft them with phosphonic acids for a flame retardant application [3, 4]. The functionalization of the HNT with 3-aminopropyltriethoxysilane and the introduction of polyethylene grafted maleic anhydride (PE-g-MA) as a compatibilizer made it possible to localize the HNT in the LLDPE phase (Figure 2).

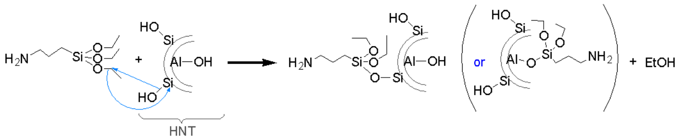

Figure 1: reaction mechanism of aminopropyltriethoxysilane and HNT

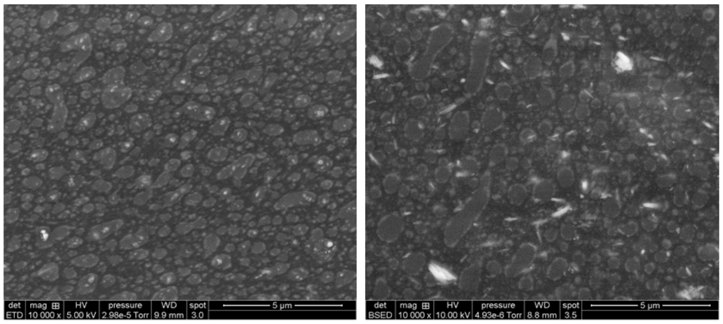

Figure 2: MEB images of LLDPE/EVA blends with HNT localized in EVA (left) and modified HNT localized in LLDPE (right)

Keywords: Halloysite, morphology, functionalization

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Synthesizing, Modifying and Using Nanoparticle Stabilisers in One-Pot to Formulate Pickering Emulsion Templates

Qixiang Jiang[1], Tommy S. Horozov[2], Alexander Bismarck[*, 1]

[1]*Institute of Material Chemistry and Research, Faculty of Chemistry, University of Vienna. Währinger Strasse 42, 1090, Vienna, Austria.*
[2]*Department of Chemistry and Biochemistry, University of Hull, Cottingham Road, Hull, HU67RX, U.K.*
[*]*alexander.bismarck@univie.ac.at*

Emulsion templates provide a versatile tool to produce macroporous polymers with well-defined pore morphologies and densities. Typically, emulsions containing monomers in a minor but continuous phase and a major internal phase are polymerised. The removal of the internal templating phase results in macroporous polymers. It is essential to stabilise the emuslion templates during their polymerisation. As compared to surfactants, (nano)particle emulsifiers are advantageous at low required loading and, therefore, cost. After polymerisation of the particle stabilised (or Pickering) emulsions, (nano)particle residues do not plasticise the resultant macroporous polymers and can introduce functionality, such as electrical conductivity, once suitable particles are used. Nevertheless, due to their intrinsic hydrophicility or hydrophobicity, most of the nanoparticles do require modification, which involves a series of liquid phase chemical reactions, purification and drying, prior to their use as emulsifiers. The particle modification proceduers demand high amount of energy, substances and time and hinder the scalability of emulsion templated macroporous polymers.

Synthesis and modification of $CaCO_3$ nanoparticles and their use as emulsifiers to formulate emulsion templates were realised in one-pot with a time frame of couple of minutes. By tuning the concentration of the nanoparticle modifier, i.e. lauric acid, the propensity of the nanoparticles were progressingly tuned, allowing them to stabilise w/o, o/w emulsion and foam templates containing a range of monomers, such as styrene, divinylbenzen and (meth)acrylate monomers. After the solidification of the templates, macroporous polymers, having closed-cell, open-cell and heirarchical pore structures, were produced. Furthermore, the scalability of the one-pot approach to produce 600 ml Pickering emulsion templates and corresponding macroporous polymers was demonstrated.

Keywords: emulsion templating, Pickering emulsions, macroporous polymers, nanoparticle modification

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Synthesis of Functional Porous Poly(ionic liquid) Membranes

Atefeh Khorsand Kheirabad[1], Jiayin Yuan[1*]

[1] *Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden* **jiayin.yuan@mmk.su.se*

Porous polymer membranes (PPMs) play a crucial, irreplaceable role in industrial production and in fundamental research, including separation, filtration, water treatment and sustainable development. The vast majority of advances concentrate on neutral or weakly charged polymers, such as the ongoing interest on self-assembled block copolymer PPMs. There is an increasing interest and need to process polyelectrolytes and ionic polymers into nanoporous polymer membranes that critically combine a high charge density with (nano)porous morphology. Additionally, engineering possible structural asymmetry simultaneously in the membrane is equally beneficial, as it would improve membrane performance by building up compartmentalized functionalities. For example, a gradient in pore size forms high pressure resistance coupled with improved selectivity. Nevertheless, developing such highly charged, porous and possibly asymmetric membranes has remained a challenge, owing to the water solubility and ionic nature of conventional polyelectrolytes, hard to process into porous state *via* common routes[1]. Recently, the Yuan group first reported an easy-to-perform production method of nanoporous polyelectrolyte membranes from poly(ionic liquid)s [2]. Building on this important but rather preliminary advance, efforts are devoted to developing new polyelectrolyte-based PPMs. This finding spawned a myriad of functional materials for promising applications, for example, catalyst support, precursors for carbon membranes for energy applications, actuator-based sensor, *etc*. Poly(ionic liquid) (PIL) is a subclass of polyelectrolytes that contains an ionic liquid moiety in the repeating unit of the polymer backbone. A unique, powerful feature of classic PILs is that their hydrophilic/hydrophobic property to a great extent, can be determined by the type of their counterions. This feature provides a practical way for designing functional materials[3] .

The aim of this research is to produce poly(ionic liquid)-based PPMs bearing task-specific functions, such as catalysis support[4], optic materials[5] and templates for inorganic membranes[6]. Both the currently established route and the to-be-developed ones will be employed for the membrane fabrication. This work is inherently interdisciplinary, as it must combine polymer chemistry and engineering, membrane and materials science for its success and will fundamentally advance the design of porous polyelectrolyte membrane for a wide scope.

Keywords: poly(ionic liquid), polyelectrolytes, porous membranes

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(Calibri, 10 pt.)Please ensure that every reference cited in the text is also present in the reference list.
Follow the format below for this purpose:

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Polymeric structures for oil in water separation

I.Krupa[1*], P.Sobolciak[1], S. Hailan[1], A. Mahmoud[1], A. Abdulgader[1], A. Popelka[1], Peter Kasak[1]

[1]*Center for Advanced Materials, Qatar University, Doha, Qatar*
[*]*igor.krupa@qu.edu.qa*

This work summarizes our recent results in a development of new polymeric media, which can be incorporated into current treatment technologies for the sorptive removal of oil from industrial wastewater, as well as can be applicable for removal of oil spills from free water. Polymer structures include i.) foams produced from paraffin wax waste formed during LDPE synthesis in Qatar Petrochemical Company, ii.) plasma treated polyethylene powder, iii.) commercial melamine foams cross-linked by $FeCl_3$, and iv) electrospun copolyamide membranes [1, 2]. The primary target application is tertiary produced water treatment for oil removal, i.e. downstream of primary and secondary oil removal unit processes (e.g. gravity separators, hydrocyclones). Target influent oil-in-water is 30 to 100 mg/L and a target effluent is <10 mg/L. Except this focus, the separation of highly concentrated oil/water mixtures (up to 60 vol.% of crude oil) was investigated, and cross-linked melamine foams shown high potential for this treatment. Finally, an applicability of polymeric foams for a removal of free oil from water surfaces was demonstrated as well.

Keywords: foams; membranes; adsorbtion; filtrartion; oil separation

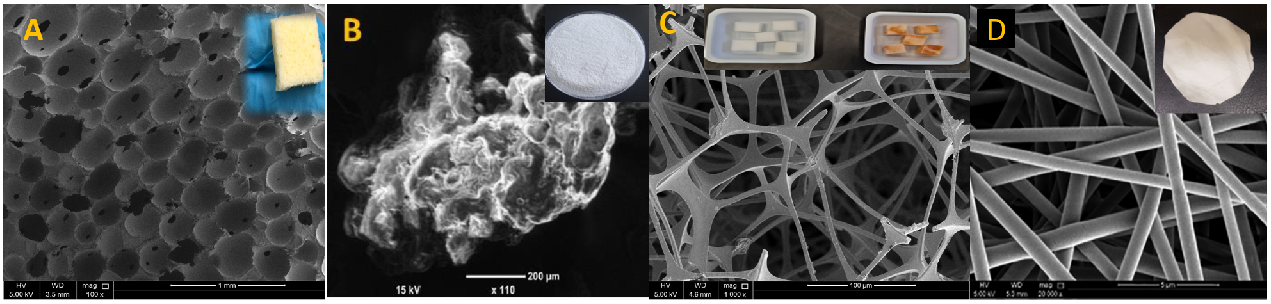

Figure 1: Paraffin wax foam (A); Plasma treated PE powder (B); crosslinked MA foam (C); copolyamide membrane (D).

Acknowledgments

This work was supported by a grant from the Qatar National Research Fund under its National Priorities Research Program (award number NPRP12S-0311-190299) and by financial support from the ConocoPhillips Global Water Sustainability Center (GWSC).

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In situ development of high aspect ratio fillers of phosphate glass for biodegradable polymer composites

O. Leclerc[1*], A. Crohare[2], V. Bounor-Legaré[1] and R. Fulchiron[1]

[1]Univ Lyon, Université Claude Bernard Lyon 1, CNRS UMR 5223, Ingénierie des Matériaux Polymères, 15 Blvd Latarjet, F-69622, Villeurbanne, France
[2]MDB Texinov, 56 Route de Ferrossière, 38110 Saint-Didier-de-la-Tour, France
**olivier.leclerc@univ-lyon1.fr*

In the actual context, the materials end-life and the control of wastes receive more attention. Thus, more and more researchers and companies look after complements or substitutes for future materials. The biodegradable polymers seem to be a good way to combine new material and ecological point of vue. Poly(butylene succinate) (PBS) is one of them. It is biodegradable and can be biosourced [1]. Its thermal characteristics such as its glass transition below ambient temperature and its melting point very close to polyethylene (115°C) make it a serious competitor. It can easily be shaped by current industrial methods.

The project presented here explores the possibility of creating new biodegradable and partially biosourced composites using PBS as a matrix. The idea is to reinforce the mechanical properties of this polymer with potentially biodegradable phosphate glass fillers. This glass, having a glass transition temperature of about 85°C, can be deformed during the polymer processing to ultimately give an organic-inorganic composite reinforced with high aspect ratio glass fillers. Precedents in this approach of *in situ* deformation have already been observed with this phosphate glass in polyethylene [2] or the creation of silica fibrils from sol-gel formulation in polypropylene [3].

The work presented here concerns the synthesis of phosphate glass in the laboratory and the description of its thermal signature. Then, composites were developed by mixing PBS with varying proportions of glass fillers. The composites were finally subjected to elongation at the exit of a capillary rheometer. A composite was successfully obtained with this procedure (see Figure 1). The dispersion of the fillers and their deformation in the composite at the different stages of the process were studied by correlating them to the rheological behavior of each phase and in particular to the ratio of viscosities as a function of temperature. Finally, the impact of the glass fillers on different properties was evaluated: crystallization of PBS, rheological response of the composite and mechanical characteristics.

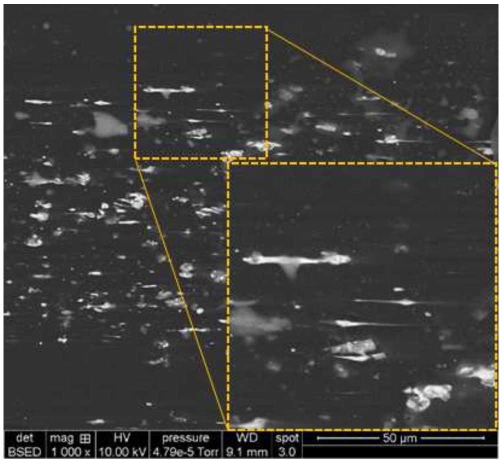

Figure 1: SEM picture of a 0.05/0.95 v/v phosphate glass/PBS composite after elongational deformation at 160°C

Thus, a new original composite was created and some of its characteristics were studied. Some questions still remain open, such as the study of the interface between the glass and the polymer matrix. This composite opens the way to new materials both in the field of biosourced and biodegradable polymers and in the structural design of future composites.

Keywords: Composite, inorganic, in situ deformation

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A General Assay to Determine Polymersome Membrane Permeability

Alisha J. Miller[1] and Rachel K. O'Reilly[1]*

[1]*University of Birmingham, Birmingham, United Kingdom*
**r.oreilly@bham.ac.uk*

Polymersomes are a class of synthetic vesicles composed of a block copolymer membrane surrounding an aqueous inner cavity. In addition to their overall size, the thickness and composition of polymersome membranes determine the range of potential applications in which they can be employed, including drug delivery systems, catalytic nanoreactors and cell mimics.[1] While synthetic polymer chemists have made great strides in controlling polymersome membrane parameters, measurement of their permeability to various analytes including gases, ions, organic molecules, and macromolecules remains a significant challenge (Figure 1). Herein, we outline the design of a new assay to quantitatively measure membrane permeability utilising a polymeric probe comprising fluorescent moieties and demonstrate its potential to be applied to different polymersome systems.

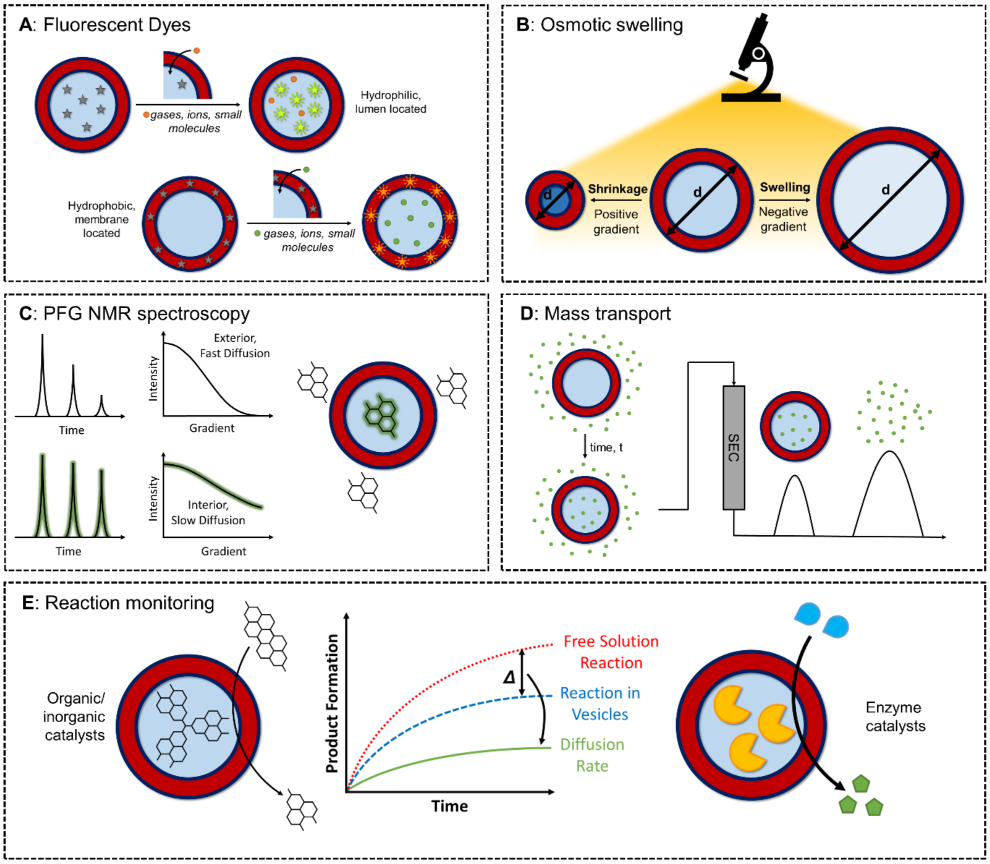

Figure 1 Reported methods for measuring polymersome membrane permeability[2]

Keywords: permeability, polymersome, fluorescence

Acknowledgments

This work was supported by the EPSRC and the University of Birmingham.

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Structural investigation of customized HM_w stereocomplex-PLA copolymers

Carmen Moya-Lopez[1], Daniel Hermida-Merino[2*], David Chapron[1], Carlos Alonso[3], Iván Bravo[3], Patrice Bourson[1]
[1] LMOPS, Université de Lorraine, Centrale Supélec, EA 4423, 2 rue Edouard Belin, Metz, 57070, France
[2] Netherlands Organization for Scientific Research (NWO), DUBBLE@ESRF, CS 40220, 38043 Grenoble Cedex 9, France
[3] Dpto. Inorgánica, Orgánica y Bioquímica, Facultad de Farmacia de Albacete, UCLM, Albacete-02071, Spain
**Daniel.hermida_merino@esrf.fr*

Poly-lactide (PLA) is a well-studied bio-based polymer that is usually synthetized by Ring-Opening Polymerization (ROP), generating two enantiomers, poly (L-lactide) (PLLA) and poly (D-lactide) (PDLA) due to the presence of a carbon chiral centre in its backbone. PLA is the bio-based polymer most widely employed in diverse fields such as food handling or biomedical applications [1]. However, the PLA applicability is slightly inferior to conventional petroleum-based polymers in terms of thermal resistance, mechanical properties and crystallinity kinetics. Different strategies have been evaluated to improve the physicochemical properties such as the use of nucleating agents to increase the crystallization rate or the equimolar blend of PLLA and PDLA enantiomers to generate Stereocomplex (SC) crystallites, which present a melting point 50 °C higher than its homocrystals (HC) counterparts due to the strong interactions between L- and D-lactyl unit sequences. However, the SC crystallization of the blended enantiomers diminishes for high molecular weight (HM_w) PLA, and enantiomeric HC are obtained instead [2].

Herein, a novel series of the long-desired HM_w stereo-diblock-copolymers of PLA were succesfully synthesized by ROP using a heteroscorpionate catalyst without the need of a co-initiator [3], achiving a full stereocomplex crystallization. Moreover, the crystallization kinetics of the designed SC-PLA derivatives were enhaced to the highest known crystallization rate by the addition of a bio-organic nucleating agent (OXA2) to retain the bio-nature of the composite, which offers a promissing processing conditions to be scale at industrial level (Figure 1A). Furthermore, the customization of the tacticity and molecular weight through the well-controlled synthesis process, enables the generation of a series of PLA-derivatives exhibiting a wide range of thermodynamic and structural properties, as evidenced by a multitechnique analysis approach (DSC (Figure 1B), SAXS/WAXS, Raman), which could potentially promote the personalization of medical applications throught the structure-properties relationship and its final applications.

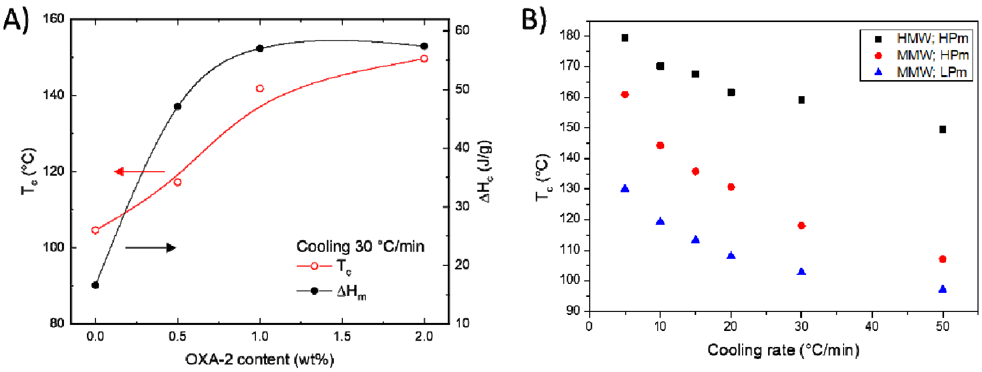

Figure 1. A) Crystallization temperature (T_c) and crystallization enthalpy (ΔH_c) as a function of OXA-2 content in a SC-PLA. B) Crystallization temperature as a function of cooling rate for three SC-PLA. HMW: High molecualr weight; MMW: medium molecular weight; HPm: High tacticity; LPm: Low tacticity.

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Functional and Responsive Self-Assembled and Photo-Cross-Linkable Triblock Copolymer based Hydrogels

E. Nicol[1]*, t. Nicolai[1], v. S. Kadam[1], a. Klymenko[1], y. Meng[1], c. Chassenieux[1], o. Colombani[1], l. Benyahia[1], j. Zhao[2], t. Narita[2]

[1] Institut des Molécules et Matériaux du Mans, UMR CNRS 6382, Université du Maine, Av. O. Messiaën, 72085 Le Mans cedex 9, France
[2] Laboratoire Sciences et Ingénierie de la Matière Molle, ESPCI Paris, PSL University, Sorbonne Université, CNRS, 75005 Paris, France
* *E-mail:* erwan.nicol@univ-lemans.fr

Amphiphilic BAB triblock copolymers are well known to self-assemble in selective solvent of the central block leading to flower-like micelles and flower aggregates at low concentration. Above a critical concentration the latter percolate resulting in the formation of a transient network. We have been able to turn such a network into a permanent one by cross-linking under UV irradiation a BAB triblock copolymer dispersed in water and based on a central poly(ethylene oxide) (PEO) block and a photo-cross-linkable outer B blocks (see Figure 1). It resulted within a few seconds into the formation of covalent hydrogel of controlled structure [1]. We applied three different strategies to improve the properties of these hydrogels by combining this photo-cross-linkable triblock copolymer (tPEO) with other hydrophilic or amphiphilic (co)polymers.

- Mixture of tPEO with an amphiphilic copolyelectrolyte (TH50) led to interpenetrated polymer self-assembled networks (IPSAN) for which the stimuli-responsiveness of both TH50 and tPEO remained. Furthermore, the mixtures displayed synergy since the percolation concentration of the individual polymer networks decreased within the IPSAN whereas their mechanical properties were enhanced when tPEO was photo-cross-linked [2].
- Mixture of tPEO with its non-polymerizable analogue led to the formation of a double network in which dynamic and permanent junctions are hybridized in the same cross-linking points. The synergy between both copolymers led a strong increase of the elastic modulus at lower polymer concentrations and to a significant increase of the fracture strain caused by the dynamic cross-links [3].
- Porous hydrogels were prepared by mixing tPEO with incompatible homopolymers such as dextran or PEO. The macroscopic phase separation could be prevented by arresting it at its first stage through the cross-linking of tPEO. The porosity of the hydrogels could be varied over orders of magnitude depending on the preparation conditions of the mixture. Microphase separation resulted in an increase of the elastic modulus of the mixtures with respect to hydrogels based on sole tPEO [4].

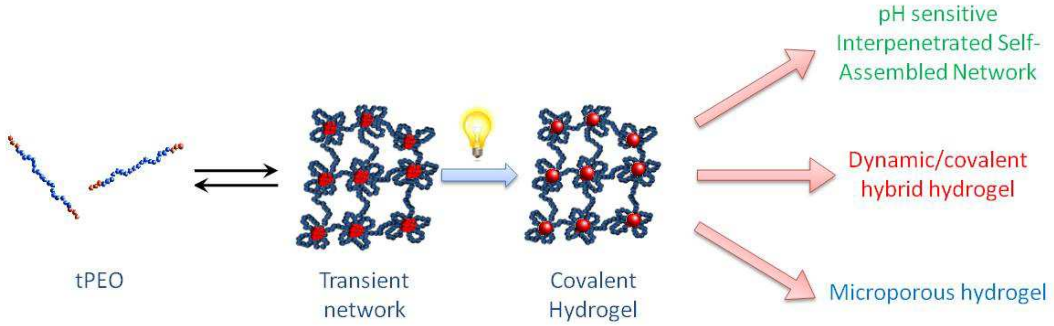

Figure 1: Schematic representation of photo-cross-linkable self-assembled hydrogels

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Smart coatings embedding mesoporous silica nanoparticles exhibiting twofold anticorrosive protection

F. Olivieri[1*], R. Castaldo[1], M. Cocca[1], G. Gentile[1], M. Lavorgna[2]

[1]*Institute for Polymers, Composites and Biomaterials - National Research Council of Italy, Pozzuoli, Italy.*
[2]*Institute for Polymers, Composites and Biomaterials - National Research Council of Italy, Portici, Italy.*
[*]*federico.olivieri@ipcb.cnr.it*

Metals protection from corrosion processes is a trending topic in several fields such as aerospace, buildings and cultural heritage. Historically, the application of sacrificial anodes was the main approach to prevent corrosion on metal substrates: typically, iron or aluminium structures were treated with chromium or zinc based coatings. However, the carcinogenity and the necessity of recurring maintenance made necessary the research of alternative strategies, including for instance metal oxide films, hybrid ceramics and polymer coatings.

Polymer coatings are excellent protective layers due to their high hydrolytic stability and adhesion to the metal substrates. Since the protection provided by a single polymeric layer is time limited, the improvement of the anticorrosive performances currenty follows more complex approaches, such as multilayer deposition or embedding of additives. This latter strategy is particularly effective, because it allows the addition of active molecules which can more efficiently prevent corrosive phenomena, realizing smart systems containing corrosion inhibitors able to tailor their release. In this context, mesoporous silica nanoparticles (MSN) are very attractive as nanocontainers for corrosion inhibitors thanks to their high chemical stability and affinity to polymer matrices, high porosity and surface area and easy preparation [1]. Their engineering in polymer coatings allows the realization of nanocomposites embedding smart stimuli-responsive nanoparticles able to release corrosion inhibitors in response to external triggers [1-2].

Here, the development of a coating containing a pH-dependent chelating complex between 1,2,3-benzotriazole (BTA), a well-known anticorrosion agent, and silver ions is presented, able to release BTA in response to pH variation associated to corrosion processes. MSN nanoparticles were loaded with BTA and capped with the BTA-silver complex. The obtained nanocarriers were embedded into an acrylic matrix, then applied on iron rebars. The engineered MSN provide active and passive barrier, due to BTA release, which forms a passivating layer on the metal surface, and silver release, available to capture chloride ions, which are able to accelerate the corrosion of the substrates (Figure 1). The validation of the anticorrosive performances of the realized coatings was performed by accelerated ageing tests, confirming the high protection of the substrate through the tailored release of BTA and the sequestering of chloride ions [2].

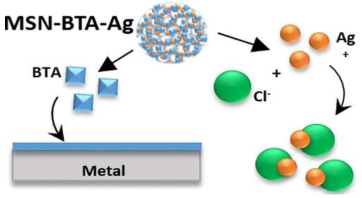

Figure 1. Twofold anticorrosion mechanism of engineered MSN-BTA-Ag.

Keywords: coatings, nanoparticles, smart, corrosion, nanocomposite

Acknowledgments: *The authors gratefully acknowledge the InnovaConcrete project funded by the European Union's Horizon 2020 Research and Innovation Programme under the grant agreement no. 760858.*

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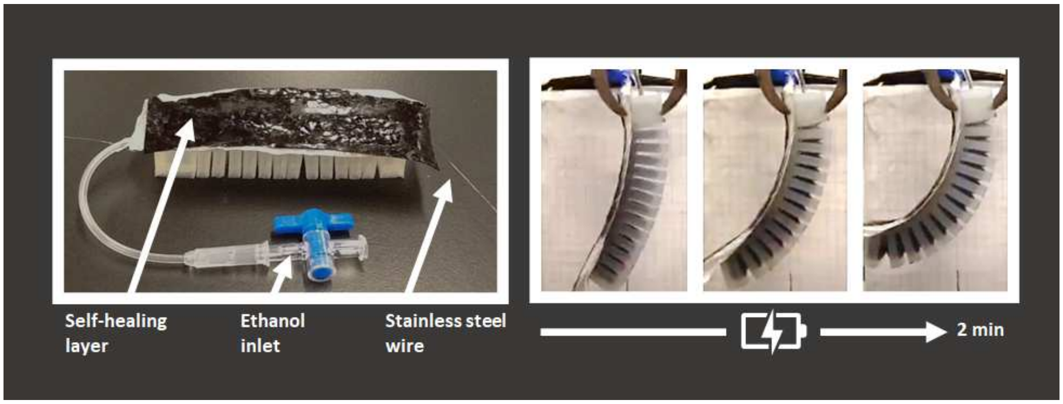
Electroactive Self-healing Soft Robotic Gripper

F. Orozco, D. Horvat, M. Miola, F. Picchioni, R.K. Bose*

University of Groningen, Groningen, The Netherlands
* *r.k.bose@rug.nl*

For the last 10 years, researchers have being reinventing the field of robotics by preparing soft robots. This approach has improves features compared to traditional rigid robots i.e. low cost, biocompatibility, adaptability to work in diverse environments, and low-hazard[1]. A common design of a soft robotic gripper is shown below. This structure is normally made of highly stretchable silicone rubbers with hollow chambers. The actuation effect is obtained by increasing the pressure inside the chamber, which can be achieved with compressed air or by phase-transition of a volatile liquid within the device, such as ethanol. For the latter, a practical strategy is to include a conductive coiled wired inside the device so that the volatile liquid can be vaporized through resistive heating.

A challenging disadvantage of soft robotic devices is their low damage resistance. Their soft flexible nature makes them prone to cuts, tear, and perforations when working with sharp objects. Therefore, self-healing features are quite attractive to implement in these soft robots[1]. Here, we prepared the hollow silicone rubber device shown below. It includes an inlet for adding ethanol, a stainless steel wire, and a self-healing layer attached to the gripping side of the device. The self-healing layer is based on polyketones that are reversibly crosslinked with the Diels-Alder reaction, so that when the layer cracks, the broken crosslinks can be reformed[1,2]. The developed soft robotic gripper actuates with voltages between 10-20 V within 2-3 minutes and successfully self-repairs microcracks at the gripping side. The actuation time is also improved upon adding carbon black into the device. However, this design has the drawback that the materials are not insulating enough. Thus, the gripping surface reaches temperatures around 100 ºC while operating, which limits its applications. Further, design improvements are to be developed.



(Left) Components of the developed soft robotic griper. (Right) Electroactive actuation of the device.

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Multiscale structure of polymerized ionic liquids by small angle neutron scattering.

T. Outerelo Corvo[1,2*], E. Drockenmuller[3], A. Chennevière[2], F. Restagno[1]

[1]Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, UMR 8502, Orsay, France
[2]CEA Saclay, Laboratoire Léon Brillouin, UMR 12 CNRS-CEA, Gif-sur-Yvette, France
[3]Université Lyon 1, CNRS, Laboratoire d'Ingénierie des Matériaux Polymères, UMR 5223, Lyon, France
[*]tiago.outerelo-corvo@universite-paris-saclay.fr

Poly(Ionic Liquid) (PIL) refer to a special type of polyelectrolyte in which each monomer unit is composed of an ionic liquid (IL). They have recently drawn significant attention since they present a unique combination of the properties of ILs with those of polymer materials. Among the former is their particular nanostructure arising from local interactions and segregation of the alkyl moiety which confers the bulk IL with either a globular or a sponge-like structure depending on the alkyl chain length [1]. On a polymer physicist point of view, the main difference between an ideal polymer melt and PILs stems from the presence of counterions and those same local interactions between IL monomer units. To understand the influence of this nanostructure on the macromolecular conformation of PIL chains, we measured for the first time the form factor of poly(1-vinyl-3-alkylimidazolium) PILs with varying side-chain length *n* and counter-anions by an extensive use of Small Angle Neutron Scattering (SANS). This technique allowed us to probe structural features of PILs chains at length scales ranging from the radius of gyration to the chain diameter and the correlation length between neighboring chains. While radii of gyration of PIL chains in dilute solutions increase with *n* due to crowding effects between monomer units, a surprising non monotonic evolution is revealed in bulk [2]. This originates from varying flexibility of the main chain and potential modulated electrostatic repulsions, either dominants for short side chains or screened by the counterions and long side chains. Moreover, the smaller scales unveil clear evidence of interdigitation of the alkyl side-chains for larger *n*. These considerations are precious insights for future applications of these polymers, particularly by exploiting their viscoelastic properties which deviate from those of ideal polymer chains.

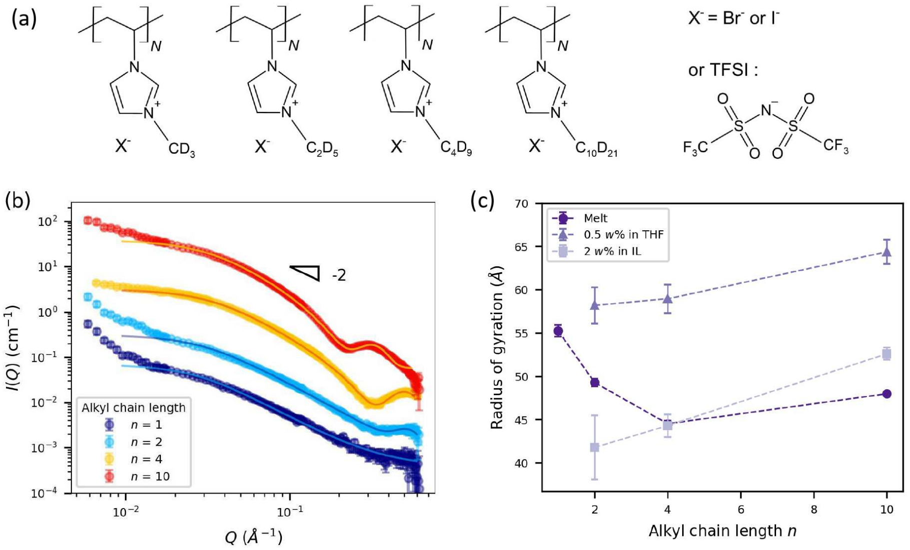

Figure: (a) Chemical structure of poly(1-vinyl-3-alkylimidazolium) PIL. (b) SANS data for melt PC$_n$VImTFSI of varying alkyl side-chain length. (c) Radius of gyration of PC$_n$VImTFSI in melt and dilute solutions determined by SANS as a function of the side chain length n.

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Transformer-Induced Metamorphosis of Polymeric Nanoparticle Shape at Room Temperature

Kostas Parkatzidis,[1] Nghia P. Truong,[1] Athina Anastasaki[1]

[1]*Laboratory of Polymeric Materials, Department of Materials, ETH Zurich*
Vladimir-Prelog-Weg 5, Zurich 8093 (Switzerland)
* *Athina.anastasaki@mat.ethz.ch*

Controlled polymerizations have enabled the synthesis of a wide range of amphiphilic block copolymers which can form nanostructured materials with different shapes exhibiting distinct properties and performance.[1] Despite the importance of shape, current strategies that allow for the efficient morphological transformation are limited in polymer scope, often alter the chemical structure, operate at high temperatures, and can be fairly tedious and time-consuming. Herein we present a rapid and versatile morphological transformation strategy which operates at ambient temperature and without impairing the chemical structure of the resulting morphologies. By simply adding a small amount of a molecular transformer (i.e. small organic molecule) in an aqueous solution of polymeric nanoparticles, a rapid evolution to the next high-ordered morphology was observed within seconds, yielding a range of nanoparticles morphology from the same starting material. Significantly, this approach can be applied to nanoparticles produced by disparate block copolymers (i.e. with different cores and coronae) obtained by various synthesis techniques, including emulsion polymerization, polymerization-induced self-assembly and traditional solution self-assembly.[2,3]

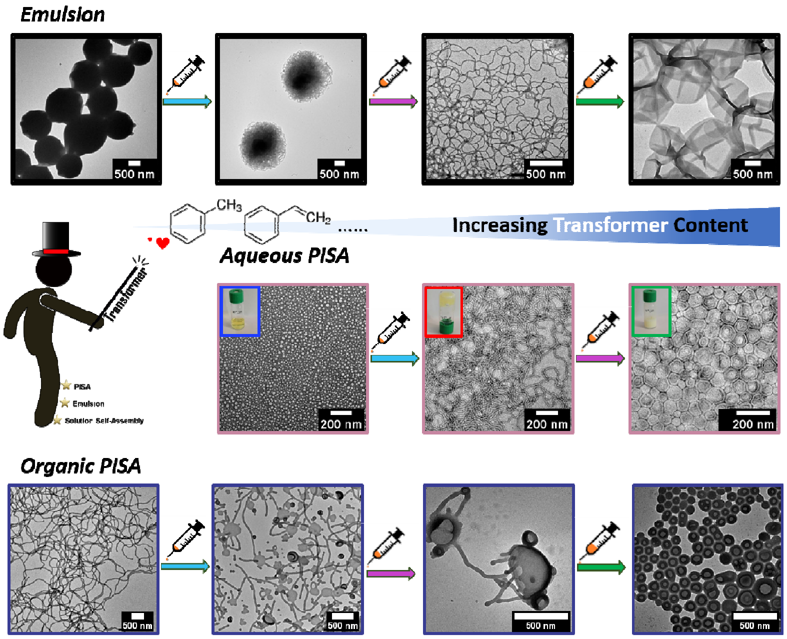

Figure 1: Transformer-Induced Metamorphosis of Polymeric Nanoparticle Shape at Room Temperature: application in nanoparticles obtained via emulsion polymerization, aqueous PISA and organic PISA

Keywords: Block-copolymers, Controlled radical polymerization, Solution polymer self-assembly, Polymeric nanoparticles, PISA, Emulsion polymerization, Morphological transformation

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Probing the Multifunctional Performance in ZnFe2O4/BaTiO3/Epoxy Resin Hybrid Nanocomposites

A. C. Patsidis[1*], S. Gioti[1], A. Sanida[1], G. Mathioudakis[2], G. C. Manika[1] Th. Speliotis[3], G. C. Psarras[1]

[1]*Smart Materials & Nanodielectrics Laboratory, Department of Materials Science, School of Natural Sciences, University of Patras, Patras 26504, Greece*
[2]*Institute of Chemical Engineering Sciences (ICE-HT), Foundation for Research & Technology-Hellas (FORTH), Stadiou Str., Platani, P.O.Box 1414, GR-26504 Patras, Greece*
[3]*Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", Aghia Paraskevi, Athens 15310, Greece*
**patsidis@upatras.gr*

Polymer matrix hybrid nanocomposites is a very promising class of materials for the development of multifunctional or even smart engineering systems. Multifunctional performance can be described or defined as the integration of various desirable and mutually supplementary properties in a single materials' system [1-4]. This system should respond autonomously under different loading conditions at service. Mechanical sustainability, suitable thermal response, tunable electric conductivity, variable electric polarization and dielectric permittivity, magnetic properties, thermally induced phase changes are parts of the overall multifunctional behaviour. Moreover, materials exhibiting smart performance are able to tune their behaviour responding to an external or internal stimulus. Certain properties of these systems can be varied in a controllable way, such as stiffness, shape, damping capacity, natural vibration frequency, polarization, conductivity, energy storing efficiency etc.

In the present study ceramic ferro-/piezo-electric ($BaTiO_3$) and ferromagnetic ($ZnFe_2O_4$) particles are embedded in a polymer matrix. Morphology, thermal properties, static and dynamic mechanical behaviour, dielectric response, conductivity, magnetic properties and induced multifunctionality are investigated by means of several experimental techniques. Furthermore, nanoinclusions are able to service as inherent nanocapacitors, where energy could be stored and retrieved. The ability for storing and retrieving energy is investigated under DC conditions and the efficiency of the process is evaluated via the coefficient of energy efficiency [5,6].

The physical properties of the employed reinforcing phases synergistically are exploited in the hybrid composites performance. Both phases contribute to the improvement of mechanical, thermal, dielectric properties, and energy storing/retrieving ability. Furthermore, barium titanate adds functional performance by its "molecular engine" and the transition from the polar ferroelectric phase to the non-polar paraelectric phase, inducing controllable polarization, while zinc ferrite induce magnetic properties.

Acknowledgments

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Development of innovative thermoplastic self-healing polymer blends for structural composites

D. Perin*, A. Dorigato, A. Pegoretti

Department of Industrial Engineering and INSTM Research Unit, University of Trento, Via Sommarive 9, 38123 Trento, Italy
**e-mail corresponding author: davide.perin-1@unitn.it*

The state of the art of self-healing technologies for the development of composites possessing self-healing properties are primarily attempting to mimic the healing mechanisms developed by nature [1]. However, self-healing materials are generally characterized by a limited technology readiness level [2]. In this work, a comprehensive characterization of novel intrinsic self-healing polymer blends, composed of a polyamide 6 (PA6) matrix and a cyclic olefinic copolymer (COC) was performed for the first time. The produced blends could be potentially used as matrices for multifunctional structural composites with self-healing capability. At this aim, PA6/COC blends at different relative contents were prepared by melt compounding and characterized from a microstructural, rheological, and thermo-mechanical point of view. Rheological measurements evidenced that the complex viscosity of the produced blends increased by increasing the COC content. From scanning electron microscope (SEM) micrographs, it was possible to highlight the immiscibility of all the prepared blends and the lack of interfacial adhesion between the constituents. The immiscibility of the produced blends was also confirmed by the differential scanning calorimetry (DSC) measurement. Consequently, upon COC addition the mechanical properties of the PA6 matrix slightly decreased. In particular, the elastic modulus decreased from 3.1 GPa to 2.5 GPa and the elongation at break from 9 % to 4 %, with a COC content of 30 wt%. In order to determine the healing efficiency of the system, the plane-strain fracture toughness of these blends was evaluated both in quasi-static and impact configurations. The presence of COC domains inside the PA6 slightly decreased the fracture toughness from 2.3 MPa $m^{1/2}$ of neat PA6 up to 2.1 MPa $m^{1/2}$ of PA6 with a COC amount of 30 wt%. The broken samples were then thermally healed at 140 °C (i.e., above the glass transition of COC) applying a pressure of 0.5 MPa. It was demonstrated that, thanks to the presence of the COC domains homogeneously distributed within the PA6 matrix, the blend containing 30 wt% of COC showed healing efficiency values up to 12 % in quasi-static mode and 41 % in impact mode. Hence, it can be concluded that the healing capability of the prepared blends was positively influenced by the immiscibility of the constituents, but also negatively affected by the lack of interfacial adhesion between COC domains and the PA6 matrix. Thus, different compatibilizers will be considered in the future to improve the mechanical properties of the COC/PA6 interphase between COC domains and PA6 matrix and the thermal mending capability of these blends.

Keywords: Thermoplastic, blends, self-healing, composites, multifunctionality.

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$SrFe_{12}O_{19}$/$BaTiO_3$/Epoxy Resin Hybrid Nanocomposites with Integrated Multi-Functionality

S. Gioti[1], A. Sanida[1], G. Mathioudakis[2], G. C. Manika[1], A. C. Patsidis[1], Th. Speliotis[3], G. C. Psarras[1*]

[1]*Smart Materials & Nanodielectrics Laboratory, Department of Materials Science, School of Natural Sciences, University of Patras, Patras 26504, Greece*
[2]*Institute of Chemical Engineering Sciences (ICE-HT), Foundation for Research & Technology-Hellas (FORTH), Stadiou Str., Platani, P.O.Box 1414, GR-26504 Patras, Greece*
[3]*Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", Aghia Paraskevi, Athens 15310, Greece*
[*]*G.C.Psarras@upatras.gr*

Materials exhibiting, in tandem, advanced structural/mechanical, thermal, electrical, and magnetic properties are required and welcomed in current and future high-tech applications. This class of materials should be able to respond with versatility to various environmental stimuli or signal controls. The key characteristic of these materials is not the nominal value of a specific mechanical or physical property (like Young's modulus, conductivity, magnetic permeability etc.), but their ability to execute functions/operations. Thus, functionality and even more multi-functionality is the major aspect. Multi-functional and adjustable performance cannot be found in monolithic materials and occurs in hybrid composites [1,2].

Functional materials represent a class of materials which can execute certain functions (operations) under the influence of an external (environmental) stimulus or sign control. Active dielectrics, such as piezoelectrics and ferroelectrics, are included in this category [3-5].

Multi-functionality is the combination of different desirable properties in a materials' system, which should exhibit all necessary responses under various loading conditions at service. Certain properties of these systems should be varied in a controllable way, such as stiffness, shape, damping capacity, natural vibration frequency, polarization, conductivity, energy storing efficiency etc. [6].

In this study hybrid nanocomposites are developed by embedding ferroelectric (BaTiO3) and magnetic (SrFe12O19) particles in an epoxy resin. By these means, multi-functionality is integrated since, besides the enhancement in mechanical, thermal, and dielectric properties, BaTiO3 particles induce variable polarization because of their ferroelectric to paraelectric transition and SrFe12O19 particles induce magnetic response [3-6]. In addition, embedded nanoparticles act as a distributed network of nanocapacitors where energy can be stored and retrieved. Optimum performance related to the synergy of the integrated physical mechanisms in the developed composites is analyzed and discussed.

Acknowledgments

The research work was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the "First Call for H.F.R.I. Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment grant" (Project Number:2850).

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Tailoring of novel benzoxazine-based thermosetting matrices incorporating carbonaceous particles for innovative broad-range pressure sensors

H. Puozzo^{1,2*}, L. Bonnaud^{2}, S. Saiev^{1}, D.Beljonne^{1}, R. Lazzaroni^{1}

[1]*Laboratory for Chemistry of Novel Materials (LCNM)*
[2]*Laboratory of Polymeric and Composite Materials (LPCM)*
Center of Innovation and Research in Materials & Polymers (CIRMAP-Materia Nova)
University of Mons (UMONS), 20 Place du Parc, B-7000 Mons, Belgium
**Hugo.PUOZZO@umons.ac.be*

In prosthetics and biomedical applications, the development of pressure sensors and, in particular, of electronic skin, is fundamental to the interfacing between human bodies and the outside world [1]. To mimic the tactile sensing properties of natural skin, one should develop large arrays of pixels, each one acting as an independent pressure detector supported on a flexible and stretchable substrate. This study investigates benzoxazines as the central platform for the matrix formulation.

Polybenzoxazines are a novel class of thermosetting phenolic resins that possess some unique features, namely regarding their thermomechanical performance and as high-performance polymers [2,3], and can be chemically tuned on purpose. Despite their outstanding characteristics, they are often intrinsically brittle and have been the subject of many investigations aiming at improving their toughness and flexibility [4]. Among others, two types of strategies have been successfully adopted, copolymerization between benzoxazine precursors and amines [5] and the incorporation of flexible segments in the resin precursors [6]. In the former case, it has been reported that amine functions can easily react with benzoxazine via ring-opening addition reactions. The benefits of this strategy are the possibility to decrease the curing temperature, to bring flexibility into the system and, consequently, to improve the material performance. In the latter case, the incorporation of flexible segments into the main chains prompts relatively high-molecular weight benzoxazine precursors that are liquid at room temperature and therefore easily processable into thin films [6]. These long chain benzoxazine may thus exhibit a combination of the thermoplatic and thermoset properties, such as flexibility, processability and crosslinking.

In the present work, a new trifunctional benzoxazine, named PtPA, was elaborated. After full curing, the resulting resin pPtPA exhibits a glass transition temperature (Tg) of about 127°C and a modulus (E') at room temperature of about 80 MPa as determined by dynamic mechanical analysis (DMA). To modulate these properties, the PtPA precursors were then copolymerized with different chain extenders that are amine-terminated, in particular Jeffamines®. At the same time, a molecular simulation was also carried out and confirmed the experimental values determined by DMA for all the developed systems. In addition, new benzoxazine precursors based on PDMS amine-terminated were also synthesized and evaluated. A Tg as low as -100°C and a E' below 1 MPa were obtained after full curing. These various benzoxazine precursors were then filled with carbonaceous particles in order to turn them into electrically conductive thermoset resins. We believe these newly developed materials are great promise for wide-range pressure sensing applications.

Keywords: benzoxazine, thermosets, carbonaceous particles, flexible matrices, pressure sensor

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Magnetorheological functional response of thermoplastic elastomers with different soft magnetic nanofillers

Carmen R Tubio[1], Ander García Díez[1], Ainara Gómez[2], Joanes Berastegi[2], M. Mounir Bou-Ali[2], Jon Gutiérrez Etxebarria[1,3]and Senentxu Lanceros-Mendez[1,4]

[1]BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940, Leioa, Spain
[2]Mechanical and Industrial Production Department, Faculty of Engineering, Mondragon University, Loramendi 4, 20500 Arrasate-Mondragón, Spain
[3]Faculty of Science and Technology, University of the Basque Country, 48080 Bilbao, Spain
[4]IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Spain
**Corresponding Author's carmen.rial@bcmaterials.net*

Magnetorheological elastomers (MREs) represent an increasingly requested class of magnetically responsive smart materials [1]. Developing MREs with a range of tailored properties is essential for the growing demands of a wide spectrum of applications in areas such as automotive, healthcare, sensors and actuators. Thermoplastic elastomers (TPEs) are a good candidates for the development of magnetorheological composites due to their ability to withstand large deformations, being flexible and even stretchable In addition, studies exploring the fabrication of MREs with nanosized fillers are still scarce [2], being most of the reports based on the use of micrometric fillers. Nevertheless, the use of nanoparticles can lead to advantages in terms on tuning of the magnetorheological response and processability by additive manufacturing technologies. In this work, novel MREs consisting of styrene-*b*-(ethylene-co-butylene)-*b*-styrene (SEBS) thermoplastic elastomer with different soft-magnetic nanofillers, including $CoFe_2O_4$, Fe_3O_4, Co, Ni, and $Ni_{80}Fe_{17}Mo_3$, have been developed. Their morphology, mechanical and thermal properties were tested and evaluated. Results were interpreted in view of the effect of particle type on the mophology variations, dispersion, degradation process, thermal stability and mechanical properties such as elastic modulus, and recovery under the applied stress. In addition, the MREs composites were characterized in terms of magnetic properties via vibrating sample magnetometer (VSM) and the rheological properties using oscillation tests under different magnetic fields. It s shown that magnetorheological (MR) effect can be tuned by properly selecting the magnetic filler, reaching values between 17% and of 8% for the Fe_3O_4 and $Ni_{80}Fe_{17}Mo_3$ composites, respectively. This study is relevant as it expands possibilities in designing advanced MREs-based devices with improved magneto-mechanical properties.

Keywords:
Smart materials, magnetorheological elastomer, magnetic properties,

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Water absorption and plasticization in non-isocyanate polyurethane – POSS hybrid networks

Konstantinos N. Raftopoulos[1*], Izabela Łukaszewska[1], Carlos Bujalance Calduch[1,2], Piotr Stachak[1], Sebastian Lalik[3], Edyta Hebda[1], Monika Marzec[3], and Krzysztof Pielichowski[1]

[1] *Department of Chemistry and Technology of Polymers, Cracow University of Technology, Kraków, Poland*
[2] *Departamento de Ingeniería Química y Nuclear, Universitat Politècnica de Valencia (UPV), Valencia, Spain*
[3] *Institute of Physics, Jagiellonian University, Kraków, Poland*
[*]*konstantinos.raftopoulos@pk.edu.pl*

The traditional route for the polyurethanes synthesis is based on diisocyanates, which suffer from certain drawbacks. Namely their synthesis involves the highly explosive and toxic phosgene, they tend to react with environmental moisture, and they are potentially toxic if not fully reacted. Moreover, the resulting polyurethanes are known for inferior hydrolytic stability [1]. For these reasons, isocyanate-free routes are sought for the production of polyurethane.

A promising approach is the reaction between amine and five membered cyclic carbonate groups [2]. This actually results in a hydroxyurethane linkage, i.e. a urethane group accompanied by a hydroxyl group attached on a nearby carbon atom. This is the route we used in this work, to sythesize a poly(hydroxy urethane) network based on an oligomeric poly(propylene oxide) diamine, putrescine, and a trifunctional cyclic carbonate. The matrix was reinforced by chemical incorporation of polyhedral oligomeric silsesquioxanes (POSS) on the basis of standard epoxy chemistry, using two architectures: 1) POSS with 3 epoxy groups, able to react with amine, substituted part of the tri-functional carbonate, giving a network topology similar to the matrix and 2) POSS moieties with only one epoxy functionality providing a "looser" network. For low POSS contents (5 wt%) the changes in topology were reflected on the glass transition of dry materials. Both differential scanning calorimetry and dielectric spectroscopy showed that mobility slowed down in the network reinforced with tri-functional POSS. In the "loosened" network, a marked decrease in fragility of the dynamic glass transition (α relaxation) leads to an interesting situation where calorimetric T_g drops with increasing POSS content while α relaxation slows down in the frequency range covered by the experiment.

The materials were conditioned at varying levels of environmental relative humidity, from 0 to 98%, and their water uptake and glass transition temperature were recorded. It was found that the materials are significantly more hydrophilic than conventional polyurethanes, with the matrix absorbing ~65 wt% (per dry mass) of water at 97% relative humidity. The absorbed water causes a marked plasticization effect, with glass transition temperature dropping by ~80 K from 0 to 97% relative humidity. Both POSS inhibit water uptake to some extent albeit in a non monotonic way. As a result, the plasticization is also inhibited; however, this is not the only influence of POSS on plasticization, but more phenomena should be considered.

Keywords: Non-Isocyanate PU, POSS, glass transition, plasticization, DSC, dielectric spectroscopy.

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Investigation of the Effect of Magnesium Salts with Chaotropic Anions on the Swelling Behavior of PNIPMAM Thin Films

J. Reitenbach[1*], C. Geiger[1], P. Wang[1], A. Vagias[2], R. Cubitt[3], D. Schanzenbach[4], A. Laschewsky[4], C. M. Papadakis[5], P. Müller-Buschbaum[1,2]

[1]Lehrstuhl für Funktionelle Materialien, Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany
[2]Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstr. 1, 85748 Garching, Germany
[3]Institut Laue-Langevin, 71 Avenue des Martyrs, CS 20156, 38042 Grenoble Cedex 9, France
[4]Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany
[5]Physik weicher Materie, , Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany
julija.reitenbach@ph.tum.de

Thermoresponsive polymer thin films have gained a lot of attention in the past decades due to their attractiveness for a wide range of applications. A variety of polymers showing LCST- or UCST-type behavior are known, and their transition temperatures can be influenced by various factors such as molar mass, end groups, copolymerization, or by the addition of salts. For polymers in aqueous solution, it is shown that the folding of the polymer chains can be strongly influenced by the type of salt. This observation follows a trend called the Hofmeister series, which is generally more pronounced for anions than for cations. Until today the origin of the empirically found Hofmeister series is still under debate. It remains an open question, whether the effect can be attributed solely to intrinsic properties of the ions themselves, or is of more complex nature, also affected by interactions between the ions and their surrounding environment, i.e., the solvent and macromolecules, such as polymers and proteins.

To further elucidate the effect of Hofmeister salts, we investigate thin films of poly(*N*-isopropyl methacrylamide) (PNIPMAM) with different magnesium salts ($Mg(ClO_4)_2$ and $Mg(NO_3)_2$) within a water atmosphere at a constant temperature. The advantage of thin films compared to polymers in solution or in bulk is that a certain mechanical stability is given, with only little loss in responsiveness of the system. [1,2] However, the complexity of the system is further increased for thin films due to their interactions at the interfaces. Via *in situ* time-of-flight neutron reflectometry (ToF-NR) measurements the swelling behavior of the thin films are investigated on a macroscopic level, where it is found, that the different salts have a significant impact on the swelling behavior. To gain further insights on a molecular level, additional *in situ* Fourier-transform infrared spectroscopy (FTIR) measurements are performed. It is observed, that the type of salt highly affects the hydration around functional groups and therefore the swelling behavior of PNIPMAM thin films.

Keywords: Thin Films, PNIPMAM, Hofmeister salts, ToF-NR, FTIR

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New Organophilic Montmorillonites with Lactic Acid Oligomers and Other Environmentally Friendly Compounds

K. Rucińska[1]*, Z. Florjańczyk[2], M. Dębowski[2], T. Gołofit[2], R. Malinowski[1]

[1]Łukasiewicz Research Network—Institute for Engineering of Polymer Materials and Dyes, Toruń, Poland
[2] Faculty of Chemistry, Warsaw University of Technology, Warsaw, Poland
** katarzyna.rucinska@impib.lukasiewicz.gov.pl*

The aim of this study was to find new greener ways to modify montmorillonite (Mt). Mt belongs to a group of natural aluminosilicates with a 2:1 layered structure. Montmorillonite is characterized by high water absorption – it can absorb five times more water than it weighs, simultaneously increasing its volume up to fifteen times . The interlayer spacing of Mt can be modified by introducing different cations or molecules into its structure. Different inorganic cations (acting as catalytic layer precursors), or organic cations (*e.g.*, those derived from quaternary ammonium salts) can be easily incorporated between the Mt layers thus altering the properties of the macroscopic material. The stability of organophilized montmorillonite can be improved, other types of organic cations *e.g.*, phosphonium, imidazolium, or arylammonium cations. The resulting materials have been extensively tested and are used as components of polymer composites.

New organophilic montmorillonites containing oligomers of lactic acid and other compounds, such as citric acid, stearic acid, maleic anhydride, pentaerythritol and ε-caprolactone, were synthesized and characterized. These materials were characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and elemental analysis, whereas their swelling capacity was also measured in water. In all tested samples, an increase in the Mt interlayer distance by *ca.* 12,8–20,1 Å resulting from intercalation of the modifying substance was found by means of XRD. Elemental and FTIR analyses showed that all of the tested samples contained an organic segment in the Mt structure. TGA showed that Mt modified with lactic acid oligomers, stearic acid or ε-caprolactone had the highest thermal stability. The lowest swelling capacity was observed in the samples modified with a lactic acid oligomer, stearic acid or ε-caprolactone, and these values were 2-3 times lower than that for the unmodified sodium Mt.

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Chitosan/Graphene Oxide Aerogels for Broad-Spectrum Water Remediation

Martina Salzano de Luna[1*], Chiara Santillo[2], Marino Lavorgna[2]

[1]*Department of Chemical, Materials and Production Engineering, University of Naples Federico II, Piazzale V. Tecchio 80, 80125 Naples, Italy.*
[2]*Institute for Polymers, Composites and Biomaterials, National Research Council of Italy, Piazzale E. Fermi 1, 80055 Portici, Italy.*
[*]*martina.salzanodeluna@unina.it*

Biopolymers are often regarded as promising materials for water purification purposes. The reason is that they possess many and different functional groups that can potentially interact with pollutant species in water [1]. Nonetheless, most of the developed adsorbents are able to target only one contaminant (or one class of contaminants) at a time. Since in real conditions many different contaminants occur simultaneously on a regular basis, novel approaches must be pursued to design adsorbent materials able to simultaneously remove different contaminants. We focus on chitosan (CS)-based adsorbents which have been largely studied for water purification from heavy metal ions and anionic organic pollutants but possess low effectiveness towards cationic species because of adverse electrostatic interaction. We addressed this issue by adding a second phase with complementary adsorption capacity, namely graphene oxide (GO). GO nanosheets, indeed, have epoxy, hydroxyl and carboxyl groups on the basal planes and at the edges that can bind cationic compounds via electrostatic interactions. In particular, we developed nanocomposite CS/GO aerogels by freeze casting. Aim of this study is demonstrating how each step of the preparation procedure has to be carefully controlled to maximize the final performances [2]. In particular, we focused on the freezing protocol of CS/GO mixtures and the chemical crosslinking step to tailor the material microstructure and, through it, the properties of the nanocomposite aerogels (Figure 1). The adsorption behaviour of the optimized CS/GO aerogels was investigated through batch experiments, and the broad-spectrum adsorption capacity was assessed by using different kinds of model pollutant molecules.

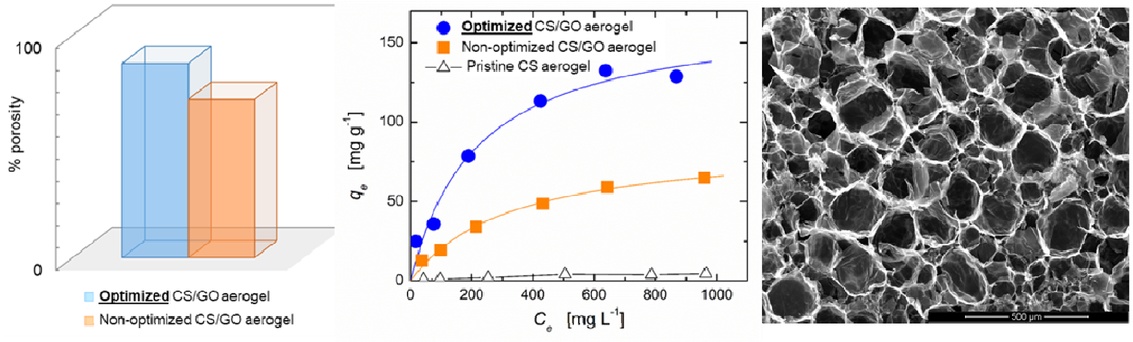

Figure 1. Percentage porosity (left) and adsorption isotherms with methylene blue dye (centre) for optimized and non-optimized CS/GO aerogels. A representative SEM image of an aerogel sample is shown on the right.

Keywords: chitosan, aerogel, adsorption, graphene oxide, crosslinking, microstructure

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Preparation of linear, Y- and Ψ-shaped polymer brushes via surface-initiated polymerization

Sabrina Sant and Harm-Anton Klok*

Institut des Matériaux et Institut des Sciences et Ingénierie Chimiques, Laboratoire des Polymères, École Polytechnique Fédérale de Lausanne (EPFL), Bâtiment MXD, Station 12, 1015 Lausanne, Switzerland
**harm-anton.klok@epfl.ch*

Surface-initiated controlled radical polymerization (SI-CRP) has become an efficient tool for the preparation of polymer brushes to modify the underlying surface properties. Polymer brushes are defined as an assembly of individual polymer chains tethered by one chain end to a solid substrate. Preparing polymer brushes by SI-CRP gives control over their molecular weight, functionality and even architecture.[1][2] In this work, surface-initiated atom transfer radical polymerization (SI-ATRP) was used to extend the polymer brush architecture from linear brushes to Y- and Ψ-shaped brushes, with the polymer chains originating from a single focal point. This was achieved with the use of a homologous series of ATRP initiators. This work aims to demonstrate the simplicity to prepare these architectures by comparing the different initiator systems and efficiency in preparing both hydrophilic and hydrophobic polymer brushes and show how these different brush architectures can be characterized.

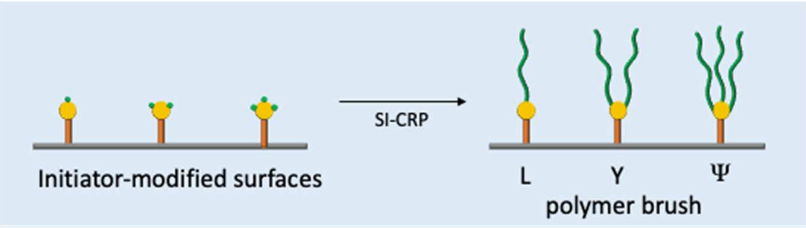

Figure 1: Illustrative strategy to prepare linear, Y- and Ψ-shaped polymer brushes.

Keywords: Polymer brushes, Surface-initiated polymerization, Thin films

Acknowledgments
This work was financially supported by the Swiss National Science Foundation (SNSF) through the National Center of Competence in Research (NCCR) Bio-Inspired Materials.

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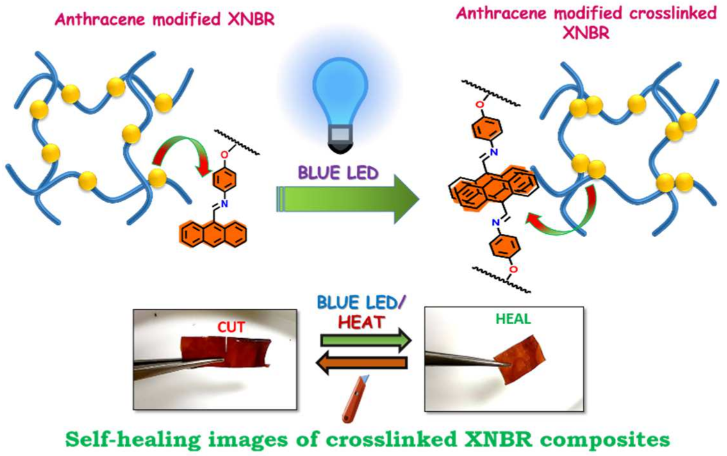
Visible-Light Responsive Self-Healable Nitrile Rubber via Non-Covalent Reversible Chemistry

Shrabana Sarkar[1], Nikhil K. Singha[1,2]*
[1]Rubber Technology Centre, Indian Institute of Technology, Kharagpur, India.
[2]School of Nanoscience and Technology, Indian Institute of Technology, Kharagpur, India.
*Email: nks@rtc.iitkgp.ac.in

The introduction of the self-healing property in the commercially available elastomers promotes the development of high-end elastomeric products with an extended lifespan and economic viability. Typically elastomers are crosslinked via chemical (by sulfur or peroxides) or UV curing processes. Interestingly, the introduction of a visible-light curing system into the elastomers will be an alternative eco-friendly route. In this case, carboxylated nitrile rubber (XNBR) [1] has been modified with light-sensitive benzylimine-functionalized anthracene (BIFA) moiety [2]. This BIFA modified XNBR undergoes crosslinking via dimerization of functionalized anthracene moiety through π-π interactions in the presence of blue LED light. The anthracene dimers undergo de-dimerization upon the thermal heating (> 130˚C) and re-conjugated with light treatment. This non-covalent reversible crosslinking provides self-healing property in the modified elastomer, as evidenced by different microscopic (optical, SEM, AFM) and mechanical analysis. Additionally, when reinforcing amine-modified nano-silica is mixed with the BIFA modified XNBR, it leads to tunable mechanical properties along with reasonable self-healing properties. This kind of modified elastomers will have potential applications in actuators, Janus material, 3D objects, etc.



A graphical depiction of reversible crosslinking in modified nitrile rubber in presence of blue light

Keywords: Anthracene, visible light, self-healing elastomer

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Water and gas transport properties of polyolefin-zeolite composites prepared by melt blending: Influence of the zeolite type and composites morphology

A. Sexton[1-2*], F. Gouanvé[1], M. Williams[2], R. de la Brosse[2], E. Espuche[1]

[1]Université Claude Bernard Lyon 1, Ingénierie des matériaux polymères UMR 5223, Villeurbanne 69622, France
[2]ADHEX, 44 Rue de Longvic, 21300 Chenôve, France
[*] *alexane.sexton@univ-lyon1.fr*

Inorganic porous fillers like zeolite can be added into polymer matrix to develop composites with controled water and gas (CO_2, O_2, He, N_2) transport properties for specific applications. Solvent cast process is generally used to prepare such materials [1]. However, from the industrial point of view, the use of organic solvents makes this technique environmentally unfriendly and technically less preferable than melt blending process. Thereby the present work aims at investigating the effect of adding two types of zeolite in a polypropylene-ethylene (PP-PE) copolymer by using melt blending process. Hydrophilic zeolite 13X and hydrophobic zeolite H^+ ZSM were selected for their pore size larger than molecular diameter of the largest studied gas.
The inorganic fillers were sucessfully incorporated by melt process into PP-PE matrix with content up to 36 % and 29 % vol. for zeolite 13X and zeolite H^+ ZSM, respectively. Defect-free hybrid films with homogeneous particle distribution were obtained. The impact of zeolite adding on the copolymer microstructure and chain mobility was investigated. Moreover detailed analysis of gas permeability, water permeability and water sorption properties were performed.
The addition of zeolite into the hydrophobic matrix led to a significant enhancement of water permeability, independently of the zeolite's nature (Figure A). On the other hand, large pore size 13X zeolite led to a slight decrease in gas permeability, while an increase of gas permeability was obtained in the presence of smaller pore size H^+ ZSM zeolite (illustrated with O_2 in Figure B). The adequacy between the experimental transport properties values and the theoretical ones, determined from Maxwell law, was discussed in the light of the composites microstructures, morphologies and of the accessibility of the zeolite porous structure for the different penetrants.

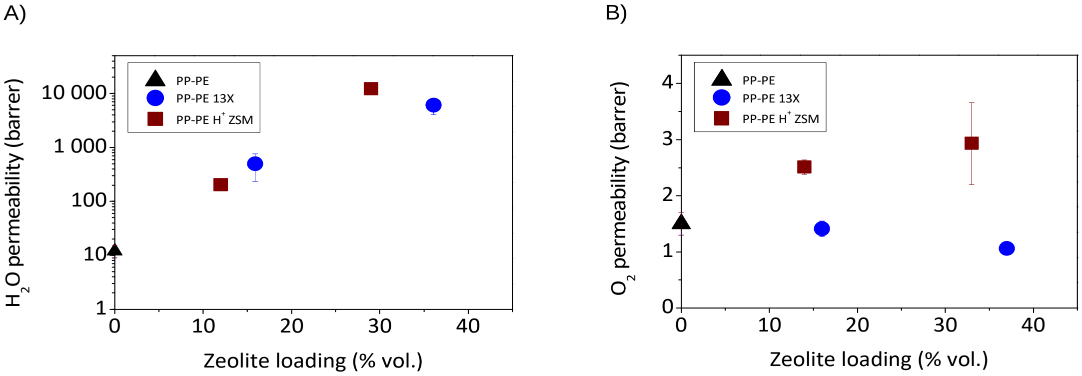

Fig. Zeolite loading influence on A) liquid water permeability and B) O_2 permeability of PP-PE matrix, PP-PE 13X and PP-PE H^+ ZSM zeolite.

Keywords: zeolite composite, gas permeability, vapor water sorption.

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Shape-Memory Materials based on Elastomer-Thermoplastic-Blends

R. Pommer[1,2], R. Saf[1], R. Supplit[3], A. Holzner[3], G. Trimmel[1*]

[1]*Institute for Chemistry and Technology of Materials, Graz University of Technology, Graz, Austria*
[2]*Polymer Competence Center Leoben GmbH, Leoben, Austria*
[3]*Semperit Technische Produkte GmbH, Wimpassing, Austria*
[*]*gregor.trimmel@tugraz.at*

Shape-memory polymers (SMPs) are stimuli-responsive materials which have the ability to recover from one or more temporary shape deformations into a predetermined, permanent configuration upon exposure to external triggers. This phenomenon is referred to as shape-memory effect (SME). Triggers can include temperature, electricity, magnetism, light or solvents. Development of SMPs has recently been driven by potential applications in numerous fields, such as construction, aerospace industry, soft robotics or biomedical devices.[1, 2] Polymer blending not only allows for the combination of favorable features of different raw materials, but also enables the cost-effective and convenient fabrication of material systems exhibiting shape-memory behavior.[3]

The present work deals with the investigation of thermo-responsive SMPs based on immiscible blends of ethylene-propylene-diene monomer rubber (EPDM) with a range of different thermoplastic materials (HDPE, PP, PP-c-PE and ULDPE).

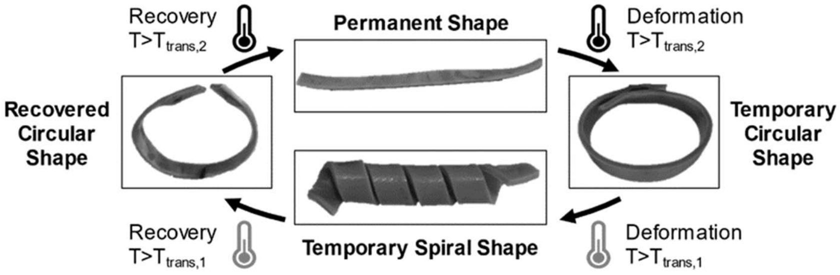

Figure 1. Triple-shape-memory cycle.

Rheological measurements and tensile tests were applied to determine cure characteristics and mechanical properties respectively. Dynamic-mechanical thermal analysis (DMTA) was utilized to comprehensively investigate thermo-mechanical features and to quantify the shape-memory effect of different processed elastomer-thermoplastic-blends. Moreover, morphological studies were carried out using atomic force microscopy (AFM). The results indicate strong temperature-dependency and tunability of shape-memory behavior by the choice of raw materials and variation of the blend ratio. Thermo-responsive triple- and multi-shape-memory behavior of selected systems was demonstrated and studied additionally.

Keywords: shape-memory polymers (SMP), functional materials, polymer blends, thermomechanical properties, multi-shape memory

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Robust self-lubricating poly(urea-formaldehyde) microcapsules designed for thermal spaying coating applications

C. Zotiadis[1], J. Patrikalos[2], D. M. Korres[1], I. Georgiopoulos[2], Ch. Sarafoglou[3], S. Vouyiouka[1]*

[1]*Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens, 157 80, Greece,* * mvuyiuka@central.ntua.gr
[2] *MIRTEC S.A., Thiva Branch, 72nd km of Athens-Lamia National Road, 34100, Chalkida, Greece.*
[3]*Shipbuilding Technology Laboratory, School of Naval Architecture and Marine Engineering, National Technical University of Athens, Zographou Campus, Athens, 157 80, Greece.*

Traditional lubricating methods are limited by working conditions, physical and chemical characteristics and durability over extended periods of usage in severe environments. New smart materials need to be developed in order to increase effectiveness and stability of lubrication, improving reliability and lifetime of manufactured products, also reducing wastes of natural resources and energy. Introducing microcapsules (MCs) containing lubricant into the surface of moving parts, significantly improves anti-friction properties and wear resistance. When the surface is subjected to friction, MCs are ruptured and the encapsulated lubricants are released, forming a boundary lubrication film that significantly reduces the friction coefficient and wear rate[1]. The aim of the current work is to produce poly(urea-formaldehyde) microcapsules (PUF MCs) with an encapsulated lubricating oil to be used in metal coating produced *via* thermal spraying. PUF MCs preparation was carried out by one stage *in situ* polymerization in an oil-water emulsion[2,3]. Key process parameters i.e. core to wall mass ratio and agitation rate were studied in respect to microcapsule characteristics. Spherical microcapsules were obtained as free-flowing white powder with a mean diameter from 57 to 88 μm, high encapsulation efficiency (up to 79 %) and increased thermal stability (onset of degradation $T_{d5\%}$ > 210 °C, maximum of thermal degradation T_d >340°C).

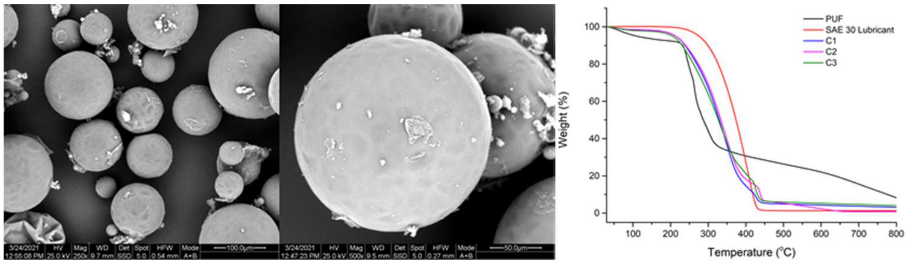

Figure 1: SEM images and TGA graph of microcapsule samples

Keywords: poly(urea-formaldehyde), microcapsules, *in situ* polymerization, self-lubrication

Acknowledgments

This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T2EDK-01883)

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Partnership Agreement
2014 - 2020

Co-financed by Greece and the European Union

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Surface Modification of Cellulose Nanocrystal (CNC) and its Dispersion in PLA matrix

Onur Nuri Arslan[1], Dilara Güntürkün[2], Burcu Özdemir[1], Aylin Bekem[3], Yonca Alkan Göksu[1], M.Reza Nofar[1*]

[1]*Sustainable & Green Plastics Laboratory, Metallurgical & Materials Engineering Department, Faculty of Chemical and Metallurgical Engineering, Istanbul Technical University, Istanbul, Turkey*

[2] *Chemistry Department, Faculty of Science and Letters,Istanbul Technical University, Istanbul, Turkey*

[3]*Metallurgical & Materials Engineering Department, Faculty of Chemical and Metallurgical Engineering, Yıldız Technical University, Istanbul, Turkey*

[*]*Corresponding Author's E-mail address : nofar@itu.edu.tr*

Increasing production and consumption of petroleum-based polymer materials around the world has led researchers towards materials with less environmental impact. Polylactic acid (PLA) is a linear aliphatic biodegradable polyester that could be obtained from natural sources. PLA is a good alternative to petroleum-based polymers that are used in many different applications. However, PLA's low melt strength and slow crytallization rate should be enhanced to increase its processability for industrial applications [1]. Among the methods used for this purpose, nanocomposites obtained by adding various nanofillers into the polymer matrix are of great importance. Cellulose nanocrystals (CNC) are biobased, biocompatible and biodegredable nanomaterials that are obtained from lignocellulosic biomass. Due to its promising features such as widespread availability in nature, low density compared to other nanoparticles, high surface area, tailorable chemical reactivity, superior mechanical and physical behavior, CNC has gained significant attention as a nanofiller for various biopolymers [2]. However, due to CNC's highly hydrophilic nature, its dispersion in hydrophobic polymers is challenging. During melt extrusion processes, CNC molecules tend to agglomerate and reduce the final mechanical properties of the matrix polymer. In order to reduce this agglomeration, CNC surface should be modified with hydrophobic molecules that could still have an interphase interaction with the matrix [3]. In this study, glycidyl methacrylate (GMA) was polymerized on CNC surface through "grafting from" technique with different monomer concentrations. Effect of poli(glycidyl methacrylate) (PGMA) chain length on the surface hydrophilicity of CNC was examined. PLA/CNC-g-PGMA nanocomposites with different CNC-g-PGMA concentrations (i.e, 1, 2 and 3 wt%) were prepared through melt mixing method. Obtained nanocomposites were examined through small amplitude oscillatory shear (SAOS) rheological analysis. The addition of CNC-g-PGMA as nanofiller in PLA matrix resulted in enhanced rheological properties. Therefore, the processability and mechanical behavior of PLA could be improved within the incorporation of surface-modified CNC.

Keywords: PLA, CNC, Surface Modification, Nanocomposites

Acknowledgments

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Surface modification of cellulose nanocrystals with benzoic acid anhydride and composites with polystyrene matrix

Alojz Anžlovar[1], Andraž Krajnc[2] and Ema Žagar[1]

[1]*Department of Polymer Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, SI-1000, Ljubljana, Slovenia*
[2]*Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia*

Recently, cellulose nanocrystals (CNC) have attracted attention of the scientific community as they are highly interesting bio-nanostructures with promising reinforcement potential in various polymer matrices. CNC are polar structures with a high concentration of surface hydroxyl groups. The surface energy characteristics of CNC need to be tuned by chemical modification to improve their compatibility with hydrophobic polymer matrices [1]. The main challenge in modifying CNC is to perform the process only on the particle surface to maintain the integrity of CNC [1]. Impressive mechanical properties of CNC make them very attractive as reinforcing nanofiller. Polystyrene (PS) is a widely used commodity polymer with an attractive price, but also with rather unsatisfactory mechanical properties. Therefore, the goal of our study was to evaluate the reinforcement potential of surface-modified CNC by preparation of PS/CNC nanocomposites. To this end, we developed and optimized the surface modification reaction of CNC with benzoic acid anhydride (BzAnh) and further the melt processing procedure to produce homogeneous PS/CNC nanocomposites with improved mechanical properties.

The CNC were surface modified with BzAnh at room temperature in a reaction time of 48 h [2]. FTIR spectroscopy confirmed the high degree of modification of CNC with BzAnh, while ^{13}C CP MAS NMR showed that the total degree of hydroxyl group modification was 16%, indicating that the degree of surface modification of CNC was very high (35 - 50%) [2]. 2D ^{1}H-^{13}C CP-HETCOR MAS NMR and ^{13}C-detected proton spin-diffusion (PSD) experiments confirmed that BzAnh reacted mainly with –CH$_2$–OH groups in the amorphous regions of CNC nanocrystals. Unmodified and BzAnh-modified CNC were used to produce nanocomposites with PS by melt processing at 200 °C. Tensile tests showed that the addition of BzAnh-modified CNC increased the stiffness and tensile strength of PS/CNC composites, while unmodified CNC deteriorated them. Addition of 5 wt% CNC to PS resulted in a 30% improvement in tensile strength and a 23% increase in stiffness [2]. The increased compatibility and improved mechanical properties of BzAnh-modified CNC were attributed to the intense entanglement of PS chains and CNC due to π–π interactions between benzene rings on PS chains and those on BzAnh-modified CNC, as shown in Fig. 1 [2].

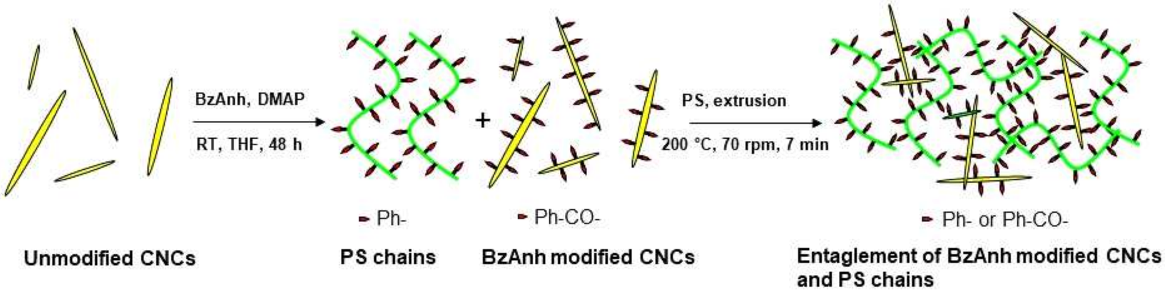

Figure 1 Schematic presentation of percolating network formation of CNC, surface modified with BzAnh, and their interaction with PS chains via π–π interactions [2]

Keywords: cellulose nanocrystals, surface modification, polystyrene, nanocomposites, melt processing

Acknowledgements *The authors acknowledge the financial support from the Slovenian Research Agency (Research Core Fundings No. P2-0145 and P1-0021).*

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HEXAGONAL BORON NITRIDE BASED MEMBRANE ARCHITECTURES FOR NANOFILTRATION

Sankeerthana Avasarala[1], Priyanka Goyal[1], Suryasarathi Bose[1*]

[1]*Department of Materials Engineering, Indian Institute of Science, Bengaluru, India, 560012*
[*]*sbose@iisc.ac.in*

Thin film composite membranes have been the state-of-the-art desalination membranes for the last few decades, but they have certain shortcomings. These disintegrate in the presence of chlorine, are highly prone to fouling, and require very high operating pressures for desalination, which even then is a very slow process. This necessitates that we look for alternative materials and membrane achitectures. Here, hexagonal Boron Nitride(hBN) sheets have been incorporated into the polymeric membrane architectures in the nanofiltration regime, to enhance the desalination performance, as well as the dye rejection, and anti-fouling performance. These membranes exploit the stability of hBN in water unlike graphene oxide, the small d-spacing, and its stable and non-toxic nature. hBN sheets have been modified and added to a polymer matrix to fabricate mixed matrix membranes. hBN sheets have been modified and deposited on a substrate as well, by utilising cross-linking agents, to use the spacing between the sheets as selective channels. Hybrid composites of hBN sheets with other nanomaterials have also been prepared to impart functionality to the active separating layer of hBN on a membranes substrate. These membranes have shown promising results for dye and salt rejection. These membranes can serve as stand-alone nanofiltration membranes or as a potential pre-filter for thin film composite membranes, thereby increasing the life of thin film composite membranes.

Keywords: hexagonal boron nitride, desalination, dye rejection, thin film composites, mixed matrix membranes.

Stretchable hydrogels from the polyelectrolyte association of hyaluronic acid and chitosan

M. Balima[1*], G. Sudre[1], A. Montembault[1]

[1] *University of Lyon, University Claude Bernard Lyon 1, CNRS, Ingénierie des Matériaux Polymères, IMP UMR 5223, F – 69622 Villeurbanne Cedex, France.*
**maeva.balima@univ-lyon1.fr*

Chitosan (CS), the only cationic polysaccharide, exhibits interesting biological properties, such as biocompatibility, biodegradability, antibacterial activity... These properties make it suitable for the development of biomedical materials. CS can interact with hyaluronic acid (HYA), an anionic biopolymer, through electrostatic interactions and form polyelectrolyte complex (PEC) hydrogels. The polyelectrolyte association of these two natural polymers at low pH (pH around 2 close to the pK_a of HYA) allows to obtain highly stretchable materials, which is quite surprising for such materials. The stretchability of these hydrogels results from a multi-scale organization revealed by SAXS at low pH: folded HYA chains able to undergo large deformation through rupture of hydrogen bonds between HYA chains, and solid-like PEC aggregates acting as physical crosslink nodes of this elastic network[1]. The aim of this work is to develop a same kind of hydrogels but obtained at neutral pH. Thus, homogeneous mixtures of high molar mass chitosan (600 kg/mol) and low molar mass hyaluronic acid (70 kg/mol) aqueous solutions were prepared with an excess of NaCl to screen the electrostatic interactions between the polysaccharides. Then, the association of the oppositely charged polyelectrolytes was triggered by desalting through dialysis in a controlled manner. Dialysis baths containing sodium acetate were performed close to physiological pH. The chain conformation in solution, the self-assembly of the polyelectrolytes, and the nanostructure of the resulting hydrogels, can be tuned by intrinsic (degree of acetylation (DA) of chitosan[2]) and extrinsic parameters (charge ratio $r = n_{-}(\mathrm{HYA})/n_{+}(\mathrm{CS})$, pH of the dialysis bath, concentration of sodium acetate). We obtained different types of materials depending on the concentration of sodium acetate in the dialysis bath. These materials were analyzed by rheological measurements and tensile tests: systems with mechanical properties similar to viscoelastic materials at high concentration of sodium acetate, and stretchable hydrogels at lower concentration with mechanical properties depending on the charge ratio *r*. The spinning of the formulations giving the most stretchable hydrogels could be then tested in order to obtain fibers with high mechanical properties.

Keywords: *chitosan, hyaluronic acid, polyelectrolyte complexes, hydrogel, stretchability*

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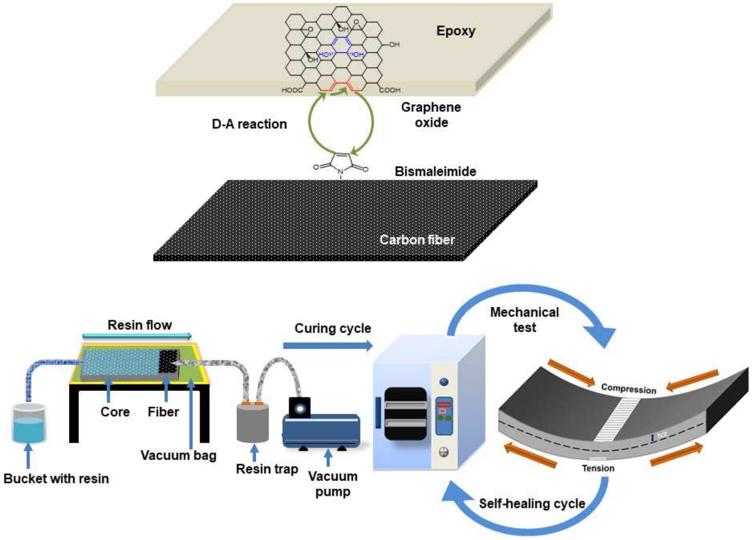
Thermoreversible Bonds and Graphene Oxide Additives Enhance the Flexural and Interlaminar Shear Strength of Self-Healing Epoxy/Carbon Fiber Laminates

Poulami Banerjee[1], S. Kumar[1]*, and Suryasarathi Bose[1]*
Department of Materials Engineering, Indian Institute of Science, Bangalore - 560012, India

Abstract:

In the current era of high strength, lightweight, and durable aircraft components, the need for carbon fiber reinforced epoxy (CFRE) laminates is highly desired owing to their high specific strength and modulus, low coefficient of thermal expansion, and tunable properties that are unmatched by other materials. However, such components' catastrophic failure occurs due to the interfacial defects and debonding, thereby reducing service life and economic viability. Therefore, there is a pressing need to enhance the mechanical properties of CFREs through matrix and fiber modifications and introduce the components' self-healing ability under a natural trigger. This study assessed the crucial role of 'thermoreversible bonds' and graphene oxide (GO) 'interconnects, which worked in tandem towards improving the interface in epoxy-based CFRE laminates. The laminates are fabricated with varying percentages of GO modified epoxy matrix (GO/CFRE) via vacuum-assisted resin transfer molding (VARTM) method. The carbon fibers were covalently modified with bis-maleimide to establish a thermo-reversible bond with the GO at the fiber-matrix interface to yield in 'interconnects'. Flexural and ILSS values for the optimized GO-modified epoxy laminates with bis-maleimide deposited carbon fibers showed a significant increase by 29.8% and 40.1%, respectively. After a self-healing cycle triggered at 60°C, they exhibited a recovery in their ILSS values up to 71%.



Keywords: Carbon fiber, Epoxy, Graphene oxide, Interface, Thermo-reversible bonds, Self-healing

Features influence of magnetic field on the structure and properties of polymer materials with metal oxides

Yuliia Bardadym

Institute of Macromolecular Chemistry of the NAS of Ukraine, Kyiv, Ukraine
yuliia.bardadym@gmail.com

Epoxy resins, an important class of thermosets, have been deeply rooted in almost everything both in industry and in our daily lives. They have excellent dimensional stability, thermal stability mechanical strength, creep resistance, electrical insulation and chemical resistance [1]. Polymer modifications are intended to impute different, typically desired properties to the new modified material properties such as enhanced thermal stability, strength, ductility, compatibility or degradability, flexibility, rigidity, melting and glass-transition temperatures etc. Physical modification is a directed change in the physical properties of polymers carried out by the transformation of their supramolecular structure under the influence of physical influences. Physical modification of polymers arises under the influence of various force fields (mechanical, electrical, magnetic, etc.). The present work aims to explore the influence of the external permanent magnetic field on the structure, thermophysical, dielectric properties of epoxy polymers and their composites with metal oxides [2].

Samples of nanocomposites were formed from epoxy resin ED-20 and triethylenetetramine. Stoichiometric ratio was 1 mole of epoxy resin to 0,18 mole triethylenetetramine. Powder CdO, PbO, Cr_2O_3 were used as fillers. The content of metal oxide was 3 vol. %. Samples of nanocomposites were subjected to curing with different conditions. The influence of constant magnetic field was $2{\cdot}10^5$ A/m. All curing processes were done at 293 – 297 K for 24 hours. Then all polymeric samples were carried out temperature stabilization at 333 ± 2 K for 24 hours. Studies of the structure, thermophysical, thermomechanical and dielectric properties of composites filled with diamagnetic or paramagnetic metal oxides formed under the influence of external constant physical field were carried.

Studies of the specific heat capacity of epoxy polymers and their composites depending on the composition and curing conditions have been carried out. In this case, the introduction of fillers into the composition of the epoxy composite contributes to a decrease in the specific heat and an increase in the glass transition temperature for the studied composites. This is explained by an increase in the packing density macrochains and free volume of epoxy polymer (EP). The glass transition temperature increases by 5 K for samples containing CdO, PbO and Cr_2O_3, and decreases by 15 K for samples filled with cadmium oxide and by 7 K for samples containing CdO.

The introduction of fillers causes an increase in dynamic modulus of elasticity, but a slight decline after the influence of constant physical field. As a result of the use of constant physical field allows to change the relative deformation of the studied filled epoxy composite materials from 5% to 15%.

For samples of EP – CdO, which was formed under the action of constant physical fields, are decrease in the destruction temperature by 50 K, the total amount of gaseous products recorded in the mass spectrum to 87 units and 18% of the total ion current. However, EP – PbO is characterized by an increase in the temperature of decomposition maxima and up to 13.8% of the total ion current. The impact of physical field on the EC - Cr_2O_3 provokes a decrease in the total ion current by 25%, the specific intensity of ion fragments up to 20%. The introduction of polyaniline into the composition of the filler leads to a significant decrease in the temperature of the maximum release of volatile components [3].

Keywords: magnetic filds, epoxy composite, oxides metals.

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Kraft Lignin and lignin-TiO_2 fillers used in rotational molded polyethylene containers

K.Bula [1*], D.Ajnbacher[1], Ł. Klapiszewski[2]

[1]*Institute of Materials Technology, Poznan University of Technology, Poznan, Poland*
[2]*Institute of Chemical Technology, Poznan University of Technology, Poznan, Poland*
[*]*Corresponding Author karol.bula@put.poznan.pl*

As a natural polymer, lignin has currently become a component with huge potential for adaptation in practical polymeric applications. Numerous advantages of lignin include, e.g., its low cost, UV-absorption, anti-oxidant activity, and capability of polymer surface energy modification. Other benefits of this bio-filler compared to synthetic fibers and inorganic particles are related to its low abrasion against plasticizing units during melt processing and lower density in comparison to mineral powders [1–3].

In this study, TiO_2-lignin dual phase fillers with varying amounts of lignin as well as pristine Kratf lignin and titanium dioxide were used as fillers to increase the performance of linear low density polyethylene (LLDPE) containers. The main experimental procedure was focused on the preparation of rectangular containers using polyethylene and its composites with 2,5 and 5% by wt. of fillers: Kraft Lignin, TiO_2, TiO_2-lignin dual phase systems with varying amounts of lignin. The rotational moded temperature into the heated chamber was set as 250 °C, the rotation time in the oven was set as 25 min., cooling phase was divided into slow cooling and fast cooling (aided by cooling fans). Differential scanning calorimetry (DSC) was used to check the crystalline structure of the composites. Microscopic observations were used to verify the filler allocation on the crosscection of the container wall. The mechanical properties of the obtained samples were validated in the compression test (Zwick/Roell Z010 universal testing machine), where compressive strength, compressive strain were checked, according to ISO 604:2002 standard. Some of the samples behaviour during compression were illustrated on the fig 1.

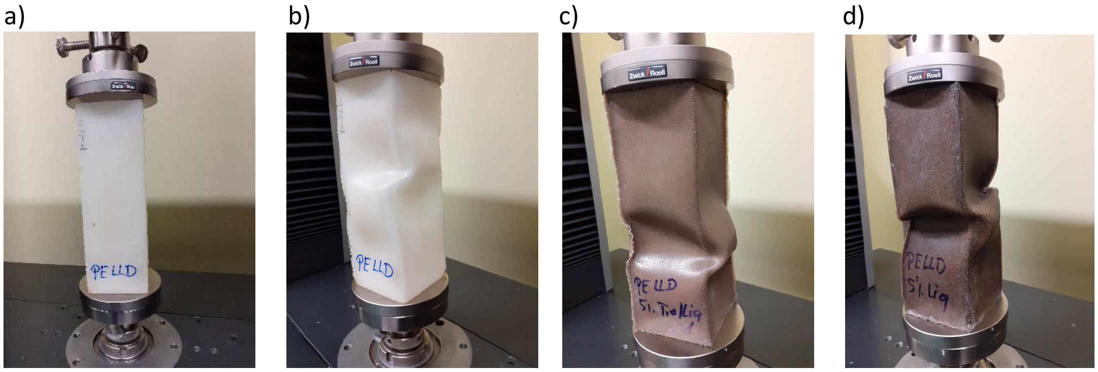

Fig. 1. Pictures of the containers compression test: a) LLDPE before test, and under test b) LLDPE, c) LLDPE 5% TiO2/Lignin, d) LLDPE 5% Lignin.

Keywords: lignin, titanium dioxide, polyethylene, rotational molding, compression test

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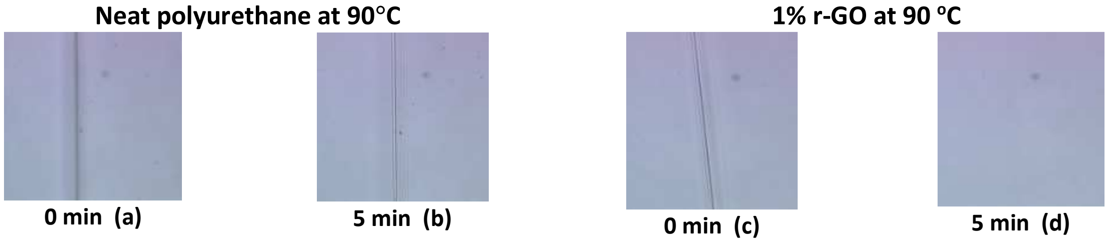
Effect of Graphitic Nanoadditives on the Self-healing Properties of Polyurethanes

K. Chrissopoulou[1,*], E. Giannakaki[1,2], M. M. Stylianakis[1,3], A. Fidelli[4], P. Krassa[4] and S. H. Anastasiadis[1,2]

[1]*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion Crete, Greece*
[2]*Department of Chemistry, University of Crete, Heraklion Crete, Greece*
[3]*Nursing Department, Hellenic Mediterranean University*
[4]*Megara Resins, Anastassios Fanis, S.A. Megara, Greece*
[*]*kiki@iesl.forth.gr*

In the last decade, waterborne polyurethanes (WBPUDs) have prevailed over the traditional solvent-based ones towards the development of environmentally friendly coatings, plasticizers and adhesives [1]. Their versatile properties in terms of soft and hard segments tunability, thermal stability, high flexibility, strong adhesion, mechanical stability and self-healing, mainly due to host–guest interactions and the presence of hydrogen bonds attracted the interest of many researchers who focused on their improvement through chemical modification, doping etc. Moreover, inorganic additives as well as graphene derivatives are widely used to reinforce the mechanical, thermal and self-healing properties of WBPUDs [2,3]. In this work, graphene oxide (GO) synthesized by a modified Hummers method, and a hydrophilic clay, Na^+MMT, were incorporated within polyurethane matrices to develop nanocomposites of different compositions. Polyurethane dispersions based on different polycarbonate and polyether polyols were used as the host material. The developed nanocomposites were thoroughly characterized through conventional spectroscopic, microscopic, surface and thermal analysis techniques, whereas their self healing ability in comparison to the respesctive of the neat polyurethanes were investigated (Figure 1), as well.


Neat polyurethane at 90°C

1% r-GO at 90 °C

0 min (a)

5 min (b)

0 min (c)

5 min (d)

Figure 1: Optical microscope images of the self-healing of a crack in a polyurethane film (and b) and a polyurethane / r-GO film with 1% of rGO (c and d)

Keywords: Waterborne polyurethanes, reduced graphene oxide, self-healing properties

Acknowledgments

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Periodic auto fragmentation of amphiphilic Tri-block copolymers microfibers into anisotropic microparticles

Nicole Edelstein-Pardo[1,3,4], Maya Molco[1,3,4], Parul Rathee[1,3,4], Gil Koren[2,3,4], Shahar Tevet[1,3,4], Shiran Ziv Sharabani[1,3,4], Roy Beck[2,3,4], Roey J. Amir[1,3,4,5*], Amit Sitt[1,3,4*]
[1]*School of Chemistry, Faculty of Exact Sciences, Tel-Aviv University, Tel-Aviv, 6997801, Israel*
[2]*School of Physics and Astronomy, Faculty of Exact Sciences, Tel-Aviv University, Tel-Aviv, 6997801, Israel*
[3]*Tel Aviv University Center for Nanoscience and Nanotechnology, Tel-Aviv University, Tel-Aviv, 6997801, Israel*
[4]*The Center for Physics & Chemistry of Living Systems, Tel Aviv University, Tel-Aviv, 6997801, Israel*
[5]*The ADAMA Center for Novel Delivery Systems in Crop Protection, Tel-Aviv University, Tel-Aviv, 6997801, Israel*
** amirroey@tauex.tau.ac.il and amitsitt@tauex.tau.ac.il*

Self-fracturing of materials due to drying is a general mechanism, which does not depend on applying external force. This natural process occurs in a variety of materials, ranging from colloidal suspensions to thin films of metals and polymers. Controlling the position and size of the fractures can be a beneficial patterning tool for different applications, however, in most systems, it is almost impossible to attain.

Here, we present a novel mechanism, based on spontaneous transverse periodic fracturing of drying of polymeric microfibers, for the formation of anisotropic microparticles of custom-made dendron-PEG-dendron amphiphilic tri-block copolymers. Upon drying of the fibers on a glass substrate, they spontaneously fracture into relatively uniform microscale tubular particles. The fracture frequency and the average fragment length are dictated by the diameter of the fibers. Furthermore, we show that the tri-block copolymer exhibits lamellar ordering in the fibers, as is indicated by X-ray scattering measurements. Fine-tuning of the hydrophobicity of the dendrons by modifying their end-groups can significantly alter the swelling and dissolving of the microparticles, hence providing control over their degradation rate.

This new method for creating anisotropic polymeric microparticles with controlled lengths and degradation times may pave the way for the simple formation of PEG polymeric particles for different applications.

Preparation of Cellulose based Nanofibrous Materials with Halochromic Function by Electrospinning

Beste Elveren[1], Manja Kurečič[1,2]

[1]Laboratory for Characterisation and Processing of Polymers, Faculty of Mechanical Engineering, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia
[2]Institute of Automation, Faculty of Electrical Engineering and Computer Science, University of Maribor, Koroska cesta 46, 2000 Maribor, Slovenia

Responsive smart polymers, sensitive to certain signals that allow them to change their physical or chemical properties, became intriguing in last decade, because of the dynamic and mostly reversible changes they introduce. Commonly, these changes are reversible when the stimulus is removed. Generally, polymers or polymers with responsive additives can be evaluated as smart responsive materials, changing their physical and/or chemical properties according to the stimuli. There are pH, temperature, photo, and electric field responsive polymers while some polymers need additives to be responsive. Chromic materials are widely being studied for the production of smart polymers, as one of the essential components in biomedicine.

A major part of the research on nanofibers for visual and optical monitoring is focused on the development of pH-sensitive membranes. pH plays an important role in a diverse set of applications, including protective clothing and safety, environmental pollution, agriculture, and the biomedical field[1-3]. However, leaching of the dye has been one of the major problems when producing halochromic polymers since most of the methods depend on weaker molecular interactions. One of the techniques to prevent leaching is to use a complexing agent and trapping the dye to the polymeric structure. Meyer et. al reported that the leaching of sulfonphthaleine based dyes decrease subsequently in the presence of poly-diallyl-dimethylammonium chloride (PDADMAC)[4, 5]. PDADMAC is a complexing agent that has been used to suppress the leaching of the dye from the polymeric matrix. It prevents the migration of dye molecule from the matrix by the ionic interactions[6].

In this study, pH responsive hybrid nanofibers will be presented by the addition of the complexing agent PDADMAC, halochromic dye will be integrated to polymers such as cellulose derivatives (e.g., cellulose acetate, etc.), to produce a spinning solution. Bromocresol green (BCG), bromothymol blue (BTB) and thymol blue (TB) will be used in this process as halochromic substances to enable the responsivity. Obtained electrospinning solutions will be characterised according to their conductivity, viscosity, and studed for their influence on fiber formation. The hybrid nanofibrous materials will be characterized by FTIR, SEM, contact angle, as well as halocromic responsiveness and leacking ability will be determined.

Keywords: halochromism, responsive nanofibers, polysaccharides, electrospinning

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Water-based aspartic acid derived vitrimer nacre-mimetic bioinspired nanocomposites

S. Engels[1*], A. Walther[2]

[1]*Johanned Gutenberg University, Mainz, Germany*
[2]*Johanned Gutenberg University, Mainz, Germany*
[*]*sjoerd.engels@uni-mainz.de*

A new waterborne vitrimer system has been imagined whereby an acrylamide-based previtrimer is prepared via free radical polymerization of an aspartic acid derivative, a methoxy triethylene glycol acrylamide, and sulfonic acid derivative as internal catalyst. By combining this linear copolymer with a crosslinker diol, *N*-methyldiethanolamine in aqueous phase and subsequent evaporative assembly, a vitrimer is prepared with elastomeric mechanical properties and fast stress relaxation rates at elevated temperatures. This vitrimer system is combined with clay nanosheets to yield nacre-mimetic bioinspired nanocomposite materials with high degrees of reinforcement. These hierarchical layered materials reach up to high values of strength and stiffness while possessing temperature-responsive properties associated with their vitrimer components. Unique properties such as recyclability, shape-locking behavior and gas-barrier properties are imagined.

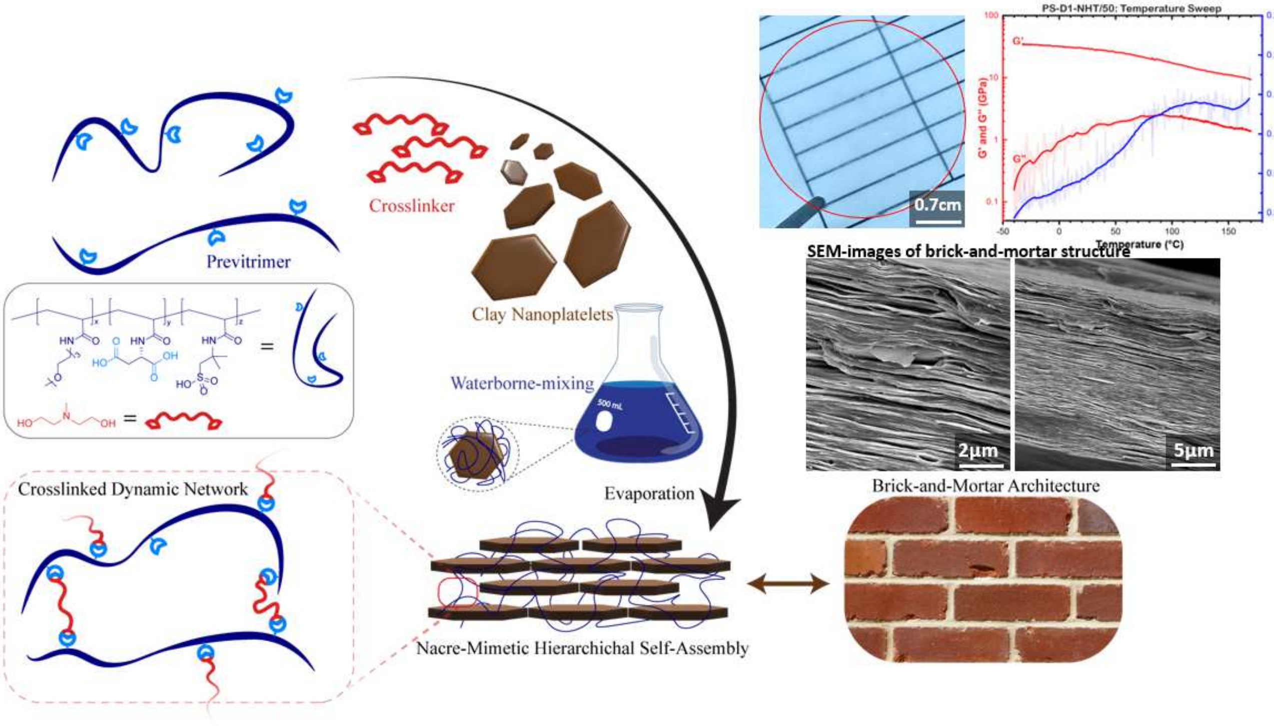

Figure 1: Preparation of nacre-mimetic vitrimer-based bioinspired nanocomposites via evaporative self-assembly to yield temperature-responsive films with a brick-and-mortar architecture.

Keywords: Vitrimer, Bioinspired, Nanocomposite, Nacre-mimetic

Acknowledgments
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Planar Photonic Crystal as Colorimetric Sensors for Smart Packaging

Andrea Escher[1], C. Tavella[1], D. Cavallo[1], D. Comoretto[1], P. Lova[1*]

[1]*Department of Chemistry and Industrial Chemistry, University of Genoa, Genoa, Italy*
[*]*Email: paola.lova@unige.it*

Monitoring the conservation status of fresh food is a challenge of growing interest for prevention of food waste and preservation of people's healt. To this end, low-cost and real-time monitoring of food degradation by-products would represent a paradigm shift for the food industry. For this purpose, colorimetric sensors for real time detection of low concentration of degradation by-products, suitable also for untrained users such as consumers, and compatible with the processing of packaging are higly interesting. Among food degradation by-products, biogenic amines, which derives from protein degradation and can induce severe intoxication even at low concentration, are higly promising analytes to accurately assess food quality.(1)
Among different technologies, opaline photonic crystals, whose color arise from the interaction between light and their submicrometric modulation of the refractive index, have been widely invesigated owing to strong color variation upon amine intercalation. In these sensors, the analites intercalates in the photonic crystal lattice modifying its pitch or the refractive index, and in turn the color of the strucutre. However, the fabrication of these systems is hardly scalable to the troughput needed by the food packaging industries. Then, polymer planar photonic crystals, also known as distributed Bragg reflectors (DBRs),(2, 3) are ideal candidates for this task. This stuctures promises indeed strong colorimetric response and can be fabricated on square meter area with technologies already employed for the processing of packaging products.(4)
In this work, we report on the detection of a prototype amine employing DBRs made of alternated thin films of a titania-polyacrylic acid hybrid (TiHy) as high refractive index medium and a blend of polystyrene and poly lactic acid (PS:PLA) as the low refractive index and as the sensitive one. In these sensor, the response is guaranteed by the aminolysis of PLA occurring upon amine intercalation in the structure. Blending the sensitive material with PS favor the formation of PLA crystallites small enough to avoid light scattering, contrary to the case of neat PLA, in which the larger crystallites induce strong light scattering and inohomegeinities in the photonic crystal structure. Moreover, coupling the polymer with the rigid hybrid material allows the structure to collapse upon PLA aminolisis, causing irreversible color fading upon amine exposure (Figure 1), which is mandatory to prevent any tampering action. These findings pave the way for real time assesment of food conservation status along the entire supply chain and after purchase.

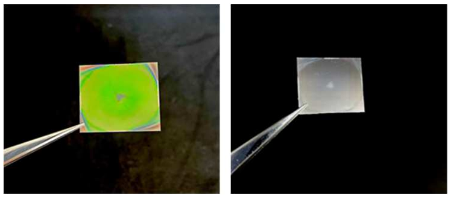
Figure 1: Before and After of a DBR PLA(PS)(High Index Inorganic Material) subject to aminolysis.

Keywords: Polymer photonic crystal, food packaging, smart packaging, biogenic amines.

Acknowledgments: *This work has been partially found by the Department of Chemistry and Industrial Chemistry of the University of Genova*

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Effect of chemical treatment of glass fibers and application pressure on the nucleation of Poly (lactide) composites

S.E. Fenni[1,2*], S.A.E. Boyer[2], A. Buur[2], O. De Almeida[1].

[1] *Institut Clément Ader (ICA), Université de Toulouse, CNRS UMR 5312, IMT Mines Albi, UPS, INSA, ISAE-SUPAERO, Campus Jarlard, Albi F-81013, France*
[2] *Mines Paris, PSL-Research University, CEMEF-Centre de Mise en Forme des Matériaux, UMR CNRS 7635, CS 10207, Rue Claude Daunesse, 06904, Sophia Antipolis Cedex, France*
**Corresponding Author: seif-eddine.fenni@minesparis.psl.eu*

Abstract

Fiber-reinforced polymer composites have attracted an increased attention in previous decades due to their enhanced mechanical properties and lightness. The mechanical performances of these composites depend strongly on the interfacial interaction and the adhesion between the fiber and the polymer matrix. On the hand, presence of such fibers in the polymer matrix leads, often, to some crystallization at the fiber interface (called fiber-induced crystallization). It is a local concept. The previously mentioned fiber-induced crystallization by-itself is known as an effective way to improve the surface adhesion between fibers and the polymer matrix [1-3].In the present study, the nucleation process and crystallization of Poly (lactide) (PLA) in contact with various chemically treated glass fibers (GF) been investigated. Three different types of chemical treatment have been applied to the GF for which we can cite: highly hydroxylated glass fibers (HCl GF), hydrophilic glass fibers (APS GF), and hydrophobic glass fibers (TMPS GF). 1. The chemistry and surface properties of these treated GF was analyzed using infrared spectroscopy and their nucleation efficiency has been deeply investigated using Polarized Optical Microscopy (POM) and Differential Scanning Calorimetry (DSC). 2. Pressure effect was additively reported on one case for further understanding.

1. Results demonstrated that various GF exhibited meaningful differences in the nucleation ability toward the PLA matrix in which, the HCl GF (highly hydroxylated GF) exhibited the highest nucleation efficiency while the TMPS GF presented the fibers with the least nucleation ability. The obtained results were in line with degree of hydrophilicity of the GFs and their compatibility with the PLA matrix. However, it should be noted that no transcrystalline structures have been observed in all the studied composites, instead, only hybrid shish-calabash structures were obtained.
2. Furthermore, the nucleation behavior of PLA on top of one selected chemically treated GF was investigated under various pressure levels. Quantitative studies showed an overall increase of the nucleation of the system with the increase of the pressure. However, the increase of the surface of the fiber-induced nucleation is always much higher than the one recorded in bulk PLA in all the investigated temperature/pressure range.

Results showed that by modifying the fiber surface chemistry, the final nucleation behavior as well as the adhesion between the fiber and the polymer matrix can be controlled. While the application of the pressure allows to understand the nucleation behavior in polymer composites under nearly real processing conditions.

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Nano vs. recycling: a study of different fillers for thermosets

M. Feuchter[1*], M. Sieberer[2], W. Kern[3]

[1]Montanuniversitaet Leoben, Institute of materials science and testing of polymers, Leoben, Austria
[2]bto-epoxy GmbH, 3300 Amstetten, Austria
[1]Montanuniversitaet Leoben, Chair of Chemistry of Polymeric Materials, Leoben, Austria
[*]michael.feuchter@unileoben.ac.at

Over the last decades the combination of nanoparticles and polymeric systems has become popular in scientific and industrial areas to enlarge the field of properties for these materials. The physical properties of the resulting nanocomposite are strongly related to the size, shape and the dispersion in the polymer matrix. Also recycling methods have become more and more interesting for scientific and industrial research institutes over the last years, especially mechanical recycling.

Fillers with sizes in the µm range and below can improve the mechanical performance of thermoset composites. Some studies have been able to ehance stiffness, strength and toughness at the same time when using nanoparticles. However, if the reinforcing particles become larger, there is usually only an improvement in one of the characteristic values mentioned and a deterioration in the others. This could be postponed by specific modifications of the particles, but these treatments are usually complex,time-consuming and cost-intensive. Due to public and financial pressure, industrial companies are increasingly forced to reuse their in-house waste or to recycle their materials internal.

The present study compares the reinforcing effect of nanoparticles with that of industry cutting dusts (because this waste fraction is already available as particles) from the epoxy resin processing industry. Silica and carbon based nanoparticles are interesting when it comes down to increase the thermal and mechanical properties of epoxy based polymer systems. To monitor the resulting properties thermo-mechanical and mechanical investigations are required.

In this work the influence of (modified and unmodified) nanoparticles on the structural, mechanical and thermo-mechanical properties of a diglycidyl ether of Bisphenol A based epoxy resin was investigated. Likewise, different waste fractions were added to these epoxy resins and the same characteristic values of these formulations were determined.

Differences in the mechanical and thermal properties were observed: the addition of fillers to the epoxy resin leads to an increase in mechanical properties, whereas thermal-mechanical properties (e.g. the glass transition temperature) are lowered. It could also be shown that the different fillers resulted in similar property profiles in the respective composite systems.

Triggered Polymersome Fusion

S. D. P. Fielden,[1*] M. J. Derry,[2] P. D. Topham[2] and R. K. O'Reilly[1*]

[1]*School of Chemistry, University of Birmingham, Edgbaston, B15 2TT Birmingham, UK.*
[2] *Aston Institute of Materials Research, Aston University, Aston Triangle, Birmingham, B4 7ET, UK*
[*]*s.fielden@bham.ac.uk*

Encapsulation of cargos into vesicle containers is key for the controlled movement of material around and between biological cells.[1] Delivery of a cargo to a specific location is possible because fusion of a vesicle's membrane to a target organelle is accelerated by attractive interactions between surface proteins.[2] This organized compartmentalization of biological cargos is essential for many processes, such as protein modification, nerve signaling and immune response coordination. The ability to reproduce such a 'parcel delivery surface' using abiotic containers would allow control over the mixing of molecular cargos in a synthetic setting. This would open new methods to control chemical reactivity at the nanoscale.

Here we present the first step to realizing such a system. This is possible by a newly discovered mechanism for triggering the fusion of synthetic vesicles formed from the assembly of amphiphilic polymers.[3] Out-of-equilibrium vesicles capable of undergoing fusion on demand can be accessed by ring-opening metathesis polymerization-induced self-assembly (ROMPISA). These vesicles relax to a more stable state by fusing together to give elongated tubular nano-objects. By tuning vesicle surface charge and membrane tension it is possible to trigger fusion by a pH switch. Furthermore, the crossed fusion of two different vesicle populations can be achieved by adjusting corona chemistry and membrane tension. The resulting fused particles have been characterized by various methods, including cryo-TEM, whilst the fusion process has been studied by in-situ SAXS. This controllable vesicle fusion process opens the possibility of targeted mixing of molecular cargos, whilst the development of more complex cascades of fusion is being investigated.

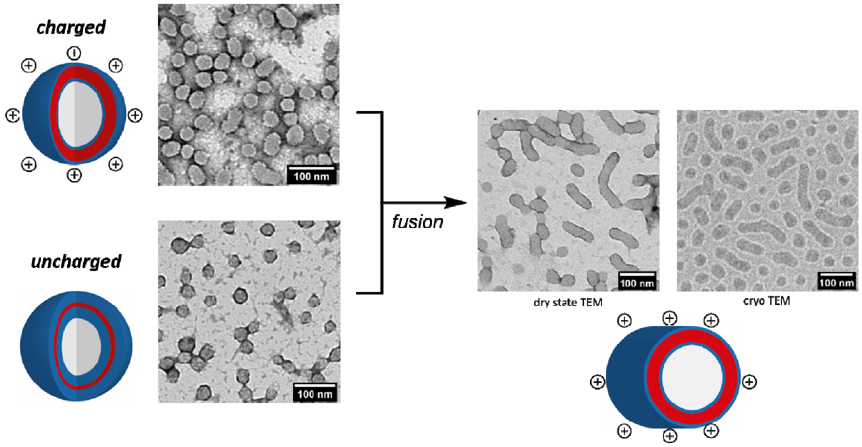

Figure 1. Selective fusion of polymersomes directed by membrane tension and surface charge

Keywords: Polymersomes, membranes, out-of-equilibrium assemblies

Acknowledgments

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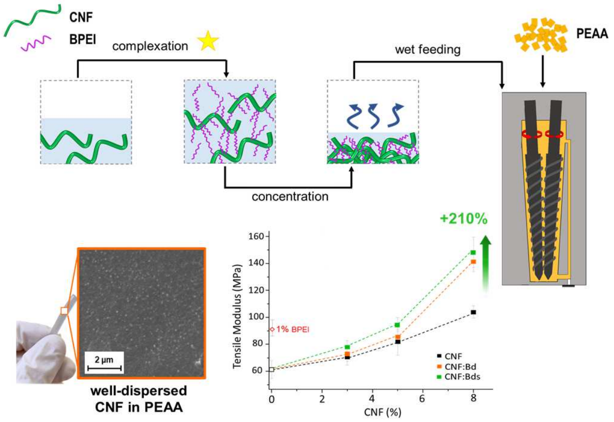
Cellulose Nanofibers – polyelectrolyte complexation to reinforce melt processed poly(ethylene-co-acrylic acid) nanocomposites

M. L. Aghemo[1], F. Carosio[1], A. Fina[1*]

[1]Department of Applied Science and Technology (DISAT), Politecnico di Torino, Alessandria, Italy
[*]Corresponding Author's E-mail*: alberto.fina@polito.it*

The apolar nature of polyolefins typically hinders the dispersion of polar particles for the preparation of nanocomposites, since the low compatibility between the two phases causes poor dispersion of the nanoparticles and weak matrix-particle interaction, which is reflected in low stress transfer. To deal with such issue, partially polar polyolefins have been proposed as matrix-particles compatibilizers. This work explores the possibility of structuring polar-groups functionalized polyolefins by dispersing polar nanoparticles. Among the wide range of nanomaterials, nanocellulose has been selected being one of the most inexhaustible, biodegradable and non-toxic nanofibers [1]. Despite great benefits, however, dispersing nanocellulose into a polymer through traditional melt blending is challenging, due to the high tendency of nanocellulose to self-interact through H-bonds among the free -OH groups on the nanocellulose free surface [2]. To overcome these limitations, an innovative water-based polyelectrolyte-complexing strategy was applied to nanocellulose to finely disperse cellulose nanofibrils (CNF) into poly(ethylene-co-acrylic acid) (PEAA). Preparation was carried out via wet feeding during melt processing, with the aim of forming a network of nanocellulose enhancing the mechanical properties of the polymer. The selected reactive complexing element was branched poly(ethylene-imine) (BPEI), bearing multiple amino groups able to interact with CNF through hydrogen bonds. SEM and rheological analysis proved improvements in the dispersion of CNF in PEAA at the different loadings (3%wt - 8%wt), without residual micrometric aggregates observable in the corresponding PEAA/CNF formulations without BPEI. Moreover, BPEI interacted not only with CNF but also with PEAA through ionic interactions between the protonated amines in BPEI and the carboxylate group on PEAA, resulting in a hybrid matrix-nanoparticle network. The combination of CNF complexation and matrix-CNF compatibilization resulted in enhanced mechanical properties of the composites, with +210% increase in tensile modulus and only -8% decrease of tensile strength with 8%wt of BPEI-complexed CNF. Hence, the network of finely dispersed CNF, compatibilized through BPEI, was shown to provide decisive improvements of its mechanical properties and thus opening new horizons in the preparation of CNF-based nanocomposites.



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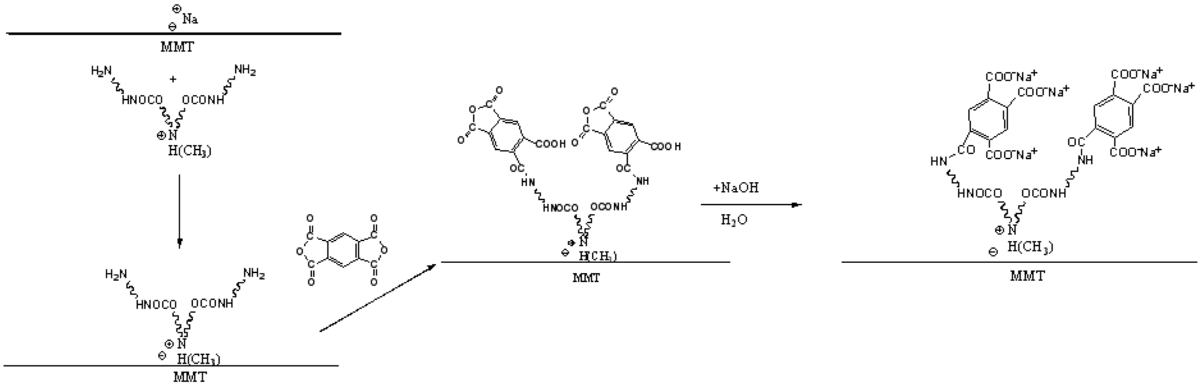
Development of organosilicate water-dispersible nanofiller for nanocomposites based on polar polymers from aqueous dispersions

Gonchar O., Travinska T., Savelyev Yu.

Institute of Macromolecular Chemistry, NAS of Ukraine
Corresponding Author's E-mail address (lexgon@ukr.net)

There is currently no single systematic approach to the development of nanocomposites based on polar polymers with MMT, due to a number of complications related to the nature and methods of synthesis of such polymers. The main difficulty in creating nanocomposites based on polar polymers is that the modified MMT, which is produced on an industrial scale, different brands of "Cloisite" manufactured by Southern Clay Products, and used to create polymer nanocomposites, has a non-polar surface. That is, the bulk of the modifiers used to modify MMT are cationic surfactants with large hydrocarbon fragments (C_{12} - C_{16}) [1]. Due to the different nature of the surface of the modified MMT and the matrix of the polar polymer, there are difficulties in the dispersion and systematic distribution of nanoparticles [2]. Given that the vast majority of polar polymers are synthesized in the process of polycondensation, researchers often use the modification of MMT with reactive compounds or directly monomers [3]. The disadvantage of such approaches is that due to the low molecular weight of the reaction compounds and monomers, the MMT surface is insufficiently covered with an organic layer.

In order to create polymer/organoclay nanocomposites based on aqueous dispersions of polymers, a method for creating a new water-dispersible organoclay was developed. This method consists in chemical modification of montmorillonite by urethane oligomer functionalized by amino groups and further surface functionalization by addition of dianhydride with subsequent hydrolysis with formation of carboxyl groups:



Keywords: montmorillonite, functionalization, nanocomposites

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Development of microfibrillated cellulose (MFC)- modified polyketone composite membranes for water purification membranes

P. Gonzalez Cortes[1*], R. K. Bose[1], Francesco Picchioni[1], Franck Quero[2].
[1]*University of Groningen, Groningen, Netherlands*
[2]*Universidad de Chile,Facultad de Ciencias Fisicas y Matematicas, Santiago, Chile*
[*]*p.a.gonzales.cortes@rug.nl*

Microfibrillated cellulose (MFC) is a biomaterial with great potential for different fields. Typical applications include textile, optical, and medical products. In addition to these, MFC has excellent potential in environmental applications, specifically for water treatment issues [1,2]. In this work, we investigate the removal of cations from water using unmodified MFC membranes. However, the lower removal capacity of these materials is a drawback. To overcome this problem, the formation of composite materials between MFC and polymers is a good alternative (Figure), improving the mechanical properties and giving more functional groups to interact with pollutants in water.

Chemically modified polyketones are materials with excellent properties (chemical or physical), making them an interesting candidate to form composites with MFC. The modified polyketones also have a significant amount of functional groups which interact synergistically with the MFC thus improving the mechanical properties of the composites. In this context, MFC/ modified polyketones composites membranes were developed, using two methodologies based on impregnation (IMP) and mixing (MIX). We will show the results of elemental analysis (EA), Fourier transformed infrarred specctra (FTIR), X-ray diffraction (XRD) ,optical microscopy, thermogravimetric analysis (TGA), and tensile tests performed on these composite materials.

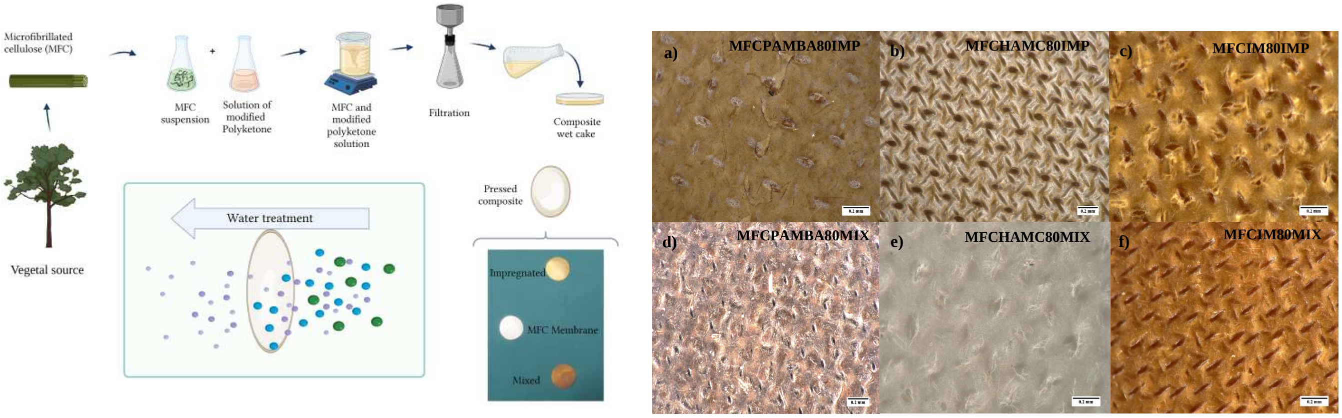

Figure. Left elaboration of composite membranes from microfibrillated cellulose and modified polyketones and right optical image of the surface of the MFC/polyketone composite membranes

Keywords: Microfibrillated cellulose (MFC), polyketone, composites materials, mechanical properties, water treatment.

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Mechanically interlocked derivatives of carbon nanotubes for reinforcement of polymethylmethacrylate

M.Gonzalez[1*], I. Isasti, M. Rivas-Carames, A. Naranjo-Chacón, M. D. Eaton, J. Villalba, M. Gonzalez-Juarez, S. Miranda, A. López-Moreno, E. M. Perez.

[1]*Imdea Nanoscience, Madrid, Spain*
[*]*Corresponding Author's E-mail: marta.gonzalez@imdea.org*

Carbon nanotubes, and in particular single-walled-carbon nanotubes (SWNTs) have been envisaged as the ideal polymer filler, due to their extraordinary mechanical properties. However, in practical terms, these expectations have not been fulfilled, due to the tendency of SWNTs to aggregate and their poor interfacial interaction with the polymer matrix. Chemical modification of the SWNT wall has been explored to try to overcome this problems, but classic supramolecular or covalent approaches have not been very successful. Our group described the synthesis of mechanically interlocked derivatives of SWNTs (MINTs).[1,2] In MINTs, the SWNTs are encapsulated within organic macrocycles, which in principle could both prevent SWNT aggregation and enhance nanotube-polymer interaction. Ineed, the reinforcement of polymers by mechanically interlocked derivatives of carbon nanotubes (MINTs) has been demonstrated in previous articles [3]. The reinforcing efficiency of MINTs in a polymethyl methacrylate (PMMA) matrix has been studied in this work. MINTs/PMMA and single wall carbon nanotubes (SWNT)/PMMA composites with different loadings (0, 1, 2, 5, 10 and 20 wt.%) have been prepared by free radical polymerization. The polymerization took place in a dispersion of either pristine SWNT or MINTs to improve the physical interaction between the fillers and the matrix.

The resulting composites was characterized by FTIR, DSC and TGA. Mechanical properties have shown that the higher the load, the greater the Young's modulus, as expected. In addition, results showed that the reinforcement of the MINTs was better at low loads, while at higher loads a greater reinforcement was obtained by the SWNTs. Furthermore, an improvement of up to 40% of the tensile stress values were obtained. This work shows that MINTs are a good alternative to reinforce PMMA, especially at low load values.

Keywords: carbon nanotubes, in situ-polymerization, reinforcement.

Acknowledgments
We acknowledge funding from Nanocore, Inc. (Copenhagen, Denmark).

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Curing Kinetics of Cyanate Ester Resin with Fullerite C_{60} and Thermal Properties of Nanocomposites Derived Thereof

O. Grigoryeva[1*], O. Starostenko[1], L. Michely[2], A. Fainleib[1], D. Grande[2]

[1]*Institute of Macromolecular Chemistry of the NAS of Ukraine, Kyiv, Ukraine*
[2]*Institut de Chimie et des Matériaux Paris-Est, CNRS-UPEC, Thiais, France*
*grigoryevaolga@*i.ua*

One of the key directions in the chemistry of fullerenes is the establishment of the laws governing their interactions with solvent molecules. Their solubility in various polymers is a separate line of fullerene dissolution chemistry. The influence of the presence of molecules with a unique structure on the physical-chemical properties of polymer nanocomposites is still poorly understood.
Dynamic DSC measurements at constant heating rate was used to characterize the effect of fullerite C_{60} on the exothermic curing reaction and thermostable cyanate ester resin (CER) formation *via* high temperature polycyclotrimerization of dicyanate ester of bisphenol E (DCBE) with fullerite C_{60} filler loading of 0.01, 0.05, 0.1, 0.5, and 1.0 wt.%. Thermal properties of the fully cured CER/C_{60} nanocomposites were evaluated using DSC and TGA techniques. The values of the exotherm onset temperature (T_0), the exotherm peak temperature (T_{exo}), reaction enthalpy (ΔH), and the values of glass transition temperatures (T_g) of the cured CER/C_{60} nanocomposites were determined. It was found that the peak temperatures shifted to higher temperatures with increasing C_{60} content, whereas the onset temperatures remained almost unchanged. Thus, one can conclude that the C_{60} particles does not significantly influence the initiation of the curing process; however, they hinder the monomer conversion to crosslinked polymer. Nevertheless, the T_g values of the final materials shifted from 274 °C for the pure cured CER to 275-290 °C for the CER/C_{60} nanocomposites depending on nanofiller content. TGA measurements showed that the CER/C_{60} nanocomposites possessed sufficiently high values of $T_{d5\%}$ ~ 441-446 °C, and $T_{d\,max}$ ~ 449-454 °C depending on fullerite C_{60} content.

Keywords: curing kinetics, cyanate ester resin, fullerite C_{60}, thermal properties

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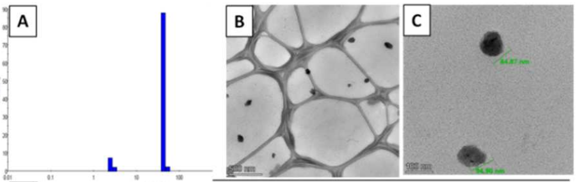
VCAM1-Targeted Nanogel Preparation to Diminish Oxidative Stress-Associated Inflammation in Atherosclerosis

R. Guner[1], I. Soyhan[1], O. Gok[1,2*]

[1]Biomedical Engineering Program, Graduate School of Natural and Applied Sciences, Acibadem Mehmet Ali Aydinlar University, Istanbul, Turkey
*[2]Department of Medical Engineering, Faculty of Engineering, Acibadem Mehmet Ali Aydinlar University, Istanbul, Turkey**
[*]ozgul.gok@acibadem.edu.tr

Atherosclerosis has been one of the most significant diseases worldwide which leads to the accumulation of lipid molecules on the arterial walls. The accumulation of lipid molecules thickens and hardens the arteries and eventually, results in serious outcomes such as myocardial infarction or ischemia [1]. Current therapies of atherosclerosis that are not targeted to damaged sites lead to not only toxicity but also lead some unwanted side effects to healthy tissues and organs. Thus, by the presented targeted drug delivery system, a novel drug monomer, that contains lipoic acid molecules, is expected to accumulate only at the damaged site of the arterial wall and will be released in a controlled and prolonged fashion. The targeting is achieved by covalent conjugation of anti-VCAM1 antibody and also, Cy-5 conjugation allows imaging of nanogels. Thus, these nanoparticles were prepared by free-radical based gelation method by using dimethacrylate-functionalized PEG polymers under UV light (365 nm) by using a water-soluble photoinitiator (I2959). 3 different molecular weights of PEG (2, 6 and 10K) were evaluated under the same gelation conditions. Nanogel formation procedure was optimized for its polymer: photoinitiator ratio, gelation time, temperature, solvent type and dilution factor. A novel monomer with three-drug molecules (LA3MA) was successfully synthesized as three lipoic acid drug molecules linked by ester bonds and a reactive methacrylate group in its structure with high purity (99.58%) and 76% yield. For drug-loaded nanogels; dilution factor, time, temperature and the amount of drug monomer (5, 10 and 20% by weight) were evaluated for optimal drug-loaded nanogels. It was found that the nanogels with a size ~100 nm were obtained with PEGDiMA polymer (6 kDa), at room temperature in 10mM pH7.4 PBS solution (Fig. 1). Polymers used at a concentration of 1mg/300µL solvent with 1:50 polymer: photoinitiator ratio by weight resulted in nanogels as a monomodal shape and with low PDI value. For *in vitro* cellular internalization assay, Cy5 dye was conjugated to the surface of amine-functionalized nanogels. Furthermore, excess amine moieties of nanogels were linked to anti-VCAM-1 antibody for targeting purposes. Cytotoxicity of drug-loaded nanogels was investigated in both L929 mouse fibroblasts and HUVEC cells at both resting states and in a state that was activated by LPS, an endotoxin to create an inflammation environment.



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LA3-MA content (%)	Size (nm)	PDI (%)	Intensity (%)	Mean zeta potential (mV)
0	42.8	4.4	90.5	-8.1
5	43.2	18.1	85.4	-0.2
10	37.0	11.8	98.2	1.5
20	56.7	19.5	92.6	8.8

Figure1. (A) Size distribution peak for PEG-based nanogel and (B and C) its TEM images; (D) Size and surface charge of drug-loaded nanogels.

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Poly(3,4-ethylenedioxythiophene)/maghemite composite: An efficient anionic dye adsorbent

S. Gupta[1,*], B. A. Zasońska[1], M. Konefał[1], E. Petrovsky[2], P. Bober[1]
[1] *Institute of Macromolecular Chemistry, Czech Academy of Sciences, 162 06 Prague 6, Czech Republic*
[2] *Geophysical Institute, Czech Academy of Sciences, 141 31 Prague 4, Czech Republic*
[*] *Corresponding Author's E-mail: guptasonal@imc.cas.cz*

With an increase in toxic and non-biodegradable wastes in water, wastewater treatment has become one of the serious environmental concerns. The ion exchange process, electrochemical treatment, flocculation, reverse osmosis and adsorption are some of the prevalent techniques used to treat contaminants, such as pesticides, heavy metals, dyes, etc. which are released from various industries.[1] Among them, adsorption is considered as an easy and inexpensive process. Conducting polymers (polypyrrole, polyaniline, poly(3,4-ethylenedioxythiophene) (PEDOT), etc.) and their composites are attaining considerable interest in the adsorption of organic dyes. [2-4]

Herein, we report the synthesis of PEDOT/maghemite (γ-Fe_2O_3) composites by chemical polymerization of 3,4-ethylenedioxythiophene (EDOT) with ammonium peroxodisulfate (APS) as an oxidant in presence of γ-Fe_2O_3 nanoparticles (Figure 1 A). The morphology of the prepared composites was studied using scanning and transmission electron microscopies. X-ray diffraction was used to detect the crystallinity in the composites. The composite prepared with the highest amount of γ-Fe_2O_3 showed the largest surface area and, thus was examined for adsorption of Reactive Black 5, an anionic dye. After dye adsorption, the PEDOT/γ-Fe_2O_3 composite was facilely separated by a magnet due to its magnetic properties, as shown in Figure 1 B.

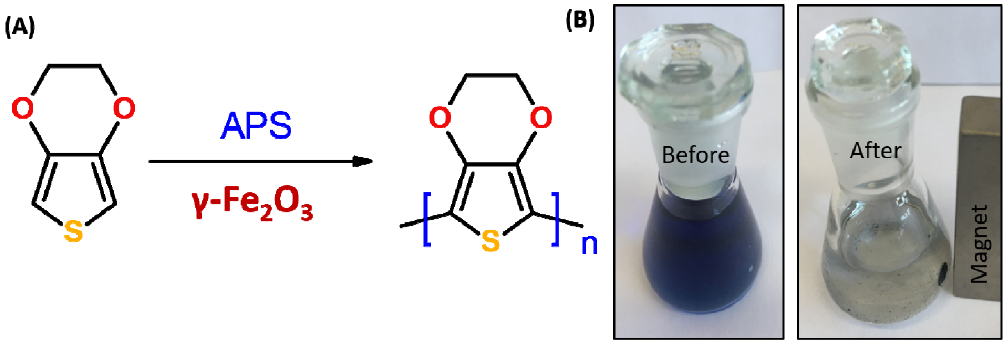

Figure 1 (A) Chemical polymerization of EDOT using APS as an oxidant in presence of γ-Fe_2O_3 nanoparticles. (B) Adsorption of anionic dye by PEDOT/γ-Fe_2O_3 composite and its separation using a magnet.

Acknowledgments

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A new image processing method for quantifying nanodispersion in silica filled rubber composites

N. Hackel[1,2*], S.M. Nagaraja[2], S. Henning[2], M. Beiner[1,2]

[1]*Martin Luther University of Halle-Wittenberg, Halle (Saale), Germany*
[2]*Fraunhofer Institut für Mikrostruktur von Werkstoffen und Systemen IMWS, Halle (Saale), Germany*
[*]*nico.hackel@imws-extern.fraunhofer.de*

The quantification of filler dispersion is important for the optimization of highly filled rubber composites and quality control in the rubber industry. Commonly used methods to quantify marcodispersion or microdispersion focus on detection and analysis of filler agglomerates having dimensions in the 2 - 100 µm and < 2 µm range, respectively. More important for the performance of rubber composites is, however, the topology of the so-called filler network, which is controlling to a large extent reinforcement and dissipation of rubber composites.[1,2] Hence, the filler network topology related to the filler dispersion on the nanoscale is of major relevance for the performance parameters of tires like rolling resistance, wet grip or abrasion. Transmission electron microscopy images are a powerful tool to analyse the filler dispersion on the nanoscale. A quantitative analysis requires, however, a quantification method combined with an automated image analysis tools. A recently proposed indirect approach[3] to compare and quantify the topology of the filler network is to determine the distribution of unfilled areas in TEM images of ultrathin sections with a thickness of about 70 nm. To increase evaluation efficiency and to minimize the influence of methodical factors, an automated image processing method was developed. Major steps of this image processing method towards the determination of unfilled areas are shown for a representative example in Fig. 1. Further details of the applied data analysis method will be discussed and histrograms showing the distribution of unfilled areas for different rubber composites will be presented. These results will be compared with data obtained by a synthetic image generator, which has been programmed to study the influence of section thickness and initial cluster size on the distribution of unfilled areas in ultrathin sections on the nanoscale.

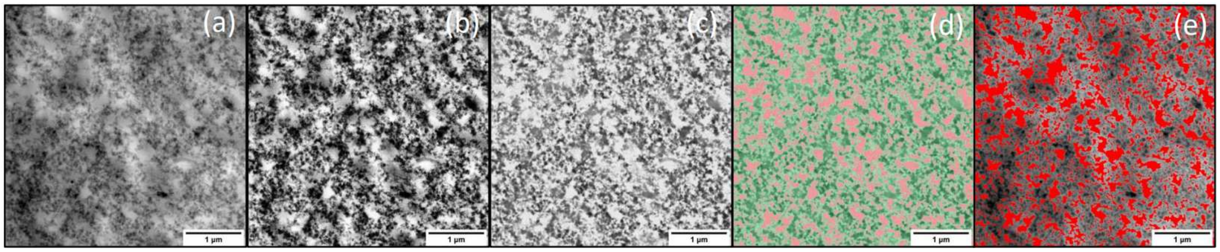

Fig. 1: Illustration of the image processing procedure with all stages: a) original, b) increased contrast, c) background subtraction, d) automated segmentation, e) unfilled regions.

Keywords: Rubber composites, Transmission electron microscopy, Filler dispersion.

Acknowledgments

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Adapting the optical reflectivity of carbon fiber reinforced polymers on the nano-scale: Matrix vs. fiber modification

Lukas Haiden[1]*, Michael Feuchter[1], Michel Barbezat[2], Amol V. Pansare[2], Andreas J. Brunner[3], Stefan Neunkirchen[4], Gerald Pinter[1]

[1] Chair of Materials Science and Testing of Polymers, Otto Glöckel-Straße 2/II, 8700 Leoben, Austria
[2] Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Mechanical Systems Engineering, Überlandstrasse 129, CH 8600 Dübendorf, Switzerland
[3] retired from Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Mechanical Systems Engineering, Überlandstrasse 129, CH 8600 Dübendorf, Switzerland
[4] Chair of Processing of Composites, Otto Glöckel-Straße 2/II, 8700 Leoben, Austria
**lukas.haiden@unileoben.ac.at*

Carbon fiber reinforced polymer (CFRP) composites are used in a wide range of applications in different industrial fields including aerospace, aviation and automotive as well as in sports equipment. These products are taking advantage of excellent mechanical characteristics combined with relatively small overall weight [1,2]. Outdoors, they are subject to environmental degradation caused, among others, by exposure to electromagnetic radiation, i.e., ultraviolet, visual and infrared. Hierarchically ordered carbon nanotubes for example have been shown to create highly absorbing surfaces, whereas snow with a complex, multi-scale porosity is providing an extremely reflective appearance in the visual and ultraviolet wavelength range [3-5]. For modifying the optical properties of CFRP's on the nano-scale, the options are matrix modification, fiber modification or a combination of both. Potential influences are the material type, shape, size and arrangement of the nanoparticles. Therefore, adapting the optical reflectivity by nanoscale modification has the potential to increase the service life of CFRP's as well as to improve mechanical properties. Furthermore, intrinsic coding of different CFRP's parts could be implemented as well [6].

For matrix modification, nanoparticles were dispersed into the epoxy resin before laminating the fibers. Fiber modification was first performed using an electrophoretic deposition process. In this case, carbon fibers were immersed into a nanoparticle suspension and an electric current was induced, providing a nanoparticle drift, in order to deposit the nanoparticles on the fibers. Furthermore, physical vapor deposition was applied to coat carbon fibers before lamination with the desired elements creating nano-scale films of different thickness on their surface. All fiber modifications were assessed with scanning electron microscopy. Modified and unmodified fibers were manufactured into CFRP's and the surface reflectivity of all samples was compared and quantified with UV/VIS measurements. Comparison with the reflectivity of nano-modified epoxy resin samples indicates significant differences between matrix and fiber modification for certain types of nanoparticles in some cases.

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Incorporation of fillers to modify the mechanical performance of inverse vulcanised polymers

Veronica Hanna[1], Peiyao Yan[1], Samuel Petcher[1], and Tom Hasell[1*]

[1]*Univerisy of Liverpool, Liverpool, England*
[*]*T0m@liverpool.ac.uk*

Sulfur is a by-product of the refinement of crude oil and natural gas, produced at over 70 million of tonnes per annum, resulting in a surplus and large overground storage of elemental sulfur.[1] The process "inverse vulcanisation" as coined by Pyun *et al.* allows for the usage of high quantities of sulfur to synthesise inverse vulcanised polymers.[2] Inverse vulcanised polymers have several applications such as construction materials,[3] self-healing materials,[4] IR transparent lenses,[5] and heavy metal capture;[6] however, they need to be further improved in their mechanical performance to widen their applications. Like with many conventional polymers, fillers can also be used to tailor the mechanical properties of inverse vulcanised polymers, for example, by increasing their tensile strength.[7] The use of the polymer, sulfur-1,3-diispropenylbenzene (S-DIB), as a model system for the addition of fillers (carbon black, cellulose microfibres, and nanoclay) at 2-10 wt.% (weight percentage) and their effect on the mechanical properties of the resutlant composite is reported herein.

Keywords: Sulfur polymers, inverse vulcanisation, fillers, mechanical properties

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Mechanical properties of flax fibers/epoxy composites for marine application

Tatjana Haramina*, Karla Pintur, Daniel Pugar

University of Zagreb Faculty of Mechanical Engineering and Naval Architecture, Zagreb, Croatia
**tharamina@fsb.hr*

One of the critical concerns regarding the acceptance of flax fibers/polymer bio-composites for marine application, as an alternative to GFRP, are their mechanical properties. A good impregnation of fibers and adhesion between components are necessary for the load transfer from matrix to fibers.

Epoxy based composites with flax fibers are prepared by means of vacuum infusion. The matrix and fibers materials are purchased by Sicomin, France and Bcomp, Switzerland, respectively. The epoxy resin of type InfuGreen 810 has 38% bio-based carbon. The ampliTex 5042 twill made of flax fibers has 500 g/m^2. The fibers are industrially treated in order to improve the adhesion between the matrix and the fibers. Mechanical properties, tested in preliminary study, were not improved when fibers were further treated with solutions of 2 to 15% NaOH in distilled water.

Composites with 4 to 10 layers of fibers were prepared and samples were cut with a water jet. The apparent interlaminar shear strength τ, tensile and flexural modulus E and strength σ were tested by means of the universal testing machine Shimadzu with frame capacity up to 50 kN (Table 1).

Table 1. Properties of composites depending on number of layers from 4 to 10.

Layers	Fibers fraction,%	σ_f MPa	E_f MPa	σ_t MPa	E_t MPa	ε %	τ MPa
4	40.43	152.44	8690.57	119.41	7288.76	5.31	15.96
5	40.45	149.14	8681.82	114.75	7321.90	5.10	16.85
6	40.73	147.54	9408.81	124.13	7469.06	6.16	17.65
7	40.77	151.31	10330.09	125.75	7694.09	6.92	16.73
8	41.14	144.62	10099.29	122.50	7337.51	8.83	16.64
9	41.28	145.52	10750.30	123.33	7116.50	8.69	16.12
10	41.38	139.71	10516.22	128.76	7060.60	9.09	15.93
CRS	-	150	5500	85	6500	-	17

The results are compared with Rules for the classification of ships, Part 24 - Non-metallic materials, published by Croatian Register of Shipping (CRS). The Rules only include properties for GFRP, and they are given in Table 1. Any alternative material is not predicted in the rules.

The composites have excellent tensile properties; however flexural tests resulted in slightly lower values than given by the CRS. Three points bending tests were applied on both τ and σ_f. The major difference in setup is that the distance between supports for τ is much smaller than that for σ_f ($l=5h$ vs. $l=16h$, where h is the average thickness). Composites with more than 7 layers of fibers have above 41 m.% of fibers, additionally there might be a problem with impregnation of fibers, when more layers are included. Their elongation at break is also higher, which might be a consequence of a lower cross-linking degree. Further investigation of composites with lower fibers fraction is needed.

Keywords: bio-composites, flax fibers, epoxy, mechanical properties, marine application

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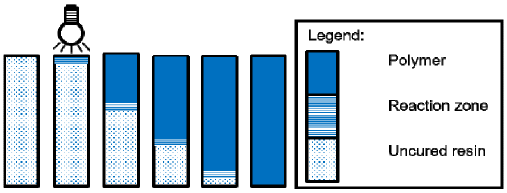
Utilization of frontal polymerization for the preparation of magnetic composites

Stefan Hirner[1,2], Margit Christa Lang[2], Peter Filipp Fuchs[2], Archim Wolfberger [2,*]

[1]*Institute for Chemistry and Technology of Materials, Graz University of Technology, NAWI Graz, Stremayrgasse 9, 8010 Graz, Austria*
[2]*Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, 8700 Leoben, Austria*
[*]*archim.wolfberger@pccl.at*

Composite materials are combinations of at least two or more components, one component illustrating the matrix and the other being in the form of (nano)particles, fibers or otherwise [1]. Polymeric composites often have technical advantages over conventional polymeric materials in terms of their mechanical properties and are therefore used in a wide range of applications, including aerospace, marine, automobile industry and biomedical applications [2]. However, polymeric composites based on thermosetting resins are mainly obtained by a heat-induced curing process which is time consuming a high amount of energy if large parts are produced [3]. These disadvantages can be avoided using novel frontal polymerization techniques (FP). FPs are a fast and energy-efficient alternative to conventional manufacturing techniques for thermosetting polymers and composites. FPs are intentionally triggered by a switchable stimulus such as UV irradiation [4]. The heat released by the triggered exothermic polymerization reaction serves as the stimulus for further polymerization or crosslinking of reactants in adjacent areas.



Schematic representation of the UV-induced frontal polymerization.

The curing of composites by frontal polymerization is often challenging because the filler content can increase the thermal conductivity on the one hand and can reduce the exothermic energy released on the other. A possible improvement or worsening of the polymerization front speed strongly depends on the filler content [5]. In this study, the motivation has been the preparation and charaterization of different magnetic composites in combintion with modeling and simulation of the curing process according to the finite element analysis including a transient heat analysis in order to compare the propagating front for filled and unfilled monomer resins [6]. Special attention has been paid to the functionalization of the particles' surfaces to avoid aggregation. FP composites with functionalized magnetite fillers were successfully prepared. An efficient UV-initiated curing by means of FP was possible and monitored via thermal imaging.

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Analysis of blends of the crystalline and the amorphous sequence of recombinant produced spider silk proteins

M. Hofmaier[1,3*], B. Urban[1], S. Lentz[4], T. Scheibel[4], A. Fery[1,3], M. Müller[1,2]

[1] *Leibniz-Institute of Polymer Research Dresden, Institute of Physical Chemistry and Polymer Physics, Hohe Straße 6, 01069 Dresden* [2] *Technical University Dresden, Chair of Macromolecular Chemistry, 01062 Dresden* [3] *Technical University Dresden, Chair of Physical Chemistry of Polymeric Materials, 01062 Dresden* [4] *University of Bayreuth, Chair of Biomaterials, Prof.-Rüdiger-Bormann Str. 1, D-95447 Bayreuth*
* *hofmaier@ipfdd.de*

Natural spider silk based, recombinantly produced spider silk proteins eADF4(Cx) have been established almost 2 decades ago.[1] The outstanding mechanical[2] and biomedically relevant[3] properties of spider silk are based on the multiblockcopolymer-like character of these proteins including hydrophilic amorphous and hydrophobic crystalline blocks. Discovering the relation between both thin pure eADF4(Cx) films varying module number x and thin blend films of corresponding amorphous and crystalline oligopeptides leads to a better understanding of folding and orientation processes in spider silk proteins.

Pure films of eADF4(Cx) ((GSSAAAAAAAASGPGGYGPENQGPSGPGGYGPGGP)x, x = 1–16) and blend films of the crystalline (pep-c: GSSAAAAAAAAS) and amorphous peptide sequence (pep-a: GPGGYGPENQGPSGPGGYGPGGP)are cast from hexafluoroisopropanol solutions on silicon substrates (Si). For eADF4(Cx) films the number of C-modules (x = 1 – 16) and for blend films the molar fraction of the pep-c (0 – 1) is varied. Both film types are characterized as-cast and after post treatment (ptm) in methanol-vapor using dichroic attenuated total reflection (ATR-) FTIR spectroscopy, circular dichroism and SFM.[4]

As-cast, all blend and eADF4(Cx) films reveale low ß-sheet (< 10 %) and high random coil content (> 80 %). After ptm, it is found that the reached β-sheet content correlates with the pep-c molar fraction until a saturation of around 60 % crystallinity is observed. Further, the observed β-sheet content in eADF4(C16) films correlates with the theoretical crystalline fraction[4, 5] and is in accordance with the β-sheet content found for the corresponding blend what makes blend systems comparable to related eADF4(Cx) proteins. An *out-of-plane* orientation relative to the surface normal of β-sheets is found for all blend and eADF4(Cx) films. In particular, higher *out-of-plane* orientation of the β-sheets is found for blend films due to better mobility of the short peptides pep-a and pep-c compared to eADF4(Cx) proteins.

Keywords: blends, recombinant spider silk proteins, dichroic ATR-FTIR spectroscopy, diblock-copolymers

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Development of carbohydrate-based composites for application in alkaline anion exchange membrane fuel cells

M. Hren[1], M. Roschger[2], V. Hacker[2], M. Nosan[3], B. Genorio[3], S. Gorgieva[1*]

[1]*Faculty of Mechanical Engineering, University of Maribor, Maribor, Slovenia*
[2]*Institute of Chemical Engineering and Environmental Technology, Graz University of Technology, Graz, Austria*
[3]*Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia*
[*]*selestina.gorgieva@um.si*

Alkaline anion exchange membrane fuel cells (AAEMFCs) are attracting increasing attention as they are promising electrochemical devices for power generation and represent a serious counterpart to the more studied proton exchange membrane fuel cells. [1] AAEMFCs, in principle, allow the use of non-precious metal catalysts, which dramatically reduces the cost per kilowatt of power in fuel cell devices. The heart of an AAEMFC is the membrane electrode assembly, which consists of an anion exchange membrane (AEM) sandwiched between an anode and a cathode. Currently, commercially available AEMs do not have satisfactory characteristics that would enable the commercial breakthrough of alkaline fuel cells. Hence the need to develop new, highly efficient, environmentally friendly and economically viable AEMs. The synthesis of synthetic polymeric AEMs is usually complex, time-consuming and environmentally unfriendly. Therefore, it is highly desirable that the membrane material be renewable and environmentally friendly. Naturally derived materials are an alternative, and chitosan (CS), cellulose nanofibrils (CNF), and nanocrystalline cellulose have been proposed as promising so far. [2], [3] They can be easily modified by attaching different moieties. Despite all the advantages presented, biopolymer-based AEMs are still not advantageous compared to synthetic AEMs, especially in terms of ionic conductivity and mechanical properties, which can be improved by the introduction of adequate fillers.

In this work, a series of chitosan-based composite membranes were developed by a simple, cost-effective solution casting method that fully complies with the principles of green chemistry. CNFs, future used as ion conductive fillers, were modified with a quaternary ammonium group-bearing agent with the intent of introducing a permanently positively charged quaternary ammonium moiety. Design of experiments was used as a tool to identify optimal combinations of influencing factors, as well as their relation within selected responses (i.e., membrane properties). The obtained chitosan-$Mg(OH)_2$ composite membranes containing modified CNF as fillers with quaternary ammonium groups were investigated for their structural properties, swelling ratio and alkaline uptake, ethanol permeability, ion conductivity, and ion exchange properties, as well as characterized in a direct alkaline ethanol fuel cell (DEFC). The resulting properties were compared to the benchmark membrane Fumatech. The obtained data indicate the applicability of the newly prepared carbohydrate-based composite membranes as AEMs in DEFC technologies.

Keywords: Anion exchange membrane, alkaline fuel cell, cellulose nanofibrils, carbohydrate composite membrane

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Mesoporous multicompartment microparticles of semi-crystalline triblock terpolymer

Nicole Janoszka[1], Suna Azhdari[1], Hui Chen[1], Deniz Coban[1], Holger Schmalz[2,3*], André H. Gröschel[1*]

[1]*Institute of Physical Chemistry, Center of Soft Nanoscience (SoN), and Center for Nanotechnology (CeNTech), Muenster, Germany*
[2]*Macromolecular Chemistry II, Bayreuth, Germany*
[2]*Bavarian Polymer Institute (BPI), Bayreuth, Germany*
[*] holger.schmalz@uni-bayreuth.de, andre.groeschel@uni-muenster.de

Confinement-Assembly of block copolymers (BCPs) is a versatile way to construct multicompartment microparticles (MMs) with various internal structures. Until now, despite of an explored range of MMs morphologies, individual microdomains or compartments have not been utilized to create porosity for selective loading or removal. Thus, generated porous MMs of ABC triblock terpolymers have potential applications in catalysis, nanomedicine, or energy storage.[1] A convenient strategy for producing mesoporous MMs is the selective removal of an individual microdomain.

In this contribution, we show the formation of MMs from semicrystalline polystyrene-*block*-polybutadiene-*block*-poly(*L*-lactide) (PS-*b*-PB-*b*-P*L*LA; SBL) or polystyrene-*block*-polybutadiene-*block*-poly(ε-caprolactone) (PS-*b*-PB-*b*-PCL; SBC) through evaporation-induced confinement assembly (EICA) and the generation of mesoporous SBL and SBC MMs by hydrolysis of the semi-crystalline P*L*LA or PCL microdomain, respectively. For that, we first used a *Shirasu Porous Glass* (SPG) membrane to generate emulsion droplets with a homogeneous size. After emulsification and EICA process, we obtained MMs predominantly with an inner structure of hexagonally packed core-shell cylinders consisting of a P*L*LA or PCL core, a PB shell, and a PS matrix. For the SBL MMs, increasing crystallinity affect the inner morphology.[2] Interestingly, the SBC MMs exhibit a transition from perforated into gyrodial structure when increasing the evaporation rate. Degradation of the SBL MMs selectively removed the P*L*LA microdomain yielding mesoporous SBL MMs with clear surface roughness (see Figure 1). We foresee that mesoporous MMs will serve as platform for nanomedical or catalytic applications as the PB microdomain can be postmodified with various functionalities in a straightforward manner, e.g., click chemistry.

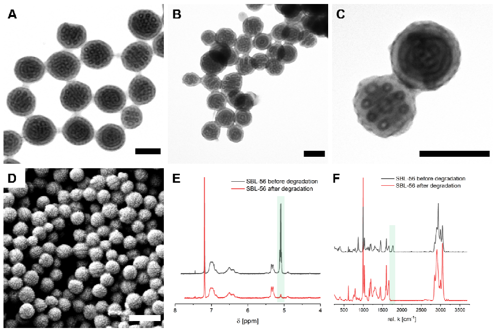

Figure 1. Degradation study of the smallest SBL-56 MMs (d_{pore}= 0.3 µm) under basic conditions in a course of 5 days. TEM overview before (A) and after (B) degradation (scale bars: 200 nm), C) TEM close-up image and D) SEM images after degradation (scale bars: 500 nm), E) ^{1}H-NMR and F) Raman analysis before (black) and after degradation (red) [2].

Keywords: 3D confinement, ABC triblock terpolymers, degradation, emulsification, microparticles

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Effect of silanized silica on crystallization of polypropylene

D. Jaska[1*], S. Zenzingerová[1], Michal Kudláček[1], R. Cermak[1], Jana Navrátilová[1], Lenka Gajzlerová[1]

[1]*Department of Polymer Engineering, Faculty of Technology, Tomas Bata University in Zlin, Vavreckova 5669, 760 01 Zlin, Czech Republic*
[*]*jaska@utb.cz*

The work deals with the crystallization study of polypropylene, which is filled with modified silica. Precipitated silica was silanized with organosilanes propyltriethoxysilane and octyltriethoxysilane. The efficiency of the activation process was evaluated by TGA. Silica treated in this way should be more compatible with non-polar polypropylene due to increased hydrophobicity and adhesion between the nanoparticles and polymer matrix. To find out this hypothesis, mixtures of polypropylene with different concentrations (0.2 wt. %, 1 wt. % and 20 wt. %) of modified and unmodified silica were prepared, which were subjected to thermal analysis using a differential scanning calorimeter. The results of non-isothermal crystallization confirmed that silanized silica acts as a nucleating agent. Adding small amount of modified silica to the polypropylene would affect the crystallization half-life.

Keywords: polypropylene, silica, silanization, non-isothermal crystalization

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Electrically conductive hybrid nanocomposites: Monte Carlo simulation and experimental study

M. Jurča[1*], M. Gořalík[2], J. Vilčáková[1], S. H. Foulger[3], C. Bubulinca[1], P. Sáha[1]
[1]*Centre of Polymer Systems, University Institute, Tomas Bata University in Zlín, třída Tomáše Bati 5678, 760 01 Zlín, Czech Republic*
[2]*Polymer Centre, Faculty of Technology, Tomas Bata University in Zlín, Vavrečkova 275, 760 01 Zlín, Czech Republic*
[3]*Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, 91 Technology Drive, Anderson, SC, USA 29625*
[*]*jurca@utb.cz*

Conductive polymer composites have many applications such as antistatic materials, lightweight shielding materials, wearable electronics and conductive glues. The electrical conductivity of nickel-filled epoxy resin (ER) composites was significantly improved by the addition of a low amount of carbon black (CB) [2] by decreasing the percolation threshold of ER/Ni composites (7.5 vol.%) [1]. E.g. the amount of Ni (8 vol. %) in ER necessary to reach 10^{-5} S/cm was decreased to only 3 vol. % with the addition of 2 vol. % of CB. The decrease of Ni content leads to low-cost production of a lighter final product, due to the lowered density of composite. Prior to physical sample preparation, ER/Ni/CB hybrid composites were simulated by the Monte Carlo method [3] (using commercial software Digimat-FE 6.1.1). Results of simulations were found to be quite precise and comparable with prepared samples. This achievement proved, that computer simulations can be successfully used to evaluate the electrical conductivity of hybrid polymer composites combining fundamentally different fillers (metal and carbon). Selected ER/Ni/CB composites were tested by lap shear test to evaluate the ability of these materials to be used as conductive glues as an alternative to soldering. Composite materials containing CB had higher adhesion than ER/Ni composites as well as neat ER. Another focus of this work is the usage of ER/Ni/CB composites for electromagnetic shielding applications. The addition of CB improved the total shielding efficiency of ER/Ni/CB composites compared to ER/Ni depending on the used concentration. This improvement can be attributed to an increase in reflective losses due to increased conductivity.

Keywords: Conductive polymer composites, computer modeling, electromagnetic shielding.

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[1] Jurča, Marek, et al. Reduced percolation threshold of conductive adhesive through nonuniform filler localization: Monte Carlo simulation and experimental study. Comp Sci and Techn, 2021, 214: 108964.
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The manufacturing of ammonia-free, low-toxic composite materials in the matrix of modified phenol-formaldehyde resins

V. Krasinskyi[1*], L. Dulebova[2], I. Gajdos[2], O. Ivanukh[1]

[1] *Lviv Polytechnic National University, Lviv, Ukraine*
[2]*Technical University of Kosice, Kosice, Slovakia*
[*]*vkrasinsky82@gmail.com*

Obtaining new types of phenol-formaldehyde polymers is of practical importance. They are used as adhesives, anti-corrosion coatings, and binders to manufacture press powders. The versatility of phenol-formaldehyde materials is due to the wide temperature range of their hardening and operation and the ability to create different performance characteristics of materials depending on the purpose. The development of polymer adhesives and protective coatings requires the creation of new polymeric materials with a given combination of properties, primarily with low toxicity, high adhesive strength, water, and chemical resistance, heat resistance. We know that, of the wide range of known modifiers of phenol-formaldehyde resins (PFR), only a tiny part of their leads to a significant improvement in the characteristics phenol-formaldehyde materials. The use of most of the proposed modifiers, along with a slight improvement in specific physical and mechanical properties, is often accompanied by a deterioration of composites' sometimes essential performance characteristics. Therefore, the problem of finding new modifiers to eliminate the shortcomings of phenol-formaldehyde compositions is relevant today.

It is assumed that the chemical modification of novolac PFR using epoxy resin and polyvinylpyrrolidone (PVP), where the hardener will be the epoxy resin, will allow the hardening of the composition without hexamethylenetetramine with the formation of a combined structure "penetrating network". As a result, the developed adhesives and anti-corrosion coatings based on such compositions will not emit during the hardening of toxic volatile products. In addition, such compositions will be characterized by high adhesive properties and heat resistance.

This work aimed to develop new low-toxic composite materials based on novolac phenol-formaldehyde resin with improved adhesion properties and heat resistance.

Studies confirm the possibility of chemical modification of novolac phenol-formaldehyde resins by polyvinylpyrrolidone and epoxy resin at temperatures higher than 120 °C. Using differential-thermal and IR-spectroscopical analyses, as well as model compounds, we showed that PFR macromolecules joint PVP in the presence of free methoxy groups of PFR of novolac type and carbonyl groups of PVP. The combined chemical network is formed determining the high thermal stability of the coating. The modification of novolac PFR by polyvinylpyrrolidone and epoxy resin creates conditions for the composition curing without urotropine. Owing to this fact we obtained thermostable non-toxic glue and paintwork materials with high technological effectiveness and adhesion, good physicomechanical properties and low water absorption. In particular, with the polyvinylpyrrolidone content from 0.5 to 1 wt% and epoxy resin from 25 to 50 wt%, the adhesive strength of the compositions increases 5-7 times.

Keywords: phenol-formaldehyde resins, epoxy resin, polyvinylpyrrolidone, modification, adhesion strength.

Acknowledgments
The work was carried out within the framework of the National Scholarship Program of the Slovak Republic.

New type of polymeric surfactants for modification of smectites and evaluation of their cytotoxicity

Zuzana Kroneková[1]*, Ľuboš Jankovič[2], Zuzana Mošková[1], Jana Madejová[2], Juraj Kronek[1]

[1] *Polymer Institute SAS, Dúbravská cesta 9, 84541 Bratislava, Slovakia;*
[2] *Institute of Inorganic Chemistry SAS, Dúbravská cesta 9, 84541 Bratislava, Slovakia*
**zuzana.kronekova@savba.sk*

Preparation of advanced functional materials based on layered silicates is drawing attention in industrial applications, as well as in the field of biotechnology and biomedicine [1]. Layered silicates are two-dimensional materials capable to form hybrid materials via confining of cationic organic moieties within the interlayer spaces of the inorganic carriers. The properties of organoclays depend largely on the type and arrangement of organic cations present in clay mineral interlayer. An important class of hybrid materials are bionanocomposites composed of biopolymers and inorganic solids, that offer biocompatibility and biodegradability, opening thus new applications in regenerative medicine and in environmentally friendly materials [2]. Here, other prospective cationic species used for modification and interaction with clay minerals are various cationic polymers (polycations). Among them, poly(ethylenimines) (PEIs), are the most widely used polycations employed in different fields of biomedicine, biotechnology and biomaterials science [4]. However, PEIs have been shown as cytotoxic to cells. On the other hand, statistical copolymers of PEI with poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline) were shown to be less cytotoxic and more suitable for biological and biomedical applications [5,6].

In this study, copolymers of poly(2-ethyl-2-oxazoline)(PEtOx) and PEI (PEtOx-co-PEI) were prepared by partial hydrolysis of PEtOx containing PEI units in the range of 9 to 55 mol%. Prepared copolymers were used for preparation of modified smectites. Biocompatibility of prepared polycations and their smectite intercalates was assed with cell viability MTT assay and cell morphology after direct contact with selected substances. We will show how the effect of cationic charge and concentration of polycations on modification of montmorillonites, the physico-chemical properties and cytotoxicity of novel hybrid materials.

Keywords: poly(ethylene imine), poly(2-etyl-2-oxazoline), montmorillonites

Acknowledgments

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Composite layers of polymer brushes and nanoparticles

F. Lange[1*], R. Jordan
[1]*Chair of Macromolecular Chemistry, Dresden, Germany*
**fred.lange@tu-dresden.de*

Porous layers of nanoparticles can be used for catalysis.[1] A possible way to obtain these layers is the incorporation of nanoparticles in polymeric scaffolds. Here we present a simple method to generate crack-free thin layers (fig. 1) with an adjustable porosity. Therefore, cationic polymer brushes are synthesized via surface-initiated copper(0)-mediated controlled radical polymerization (SI-CuCRP).[2] In the next step, these polymer layers are immersed in a suspension of negatively charged silica nanoparticles (NPs) to form composite layers.[3] A subsequent calcination step allows the removal of the polymeric scaffold which results in a porous network of the beforehand embedded nanoparticles.

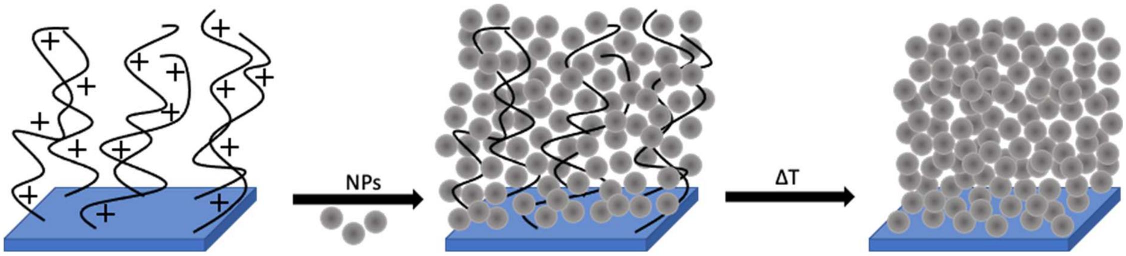

Figure 1: *Cationic polymer brushes serve as scaffold for incorporation of negatively charged nanoparticles. A subsequent calcination step removes organic compounds to form porous layers.*

The SI-CuCRP enables control over the grafting density and the thickness of the cationic polymer brushes.[4] This can be used to tailor the properties of the generated calcinated composite layers. For example, by implementing a grafting density gradient, a porosity gradient can be achieved.

In addition to that, the influence of the nanoparticle size was investigated as well as the concentration of the nanoparticle suspension while incorporation. Varying these parameters allows additional control over the thickness and porosity of the calcinated composites. Furthermore, the system was expanded by using gold and palladium nanoparticles instead of silica. This might allow the implementation of these porous layers in the field of catalysis.

Keywords: composite layers, nanoparticles, polymer brushes, porosity

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Looped Mechanophores as Stress Indicators in Polymer Networks

C. Lupfer [1*], A. Walther[1]

[1]A^{3}BMS Lab, *Active, Adaptive and Autonomous Bioinspired Materials, Department of Chemistry, University of Mainz, 55128 Mainz, Germany; DFG Cluster of Excellence @ FIT "Living, Adaptive and Energy-Autonomous Materials Systems" (livMatS), Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg, 79110 Freiburg, Germany;*

**claudius.lupfer@uni-mainz.de*

The use of mechanophores as building blocks that serve as predefined weak linkages has enabled the creation of mechanoresponsive and mechanofluorescent polymer materials, which are interesting for a range of applications including the optical detection of stress and the prediction of material fracture, fatigue and hysteresis in polymers.[1]

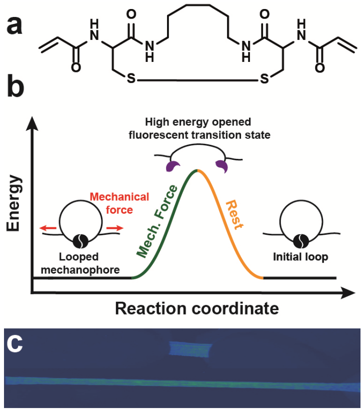

Figure 1: a) Structure of our used looped mechanosensing disulfide module. **b)** Energy landscape of the looped mechanophore. **c)** Fluorescence images of unstressed and stretched pro-fluorophore doped elastomers crosslinked with the looped mechanophore.

However, in typical mechanophores, covalent bonds are broken when polymers containing these chemical motifs are stressed, weakening the polymers in the process.

Here we show a new class of mechanophores, featuring a loop motif, that avoid this drawback by offering a safety line keeping the network topology intact after covalent bond rupture (**Fig. 1 b**).

For this we use a looped mechanophore featuring a sacrificial disulfide bond (**Fig. 1 a**). This mechanophore we embedded as crosslinkers into elastomers and solvent swollen organogels. Mechanofluorescent readout is achieved by addition of a pro-fluorophore that turns fluorescent when reacting with generated mechanoradicals. With this concept we could visualize the mechanoactivation using fluorescence microscopy (**Fig. 1 c**).

With this concept we established a new class of mechanophores that can indicate stress in polymer networks reversibly. In future trials we will exploit the high reactivity of the generated radicals for mechano-initiated downstream reactions inside polymer networks.

Keywords: mechanochemistry, molecular probes, mechanoresponsive polymers; polymer materials;

Acknowledgments

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References

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Reactivity and catalytic effect of fumarate metal organic frameworks on the thermal curing of bispropargyl ether

Siva Kaylasa Sundari [1], Shamim Rishwana [1], Arunjunai Raj Mahendran[2],
Vijayakumar C.T[3]
[1] *Department of Chemistry, Kamaraj College of Engineering and Technology (Autonomous), S.P.G.C. Nagar, K. Vellakulam-625701, Tamil Nadu, India*
[2] *Competence Center for Wood Composites and Wood Chemistry, Altenberger strasse 69, A-4040 Linz, Austria*
[3] *Department of Polymer Technology, Kamaraj College of Engineering and Technology (Autonomous), S.P.G.C. Nagar, K. Vellakulam-625701, Tamil Nadu, India*
**a.mahendran@wood-kplus.at*

Metal organic Frameworks (MOFs) are hybrid organic-inorganic materials having wide range of applications especially in the field of catalysis. MOFs has an extraordinary high surface area, tunable pore size and adjustable internal space properties[1]. Acetylene terminated polymers are gaining interest due to the need for easily processable thermally stable networks[2]. The formation of void free materials is the main advantage of bispropargyl ether monomers. The aluminum fumarate (Al_FA_A) and copper fumarate (Cu_FA_C) MOFs were synthesized and blended with bispropargyl ether (bis (4-propargyloxyphenyl) sulfone - SPE). The (SPE + 1 % MOFs) blends were characterized and they are polymerized P(SPE + MOFs). The synthesized materials are characterized using Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR), Differential Scanning Calorimetry (DSC), Thermogravimetry (TG) and Thermogravimetric analyzer coupled with Fourier Transform Infrared Spectrophotometer (TG-FTIR). The addition of both MOFs decreases the enthalpy of fusion and enthalpy of curing by 60 % which permit low temperature processability. The addition of copper MOF to SPE drastically reduced the temperature at which the thermal curing is maximum (300 °C to 252 °C). The 2-H chromenes are formed from bispropargyl ethers by Claisen type sigmatropic rearrangement. Compared to the pure SPE, the polymers resulting from hybrid systems show slower thermal degradation rate and the evolved gas analysis predicted the products formed during degradation. The sulfone as swivel group in SPE and the involvement of fumarate π-bonds of MOFs during polymerization makes the material more versatile. The investigation concludes that modifications in functionality leads to the application of these novel MOF blends for high temperature applications to produce thermally stable matrix resin for the reinforced composites. The curing temperature of SPE can also be drastically reduced.

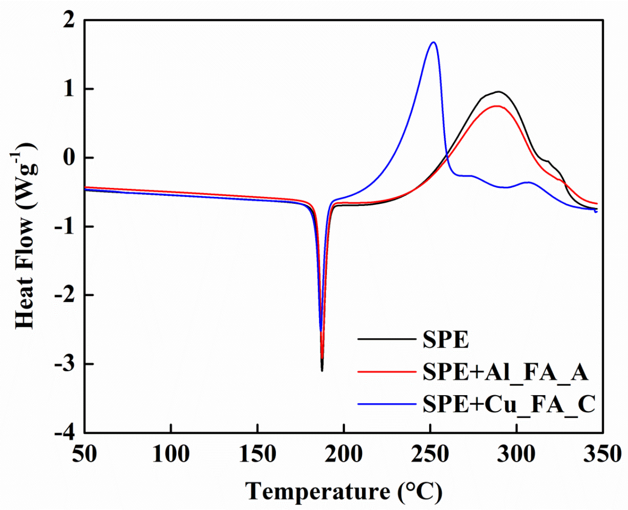

Figure 1: DSC curing curves for SPE and SPE with MOFs

Keywords: Metal Organic Framework (MOF), fumrate MOFs, catalytic effect, bispropargyl ether, high temperature application

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Filler-network related contributions to dissipation in NR/BR blends filled with carbon black

S.M. Nagaraja[1,2*], S. Henning[2], N. Hackel[1], S. Ilisch[3], M. Beiner[1,2]
[1]*Martin Luther University Halle-Wittenberg, 06099 Halle (Saale), Germany*
[2]Fraunhofer IMWS*, Walter-Hülse-Str. 1, 06120 Halle (Saale), Germany*
[3]*Synthos Schkopau GmbH, Strasse E17, 06258 Schkopau, Germany*
***sriharish.malebennur@imws.fraunhofer.de**

The focus of this study is to comprehend the factors influencing the filler network contributions to dissipation in carbon-black filled natural rubber and polybutadiene rubber blend composites (NR/BR). In recent studies, we have proposed a modified Kraus equation to resolve and quantify different contributions to dissipation by approximating the loss modulus (G'') data-dependent on dynamic shear strain amplitude.[1] The resolved filler-network related contributions to dissipation are dominant at different strain amplitude regimes as obtained from strain sweeps measured at different temperatures and frequencies. We have proposed a physical picture that describes the viscoelastic nature of filler network and supports the earlier work that concluded glassy bridges as a source for viscoelastic reinforcement in S-SBR composites filled with silica. [2] The resolved contributions to dissipation is related to: (i) deformation of intact glassy bridges in the filler network dominating at small strain amplitudes, (ii) breaking of glassy rubber bridges dominating at intermediate strain amplitudes, and (iii) contributions to dissipation which are filler network independent remaining at very large strain amplitudes.[1] The approach was further used to get deeper insights about the viscoelastic filler network and its contribution to dissipation and reinforcement. Following the similar approach we have evaluated the NR and NR/BR blend composites filled with carbon black and realized the importance of glassy bridges being a part of filler-network and obtained further insights about the two factors that are specific to the viscoelastic filler network. The data suggested that the chemical composition of the glassy bridge and topology of the filler network have a strong influence on the dissipative and reinforcement properties.[3] To further evaluate this hypothesis, in this work in-depth studies are done on NR/BR blends by varying the method the processing conditions, and an approach is developed to evaluate the filler network topology using TEM images.[4] The results shown in this poster discusses the importance of the chemical composition of glassy bridge and topology of filler network on dissipation and reinforcement in rubber composites.

Keywords: Rubber composites, Dissipation, Reinforcement, Dynamic mechanical analysis, Transmission electron microscopy.

Acknowledgments

The authors thank IB Sachsen-Anhalt and EFRE for financial support in the framework of the projects 1604/00027 and 1604/00028.

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Soft Mechanochemistry of Disulfide Crosslinked Polymer Networks

Zhao Meng and Harm-Anton Klok[1*]

[1]*First author's Institution, City, Country (Calibri, 11 pt., Italic)*
[*]*harm-anton.klok@epfl.ch (Calibri, 11 pt., Italic)*

Mechanochemistry harnesses mechanical force to facilitate chemical reactions. Traditionally, the field of polymer mechanochemistry has used methods to activate chemical bonds, which use forces that are larger than those are that are required to break a covalent bond. The effect of weaker forces, which are known to play important roles in mechanobiology, has so far been largely overlooked in polymer mechanochemistry. This subdomain of mechanochemistry, which we like to refer to as soft mechanochemistry, is exemplified by degrafting of polymer brushes [1]. There is also evidence that indicates that soft mechanochemical effects can impact the properties of crosslinked polymer networks. Very little work, however, has been done so far to systematically investigate and understand these phenomena. In this work, we have prepared disulfide crosslinked polymer networks and investigated the impact of swelling-induced tension on the disintegration of polymer networks.

Keywords: mechanochemistry, disulfide, polymer networks

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Performance Fabrics Obtained by In-Situ Growth of Metal−Organic Frameworks in Electrospun Fibers.

Maya Molco[1,2], Fabrice Laye[3], Enrique Samperio[3], Shiran Ziv Sharabani[1,2], Victor Fourman[4], Dov Sherman[4], Manuel Tsotsalas[3], Christof Wöll[3], Joerg Lahann[3], and Amit Sitt[1,2]

1. School of Chemistry and the Tel-Aviv University Center for NanoScience and Nanotechnology, Tel Aviv University, Tel Aviv, 6997801, Israel
2. The Center for Physics & Chemistry of Living Systems, Tel Aviv University, Tel-Aviv, 6997801, Israel
3. Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, 76344, Germany
4. School of Mechanical Engineering, Tel-Aviv University, Tel-Aviv, 6997801, Israel
**amitsitt@tauex.tau.ac.il*

Metal organic frameworks (MOFs) are highly porous synthetic materials, which are made of metallic ions interconnected with organic ligands. MOFs exhibit exceptional surface to volume ratio, variable pores sizes, and selective binding and hence, there is an ongoing effort to broadening their utilization in different applications

In this work, I demonstrate the development of a novel approach for fabricating freestanding MOF-embedded polymeric fibers, using the fibers themselves as microreactors for the in-situ growth of the MOFs. Two MOFs were chosen to demonstrate this method: HKUST-1, composed of copper (II) ions and benzene-1,3,5-tricarboxylic acid and ZIF-8, a member of the zeolitic imidazolate frameworks, composed of zinc (II) ions and 2-methylimidazole. The MOFs fibers are obtained via co-hydrodynamic electrospinning of polymer solutions that contain the MOF precursors. The obtained fibers are then exposed to ethanol vapor resulting in the coverage of the fibers by MOFs. The crystals' structure was confirmed by X-ray diffraction and the mass percentage of the crystals was determined by several methods. The MOF fibers obtained using this method can reach lengths of hundreds of meters and exhibit mechanical strength that allows arranging them into dense, flexible, and highly durable nonwoven meshes. The MOF crystals grow from the core of the fibers toward their outer surface and are strongly embedded inside the polymer matrix and enhances the fibers mechanical strength. The use of the MOF fiber meshes for the immobilization of the enzyme horse radish peroxidase (HRP) was examined, and the enzyme-MOF fabrics exhibit improved catalytic performance.

The MOFs embedded fibers, obtained in this work, demonstrate the use of electrospun polymeric fibers as microreactors for performing chemical reactions that modify the properties of the fibers and lead to new functionalities and hold promise for different applications including filtering, selective catalysis, and sensing, and pave the way to new and improved performance fabrics and active membranes.

Laser Microprinting of Nanoporous Materials Based on Hexagonal Columnar Liquid Crystals via Two-Photon Polymerisation

J. Monti[1], A. Concellón[2], R. Dong[3], M. Simmler[4], A. Münchinger[5], H. Nirchl[4], M. Wegener[1,5], C. Osuji[3], E. Blasco[1,6,7*].

[1]Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany
[2]Department of Chemistry, Massachusetts Institute of Technology (MIT), Cambridge, MA, USA
[3]Department of Chemical and Biomolecular Engineering, the University of Pennsylvania, Philadelphia, PA, USA
[4]Institute of Mechanical Process Engineering and Mechanics (MVM), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
[5]Institute of Applied Physics (APH), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
[6]Organic Chemistry Institute, Heidelberg University, Heidelberg, Germany
[7]Centre for Advanced Materials (CAM), Heidelberg University, Heidelberg, Germany
[*]eva.blasco@oci.uni-heidelberg.de

Nanoporous polymeric materials relying on hexagonal columnar liquid crystals (Colh LCs) are excellent candidates for size- and charge- selective membranes. However, their use as printable material remains unexplored. In our work, we propose a new approach for the fabrication of ordered nanoporous microstructures based on Colh LCs, using two-photon laser printing. To fulfill this aim, we employ, as the base of our printable ink, a photocrosslinkable hydrogen-bonded complex, that self-assemble into Colh mesophases. The presence of photopolymerisable acrylate groups at the periphery of the molecules enables a successful light-induced polymerisation printing process. We begin our investigation by the systematic study of the formation of the hydrogen-bonded assemblies and of their LC properties, and of the formulation of the Colh inks for laser microprinting. We demonstrate the conservation of the Colh arrangement through the photopolymerisation process and the later possibility to break the hydrogen-bonding interactions to afford nanoporous microstructures. Finally, we show the selective adsorption of small cationic molecules in the microstructures, which highlights the potential of the approach for the fabrication of functional nanoporous structures with a defined geometry. We believe that this first example of printable Colh photoresists will open new opportunities for the fabrication of functional porous microdevices.

New Organic-Inorganic hybrids with Enhanced Dispersibility and Photo-actuating Properties

Mosnáčková Katarína[1], Mrlík Miroslav[2], Mičúšík Matej[1], Peter Kasák[3], Mosnáček Jaroslav[1]

[1]Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia
[2]Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, trida Tomase Bati 5678, 760 01 Zlin, Czech Republic
[3]Center for Advanced Materials, Qatar University, Doha 2713, Qatar

Surface modification of carbon nanotubes by polymer coating with uniform architecture has attracted wide-spread attention because it provides access to nanoparticles with novel structures and properties. Nowadays, the controlled polymerization techniques represent a promising method suitable for achieving precise control over the structure of the grafted polymer chains with varying range of graft densities [1]. The introduction of PHEMA-g-PCL copolymer moieties to the different types of surface resulting in improvement of the physicochemical and thermo-responsive properties and thanks to biocompatible and hydrophobic characters of PCL can be uses for antitumor nanocarrier applications and tissue engineering [2,3]. Polymer hybrids consisting of the multiwalled carbon nanotubes modified with either poly(2-hydroxyethyl methacrylate) / poly(caprolactone) homopolymer or copolymer poly(2-hydroxyethyl methacrylate)-co-poly(caprolactone) (PHEMA-co-PCL) were prepared and their viscoelastic and photo-actuating properties were investigated. Carbon nanotubes modified with PHEMA homopolymer were prepared by surface initiated reversible addition and fragmentation chain transfer polymerization (SI-RAFT) in control manner resulting in the formation of core-shell nanostructures. In the second step, the pendant hydroxyls of PHEMA were used for initiation of ring opening polymerization (ROP) of ε-caprolactone leading to formation of tree-like copolymer structures. Control over the molecular characteristics of the second PCL layer was achieved by covalent tin (II) compound used as a catalyst. Two step modification led to complete covering of MWCNTs by copolymer layer resulting superior dispersibility proven by AFM. XPS and TGA were used for determination of elemental composition and the grafted polymer quantities of the resulting hybrid particles. XPS analysis confirmed the successful covalent immobilization of chain transfer agent on the MWCNTs surface and showing a significant increase in atomic oxygen content after RAFT and ROP polymerization coming from grafted polymer. The viscoelastic properties of copolymer and hybrid particles were evaluated by dynamic mechanical thermal analysis. Comparison of photo-actuating behaviour of the copolymer and copolymer modified hybrid particles was performed using thermomechanical analysis device.

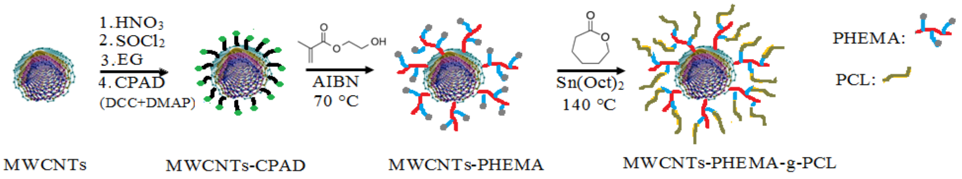

Figure 1. Schematic illustration of multistep modification of crude MWCNTs resulting in PHEMA-g-PCL copolymer grafting.

Acknowledgments

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Investigations on surface-tethered germanium based photoinitiators

Matthias Müller [1], Wolfgang Kern[1,2*], Christine Bandl [1], Micheal Haas [3], Manfred Drusgala[3]

[1] Chair in Chemistry of Polymeric Materials, University of Leoben, Otto Glöckel-Straße 2, A-8700 Leoben
[2] Polymer Competence Center Leoben GmbH, Roseggerstraße 12, A-8700 Leoben
[3] Institute of Inorganic Chemistry, Graz University of Technology, A-8010 Graz
** E-mail: wolfgang.kern@unileoben.ac.at*

Since surface initiated polymerization gained increasing interest in the last decades, the coupling of photoinitiators to surfaces and particles has become an important research topic in polymer photochemistry. To give some examples, immobilized photoinitiators are employed for surface modification, including the adjustment of surface polarity, its optical properties and reactivity as well as the fabrication of nanostructured materials by lithographic patterning. Moreover, photoactively functionalized particles are applied as low-migration photoinitiators, and for the generation of inorganic protective layers on inert polymer films and fibers. An example is the reaction of azidophenyl functionalized silica particles with polyethylene and poly(ethylene terephthalate).

In a recent study, the potential of selected acylgermanium components as photoinitiators was demonstrated. The group-14-based compounds formed germyl radicals upon irradiation with UV light (λ = 355 nm), which added to double bonds of an acrylic monomer. This new class of photoinitiators showed high photoreactivity even at low concentrations as well as considerable photobleaching, which makes them promising for high performance applications. [1]

In the present work, selected Ge-based photoinitiators were immobilized to inorganic surfaces utilizing different routes. Firstly, the direct attachment of triacylhalogermanes (X = Br and I) to polar surfaces by reaction of the Ge-halogen unit with superficial hydroxyl groups of the substrate was investigated. In a second approach the Ge-based photoinitiators were modified with functional silanes, introducing trialkoxy groups which act as coupling units in the subsequent immoblization reaction. The photoreactive surfaces were then employed in surface initiated polymerization. Thin layers of polystyrene and acrylic polymers were generated on the modified substrates. Moreover, structured polymer films were prepared, proving the high photoreactivity and efficiency of the immobilized germanium based photoinitiators in spatially resolved grafting-from reactions. The functionalized samples were investigated with regard to surface composition and reactivity, using FT-IR and XPS spectroscopy as well as optical and atomic force microscopy.

Future prospects encompass the immobilization of the germanium based photoinitiators onto inorganic particles such as silica nanoparticles in order to prepare high performance low-migration photoinitiators, which are required in the field of UV-curable printing inks for example.

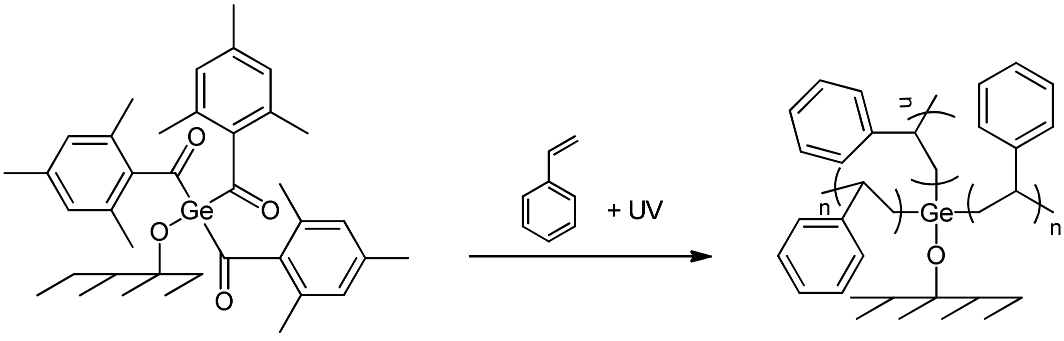

Figure 1: Schematic representation of a surface coupled Ge-based photoinitiator (left) initiating the polymerization of styrene (right)

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Layer-by-layer (LbL) assembly of calixarene modified GO and LDH nanostructures on flame retardancy and dye adsorption behavior of flexible polyurethane foams

Saman Abrishamkar [1], Abbas Mohammadi [1*], Jimena De La Vega [2], De-Yi Wang [2,3], Ehsan Naderi Kalali [4]

[1] *Department of Chemistry, University of Isfahan, Isfahan 81746-73441, I.R. Iran*

[2] *IMDEA Materials Institute, C/Eric Kandel 2, 28906 Getafe, Madrid, Spain*

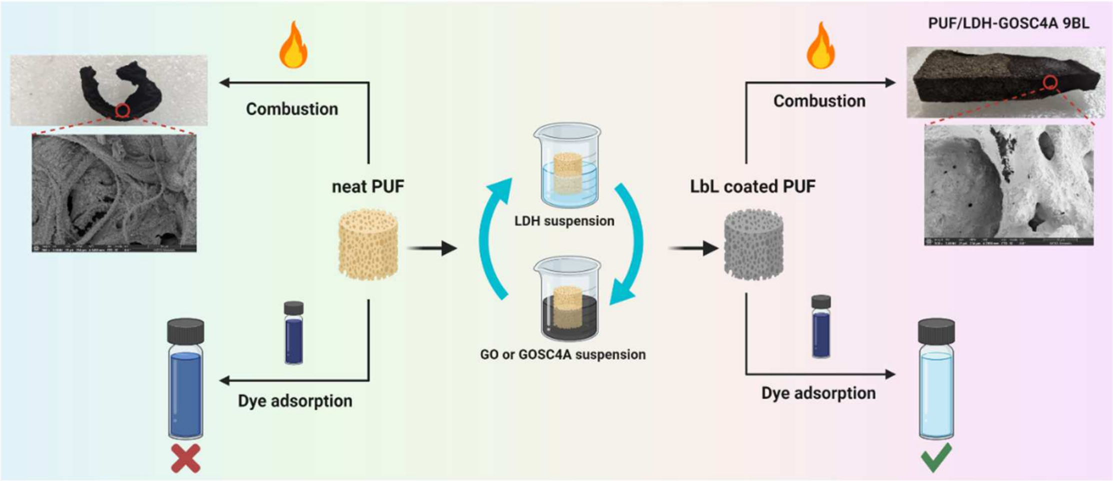
[3] *Universidad Francisco de Vitoria, Ctra. Pozuelo-Majadahonda Km 1,800, 28223, Pozuelo de Alarcón, Madrid, Spain4*

[4] *Institute of Macromolecular Chemistry, 2, Heyrovského nám. 1888, Břevnov, 162 00 Praha 6*

[*] a.mohammadi@sci.ui.ac.ir

In this project, the effect of LbL coatings based on layered double hydroxide (LDH), graphene oxide (GO), and sodium p-sulfonatocalix[4]arene modified graphene oxide (GOSC4A) on the fire resistance and dye adsorption behavior of flexible polyurethane foam was investigated. For this purpose, samples including neat PU foam and modified PU foams with 3, 6, and 9 bilayers of LDH-GO and LDH-GOSC4A coatings were prepared. SEM images of the prepared foams confirmed the presence of LDH-GO and LDH-GOSC4A coatings on the foam surface and showed that the LDH-GOSC4A layers form a denser and more uniform coating on the surface. Combustion studies of prepared foams using CCT and horizontal burning test demonstrated that at the same number of bilayers, foams including LDH-GOSC4A coatings showed better flame-retardant properties than LDH-GO coated foams. Therefore, PUF/LDH-GOSC4A 9BL foam showed the highest fire resistance, and its PHRR, THR, and TSP values decreased by 28.8, 11.8, and 36.3% compared to uncoated PUF, respectively. Methylene blue (MB) adsorption studies revealed that adsorption of MB onto PUF/LDH-GOSC4A 9BL is well consistent with the pseudo-second-order kinetic model and its maximum adsorption capacity is 38.46 mg/g based on the Langmuir isotherm equation.

Keywords: polyurethane foams, LbL assembly, layered double hydroxides, graphene oxide, flame retardancy, dye adsorption



Additive soft matter design by UV-induced polymer hydrogel inter-crosslinking

T. A. Neuendorf[1], N. Weigel[1], M. Vigogne[1], J. Thiele[1*]

[1]*Leibniz Institute of Polymer Research, Dresden, Germany*
[*]*thiele@ipfdd.de*

In recent years, stimuli-responsive hydrogels have gained tremendous interest in designing smart 4D materials for applications ranging from biomedicine[1] to soft electronics[2] that can change their properties on demand over time. However, at present, a hydrogels' response is often induced by merely a single stimulus, restricting its broader applicability. Here, the controlled hierarchical assembly of various hydrogel building blocks, each with a tailored set of mechanical and physicochemical properties as well as programmed stimulus response, may potentially enable the design and fabrication of multi-responsive polymer parts that process complex operations.

In this context, the inter-connection stability of such building blocks is equally crucial as their property since it is directly associated with the transfer of information between the building blocks. Although multiple approaches of inter-connection[3,4] and assembling[5,6] were made, they either miss out on the additive manufacturing aspect, namely the controlled stacking of assemblies into 3D objects, or mostly rely on unsaturated moieties of the respective base material to inter-connect their hydrogel structures instead on a strong building block inter-connection.

We address these challenges using a separate crosslinking mechanism based on UV-induced 2,3-dimethylmaleimide (DMMI) dimerization to inter-connect hydrogel-based building blocks. To demonstrate its versatility, we first inter-connect acrylamide-based and N-isopropylacrylamide-based millimeter-sized cubic building blocks, respectively, yielding dual-crosslinked freestanding assemblies. Second, we apply this approach to inter-connect microfluidically fabricated, micrometer-sized acrylamide-based spheres into freestanding structures.

With this work, we want to pave the way towards a new multi-material additive manufacturing technology based on hydrogel building blocks with the capability of tuning material properties at the micrometer-scale, allowing topologically complex, multi-functional materials.

Keywords: Hydrogel; Assembly; Additive manufacturing; Photopolymerization; Crosslinking; Building blocks; Droplet microfluidics

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Advanced polymerization techniques in surface modification.

Darshak Pathiwada[1,2], Jaroslav Mosnáček[1,2]

[1]Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia
[2]Centre for Advanced Materials Application, Slovak Academy of Sciences, Bratislava, Slovakia

Among the variations of ATRP that employ ppm levels of catalyst (e.g. ARGET-ATRP, SARA-ATRP, ICAR-ATRP), PhotoATRP is receiving significant notice due to its low cost of operation, enhanced tolerance towards oxygen, milder reaction conditions, and provides temporal control over the polymerization. It also further eliminates the use of additional chemicals [1, 2]. Surface modification using polymers via surface-initiated atom transfer radical polymerization (SI-ATRP) can impart desired properties such as antifouling and antimicrobial, functionality, lubrication, corrosion resistance etc. The above-mentioned characteristics of photoATRP in surface modification via SI-PhotoATRP can make it an extremely valuable tool for the synthesis of well-controlled polymer brushes over large areas by using minimal reaction volumes [3].

In the present work, polymer brushes are synthesized on a silica wafer (SiO_2). Initially, ATRP initiator motifs are attached to the silica substrate by using vapour deposition, these act as initiator sites for the development of polymer brushes. Various studies are needed to understand the effects of catalyst concentration, the intensity of light, oxygen concentration on the growth of polymer brushes. The surfaces were modified by functional polymers including polymers from renewable monomers such as α-methylene-γ-butyrolactone (MBL). These functional polymers can be used for subsequent post functionalization of the surfaces.

Keywords: Surface modification, PhotoATRP, SI-photoATRP, Functional polymers.

Acknowledgments

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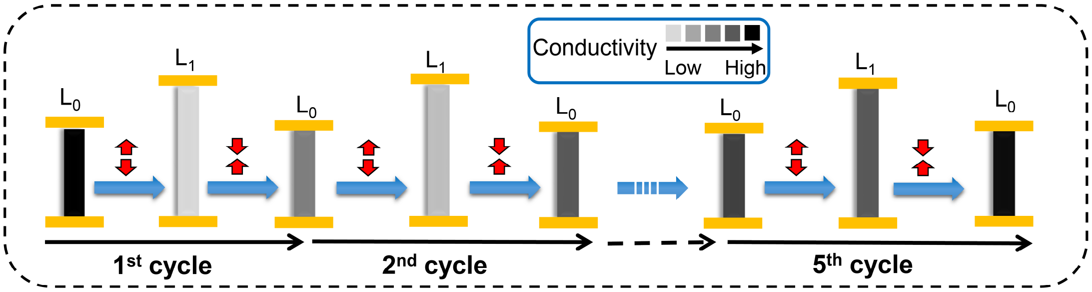
Electrical conductivity behavior of thermoplastic starch-based composite during cyclic deformation

Hamed Peidayesh[1], Katarína Mosnáčková[1], Zdenko Špitalský[1], Abolfazl Heydari[1], Alena Opálková Šišková[1,2], Ivan Chodák[1*]

[1]*Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia*
[2]*Institute of Materials and Machine Mechanics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 13 Bratislava, Slovakia*
[*]*Ivan.chodak@savba.sk*

Conductive polymer composites (CPCs) are designed by mixing an insulating polymeric matrix with conductive fillers. Substantial effort has been devoted in the past decade to understanding the features of CPCs with respect to conductivity changes under external stimuli, such as thermal, electrical, mechanical, or chemical stresses [1]. Mechanical deformation is likely the most important factor that affects the structure of the conductive pathways. On the other hand, polymers from renewable resources as matrices for solid conducting composites have been considered. Thermoplastic starch (TPS) has attracted the attention of many researchers in the biopolymer industry since it is abundant in nature, cost-effective, available from renewable resources, and biodegradable [2]. However, the dependence of electrical conductivity on mechanical deformation for TPS-based composite has not yet been investigated in similar experiments using online measurements.



Online measurement of conductivity changes during cycling deformation [3]

Herein, this contribution is focused on investigating the changes in electroconductive paths during cyclic deformation of electroconductive TPS-based composites. TPS-based composites filled with various carbon black (CB) contents were prepared through melt processing. With increasing CB content, the tensile strength and Young's modulus were found to increase substantially. We found a percolation threshold for the CB loading of approximately 5.5 wt% based on the rheology and electrical conductivity. Both the electrical conductivity and mechanical properties were recorded in parallel using online measurements. The electrical conductivity increases or at least remains constant during five runs of repeated cyclic mechanical deformations to constant deformation below strain at break, indicating more perfect recovery of conductive paths and their new formation.

Acknowledgments

This study was supported by projects VEGA 1/0751/21, APVV 20-0593, and project M--ERANET En--ActiveETICS.

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Morphology and thermal properties of Poly(3-hydroxy butyrate) produced by microbial fermentation and filled with β-tricalcium phosphate

Konstantinos N. Raftopoulos[1*], Tomasz M. Majka[1], Ewa Szefer[1], Adam Szeligowski[2], Tomasz Witko[2], Olga Zastawny[2], Adam Kaczmarski[2], Aneta Zima[3], Ewelina Cichoń[3], Szymon Skibiński[3], Joanna Czechowska[3], Anna Ślósarczyk[3], Maciej Guzik[3], and Krzysztof Pielichowski[1]

[1]*Department of Chemistry and Technology of Polymers, Cracow University of Technology, Kraków, Poland*
[2]*Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków, Poland*
[3] *Department of Ceramics and Refractories, AGH University of Science and Technology, Kraków Poland*
[*]*konstantinos.raftopoulos@pk.edu.pl*

Poly(3-hydroxy butyrate) (P(3HB)) is a biocompatible polymer which has been proven suitable for hard tissue regeneration applications [1]. This polymer can be obtained form biological fermentation processes, and seve as a matrix for the production of composites with ceramic components for the purpose of tailoring its physical, chemical and biological properties to the specific needs of the application at hand. Another parameter that has a significant impact for this kind of applications is the actual physical form of the resulting composite.

In this work, P(3HB) was obtained via microbial fermentation in a biorefinery module, from glycerol, a hydrolysis product of rapeseed oil. It was subsequently modified by β-tricalcium phosphate (β-TCP). The inclusion of this ceramic additive allowed the production of biopolymer-ceramic composites, which can be applied in the regeneration of cartilage tissue or other advanced non-implantation composite materials. The composites were produced both with standard polymer processing (extrusion), as well as with a wet-spinning approach. The first method provided solid like materials, while the second one produced foam-like materials, which are considered more appropriate for tissue regeneration applications.

The obtained materials were characterised regarding their micromorphology with Scanning Electron Microscopy. Their crystal structure was characterised by X-ray diffraction. Moreover the impact of the filler on the glass transition and crystallinity was studied by Differential Scanning Calorimetry.

Filler dispersed well in the matrix, and it is interesting to observe significant similarities in the crystal structure of the two components, polymer and filler.

Keywords: poly(3 hydroxy butyrate), β-TCP, XRD, DSC

Acknowledgments

This work has been financed by the National Centre for Research and Development in Poland within the strategic research and development program "Modern material technologies" – TECHMATSTRATEG, Project: "Technologia biorafinacji olejów roślinnych do wytwarzania zaawansowanych materiałów kompozytowych" "Nowoczesne technologie materiałowe" – TECHMATSTRATEG2/407507/1/NCBR/2019

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Marrying synergy- and plasmonic-enhancement on bio-based hydrogels for hydrogen generation

O.Ramírez[1,2,3*], S. Bonardd[2,3], C. Saldías[1], D. Díaz Díaz[2,3*], A. Leiva[1*].

[1]*Departamento de Química Física, Pontificia Universidad Católica de Chile, Santiago, Chile.*
[2]*Departamento de Química Orgánica, Universidad de la Laguna, La Laguna, Spain.*
[3]*Instituto Universitario de Bio-Orgánica Antonio González, Universidad de la Laguna, La Laguna, Spain.*

**O. Ramírez: ogramirez@uc.cl*

Environmetally friendly materials and sustainable fuels are key to face nowadays issues. In this sense, here we have developed bio-based calcium crosslinked alginate beads superficially modified by plasmonic bimetallic nanoparticles (BNPs) to carry hydrogen generation reactions, as an environmetally friendly fuel, in replacement of fossil fuels. The incorporated BNPs gave interesting optical absorption properties relaying in the visible range of the light spectra to the hydrogels, with a tunable depedance on the metallic composition of the nanoparticles, phenomenon attributed to the localized surface plasmon resonance of the bimetallic nanoparticles (LSPR). The synthesized materials were highly active for the the hydrolysis of ammonia borane, a well known hydrogen storage molecule, as an hydrogen generation reaction, in which the BNP showed and enhanced activity in comparisson with its monometallic counterparts, suggesting a synergic behavior. Additionally, due to the optical properties of the material, the catalytic process was enhanced by irradiating the reaction vessel with low intensity white LEDs, figure 1, enhancement related to the LSPR of the nanoparticles, accelerating the reaction by a hot-electron transfer to the surface adsorbed reactants, as demonstrated by other autors [1].

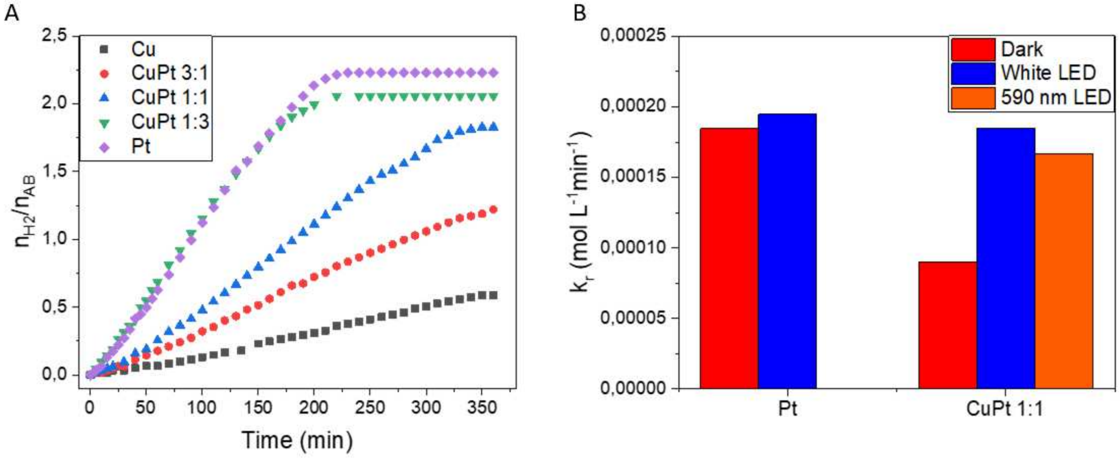

Figure 1. (a) Hydrogen generation profile using hydrogels with different catalytic loads, and (b) Pt and CuPt 1:1 light enhancement kinetic rate.

Keywords: Alginate hydrogel, hydrogen, synergy, light enhancement.

Acknowledgments
O. Ramírez thanks to ANID Doctorado nacional Scholarship 21191002.

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Conjugated Microporous Polymer Coated Silica Spheres for enhanced Adsorption of Diclofenac

Berthold Reis[1*], Kai Pfefferkorn[1] , Christoph Beutner[1], Konstantin Borchert[1], Christine Steinbach[1], Dana Schwarz[1], Simona Schwarz[1]

[1] *Leibniz-Institut für Polymerforschung Dresden e. V., Dresden, Germany*
[*]*reis@ipfdd.de*

Conjugated microporous polymers (CMPs) consist of π-conjugated repetition units in a network with numerous favorable properties, such as high chemical and physical stability, high specific surface areas, and large adsorption capacities towards organic pollutants like pharmaceutics and dyes[1,2]. The bottleneck for large scale production proved to be the synthesis requiring elaborate conditions, whilst only rendering output in the low gram of milligram scale[2,3]. Herein, an inexpensive method to increase the production volume whilst preserving the beneficial adsorption properties towards the pharmaceutical compound diclofenac is reported[4]. The micropores of the synthesized CMP assist adsorption on the surface but hinder a diffusion into the volume of the material. By coating the CMP around commercially available silica spheres the surface area accessible to the organic pollutants, such as diclofenac, is drastically extended while the total produced mass significantly increased (Figure 1).

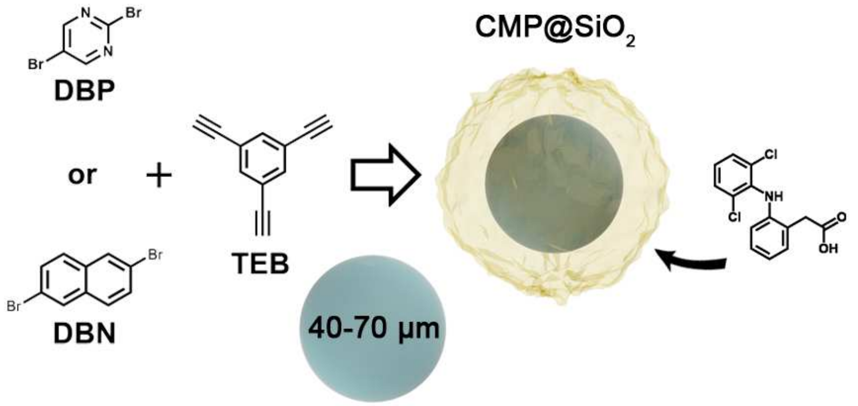

Figure 1 – **Coating of silica spheres (40-70 µm) with two different CMPs based on the Sonogashira coupling of 1,3,5-triethynylbenzene (TEB) with 2,5-dibromopyrimidine (DBP) and 2,6-dibromonaphthalene (DBN), respectively.**

Keywords: conjugated microporous polymers, silica spheres, hybrid materials, diclofenac adsorption

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Peapod-structured Polymeric Tubular Microreactors: Utilizing Mesoporous Silica Nanoparticles as Generic Holders for Catalytic Species

Tomer Reuveni[1,2], Inbar Anconina[1,2] and Amit Sitt[1,2*]

[1]*Department of Physical Chemistry, School of Chemistry, Faculty of Exact Sciences, Tel-Aviv University, Tel-Aviv, Israel*
[2]*Tel Aviv University Center for Nanoscience and Nanotechnology, Tel-Aviv University, Tel-Aviv, Israel*
[*]*amitsitt@tauex.tau.ac.il*

Tiny vessels of microscale dimensions that can host chemical reactions, aka Microreactors (MRs), have raised considerable interest due to their advantages over conventional macroscale reactors, which include efficient heat and matter transfer, confinement of aggressive environments, efficient cascading of reactions, and establishment of parallel architectures.

In this work, we present a novel type of tubular polymeric catalytic microreactors, which utilize mesoporous silica nanoparticles (MSNs) as generic carriers for catalytic species in electrospun polymeric microfibers. In this approach, first, a catalyst is embedded in the MSNs. Next, the MSNs are dispersed in a viscous solvent, and the dispersion is electrospun using concentric needles, resulting in a core/sheath architecture in which the MSNs are homogeneously dispersed within a hollow polymeric fiber in a peapod architecture.

Using this approach, we developed a generic methodology for loading catalysts into hollow microfibers using MSNs as holders and demonstrated the fabrication of microreactors that utilize catalysts while examining their performance in catalyzing the decomposition of hydrogen peroxide to oxygen inside the microtubular cavity.

This new methodology demonstrated here is extremely general and generic and can provide the means to develop new and diverse tubular microreactors with high catalytic performance, making it attractive for a large range of biological, chemical, and industrial applications.

Dual thermoresponsive Zwitterionic Microgels with controlled distribution of zwitterionic groups and its Anti-fouling properties

Pabitra Saha,[1,2,*] Ritabrata Ganguly,[2] Nikhil K. Singha,[2] Andrij Pich[1]

[1]DWI-Leibniz Institute for Interactive Materials, Aachen, Germany, 52056
[2] AVT.CVT RWTH Aachen University, Aachen, Germany, 52074
[2]Rubber Technology Centre, Indian Institute of Technology Kharagpur, India, 721302
[*]Corresponding author E-mail address: saha@dwi.rwth-aachen.de, pabitra.saha@avt.rwth-aachen.de

Microgel, a smart class of material has drawn attention in the past few years due to its response to external stimuli like temperature, pH, and ionic strength of the solution. Among them one type of polymer becomes soluble and the other becomes insoluble in water upon heating displaying upper critical solution temperature (UCST) (e.g. poly(sulfobetaine), PSB) and lower critical solution temperature (LCST) (e.g. poly(*N*-vinylcaprolactam), PVCL), respectively. Polyzwitterions, electrically neutral polymers are biocompatible, biodegradable, and non-cytotoxic in nature and the presence of zwitterionic pendant group in the main backbone makes them stable against temperature and pH variations and strong hydration capability in salt solution promote them to be used as interfacial bio-adhesion resistance material.[1]

Herein, we developed a synthetic strategy to synthesize dual-temperature-responsive low surface fouling zwitterionic microgels. Statistical poly(*N*-vinylcaprolactam-*co*-glycidyl methacrylate) copolymers were synthesized by RAFT polymerization and post-modified by thiol-epoxy click reaction with thiol end-group-modified poly(sulfobetaine) macro-RAFT (PSB-SH) to obtain poly(*N*-vinylcaprolactam-*co*-glycidyl methacrylate)-*graft*-poly(sulfobetaine) (PVCL-*co*-PGMA-*g*-PSB) graft copolymers. Synthesized graft copolymers were cross-linked by diamine cross-linker in water-in-oil (w/o) inverse mini-emulsion to obtain zwitterionic microgels.[2] Using this approach, we synthesized microgels with unique microstructure and uniform distribution of poly(sulfobetaine) chains, which exhibits tunable dual-volume phase transition (UCST-LCST) temperatures. The microgels also showed excellent antifouling property reflected in strongly reduced protein absorption on a microgel-coated surface.

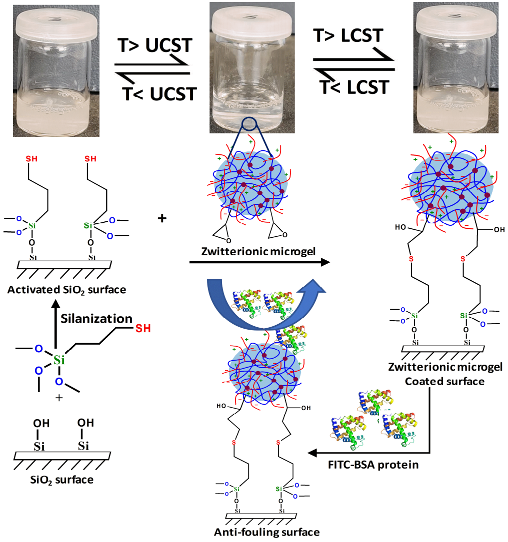

Figure 1: Dual thermoresponsiveness of zwitterionic microgels and their anti fouling activity after covalently coated on activated silica wafer

Keywords: RAFT polymerization, Hydrophilicity, Copolymers, Microgels, Polyzwitterion, UCST-LCST

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The effect of a secondary particle on self-healing and electromechanical properties of polymer composites based on Carbon Black and Diels-Alder networks

Fatemeh Sahraeeazartamar[1*], Ellen Roels[1], Seppe terryn[1], Ali Safaei[1], Guy Van Assche[1], Bram Vanderborght[1], Joost Brancart[1]

[1]*Vrije Universiteit Brussel, Brussels, Belgium*
[*]*fatemeh.sahraeeazartamar@vub.be*

Nowadays with the development of modern electronics techniques, materials that exhibit both self-healing and conductive properties can be expected to offer obvious advantages in self-healing electronics and soft robotics, However, in the design of an electrically conductive polymer composite, the most challenging issue is to optimize the concentration of conductive filler to compromise the electrical properties and chain mobility required for self-healing properties. In this work, the effect of organo-modified Nanoclay Cloisite 15A on the improvement of electrical conductivity and self-healing properties of polymer matrix composites based on Carbon Black ENSACO 360G and Diels-Alder polymer network DPBM-FT5000 with Furan to Maleimide stochiometric ratio of 0.6 was studied. The study was performed to optimize the content of Carbon Black and Cloisite 15A in which the polymer composite shows good electrical and self-healing properties. The percolating network of conductive particles led to decent electrical conductivity hybrid composites around 7.5 wt.% CB. It was concluded that depending on the CB content, the addition of Cloisite 15A can improve the electrical, mechanical, and rheological properties of composites synergistically. More importantly, the presence of Cloisite 15A increased the mechanical self-healing efficiency of polymer composites after healing at 90 °C for 1 hour. Moreover, the electromechanical properties of selected hybrid composites were studied in terms of resistance-strain behavior. The composite fiber containing 10% CB presented high sensitivity and a positive piezoresistive response in a range of 20-250% strain. The fiber was further embedded in an insulating Diels-Alder network for strain sensor applications. These promising results suggest the use of studied electrically conductive and self-healing hybrid composites for deformation and damage sensing applications in soft robotic.

Keywords: Polymer Matrix Composite, Hybrid Composite, Self-healing Polymer, Diels Alder Network, Carbon Black, Nanoclay, Electromechanical Behavior, Sensing

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Preparation and properties of CO_2 capture membranes based on poly(ether-block-amide) copolymers

G.S. Medeiros[1*], J. Peter[1], Robert Valek[2], Ondrej Hák[2]

[1] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic.*
[2] *MemBrain s.r.o., Pod Vinici 87, Straz pod Ralskem, Czech Republic*
[*]*santos@imc.cas.cz*

The high rate of carbon dioxide emmissions at the atmosphere has been increased over the last decades leading to a high impact at the global warming, one of the main sources of such effect comes from flue gases of thermal power plants [1]. The use of separation membrane technology for CO_2 capture has been promissoring due to the low energy requirement for its production and operation. The final performance of such membranes technology is directly influenced by the membrane material, its structure, thickness, configuration and design of membrane modules[2].

The top-down approach is one of the methods used to fabricate a specific membrane configuration. This method concerns the coating of the selective polymer (from a solution), onto a porous substrate, that can be in configuration of flat sheet or hollow fibers, providing mechanical strengh and support to selective layer. Tested substrates for this purpose were made from polyacrylonitrile (PAN), poly(ether sulfones) (PES), polysulfones (PSf) and poly (vynylidene fluoride) (PVDF)[3].

In this work some characteristics are explored, such as surface conditions to improve an efficient gas separation, especifically for CO_2/N_2. Surface variables such as the pore size distribution of hollow fibers of polysulfone (PSF) or PES (commercial type UDEL P-3500) were investigated. The BET isotherms of different PSF membranes prepared under different processing conditions (P10_2C and P10_4V) shows that a wide distribution of pore size and large pore sizes inhibied an efficient performance of the gas separation. Therefore the neat P10_4V fibers with a narrow distribution of pore size has a higher selectivity, than P10_2C. One possibilitiy to eliminate the surfaces defects is to coat the substrate with a "gutter layer" to prevent the intrusion of the selective layer into the pores and provide a smooth surface for the main layer.

Polydimethylsiloxane it is one of the gutter layers widely applied [4].However, when the selective layer is a polar polymer the surface interaction is weak, what can spoil a good performance of gas separation. A modification of the surface by plasma treatment in different systems were applied at PDMS layer to contribute to a better surface interaction [5]. The increase of surface energy shows an efficient modification of PDMS surface reducing the hidrophobicity by 50%, and therefore a better interface with the active layer, the commercial copolymer poly(ether block amide) (PEBAX1657).

Moreover the surface parameters for a defect free membrane the use of nanoparticles, additives and functionalizations at the active layer has been studied to enhance permeability and selectivity. The strategy for inserting an additive with ethylene oxide groups, as pentaerythritol ethoxylate, at PEBAX, was then carried out, providing a good interaction between the ether oxygen linkages groups with CO_2. Different weight concentrations were investigated and the amount of 20wt% of ethylene oxide compound enables an increase of selectivity for CO_2/N_2, without modification of mechanical strength.

Keywords: CO_2 capture, hollow fibers membranes, plasma treatment, PEBAX;

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Synergistic effect of the strength increasing of fiberglass by reinforcing epoxy binder with carbon nanotubes

M.T. Kartel[1,3], Yu.I. Sementsov[2,3*], O.A. Cherniuk[3], E.M. Demianenko[3], Yu.V. Grebelna[3], S.M. Makhno[2,3], M.I. Terets[3], S.V. Zhuravskyi[2,3]

[1] *Ningbo University of Technology, Ningbo, China,*
[2] *Ningbo Sino-Ukrainian New Materials Industrial Technologies Institute, Ningbo, China,*
[3] *O. Chuiko Institute of Surface Chemistry, NAS of Ukraine, Kyiv,*
[*] *ysementsov@ukr.net*

The excellent ratio of performance (strength) to weight of fiberglass on epoxy binder determines their use in aerospace, automotive and shipbuilding industry, sports equipment, and more recently - in unmanned aerial vehicles. In this work, the interaction of epoxy binder with amine hardener with the surface of the nanocarbon filler (multilayer carbon nanotubes) was investigated by experimental and quantum chemical methods. In this case, the strength of fiberglass is lower the more oxygen-containing groups are contained on the surface of CNT.Explanation of this effect is given by quantum chemical calculations of the interaction of pure and oxidized model surface of CNT (graphene-like planes) with hardener molecule (triethylenetetramine) [1]. The energy of the intermolecular interaction of triethylenetetramine with the model of the oxidized outer surface of CNT is greater than the same value for complexes with non-oxidized surface. Thus oxidized CNT impairs the interaction of the hardener with the epoxy resin. On the other hand, it is known that OH groups are a catalyst for the polymerization of epoxy resins, ie they are able to activate epoxy groups and cause the transition complex in the reactions of amine hardener with epoxy resin [2]. Thus, the introduction as a filler of unoxidized CNTs in the hardener and oxidized CNTs in the epoxy resin leads to a synergistic effect of increasing the strength of fiberglass. Experimental results for determining the strength of fiberglass depending on the content of oxidized and non-oxidized CNTs are given in Table 1.

Table 1. Tensile strength of model samples of fiberglass depending on the content of CNTs and oxidized CNTs

№	Component of the composition	CNT content, % wt.		* Total CNT content, % wt.	Tensile strength, MPa	Change in strength limit %
		not oxidized	oxidized			
1	Epoxy resin	0	0.25	0,25	46,0	70
	Hardener	0,25	0			
2	Epoxy resin	0	0,1	0,15	40,0	48
	Hardener	0.3	0			
3	Epoxy resin	0	0,1	0,5	51	89
	Hardener	1,5	0			
4	Epoxy resin	0	1,0	1,0	56	107
	Hardener	1,0	0			
5	Epoxy resin	0	2,5	1,9	39,0	44
	Hardener	0,3	0			
6	Epoxy resin	0	2,5	2,2	28,5	5,6
	Hardener	1,5	0			
7	Epoxy resin	0	0	0	27,0	—
	Hardener	0	0			

* in terms of solid resin

Keywords: carbon nanotubes, fiberglass, epoxy binder with amine hardener

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Polymeric nanocomposites with hybrid nanofillers

A. Stepura[1*], M. Procházka[1], G. Gentile[2], M. Lavorgna[2], M. Avella[2], M. Omastová[1*]

[1]*Polymer Institute, Slovak Academy of Sciences, Dubravska cesta 9, 845 41 Bratislava, Slovakia*
[2]*Institute for Polymers Composites and Biomaterials of National Research Council of Italy, Napoli, Italy*
anastasiia.stepura@savba.sk, maria.omastova@savba.sk

Nanocomposites are of great interest in recent years. Polymer nanocomposites are an important category of materials, whose properties are inaccessible with individual components acting alone. These nanocomposites have a promising potential for a broad kind of applications. Amongst several polymeric matrices used for the realization of polymer nanocomposites, recently HAVOH – high amorphous polyvinyl alcohol, commercialized under the name G-polymer, has been proposed [1]. HAVOH is a polyvinyl alcohol modified with diol monomers. Its prominent properties include biodegradability, water solubility, ease melt processing and excellent oxygen barrier property. HAVOH is mainly used in food and medical packaging. As concerning the fillers used to realize polymer nanocomposites, MXenes are gaining an increasing attention. MXenes are 2D inorganic nanoparticles, which are layered structures of transitional metal carbides, nitrides or carbonitrides. Its general formula is $M_{n+1}X_nT_x$, where M stands for transitional metal, X is for carbon or nitrogen, and T_x represents surface termination group, that are mostly *=O, -F, -OH*. MXenes possess outstanding properties such as high electrical conductivity, big energy capacitance, absorption of microwaves etc. [2]. Single-walled carbon nanotubes (SWCNTs) are one of possible forms of carbon nanotubes. Ordering of carbons in SWCNTs defines whether its electronic behavior will be as in semiconductor or as in metal [3].

In this work we report preparation of 3 series of composite samples – HAVOH/MXenes, HAVOH/SWCNTs and HAVOH/SWCNTs/MXenes. The range of fillers concentrations varied from 1.0 to 5.0 wt. %. All samples were prepared by solvent casting method. SWCNTs were sonicated for 1 hour in water with ultrasonic probe, and afterwards it was transferred onto magnetic stirrer. Then HAVOH pellets were added straight into that mixture for its dissolving at 50-90 °C. In case of ternary HAVOH/SWCNTs/MXenes composites, calculated amount of water-based MXene solution was also added. After this mixing composite was poured out into Teflon Petri dish and left on an open air for few hours and then put into vacuum drier at total water evaporation. Dried films were pressed between two hot plates at 220 °C.

Three series of composites together with neat matrix were measured with broadband dielectric spectroscopy (BDS) using Novocontrol Concept 40 (Germany). As it is typical for polymers, neat HAVOH matrix was not conductive. When only 1.0 wt. % of SWCNTs was added, conductivity reached 10^{-6} S/cm. HAVOH/MXenes composites reached conductivity 10^{-7} S/cm in the semiconductor zone, when 5.0 wt. % of the filler was used. Even 3 orders higher values were received for ternary HAVOH composite, where both 3.0 wt. % of 1D carbon nanotubes and 1.0 wt. % of 2D MXenes were added simultaneously. In this case it can be explained with synergetic effect of the fillers, when long and flexible carbon nanotubes help to increase number of contacts between single sheets of MXenes. This was also confirmed with scanning electron microscopy (SEM) study of composite samples. These composites in the future can be used as conductive materials in the EMI-shielding and coatings.

Keywords: MXenes, single-walled carbon nanotubes, high amorphous vinyl alcohol, polymeric nanocomposites, electrical conductivity

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Structure and properties of epoxy composites filled with graphene reduced oxide/iron oxide hybrid nanoparticles

Anastasiia Kobyliukh[1,2]*, Yevgen Mamunya[2*], Andrii Misiura[3], Karolina Olszowska[1], Marcin Godzierz[1], Sławomira Pusz[1], Urszula Szeluga[1]

[1]Centre of Polymer and Carbon Materials, Polish Academy of Sciences, M. Curie-Skłodowskiej 34, Zabrze,
[2]Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, 48 Kharkivske chaussee, 02160, Kyiv, Ukraine
[3]Taras Shevchenko National University of Kyiv, Faculty of Physics, 4 Prospekt Hlushkova, Kyiv 03022, Ukraine
**akobyliukh@cmpw-pan.edu.pl, ymamunya@ukr.net*

The application of conductive fillers (e.g., metal compounds or carbon particles) in an electrically insulating polymer matrix is a simple way to initiation of electrical conductivity therein and consequently to produce conductive polymer composites (CPCs). The easy processing, tunable electrical properties (10^{-8}–10^{6} S/m), enhanced mechanical properties and relatively low manufactiring costs make CPCs attractive research topic both for the academic and industrial communities [1]. Recently, the use of hybrid fillers makes possible to achieve the characteristics of composites more advantageous than in the case of individual fillers. Such hybrid fillers can be metal-carbon, metal-metal or carbon-carbon [2]. Particularly interesting is the preparation of polymer composites containing hybrid fillers with magnetic properties. Then, under magnetic field, it is possible to obtain composites with an oriented arrangement of filler particles which results in better electrical conductivity, thermal conductivity, and other characteristics of CPCs.

The aim of this work was to characterize the structure, thermomechanical properties and electrical conductivity of multifunctional epoxy composites with hybrid filler based on reduced graphene oxide nanoplatelets (GNPs) coated with iron (III) oxide (IO3) and iron (II) oxide (IO2) nanoparticles (NPs). The structure of fillers was determine by X-ray diffraction (XRD), Raman spectroscopy and scanning and transmission electron microscopes (SEM-EDS, TEM). Two types of epoxy composites were prepared: (1) with random distribution of filler NPs obtained by typical magnetic and ultrasonic mixing methods and (2) with partially arranged distribution of filler NPs obtained under external magnetic field. The partial arrangement of graphene sheets coated with IO NPs was confirmed by increased area ratio of G band to D band in Raman spectra of composites. The effect of the structure and the content of filler NPs on percolation threshold of electrical properties as well as on thermal stability, glass transition temperature and dynamic elastic modulus was studied. The influence of magnetic treatment on the properties of epoxy composites was also studied in terms of their applicability as thermally and electrically conductive polymer composites with enhanced mechanical strength .

Keywords: graphene/iron oxide hybrids, epoxy composites, thermomechanical properties, electrical conductivity, electrical percolation threshold

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Harnessing light to create functional, three-dimensional polymeric materials: multitasking initiation systems as the critical key to success

W.Tomal[1*], J. Ortyl[1,2,3]

[1] *Cracow University of Technology, Faculty of Chemical Engineering and Technology, Warszawska 24, 31–155 Cracow, Poland*
[2] *Photo HiTech Ltd., Bobrzyńskiego 14, 30–348 Cracow, Poland*
[3] *Photo4Chem, Lea 114, 30-133 Cracow, Poland*

Composite materials are a class of multifunctional materials that are immensely popular due to their beneficial properties. Particularly noteworthy are nanocomposite materials, in which the addition of a filler with a dimension at the nanoscale significantly changes the final properties of the product, such as improves its thermo-mechanical properties, increases heat resistance, provides conductive properties and many others. Photopolymerization technique is one of methods for obtaing composite materials, that makes it possible to print nanocomposite materials of desired geometries, at reasonable printing rates, with no need of further mechanical processing of the finished element. The numerous difficulties caused by the presence of nanometric filler in the resin make the fabrication of nanocomposite materials via techniques such as DLP is still a challenge for both the scientific and industrial environments.

In the course of research, we have demonstrated that the use of a suitable initiating system plays a key role in photopolymerization processes and can extend the application capabilities of raw materials in which it is used. The newly synthesized compounds presented in this work push the performance of photoinitiation and photopolymerization processes to an even higher level. Their implementation in 3D printing allows, among others, to reduce the processing time, print thicker layers up to a millimeter range, or improve the printing accuracy even for nanocomposites with a high content of wide-range absorbing nanofillers such as carbon nanotubes. Our study also proves the feasibility of printing viscous resins without the need for lowering the viscosity with reactive diluents, which further extends the versatility of this additive manufacturing technique and effectively oppose the increased viscosity often accompanying the addition of nanofillers.

Keywords: Photoinitiating system, Photopolymerization, CNTs nanocomposites, Real-time FTIR, Photo-rheology, 3D-VAT printing, DLP printing, Laser 3D printing

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Effect of nanowires and nanofibers on properties of photocrosslinked lginate nanocomposite hydrogels

B. F. Urbano*, M. Cordero, C. Ruiz
Departamento de Polímeros, Universidad de Concepción, Concepción, Chile.
*Corresponding author: burbano@udec.cl

One-dimensional nanoparticles represent an exciting type of filler for obtaining nanocomposite hydrogels (NCgels) due to their high aspect ratio. Most researchers study materials reinforced with continuous fibers, while discontinuous fibers are less reported. This work aimed to study the influence of low aspect ratio one-dimensional nanoparticles. We synthesized nanocomposite hydrogels via photopolymerization of methacrylated alginate macromonomers and aluminum oxide nanoparticles, nanowires, and nanofibers as fillers. Our literature review revealed no studies on the effect of the aspect ratio or length of 1D nanoparticles in hydrogels. We study the effect of 1D nanoparticles with a low aspect ratio (< 50) on the rheological properties, swelling, and thermal properties of NCgels. Unlike composite materials reinforced with continuous fibers, the use of short fibers leads to different behaviors. In composites with short fibers, stress transfer occurs not only at the cylindrical surface of the fiber but also at the fiber ends. In contrast, if the fiber length is much longer than the length where stress transfer occurs, the effect of the fiber ends can be neglected. We hypothesise that short fiber length and even low aspect ratio nanoparticles will have an influence on the properties of hydrogels, such as swelling, rheological and thermal properties. Aluminum oxide nanoparticles, nanowires, and nanofibers were employed as fillers, which differed only in their length. Sodium alginate, which has been widely used due to its nontoxicity and biocompatibility, was used as a matrix[1].

It was shown that nanofibers provided better hydrogel reinforcement due to a greater restriction on the mobility of the polymer chains (and nanoparticles itself) during the application of shear stresses, i.e., the nanocomposites showed an increase in shear modulus (8-fold increase); however, the yield and creep deformation decreased significantly, revealing a glassier structure associated with a more connected macromolecule network. Other studies involved swelling and thermal properties. Regarding swelling properties, the higher aspect ratio nanoparticles significantly decreased the hydrogel water absorption capacity (2.5-fold), but both nanoparticle types produced a decrease in the water diffusion coefficient. Finally, through thermal degradation kinetics studies, it was shown that the activation energy increases at conversions above 0.5, demonstrating a higher energy barrier for decarboxylation, dihydroxylation, decarbonylation, and glycosidic bond scissions, which was attributed to alginate chain-nanoparticle interactions [2].

Keywords: 1D nanoparticles, Nanocomposite hydrogels, aspect ratio.

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Poly(2-oxazoline) amphigels for cleaning of gelatin photography

Z. Vargová[a,b], V. Jančovičová[b], Z. Cseriová[a], R. Tiňo[b], K. Vizárová[b], M. Reháková[b], J. Kronek[a*]

[a]*Department for Biomaterials Research, Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, Bratislava, Slovakia; *juraj.kronek@savba.sk*
[b]*Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, Bratislava, Slovakia*

In the past, wet cleaning techniques were mainly used to preserve cultural heritage objects, specifically photographs. However, immersion of a photography in the water or the application of water to its surface may cause irreversible changes on photography. [1] Therefore, it was challenging to develop a technique that does not damage the original surface layer during the cleaning process, or later during storage.

In conservation practice, the possibilities of gels application for cleaning of cultural heritage objects are increasingly published. [2] The main advantage of gels lays in the high ability to retain solvents throughout the gel volume. The other benefits of gels are their higher mechanical resistance and safe cleaning of artifacts and even water-sensitive substrates because the cleaning effect of gels is limited only to the surface of objects. The most used gel for cleaning is agar gel due to its low price and easy prepartion. However, during using agar gel, much of the water diffuses into the photography substrate. [2] [3]

This work was focused on the preparation of amphigels based on poly(2-oxazolines) (POx) and their application in the cleaning of gelatin photographs. POx belong to a class of synthetic polymeric materials that are mainly used in biomedical applications for their properties, as biosafety, non-toxicity and high structural diversity. Gels based on POx represent an interesting materials for various applications. However, no attention was given to applications of these gels for cleaning of cultural heritage objects. [4] For this purpose, two amphiphilic statistic copolymers poly[$(\mathrm{MeOx})_x$-*stat*-$(\mathrm{EnOx})_{1-x}$] with different composition were prepared in living ring-opening polymerization of 2-ethyl-2-oxazoline (EtOx) with 2-(3-butenyl)-2-oxazoline (EnOx). We selected ratios of monomers (EtOx and EnOx) in copolymer equal to 90:10 and 80:20 in order to adjust polarity of resulting amphigels and also their cross-linking density. Amphigels were prepared by photoinduced thiol-ene click reaction of copolymers with 3-propanedithiol (PropDiSH) in four different copolymer/PropDiSH ratios. The prepared amphigels were characterized by the degree of swelling in different solvents, measurement of mechanical properties, surface energy ,and by IR spectroscopy. The cleaning efficiency was evaluated by non-destructive methods as ATR-FTIR spectroscopy, colorimetry and reflectance. The main benefit of prepared amphigels lays in fine tunning of their properties, such as the degree of swelling in different solvents, the mechanical resistance, or surface properties, what can significantly affect the process of the cleaning.

Keywords: gelatin photography, cleaning, amphigels, poly(2-oxazoline)

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Studying the Reactivity of Micellar Nanoreactors for Palladium Mediated Depropargylation Reaction in Aqueous Media

Shreyas Wagle[1, 2*], Roey J. Amir [1, 2, 3, 4]

[1] *Department of Organic Chemistry, School of Chemistry, Faculty of Exact Sciences*
[2] *Tel-Aviv University Center for Nanoscience and Nanotechnology*
[3] *ADAMA Center for Novel Delivery Systems in Crop Protection, Tel-Aviv University, Tel-Aviv 6997801, Israel,*
[4] *The Center for Physics and Chemistry of Living Systems, Tel-Aviv University, Tel-Aviv 6997801, Israel.*
[*]*wagle@tauex.tau.ac.il*

Biorthogonal chemistry is a powerful tool for therapeutic and imaging applications as it facilitates in-vivo transformations of molecules, which do not occur through naturally occurring bioprocesses. Since many of biorthogonal reactions are based on transition metal chemistries, tranfering them to an aqueous setup is major challenge as the surrounding water molecules could poison the catalyst in addition to issues of solubilizing the reagents.

Polymeric self-assemblies, such as micelles, can act as nanometer-sized flasks to solubilize and offer the necessary lipophilic environment for conducting these reactions[1] that will help us in activating prodrugs at the intended site potentially reducing the side effect. Considering the huge potential of such systems, we wanted to systematically explain the effect of tuning the structure of the micelles on the reaction kinetics in an aqueous environment.

Towards this goal, we designed a set of palladium-embedded micelles[2], made from PEG-dendron amphiphiles and studied their ability to facilitate palladium mediated depropargylation reactions[3] of model substrates. Using dendrons as the hydrophobic block granted us the ability to fine-tune the hydrophobicity of the dendritic end-groups and study their effect on conducting depropargylation reactions in complex biological setting. Our results show how modification of the core of the nanoreactors affect the stability and can be used as a tool for optimizing the reactivity and selectivity of nanoreactors.

Keywords: biorthogonal chemistry, micellar nanoreactors, polymer-dendron amphiphiles

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Construction of Eukaryotic Cell Biomimetics Based on Polymersomes and Proteinosomes

D. Wang[1,2], S. Moreno[1], B. Voit[1,2], D. Appelhans[1*]

[1]*Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany*
[2]*Technische Universität Dresden, Dresden, Germany*
[*]*applhans@ipfdd.de*

The design and construction of integrated chemical ensembles for modelling complex biological systems and exploring the origin of life is attracting considerable interest in a wide range of research communities[1-2]. Inspired by the hierarchically structured architecture of eukaryotic cells, the concept of compartmentalization has been widely introduced into the construction of artificial protocells[3-4], enabling performance of complex multi-step biochemical reactions within a confined environment without causing the formation of undesired by-products and incompatibilities between the catalytic steps. Reproduction of cell-like multicompartmental micro-sized structures via a bottom-up approach not only provides insight into the fundamental processes in natural cells, but also paves the way for the development of next-generation of protocells as well as their potential application in biomedicine and bioengineering.

This work will present a facile strategy for the construction of hierarchically structured biomimetic eukaryotic cells through the spontaneous encapsulation of alkaline phosphatase-loaded polymersomes (Psomes-ALP) as artificial organelles, together with functional native enzymes, into microscale proteinosome-based microcompartments. Due to the pH-responsiveness of alkaline phosphatase in activity, the created pH detecting artificial organelles are capable of differentiating between low concentrations of extracellular glucose in a time-dependent manner, mimicking subtle changes in the extracellular environment in biomimetic eukaryotic cells[5]. In addition, the potential of Psomes-ALP was further explored to enhance the structural and functional complexity of current cell-like microstructures. The dephosphorylation of precursors, NAPffkYp(NBD), by Psomes-ALP leads to the formation of supramolecular hydrogel within proteinosomes, which affords the opportunity to manipulate the morphology of protocells and the activity of nested enzymes. The self-production of a skeleton-like matrix by an internally generated reaction offers insights into how these integrated structures might have been assembled within a prebiotic context.

Keywords: Multicompartments, Polymersomes, Proteinosomes, Glucose Detection, Nanofiber Formation

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A thermoresponsive poly(2-oxazoline)-based molecular brush in aqueous solution: effect of a cononsolvent

Bahar Yazdanshenas[1*], Christoph Spies[1], Clemens Sachse[2], Stefano Da Vela[3], Rainer Jordan[2], Christine M. Papadakis[1]

[1]Technische Universität München, Physik-Department, Garching, Germany
[2]Technische Universität Dresden, Fakultät Chemie und Lebensmittelchemie, Dresden, Germany
[3]European Molecular Biology Laboratory c/o DESY, Hamburg, Germany
[*]bahar.yazdanshenas@ph.tum.de

Molecular brushes are a type of graft polymers with polymeric side chains attached to each repeat unit of a linear polymer backbone. The high grafting density gives the molecular brushes a rather compact structure, that affects their physical properties. For example, when the side arms are thermoresponsive in aqueous solution, the cloud point T_{CP} of the molecular brush is shifted with respect to the linear analogue. Here, we investigate a poly(2-oxazoline)-based molecular brush, P*i*POx$_{100}$-*g*-PEtOx$_{17}$, with thermoresponsive poly(2-ethyl-2-oxazoline) (PEtOx) side chains and a poly(2-isopropenyl-2-oxazoline) (P*i*POx) backbone. Poly(2-alkyl-2-oxazoline)s are well-known for their biocompatibility and tunable thermoresponsivity, which strongly depends on the alkyl substituent, the polymeric architecture, and concentration. We previously found that, in water, T_{CP} of a P*i*POx$_{100}$-*g*-PEtOx$_{17}$ molecular brush is suppressed from ca. 60 °C, the value for linear PEtOx, to ca. 40 °C [1].

In this work, we study the effect of the cosolvent ethanol on the solubility of this molecular brush at a concentration of 10 g L^{-1}. Water-ethanol solvent mixtures are known to exhibit abnormal mixing properties and were demonstrated to result in increase of solubility for several types of poly(2-oxazoline)s [2]. Turbidimetry revealed a drastic increase of T_{CP} with increasing ethanol fraction. Dynamic light scattering (DLS) showed that by addition of 20 vol % ethanol, aggregates appear already below T_{CP}, in coexistence with individually dissolved molecular brushes. Moreover, a morphological study by synchrotron small-angle X-ray scattering (SAXS) showed that, below T_{CP}, the molecular brushes assume a compact shape.

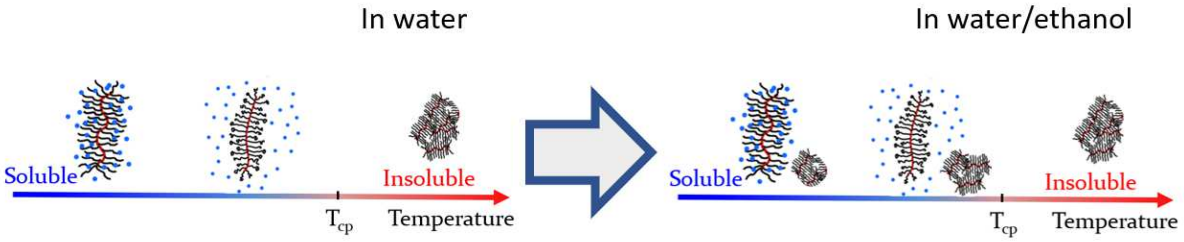

Figure 1: Schematic representation of solubility behavior of the molecular brush in pure H_2O (left) compared with the one in an 80:20 water/ethanol v/v solvent mixture (right)

Keywords:
Molecular brushes, thermoresponsive polymers, dynamic light scattering, small-angle X-ray scattering

Acknowledgments
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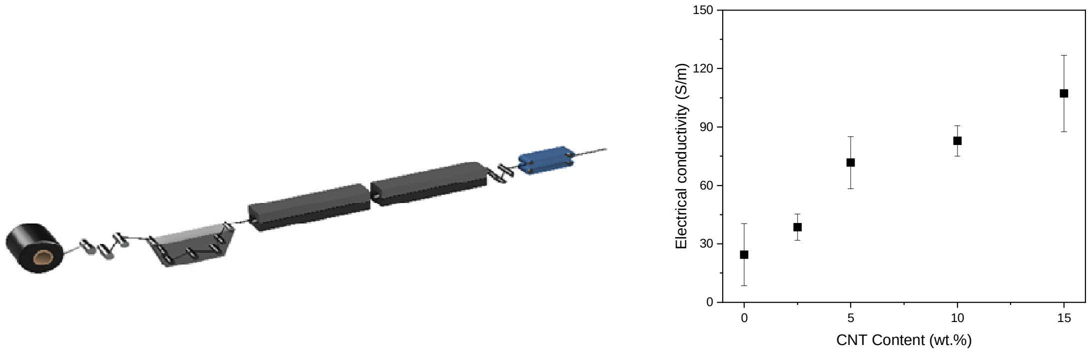
Hierarchical composites with high CNT loaded solid epoxy resins

Neptun Yousefi[1], Sandra J. Fisher[2], Christoph Burgstaller[3], Milo S.P. Shaffer[2], and Alexander Bismarck[1,4*]

[1]Polymer and Composite Engineering (PaCE) Group, Institute of Materials Chemistry, Faculty of Chemistry, University of Vienna, Währinger Straße 42, A-1090 Vienna, Austria
[2]Department of Chemistry, Imperial College London, South Kensington, London, SW7 2AZ, UK
[3]Transfercenter für Kunststofftechnik (TCKT), Franz-Fritsch-Straße 11, A-4600, Wels, Austria
[4]Department of Chemical Engineering, Imperial College London, South Kensington, London, SW7 2AZ, UK

Although primarily employed as protective coatings, solid epoxy formulations are promising materials as they are typically much cheaper than liquid epoxy resins commonly used in composite production. Applications of composites are usually dominated by their compression strength and interlaminar shear strength. To exploit this, we have investigated the use of solid epoxy resins with high carbon nanotube (CNT) loadings in composite manufacturing. CNT reinforced resins have improved modulus and strength [1]; using these nanocomposites as the matrix for conventional carbon fibres results in hierarchical composites with improved matrix-dominated properties. Other functional improvements, such as an increased through-thickness electrical conductivity, were also anticipated. As such, the development of a novel manufacturing method exploiting high CNT loaded solid epoxies has the potential to improve the performance of the composite [2].

Different epoxy resins were formulated by mixing solid epoxy, hardener and CNTs (up to 20 wt.%) at elevated temperature. Microscopic imaging confirmed a homogenous dispersion of CNTs in solid epoxy resins. Tensile properties of nanocomposites were determined. A wet powder impregnation method was used to produce solid epoxy reinforced prepregs with a high carbon nanotube loading fractions. The prepregs were consolidated into laminates with fibre volume fraction of 57%. Both interlaminar shear strength and compression strength of the hierarchical composites improved by almost 19% and 31%, respectively. The through-thickness electrical conductivity of the hierarchical composites were enhanced significantly when compared to the control composites.



High carbon nantube reinforced composites

Keywords: Thermosetting resins, Carbon nanotubes, Carbon fibre reinforced composites,

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Flow-driven fabrication of calcium phosphate/alginate composites

R. Zahorán[1*], P. Kumar[1], D. Horváth[2] and Á. Tóth[1]

[1]*Department of Physical Chemistry and Materials Science, University of Szeged, Szeged, Hungary*
[2]*Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary*
[*]*rekazahoran@gmail.com*

Synthesis of composites has always been an important research field growing parallel with the developing medical and industrial technologies. The wide range of applications requires advanced planning of the composites, which should go beyond experimenting in batch reactions only. In the emerging field of chemobrionics,[1] materials exhibiting spatiotemporal chemical structures are constructed under far-from-equilibrium conditions. Metal silicate membranes as typical chemical gardens are produced when metal salts are injected into water glass solutions. Recently, metal-ion-modulated chitosan hydrogel tubules [2] have been achieved with the same flow-injection technique. This method enables us to modify the physico-chemical properties of the matter by simply varying physical parameters like flow rate or density gradient.

We have investigated tubular hydrogel formation in the reaction between an aqueous solution containing an organic constituent (sodium alginate) mixed with an inorganic component (sodium phosphate) and a solution of calcium chloride. Alginate, a commonly used material in food industry, is an anionic polysaccharide with many favorable properties that can form a gel via sol-gel transition in the presence of divalent ions such as Ca^{2+}. In addition, calcium phosphates are of great interest due to their relevance in nature (teeth, bones, etc.). Using a three-dimensional flow-injection method, we have created composite tubes by varying not only chemical composition but also injection rate. The observed structures are summarized in dynamical phase diagrams. To distinguish between the two possible precipitation pathways (amorphous calcium phosphate or tricalcium phosphate), equilibrium calculations have been carried out along with various spectroscopic analyses. Furthermore, we have characterized the gelation in different alginate-phosphate compositions, identified the driving forces, and, as the gels can serve as membranes, we have determined their electrochemical properties. The microstructure of the composites has been studied by rheology, Raman spectroscopy, and X-ray µCT.

These composites prepared under biomimetic conditions may be useful for designing adaptive soft materials.

Keywords: chemobrionics, alginate, calcium phosphate, chemical garden, biomimetic hydrogels

Acknowledgments

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Artificial cell structure with pH regulation and cytosolic pH self-monitoring

K. Zhang,[1,2*,] S. Moreno,[1] B. Voit,[1,2] D. Appelhans[1]
[1] *Leibniz-Institut für Polymerforschung Dresden e. V., 01069 Dresden, Germany*
[2] *Organic Chemistry of Polymers, Technische Universität Dresden, 01062 Dresden, Germany*
Zhang-kehu@ipfdd.de

Structures and functions of eukaryotic cells with an outer permeable membrane, a cytoskeleton, and functional organelles can be perfectly presented and imitated by a multi-compartmentalized protocell containing diverse synthetic organelles, such as pH-responsive polymersomes (Psomes), liposomes, coacervates or dendrimersomes in various large-sized giant unilamellar vesicles.[1-5] Herein, two kinds of artificial organelles with stimuli-trigged regulation ability and orthogonal-responsive membranes, glucose oxidase-(GOx)-loaded Psomes A (GOx-Psomes A)[6] and urease-loaded Psomes B (Urease-Psomes B),[6] and a pH-sensor (Dextran-FITC) are encapsulated into proteinosomes by pickering emulsion method to construct a polymersomes-in-proteinosome system. Adding fuels (glucose or urea) outside the protocell penetrate the membrane of proteinosomes and enter into GOx-Psomes A and Urease-Psomes B to produce chemical/biological signals (gluconic acid or ammonia) resulting in a decrease or an increase of pH. This will counteract the catalytic “switch on” or “switch off” of enzyme-loaded Psomes A and B owing to their different pH responsive membranes. Thus, Dextran-FITC can immediately detect slightly cytosolic pH changes by fluorescence intensity. Overall, this approach shows heterogeneous polymersomes-in-proteinosome architectures with feedback-induced, oscillating pH-regulating and pH self-monitoring for several cycles ability for mimicking structures and metabolisms of eukaryotic cells. In the future, we aim to realize the reversible clusters of artificial organelles in protocell under external stimuli.

Keywords: artificial organelles, polymersome-in-proteinosome, pH regulation, pH self-monitoring

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In-Situ Formation of Polystyrene and Polystyrene-*b*-Polyisoprene Grafted Silica Nanoparticles

F. Aldakheel, K. Ntetsikas, N. Hadjichristidis*

Polymer Synthesis Laboratory, KAUST Catalysis Center, Physical Sciences and Engineering Division,
King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia.
Nikolaos.Hadjichristidis@kaust.edu.sa

Abstract: Polymer/silica hybrid materials have attracted the attention of researchers due to the improved mechanical, thermal, electrical, and magnetic properties resulting from the coupling of each individual component. The synthesis of these materials can be achieved either by "grafting-from" or "grafting-to" approaches. The "grafting-from" approach is also known as surface-initiated polymerization (SIP), as the polymer chain is growing from a surface anchored initiator. While in the "grafting-to" approache, end-functionalized polymer chains are directly bonded to the surface via coupling reactions.[1] Here, we report a novel approach which is the *in-situ* formation of silica nanoparticles grafted with homopolymers or copolymers (polymer@SiO_2). The precursor homopolymers or copolymers bearing tetraethyl orthosilicate (TEOS) end groups were synthesized by high vacuum anionic polymerization techniques. Polymer nanocomposites were then fabricated by melt or solution mixing of the polymer@SiO_2 with commercial polystyrene (PS) or thermoplastic elastomer (TPE) matrices. PS or polystyrene-b-polyisoprene (PS-*b*-PI) were first synthesized with different molecular weights and then terminated with TEOS. Subsequently, silica grafted with polymer chain was formed *in situ* by hydrolysis and condensation reactions of the terminal TEOS groups.[2] The molecular characteristics of PS-TEOS and PS-*b*-PI-TEOS were determined by ^{1}H NMR, SEC and MALDI-TOF. The formation of PS@SiO_2 and PS-*b*-PI@SiO_2 nanoparticles was verified by FT-IR, solid state ^{29}Si NMR/^{13}C CP/MAS NMR, TEM, TGA, and DLS. Nanocomposites of PS were prepared by extrusion of PS/SiO_2-NPs or PS/PS@SiO_2-NPs blends. Nanocomposites of TPE (PS-*b*-PI-*b*-PS) were prepared by mixing SiO_2-NPs or PS-*b*-PI@SiO_2 with TPE solutions and evaporation. In Figure 1 only the TEM images of the PS@SiO_2 and PS-*b*-PI@SiO_2 are given. Tensile tests were performed to investigate the effect of the polymer@SiO_2 (filler) on the mechanical characteristics of the filler/matrix blends.

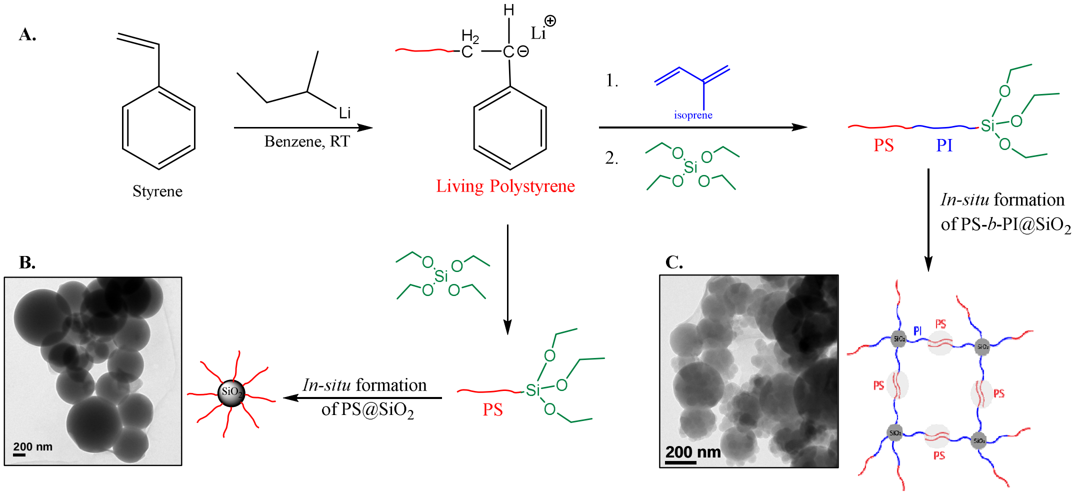

Figure 1. A. *Schematic representation of the in-situ formation of silica nanoparticles grafted with PS or PI-b-PS,* **B.** *TEM image of* $PS_{3k}@SiO_2$, **C.***TEM image of* PS_{3k}*-b-*$PI_{3k}@SiO_2$.

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Interpolyelectrolyte complexes chitosan based. Encapsulation of fungicide agents of nitroeguenol derivatives. A physicochemical study

N. Alvarado[1*], D. Díaz[2], R. Plaza[2], F. Santana[3]

[1]*Instituto de Ciencias Químicas Aplicadas, Facultad de Ingeniería, Universidad Autónoma de Chile, Chile*
[2]*Química y Farmacia*, *Facultad de Ciencias de la Salud, Universidad Autónoma de Chile, Chile*
[3]*Ingeniería Civil Química, Facultad de Ingeniería, Universidad Autónoma de Chile, Chile*
**nancy.alvarado@uautonoma.cl*

The interpolyelectrolyte complexes (PECs) are a type of nanoaggregates widely used in several fields mainly as carriers or reservoirs of bioactive molecules. These systems are formed by anionic and cationic polyelectrolytes [1]. These structures are highlighted for being capable of generating two environments in just one structure: hydrophilic and hydrophobic environments. These characteristic is very attractive since it is possible encapsulates compounds soluble in organic solvent to be applied in aqueous medium. In this sense, a serie of nitro-eugenol derivatives (NEd) has been tested against *Botrytis cinerea*, previously and, the results showed promissing effects against this fungus.

Here it is presents two new formulations environmentally friendly of a series of PEC chitosan based, with the incorporation of synthetic nitro-eugenol derivatives (NEd) to be applied as a potential biofungicide (Figure 1). These formulations were constituted by chitosan, which was used as cationic polyelectrolyte, meanwhile copolymers of maleic anhydride-α-olefins (1-hexene; 1-octene) family were used as anionic polyelectrolytes. The results showed that the PECs systems were successfully obtained. The incorporation of NEds in PECs were effectively carried out. The physichemical characterizations showed that the structure of anionic polyelectrolyte influences in the encapsulation of the NEds.

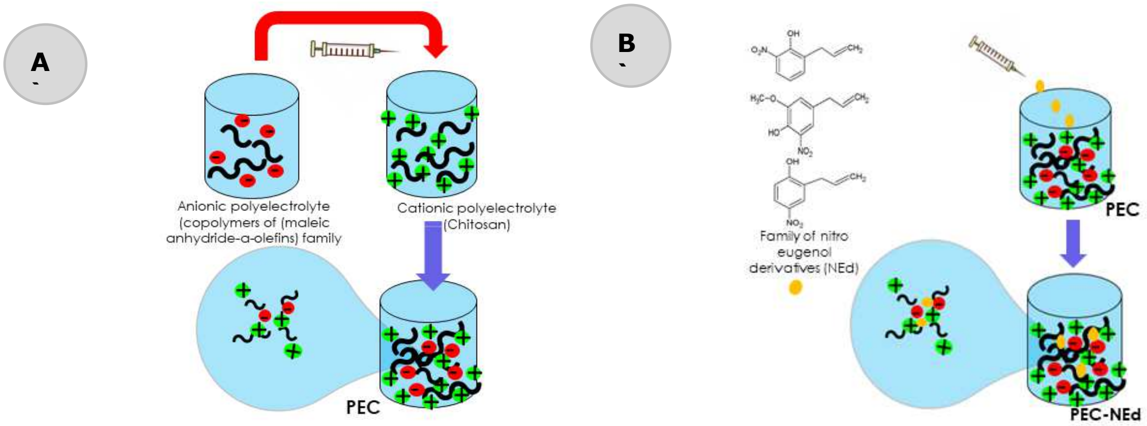

Figure 1. Schematic description of the preparation of PECs-NEDs. A) PEC formation and B) Incorporation of NEd on PEC for PEC-NEd formation.

Acknowledgments

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Polymers for Opto-electronic and Energy Applications

Operando studies of morphological degradation in polymer-based organic solar cells

Peter Müller-Buschbaum[1,2,*]

[1]Lehrstuhl für Funktionelle Materialien, Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany
[2]Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstr. 1, 85748 Garching, Germany
** E-mail: muellerb@ph.tum.de*

Based on novel conjugated semiconducting polymers, organic solar cells are an interesting alternative to conventional silicon based solar cells as they feature new possibilities in fabrication and utilization. Using wet chemical processing, they can be manufactured with large-scale production methods such as roll-to-roll printing. They are light-weight and flexible, which offers novel ways for building integration of use in off-grid applications. However, in terms of large-scale usability, one of the major challenges for polymer-based organic solar cells is to overcome their relatively short lifetime, as compared to their inorganic counterparts. To gain a deeper understanding of organic solar cell degradation with respect to changes in the active layer morphology, we present operando studies during the first hours of operation. The studies reveal information on both, its evolving current-voltage characteristics and the changes of the active layer morphology in the organic solar cells. For that purpose, advanced x-ray scattering methods (GISAXS / GIWAXS measurements) and current-voltage (IV) tracking of the operating solar cell are performed simultaneously to gain fundamental understanding. Starting from an optimized morphology of the active layers in terms of highest device efficiencies, depending on the donor-acceptor system, different morphological degradation pathways are identified. Either a mixing or a demixing process can occur during degradation and cause changes of the active layer morphology. The altered morphology is less optimal for charge transport through the active layer due to poor percolation in a too fine morphology or a poor splitting of excitons in a too coarse morphology. Different examples for both degradation pathways will be discussed. Moreover, the impact of additives on device performance, stability and degradation pathway will be investigated.

Keywords: organic solar cell, semiconducting polymer, conjugated polymers, degradation

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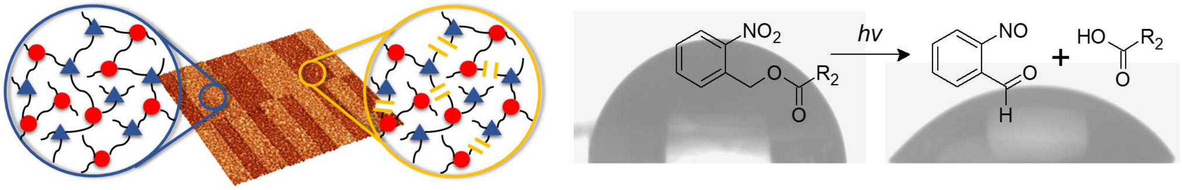
Stimuli-responsive photopolymer networks

E. Rossegger[1], T. Griesser[2], S. Schlögl[1*]

[1]*Polymer Competence Center Leoben GmbH, Leoben, Austria*
[2]*Institute of Chemistry of Polymeric Materials, Montanuniversitaet Leoben, Leoben, Austria*
[*]*sandra.schloegl@pccl.at*

Advancing from polymers with structural and passive functions, the present work highlights the design of stimuli-responsive photopolymers by introducing molecular switches into the network structure. In particular, photo-cleavable chromophores such as *o*-nitrobenzyl ester (*o*-NBE) groups are applied to design photopolymers, which change specific material properties after exposure to UV-light.[1] Along with a spatially controlled change of bulk properties (e.g. thermo-mechanical properties and solubility), *o*-NBE chemistry is also used to create multi-gradient surfaces allowing a directed motion of liquids.[2,3]



Tuning bulk and surface properties of photopolymers via UV-induced photocleavage of *o*-nitrobenzyl ester chromophores.

Whilst the introduction of *o*-NBE links enables a "one-time" switch of the material properties, synthesis routes further involve the preparation of photo-responsive dynamic polymer networks. By introducing the photo-switches in dynamic polymer networks, which undergo catalyzed bond exchange reactions at elevated temperature, microstructures can be repeatedly written at the same area of thin films by photolithography and erased by a thermal annealing step.[4] In addition, by using selected photolatent catalysts, topological rearrangements are activated in vitrimers on-demand by light exposure.[5,6] This is a versatile strategy to fabricate intrinsically healable soft active devices, which are able to undergo locally programmable shape change.

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Towards efficient and sustainable light sources: radiative rate engineering by polymer planar microcavities

H. Megahd[1], P. Lova[1], S. Sardar[2], C. D'Andrea[2,3], A. Lanfranchi[1], B. Koszarna[4], M. Patrini[5], D. T. Gryko[4], D. Comoretto[1*]

[1] *Dipartimento di Chimica e Chimica Industriale, Università di Genova, Genova, Italy*
[2]*Center for Nano Science and Technology@PoliMi, Istituto Italiano di Tecnologia, Milano, Italy*
[3] *Dipartimento di Fisica, Politecnico di Milano, Milano, Italy*
[4]*Institute of Organic Chemistry of the Polish Academy of Sciences, Warsaw, Poland*
[5]*Dipartimento di Fisica, Università di Pavia, Pavia, Italy*
davide.comoretto@unige.it

Controlling emitters radiative rate in lightening devices is fundamental to boost their efficiency.[1] This effect enhance photoluminescence (PL) kinetics and intensity, and can be obtained embedding a fluorophore in nanostructures confining photons in both space and time. In these terms, planar microcavities are among the most studied configurations, consisting of two dielectric mirrors reflecting specific wavelengths separated bya submicrometric spacing layer.[2] The latter contains the emitter and introduces allowed modes that enhance the PL within the mirrors reflectance region at the cavity modes. However, up to date only inorganic systems, which forbid flexible devices, have shown radiative rate control.

Unlike inorganics, the solution-processing of flexible polymers does not require energy-consuming high temperature and vacuum conditions.[3] As such, achieving this effect in polymer systems has been of interest, yet challenging due to the low dielectric contrast they offer. We report the first confirmed radiative rate change in all-polymer microcavities thanks to dielectric mirrors pairing polyvinylcarbazole (PVK) with the low index perfluorinated polymer Aquivion® (AQ), giving the highest refractive index contrast in such systems to date. The microcavity consists of two polymer mirrors sandwiching a stable diketopyrrolopyrrole derivative (DPP) blended with polystyrene (PS) (Fig.1a inset). The PL intensity at the cavity mode at 717 nm increases by a 40-fold when compared to an identical film on glass (Fig1.a). More importantly, PL lifetime variation (Fig1.b) paired to external quantum efficiency data validates a change in the radiative lifetime. Comparing the microcavities with a series of reference allowed excluding any extrinsic effect.

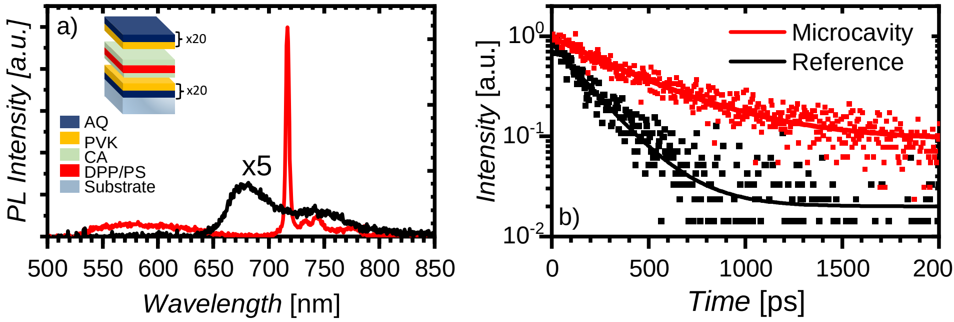

Figure1. a) Microcavity (red) and reference film (black) fluorescence; b) fluorescence decay for the microcavity (red) and reference film (black).

Keywords: Nanostructured polymers, polymer devices, photoluminescence efficiency, Purcell effect

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Synthesis of Bi_2Te_3 nanotubes to prepare thermoelectric polymer hybrid composite

A. Baimyrza[1], R. Retoux[2], B. Fiedler[3], F. Gascoin[2], C. Lemouchi[1], L. Le Pluart[1]

[1] *Normandie Univ, ENSICAEN, UNICAEN, CNRS, LCMT, Caen, France*
[2] *Normandie Univ, ENSICAEN, UNICAEN, CNRS, CRISMAT, Caen, France*
[3] *Hamburg University of Technology, Institute of Polymers and Composites, Hamburg, Germany*
**aigerim.baimyrza@ensicaen.fr*

Bi_2Te_3 is one of the most suitable thermoelectrical (TE) materials for near room temperature application[1] as its figure of merit is around 1. Nanotubular morphology has potential to demonstrate better TE performance due to quantum confinement effect and preferential phonon scattering[2] as well as to strongly decrease the percolation threshold due to high aspect ratio. Herein, we studied the influence of morphological content of the Bi_2Te_3 nanoparticles and the aspect ratio of Bi_2Te_3 nanotubes on the properties of Bi_2Te_3 /epoxy resin (RIMR-135/RIMH-137) hybrid composites. The influence of composite incorporation method on the final properties of material also was investigated by comparing two methods: speedmixing and infusion. The infusion method, earlier developed for CNT/epoxy thin films[3], was adopted for the first time for Bi_2Te_3 nanotube fillers. It relies on preparation of Bi_2Te_3 buckypellet and further infusion of it by resin and subsequent curing. So far only thin films of Bi_2Te_3/isolating matrix hybrids were reported, while our method allows to prepare bulk samples of any thickness.

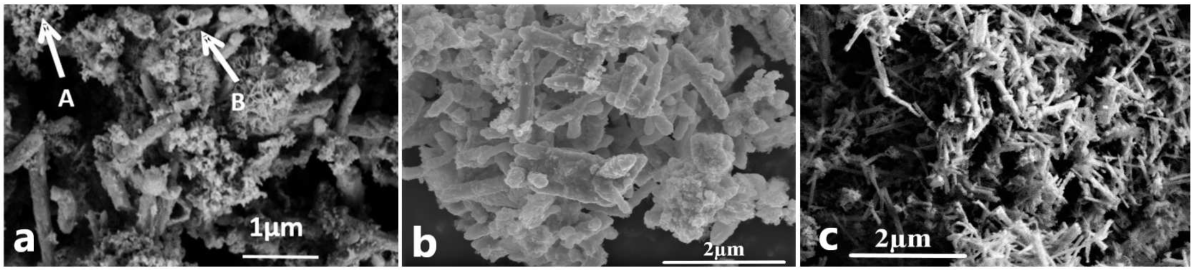

Figure - 1. SEM images of Bi_2Te_3 nanoparticles synthesised by different mechanisms: a – Bi_2Te_3 synthesised by rolling-up mechanism: A – isotropic particles, B – nanotubes; b – Bi_2Te_3 synthesised by diffusion mechanism; c – Bi_2Te_3 synthesised by diffusion mechanism with additional surfactant

In order to obtain Bi_2Te_3 fillers two methodologies to synthesise Bi_2Te_3 nanotubes were developed. First method involves formation of tubular morphology via rolling-up mechanism and produces pure Bi_2Te_3 phase morphologically consisting of isotropic particles and 30% of nanotubes[4] (Figure-1, a). In the second method tubular morphology is formed by diffusion of Bi-precursor into Te-rod templates, formed in-situ. This method yields nanoparticles with 80% of tube content (Figure-1, b). Application of additional surface in the second method leads to increase of the nanotube content up to 100% and also increases the aspect ratio of the particles (Figure-1, c). The advantages of both developed methods are relatively mild reaction conditions (reflux at 90°C, inwater) and easy scalability. Phase purity of Bi_2Te_3 particles was confirmed XRD and EDX, morphology was analysed by SEM and hollow structure of some closed tube confirmed by HRTEM analysis.

Keywords: Bismuth telluride nanotubes, epoxy resin, thermoelectrical materials, hybrid composite

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Phosphorus containing sulfonated polytriazoles via Click polymerization: Synthesis, properties and proton exchange membrane applications

A. Ghorai[1], H. Komber[2], B. Voit[2], S. Banerjee[1]*

[1]*Materials Science Centre, Indian Institute of Technology Kharagpur, Kharagpur - 721302, India*
[2]*Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse. 6, 01069 Dresden, Germany*
* *S. Banerjee (susanta@matsc.iitkgp*.ac.in)

The proton exchange membrane (PEM) is considered one of the vital components of fuel cells. A PEM is a solid electrolyte for proton transfer and prevents fuel crossover between the cathode and anode. The necessary characteristics of efficient PEM materials are high thermal, mechanical, and chemical stability, phase segregated morphology and high proton conductivity with better management abilities. In this regard, a variety of sulfonated polymer membranes were designed and prepared and their performances were examined as alternate PEM materials to sulfonated tetrafluoroethylene-based fluoro-copolymers.

The copper-induced azide-alkyne click polymerizations are found to be an easy and facile method to prepare sulfonated polytriazoles. To achieve balanced qualities among proton conductivity, chemical stability, and water management, several types of heteroatoms (oxygen, nitrogen, and phosphorus) have been included in the polymer chains by adding numerous common chemical moieties.[1,2] The incorporation of phosphine oxide moieties into polymer chains aids in the formation of a higher-quality polymer membrane with efficient proton transport, high thermal and mechanical stability, and adequate water retention. Additionally, triaryl phosphine oxide units in polymers also increase the oxidative stability by reducing the attack by peroxide radicals.[3] Hence, the phosphorus-containing polymers are emerging as a strong contender in the PEM spectrum based on their overall membrane properties.

Our group has prepared several new phosphorus-containing monomers and polytriazoles thereof shown in Figure 1. The synthesized polytriazoles were structurally characterized by NMR and FT-IR techniques. Transparent and flexible membranes were fabricated from these polymers adapting conventional solution casting process is used and their different PEM characteristics were thoroughly investigated. The membranes demonstrate a superior set of PEM properties than many other similar polytriazoles without any phosphine oxide moieties and several of the membranes showed promise towards their application in fuel cells.

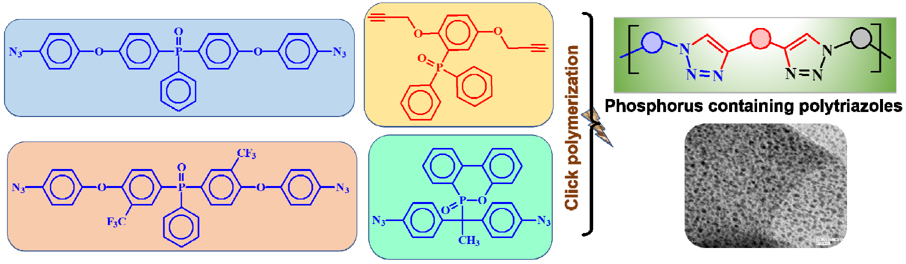

Figure 1: Phosphorus containing polytriazoles from different diazides and dialkyne

Keywords: Phosphorus, Polytriazole, Click polymerization, Membrane, Proton exchange membrane

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Amphiphilic Polymer Co-networks as a Matrix for Wearable Energy Harvesting Devices

Chieh-Szu Huang[1,2], René M. Rossi[1], Maksym Kovalenko[1,2], L. F. Boesel[1,*]

[1] *Empa, Swiss Federal Laboratories for Materials Science and Technology, St. Gallen, Switzerland*
[2] *ETH – Swiss Federal Institute of Technology Zürich, Zürich, Switzerland*
luciano.boesel@empa.ch

In recent years, luminescent solar concentrators (LSCs) have attracted considerable attention for their advantages in absorbing diffusive light and increasing the cost-effectiveness of solar cells; however, the integration and compatibility with wearable photovoltaics and the energy transfer (ET) efficiency still require improvement.

In our current work [1], amphiphilic polymer co-networks (APCNs) are employed as polymer matrices for wearable LSCs owing to their flexibility and wearability (Fig. 1, left). Furthermore, with the assistance of APCNs' nanophase separated hydrophobic and hydrophilic domains, hydrophobic (Lumogen Red, acceptor) and hydrophilic (fluorescein, donor) luminescent materials are loaded in adjacent nanometer-separated domains. This results in high ET rates and broaden the acceptor's absorption range, rendering a more efficient down conversion emission.

With this straightforward synthesis procedure, we could achieve high ET rates between dye pairs via FRET and photon recycling. These two energy transfer mechanisms were confirmed by steady-state and dynamic photoluminescence methods, showing a ~100% total ET between donors and acceptors.

Applying the loaded APCN as a coating, we were able to increase the efficiency of flat solar cells by matching its absorption profile with the emission range of the dye pairs (e.g. pc-Si PVs PCE increased of 14.5% in the excitation range of 375-550 nm, Fig. 1, right). The developed nanostructure-assisted ET system can be directly extended to a wide variety of luminescent materials including dyes (Rhodamine B, HPTS, DCM, and Lumogen Yellow) and quantum dots (CsPbBr3 and CdSe/ZnS). The re-emitted photons are monitored via geometry photoluminescence measurement and Monte Carlo ray tracing simulation, indicating the APCNs LSC vertically-tandem attached to the flexible photovoltaics can effectively increase the light absorbing area and be beneficial to the optimal utilization of incident light.

This novel APCN could find potential uses in the energy-harvesting field, serving as wearable LSCs for the next generation of flexible and wearable photovoltaics. As an example, we recently proposed the use of the APCNs with fiber-based solar cells (FSC), achieving an increase of 84% in the PCE of a textile device with five FSC due to the side-attachment of the APCNs.[2]

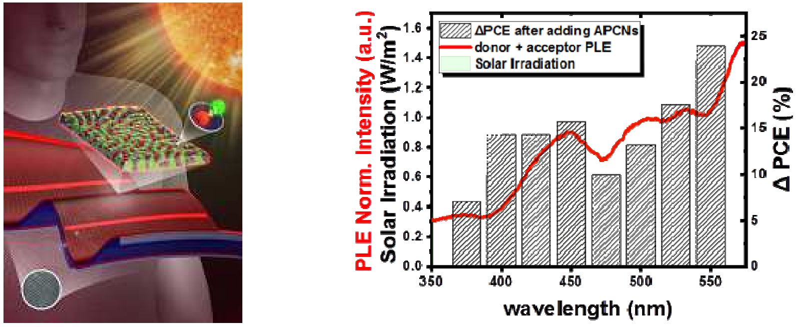

Figure1. (Left) Concept of a wearable energy harvesting textile. (Right): enhancement of the PCE in planar solar cells due to ET in APCNs.

Acknowledgments

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Chemical vapor deposition of polypyrrole for energy storage and sensor applications

Afshin Dianatdar, Adrivit Mukherjee, Mart Hendriksen, Ranjita K. Bose*

Department of Chemical Engineering, University of Groningen, The Netherlands
**r.k.bose@rug.nl*

Chemical vapor deposition (CVD) is a well-known technique for the synthesis of inorganic coatings and thin films. In milder variants of CVD, known as initiated CVD and oxidative CVD, organic polymers can be synthesized. The monomer in addition to an initiator or oxidant are introduced into a vacuum reactor in the vapor phase, after which they undergo a one-step surface polymerization to yield solid thin films or coatings. The advantages of these techniques are the ability to produce multilayered films and devices on a variety of delicate or porous substrates resulting in a high degree of coating conformality.

In this work we will present recent results on synthesis of polypyrrole using oxidative chemical vapor deposition (oCVD) where polymer synthesis, doping, and film formation were combined in a single processing step. By carefully tuning the reaction parameters of deposition temperature, reactor pressure and oxidant to monomer flow rate ratio, homogeneous polypyrrole films with a record conductivity of 180 S cm^{-1} for a solvent-free method were produced. These polymers were used further for two applications: sensors and energy storage. For the piezoresistive strain sensors, polypyrrole was coated onto flexible substrates with porosities on different scales such as electrospun fiber-mats, phase-separated hydrogel membranes as well as 3D printed lattices. These substrates allowed us to obtain sensors with tunable mechanical and electrical properties. The results of the piezoresistive strain sensing behavior, gauge factors and cyclic stability will be shown. For the electrochemical energy storage electrode, polypyrrole was coated on a commercially available carbon fiber mat. The electrodes were characterized via cyclic voltammetry, galvanostatic charge-discharge measurements, and cyclic thermal stability tests. In summary, this presentation will highlight recent advances of using oCVD to synthesize polypyrrole for sensor and energy applications.

Keywords: chemical vapor deposition, energy storage, polypyrrole, coating

Monodisperse Polypeptoid Application in Silicon Deterministic Doping

R. Chiarcos[1*], M. Laus[1], V. Gianotti[1], D. Antonioli[1], V. Ospina[1], M. Perego[2]

[1]*Università del Piemonte Orientale, Alessandria, Italy*
[2]*IMM-CNR, Agrate-Brianza, Italy*
[*]*riccardo.chiarcos@uniupo.it*

The mad rush to technological enhancement requires the production of transistors with complex shapes and dimensions of only few nanometers in order to increase power and speed of microelectronic devices. In an electrical circuit, transistors play the role of fondamental units that cells have in our body. From an industrial point of view, these devices have to be extramely small and, at the same time, perfectly homogeneus with each other, thus requiring an extreme control of the amount and position of dopant atoms in the semiconductive substrate.

Some years ago, our research group introduced an innovative doping process based on polymers characterized by a chain-terminal containing a phosphorus dopant atom and reactive with the semiconductive substrate[1]. The grafting of these functional polymers to the substrate lays on the silicon surface phosphorus atoms with the opportunity to tune the amount of the atoms simply by modifying the molecular weight of polymeric carriers. Despite the system gave very promising results, some nuisance came from the non-perfect reproducibility of the polydispersity of the samples in successive synthetic preparations. In this context, it is necessary to stress that polydispersity playes a major role during the grafting to process because of the preferential grafting of short chains over the longer chains[2,3].

Nowadays only nature can synthesize perfectly monodisperse macromolecules, e.g. DNA and polypeptides. Fortunately, R. Merrifield (Nobel prize in 1984) developed a Solid-Phase based method able to automatically synthesize polypeptides with high precision. Furthermore, the Solid-Phase approach was extended by Zuckermann to the synthesis of polypeptoids, which are close cousins of polypeptides but soluble in organic solvents[4].

This approach was recently explored by our group. In this contribution the synthesis and the grafting to characteristics of phosphorus-containing polypeptoids with 5, 10, 15 and 20 units will be presented. The effectiveness of these molecules in the silicon doping process will be also compared to the performance of dopant containing polystyrene and polymethylmethacrylate samples prepared by ARGET- ATRP.

Keywords: doping, “grafting to” reaction, polypeptoids, precision polymers

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Conjugated copolymers and their hybrid layers with interesting properties for optoelectronics

V. Cimrová*, V. Pokorná, P. Babičová, D. Výprachtický

Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic
**cimrova@imc.cas.cz*

Conjugated semiconducting polymers, particularly third generation donor-acceptor (D-A) copolymers, are of interest due to their many potential applications, namely, in photonics and optoelectronics, such as in light-emitting diodes, photovoltaic devices, photodetectors, organic field-effect transistors, sensors, optical switches, electrochromic devices, optical power limiters, and batteries, due to their specific physical, optical, and electronic properties.

In this contribution, series of donor-acceptor copolymers with interesting properties for the above mentioned applications and their hybrid layers with silver nanoparticles or perovskite will be reported. For the application of the copolymers, it is important to understand how their photophysical, electronic and electrochemical properties can be tuned by various combinations of donor and acceptor units or via attachment of different side chains on the acceptor or donor units. Therefore, we have synthesised and characterized donor-acceptor copolymers containing various electron acceptor (based on thienothiadiazole, difluorobenzothiadiazole and perylenetetracarboxydiimide) and with various electron-donor units (9,9-bis(alkyl)fluorene, 2,5-dialkyl- or 2,5-dialkyloxy- substituted 1,4-phenylene, bithiophene and carbazole derivatives) in the polymer backbone bearing various side chain combinations. Their properties (photophysical, electronic, photo- and electro-luminescent, spectroelectrochemical, electrical, photoelectrical, etc.) in solutions, thin films, polymer blends and/or hybrid systems were studied. The results are reported and discussed in relations to the copolymer backbone structure, side chain nature and their combinations, and also molecular weight. The thianothiadiazole-based D-A copolymers possess low bandgap, high electron affinity and exhibit interesting reversible electrochromic behavior. Optical switching was demonstrated and it was shown that response times depend on the donor unit nature. Performance of photovoltaic devices also depend on the nature of side alkyl chains. The difluorobenzothiadiazole-based D-A copolymers with higher bandgap show intense photoluminescent and interesting electroluminescent properties. The perylenetetracarboxydiimide(PDI)-based donor-acceptor copolymers exhibit interesting photophysical and redox properties promising for various applications. Using PDI-based copolymers, we succeded in formation hybrid layers with homogenous silver nanoparticles (Ag-NPs) coverage. The hybrid layers were prepared during reduction by electrochemical doping of pristine copolymer layers, using silver nitrate. The Ag-NPs coverage and size depended on the hybrid layer preparation conditions and on the copolymer composition. Stable Ag-NPs with an average diameter < 100 nm were formed on the surface. Significant improvements in light absorption due to the plasmonic effects of Ag-NPs were observed. The metallic character of the Ag-NPs was proven by X-ray photoelectron spectroscopy. Such hybrid layers have the potential for various photonic and electronic applications, particularly in photovoltaics, sensing, or catalysis. Polymers with heteroatoms such as nitrogen or oxygen are also interesting for hybrid materials with perovskites (methylammonium or formamidinium lead halide). Polymer-perovskite hybrid layers were prepared by spin-coating either in one- or two-steps depending on the solubility of selected copolymers. Their properties will be reported and disscused. Copolymer-perovskite combination can improve stability of perovskite and additional copolymer layers can also serve as electron- or hole-transporting layers in optoelectronic devices.

Keywords: conjugated polymers, hybrid layers, photophysics, spectroelectrochemistry, optical switching, electroluminescence, photovoltaics

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Three-component approach of solid polymer electrolytes based on zeolites and ionic liquid for high-performance lithium-ion batteries

J. C. Barbosa[1,2,3], D.M. Correia[1,3], M. Salado[4], A. Fidalgo Marijuan[4], R. Gonçalves[5], S. Ferdov[1,2], V. de Zea Bermudez[3], C. M. Costa[1,2,6]*, S. Lanceros-Mendez[4,7*]

[1]Physics Centre of Minho and Porto Universities (CF-UM-UP), University of Minho, 4710-057 Braga, Portugal
[2]Laboratory of Physics for Materials and Emergent Technologies, LapMET
[3]Department of Chemistry and CQ-VR, University of Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal
[4]BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain.
[5]Center of Chemistry, University of Minho, 4710-057 Braga, Portugal
[6]Institute of Science and Innovation for Bio-Sustainability (IB-S), University of Minho, 4710-057 Braga, Portugal
[7]Ikerbasque, Basque Foundation for Science, 48009 Bilbao, Spain
[*]Corresponding Author's: cmscosta@fisica.uminho.pt and senentxu.lanceros@bcmaterials.net

Lithium-ion batteries emerge as the most suitable candidates as effective energy storage systems for a wide range of applications, such as smartphones laptops, electric vehicles, and home storage systems. However, there are some issues to solve associated with the application of conventional lithium-ion batteries, especially due to the use of liquid components in their constitution, namely electrolytes, that are highly reactive and easily flammable. In this context, solid polymer electrolytes arise as an effective alternative to overcome these issues, by eliminating the necessity to use liquid electrolytes. However, several problems need to be solved before solid polymer electrolytes turn into a real and effective option for being implemented in commonly used devices. However, solid polymer electrolytes are still lagging behind in some critical issues such as cycling stability and ion conductivity [1].

In this work, we present the development of new solid polymer electrolyte based on a three-component approach, using a polymer matrix and two combined fillers, an ionic liquid ([BMIM][SCN], [EMIM][TFSI], [BMIM][N(CN2)]) and a zeolite (clinoptilolite, MFI, ETS-4). Different preparations methods, ionic exchange of zeolites, ionic liquid types were studied to evaluate their influence in the properties and performance of the solid polymer electrolyte [2].

These solid polymer electrolytes show promising results, with suitable room temperature ionic conductivity (0.19 mS.cm^{-1}) and excellent battery performance (160.3 mAh.g^{-1} at C/15) over prolonged charge/discharge cycles.

Keywords: zeolites, ionic liquid, solid polymer electrolytes, lithium-ion batteries

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Full colour photonic pigments by confined block copolymer self-assembly

A. Dodero[1*], K. Djeghdi[1], V. Bauernfeind[1], M. Airoldi[1], B. Wilts[2], C. Weder[1], U. Steiner[1], I. Gunkel[1]

[1]*Adolphe Merkle Institute, University of Fribourg, Fribourg, Switzerland*
[2]*Department of Chemistry and Physics of Materials, University of Salzburg, Salzburg, Austria*
[*]*andrea.dodero@unifr.ch*

Photonic pigments are one of the most exciting topics in optics as they are expected to lead to a pure, long-lasting and brilliant colouration making them ideal candidates for future paints, cosmetics, displays, and advanced photonic devices.[1] Till now, most efforts focused on amorphous packings of colloidal crystals whose applicability is however hindered by their poor colour purity, limited scalability and whitish appearance.[2,3] Here we present the robust and versatile fabrication of non-iridescent photonic pigments based on the 3D confined self-assembly of block copolymers via emulsification (Figure 1a). The main approach consists of preparing concentric lamellar structures (Figure 1b) whose periodicity can be controlled by adding specific swelling agents enabling the formation of supramolecular comb-like assemblies (Figure 1c).[4] Thus, photonic pigments with colour brightness, full-spectrum tunability, angular independence and reflectance up to 100% were achieved (Figure 1d). Taking inspiration from nature,[5] photonic particles combining structural colouration and broad-band absorption were also investigated. Specifically, the addition of small quantities of black absorbers within the photonic particles was proved to significantly reduce the intrinsic incoherent light scattering leading to an overall higher colour vividness and purity. In conclusion, the developed photonic pigments represent a rich playground for further advances in the thriving field of structural colouration and pigment technology.

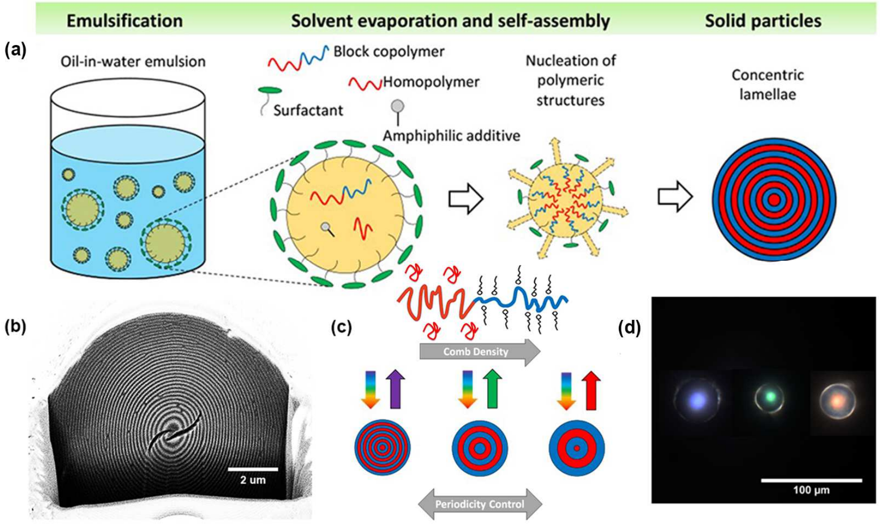

Figure 1. (a) Schematic of concentric lamellae photonic particles preparation. **(b)** Concentric lamellar morphology. **(c)** Colour tunability via the control of supramolecular comb-like assemblies. **(d)** Optical microscopy images of full-spectrum photonic particles.

Keywords: photonic pigments, block copolymers, self-assembly

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Development of Polymer Electrolytes Complementary to Model Active Systems for Polymer-based Batteries

L. Ehrlich[1,2*], P. Uhlmann[1], U. L. Muza[1], A. Lederer[1,3], D. Pospiech[1]

[1]*Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Deutschland*
[2]*Organic Chemistry of Polymers, Technische Universität Dresden, 01069 Dresden, Germany*
[3]*Department Chemistry and Polymer Science, Stellenbosch University, 7602 Matieland, South Africa*
[*]*ehrlich@ipfdd.de*

Nowadays, sustainability is a widely discussed topic in the field of energy supply and storage. There are many highly developed technologies designed to make life more environmentally friendly and economical, in particular in the field of battery research by replacing current lithium-ion technology with more environmentally friendly alternatives.
The aim of this study is to develop a solid-state polymer redox battery consisting of polymeric active materials and a chloride-conducting polymer electrolyte (PEL) which is based on ionic liquid monomers and is exactly designed for the redox system *p*(TEMPO) (cathode)/p(viologen) (anode). The PEL will find application in the form of thin films of linear homopolymers or crosslinked polymers (Figure 1), respectively, synthesized by radical polymerization methods. The properties of the PEL can be influenced by their chemical structure to obtain high ionic conductivities ($\sigma = 10^{-4}$ S/cm) and low glass transition temperatures ($T_g < 0$ °C), necessary to ensure high segmental mobility.[1,2] The results show that an increasing amount of crosslinker leads to the reduction of the ionic conductivities. Furthermore, a longer alkyl spacer chain in the substituent leads to a decrease of T_g. Lower T_g values result in higher ionic conductivites because higher flexibility supports ion mobility.

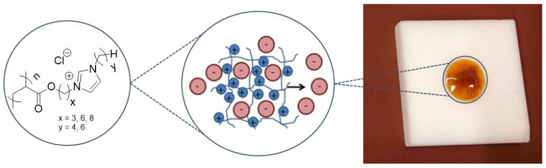

Figure 1: Ionic liquid polymer network designed as solid electrolyte for redox batteries.

Detailed characterization by NMR spectroscopy, Electrochemical Impedance Spectroscopy (EIS), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and voltammetric measurements demonstrate the chemical, thermal and electrochemical stability of the PELs. Furthermore, we study the soluble linear homopolymers with respect to their molar masses. The determination of the molar masses by means of Size Exclusion Chromatography (SEC) is very challenging, due to interaction of the ionic polymers with the stationary phase of SEC-columns. Therefore, a special method called Thermal Field Flow Fractionation (ThFFF) was employed for the first time demonstrating great potential for characterizatioin of these challenging materials. With this method we show that the polymers synthesized by radical polymerization possess distributions in the high molar mass range.

Keywords: organic batteries, ionic liquids, polymer electrolytes, ThFFF

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Examples on Graphitic Carbon Nitride in Synthetic Polymer Chemistry

C.Esen[1], B.Kumru[2*]
[1,2]Max Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, Am Mühlenberg 1, 14476 Potsdam, Germany
cansu.esen@mpikg.mpg.de, baris.kumru@mpikg.mpg.de.

The urge of light harvesting has a great importance ever since we reached the ultimate level of pollution and energy shortage nowadays. To the fact that, association of photochemistry and polymers plays a crucial role in fabrication of advanced processes and materials. Metal-free polymeric semiconductor graphitic carbon nitride (g-CN, g-C_3N_4 as ideal formula) grants photoactivity into polymeric networks when it is either embedded or covalently linked. Not only the ease of synthesis method (cheap and abundant nitrogen rich precursors treated via thermal condensation around 550 °C) but also adjustable optical properties span from absorption, band gap and photoluminescence via pre/or post modifications, stands out g-CN among current metal-based photocatalysts. However, immobilization of g-CN into stable surfaces has been a quite challange due to the weak dispersibility based on strong pi-stacking of graphitic nanosheets, which in return hinders potential scale-up options. Herein, three articles will exhibit the utilization of g-CN in i) resin formation, ii) hydrophobic hydrogel formation and iii) processable oligoEDOT synthesis. To begin with, polymer beads named poly(styrene-co-divinylbenzene, PS-DVB) are firstly endowed with photoactivity by integration of organo-dispersible g-CN (vTA-CMp) via suspension photopolymerization. Afterwards, resulting tunable beads were employed as recyclable photocatalysts as underlined by RhB dye photodegradation experiments (figure 1a).[1] In other study, we synthesized a hydrogel scaffold via redox induced free radical polymerization in which g-CN nanosheets were embedded. Taking the advantage of the photoactivity, under visible light irradiation, we can graft biocompatible hydrophobization agent resulting in hydrophobic hydrogel from a super hydrophilic nature. Such a system showed delayed nutrient release in aqueous environments that is highly desired in agricultural delivery systems.[2] Additionally, photoactive hydrogel scaffold can be swollen with secondary monomer-crosslinker solution to form functional IPN-style interlocked hydrogels under visible light (figure 1b).[2] Lastly, we will demonstrate the use of g-CN as a heterogeneous redox photoinitiator to synthesize a non-doped oligo 3,4-ethylenedioxythiophene (oligoEDOT) via oxidative photopolymerization under visible light. So-formed oligo-EDOT material has shown facile processability to produce films and coatings, that can be post-doped to form conductive surfaces. Addition of excess g-CN in the polymerization media forms PEDOT coated g-CN via surface polaron, that is highly attractive for photocatalysis (figure 1c).[3] This abstract elucidates only few examples with a great potential that can be harnessed by the combination of g-CN and polymer materials. Despite the field is still infant, one can expect a greater contributions to form scalable and facile syntetic routes to form advanced polymeric materials.

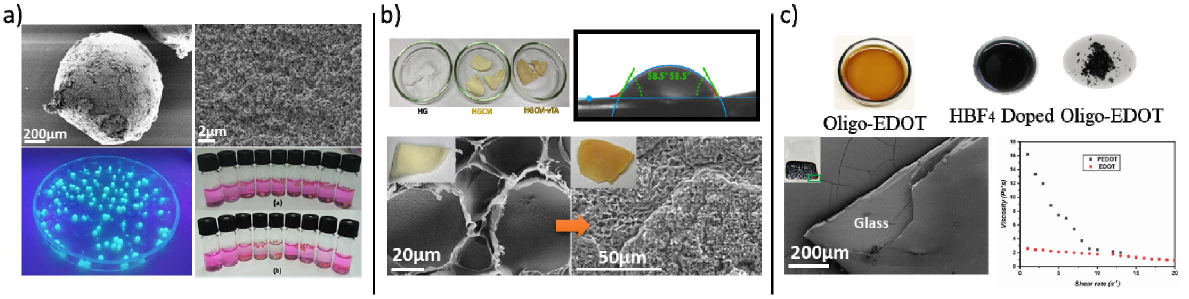

Figure 1. Suspension photopolymerization of poly(styrene-co-divinylbenzene) integrated with organo-dispersible g-CN (vTA-CMp) (a), g-CN embbeded hydrogel and its hydrophobized analog synthesis via in-situ photo grafting (b), oxidative photopolymerization of EDOT via g-CN (c).

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Naturally-derived biopolymer electrolyte for Zn-air batteries

E. García-Gaitán,[1,2,3] I. Cantero,[2] D. González,[2] and N. Ortiz-Vitoriano[1,4]

[1] Centre for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Alava Technology Park, Albert Einstein 48, 01510, Miñano, Spain
[2] CEGASA Energía SLU, Marie Curie, 1, Parque Tecnológico de Álava, 01510 Miñano, Spain
[3] University of the Basque Country (UPV / EHU), Barrio Sarriena, s / n, 48940 Leioa, Spain
[4] Ikerbasque, Basque Foundation for Science, María Díaz de Haro 3, 48013, Bilbao, Spain

High energy demand and concerns about climate change have urgently promoted a transition from fossil fuels to clean renewable energy. Rechargeable lithium batteries, currently on the market, are a good alternative to fossil fuels; however, its use in stationary energy storage systems involves a great cost, being necessary to seek new highly competitive technologies at a lower cost. In this sense, Zn-air batteries are attracting a great deal of attention thanks to: (1) Zn abundance in the earth's crust which is one of the most abundant minerals; (2) high energy density (6136 W h L^{-1}) and a relatively high specific energy (1218 Wh kg^{-1}); (3) low cost and (4) operational safety. [1] Currently, Zn-air batteries suffer from leakage or evaporation due to the liquid nature of the electrolyte and the open-system set-up which causes a decrease in the performance and hence short cycle life [1, 2, 3]. This challenge, however, can be overcome by the use of solid electrolytes with similar properties to those reported in liquid systems thanks to the use of gel-based polymer electrolytes.

In this work, we present the development of a novel solid electrolyte, based on a natural, linear, and biodegradable polymer. The biopolymer soaked in a saline solution forms a suitable gel to be used as a solid electrolyte, which also works as a separator in Zn-air batteries. In this study, its manufacture and characterization will be presented, as well as its electrochemical performance in a Zn-air battery. This electrolyte presents a conductivity of $4.5x10^{-1}$ S·cm^{-1}, similar to the commonly used liquid alkaline (KOH) electrolyte (8M KOH solution presents a conductivity of 6.1x10-1 S·cm^{-1}). [4] The electrochemical testing in a Zn-air battery shows excellent performance and higher Zn extraction when compared with other solid electrolytes. [3] Moreover, it does not liquefy, and its mechanical properties are maintained after being subjected to a constant discharge until battery failure.

Keywords: Zn-air, bioelectrolyte, biopolymer, batteries, metal-air, ionic conductivity.

Acknowledgements

This project (RTC-2017-6238-3 AEI / FEDER, EU) is funded by the Ministry of Economy and Competitiveness and by the European Regional Development Fund FEDER. E. Garcia thanks the Basque Government for the Beca Bikaintek 01-AF-W2-2019-00003.

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Polyanion Star-shaped Macromolecules as Additives for High Performance Single-ion Electrolytes

E. Glynos[1,2*], G. Nikolakakou,[2,3] C. Pantazidis,[4] G. Sakellariou[4]

[1] *Departement of Materials Science and Technology, University of Crete, 71003 Heraklion, Crete, Greece*
[2]*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1385, 71110 Heraklion, Crete GR, Greece*
[3]*Departement of Chemistry, University of Crete, Heraklion, 700 13 Heraklion, Crete, Greece*
[4]*Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece*
[*]*eglynos@iesl.forth.gr, eglynos@materials.uoc.gr*

Single-ion solid polymer electrolytes (SPEs) could be a real "game-changer" as they represent the ultimate solution to the safety issues associated with the use of flammable and toxic liquid electrolytes in commercial Li-ion batteries. Most importantly, SPEs hold the key for the realization of high energy-density Li-metal batteries, as they are chemical stable towards Li metal while their mechanical resistance could reduce, or even suppress Li dendrite formation and eliminate the associated safety hazards and the catastrophic failure of the battery. Conventional SPEs, that are formed by mixing Li salt with a polar polymer host that dissociates the lithium salt, are dual ion conductors (both the cation and anions are mobile) with a very low Li$^+$ transference number ($r_+ \sim 0.5$), which leads to strong ion concentration gradient with deleterious and catastrophic effects for a lithium battery. Despite the considerable research effort in SPEs, the development and realization of their potential has been hampered by the inability to design materials that possess simultaneously, high ionic conductivity, good mechanical properties, and cation transference number close to unity (i.e. single-ion solid polymer electrolytes, $r_+ = 1$). In this talk, we introduce the use of novel, stiff/glassy, polyanion particles, composed of high functionality poly(lithium 4-styrenesulfonyl trifluoromethylsulfonyl imide), PSTFSILi, star-shaped polymers as additives to liquid, low molecular weight poly(ethylene oxide), PEO, electrolytes for the synthesis of SPEs that are single-ion by design while exhibit an unprecedented combination of high modulus and ionic conductivity, at room temperature. The resulting single-ion SPEs exhibit simultaneously higher conductivity and mechanical strength compared to their linear PSTFSILi blend analogues. Key to their performance is the morphology that stems from the ability of the PSTFSILi nanoparticles to disperse within the liquid PEO electrolyte, permitting the development of a highly interconnected network of pure liquid PEO that promotes to high ionic conductivity.

Keywords: single-ion polymer electrolytes, nanostructured materials, polyanion star polymers

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Ευρωπαϊκή Ένωση
Ευρωπαϊκό Ταμείο
Περιφερειακής Ανάπτυξης

ΕΛΛΗΝΙΚΗ ΔΗΜΟΚΡΑΤΙΑ
ΥΠΟΥΡΓΕΙΟ
ΑΝΑΠΤΥΞΗΣ ΚΑΙ ΕΠΕΝΔΥΣΕΩΝ
ΕΙΔΙΚΗ ΓΡΑΜΜΑΤΕΙΑ ΔΙΑΧΕΙΡΙΣΗΣ
ΠΡΟΓΡΑΜΜΑΤΩΝ ΕΤΠΑ, ΤΣ & ΕΚΤ
ΕΙΔΙΚΗ ΥΠΗΡΕΣΙΑ ΔΙΑΧΕΙΡΙΣΗΣ ΕΠΑνΕΚ

ΕΠΑνΕΚ 2014-2020
ΕΠΙΧΕΙΡΗΣΙΑΚΟ ΠΡΟΓΡΑΜΜΑ
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Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

Improving the Ionic Conductivity of Block Copolymer Electrolytes by Interfacial Engineering

C. Prado Martínez[1], M. Airoldi[1], U. Steiner[1], and I. Gunkel[1*]

[1]*Adolphe Merkle Institute, Fribourg, Switzerland*
[*]*ilja.gunkel@unifr.ch*

Block copolymer electrolytes for Li-ion batteries promise a combination of a high elastic modulus and good ionic conductivity, circumventing a range of issues with liquid electrolytes [1]. Unfortunately, their conductivity performance often lies much below the expected morphology-driven value, which limits their utility for lithium batteries [2]. We recently uncovered that the wetting behavior of the block copolymer on the electrode has a very strong effect on the overall conductivity [3]. Here we show that the conductivity in lamellae-forming polystyrene–*block*–poly(ethylene oxide) (PS-*b*-PEO) block copolymers – arguably the work horse of the community for decades – can be significantly increased by engineering the electrode-electrolyte interface.

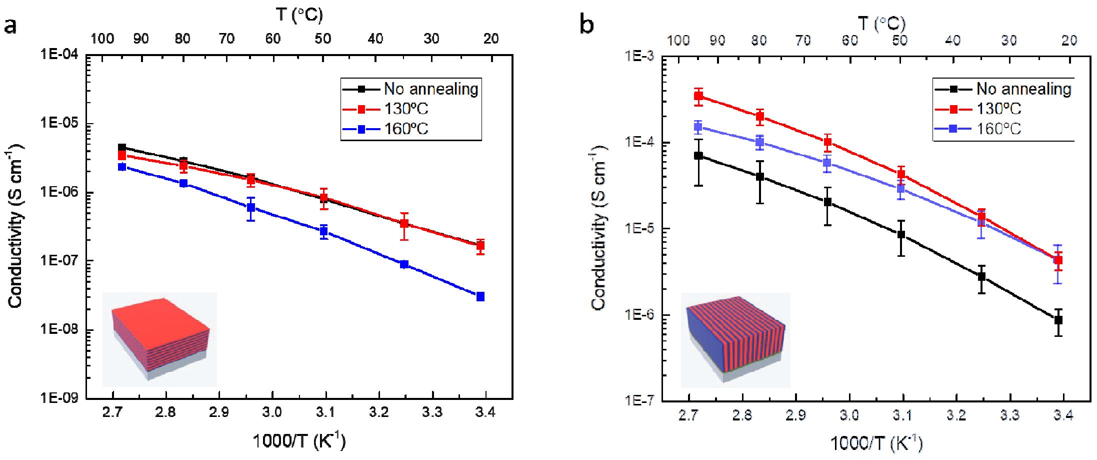

Figure 1: Conductivity of 800 µm thick lamellae-forming PS-*b*-PEO films in symmetrical stainless steel cells with Li-ion concentration of r = 0.08. Annealing the samples for one hour at indicated temperatures leads to a drop in conductivity (a), while the same electrodes surface-modified with neutral random copolymer brushes of PS/P2VP cause an increase in the conductivity (b). Cartoon insets show surface-parallel lamellae for preferential electrode wetting on stainless electrodes (a), while surface-perpendicular lamellae on stainless steel surface-functionalized with a polystyrene/poly(2-vinylpyridine) (PS/P2VP) brush layer that renders the surface neutral for the block copolymer (b). While surface-parallel lamellae are expected to significantly limit transport of lithium ions, a surface-perpendicular orientation promotes ionic transport.

Keywords: block copolymer electrolytes, random copolymer brushes, lithium batteries, electrochemical impedance spectroscopy

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Redox-active Ru-polymetallaynes for multi-state electrochromic memory application

P. Y. Ho[1, 2], E. Dmitrieva[3], O. Ditzer[1,2], N. Sun[1], O. Guskova[1], F. Lissel[1,2*]

[1]Leibniz-Institut für Polymerforschung (IPF) Dresden e.V., Dresden, Germany
[2]Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, Dresden, Germany
[3]Leibniz-Institut für Festkörper- und Werkstoffforschung (IFW) Dresden, Dresden, Germany
**lissel@ipfdd.de*

Materials that can exhibit multiple states (e.g. oxidation states) in solid-state are vital prerequisite to achieve highly-compact memory capacity. From a practical point of view, the change of states should preferably be at low voltage. Ruthenium (Ru)-acetylide-based materials are promising candidates due to their redox-activity and electron-rich character[1], yet they have never been studied for solid-state multi-state memory application, probably due to the lack of a reliable and simple synthetic route for this class of materials. Recently, we successfully synthesized three redox-active and solution processable Ru-polymetallaynes using a facile dehydrohalogenation polymerization method previously demonstrated by our group[2]. The polymer layout is a Wolf Type-III system, i.e., the redox-active metal centers are covalently included in the sp^2/sp^3 conjugated polymer backbone. By modifying the organic bridging ligands (i.e. rigidity, redox-matching), the interaction between Ru centers (metal-metal interaction) can be modulated to afford materials with additional intermediate mixed-valence states and low metal-based oxidation potential as indicated by experimental (CV, *In-situ* EPR, SEC analysis) and theoretical (DFT) results. The polymers were then investigated in electrochromic devices to access stability over cycles and state retention time.

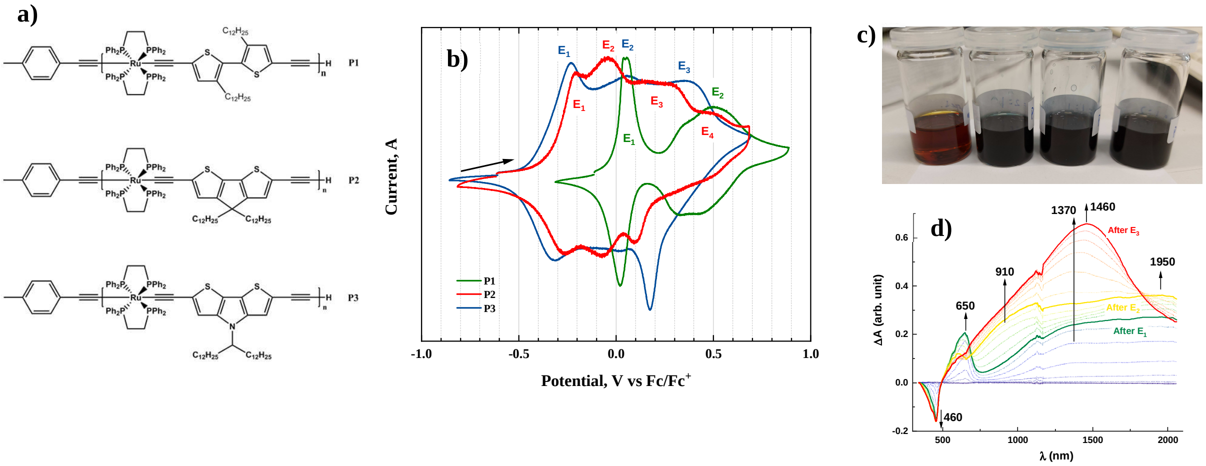

Figure 1. a) Structures of P1-P3, **b)** CVs of P1-P3, **c)** color change of P3 at different oxidation states (dopant: F_4-TCNQ, color change: brown (left), dark blue (second left), black (second right) and dark brown (right)) and **d)** SEC analysis of P3 thin film.

Keywords: Ruthenium-acetylide, ruthenium-polymetallaynes, multi-state memory, mixed-valence

Acknowledgments

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Aerosol Jet Printing of Benzocyclobutene-based Inks for Electronic Applications

F. Iervolino[1*], R. Suriano[1], M. Scolari[2], I. Gelmi[2], L. Castoldi[2] and M. Levi[1]

[1] *Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, Milan (MI) 20133, Italy*
[2] *STMicroelectronics, Via Camillo Olivetti, 2, Agrate Brianza (MB), 20864, Italy*
[*] *filippo.iervolino@polimi.it*

Aerosol jet printing (AJP) is a non-contact, maskless digital fabrication technology that allows the fabrication of complex features in an additive fashion. AJP is based on the ejection of an aerosol stream, which is focused on the substrate. AJP can process a wide variety of materials, e.g., metallic, ceramic and polymeric inks. [1] The vast majority of the works in the literature focuses on the AJP of inks containing silver nanoparticles, graphene or carbon nanotubes, while few works investigate the use of polymeric inks. In this work, we study the AJP of benzocyclobutene (BCB)-based inks. BCB is a thermoset polymer widely used in the electronic industry for wafer bonding, MEMS and packaging applications. Usually, BCB is applied by spin-coating. However, spin-coating needs to be coupled with a lithographic process when complex patterns need to be fabricated. [2] AJP represents a valuable alternative since it allows to fabricate the desired pattern in one step. Another advantage of AJP is the feasability of obtaining patterns with a relatively high thickness by adjusting both the process parameters and printing multiple layers. [3] In the current study, we investigate the formulation and characterization of BCB-based inks. Then, the effect of the processing parameters is evaluated printing the smallest possible features, i.e., a line pattern. In particular, the effect on the line width and thickess is considered. Squares patterns are also printed to evaluate the print quality for a 2D-like pattern, as shown in Figure 1a. The printed squares have a thickness ranging from 1.5 to 40 µm using just a single layer, proving the high versatility of AJP. Furthermore, Figure 1b shows the feasability of printing complex patterns with relatively small features. Finally, the adhesive properties of the printed BCB coating are evaluated by mean of pull-off and shear tests.

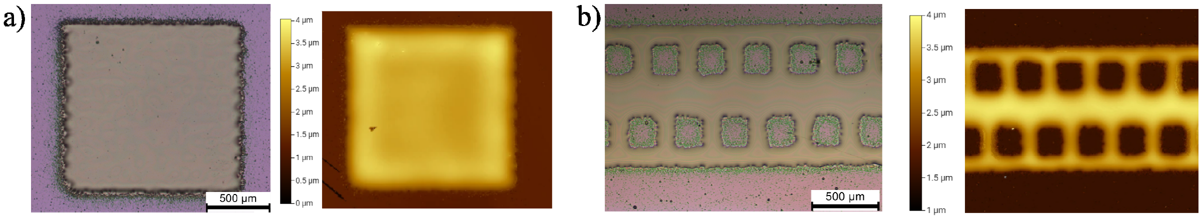

Figure 1. Optical miscrocpy and optical profilometry of a) a square pattern and b) a complex pattern printed with aerosol jet printing

Keywords: additive manufacturing, aerosol jet printing, benzocyclobutene, polymeric adhesive

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This work was supported by the Joint Research Centre scientific partnership between Politecnico di Milano and STMicroelectronics. The authors acknowledge the availability of experimental facilities at PoliFAB, the micro- and nanofabrication facility of Politecnico di Milano.

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In situ study of printing donor: acceptor polymer blends for photovoltaic applications

X. Jiang[1*], P. Chotard[1], K. Luo[1], S. Tu[1], M. A. Reus[1], S. Yin[1], J. Reitenbach[1], C. L. Weindl[1], M. Schwartzkopf[2], S. V. Roth[2], P. Müller-Buschbaum[1,3]

[1]Lehrstuhl für Funktionelle Materialien, Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany
[2]Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany
[3]Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstr. 1, 85748 Garching, Germany
[*]E-mail: xinyu.jiang@ph.tum.de

With the advantages of highly tunable molecular energy levels and light absorption spectra, organic solar cells (OSCs) using non-fullerene accepters have achieved power conversion efficiencies over 18%. However, these best efficiencies are still behind that of traditional silicon solar cells, in particular in case of printed OSCs, which demonstrates the need for further intensive investigations. The performance of OSCs is strongly influenced by the morphology of the active layer, which forms during the device fabrication. Therefore, understanding the mechanisms of the structure forming processes of the active layer is key for gaining more fundamental understanding and thereby enabling a device optimization. [1] Herein, we compare chlorobenzene (CB) and chloroform (CF) used as host solvents for printing the neat films of the novel wide-bandgap donor polymer PDTBT2T-FTBDT, the small molecule non-fullerene acceptor BTP-4F as well as the respective PDTBT2T-FTBDT: BTP-4F blend films, which are used as active layers in OSCs. [2] Using CF, OSCs with a high power conversion efficiency of up to 13.2 % are reached in ambient conditions. In comparison to CB printed blend films, the active layer printed out of CF has a superior morphology and a more pronounced face-on orientation of the crystallites, resulting in an enhanced exciton dissociation and suppressed non-radiative charge carrier recombination. For tracking the mechanism of the structure formation of polymer domains, we use in-situ grazing incidence wide-angle X-ray scattering (GIWAXS) and UV-vis techniques. Based on in situ studies of the slot-die coating process of the PDTBT2T-FTBDT: BTP-4F films, the details of the film formation kinetics are clarified, which cause the superior behaviour for CF compared to CB printing due to balancing the aggregation and crystallization of donor and acceptor materials.

Keywords: slot-die coating, non-fullerene organic solar cells, in situ UV-vis, in situ GIWAXS

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Zwitterionic polymer-based platforms for sustainable energy and advanced applications

P. Kasak[1*]

[1]*Center for Advanced Materials, Qatar University, POBox 2713, Doha, Qatar.*
[*]*Peter.kasak@qu.edu.qa*

Zwitterionic polymer materials, possessing balanced charges in each monomer unit, turn out to be a benchmark for antibiofouling material [1,2] with unique solution and surface properties [3]. This contribution is focused on fabrication and application of zwitterionic polymers and their copolymers. Such type of polymers offers controlled solution (upper critical solution temperature), cell adhesion materials and (bio)sensing platform. Furthermore, sustainable osmotic engine based on zwitterionic hydrogel material fuelled by salinity gradient will be presented. Moreover, discussion on modification of polymeric backbone to sulfobetaine-based polydisulfides allowing tunable depolymerization kinetics and modulable solution properties and surface wettability will be performed.

Keywords: zwitterionic polymers, osmotic engine, polydisulfides.

Acknowledgments

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Formation of stable heterojunction by sequential solution deposition of conjugated polymer and small molecule

Suhyun Min[1], Seung Hee Han[1], Chanju Park[1], Jinhan Cho[2], Kyungkon Kim[1]*

[1]*Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760, Republic of Korea*
[2] *Department of Chemical & Biological Engineering and KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, Republic of Korea*
**kimkk@ewha.ac.kr*

With rapid advances in the development of new conjugated polymers, non-fullerene acceptors, the power conversion efficiency (PCE) of organic photovoltaics (OPVs) has been increased over 17%. However, a major drawback for the commercialization of OPVs is their long-term stability under continuous operation. Especially, OPVs suffer from a rapid decrease in PCE during initial device operation, which is known as the "burn-in loss". It is considered that the origin of the burn-in loss is mainly related with the instability of the heterojunction morphology at bulk and/or interface. In this contribution, I would like to introduce a strategy to improve heterojunction morphology through the construction of heterojunction by sequential deposition of conjugated polymer donor and conjugated small molecule acceptor.

Keywords: organic solar cell, sequential depostion, stability

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Polymer composites as a promising solid electrolytes in energy applications.

Sylwia Kozdra [1, 2, *], Łukasz Florczak [2], Ireneusz Opaliński [2], Piotr Szałański [2], Adrianna Wójcik [1, 3], Małgorzata Możdżonek[1], Paweł Piotr Michałowski [1]

[1]*Łukasiewicz Research Network – Institute of Microelectronics and Photonics, Aleja Lotników 32/46, 02-668 Warsaw, Poland*
[2]*Rzeszów University of Technology, Faculty of Chemistry, Powstańców Warszawy 12, 35-959 Rzeszów, Poland*
[3]*Warsaw University of Technology, Faculty of Physics, Koszykowa 75, 00-662 Warsaw*
[*]*Sylwia.Kozdra@imif.lukasiewicz.gov.pl*

Polymer composites with advanced properties, especially conductive composites are constantly tested for applications as solid polymer electrolytes (SPE) [1]. Solutions to improve the current energy applications are desirable because of increasing safety and performance requirements. Polymers with the addition of lithium salts perfectly meet the safety criteria, but their efficiency is insufficient for practical applications due to too low conductivity [2]. The selection of SPE ingredients and production methods have a decisive influence on its final properties and functionality.

In this work, polymer composite with different amounts of lithium perchlorate in PVDF polymer matrix was tested as SPE. The crucial property: ionic conductivity of the obtained SPEs was compared and differences related to the amount of lithium compound were noticed (Fig 1). Significant differences in conductivity values indicated changes in mechanisms of ions transport and were explained by simultaneously observed changes in the chemical, and crystal structure. An unexpected increase in the conductivity value was observed, indicating the existence of an optimum ratio of the composite components. It has also been shown that the method of preparing the composite is extremely important. Intensive mixing ensures an optimal level of homogeneity, especially important for conductive properties. Using the Secondary Ion Mass Spectrometry technique the distribution of lithium in the polymer matrix was investigated which clearly indicated that crucial differences in SPE conductivity were related to the lithium distribution.

The conducted research shows the potential of polymer composites based on PVDF and $LiClO_4$. The method of producing SPE, especially the use of high-energy mixing with optimally selected process parameters, is a potential solution to the problem of low conductivity of polymer composites.

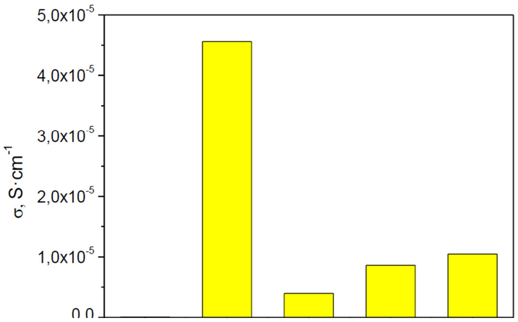

Fig. 1 Conductivity of SPE with increase amount of $LiClO_4$

Keywords: polymer composites, high-energy mixing, solid polymer electrolytes, energy applications

Acknowledgments

This work was supported by the National Science Centre within the SONATA14 (grant no. 2018/31/D/ST5/00399)

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Polycarbonate and poly ether ether ketone composites with hybrid carbon nanotube fillers for thermoelectric application

B. Krause* [1], I. Konidakis [2], H. Reith [3], E. Stratakis [2], P. Pötschke [1]

[1]*Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany*
[2] *Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology-Hellas (FORTH), Heraklion-Crete, Geece*
[3] *Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden e.V., Dresden, Germany*
**krause-beate@ipfdd.de*

The incorporation of carbon nanotubes (CNTs) within suitable polymer matrices offers a great platform for the development of electrical conductive composites which are also of interest as thermoelectric materials. Previous studies have shown that the thermoelectric properties of such composites depend not only on the type of CNTs but also on the type of the polymer matrix [1-3]. Singlewalled CNTs (SWCNTs) are particularly suitable for achieving high Seebeck coefficients S. Branched multiwalled CNTs (MWCNTs) lead to very high electrical conductivities σ of the composites due to their very good dispersion behaviour. With the target of a high power factor PF ($PF = \sigma \cdot S^2$), the values of both S and σ should be high.

The aim of the present study was to improve the thermoelectric properties of composites by combining CNT types that lead to high Seebeck coefficients and other CNT types that lead to high conductivities. Such composites with hybrid CNT fillers (CNT contents in the range of 0.5 to 5 wt%) were prepared by melt compounding with polycarbonate (PC) and poly ether ether ketone (PEEK) as polymer matrices. The highest Seebeck coefficient values were found at 0.75 wt% SWCNT Tuball^{TM} with 39.5 µV/K in PC and 61.3 µV/K in PEEK composites. Next to the thermoelectric characterization of both single- and hybrid-CNT filled composites also the mobility of the charge carriers was investigated by Hall measurements for selected composites. Ultrafast laser time-resolved TAS was employed to thoroughly investigate the exciton dynamics and corresponding charge carrier lifetimes within the developed PC/CNT composites. The findings of this study shed light on the physical origins of the thermoelectric conversion efficiency, upon providing evidence of how it is related with the excitonic characteristics of the incorporated CNTs. It was found that the Seebeck coefficient of both single and hybrid-filler composites exhibits a direct correlation with the exciton lifetime of the CNTs, while being independent of the CNT concentration within the polymers. Such correlation was already described in [3] for polypropylene based composites filled with SWCNT and nitrogen-doped MWCNTs.

Keywords: polymer composites, thermoelectric, carbon nanotubes

Acknowledgments

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Polymeric Photonic Crystals for Passive Thermal Management

A. Lanfranchi[1*], H. Megahd[1], P. Lova[1], D. Comoretto[1]

[1]*Università degli Studi di Genova, Genoa, Italy*
[*]*davide.comoretto@unige.it*

Thermal shielding is becoming of increasing importance for the reduction of energy consumption in buildings, higher efficiency of greenhouses and conservation of food and beverage.[1,2] In this work, we report on the use of full-polymer planar photonic crystals as selective reflectors for near-infrared radiation (NIR), which is mainly responsible for the radiative heating of objects from sunlight. Indeed, several materials, including moisture, absorb light in this spectral range and generate heat upon absorption.[3]

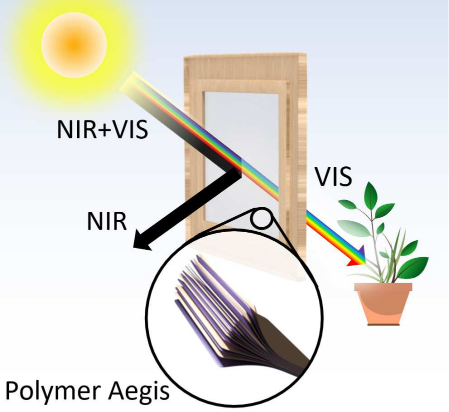

Figure 1. Schematic of Polymer aegises' functioning, reflecting NIR light and transmitting VIS one.

The multi-layered structures are made of low-cost, flexible and versatile polymer films designed and fabricated to selectively reflect NIR radiation, yet keeping high transparency in the visible range. This is possible thanks to a fine enginering of their sub-micrometric periodicity, which induces light interacion phenomena detectable as spectral region with intense reflectance. These structures, which we call "aegises" referring to the invulnerable goat pelt of Greek mythology, were fabricated by spin-coating of poly(*N*-vinylcarbazole) as the high refractive index medium and either cellulose acetate or polyacrylic acid as the low index one.[4,5] Different structures were realized to match the absorbance spectra of materials with NIR absorbance. All of them were tested as thermal shields measuring the temperature variation of different materials upon irradiation. These tests demonstrates that our polymer structures can reduce heating by more than 15% with respect to uncoated glass. Considering the ease to scale-up the fabrication on very large area by co-extrusion,[3] these results promising for lowering buildings energetic consumption and for best conservation of food and beverages.

Keywords: Energy Efficiency, Thermal Shielding, Dielectric Mirror, Multilayer, Photonic Crystal, Near Infrared, Reflector

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Sulfonylimide-Based Single-Ion Conducting Polymer Electrolyte for High-Voltage Lithium-Metal Batteries

Hai-Peng Liang, Zhen Chen, Stefano Passerini, Dominic Bresser

Helmholtz Institute Ulm (HIU), Helmholtzstrasse 11, D-89081 Ulm, Germany
Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany
**hai-peng.liang@kit.edu*

Lithium-metal batteries are theoretically providing the highest energy density possible.[1] However, the potential formation of lithium dendrites and the subsequent short circuiting of the cell, resulting in a thermal runaway, pose a severe safety issue.[2–4] This can be addressed by replacing the conventional liquid electrolyte with solid ionic conductors. In this regard, single-ion conducting polymer electrolytes (SIPEs) are considered particularly attractive due to the elimination of the detrimental reversed cell polarization and the uniform Li^+ flux.[5,6] Commonly limited by the oxidative stability at elevated electric potentials, however, SIPEs are rarely investigated in lithium-metal batteries employing high-voltage layered cathodes.[7]

Herein, we present a novel single-ion conductor synthesized from the copolymerization of two functional lithium salts. The self-standing polymer membrane provide a wide electrochemical stability window of up to 5.2 V, suitable ionic conductivity (0.24 mS cm^{-1} at 20 °C and 0.37 mS cm^{-1} at 40 °C), and excellent (electro)chemical compatibility with both lithium-metal anodes and Ni-rich $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NMC_{622}) cathodes. As a result, this new polymer electrolyte enabled very stable cycling of high-energy Li||NMC_{622} full-cells with high cell voltage of 4.3 V and a capacity retention of 91.5% after more than 250 cycles at 1C.

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The phase behavior and state diagram of PBTTT and novel derivatives in mixtures with $PC_{61}BM$ for organic near-IR photodetectors

Z. Liu[1]*, J. Vanderspikken[2,3], K. Van Der Flaas[4], M. Hamid[4], E. Nies[4], B. Goderis[4], K. Vandewal[2,3], W. Maes[2,3], B. Van Mele[1] and N. Van den Brande[1]

[1]*Vrije Universiteit Brussel, Physical Chemistry and Polymer Science, Brussels, Belgium*
[2]*Hasselt University, Institute for Materials Research (IMO-IMOMEC), Diepenbeek, Belgium*
[3]*imec, Associated Laboratory IMOMEC, Diepenbeek, Belgium*
[4] *KU Leuven, Polymer Chemistry and Materials Division, Leuven, Belgium*
* *zhen.liu@vub.be*

The intermolecular charge transfer (CT) state formed at the interface between the donor (D) and the acceptor (A) is crucial for the device performance of organic cavity-based near-infrared (NIR) photodetectors. In such a device, a high interfacial contact area between D:A is required because it significantly promotes the CT absorption [1]. PBTTT:$PC_{61}BM$, a well-known benchmark system, is selected because the intercalation of the fullerene acceptor between the side chains of the polymer donor maximizes the D:A contact [2]. Two novel PBTTT derivatives were developed to further lower the energy gap between the HOMO of the donor and the LUMO of $PC_{61}BM$, and thus extend the CT absorption of the device more into the NIR [3].

In this research, Rapid Heat-Cool DSC (RHC) and temperature-resolved synchrotron XRD are combined for the construction of state diagrams. As the phase behavior and morphology of the D:A mixtures directly affect the device performance, it is important to construct state diagram which reveal the composition-temperature-phase behavior relationships of the blends [4]. RHC has been proven to be a well-suited technique for the construction of the state diagram, as it allows a relatively wide range of heating and cooling rates up to 2000 K/min [4]. Temperature-resolved synchrotron XRD allows to study the structural changes accompanied by thermal transitions as a function of temperature. With the help of synchrotron XRD results, the complex phase behavior, including formation of cocrystals and eutectics, of the PBTTT:$PC_{61}BM$ benchmark system is revisited, and compared to the systems based on the novel derivatives. Furthermore, it is also found that homocoupling, a common defect arising from the synthesis of these donor materials, plays a crucial role in the intercalation behavior.

Keywords: organic near-IR photodetectors, state diagram, cocrystal, eutectic, rapid heat-cool DSC, synchrotron XRD, homocoupling

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High dielectric contrast hybrid polymer-inorganic planar photonic crystals

S. Bertucci[1], H. Megahd[1], A. Escher[1], A. Dodero[1], S. Fiorito[2], M. Patrini[3], F. Di Stasio[2], D. Comoretto[1], P. Lova[1*]

[1]Università di Genova, *Dipartimento di Chimica e Chimica Industriale, Genova, Italy*
[2]*Istituto Italiano di Tecnologia, Morego (GE) Italy*
[3]Università di Pavia, *Dipartimento di Fisica, Pavia, Italy*

[*]*paola.lova*@unige.it

In the last decades a large effort has been paid to replace widespread inorganic photonic crystals with polymer ones. The interest in these structures arises from their ability to modify photon flow thanks to the periodical modulation of refractive index.[1-3] This peculiarity has indeed been largely employed for several tecnological applications including emission control, photon recycling, light harvesting enhancement, and sensing.[1] While inorganic structures, thanks to high dielectric contrast, provide undiscussed performances, polymer ones are easier to fabricate and possess mechanical properties otherwise unconceivable.[1] Thus, mantaining the polymers' processability yet obtaining the performance of inorganics is a highly sought goal in the in the field.

In this work, we report on the solution processing of high dielectric contrast photonic structures with processability and mechanical properties typical of polymers and performances of inorganic materials commonly processed with high vacuum technologies (Fig. 1). The new structures are obtained by spin-coating coupled to coss-linking of metal alcoxides and polymer matrices, thus allowing new hybrid materials with easily tunable refractive index. We demonstrate the compatibility of these materials with several conjugated and dielectric polymers to fabricate functional photonic structures and their use for emission control, sensing, and light harvesting enhancement in photocatalytic systems.

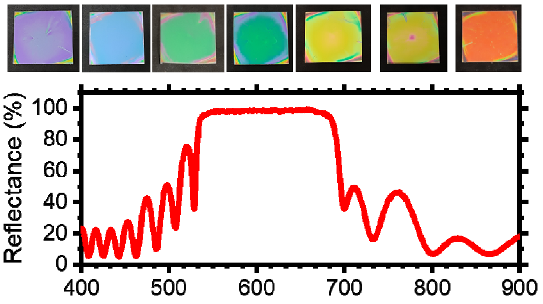

Figure 1: digital photographs (top) and a typical spectrum of a hybrid photonic structure.

Keywords: Hybrid photonic structures, composites, solution processing.

Acknowledgments: *This work has been partially founded by the Department of Chemistry and Industrial Chemistry of the University of Genova*

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Exploring the Effects of Hydrogen Bonding in poly(β-amino ester) based Solid Polymer Electrolytes for Lithium-ion Batteries

O. Majumdar[1*], T.Melander Bowden[1]

[1]*Uppsala University, Uppsala, Sweden*
*[*orpita.majumdar@kemi.uu.se](mailto:orpita.majumdar@kemi.uu.se)*

Ionic conductivity of Solid Polymer Electrolytes (SPEs) is yet to meet the requirements of the future energy-storage devices, indicating significant hurdles to progress. Intermolecular interactions like hydrogen bonding in SPEs can play a vital role in lithium ion mobility and conduction. The polar groups in the SPE could interact with the hydrogen bonds, thereby reducing the interaction strength with lithium ion, leading to an increase of free lithium ion. Thus, lithium ion channels can be formed, presenting a convenient path for lithium ion transport. Simultaneously, hydrogen bond interactions can disrupt the regular arrangement of the conducting segment and reduce the crystallinity of the polymer, resulting in an increase in ionic conductivity and lithium-ion transference number. Furthermore, the existence of hydrogen bonds can play an important role in improving the mechanical properties of the SPEs.[1], [2]

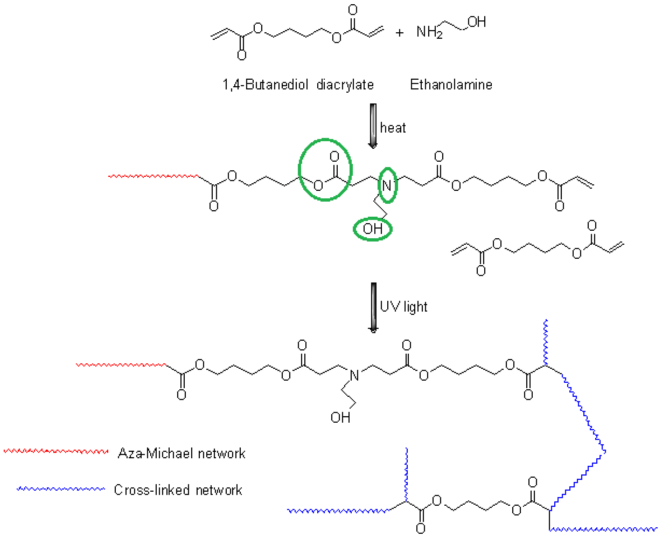

Figure 1: Reaction Scheme

In this work, the synthesis of poly(β-amino ester) based SPE from off-stoichiometric acrylate-amine formulations is demonstrated using a dual-curing, catalyst and solvent free approach. [3], [4] The synthesized polymers are hypothesized to have better mechanical properties and improved ionic conduction due to the existence of hydrogen bonding and hence are evaluated as a new class of SPEs. The glass transition temperature (onset) for a free-standing and easy to handle film of the polymer (1.3:1 acrylate-amine ratio) with and without 30 wt% salt is showed to be -15 °C and -40 °C respectively with DSC measurements. The hydrogen bonding interactions of the polymer can be investigated by IR spectroscopy. The polymer chain can facilitate the movement of both the anion and the cation owing to the presence of the different functional groups, highlighted in green in the reaction scheme. Additionally, these SPEs can be easily modified by changing the monomer structure and the stoichiometry of the formulations giving rise to a range of mechanical and thermal properties.

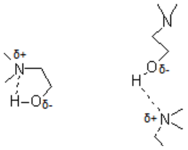

Figure 2: Intra- and Inter-molecular H-bonding

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Novel Bisphenol-Derived Single-Ion Conducting Polymer Electrolytes for High-Energy Lithium Batteries

A. Mayer[1,2,*], S. Passerini[1,2], and D. Bresser[1,2]

[1]*Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*
[2]*Helmholtz Institute Ulm (HIU), Ulm, Germany*
**alexander.mayer@kit.edu*

In order to broaden and strengthen the future application of lithium batteries, it is essential to further increase their energy density without compromising their safety.[1] In this regard, the use of metallic lithium as an anode material is considered to be the next big step forward in battery research, but this requires the realization of electrolyte materials with high electrochemical stability towards lithium, while simultaneously suppressing dendritic lithium deposition.[2] Research in this field mainly focuses on solid electrolytes nowadays, such as ceramics or polymers. For the latter, the achievement of suitable ionic conductivities at ambient temperature, however, is a great challenge.[3] In addition, the use of polymer-based electrolytes like, for instance, the well-known poly(ethylene oxide) (PEO) mixed with a lithium conducting salt is commonly limited to “low-voltage” cathode materials such as $LiFePO_4$ due to the limited electrochemical stability towards oxidation.[3] Recently, we have reported a new single-ion conducting multi-block copolymer electrolyte system with high ionic conductivity of about 1 mS cm^{-1} at ambient temperature, long-term stable lithium cycling, and excellent electrochemical stability even towards $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC_{811}) cathodes.[4,5] Herein, we present our most recent results on the further development of such non-flammable multi-block copolymer systems, incorporating highly mobile molecular transporters (e.g., ethylene carbonate (EC) or propylene carbonate (PC)). Following a concise review of our work on poly(arylene ether) multi-block copolymers within the last years, our most recent advances in this field will be presented, including a new branch of ionomers based on commercially available bisphenol derivatives. This approach provides the unique opportunity to investigate the influence of the monomer substitution pattern on pivotal properties of these electrolyte systems, such as the electrochemical stability or ionic conductivity. Moreover, a comparative analysis of their (electro)chemical, mechanical, and thermal properties will be presented. Eventually, the potential scale-up and commercial use will be briefly discussed, including a suitable recycling concept.

Keywords: block copolymer, electrolyte, single-ion conductor, lithium battery

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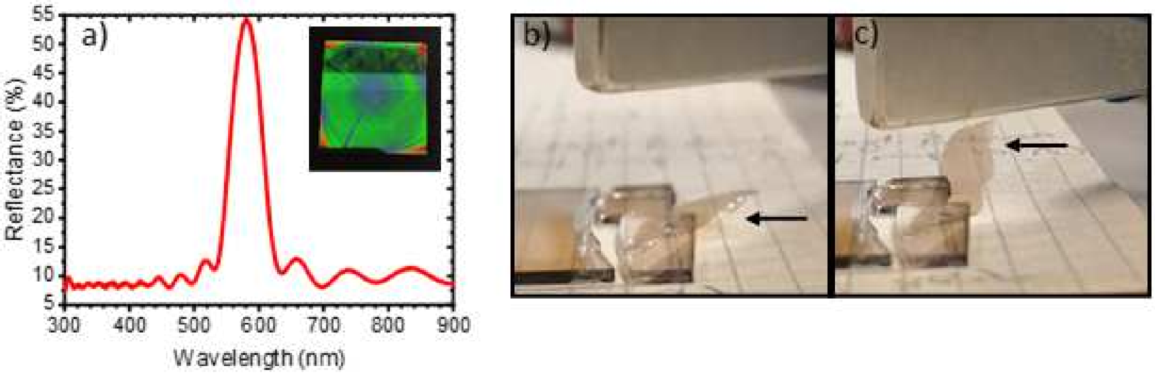
Magnetic Nanocomposite Polymer Photonics

H. Megahd[1], S. Slimani[1,2], D. Peddis[1,2] , P.Lova[1], D.Comoretto[1*]

[1]*Dipartimento di Chimica e Chimica Industriale, Università di Genova, Genova, Italy*
[2]*Institute of Structure of Matter, Italian National Research Council (CNR), Rome, Italy*
[*]*davide.comoretto@unige.it*

Magnetic polymer-inorganic composites are increasingly researched thanks to their unique responsiveness, mechanical flexibility, processability, and interesting functionalities.[1, 2] Their implementation in polymer photonic structures would then represent a viable route to simple and low-cost actuators and optical sensors. While various blends have been reported, obtaining the transparency requested in photonics is a challenging task.[3] To this end, monodispersed magnetic nanoparticles with controlled size and morphology are mandatory. In particular, particles in the superparamagnetic regime (i.e., M_r=0, H_c=0) enable responsive composites with low loading, yet avoiding light scattering, and maintaining transparency and magnetic responsiveness.

In this work, we report on new photonic crystal structures embedding polystyrene and polyvinylcarbazole composites incorporating cobalt ferrite ($CoFe_2O_4$) nanoparticles. More importantly, we demonstrate their utilization for fabricating magnetically responsive translucent dielectric mirrors. These mirrors, which are a subset of photonic crystals, consist of alternating layers of different dielectric materials with a periodicity comparable to the wavelength of visible light.[4] The interference effects between light refracted and reflected at the layer interfaces give rise to strong reflection phenomena, associated with a bright structural color. The magnetic blends show excellent homogeneity and processability, enabling their spin-coating into regular submicrometric thin films with excellent optical properties. Constructing multi-layered stacks of the magnetic composite and cellulose acetate, a compatible polymer, resulted in highly reflective, magnetically responsive, and flexible self-supporting photonic crystals (Figure 1.a). Panels b and c show a freestanding film bending under the influence of a magnet. These responsive structures can be promising for applications concerning opto-mechanical actuation.



Figures 1. a) Reflectance of PS-NP/CA DBR with photo of the sample in inset. Mechanical actuation of free-standing (b) without and (c) under the influence of an external magnetic field.

Keywords: nanostructure polymers, nanocomposites, responsive polymers, polymer photonics

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Incorporation of Fluorescent Dyes and Nanoplatelets in PMMA Microfibers Prepared by Stable Jet Electrospinning

F. Li[1,2], H. -A. Christ[2], P. Y. Ang[1,3], H.-H. Johannes[1,3], W. Kowalsky [1,3], L. F. Klepzig[1,4], J. Lauth[1,4], M. Hohgardt[5], X. Liu[1,5], P.J. Walla[1,5], H. Menzel[1,2*]

[1]*Cluster of Excellence PhoenixD (Photonics, Optics, and Engineering – Innovation Across Disciplines), Hannover, Germany*
[2]*Institute for Technical Chemistry, Technische Universität Braunschweig, Braunschweig, Germany*
[3]*Institute for High Frequency Technology, Technische Universität Braunschweig, Braunschweig, Germany*
[4]*Institute of Physical Chemistry and Electrochemistry, Leibniz Universität Hannover, Hannover, Germany*
[5]*Institute for Physical and Theorectical Chemistry, Technische Universität Braunschweig, Braunschweig, Germany*

**h.menzel@tu-braunschweig.de*

Light-emitting or other active polymer fibers, prepared from polymers embedding chromophores or functional nanoparticles, are suitable for various applications in advanced photonics and sensing technologies.[1-2] Electrospinning is a promising method for preparation of such active polymeric nanomaterials. However, while electrospinning is a facile process for incorporating dyes or nanoparticles into the fiber matrix material to adjust the optical properties, it is also a delicate process that is influenced by a whole range of parameters. Moreover, although classical electrospinning produces very thin fibers, due to the typical whipping they tend to be deposited in a disordered manner as a nonwoven and can then no longer be manipulated easily. However, by adjusting the parameters electrospinning can also be performed in the stable jet mode, which produces somewhat thicker fibers but deposits them as highly aligned fiber bundles.[3] The method has to be optimized to produce smooth and uniform fiber surfaces and to control fiber thickness and orientation.

Microfibers were prepared by stable jet electrospinning from polymethylmethacrylate (PMMA) with Rhodamine B as potential laser dye and the fibers were investigated regarding amplified stimulated emission.[3] At the same time, also two-dimensional semiconductor nanoplatelets (CdSe/CdS) were embedded in PMMA microfibers. Highly aligned fibers with an orientation of the nanoplatelets were obtained. Dominant anisotropic emission along the fibers was achieved, which is expected to have superior performance for the applications in waveguides and fiber lasers.

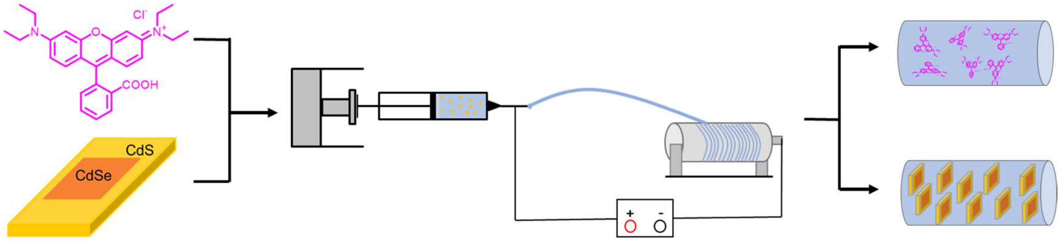

Figure 1: Schematic of the Linear jet electrospinning of PMMA with Rhodamin B and with fluorescent nanoplatelets, respectively

Keywords: polymer matrix, laser dyes, fluorescent nanoplatelets, stable-jet-electrospinning, fiber laser

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Uncovering the impact of coordination chemistry on cation transport in polymer electrolytes

Jonas Mindemark[1*]

[1]*Department of Chemistry – Ångström Laboratory, Uppsala University, Uppsala, Sweden*
[*]*jonas.mindemark@kemi.uu.se*

Since the dawn of the research field of ion transport in polymer materials, there has been a heavy focus on materials based on polyether matrices and in particular poly(ethylene oxide) (PEO). While important lessons have been gained – such as the dependence on amorphous structures and chain dynamics for fast ion transport – the one-sided focus on PEO as the ion-solvating matrix has largely obscured the effects of the coordination structure on the movement of ions in polymeric materials. Instead, the prevailing models for ion transport emphasize the coupling of the cation movement to the segmental dynamics of the polymer host. This is indeed an important cornerstone of the phenomenon of ion transport in polymers, but recent research has uncovered additional aspects that are equally important to understand and control in order to optimize materials for fast ion transport. As one of these factors, the coordination structure and the strength of the ion–polymer interactions have a notable impact on ion transport, with a direct correlation between the coordination strength and the cation transference number, as measured both electrochemically and with electrophoretic NMR. [1] This improved understanding has been enabled both by the implementation of new materials with a wider range of coordinating motifs and differences in coordination strength, and by the development of methods that allow for determination of the coordination strength.

This presentation will account for our recent efforts into uncovering the effects of coordination chemistry on the transport properties of polymer electrolytes, how this brings us closer to painting a complete picture of the mechanism of ion transport in solvent-free polymers and how it can be applied to tailor materials for more efficient cation conduction. [2] While it is natural to start this discussion with Li^+ coordination and transport, it is also interesting to expand it further towards for example Na^+ and Mg^{2+}, [3, 4] which are interesting not only as next-generation battery systems, but also from the point of view of creating a more complete and fundamental understanding of the ion transport phenomena in these systems.

Keywords: polymer electrolytes, ion transport, coordination

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Piezoresistive Polymer Composites via Oxidative Chemical Vapor Deposition of Polypyrrole on Flexible Substrates

A. Mukherjee[1], S.Selenica[1], J. Es Sayed[2], A. G. P. Kottapalli[3], M. Kamperman[2], R. K. Bose[1*]

[1]*Product Technology, Department of Chemical Engineering, Engineering and Technology Institute Groningen (ENTEG), University of Groningen, Groningen, The Netherlands*
[2]*Polymer Science, Zernike Institute of Advanced Materials (ZIAM), University of Groningen, Groningen, The Netherlands*
[3]*Advanced Production Engineering, Engineering and Technology Institute Groningen (ENTEG), University of Groningen, Groningen, The Netherlands*
[*]*r.k.bose@rug.nl*

Conductive polymer composites (CPCs) have attracted growing attention for a variety of biomedical applications that rely on both electrical conductivity and flexibility such as in wearable electronics for human movement monitoring.[1] Typical CPCs consist of an intrinsically conductive polymer (ICP), such as polypyrrole (PPy), and an insulating flexible polymer matrix. ICPs exhibit strong electrical conductivities owing to their highly conjugated structure, however, they are also brittle and insoluble, leading to difficulties in manipulation and processing.[2] Our work explores the fabrication of CPCs using oxidative chemical vapor deposition (oCVD) to incorporate conductive PPy onto flexible substrates. oCVD is a solvent free technique that can accomplish conformal coatings of doped ICPs onto delicate microstructures in a single processing step.[3] As a vapor phase technique, operated under mild conditions, oCVD circumvents several challenges faced by conventional solution processing such as dewetting, solvent damage etc. We have utilised these advantages to develop CPCs by oCVD of PPy on various porous polymeric substrates such as polyelectrolyte hydrogels, electrospun fiber-mats and 3D printed elastic lattices. SEM and FTIR investigations show that the porous microstructure allows homogeneous deposition of ultra-thin coatings of doped PPy throughout the matrix of the substrate, rendering them electrically conductive while afflicting minimal alterations on the mechanical properties. The mechanical and electrical properties of the fabricated CPCs can be further tuned by controlling the thickness of the PPy coating. The engineered CPCs demonstrate piezoresistive behaviour with high strain sensitivities for large deformation ranges and good cyclic stability. Hence, our results present them as prominent candidates to design wearable and flexible piezoresistive strain sensors.

Keywords: conductive polymer composites, conductive polymers, flexible electronics, oxidative chemical vapor deposition, hydrogel, strain sensors

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Polar Amorphous Polymers: Synthesis and Response to Different Stimuli

Yauhen Sheima,[1,2] Johannes von Szczepanski,[1,3] Patrick Danner,[1,3] Francis Owusu,[1,2] Mihail Iacob,[1] Elena Perju,[1] Frank Nüesch,[1,2] Dorina M. Opris[1*]

[1]Swiss Federal Laboratories for Materials Science and Technology Empa, Dübendorf, Switzerland
[2]Ecole Polytechnique Fédérale de Lausanne EPFL, Lausanne, Switzerland
[3]Department of Materials, ETH Zürich, Zurich, Switzerland
[*]dorina.opris@empa.ch

When heated, a solid polar amorphous polymer (PAP) passes through the glass transition.[1] The glass transition temperature, T_g, represents the point of a critical property change. Below T_g the PAP has an elastic modulus in the GPa range and thus does not deform much under mechanical stress, the polar dipoles are frozen and do not orient in an external electric field. Above T_g, PAP can reversibly change its shape under mechanical stress when properly cross-linked.[2,3] Additionally, the dipoles are mobile and thus respond to an electric field. The challenge is to prepare PAP with high polarity yet sufficiently low T_g to allow room temperature elasticity.[4] Such materials can be used as active dielectrics in electrically responsive elastic capacitive devices.[2] Because of their simple manufacturing, silent operation, large force generated, easy and tuneable actuation by the applied voltages, these devices are most suitable for artificial muscles and soft robots.[5] This presentation will give an overview of how we synthesize such responsive materials, overcome problems when manufacturing devices, and optimize their performance.

Keywords: polar polymers, high dielectric permittivity polymers, high dielectric constant polymers, elastomers, dielectric elastomer actuators, electrically responsive polymers

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Polymer memristors for neurosynaptic elements

J. Pfleger[1*], Y. R. Panthi[1,2], A. Pandey[1,2], D. Výprachtický[1] and I. Šeděnková[1]

[1]Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovsky Sq. 2,
162 06 Prague 6, Czech Republic;
[2]Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3,
120 00 Prague 2, Czech Republic
[*]*pfleger@imc.cas.cz*

Memristors with neurosynaptic functionality take a continuity of resistance values with synaptic weights modulated by the number and frequency of homogeneous spikes. In order to mimic neural synapse memristors must exhibit analog properties including non-abrupt switching transitions, continuously variable resistance states, and predictable response. We prepared poly(methacrylamide) derivative with charge transporting group separated from the polymer backbone by an alkyl chain (see Fig. 1, left) and show that it can change electrical characteristics from bistable to analog behavior, depending on the layer thickness, electrode material and applied voltage range.

The polymer was prepared by a radical polymerization of N-(3-(9H-carbazol-9-yl)propyl)methacryl- amide using azobisisobutyronitrile as a radical initiator. The molar mass of the polymer was influenced by reaction temperature but it was still relatively low (Mw = 6000, Mn = 4000, D = 1.50). Glass transition temperature of the polymer is 130 °C and it is stable at higher temperatures up to 300 °C.

We show the preparation and properties of simple organic memristor elements based on thin films of the polymer, which can be prepared using common laboratory casting techniques as spin casting, slot die or dip coating, or screen and inkjet printing in the manufacturing scale. When prepared with Au top electrode and after annealing at 120 °C, it showed a memristive behaviour that mimic the neurosynaptic plasticity (see Fig. 1, right and bottom)

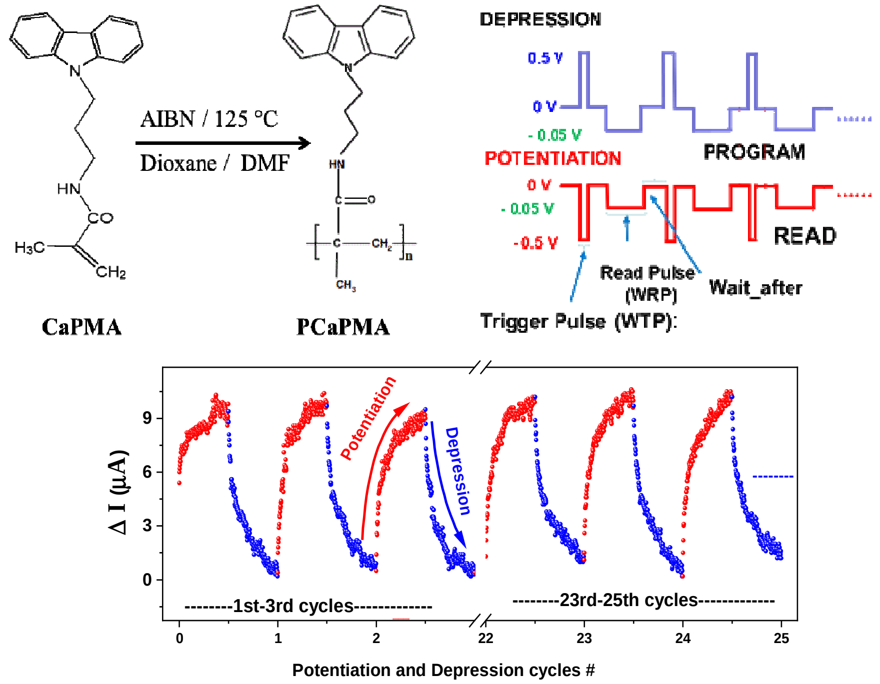

Figure 1: Chemical structure of poly(N-(3-(9H-carbazol-9-yl)propyl)methacrylamide) and neurosynaptic behavior of Au/polymer/ITO sandwich sample.

Acknowledgments

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Improved piezoresistive strain sensor characteristics of conductive polymer composites by using polymer blends as matrix

X. Tang[1,2], J. Pionteck[1*], B. Krause[1], P. Pötschke[1*], B. Voit[1,2]

[1]*Leibniz Institut für Polymerforschung Dresden e.V., Dresden, Germany*
[2]*Organic Chemistry of Polymers, Technische Universität Dresden, 01062 Dresden, Germany)*
[*]*pionteck@ipfdd.de, poe@ipfdd.de*

The electrical conductivity of conductive polymer composites (CPCs) results from interconnected conductive fillers and can be controlled by varying the constituents of the CPCs, their concentrations, preparation conditions, and other factors. When stress is applied to the material, the shape of the specimen and the connectivity of filler networks vary and thus the conductivity changes, which can be measured and correlated to the applied force or strain. Typically, tensile deformation increases the filler-filler distances which increases the electrical resistance. The relative resistance change, expressed as $\Delta R/R_0$ (ΔR: resistance change; R_0: initial resistance) correlates with the applied stress or strain, thus enabling the use of CPCs as piezoresistive sensors.

Unfortunately, CPCs exhibit non-linear, exponential-like dependencies of R on the applied strain which limits the range of measurable strains due to excessive increase in electrical resistance at higher strains. Thus, there is a general need to increase the linearity of the sensing signal combined with high signal intensity. For that, we used carbon nanotubes (CNTs, filler amount 0.75 - 2 wt%)) as fillers and polymer blends as matrix. The melt-mixed blends consist of different proportions of semi-crystalline poly(vinylidene fluoride) (PVDF) and either amorphous poly(methyl methacrylate) (PMMA) [1] or semi-crystalline poly(butylene succinate) (PBS) [2]. For analysing the effect of the anisoptropy of the conductive filler on the sensor properties, also carbon black (CB, 3 or 4 wt%) was used as nearly isotropic filler. Both blend combinations are miscible in the molten state and phase separate during cooling driven by partial crystallization. The crystallization of PVDF (and PBS in the PVDF/PBS blend) is affected by the second polymer and by the filler. Furthermore it depends on the composition and the preparation conditions. After solidification, in PVDF/PMMA blends, CNTs are located in the region outside but close to the PVDF crystals, while CB locates in the PMMA-rich amorphous phase. In PVDF/PBS/CNT blends, both filler types are located in the amorphous PBS-rich phase, surrouned by PBS crystals.

In this work we correlate the different morphologies of the polymer blend composites with their elctrical conductivities and sensing parameters and demonstrate that by proper choice of the blend compositon, filler type, filler content, and processing parameters the linearity of the sensing signal as well its intensity can be improved compared to single-polymer composites, allowing the development of CPC-based strain sensors that can be adapted to specific application requirements.

Keywords: conductive polymer blend composites, piezoresistive behavior, strain sensing

Acknowledgments

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Magnetically and optically responsive anisotropic hydrogels based on core-shell Fe_3O_4@Au nanorods

Mikel Rincón-Iglesias[1], Senentxu Lanceros-Méndez[1,2], Erlantz Lizundia[1,3], Javier Reguera[1]

[1]*BCMaterials, Basque Center for Materials, Applications, and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain.*
[2]*Ikerbasque Basque Foundation for Science Bilbao 48009, Spain*
[3]*Life Cycle Thinking Group, Department of Graphic Design and Engineering Projects. University of the Basque Country (UPV/EHU), Plaza Ingeniero Torres Quevedo 1, 48013 Bilbao, Biscay, Spain*
**mikel.rincon@bcmaterials.net*

Multifunctional hydrogels that respond to a range of stimuli are of interest for soft electronics, biological applications, hyperthermia, sensors and actuators, among others. The development of agarose hydrogels combined with Au-coated magnetite (Fe_3O_4) nanorods (NRs) is reported. The anisotropic shape of the nanoparticles enables their magnetic orientation within the hydrogel matrix, to tune the magnetic and optical response.

The fabrication of the hydrogels involves several steps, starting with the synthesis of Au-coated magnetic NRs. Fe_3O_4 NRs of different sizes were synthesized by solvothermal method. Then, NRs were functionalized with aminopropyltriethoxysilane (APTES) and 3 nm Au nanoparticles were mixed with NRs and stacked on their surface forming a core-satellites structure. The Au-coating was controlled by adding extra amounts of gold until a complete shell was formed (Fe_3O_4-NR@Au).

Agarose was selected for the preparation of hydrogels due to the simplicity of fabrication by microwave heating and the formation of extensive physical crosslinks between its chains, yielding a mechanically robust three-dimensional structure. The Fe_3O_4-NR@Au were included in a hot fluidic solution of agarose and the composite solution was introduced inside a magnetic field in order to orient the Fe_3O_4-NR@Au in specific directions. The matrix was able to arrest the particles after the gelation.

Magnetic characterization of NRs and Fe_3O_4-NR@Au demonstrated the successful orientation of the particles inside the matrix exhibiting different magnetic parameters, where saturation magnetization was reached at lower magnetic fields for parallel orientations and the highest for perpendicular directions, while randomly distributed particles showed a contribution of both. In addition, AC hysteresis loops were measured and the specific absorption rate (SAR) was calculated as a function of the applied magnetic field. The maximum SAR value, obtained at high magnetic fields, was also dependent on the orientation, achieving the highest values for the case of parallel configuration and the lowest ones for the perpendicular case. Thus, the obtained results demonstrate the possibility of fine-tuning the magnetothermal effect by varying the angle of application of magnetic fields. Finally, photothermal transduction was also obtained, reaching a temperature increase above 20 °C for a low light power of 0.2 W. [1]

Keywords: magnetic nanorods; anisotropy; core-shell; agarose; hydrogels; hyperthermia

Acknowledgments

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Hybrid Crosslinked Polymer Electrolytes with Grafted Ions for Li-Battery

S. Issa [1], R. Jeanne-Brou [2], S. Mehan [3], D. Devaux [2], F. Cousin [3], D. Gigmes [1],
R. Bouchet [2], T. N. T. Phan [1*]

[1] Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire-UMR 7273, Marseille, France
[2] Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, Grenoble, France
[3] Laboratoire Léon Brillouin, Université Paris-Saclay, CEA-CNRS UMR 12, Gif-sur-Yvette, France
[*] *trang.phan@univ-amu.fr*

Lithium metal with its high specific capacity and low redox potential is seen as the next reference material for negative battery electrode. However, the nucleation and growth of Li dendrite through the electrolyte, leading to battery failure, remain the major drawback that limits its widespread use [1]. Theoretically, the nucleation of Li dendrites can be prevented by increasing Li cation transference number (t^+) [2] while stiff electrolyte can mitigate their growth. The latter is clearly in favour of solid-state electrolytes. Among different solid electrolytes, hybrid solid electrolytes (HSEs) combining the advantages of inorganic and polymer electrolytes, are considered as the promising ones [3]. However, significant improvements for constructing a good dispersion method need to be made to overcome severe agglomeration of inorganic filler within polymer matrix. In this study, we prepared new HSEs using alkoxide silanes functionalized with lithium salt and functional poly(ethylene oxide) (PEO) to generate homogenous nanostructured organic-inorganic hybrid materials (Fig 1). This new material combines an organic crosslinked PEO network ensuring the ionic conductivity and inorganic (SiO_2) crosslinking site reinforcing the mechanical properties where highly delocalized anion are grafted [4]. One of the aims of this work is also to study the influence of inorganic/organic and [EO]/[Li] ratios on the thermal, mechanical and electrochemical properties of the new HSEs. A special attention has been devoted to characterizing and analyzing the HSEs in order to establish structure-properties relationship.

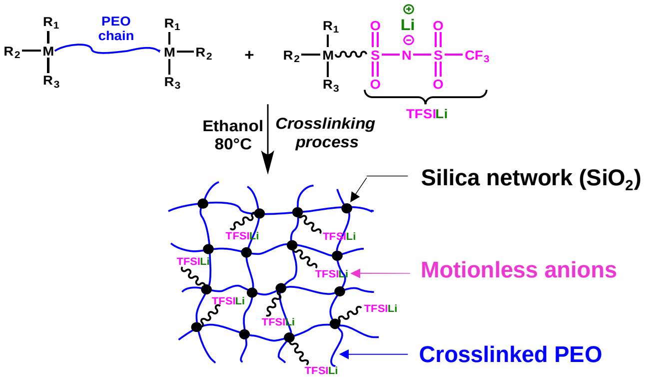

Figure 1. Synthesis process and expected structure of hybrid crosslinked PEO-based electrolyte

Acknowledgments

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Ordered positioning of conjugated polymers and polyelectrolytes on the surface by synthesis of binary mixed polymer brushes

K. Wolski[1*], J. Smenda[1], A. Grobelny[1], P. Dąbczyński[2], M. Wytrwał-Sarna[3], M. Marzec[3], S. Zapotoczny[1]

[1] *Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Krakow, Poland*
[2] *Jagiellonian University,* Faculty of Physics Astronomy and Applied Computer Science*,* Łojasiewicza 11, 30-348 *Krakow, Poland*
[3] *Academic Centre for Materials and Nanotechnology, AGH University of Science and Technology, Kawiory 30, 30-055 Krakow, Poland*
[*] *wolski@chemia.uj.edu.pl*

The formation of polymer blends, composites or copolymers often enable production of materials with better properties than those based on single components. One can mention here the development of poly(3,4-ethylenedioxythiophene) and poly(sodium 4-styrenesulfonate) (PEDOT:PSS) blend which was the true breakthrough in the field of conjugated polymers as PEDOT:PSS is the most widely used material in organic electronics nowadays. Highly conductive yet insoluble and infusible PEDOT when obtained in the presence of PSS forms stable water dispersion that could be easily processed and used e.g., for production of thin polymer films demonstrating exceptional stability and electrical properties. In consequence, PEDOT:PSS is considered as a promising material for replacing rare inorganic conductors in different applications such as: solar cells, light-emitting diodes etc.

The spatial distribution of components in polymer blends/composites is often difficult to control. The same concerns achievable range of compositions e.g., weight ratios of both polymers. As a consequence, PEDOT:PSS films demonstrate out of plane conductivity (important in certain applications) up to several orders of magnitude lower than in-plane one, due to the lamellar structure with ellipsoidal PEDOT domains surrounded by PSS [1].

We propose here a novel synthetic strategy based on surface-initiated reversible deactivation radical polymerizations for production of conjugated binary mixed polymer brushes. The developed structures with neighboring conjugated polymers (CPs) and polyelectrolytes (PELs) grafted on the same surface ensured production of ordered thin films with CPs chains surrounded by PELs and perpendicularly oriented with respect to the surface. The obtained materials mimic the PEDOT:PSS and at the same time take the advantages of unique conformation of surface-grafted polymers. SIMS profiling, AFM nanoIR and AFM nanomechanical mapping in air and selective solvents provided precise insight into surface dynamics and interactions of CPs with PELs. It was indicated that vertical and horizontal phase separation and hence intermolecular mixing of both components could be controlled by the post synthesis chemical modifications.

Keywords: binary mixed polymer brushes, Atomic Force Microscopy, conjugated polymers, surface-initiated polymerizations, PEDOT:PSS

Acknowledgments

The project was supperted by the National Science Center in Poland (SONATA 14, Grant No. 2018/31/D/ST5/00868).

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Molecular-Orientation-Dependent Transient Behaviors of Organic Mixed Ionic–Electronic Conductors

Ji Hwan Kim[1], Roman Halaksa[1], Christian B. Nielsen*[2], and Myung-Han Yoon*[1]

[1] *School of Materials Science and Engineering Gwangju Institute of Science and Technology 123 Cheomdangwagi-ro, Buk-gu, Gwangju 61005, Republic of Korea*
[2] *2Department of Chemistry, Queen Mary University of London, London E14NS, United Kingdom*
**mhyoon@gist.ac.kr*

Despite the growing interest in organic mixed ionic–electronic conductor's dynamic behaviors at the frequency domain, there exist very few studies on the effect of their microstructural characteristics on ion-mediated transient responses of corresponding organic electrochemical transistors (OECTs). In this research, we developed a model mixed conducting polymer system with different molecular orientations and investigated the effect of molecular orientation on ion-mediated transient OECT behaviors. Two polymers with similar mixed conductivity and electrochemical characteristics except molecular orientation were successfully synthesized by varying the co-monomer unit (2,2'-bithiophene or phenylene) used in conjunction with a novel 1,4-dithienylphenylene-based monomer. The comprehensive electrochemical analysis suggests that the molecular orientation affects the length of the ion-drift pathway, which is directly correlated with ion mobility, resulting in different OECT transient responses. These results provide general insights into the molecular-orientation-dependent ion movement characteristics of polymeric mixed conductors as well as material/device design principles.The text should be 11-point Calibri in the single-column format in A4 paper with margins 2cm on all sides. Keep the layout of the text as simple as possible.

Keywords: molecular orientation, organic mixed ionic-electronic conductors, organic electrochemical transistors

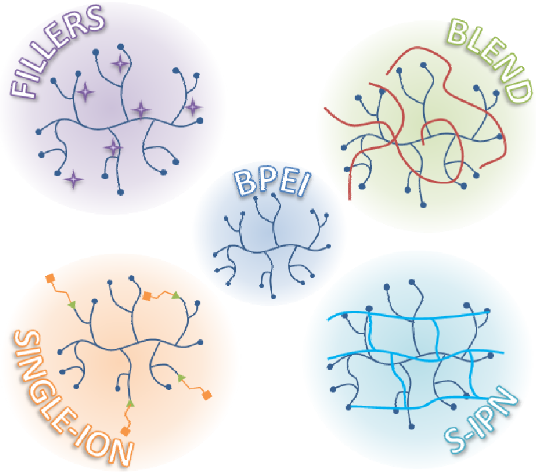
N-rich Ionic Conductive Polymers for Li-ion Batteries

L. Artigues[1,2]*, V. Chaudoy[1], V. Lapinte[2], L. Monconduit[2]

[1]*Renault Group, Guyancourt, France*
[2]ICGM*, Montpellier, France*
**lucie.artigues@renault.com*

Expectations for the next generation of electrical vehicles batteries are continuously increasing in terms of autonomy, environmental impact, time of charge or cost. All-solid-state systems where a liquid electrolyte is replaced by a solid electrolyte are a promising opportunity for the future Li-ion batteries. The two types of solid electrolytes are based on inorganic materials or polymers. In this work, solid polymer electrolytes are studied. Poly(Ethylene Oxide) (PEO) is the gold standard electrolyte polymer with an ionic conductivity of 0.36 mS.cm-1 at 60 °C in presence of lithium salt (e.g. lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)) [1] benefiting of a low glass transition temperature, about -60 °C. One drawback is the crystallinity which decreases the ionic conductivity and consequently the electrochemical performances.

Our objective is to explore some alternative polymers to PEO in solid polymer electrolytes in particular Poly(EthyleneImine) (PEI), a nitrogen-rich polymer, structurally equivalent to PEO. The higher electrodonor character of nitrogen related to oxygen favors the salt dissociation by a stronger coordination of Li+ in PEI than in PEO as already modeled [2]. Branched PEI (bPEI) is an attractive candidate because totally amorphous with a low Tg about -50 °C, thermally stable (above 300 °C) with an electrochemical stability window up to 4.5V vs Li. Nevertheless, the ionic conductivity in presence of LiTFSI is still insufficient, 8.10-4 mS.cm-1 @ RT. Thus, the mechanical strength of the self-standing PEI polymer films must be enhanced as well as the conductivity. We considered different strategies like i) blends with more rigid N-rich polymers like polyoxazolines or ii) semi-InterPenetrated Networks (s-IPN) resulting from mobile free PEI chains entangled in a resistant mechanically network of methacrylated PEO. Another pathway consists in hybrid electrolytes by adding inorganic fillers in PEI matrix. Depending on the nature of the fillers, the acidity of their surface and their size, Li ions will be able to interact with them and their transport can be improved. Three fillers were tested and an increase in conductivity was observed at room temperature. All these routes will be detailed to demonstrate the potential contribution of nitrogen-rich polymers in Li-ion batteries.



Possible improvement for Polyethylenimine-based solid polymer electrolytes

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Eumelanin Polymers and Derivatives for Energy Applications

N. Al-Shamery[1,2], X. Gong[1], S. Morgenschweis[2], P. S. Lee[1*]

[1]School of Materials Science and Engineering, Nanyang Technological University, 639798, Singapore
[2]Kekulé Institute of Organic Chemistry and Biochemistry, University of Bonn, 53121 Bonn, Germany
*noah.al.shamery@gmail.com, *pslee@ntu.edu.sg*

Over the last decade, the interest in using eumelanin polymers specifically as a material class for applications in technological and biomedical settings has increased drastically [1]. The most recent efforts in synthesis of derivatives for battery device applications have mostly focused on increasing their solubility for film processibility, as the short chains of unmodified eumelanin that also form tetramers are mostly insoluble in water [2]. Thus, a vast number of potential derivatives have yet to be studied more deeply that could potentially help in understanding the redox chemistry of eumelanin based on the polymer structures. Here, synthetic eumelanin (melanin-*Syn*) polymers were chemically modified to include *tert*-butyloxycarbonyl protecting groups added to the indole N-1 nitrogen atoms of the monomers building porphyrin-like structures in the tetramers, giving the derivative melanin-*Boc*. The goal was to investigate the importance of metal ion chelation by the secondary amine groups through a functionalized eumelanin. The eumelanin derivative was coated on a conductive carbon paper cathode and tested with a zinc anode in a two-electrode coin cell-system, using $ZnSO_4$ in deionized H_2O as electrolyte. The role of the amine groups will be elucidated by comparing electrochemical properties of the polymers melanin-*Syn* and melanin-*Boc* in electrolytes of different concentration. Cyclic voltammetry-, galvanic charge-discharge-, and battery cycling measurements were carried out. Furthermore, the substances were characterized and compared using NMR-, FTIR-, SEM-, and UV-Vis experiments. The indole nitrogen atoms were found to play an important role in charge transfer processes of melanin-based energy storage systems. The implications of the differences between melanin-*Syn* and melanin-*Boc* for choosing new melanin derivatives will be discussed.

Keywords: melanin, eumelanin, polymer, derivative, battery, device, electrochemistry, chelation.

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Effect of inorganic charges (Bi_2O_3 and Bi $(NO_3)_3$) on the thermoelectric properties of polypyrrole

Z. Bekkar Djelloul Sayah [1,2*], A. Mekki [1], Y. Bourenane cherif [1], J-F. Durastanti [2]

[1] *Ecole Militaire Polytechnique, Bordj El Bahri - Algiers, Algeria*

[2] *Laboratoire CERTES - Université Paris-Est Créteil - IUT de Sénart-Fontainebleau, Lieusaint, France*
**Corresponding Author: zakaria.bekkardjelloulsayah@emp.mdn.dz ; bekkar_zakaria@yahoo.fr*

The use of systems which permit the recovery and the conversion of waste heat into useful energy has become the concern of many researchers in the world, who try to put forward promising new methodologies to convert residual heat into useful energy, leading to the generation of electricity; this principle is commonly referred to as "Thermoelectricity". In fact, thermoelectric devices are now of a lightweight character comparatively to the earlier apparatus used in the field, owing to the absence of vibrations and noise related to a compressor, and the use of tiny materials considered as the beating heart of the whole process. Moreover, they could use several heat source, including residual and solar heats **[1]**.

Indeed, one dimensionless factor, called the figure of merit (ZT), can give an estimation of the thermoelectric materials performances. It relates the three characteristics of electrical conductivity (σ), thermal conductivity (κ), Seebeck coefficient (*S*) as well as the working temperature T, ($ZT = (S^2 \times \sigma / \kappa) \times T$); an efficient material must therefore have both a high electrical conductivity, a significant Seebeck coefficient and a low thermal conductivity **[2]**.

Improvement of the ZT involves optimizing the concentration of the charge carriers via donor or acceptor dopants atoms **[3]**.

The interest aroused by the use of polymeric thermoelectric materials justifies the purpose of this study for the synthesis of a thermoelectric semiconductor polymer, in this case polypyrrole, and emphasize the study of the influence of inorganic dopants, namely bismuth oxide (Bi_2O_3) and bismuth nitrate ($Bi(NO_3)_3$), on its thermoelectric properties.

In this work, polypyrrole was chemically synthesized in two factions, neat ones and filled with inorganic charges, at different molar ratios (Charge: Monomer) of (1:10), (1:15), (1:20) and (1:25).

A series of structural and morphology characterizations were carried out on the elaborated products, to determine their chemical, by Infrared spectroscopy with Fourier Transform (FTIR) and by Scanning Electron Microscopy (SEM).

The thermoelectric performances of the studied composites were evaluated by measuring the electrical and thermal conductivities, the Seebeck coefficient and the figure of merit (ZT).

The high values of the figures of merit ZT at room temperature, are obtained for the material prepared based on Bi_2O_3 and Bi $(NO_3)_3$, at molar ratio (Charge: Monomer) of (1:10). They are equal to ($1,45.10^{-5}$) and ($1,8.10^{-6}$), respectively. These results are superior to those found for neat polypyrrole alone which is ($1,68.10^{-7}$) **[4]**.

Keywords: Thermoelectricity, conductive polymers, thermoelectric composites, improvement of thermoelectric performance, inorganic charges.

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Solution-processable hole-transporting polymers: synthesis, doping study and crosslinking induced by UV-irradiation or Huisgen-click cycloaddition

Enrique Caldera-Cruz[1,2], Kenan Zhang[1,2], Takuya Tsuda[1], Roman Tkachov[3], Tetyana Beryozkina, Nataliya Kiriy[1], Brigitte Voit[1,2], Anton Kiriy[1]

[1]*Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany*
[2]*Organic Chemistry of Polymers, Technische Universität Dresden, 01062 Dresden, Germany*
[3]*Fraunhofer-Institut für Werkstoff- und Strahltechnik, Winterbergstr. 28, 01277 Dresden, Germany*
[4]*TOSLab, Ural Federal University, Mira str., 28, 620002 Yekaterinburg, Russia*

The precise fabrication of high performance, multilayered organic light-emitting diodes (OLEDs) by vacuum deposition has contributed to the development of this technology in the past decades. The alternative solution-based processes offer the possibility of cheap and scalable fabrication of large-area devices [1]. However, the degradation of preceding layers during the subsequent depositions (by dissolution or intermixing) is a challenge for the fabrication of multilayers by solution processing. One possibility to circumvent this issue is the use of crosslinkable materials [2].

In this work a pair of hole-conducting polymers comprising 3,6-linked carbazole and meta-linked anisole derivatives were synthesized and characterized. The polymers P1 and P2 feature solubilizing moieties and reactive azide and alkyne side-groups, repectively, complementarily for cross-linking (figure 1a). The polymers can be cross-linked either by thermal annealing at relatively low temperatures in the 85-110 °C range, or by ultraviolet-irradiation (UV). A general applicability of the latter for a photolithographic patterning of the hole conducting polymer was proven. The polymers have an ionization potential (IP) of 5.8 eV, close to the IP of a small-molecule hole-conductor tris(4-carbazoyl-9-ylphenyl)amine (TCTA). Unlike the commercial 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), the strong dopant hexacyano-trimethylene-cyclopropane (CN6CP), can efficiently p-dope the polymers to increase their conductivity by 5-6 orders of magnitude (figure 1b).

Our results suggest that the synthesized polymers are promising candidates for their use in solution-processable OLEDs as hole-injection layers (HIL) and hole-transport layers (HTL) materials [3].

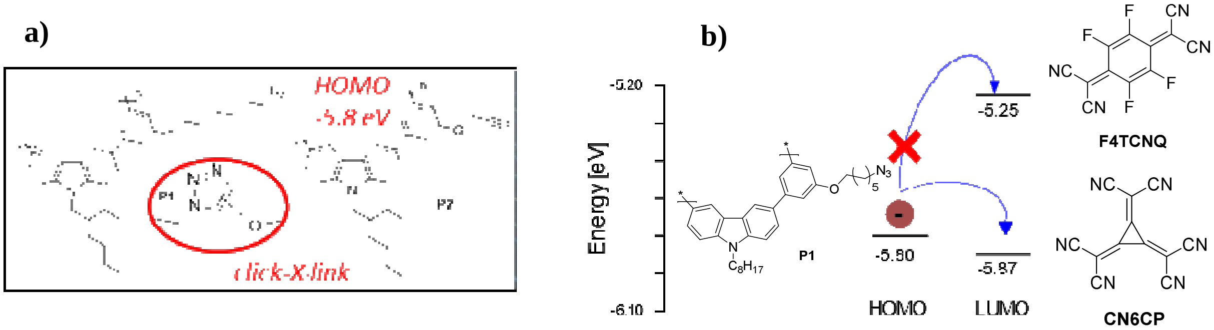

Figure 1. (a) Chemical structure of P1 and P2, as well as a depiction of the crosslinking reaction, (b) Schematic representation of p-doping process and the energy levels of P1, F4TCNQ and CN6CP.

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Layer-by-Layer Assembled Textile Electrodes for Water-Splitting Reaction

Yunji Ko, Jinhan Cho*

Dept of Chemical & Biological Eng, Korea University, Seoul, South Korea (Calibri, 11 pt., Italic)
**jinhan71@korea.ac.kr*

For the practical use of water electrolyzers using non-noble metal catalysts, it is crucial to minimize the overpotentials for the hydrogen and oxygen evolution reactions. Here, we introduce cotton-based, highly porous electrocatalytic electrodes with extremely low overpotentials and fast reaction kinetics using metal nanoparticle assembly-driven electroplating. Hydrophobic metal nanoparticles were layer-by-layer assembled with small-molecule linkers onto cotton fibrils to form the conductive seeds for effective electroplating of non-noble metal electrocatalysts. This approach converts insulating cottons to highly electrocatalytic textiles while maintaining their intrinsic three-dimensional porous structure with extremely large surface area without metal agglomerations. To prepare hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) electrodes, Ni was first electroplated onto the conductive cotton textile (HER electrode), and NiFe was subsequently electroplated onto the Ni–electroplated textile (OER electrode). The resulting HER and OER electrodes exhibited remarkably low overpotentials of 12 mV at 10 mA cm^{-2} and 214 mV at 50 mA cm^{-2}, respectively. The two-electrode water electrolyzer exhibits a current density of 10 mA cm^{-2} at a low cell voltage of 1.39 V. Additionally, the operational stability of our device is well maintained even at an extremely high current density of 1 A cm^{-2} for at least 100 h.

Keywords: layer-by-layer assembly, water-splitting, electrocatalytic textile

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Investigation of hybrid perovskite and conjugated polymer thin layers

V. Pokorná[1], M. Guessmi[1], S. Eom[2], S. Gupta[1], D. Výprachtický[1], Y. Kang[2], and V. Cimrová[1*]

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic*
[2]*Department of Chemistry, Hanyang University, Seoul 04763, Korea*
[*]*cimrova@imc.cas.cz*

Organic-inorganic perovskites has emerged as a highly promising class of semiconductor for optoelectronic device applications, such as solar cells, light-emitting diodes, and photodetectors due to the many advantages including their low-cost, facile synthesis, solution processability, high absorption coefficient in the visible region, ease of bandgap tuning, and high luminescence quantum yield. However, the chemical instability of perovskite active layers has been a significant hindrance to the widespread commercialization of this technology. It is known that perovskites degrade in the presence of humidity, light, or oxygen, therefore the research on improvement of their stability is of interest.

In this contribution, we report on preparation, characterization and photophysical properties of thin films made of organic-inorganic perovskites (methylammonium lead iodide ($MAPbI_3$) or bromide ($MAPbBr_3$) and formamidinium lead iodide ($FAPbI_3$) or bromide ($FAPbBr_3$)) and their hybrid systems with selected conjugated polymers in order to improve their stability and properties. One and two step spin-coating methods were used for the perovskite thin film preparation. Thin perovskite and hybrid films were prepared either from blend solution or by multistep spin-coating of the layers. Photophysical properties of thin films including their stability were studied by means of absorption and photoluminescence (PL) spectroscopies, and their morphological properties by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Precursors with larger cations – carbazole(Cz)-based (3-(*9H*-carbazol-9-yl)propan-1-aminium iodide) and perylene-3,4,9,10-tetracarboxydiimide (PDI)-based (2,2'-(1,3,8,10-tetraoxoanthra[2,1,9-*def:*6,5,10-*d'e'f'*]diisoquinoline-2,9(1*H*,3*H*,8*H*,10*H*)-diyl)diethanaminium bromide and iodide) were synthesized and characterized for preparation of 2D perovskite layers. Poly{[9,9-dioctylfluoren-2,7-diyl]-*alt*-[2-(3,5-di-*tert*-butyl-phenoxysulfonyl)-1,4-phenylene]}(PFBPSOP), copolymer soluble in dimethylformamide (DMF) was prepared and characterized for one-step layer preparation. Perylenetetracarboxydiimide(PDI)-based, carbazole(Cz)-containing and difluorobenzothiadiazole (DFBT)-containing copolymers were used for fabrication of hybrid layers with the aim to improve their stability. They were successfully used for dripping in two-step preparation method. PDI-based and Cz-containing copolymers are interesting as additional layers not only to improve stability, but also as electron- or hole-transporting layers for devices, respectively. The influence of solvent and coating conditions on the film quality was investigated. Various combinations of the solvents were tested to get good film quality. Concerning to 2D perovskite layers, films of good quality were succeeded using Cz-based larger cation, however the films with PDI-based larger cation were too rough even after several optimization processes. We succeeded in the preparation of good quality films using blend of perovskite $FAPbBr_3$ and DMF-soluble copolymer PFBPSOP by one-step preparation method. The presented results of photophysical and morphological studies will be discussed in relation to the composition and film preparation method using various solvents. Further, the materials under study were tested as active layer in photovoltaic and light-emitting devices and their characteristics were measured.

Keywords: organic-inorganic perovskite, conjugated polymers, hybrid layers, photophysics, electroluminescence, photovoltaics

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Sustainable carrageenan based separators for lithium-ion batteries

J.P. Serra[1], A. Fidalgo-Marijuan[2], J. Teixeira[1,3], L. Hilliou[4], R. Gonçalves[5], K. Urtiaga[6],
A. Gutiérrez-Pardo[7], F. Aguesse[7], C.M. Costa[1,8,*], S. Lanceros-Mendez[2,9]

[1]*Physics Centre of Minho and Porto Universities (CF-UM-UP), University of Minho*
7 4710-057 Braga, Portugal
[2]*BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU*
Science Park, 48940 Leioa, Spain
[3]*Institute of Science and Innovation for Bio-Sustainability (IB-S), University of Minho,*
4710-057 Braga, Portugal
[4]*IPC - Institute for Polymers and Composites, Universidade do Minho, Campus de*
Azurem, 4800-058 Guimarães, Portugal
[5]*Centre of Chemistry, University of Minho 4710-057 Braga, Portugal*
[6]*Department of Geology, Universidad del Pais Vasco (UPV/EHU), 48940, Leioa, Spain*
[7]*CIDETEC, Basque Research and Technology Alliance (BRTA), Paseo de Miramón, 196, 20014 Donostia-San Sebastian, Spain*
[8]*Laboratory of Physics for Materials and Emergent Technologies, LapMET*
[9]*Ikerbasque, Basque Foundation for Science, 48009 Bilbao, Spain*
[*]*Corresponding Author's: cmscosta@fisica.uminho.pt and senentxu.lanceros@bcmaterials.net*

The rapid technological evolution and population growth demand more sustainable materials compatible with the circular economy paradigm. Natural polymers, a class of materials produced by biological and renewable resources, represent an important opportunity for the development of more sustainable technologies [1].

Carrageenan's are sulphated polysaccharides that occur as matrix material in several species of red seaweeds of the class Rhodophyceae and show interesting characteristics to be used in a large variety of applications. The present work presents the development of separator membranes for lithium-ion batteries (LIBs) applications based on lyophilized carrageenan with different initial polymer concentrations (1 and 4wt.%).

The samples were evaluated in terms of morphology, physical-chemical characteristics, thermal behavior, mechanical and electric and ionic proprieties in order to evaluate their applicability for separator membranes in LIBs. The half-cells prepared with 4wt% carrageenan content show good cyclability and a discharge capacity of 145 mAh.g^{-1} at C/10-rate, demonstrating excellent battery performance.

Keywords: carrageenan; separator; sustainability; lithium-ion batteries; energy storage systems

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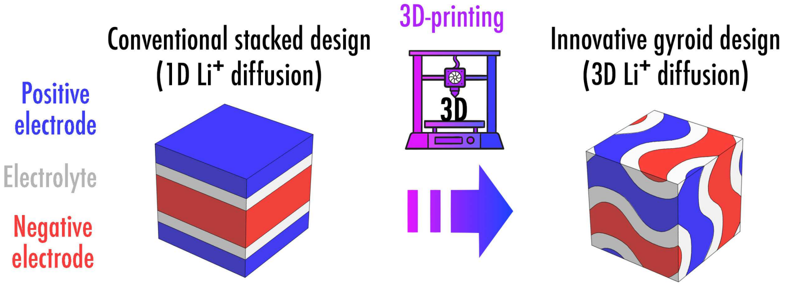
3D printed polymer electrolytes for lithium-ion batteries

Arkadiusz Czerwiński, Paweł Suchomski, Ewa Zygadło-Monikowska
Warsaw University of Technology, Faculty of Chemistry, Warsaw, Poland

The most common power sources in mobile devices and electric cars are lithium-ion batteries. Unfortunately, among the many advantages such as high specific capacity and current density, lithium-ion cells have one main disadvantage - low safety of use. Most lithium-ion batteries contain liquid electrolytes containing volatile and flammable organic solvents, which can be dangerous especially in the event of unsealing battery (e.g. in a car accident) leading to fire or explosion. Our research is focused in obtaining polymer electrolytes that do not contain liquids components (solid polymer electrolytes – SPE) or contain liquid electrolyte trapped in a crosslinked polymer network (gel polymer electrolytes – GPE). Polymer electrolytes obtained by our group can be formed using 3D printing techniques, leading to the manufacture of electrolytes of custom shape, precisely suited to the shape of the electrodes and the individual requirements of the end user. Research is underway to demonstrate a more efficient ion conduction mechanism with a three-dimensional structure of polymer electrolyte and electrodes, compared to classic sandwich type structure[1]. Despite the many advantages, known solid polymer electrolytes are not commonly used due to their low ionic conductivity, which limits the possibility of using them to low current battery mostly. To increase the conductivity, we used non-volatile, star-shaped polymers plasticizers as well as polycarbonates to obtain conductivities of the order of 10^{-4} S/cm at room temperature, which is a result close to the commonly used liquid electrolytes. Our research focuses mainly on the synthesis and characterization of polymers and polymer plasticizers with properties that can be used in lithium-ion batteries and at the same time can be processed with 3D printing techniques.



Scheme of a conventional Li-ion battery (one direction Li+ diffusion) vs 3D-printing gyroid design (three directions Li+ diffusion) [1]

Keywords: polymer electrolytes, lithium-ion, 3D printing, SPE, GPE, li-ion

Acknowledgments
Research was funded by (POB Energy) of Warsaw University of Technology within the Excellence Initiative: Research University (IDUB) programme.

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Synthesis of a novel reactive dopant for organic semiconductors

Simon Enders[1], Roman Tkachov[3], Brigitte Voit[1,2], Anton Kiriy[1]

[1]Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany
[2]Organic Chemistry of Polymers, Technische Universität Dresden, 01062 Dresden, Germany
[3]Fraunhofer-Institut für Werkstoff- und Strahltechnik, Winterbergstr. 28, 01277 Dresden, Germany

Efficient doping of organic semiconductors is an indispensable part of modern organic electronics. Especially for advanced applications such as OFETs and OLEDs, polymeric semiconductors are already used in technology worldwide, and the appropriate doping of polymeric semiconductors is of crucial importance for their performance. One problem with doping polymeric semiconductors is the tendency of the charged dopant molecules present after molecular doping to migrate through the polymer film under the influence of an electric field or by diffusion [1]. For example, p-n junctions become unstable under application conditions [2]. Covalently binding a dopant to the polymeric semiconductor could circumvent this problem.

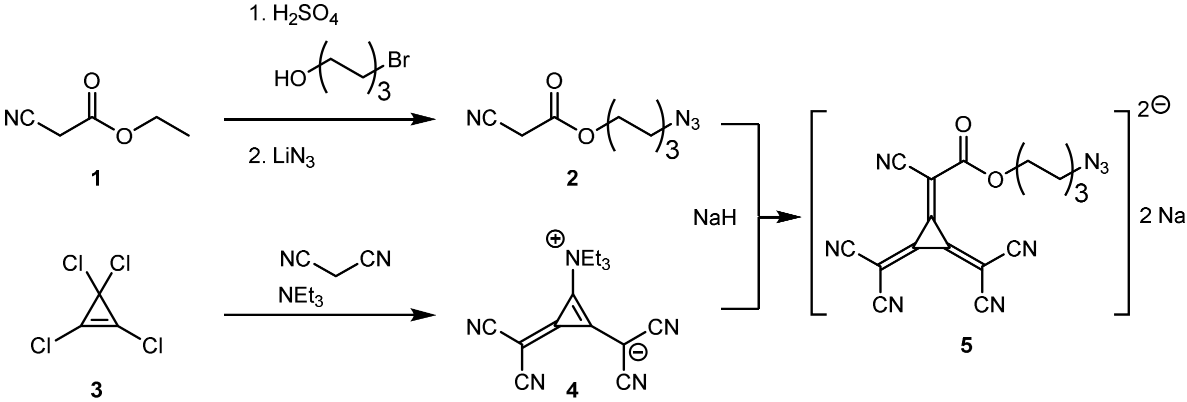

Fig. 1 Synthesis scheme of CN5HexN3-CP-2Na

Here we would like to present the synthesis of a new dopant molecule CN5HexN3-CP-2Na (5) that can be covalently bound to alkyne groups of corresponding polymeric semiconductors via thermal Huisgen cycloaddition and copper-catalyzed click reactions. A suitable semiconductive polymer containing pendant alkyne groups was developed and will be modified with the dopant to yield a new self-compensated polymer.

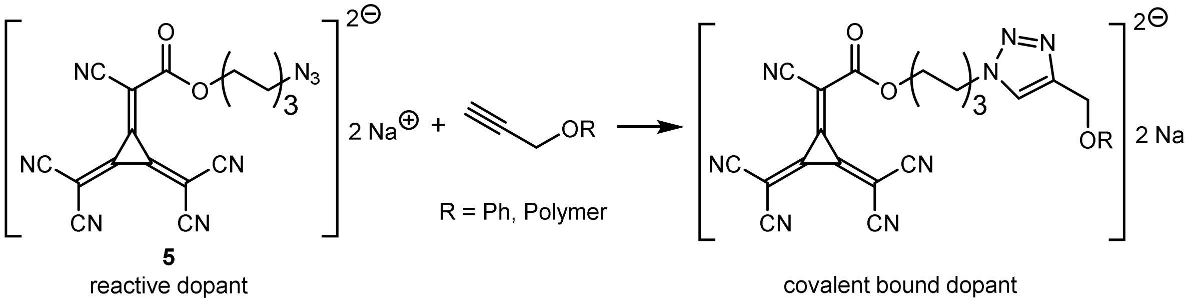

Fig. 2 Covalent binding of dopant with model substrate, done with both Huisgen-Cycloaddition and Cu-catalysed click-reaction

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A study of the ease of processing of polymer compositions for positive electrodes in all solid state batteries

Author's Name (Calibri, 12 pt.) e.g. A. Flament[1,2*], P. Bernard[2], C. Carrot[1], M. Desse[1]
[1]*Univ Lyon, UJM-Saint-Etienne, CNRS, IMP UMR5223, F-42023 Saint-Etienne, France*
[2]*Groupe Renault, 78820 Guyancourt, France*
[*]*augustin.flament@univ-st-etienne.fr*

The climate emergency requires to review our lifestyles, particularly those related to transport. Electric vehicles is part of the solutions provided that efficient energy storage is achieved. The choice of all-solid state lithium-ion batteries on a polymer basis stands out for its ability to combine autonomy and safety and ease of process. The challenge of all-solid state batteries is to ensure ionic and electronic functional conductive properties through pathways within the matrix via the addition of various constituents depending on the type of electrode (carbonaceous fillers, lithium salts, active materials for Li intercalation).
In this work, an internal mixer was used to rationalize the mixing of the constituents of a positive electrode in blends within a polymer binder also playing the role of the solid electrolyte. Ionic and electronic conductive properties require the addition of a large amount of various fillers. Therefore, parameters such as torque and temperature are clues to the flow of the final material during its processing especially in view of the extrusion of solid positive electrodes.
The polymer-lithium salt mixture was prepared first and the effect of successive additions of the active filler (lithiated nickel-manganese-cobalt oxide type) and carbonaceous conductive additive was studied. The impact on some functional properties was also shown. The addition of fillers acts to increase the viscosity and comparison was performed with the models of Krieger-Dougherty. Lithium salt was found to have a positive effect in the reduction of self-heating during the processing.

Synthesis of functional gradient polymers though chemical vapor deposition

G. Fortunato[1], A. Mukherjee[1], P. Raffa[1], F. Picchioni[1], R.K. Bose[1*]

[1] *Product Technology, Department of Chemical Engineering, Engineering and Technology Institute Groningen(ENTEG), University of Groningen, Groningen, The Netherlands*

[*] *r.k. bose@rug.nl*

Gradient polymers represent a promising class of materials whose composition progressively changes along one or more directions resulting in a gradual change of materials properties. As widely observed in natural systems, the gradient plays a key role in binding two materials with mismatching mechanical properties (e.g. soft-stiff) where the presence of interfaces would cause poor stress dissipation and premature failure. Gradient polymeric structures can be typically obtained through a controlled addition of different monomers, as in deposition techniques. [1]Thermally initiated chemical vapor deposition (iCVD) stands out among them, in particular when targeting compositional gradients at the nanoscale, in a single step. Being solvent-free and operated under mild conditions, the deposition is highly controlled and the properties of the resulting films are precisely tuneable. Furthermore, the free radical process allows for a wide choice of unsaturated species as monomers. [2] In particular, the incorporation of functional monomers as vinyl cinnamate or allyl methacrylate allows for post modification by irradiating the film with UV radiation at selected wavelengths. [3] In this work we explore the possibility to fabricate a compositional and mechanical gradient into polymer films through iCVD followed by UV-crosslinking.

Thin films (up to 2 microns thickness) were fabricated by depositing allyl methacrylate (AMA) combining with a series of alkyl methacrylates. The quality and homogeneity of films was studied through SEM and profilometry. FTIR and XPS confirmed the gradient in composition and the retention of allyl functional groups in the polymer. Post-modification (crosslinking) was studied as a function of the irradiation wavelength and time exposure through FTIR and XPS. Mechanical properties were assessed in terms of nanoindentation. Irradiation through a photomask confirmed the possibility of a spatial control on crosslinking, suggesting the possibility to create more complex patterns via lithography.

Keywords: solventless synthesis, chemical vapour deposition, post-modification, crosslinking, additive manufacturing, gradient poymers

Acknowledgments

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Pla/carbon nanotubes composites for thermoelectric application: relation between elaboration, structure and properties

V-H. Vo Le[1], C. Binet[1], J.-F. Brun[1], V. Gaucher[1*]
[1]*Univ. Lille, CNRS UMR 8207 - UMET - Unité Matériaux et Transformations, F-59655 Lille, France*
[*]*Corresponding author: valerie.gaucher@univ-lille.fr*

Thermoelectrics are materials that can be used to convert heat directly into electricity via the thermoelectric Seebeck effect. To optimize the efficiency of thermoelectric materials, it is necessary to maximize the dimensionless figure of merit $ZT = \frac{\sigma S^2}{\kappa} T$, where σ is the electrical conductivity, κ the thermal conductivity, S the Seebeck coefficient, and T the temperature. Therefore, thermoelectric materials must exhibit a high electrical conductivity, a high Seebeck coefficient, and a low thermal conductivity[1]. Within this framework semiconducting materials are the best thermoelectrics. During the last decade, organic thermoelectrics have emerged as a relevant alternative to inorganics for low temperature waste heat harvesting applications (T<500 K) including carbon nanotubes/polymer based nanocomposites[2,3].

In this study, nanocomposites based on a Poly(lactic acid) (PLA) filled with different percentages of carbon nanotubes (CNTs) (up to 10 wt%) were prepared to investigate their thermoelectric properties at room temperature with a particular attention to the influence of elaboration process. For this, an amorphous and a semi-crystalline grade of PLA, and Multi-walled carbon nanotubes have been chosen. Extrusion or solution mixing, followed by hot-pressing process are being used to prepare thick PLA/CNTs samples (typically about 500 µm in thick).

Differential Scanning Calorimetry (DSC) and X-Ray scattering results have shown that both grades of PLA are amorphous in all the composites whatever the elaboration process used. Regarding the thermoelectric properties, as expected, CNTs significantly improve electrical conductivity by several orders of magnitude as soon as the CNT fraction is higher than the percolation threshold (below 2 wt% CNT). The higher value for the electrical conductivity measured in this study was around 10^2 S/m with 10 wt% CNT. Note that the in-plane electrical conductivity of all PLA/CNTs appears 10-100 times higher than the values from cross-plane whatever the elaboration process used. By contrast, thermal conductivity is contained and slowly increases with the addition of CNT: κ increases from around 0.2 for pristine PLA to 0.40 W/m.K with 10 wt% CNTs. Finally, the Seebeck coefficient is ranging from 10 to 12 µV.K^{-1} and does not seem to be dependent on the elaboration process either.

Keywords: Electrical conductivity, Thermal conductivity, Seebeck coefficient

Acknowledgments: The authors are indebted University of Lille and Région Haut-de-France for funding the PhD thesis. Financial support from Région Nord Pas-de-Calais and European FEDER for SAXS/WAXS laboratory equipment is also gratefully acknowledged.

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Optical properties of vacuum-deposited fluoropolymer thin films

K. Grytsenko, Y. Kolomzarov, P. Lytvyn, O. Kondratenko, E. Bortchagovsky
V.E. Lashkaryov Institute of Semiconductor Physics, pr. Nauki 41, 03650 Kyiv, Ukraine

Fluopolymer (FP) thin films already find applications as protective and dielectric layers in novel devices, including organic light emitting diodes, surface plasmon resonance sensors and photovoltaics. Deposition of polytetrafluoroethylene (PTFE) thin films from a gas phase allows to produce PTFE films on any substrate, avoiding anti-wetting conditions during deposition from a liquid phase. Deposition by low temperature plasma (LTP) usually leads to the formation of PTFE films with rough surfaces, sometimes with inclusions of drops formed in the gas phase at a comparatively high pressure necessary for LTP. Decomposition-evaporation of bulk FP in a high vacuum with the consequent activation of vapor by a cloud of accelerated electrons (EVD) method was designed namely for the production of smooth transparent FP thin films for optical applications. 40,68 MHz LTP was used at low pressure during EVD.

Refractive index of the PTFE thin films deposited by EVD was in 1,15 -1,39 range dependent on deposition conditions such as pressure and electron activation power. The higher the pressure and activation current, the lower the refractive index. However the films deposited by EVD changed their refractive index under the action of elevated temperature. Application of LTP at low pressure during EVD led to the formation of more smooth PTFE films, stable at an elevated temperature. The hardness of the PTFE film also increased. The higher the pressure during combined (EVD + LTP) deposition the rougher the film surface. The combined deposition also allows to coat nanostructured relief on plastic surfaces. Deposited by EVD the FP "film" showed ant-wetting behavior, while EVD+LTP formed conformal coating onto ridges, slopes and grooves of the plastic nanostructure. The refractive index and absorption coefficient of the PTFE films measured in the 200 nm – 2500 nm diapason will be presented and discussed.

Polychlorotrifluoroethylene (PCTFE) showed the reverse behaviour under the action of LTP during EVD. Films deposited by EVD+LTP consisted of large fibrils. Films deposited by EVD only were smooth with a refractive index in the 1,39 – 1,45 range depending on deposition conditions. Figure shows the transmission spectra of PTFE and PCTFE films.

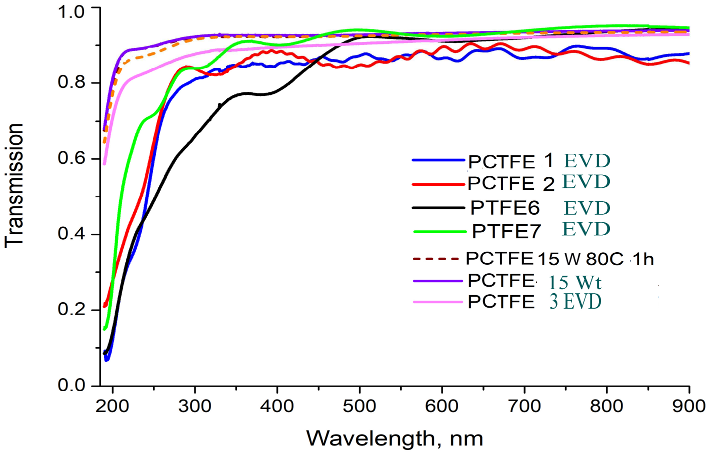

Figure. Transmission spectra of PTFE and PCTFE films produced at various conditions.

The transmission of all FP films deposited by EVD and EVD + RF was between 90 and 100 % in the visible region. PTFE film deposited at lowest pressure by EVD+LTP showed a little transmission increase after annealing in air. PTFE films deposited at intermediate pressure showed no changes in transmission after annealing. PCTFE films were more transparent than PTFE films.

Conclusions: The transmission and refractive index of FP can be purposefully controlled by the choice of optimal deposition conditions and FP material as well.

Synthesis of high performance supercapacitor electrode materials based on ICP/carbon composites

E. Inci[1], J. Keskinen[2], M. Mäntysalo[2], D. Lupo[2], J. Pionteck[1*]

[1] *Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany*
[2] *Faculty of Information Technology and Communication Sciences, Tampere University, Tampere, Finland*
[*]*pionteck@ipfdd.de*

Nowadays, the rapid growth of portable electronics and hybrid electric vehicles propels the development of electrochemical capacitors, also known as supercapacitors (SCs), to the forefront of research [1]. Current research on electrochemical capacitors aims to increase power and energy density while also lowering fabrication costs and using environmentally friendly materials. Electrochemical capacitors are classified as electrical double-layer capacitors (EDLCs) or pseudocapacitors based on their charge storage mechanism and active material type [2]. Carbon materials with a high specific surface area are commonly used in EDLCs. EDLCs charge and discharge via rapid ion adsorption and desorption [3]. On the other hand, pseudocapacitors are fast and reversibly chargeable by redox reactions of transition metal oxides or intrinsically conductive polymers (ICPs) [4].

Polyaniline (PANI) is the most promising potential electrode material candidate of the available ICPs, because of its low cost, ease of production, and relatively high conductivity. However, similarly to other conducting polymers, PANI has a low power density and instability during the electrochemical reactions. Therefore, highly dispersed PANI on a support material with good conductivity and a large surface area (such as graphene derivatives) should be a promising strategy to increase the capacitive capabilities of PANI.

In this study, our aim is to produce PANI/carbon composites with high energy density and high capacitance for SC electrode materials. PANI/carbon composites are synthesized by *in-situ* chemical oxidation polymerization of aniline in presence of different carbon materials. Morphological, electrical and electrochemical properties of various prepared materials are currently being examined in order to select the most appropriate electrode material for preparation of printable, long lasting supercapacitor electrodes. The electrochemical behaviour of the prepared electrode materials was first tested using sulfuric acid as electolyte in a three electrode or symmetric two-elctrode set-up. From selected PANI/carbon samples, pastes were prepared and applied for preparation of electrodes by the doctor blade method. Their electrochemical behavior was analyzed in symmetric and asymmetric two-electrode supercapacitors with neutral electrolyte. The data obtained were compared with the tests made using acidic electrolytes to analyse the effect of the electrolyte on the electrochemical performance. First results will be presented.

Keywords: supercapacitor, carbon, polyaniline, energy storage

Acknowledgments
This work is part of the InComEss (INnovative polymer-based COmposite systeMs for high-efficient Energy Scavenging and Storage) project and receives funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement Number 862597.

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Micro-sized silicon/carbon composite anode for Li-ion battery with Facile Preparation

N. Çakmakçı, J. Park, H. Kim, H. Song and Y. Jeong*

Department of Organic Materials and Fiber Engineering, Soongsil University, Seoul, South Korea
* *yjeong@ssu.ac.kr*

Lithium-ion batteries (LIBs) are one of the most used energy sources for portable devices nowadays. Many studies have been focused on finding cost-effective and high-capacity LIBs for electric vehicles (EVs) and energy storage systems (ESSs) to meet demand [1]. Graphite has been the conventional LIB anode material for decades thanks to its low volumetric expansion rate and good stability. However, graphite has a low theoretical capacity, making it an insufficient material for high-capacity LIBs [2]. Unlike graphite, silicon has nearly ten times higher theoretical capacity and higher energy density as anode material for LIBs [3]. In addition to this, silicon is non-toxic and inexpensive owing to its abundant reserves [4]. Nonetheless, silicon has poor cyclability due to the large volume change during charging/discharging [5]. Carbon coating is an effective and simple method compared to etching and ball-milling to overcome the volume expansion, cracking, and pulverization of silicon during cycling [6]. In this study, the silicon-carbon composite anode material is prepared using micro-sized silicon with a polymer coating method. The carbon layer onto multiple silicon particles is formed by the carbonization of PVA. Also, the void space between silicon particles and the carbon layer is formed with pyrolyzed PMMA for extra support to suppress volume exchange. Additionally, acetylene black (AB) is introduced into the void space to improve the electrical contact. As a result, our Si/C composite (Si/void/AB/C) shows a high reversible capacity of 1235 mAh g^{-1} after 400 cycles at 0.5 C rate and a high coulombic efficiency of 99.7%.

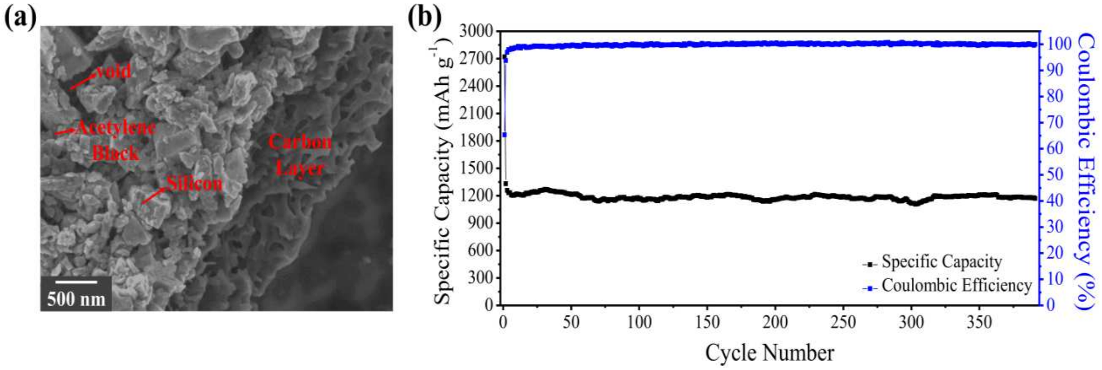

Fig. (a) The cross-section SEM image of the Si/void/AB/C composite and (b) cycling performance of the Si/void/AB/C composite.

Keywords: Lithium-ion battery, silicon, carbon, Si-C composite, acetylene black

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Enhancement in the barrier properties of ZIF- 67 modified PET

Jinu Joji[1], Varun Adiga [2], Praveen C Ramamurthy[3], and Hasitha Weerasinghe[4]

[1,3]Department of Materials Engineering, Indian Institute of Science Bangalore, India
[2,3] Interdisciplinary center for energy and research Bangalore, India
[4] commonwealth scientific and industrial research organization, CSIRO, Australia

The Long-term stability of perovskite solar cells under ambient is a major challenge [1]. To minimize this challenge various barrier materials like glass, and polymers are used as encapsulants[2]. The specific barrier performance can be enhanced by the addition of functionalized nanoparticles. Like metal oxides, MOFs, etc. Here in this work, barrier properties of polyethylene terephthalate (PET) coated with Zeolite Imidazolium framework (ZIF- 67) was evaluated. The synthesized ZIF- 67 was mixed with polyvinyl alcohol(PVA) and coated on a PET sheet.

The properties ZIF- 67 coated PET and neat PET were compared. The thickness of the PVA-ZIF- 67 coatings was found to be 3-5 μm from profilometry measurement. The surface roughness was 8-12 nm which was calculated by atomic force microscopy. The water vapor transmission rate (WVTR) was assessed using Cavity ring-down spectroscopy (CRDS). Compared to neat PET, PVA-ZIF- 67 coated PET sheet has shown a one-order reduction in moisture permittivity (Figure 3). The WVTR of the Neat PET sheet is almost ~10.5gm/m^2/day and for the modified, it shows around ~0.2316gm/m^2/day (Figure 1). Thus, the moisture stability of ZIF- 67 accounted for the reduction in WVTR of PET[4].

Keywords: ZIF- 67, PET, WVTR

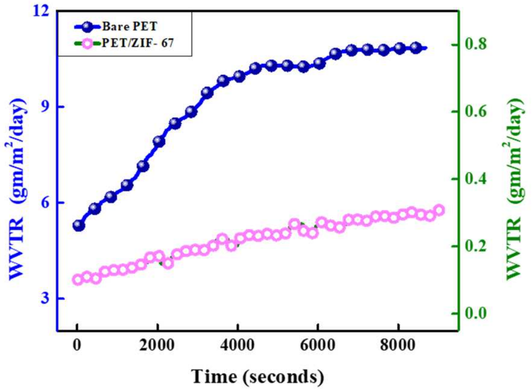

Figure 1:Barrier properties of PET vs PET-67

Acknowledgments

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Design of ionenes based on ionic liquid functional monomers and their applications to a solid polymer electrolytes of lithium-ion batteries

Minjae Lee,[1] Jong Hyeok Park,[2] Sang Young Lee[2]

[1]*Kunsan National University, Gunsan, S. Korea*
[2]*Yonsei University, Seoul, S. Korea*
[*]*Corresponding Author's E-mail address: minjae@kunsan.ac.kr*

The text should be 11-point Calibri in the single-column format in A4 paper with margins 2cm on all sides.
Keep the layout of the text as simple as possible.
The maximum length of the abstract is one page A4.
Figures and tables can be embedded in this section. Caption (Calibri, 8 pt., Bold) should be given below the figures & above the tables.
The file must be saved in the format MS Office Word (doc, docx, **NOT pdf**).
The name of presenting author should be underlined.

New ionic polymers for a solid-state electrolyte of litium-ion batteries are a key material for high electrochemical performances. Many types of ionic polymers have been reported, and our research group also designed and synthesized various ionic polymers, which are polymerized from ionic-liquid monomers. In this study, main-chain ion conducting ionenes are prepared and characterized. From dihydroxyl ionic liquid monomers and proper diacid chlorides or diisocyanates, the polycondensation reactions gave the ionic polyesters or polyurethanes respectively. Chemical structures were varied by different anions, different lengh between two ionic salt units, and different organic heterocyclic cation structures. Some of the ionenes were semi-crystalline, but the others are amorphous; the morphologies are dependent on the polymer's chemical structurues. Detail characterization studies of the linear ionenes will be discussed in the presentation. The solid polymer electrolytes made of the new synthesized ionenes were applied to lithium metal batteries. Free standing films can be prepared from the polymer electrolyte compositions. The highest ionic conductivity during the electrolyte films is up to 4.2×10^{-1} mS cm^{-1}. The lithium metal battery cell performances are more than comparable and detail battery test results will be discussed in the presentation.

Keywords: (optional, Calibri, 11 pt.) Polymer electrolyte, ionic polymer, lituim-ion battery, solid-state electrolyte

Acknowledgments

Co-workers, Prof. J. H. Park and Prof. S. Y. Lee in Yonsei University, S. Korea. This research was supported by Creative Materials Discovery Program through the National Research Foundation of Korea(NRF) funded by Ministry of Science and ICT(2018M3D1A1058624).

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Layer-by-layer Deposition of 2D CdSe/CdS Nanoplatelets in Polymer Matrices as Fluorescent Composite Material

F. Li[1,2*], L. F. Klepzig[1,3], J. Lauth[1,3], H. Menzel[1,2]

[1]*Cluster of Excellence PhoenixD (Photonics, Optics, and Engineering – Innovation Across Disciplines), Hannover, Germany*
[2]*Institute for Technical Chemistry, Technische Universität Braunschweig, Braunschweig, Germany*
[3]*Institute of Physical Chemistry and Electrochemistry, Leibniz Universität Hannover, Hannover, Germany*
[*]*fuzhao.li@tu-braunschweig.de*

Two-dimensional semiconductor nanoplatelets (NPLs) have been recognized as one of the most promising luminescent materials over the past few decades, owing to their size dependent optical properties and anisotropic light emission.[1] By controlling the NPLs orientation, macroscopically polarized emission could be achieved.[2] The realization of these NPLs into applications usually demands appropriate fabrication. Using polymers as matrices to incorporate NPLs is a promising way to produce composite materials. By doing this, not only the NPLs can be immobilized and protected by an enclosing matrix, but also a well-defined orientation of NPLs can be achieved.[3]

In our recent work, a layer-by-layer dip-coating technique was applied to sequentially deposite NPLs and polyelectrolytes (PELs) for preparation of fluorescent thin films. Electrostatic interactions were used as main driving forces for the formation of multilayers. By optimizing parameters, NPLs can be adsorbed as well-separated submonolayers and lie flatly on the substrates. Optical properties of NPLs were maintained after the formation of composite films. Film thickness as well as surface roughness were influenced by using different PELs and pH conditions.

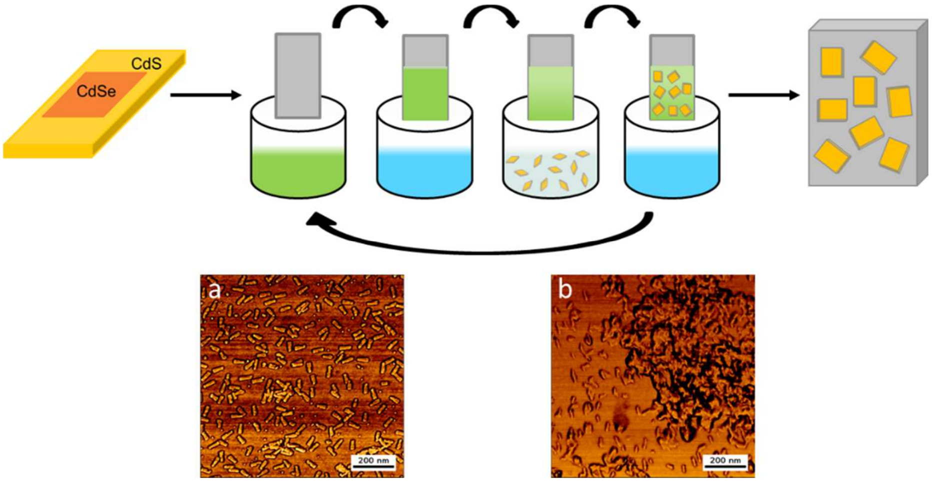

Figure 1: Schematic illustration of a layer-by-layer deposition process with CdSe/CdS NPLs and PELs. AFM phase images of one NPLs/PELs bilayer using (a) poly(diallyldimethylammonium chloride) as PEL with a pH of 10 and (b) poly(ethylenimine) as PEL with a pH of 6.

Keywords: polymer matrix, nanoplatelets orientation, layer-by-layer deposition, composite material

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Effects of lithium salts on the dimerization of UPy motifs in self-healing polymer electrolytes

Cuc Thu Mai[1*], Guiomar Hernández[1], Kristina Edström[1], Jonas Mindemark[1]

[1]*Department of Chemistry, Ångström Laboratory, Uppsala university, Uppsala, Sweden*
[*]*cuc.mai@kemi.uu.se*

Polymers hold great promise for replacing conventional liquid electrolytes in lithium batteries, and network architectures enable the modulus to be tuned semiindependently of conductivity.[1] Cross-linked polymer networks via dynamic bonding offer the additional benefits of recyclability and self-healing in response to physical damage.[2,3] Among dynamic bonding systems, hydrogen bonding has attracted great interest for the fabrication of polymers with self-healing capabilities. Reinforced electrolyte networks fabricated with self-complementary hydrogen bonding ureiodopyrimindinone (UPy) motifs have been previously studied and shown to exhibit enhanced ionic conductivity and cycling performance as well as mechanical properties.[2-4] The negative effect of lithium salt, LiTFSI on the mechanical stability of self-healing polymer electrolyte was reported once before but little explanation has been provided. Recognizing that, in this work, the focus is on elucidating the hindering effects of lithium salts (LiTFSI, $LiPF_6$) on the self-healing capability of UPy-based electrolytes. Finally, we want to discuss the prospects of self-healing polymer electrolytes in lithium metal batteries, emphasizing the practical challenges that remain to be addressed.

Keywords: self-healing, polymer electrolyte, hydrogen bonding, lithium metal anode.

Acknowledgments

The authors acknowledge financial support from the Knut and Alice Wallenberg Foundation.

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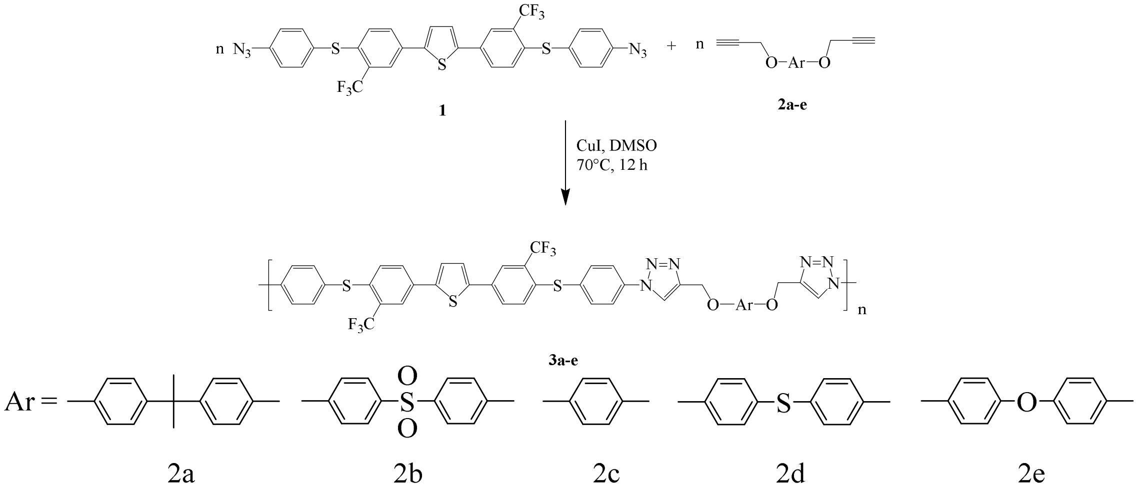
Sulfur containing high refractive index polytriazoles for optoelectronic applications

K. Mazumder[1], H. Komber[2], E. Bittrich[2], B. Voit[2*], S. Banerjee[1*]

[1]*IIT Kharagpur, Kharagpur, India*
[2]*IPF Dresden, Dresden, Germany*
[*]*voit@ipfdd.de*
[*]*susanta@matsc.iitkgp.ac.in*

The past few decades have seen remarkable advances in the field of opto-electronics and the need to develop highly functional materials has become utmost relevant. Polymeric materials having inherent high refractive indices (RI) are of greater significance due to the huge diversity of applications they provide in optical applications, which include OLEDs, lenses, waveguides, prisms, etc. Polytriazoles fall in the category of high performance polymers by virtue of their excellent thermal and thermos oxidative stability and chemical resistance. Polytriazoles also ensure the ease of synthesis via Cu(I)-catalysed azide-alkyne cycloaddition reactions.[1] The click polymerizations between an azide and an alkyne system using Cu(I) catalyst provide facile synthesis technique to prepare polytriazoles in mild reaction conditions. Furthermore, fluorine containing polymers are known for their ease of solubility without compromising their thermal stability. The presence of bulky –CF_3 moiety helps to increase the solubility of the polymer, decreasing the intramolecular chain interactions.[2] This proposal focuses on the preparation of a sulfur containing diazide monomer (**1**) and its click reactions with dialkyne monomers (**2a-e**) to prepare a series of high refractive index poytriazoles (**3a-e**) in presence of Cu(I) catalyst in mild reaction conditions and study the refractive indices of the final polymer materials.



Scheme 1. Synthesis scheme and structure of polytriazoles, 3a-e.

Keywords: Polytriazoles, sulfur containing polymers, optical applications, high refractive index

Acknowledgments

IIT Kharagpur, IPF Dresden, DAAD

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Colloidal assemblies of core-shell hydrophilic spherical and spheroidal particles

Damian Mickiewicz[1*], Mariusz Gadzinowski[1], Witold Szymański[2], Teresa Basinska[1], Stanislaw Slomkowski[1]

[1] *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, H. Sienkiewicza 112,*
90-363 Lodz, Poland
[2] *Technical University of Lodz, Institute of Materials Science and Engineering, Stefanowskiego 1/15,*
90-924 Lodz, Poland
**dmi@cbmm.lodz.pl*

Assemblies of spherical polymer particles are already well known and have been used as elements of optoelectronic devices, nanolithography reagents, and parts of biosensors. Knowledge on formation of setups composed of particles with shape anisotropy, and their properties compared to spherical particles are very scarce.

The aim of these studies was preparation of the spherical and spheroidal hydrophilic core-shell polymer particles and formation of their multidimensional assemblies. The spheroidal particles containing polyglycidol in the interfacial layer (P(S/PGL)) were prepared from the spherical ones. The hydrophilic P(S/PGL) microspheres (with D_n=408 nm) were synthesized by emulsion copolymerization of styrene and polyglycidol macromonomer, using potassium persulfate as an initiator. To prepare spheroidal particles the microspheres were embedded in poly(vinyl alcohol) (PVA) film. The 1 cm -wide stripes of the film containing particles (with conc. ca. 5 wt%) were uniaxially slowly stretched at 120 °C (i.e. above Tg of polystyrene and PVA) to the required length. Finally, the spheroidal particles were isolated by dissolving the film in water. The particles were characterized by SEM, DLS, EA, XPS. From the relation between the film elongation and particles aspect ratio (AR) it was found that AR increased in direct proportion to elongation for AR in the range 1-8. The microspheres' and spheroids' assemblies (see Fig.1) were prepared on silicon supports from particles suspension in water containing EtOH in the concentration range 0-30 vol%. The results of 3D assemblies studies revealed that morphology the assemblies, their optical and mechanical properties are related to particle aspect ratio and concentration of ethanol in particles aqueous suspension (see Figure 1 a,b).

Keywords: polymer particles, colloidal assemblies, photonic crystals, multilayers

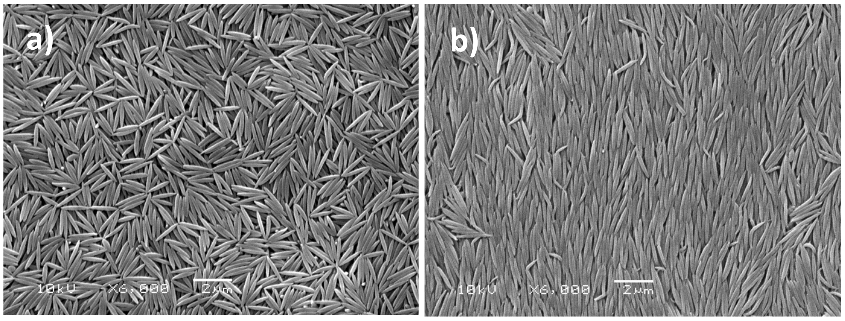

Figure 1. Asemblies of P(S/PGL) spheroids (AR=6,41), a) 0% EtOH, b) 20% EtOH.

Acknowledgments

The authors express their gratitude for financial support from National Science Centre (Poland) grant Nr UMO- UMO-2018/29/B/ST8/01721.

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Composite polymer electrolyte membrane for fuel cells and battery application

Phumlani Msomi*

[1]*Department of Chemical Scinces, University of Johannesburg, Johannebsurg, South Africa*
[2] *Centre for Nanomaterials Science Research, University of Johannesburg, Johannesburg, South Africa*
[3]*Research Centre for Synthesis and Catalysis, Department of Chemical Sciences, University of Johannesburg, Johannesburg 2028, South Africa*

**Corresponding pmsomi@uj.ac.za*

Renewable energy technologies such as fuel cells and batteries are noticeable the preferred technologies for energy generation and storage. This has prompt research to focused on these technologies and advance their sustainability, power output and storage capacity. Both these energy technologies, in their heat, have a polymer electrolyte membrane which can enhance their power and energy production. This work discusses the fabrication, application and need of polymer electrolyte membrane in both fuel cells and batteries. The polymer electrolytes properties in this work are enhanced using different nanostructured materials and applied in fuel cells and Metal-air barriers.

Keywords: Fuel cells, Battries, polymer electrolytes, nanomaterials

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Solvent-free conductive coatings containing chemically coupled particles for functional textiles

Jagadeshvaran P L[1], Kamlesh Panwar[2], Indumathi Ramakrishnan[2], Suryasarathi Bose[1]*

[1] *Department of Materials Engineering, Indian Institute of Science, Bangalore, India 560012*
[2] *Resil Chemicals Pvt. Ltd., Bommasandra Industrial Area, Bangalore, India 560099*
**Corresponding Author's E-mail address: sbose@iisc.ac.in*

The surge in the usage of wireless electronics and communication devices has engendered a different form of pollution, viz. the electromagnetic (EM) pollution and yet another serious issue, electromagnetic interference (EMI). There is a legitimate need to develop strategies and materials to combat this issue, otherwise leading to dreadful consequences. Functional textiles have emerged as the modern materials to help attenuate EM waves due to the numerous advantages – flexibility being the most important. In addition to this, there is an inherent advantage of multiple interfaces in coated fabrics that can engender significant attenuation. Herein we report a coating having multifunctional properties – capable of blocking both UV and EM radiation (predominantly of the microwave frequencies) with flame-retarding properties. The layer described here comprises iron titanate(FT) synthesized from its sustainable precursor – ilmenite sand and carbon nanotubes (CNT) dispersed in waterborne polyurethane. It is worth noting that FT's use as a multifunctional material is being reported for the first time. It was observed that a single layer of coated fabric shows EMI shielding effectiveness of -40 dB translating to 99.99% attenuation and similarly a UV blocking of 99.99% in the wavelength ranging from 200-400 nm. The microwave shielding properties of the fabric were demonstrated using a Bluetooth module – where the coated fabric was able to block the incoming Bluetooth signals to the module from a mobile phone. Besides, the coated fabrics exhibited phenomenal enhancement in thermal stability - a five percent increase in the limiting oxygen index (LOI) was observed upon the application of the coating. Such exceptional properties complement cotton fabrics' existing utility, thereby extending their use to specialty applications.

Keywords: Multifunctional coatings, EMI shielding, UV blocking, iron titanate, CNT, waterborne polyurethane, cotton fabrics

Memristive Behavior of Polymethacrylamide with Carbazole Side Groups

Y. R. Panthi[1, 2], J. Pfleger[1*], D. Výprachtický[1], Ambika Pandey[1,2], M. A. Thottappali[1,2], I. Šeděnková. [1]

[1] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského nám. 2, 16206 Prague 6, Czech Republic;*

[2] *Faculty of mathematics and physics, Charles University, Ke Karlovu 3, Prague 2, Czech Republic*

[*]*pfleger@imc.cas.cz*

A memristor is principally a resistor-like device composed of an active layer sandwiched between two electrodes whose resistance is dependent on the magnitude and the direction of the previously applied voltage. Contrary to the electronic memory devices, which exhibit only two distinct electrical conductance states assigned to logic 0 and logic 1 in the binary system, the memristor device exhibits memory with a gradual conductance change over the multiple operations [1]. It has been shown recently that such properties can be utilized in neuromorphic computing and synaptic learning [2].

Here, we report on the synthesis of poly[N-(3-(9H-carbazole-9-yl)propyl)methacrylamide] (PCaPMA) and its properties when employed in a memristive system. When the thin film of the PCaPMA is sandwiched between indium tin oxide (ITO) and aluminum/gold electrodes, it exhibits a distinct bi-state resistive switching at specific distinct voltages. These switching and bi-stable conduction are explained in the frame of phenomena in the polymer close to its electrical breakdown. Utilization of such phenomena in electronic memory devices was evaluated, showing the ON/OFF current ratio exceeding 100 and excellent reproducibility and persistence. Contrary, at the lower voltages far from the electrical breakdown, the device showed a gradual decrease of resistance during multiple applications of voltage sweeps/pulses and reversible behavior during a subsequent application of voltage cycles of reverse polarity. Such changes depend on the frequency and width of applied pulses and mimic the learning/forgetting properties of biological neurosynapses. The working mechanism of multiple changes of the resistive state, also showing synaptic plasticity, has been assigned directly to manipulating the redox state of the functional carbazole unit attached to the polymer backbone [3]. The percolation behavior is controlled by voltage-induced conformational changes of these heterocycles and the trapping/detrapping of charges in the polymer bulk. The stabilization of the pendant group by physical crosslinking between amide and carbonyl groups via hydrogen bonds plays a crucial role in exhibiting the nonvolatile resistive memory.

Keywords: Memristor, neuromorphic computing, synaptic learning, bi-state resistance, carbazole, conformational changes, charges trapping/detrapping.

Acknowledgments

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Reinforcing solid polymer electrolytes with cellulose nanofibers for high mechanical strength and high ionic conductivity

Cristina Prado-Martínez[1], Isabella Mombrini[2], Preston Sutton[1,3], Aristotelis Kamtsikakis[1], Worarin Meesorn[1], Gilberto Siqueira[4], Ullrich Steiner[1], Ilja Gunkel[1*]

[1]*Adolphe Merkle Institute, Fribourg, Switzerland*
[2] *Electrochemical Innovation Lab, London, U.K. & ESRF - The European Synchrotron, Grenoble, France*
[3]*Present address: BeDimensional S. p. A., Via Lungo Torrente Secca 30R, 16163 Genova, Italia*
[4]*Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland*
[*]*ilja.gunkel@unifr.ch*

Moving towards sustainable energy storage is one of the great challenges of our era. While lithium-ion batteries already play an important role in this transition, new materials and methods are necessary to advance this current technology and meet future goals[1]. Solid polymer electrolytes (SPEs) are a potential key compoment in safer batteries with higher power. However, SPEs currently still do not simultaneously meet the requirements of providing high ionic conductivity and high mechanical stability, which are antagonist features in SPEs.

In our research we show that a SPE with high ionic conductivity – polyethylene oxide-epychlrohydrine copolymer (EO-EPI)[2] can be signficantly reinforced with cellulose nanofibers (CNFs) without compromising its conductivity. By tuning the composition of these CNF-reinforced SPEs, we were able to increase the storage modulus of the copolymer by a factor of 70 without any significant reduction in the ionic conductivity (**Figure 1**). Additionally, we evaluated the electrochemical stability of the SPE by cylic voltammetry and galvonostatic cycling in a symmetrical Li/SPE/Li cell and confirmed that the system is capable of moving lithium ions back and forth in a stable way for several days without a significant capacity loss. Therefore, the combination of the improved mechanical strength, a very competitive ionic conductivity and good cyclicability makes this nanocomposite material a very promising candidate for the use as an SPE in next-generation lithium batteries.

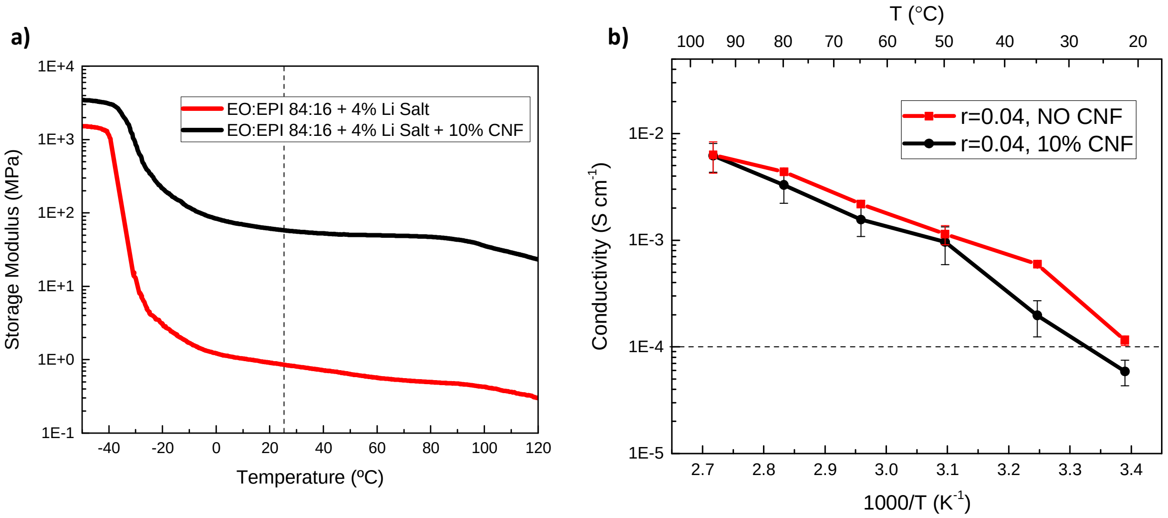

Figure 1. Mechanical strength and ionic conductivity of CNF-reinforced EO-EPI SPEs a) Storage modulus E' vs temperature for EO-EPI SPEs, with and without CNFs. **b)** Comparison of the temperature-dependent conductivity of the EO-EPI SPEs with and without CNFs.

Keywords: Lithium batteries, solid polymer electrolytes, cellulose nanofibers, DMA, conductivity, impedance, cyclic voltammetry, electrochemistry, galvanostatic cylcing

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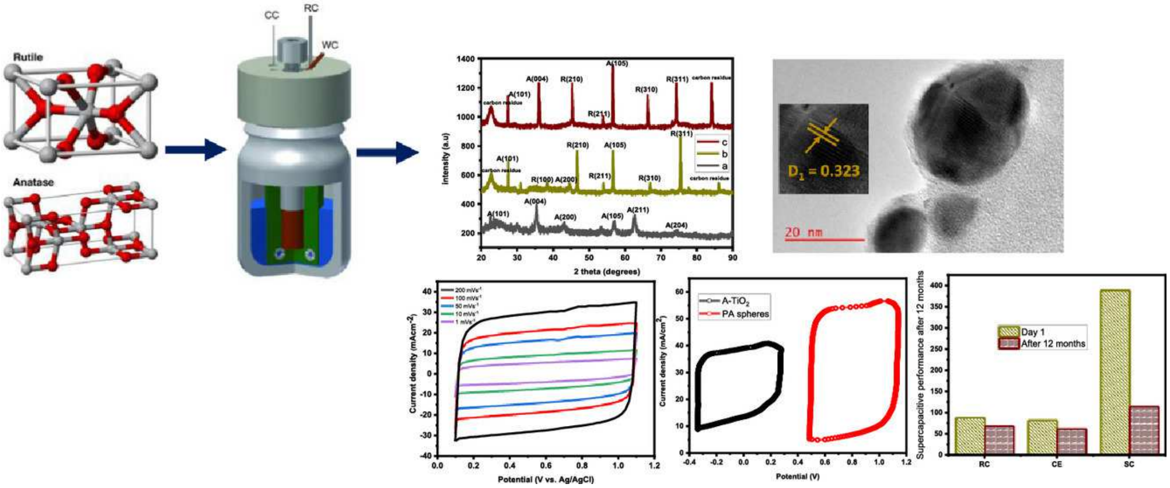
Starch built TiO2 nanoarchitecture with mixed anatase and rutile phase for high energy density supercapacitor electrode

OD Saliu, M Mamo, P Ndungu, J Ramontja*

University of Johannesburg, Johannesburg, South Africa
**jamesr@uj.ac.za*

TiO_2 nanoparticles are generally known to have low capacity and poor cycle life when used for supercapacitor electrodes. This work improved the overall energy storage ability of TiO_2 nanoparticles by growing them on an activated starch template, which creates polyhydroxylated points that act as nucleation sites for stable nanoparticle growth. The calcined products were studied for phase changes using XRD, TEM, and Raman. Consequently, a balance between the anatase and rutile phase in the TiO_2 nanoparticles led to the highest energy storage capacity. The calcination resulted in lowered crystallite sizes, and the activated starch template imparted surface oxygen groups that contributed to enhanced supercapacitive performances. In this work, the TiO_2 synthesized on an activated starch template is referred to as A-TiO_2, the TiO_2 grown on un-activated starch was U-TiO_2, while the reference TiO_2 synthesized without a template was referred to as unsupported-TiO_2. A-TiO_2, which has 72% anatase and 28% rutile, had the best result and showed specific capacitance as high as 388 Fg^{-1}, energy density as high as 194 Wh Kg^{-1}, a power density of 4473 W Kg^{-1}, ESR of 0.53 ohms, and retention capacity of 99% after 20,000 cycles.



Keywords: Supercapacitors, Anatase, Rutile, TiO_2, Activation, Conductive biopolymer, Activated starch

Acknowledgments

Authors wish to acknowledge the National Research Foundation (South Africa) Thuthuka program, the centre for Nanomaterials Science Research at the Department of Chemical Sciences (University of Johannesburg), and the URC (University of Johannesburg) for funding this work.

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Singlet fission induced by singlet-singlet annihilation in a metallo-supramolecular polymer of α,ω−bis(tpy)terthiophenes with Zn^{2+} ion coupler

M. A. Thottappali[1], M. Menšík[1], D. Rais, P. Guloglu[1], P. Toman[1], J. Pfleger[1]
[1]*Institute of Macromolecular Chemistry, Prague, Czech Republic.*

Singlet fission (SF) is a photo-induced process, in which two triplet excitons are generated from a singlet exciton. SF thus transforms high energy photon to less energetic longer lived species that can be utilized, for example, for better light harvesting in photovoltaic devices, utilizing also energy that would be otherwise dissipated to heat. Metallo-supramolecular polymers (MSPs) attracted considerable attention in the field of optoelectronics due to their unique properties like possibility of the post-synthesis tuning, reverse assembling, and self-healing. It has been reported recently [1] that thin films of MSP based on α,ω−bis(tpy)terthiophene unimers assembled with Zn^{2+} ion couplers (TT-Zn) facilitate a SF process upon photoexcitation.

The time-resolved transient absorption studies of thin films of TT-Zn (Fig. 1) proved that the SF process occurs after the photoexcitation at 330 nm, leading to a higher excited state S_n. Contrary, after the photoexcitation to the state S_1 using a laser pulse at 440 nm, excitons decay by singlet-singlet collisions [2]. It has been confirmed by both the dependence of the decay rate on the pump fluence and by the power-law decay of singlet excitons in time. It has been shown that the process of the singlet-singlet annihilation is accompanied by several subsequent processes (Fig. 1, right) [2]. First, the singlet-singlet annihilation is controlled by the Förster process $S_1 + S_1 \rightarrow S_0 + S_n$, and not by the diffusion. Second, after this Förster energy transfer one of the unimers is deexcited, while the second one is excited to a higher excited state, similarly to the photoexcitation at the wavelength 330 nm. The resulting S_n state undergoes the SF process, during which the triplet pair is formed. Subsequently, the hot triplet pair can dissociate and two independent triplets move by a slow diffusion process. In the last stage, the two triplets annihilate, which can possibly explain a weak signal of singlets in very long-time delay after photoexcitation. The time dependences of the triplet states formation prove that the triplets are not formed by the inter-system crossing ($S_1 \rightarrow T_1$) but the rate of their formation is fully controlled by the singlet-singlet annihilation. The time evolution of the diffusion coefficients of triplets was also determined showing apower-law decrease in time and faster decrease with increasing initial pump fluence. Thus, in thin films of TT-Zn, the transition rate from singlets to long-lived triplet excitons increases with the initial excitation density.

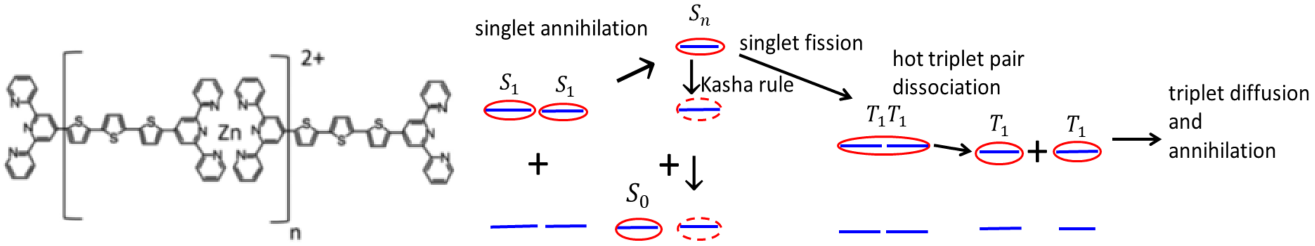

Fig. 1. Left, scheme of the metallo-supramolecular polymer of α,ω−bis(tpy)terthiophenes with Zn^{2+} ion couplerss. Right, subsequent processes of the singlet-singlet annihilation, higher singlet state formation, singlet fission, triplet pair dissociation, triplet diffusion and annihilation.

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Tuning Hydrogen-Bond Derived Supramolecular Assembly in Bifunctional α-Oligothiophenes

R. Thümmler[1], F. Lissel[1,2*], B. Voit[1,2]

[1]*Leibniz Institute of Polymer Research Dresden e.V., Dresden, Germany*
[2]*Faculty of Chemistry and Food Chemistry, Dresden Technical University, Dresden, Germany*
[*]*lissel@ipfdd.de*

Molecular Organic Semiconductors (OSCs) present a promising alternative to established inorganic materials due to the accessibility of diverse, well-defined and highly regular structures composed of abundant elements. Additionally exhibiting inexpensive solution-processability, OSCs allow the utilization of high-throughput techniques, such as printing, for device fabrication [1,2]. The high (electro)chemical stability and suitable charge-carrier mobilities of oligothiophenes, in combination with facile functionalization routes, render them a convenient class for the exploration and establishment of structure-property relationships [2-4].
The aim of this work is the synthesis of dynamic supramolecular structures based on bifunctional linear all-α-oligothiophenes with varying backbone lengths. Incorporating multiple hydrogen bonding sites on the oligomers allows to build crosslinked and responsive networks, and the weak bonding character can potentially enhance resilience towards mechanical deformation as well as conclusively enabling self-healing properties. As minimal changes in the material's molecular weight upon the introduction of functional groups are favorable in order to maximize the thiophene's gravimetric capacity, the choice of H-bonding motifs, each composed of donor (D) and acceptor (A) sections, is guided by limiting their size. As functional groups for the self-complementary double (AD) and quadruple (AADD) H-bonding sites, carboxyl groups and 2-Ureido-4[*1H*]-pyrimidinone will be used, respectively. To incorporate triple hydrogen bonds, the introduction of different substituents, namely 2,6-dihydroxypyridine (DAD) and *1H*-pyrrole-2,5-dione (ADA), is needed.

Keywords: Oligothiophene, Hydrogen-Bond, Self-Assembly, Supramolecular Polymer, Organic semiconductor

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Electropolymerized Nanostructured Polypyrrole Films

D.V. Tumacder[1,2,*], P. Bober[1]

[1]Institute of Macromolecular Chemistry, Czech Academy of Sciences, 162 06 Prague 6, Czech Republic
[2]Faculty of Science, Charles University, 128 43 Prague 2, Czech Republic
** E-mail: tumacder@imc.cas.cz*

Polypyrrole (PPy) is a promising conducting polymer due to its excellent electronic and ionic conductivity, electroactivity, and its other unique properties relevant for various applications. Recently, the studies have been focused on the controlling of its morphology and enhancing its electronic and electrochemical properties by introducing structure guiding agents like organic dyes during polymer chemical synthesis [1]. The incorporation of dyes, such as safranin [2,3] and acid blue [4,5] leads to the formation of PPy nanofibers or nanotubes with enhanced conductivity.

In this study, PPy, PPy-safranin and PPy-acid blue 25 films were electropolymerized through cyclic voltammetry in 0.2 M HCl aqueous solution with a potential window of –0.30 to 0.75 V versus Ag/AgCl reference electrode for 25 cycles at a scan rate of 20 mV/s [6,7]. Morphology, electroactivity, and capacitive behavior of the films were studied using scanning electron microscopy, cyclic voltammetry, and Raman spectroscopy. Typical globular structures were formed for the electropolymerized PPy film. The presence of safranin in PPy forms cauliflower-like nanostructures while nanofibrillar structures are observed in the presence of acid blue 25. Bipolaron:polaron ratio of PPy-safranin and PPy-acid blue 25 films has increased indicating better order of chain organization as compared to pristine PPy. Moreover, the effect of safranin and acid blue 25 augmented the electroactivity of the films with an areal capacitance higher than PPy film. PPy-acid blue 25 possessed the highest areal capacitance among the prepared films. The electrochemical stability of PPy was improved from 84% capacitance retention to 89% and 99% with the presence of acid blue 25 and safranin, respectively. Hence, the incorporation of organic dyes like safranin and acid blue 25 to pyrrole electropolymerization stimulated the growth of nanostructured PPy with improved electroactivity.

Keywords: Polypyrrole, eletropolymerization, safranin, acid blue 25

Acknowledgments

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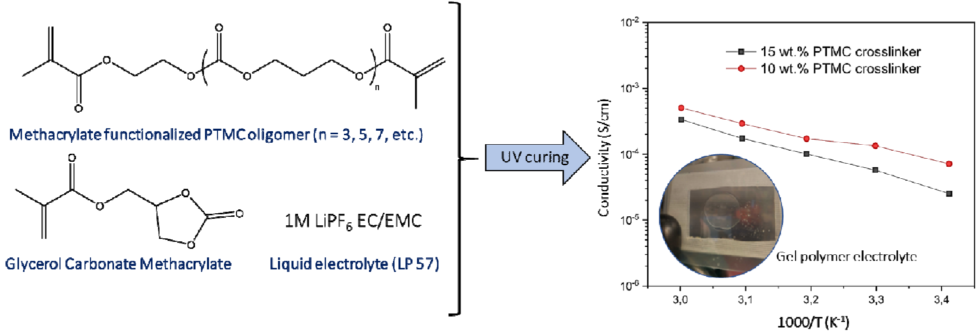
Gel Polymer Electrolytes Based on Methacrylate End-Capped Poly(trimethylene) Carbonate Oligomers for Lithium Batteries

Vidyanand Vijayakumar[1*], Daniel Brandell[1], Jonas Mindemark[1]
[1]Department of Chemistry - Ångström Laboratory, Structural Chemistry Unit, *Uppsala University, Uppsala, Sweden.*
[*]*vidyanand.vijayakumar@kemi.uu.se*

High molecular weight (> 10000 g/mol) linear poly(trimethylene carbonate) (PTMC) is a well-established polymer host used in solid-state polymer electrolytes for lithium battery application. Despite possessing several interesting electrochemical features as suitable electrolytes, the slow polymer chain dynamics of high molecular weight PTMC is often unfavorable for fast ion conduction.[1] Herein, we aim at designing and exploring the prospects of low molecular weight linear PTMC oligomers (< 2000 g/mol) as an alternative to the conventional high molecular weight linear PTMC polymers used in polymer electrolytes. The oligomeric PTMC expects to improve the polymer host's amorphous character, fastening the chain dynamics beneficial for enhanced ion transport in both solid-state and gel polymer electrolytes. However, the oligomeric PTMCs suffer from poor mechanical stability. They exist as viscous liquids at room temperature, unlike the solid/semi-solid high molecular weight PTMC counterparts, preventing the conventional solution/melt casting methods from processing them into self-standing polymer electrolyte membranes. In this regard, this work deals with tweaking the structure of low-molecular-weight linear PTMC oligomers by end-capping with methacrylate functionalities, making them prone to free-radical polymerization on ultraviolet (UV)-light irradiation (Scheme 1).[2] The functionalized PTMC crosslinker oligomers are viscous liquids easily soluble in carbonate-based organic liquid electrolytes. A precursor solution based on methacrylate-end-capped PTMC and another methacrylate monomer called glycerol carbonate methacrylate (GCMA) in the presence of LP57 liquid electrolyte (1M $LiPF_6$, EC/EMC) delivers gel polymer electrolytes with solid-like operability on UV-light-assisted free-radical crosslinking process. The preliminary results indicate the gel polymer electrolytes possess room temperature ionic conductivity in the range of 0.1–0.01 mS/cm.



Scheme 1: Structure of the linear and functionalized PTMC oligomers and the illustration of UV-light crosslinking for polymer electrolyte processing.

Keywords: Lithium-ion batteries, polymer electrolytes, ionic conductivity, electrochemical stability

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Oxygen heteroatom enhanced sulfur-rich polymers synthesized by inverse vulcanization for high-performance lithium-sulfur batteries

Haoran Wang[1,2], Bowen Zhang[1], Romy Dop[1], Peiyao Yan[1], Alex R. Neale[2], Laurence J. Hardwick[2*] and Tom Hasell[1*]

[1]*Department of Chemistry, University of Liverpool, Liverpool, UK*
[2]*Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool, UK*
[*]*hardwick@liverpool.ac.uk*; [*]*T.Hasell@liverpool.ac.uk*

The "shuttle effect" is one of the key issues to overcome for the commercialization of Lithium-sulfur (Li-S) batteries.[1] A "chemical confinement" strategy has been recognized as one of the most efficient way to alleviate the dissolution of long-chain lithium polysulfides.[2] Here, Sulfur-rich polymers, synthesized through inverse vulcanization[3,4], with tunable heteroatom containing crosslinkers were investigated as the active S containing cathode material within Li-S cells. The polymers possess up to 73% active sulfur while, importantly, not containing any unreacted, crystalline sulfur. Li-S cells based on the polymers achieve specific capacities of 1206 mAh gs^{-1} for an active material polymer containing 80 wt% sulfur, with 10 wt% of a structural crosslinker (dicyclopentadiene), and 10 wt% of an oxygen containing crosslinker (ethylene glycol dimethacrylate). The high capacity achieved within this composition is associated with of this sample, in a higher average sulfur rank within the polymer structure. Furthermore S-polymers with heteroatomic crosslinkers exhibited lower capacity fade (0.093% per cycle) compared with polymers without functionalized heteroatomic crosslinkers (0.165% per cycle) and elemental sulfur (0.312% per cycle). X-ray photoelectron spectroscopy highlights the inherent binding between the ester group carbonyl oxygen within the crosslinker to the long-chain lithium polysulfides, which may inhibit dissolution of these intermediates.

Keywords: Li-S cells, chemical confinement, sulfur-rich polymers, inverse vulcanization, oxygen heteroatoms

Acknowledgments

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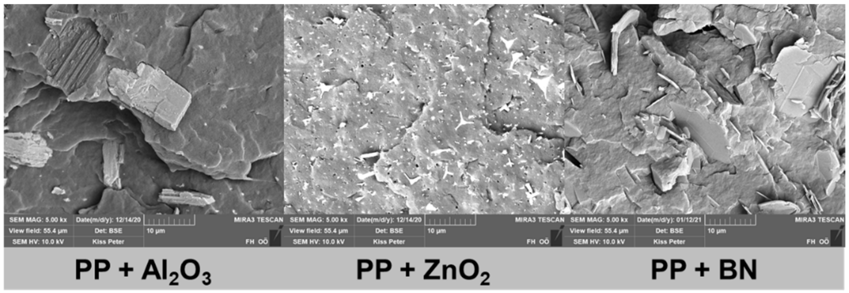
Relationship between the interface of matrix and filler and the thermal conductivity as well as the mechanical properties of the composite

Nina Wolfsgruber [a d *], Christoph Burgstaller [a], Andreas Tanda [b], Peter Kiss [c], Vasiliki-Maria Archodoulaki [d]

[a] *Transfercenter für Kunststofftechnik GmbH, Franz-Fritsch Straße 11, A 4600 Wels, Austria*
[b] *O.K.+Partner, Matzigthalstraße 21, A 4663 Laakirchen, Austria*
[c] *University of Applied Science Upper Austria Campus Wels, Stelzhamerstraße 23, A 4600 Wels, Austria*
[d] *TU Vienna Institute for Materials Science, Getreidemarkt 9, A 1060 Wien, Austria*
[*] *nina.wolfsgruber@tckt.at*

A continuing trend in plastics technology is the integration of functions with simultaneous miniaturization of components, especially in electrical components such as headlights or charging columns. This miniaturization increases power density, and heat must be dissipated to avoid damaging the components[1]. One promising option here are electrically insulating, thermally conductive plastics, as these can be brought into direct contact with the electronic components. However, the properties of such polymer matrix composites of fillers and plastics are currently not satisfactory, since above all the achievable thermal conductivities are very limited despite the use of highly thermally conductive fillers. Not only the material itself, but also the quantity, size and shape of the filler strongly influence the thermal conductivity. For example, a mixture of elongated particles or platelets with a spherical filler can achieve a significant improvement in thermal conductivity, since the different particle shape creates thermal conduction paths that improve thermal conductivity[2 3].



SEM images of PP with different fillers

The aim of this work is to understand the interaction of filler and matrix at the interface. We prepared compounds from four different matrices and four different fillers to investigate the mechanical properties and the thermal conductivity and to get a better understanding of the interaction between the filler and the matrix. In order to be able to better describe the processes at the interface, acoustic emission tests were carried out on the test specimens during the tensile test. An attempt was also made to describe the measured values by means of a mathematical model in order to obtain information about the interaction between matrix and filler at the interface. We found that the largest influence on the thermal conductivity is the particle shape of the filler. This correlation is also found for the mechanical properties.

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Using sound to synthesize covalent organic frameworks in water

Wei Zhao[1,2], Peiyao Yan[1], Haofan Yang[1,2], Mounib Bahri[3], Alex M. James[1], Hongmei Chen[1], Lunjie Liu[1], Boyu Li[1], Zhongfu Pang[1,2], Rob Clowes[1], Nigel D. Browning[3], John W. Ward[1,2*], Yue Wu[1*] & Andrew I. Cooper[1,2*]

[1] *Materials Innovation Factory and Department of Chemistry, University of Liverpool, Liverpool, UK*
[2]*Leverhulme Research Centre for Functional Materials Design, Materials Innovation Factory and Department of Chemistry, University of Liverpool, Liverpool, UK*
[3]*Albert Crewe Centre for Electron Microscopy, University of Liverpool, Liverpool, UK*
[*]*Corresponding Author's E-mail address: john.ward@liverpool.ac.uk; yue.wu@liverpool.ac.uk; aicooper@liverpool.ac.uk*

Covalent organic frameworks (COFs) are typically synthesized using solvothermal conditions (>120 °C, >72 hours) in harmful organic solvents.[1] Here we report a strategy to rapidly (<60 minutes) synthesize imine-linked COFs in aqueous acetic acid using sonochemistry and thus avoid most of the disadvantages of solvothermal methods.[2] Using the sonochemical method, we synthesized to our knowledge previously unreported COFs. The crystallinity and porosity of these COFs is comparable to or better than those of the same materials made by established solvothermal routes. The sonochemical method even works in sustainable solvents, such as food-grade vinegar. The generality of the method is shown in the preparation of a 2D COF with pendant functionalization and of a COF with 3D connectivity. Finally, a COF synthesized sonochemically acts as an excellent photocatalyst for the sacrificial hydrogen evolution from water, showing a more sustained catalytic performance compared with that of its solvothermal analogue. The speed, ease and generality of this sonochemical method together with improved material quality makes the use of sound an enabling methodology for the rapid discovery of functional COFs.

Keywords: Covalent organic frameworks, sonochemistry, photocatalyst hydrogen evolution.

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Electrochromic properties of iron (II) metallo-supramolecular polymers

U. Acharya[1*] , A. Šturcová[1], A. Chernyshev[2], J. Zedník[2], J. Vohlídal[2], J. Pfleger[1]

[1] *Institute of Macromolecular Chemistry, Czech Academy of Sciences, 162 06, Prague 6, Czech Republic*
[2]*Faculty of Science, Charles University, 128 40 Prague 2, Czech Republic*
[*]*acharya@imc.cas.cz*

Electrochromic (EC) materials have gained vast attention recently due to a wide range of applications like optical displays and switching devices, smart windows, camouflage objects, flexible electronics, smart textiles, robotics, etc. [1]. Various electrochromic materials are already known, such as polyoxometalates, transition metal oxides, coordination compounds, and conducting polymers [2]. Nowadays, metallo-supramolecular polymers (MSPs) are gaining increasing attention as EC materials due to easy processability, stability, and reversible switching between different oxidation states.

In this work, new MSPs derived from unimers with thieno[3,2-b]thiophene central unit, bis(tpy) end groups linked through various linkers (none, ethynediyl, 1,4-phenylene, and 2,2´-bithophene-5,5´-diyl) are presented [3]. The Fe-MSP films were prepared by spin-casting on Indium Tin Oxide (ITO) glass and characterized by atomic force microscopy, cyclic voltammetry, UV-Vis, and Raman spectroscopies.

The relation between the structure and electrochromic performance of unimers and related Fe(II) MSPs revealed that, among studied MSPs that derived from the unimer with no linker showed the highest optical contrast and coloration efficiency (CE = 641 $cm^2\ C^{-1}$) as well as the fastest optical response. This makes it an excellent candidate for a use in electrochromic devices. The electro-chemical oxidation by the applied voltage resulted in the reversible changes in the Raman spectral pattern of this MSPs consisting in the dumping of the bands belonging to the thieno[3,2-b]thiophene central unit. .

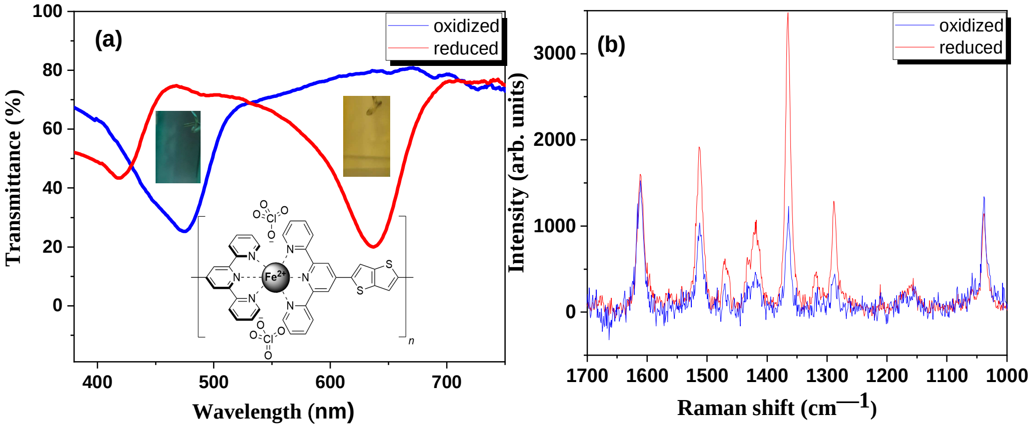

Fig: (a)Photographs, structure and UV/vis transmittance spectra (adapted from reference 3) (b) RAMAN spectra of Fe-MSP EC film.

Acknowledgments

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Roll-to-Roll printing of magnesium oxide embedded in PVA matrix as an efficient moisture barrier for Organic Photovoltaics

Varun Adiga[1] , Hasitha Weerasinghe[2], Praveen C Ramamurthy[3*]

[1] *Indian Institute of science, Bengaluru, India*
[2] *Commonwealth Scienctific and Industrial Research Organization, Victoria, Australia*
[3] *Indian Institute of science, Bengaluru, India*
[*] *onegroupb203@gmail.com*

Advances in Organic photovoltaic devices (OPVD) and their stability through ultra-high moisture barrier packaging films have led to various cost-effective developments [1][2]. Moisture barriers have numerous well-known applications in the field of electronics, food packaging, pharmaceutical, etc [3][4]. In this work, an attempt is made to incorporate magnesium oxide (MgO) nanoparticles in polyvinly alcohol (PVA) matrix to achieve lower water vapor transmission rates (WVTR) to lower the degradation in OPVD. The films printed/coated through Roll-to-Roll (RTR) technique onto PET films were tested for optical transparency and found ~80% around visible region. The morphology of these films were performed using scanning electron microscope and atomic force microscopy which exhibits the nanoparticle behaviour of the filler material. The RTR printed MgO embedded in PVA matrix (MEP) which was coated onto PET films of 150µm showed excellent transparency in the visible region, thereby showing its capability of packaging not only in electronic application as well as in food and pharmaceutical packaging. Additionally, WVTR tests through cavity ringdown spectroscopy technique confirms two orders lower moisture barrier property than that of neat PET films as shown in figure 1 suggesting a good hermetic seal for future OPVD.

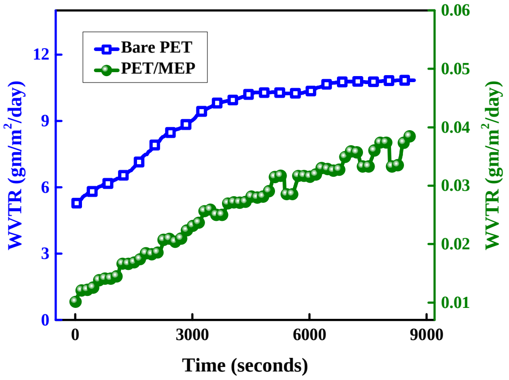

Fig. 1 WVTR of MgO embedded in PVA matrix coated on PET along with bare PET using CRDS technique.

Keywords: polymer, moisture barrier, water vapor transmission rate, cavity ringdown spectroscopy, roll-to-roll printing

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Physics, Physical Chemistry, and Characterization of Polymers

Magneto-polymer hydrogels with large length changes in response to magnetic stimuli

F.J. Vazquez-Perez[1], C. Gila-Vilchez[1], J.D.G. Duran[1], A. Zubarev[2], L. Alvarez de Cienfuegos[3], L. Rodriguez-Arco[1], M.T. Lopez-Lopez[1]*

[1]*Universidad de Granada, Departamento de Física Aplicada, Granada, Spain*
[2]*Ural Federal University, Department of Theoretical and Mathematical Physiscs, and M N Mikheev Institute of Metal Physics, Ural Branch of the Russian Academy of Science, Ekaterinburg, Russia*
[3]*Universidad de Granada, Departamento de Química Orgánica, Granada, Spain*
**modesto@ugr.es*

Among the different stimuli for remote control of soft actuators, magnetic stimuli stand out for their ease of application, tunability, fast response, and deep and safe penetration in most media. This field of soft actuators that respond to magnetic stimuli has been largely dominated by elastomers, although recently, research interests are moving towards polymer hydrogels, with the emergence of some excellent actuators based on hydrogels made from natural polymers [1-2]. Nevertheless, the actuation of hydrogels is a challenging field, such as achieving significant and reliable responsiveness. Furthermore, most soft actuators primarily experience bending and twisting movements, whereas actuators that undergo reversible changes in length or volume in response to an applied magnetic field are rare.

In this work, we demonstrate that magnetic hydrogels prepared by dispersing magnetic particles within an incipiently formed physical matrix of alginate fibres greatly change their length in response to an applied magnetic field [3]. To quantify this responsiveness to magnetic stimuli, we first analysed the length changes of these hydrogels during the process of magnetization. We found that the length changes achieved by hydrogels with a low degree of network crosslinking, and thus low stiffness (Young's modulus), were much larger than any of the previously reported values for magneto-polymer composites with similar particle loading and under comparable magnetic field strengths. However, increasing the level of crosslinking of the alginate hydrogels resulted in higher Young's modulus, which in turn restricted the responsiveness to the applied magnetic field. We also found that, in addition to the elasticity of the matrix, the responsiveness can also be modulated by modifying the concentration of magnetic particles or the distribution of particles within the hydrogel. Furthermore, we present a theoretical model that demonstrates that the aggregation of particles into clusters, together with the softness of the network of alginate fibres, was responsible for such high length changes. Finally, as a proof-of-concept application, we present a valve containing a magnetic gel that can be opened and closed remotely by the action of a magnetic field. To conclude, our results demonstrate that an adequate design at the microscale of magnetic hydrogels is the basis for obtaining large and reversible length changes at the macroscale in response to magnetic stimuli.

Keywords: alginate, magnetic particles, composite hydrogel, soft actuator, microstructural properties, mechanical behaviour

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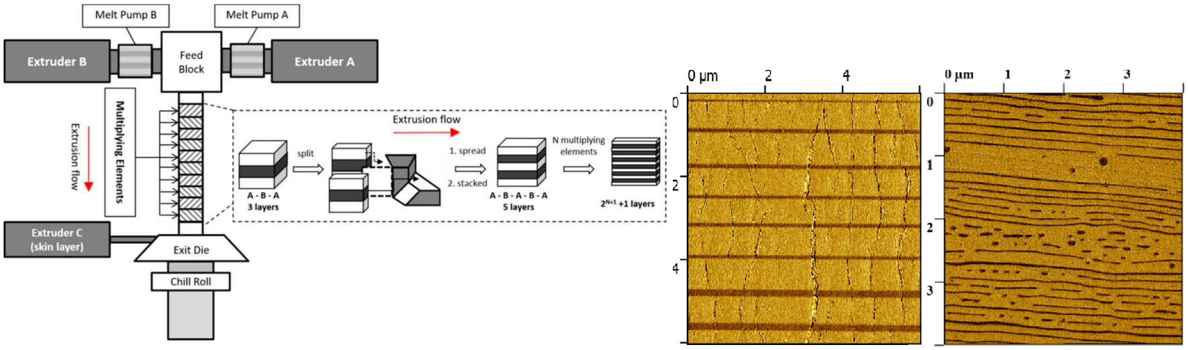
Interfaces and interphases in multilayer polymer films

G. Miquelard-Garnier[1,*], C. Sollogoub[1], A. Guinault[1], J. Peixinho[1], A. Bironeau[1], M. Chebil[1], Q. Beuguel[1], A. Dmochowska[1]

[1] *Laboratoire PIMM, CNRS, Arts et Métiers Institute of Technology, Cnam, HESAM Université, 75013 Paris, France*
[*]guillaume.miquelardgarnier@lecnam.net

In this talk, we will focus on multilayer polymer films obtained from multilayer coextrusion, from the point of view of their interfaces. This process allows the fabrication of films in which thousands of alternating layers of two (or more) polymers are stacked atop one another where each layers have a nanometric thickness. First we will describe briefly how the process works and potential applications of such films [1], and will then focus on its limitations: when pushed to the nanoscale limit, interfacial instabilities occur and lead to layer breakup [2]. Simple experiments and physical models about the nature of these instabilities will be presented. [3-6] In a last part we will focus on the rheological properties of compatibilized interfaces (interphases) in such films. [7]



Left: schematic of the multilayer coextrusion process. Right: AFM images of nanolayered films (continuous layers in the left image, broken nanolayers in the right image)

Keywords: interfaces, interphases, multilayer coextrusion, interfacial instabilities, ultra-thin films

Acknowledgments

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The Analytical Ultracentrifuge: From Structural Resolution of Polymer Systems to Nanomedicines

G. Cinar[1,2], O.J. Valderrama[1,2], I.Nischang[1,2*]

[1]*Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstr. 10, 07743 Jena, Germany*
[2]*Jena Center for Soft Matter, Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany*
[*]*ivo.nischang@uni-jena.de*

The origins of colloid and polymer science date back to approximately 100 years ago. These were accompanied by the development of experimental opportunities to study disperse systems. A key experimental approach and instrument finding its origin at that time is an analytical ultracentrifuge (AUC).[1] The inception of the AUC also coincided with the rise of the macromolecular hypothesis by Hermann Staudinger with his paper entitled "Über Polymerisation" in 1920, which laid the foundation of the term "polymerization" and the understanding of polymers as high molar mass molecules. Primarily, the AUC was developed as a tool for the characterization of particles, proteins, and macromolecules of natural origin. Together with modern numerical opportunities, it matured from a classical and powerful technique in the area of biophysics directed toward new apllications in polymer, colloid, and materials science. Alongside, it is accepted as a characterization tool by the European Medicines Agency (EMA) and Food and Drug Administration (FDA).

Based on the above perspective, the modern application of an AUC enables characterization of solution components starting from materials of only a few thousand g mol^{-1} up to the maximum of the colloidal size range.[1] This is particularly enabled by the widely adjustable rotor speeds and, consequently, centrifugal forces. These modern experimental opportunities are enabled by multidetection as well as the robust application of a variety of temperatures.

After introducing general polymer and colloid parameters determinable by an AUC in a simplified fashion,[1] the AUC's modern experimental opportunities developed and utilized in our contemporary research on new systems are featured. Examples concern polymers,[2] dynamics of polymer (self-)assemblies containing cargo[3,4] as well as medical nanoparticles containing drug and targeting dye moieties.[5] For the latter, the study of dynamic processes such as material stability in a variety of solutions, the material-biofluid interactions, and material erosion are highlighted.

Keywords: analytical ultracentrifugation, medical nanoparticles, micelle, nanomedicine, polymer

Acknowledgments

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Highly Tunable Nanostructures in a Doubly pH-Responsive Pentablock Terpolymer in Solution and in Thin Films

F. A. Jung[1],C. Tsitsilianis[2], C. M. Papadakis[1*]

[1]*Technical University of Munich, Physics Department, Soft Matter Physics Group, 85748 Garching, Germany*
[2]*University of Patras, Department of Chemical Engineering, 26504 Patras, Greece*
[*]*papadakis@tum.de*

Multiblock copolymers with charged blocks are complex systems, which show great potential for enhancing the structural control of block copolymers. We investigate a pentablock terpolymer PMMA-*b*-PDMAEMA-*b*-P2VP-*b*-PDMAEMA-*b*-PMMA, that contains two types of midblocks, which are weak cationic polyelectrolytes, namely poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) and poly(2-vinylpyridine) (P2VP), and these are end-capped with short hydrophobic poly(methyl methacrylate) (PMMA) blocks [1]. The self-assembly behavior of this type of charged multiblock copolymer in dilute aqueous solution and in thin films is discussed in dependence on the degrees of ionization of the P2VP and PDMAEMA blocks, which are altered in a wide range by varying the pH value. High degrees of ionization of both blocks prevent structure formation, whereas microphase-separated nanostructures form for partially charged and uncharged states. In solution, the nanostructure formation is governed by the dependence of the solubility of the P2VP block and the flexibility of the PDMAEMA blocks on the degree of ionization. In contrast, in thin films, the dependence of the segregation strength on the degree of ionization is key. Furthermore, the solution state plays a crucial role in the film formation during spin-coating. Overall, both the mixing behavior of the three types of blocks and the block sequence, governing the bridging behavior, result in strong variations of the nanostructures and their repeat distances.

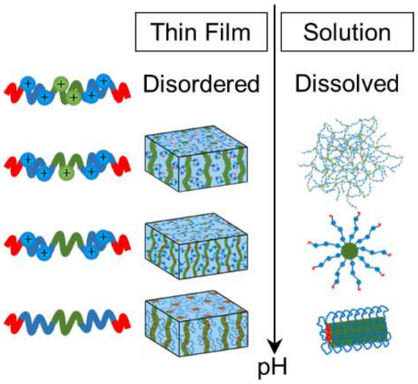

Figure 1. *Schematic representation of the charge state of the pentablock terpolymer along with the thin film and solution structures in dependence on the degrees of ionization of the two midblocks.*

Keywords: block polymers, pH-responsive polymers, scattering methods

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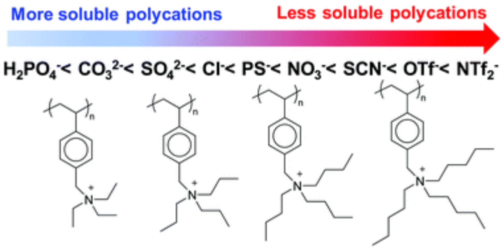
Responsive polycations with hydrophobic counterions

Vikram Baddam[1], Erno Karjalainen[2], Heikki Tenhu[1]

[1]*University of Helsinki, Finland*
[2]*VTT Technical Research Centre of Finland*

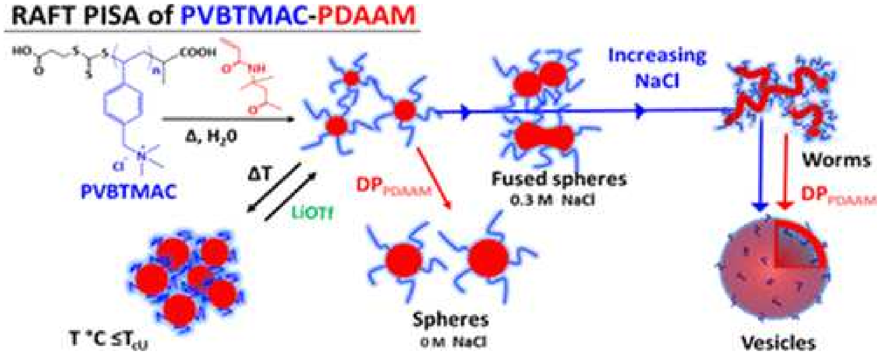
The balance of electrostatic and hydrophobic interactions affects thermal behavior of polyelectrolytes in water. A nice example of this is a series



where only the polymer with ethyl substituents shows UCST, the rest are LCST polymers. Different salts have different effects and thus, the phase separation temperatures can be varied in a wide range.[1]

This presentation concentrates on a polycation poly(vinylbenzyl trimethylammonium triflate), PVBTMA, and first, on block copolymers of the polycation and PEG. The counterion in this case was hydrophobic triflate, which reduces the solubilities of the polymers, and in aqueous triflate solutions they show UCST behavior. The phase separation process upon cooling aqueous PEG-PVBTMA-OTf is, however, complicated and strongly dependent on the length of the cationic block. When the polymers phase separate, particles are formed. The mechanism of colloidal stability depends on the cationic block length.[2-3]

A better soluble chloride of the polycation, PVBTMA-Cl has been used as a macroinitiator in PISA polymerization of diacetone acrylamide (DAAM). A whole spectrum of particle morphologies was obtained simply by adjusting the salt (NaCl) concentration. In aqueous triflate solutions the PVBTMA chains on particle surfaces respond to temperature, and interestingly, under certain conditions they show two-step transitions.[4]



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Development of Functional Surfaces with Controllable Wettability and Water Adhesion

Spiros H. Anastasiadis[1,2,*,#]

[1] *Institute of Electronic Structure & Laser, Foundation for Research & Technology-Hellas, 70013 Heraklion, Crete, Greece*
[2] *Department of Chemistry, University of Crete, 71003 Heraklion Crete, Greece*
[*]*spiros@iesl.forth.gr*

The design of multifunctional surfaces based on biomimetic structures has gained the interest of the scientific community. Such biomimetic structures can be achieved by using suitable coatings onto appropriately micro/nano-structured substrates. Hierarchically roughened surfaces can be prepared by irradiating a mettalic or semiconductor surface using ultrafast (femtosecond) laser or by utilizing a polymer nanocomposite coatings when a soft substrate surface is to be modified; suitable chemistry of the coatings provides the desired functionality. We will demonstrate three different cases: (a) The utilization of end-anchored polymer chains onto hierarchical Si surfaces results in surfaces that exhibit reversible and controllable wettability to temperature and/or pH from the "parahydrophobic" behavior of natural plant leaves all the way to superhydrophilic properties in response to external stimuli [1]. (b) The use of polymer nanocomposite coatings onto polymeric substrates, where the inorganic particulate additives create the appropriate roughness and the polymer matrix provides the proper functionality, can produce superhydrophobic and water repellent surfaces as well as superoleophobic ones [2]. (c) Allowing a laser irradiated metallic surface to remain under low temperature heating or under moderate vacuum, which can lead to the development of superhydrophobic and, even, water repellent metal alloy surfaces; the ones that remained under vacuum were water-repellent (superhydrophobic with very low water adhesion), whereas the ones that underwent thermal processing exhibited superhydrophobicity with high water adhesion [3].
In collaboration with M. A. Frysali, Th.-M. Chatzaki, F. Krasanakis, L. Papoutsakis, K. Chrissopoulou, F. Gojda, M. Loulakis, S. Tzortzakis

Keywords: functional surfaces, responsive surface, superhydrophobic surface, water-repellence, contact angle, laser irradiation

Acknowledgments
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Synthesis and Self-Assembly in Aqueous Media of Amphiphilic Bottlebrush Block Copolymers Towards Anisotropic Dynamic Aggregates

Julien Rosselgong[1, 2], Guillaume Declerc[1], Gireesh Kumar Balakrishnan Nair[2], Christophe Chassenieux[2], Maud Save[1], Elise Deniau[1,2]

[1] *CNRS, Université de Pau & des Pays de l'Adour, E2S UPPA, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, IPREM, UMR5254, 64000, PAU, France.*
[2] *CNRS, Le Mans Université, Institut des Molécules et Matériaux du Mans, IMMM, UMR6283, 72000, LE MANS, France.*
**elise.deniau@univ-pau.fr*

The goal of the present work is to synthesize amphiphilic block copolymers containing a brush block that can exhibit reversible pH-controlled self-assembly in aqueous media into anisotropic nanostructures at equilibrium. To address this challenge, bottlebrush diblock copolymers of *tert*-butyl acrylate (*t*BA) and *n*-butyl acrylate (*n*BA) are synthesized by using two successive reversible deactivation radical polymerization (RDRP) techniques prior to be acidolyzed to provide the amphiphilic copolymers. Nitroxide mediated polymerization (NMP) makes possible to synthesize the P*t*BA-*b*-(P*t*BA-*co*-BiBEA) (for ethyl 2-2-bromoisobutyryloxy acrylate) block copolymer backbone as precursor of the bottlebrush diblock copolymer. This RDRP method was chosen for its ability to polymerize the BiBEA inimer without interfering with the halide function[1] and for the absence of dissociation of the alkoxyamine chain end during next atom transfer radical polymerization (ATRP) step carried out at room temperature. Based on literature,[2] P(*t*BA-*co*-*n*BA) polymer brushes were synthesized by "grafting from" ATRP at low temperature with specific catalyst concentration in order to favor copper-catalyzed radical termination and hence avoiding macroscopic gelation of polyacrylate brushes. It is expected to tune the number of brushes by the fraction of BiBEA inimer. Each graft contains a fraction of *t*BA/*n*BA units with a composition of 50/50 in order to synthesize tempered hydrophobic blocks[3] after selective acidolysis of *t*BA into acrylic acid (AA) units. Thanks to both *i.* the bottlebrush structure, which allows constraining the packing parameter of the self-assemblies with a flat curvature, and *ii.* the strategy of decreasing the interfacial tension of the hydrophobic blocks by incorporating hydrophilic pH-sensitive AA units, the amphiphilic bottlebrush copolymers are expected to self-assemble in water within polymeric worm-like micelles at thermodynamic equilibrium. We will describe the synthesis of amphiphilic bottlebrush block copolymers comprising a PAA hydrophilic block and a tempered hydrophobic P(*n*BA-*co*-AA) brush block and show preliminary results on the self-assembling behaviour of di- and triblock copolymers dispersed in water characterized by light scattering and CryoTEM.

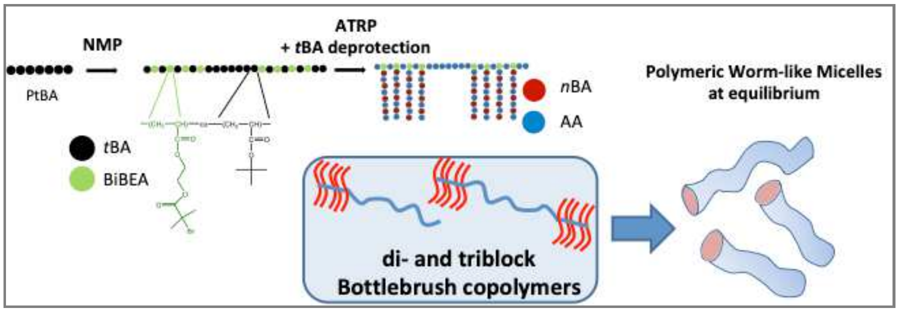

Figure. Synthesis of amphiphilic bottlebrush block copolymers leading to worm-like micelles in water.

Keywords: Amphiphilic Block Copolymers, Bottlebrush, RDRP, Dynamic, Self-assembly.

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Limits on the acceleration of the photooxidation of low-density polyethylene

J-L Gardette, J. Christmann, S. Therias*

Université Clermont Auvergne, CNRS, Clermont Auvergne INP, ICCF, F-63000 Clermont-Ferrand, France
sandrine.therias@uca.fr

The aim of this work was to evaluate the influence of light intensity on the rate of photooxidation of polyethylene. This is part of a general study performed with the objective of understanding the limits and accuracy of accelerated artificial weathering and the relevance of "highly" accelerated UV weathering tools.
The effect of irradiance on the rate of a photochemical process can be characterized by the reciprocity. A material obeys reciprocity if the degradation is a function of the total radiant energy and not a function of the rate at which the energy is applied. The reciprocity law can be described as:
I t = constant, with I = irradiance and t = exposure time.
The rates of photochemical processes as a function of light intensity usually follow the Schwarzschild law:
$k = A\, I^p$
where k is the reaction rate, A is a proportionality constant, I is intensity (or irradiance), and p is the Schwarzschild coefficient, which is an experimentally derived number. This may also be written as:
$I^p\, t$ = constant
When p =1, Schwarzschild's law becomes the reciprocity law.

Polyethylene films were subjected to accelerated photooxidative experiments at various UV light intensities from 1.1 up to 300 W.m^{-2} in the rage 300-400 nm, at a constant temperature fixed at 60°C. The rate of photo oxidation were measured by monitoring the amounts of carbonylated photoproducts using IR spectroscopy. Figure 1 shows the results obtained.

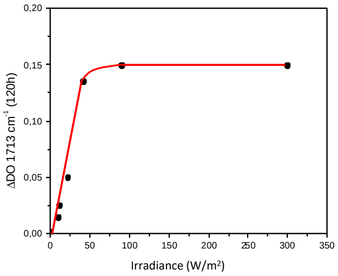

Figure 1. Absorbance after 120 hours of exposure as a function of the irradiance (PE films 100 microns)

The results show that no acceleration of the photooxidation was observed for irradiances above 50 W.m^{-2}, which means that the Schwarzschild coefficient was equal to 0. For lower levels of irradiance, the Schwarzschild coefficient p was always below 1 and approached 0.5. Considering the photooxidation mechanism, this is explained by the fact that recombination and/or disproportionation are faster than propagation as a result of excessive free radical generation resulting from light absorption at high irradiance levels.

Keywords: polymers; durability; photo- oxidation; accelerated ageing; reciprocity

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Diblock dialternating terpolymers by one-step/one-pot highly selective organocatalytic multimonomer polymerization

Jiaxi Xu, Xin Wang, Nikos Hadjichristidis*

[1]Polymer Synthesis Laboratory, Physical Sciences and Engineering Division, KAUST Catalysis Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia
**Corresponding Author's E-mail address: nikolaos.hadjichristidis@kaust.edu.sa*

Block copolymerization technology has attracted considerable interest in commercial applications as it combines the unique characteristics of each segment in the same molecule. By controlling the composition, molecular weight/molecular weight distribution, and structure of each component, the properties of the final block copolymers can be adjusted. This is why block copolymers are widely used in the industrial sectors of thermoplastic elastomers, drug delivery, membranes, lithography, and mesoporous materials. Therefore, the synthesis of well-defined block copolymers from a mixture of monomers without additional actions ("one-pot/one-step") is an ideal and industrially valuable method.[1,2] In addition, the presence of controlled alternating sequences in one or both blocks increases the structural diversity of polymeric materials but, at the same time, the synthetic difficulty.[3] Here, we discuss the synthesis of perfect diblock dialternating terpolymers having a sharp junction between the two blocks, with highly-controllable molecular weights and narrow molecular weight distributions ($Đ < 1.08$) by a "one-pot/one-step" ring-opening terpolymerization of a mixture of three monomers (*N*-sulfonyl aziridines; cyclic anhydrides and epoxides), with tert-butyliminotris(dimethylamino)phosphorene (*t*-BuP$_1$) as catalyst. The organocatalyst alternates between two distinct polymerization cycles without any external stimulus, showing high monomer selectivity and kinetic control. The proposed mechanism is based on NMR, *in situ* FTIR, SEC, MALDI-ToF, reactivity ratios, and kinetics studies.[4]

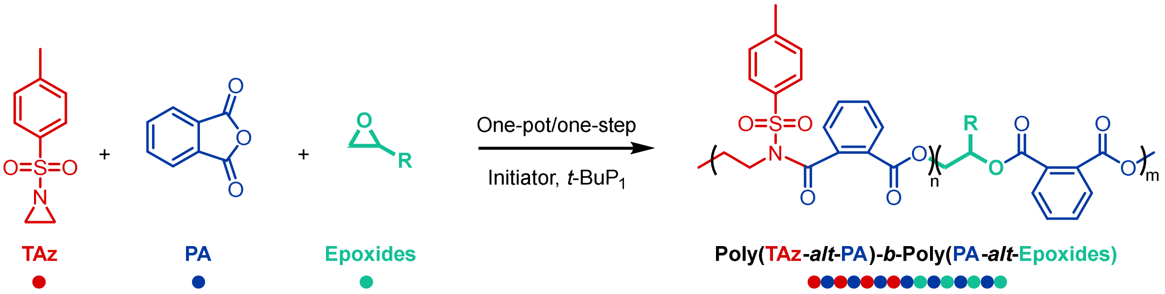

Figure 1. Terpolymerizations of *N*-sulfonyl aziridines, cyclic anhydrides, and epoxides towards diblock dialternating terpolymers.

Keywords: One-step/one-pot, Ring-opening alternating terpolymerization, Organocatalyst, Diblock dialternating terpolymers

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In-depth understanding of the adsorption of charged nanolatexes onto cellulose model surfaces

A. E. Alexakis[1,2] *, M.R.Telaretti Leggieri[1], T. Benselfelt[3], L. Wågberg[3] and E. Malmström[1,2]

[1]*KTH Royal Institute of Technology, School of Engineering Sciences in Chemistry, Biotechnology and Health, Department of Fibre and Polymer Technology, Division of Coating Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden*
[2]*Wallenberg Wood Science Centre (WWSC), Teknikringen 56, SE-100 44 Stockholm, Sweden*
[3]*KTH Royal Institute of Technology, School of Engineering Sciences in Chemistry, Biotechnology and Health, Department of Fibre and Polymer Technology, Division of Fibre Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden*
**Corresponding Author's E-mail address; aleale@kth.se*

Hitherto, cellulose modification has been primarily focused on chemical treatments involving grafting from and grafting to techniques when targeting biocomposite applications. However, physical modification (physisorption) involving latex nanoparticles, provides a versatile alternative. These nanolatexes are primarily synthesized via emulsion polymerization where low molecular weight surfactants are used to stabilize the hydrophobic core. However, the lack of covalent bonding between the surfactant and the hydrophobic polymer may lead to unfavorable effects, such as the migration of the former [1]. Nowadays, controleld radical polymerization techniques, such as reversible addition-fragmentation chain-transfer (RAFT) polymerization have been employed for the synthesis of such nanoparticles. Specifically, RAFT-mediated polymerization-induced self-assembly (PISA) in water exhibited great versatility on the chemistry of the produced nanolatexes [2]. Briefly, a hydrophilic polymer is chain extended in water with a hydrohpobic monomer resulting in the formation of amphiphilic diblock copolymers which in extension self-assemble producing nanosized colloidal particles. This approach, provides an holistic control over their final properties on-demand and thus these nanoparticles can act as model systems. Previously in our group, charged nanolatexes produced via RAFT-mediated PISA have been used in the compatibilization of cellulosse and cellulose nanofibrils in coating and composite applications [3,4]. However, there is a lack of an in-depth understanding of the key parameters that dominate their adsorption on the aforementioned substrates. In this work, cationically charged nanolatexes with varying surface charge and size were adsorbed onto anionically charged cellulose model surfaces (Figure 1). Their adsorption was monitoed by stagnation point reflectometry (SPAR) and quartz crystal microbalance with dissipation (QCM-D). Finally, their film formation properties were also investigated by field emission scanning electron microscopy (FE-SEM) and contact angle measurements.

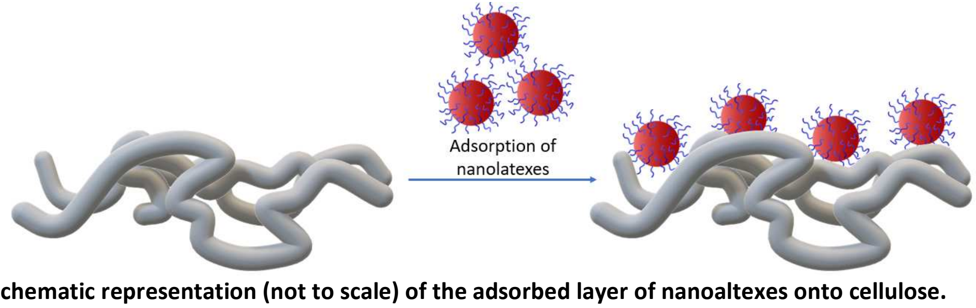

Figure 1: Schematic representation (not to scale) of the adsorbed layer of nanoaltexes onto cellulose.

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Cationic quaternary ammonium stabilizers in PISA: control of particle morphology with salt, hydrophobic counterions and temperature

V. Baddam, L. Välinen, L. Kuckling, H. Tenhu*
Department of Chemistry, University of Helsinki
**heikki.tenhu@helsinki.fi*

Polymerization-induced self-assembly (PISA) is now widely used to synthesize block copolymer particles with various morphologies like spheres, worms, and vesicles. In PISA, the block copolymers undergo in situ self-assembling during the polymerization of core-forming monomers. The final morphology depends on several parameters like the chemical composition of hydrophilic and hydrophobic blocks, temperature, solvent, salt, and pH [1]. Often spherical particles are obtained when strong polyelectrolytes are used as stabilizers. However, higher-order morphologies can be achieved when the charge density in the corona is diluted with nonionic co-stabilizers [2]. A full morphological spectrum can also be achieved by screening the charges with NaCl when styrene-based polycation is used as the stabilizer block [3].

Herein, we discuss the copolymerization of diacetone acrylamide (DAAM) with three chemically different polycation stabilizers. Styrene-based poly((vinylbenzyl) trimethylammonium chloride), PVBTMAC, and two more hydrophilic ones, poly((2-(methacryloyloxy)ethyl) trimethylammonium chloride), PMOTAC, and poly((3-acrylamidopropyl) trimethylammonium chloride) were chain extended with DAAM in aqueous salt solutions. When PVBTMAC is used, the particle morphologies transformed from spheres to cloudberries to vesicles with increasing the salt concentration at constant target DP of PDAAM. The particles obtained with either long PVBTMACs or using more hydrophilic cation chain transfer agents mainly build either spherical or raspberry-like morphologies. In the presence of LiOTf, styrene-based polycations undergo phase separation (UCST-type) upon cooling, whereas PMOTAC and PAMPTMAC are well soluble at any temperature. The morphologies of the particles change when the polymerization is conducted in aqueous LiOTf solutions at 70° C; fused spheres or even vesicles were observed in the case of short PVBTMAC. Upon cooling, the spheres fuse together or build worm-like networks. The particles obtained with the other two polycations do not respond to triflate and temperature.

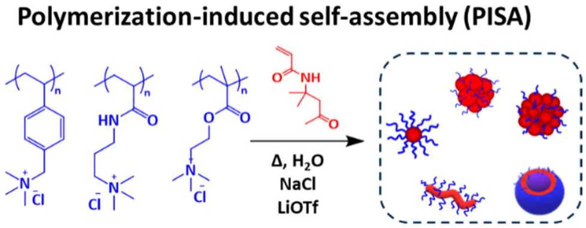

Figure 1. RAFT dispersion polymerization of DAAM with polycation CTAs, particles with various morphologies.

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Development and characterization of functional polymer coatings for temperature monitoring of battery systems in electric vehicles

D. Bautista-Anguís[1*], A. Wolfberger[1], S. Schlögl[1]

[1]*Polymer Competence Center Leoben GmbH, Leoben, Austria*
[*]daniel.bautista@pccl.at

The market share of battery electric vehicles (BEVs) has considerably increased during the last years due to global efforts for reducing CO_2 emissions. As a consequence, there is a high demand to monitor and prevent possible over-temperature of their batteries and other critical components during their service life which will assure their proper performance as well as the safety of passengers.

The use of temperature-responsive polymers in combination with low-cost metal oxide (MOx) gas sensors emerges as a promising and economically viable solution for indirect temperature monitoring of battery systems. In order to have a proper function of this concept, the developed functional polymer must release traceable gases at defined temperatures that can be easily detected by the MOx sensor.

To achieve the release of a sufficient amount of tracer gases at critical temperatures, two different approaches were studied. In the first approach, two azo-compounds, namely 1,1'-azobis(cyclohexanecarbonitrile) (ABCN) and azobisisobutyronitrile (AIBN) with decomposition temperatures in the range of 80°C - 150°C were introduced into polyurethane matrix coatings. The decomposition temperatures and the released gases of both azo-compounds were studied by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) and thermal desorption coupled to gas chromatography and mass spectrometry (GC-MS) and evolving gas analysis spectroscopy (EGA), obtaining similar values and a good correlation between the techniques.

As second approach, short chain thiols were used as cleavable functional groups for isocyanate-based polyurethane formulations. [1] Model compounds of 4,4'-methylenediphenylene isocyanate MDI, blocked with short-chain thiols were initially prepared to study their deblocking temperature by means of the aforementioned techniques. A functional polyurethane based on a polymeric MDI and a polyol coating with the most suitable thiol was prepared and characterized as a possible solution for the monitoring of battery systems.

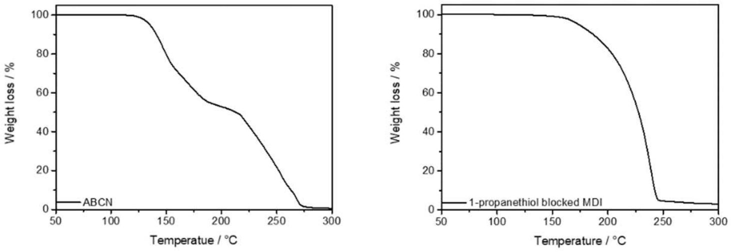

Figure 1: Thermal decomposition of ABCN and 1-propanethiol blocked MDI

Keywords: azocompounds, thiols, polyurethane, thermosensitive coatings, thermal characterization

Acknowledgments

The research work was performed within the cooperative R&D project "Galion" (*FFG Project No. 871676*) at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the Energy Research Programme funded by the Climate and Energy Fund of the Austrian Federal Government with contributions by VIRTUAL VEHICLE Research GmbH, Samsung SDI Battery Systems GmbH, Sensirion AG, Graz University of Technology and UnravelTEC OG. The PCCL is funded by the Austrian Government and the State Governments of Styria, Lower Austria and Upper Austria.

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Will the PVC Book Covers in Depositories Survive us?

R. Kalousková, L. Malinová, V. Benešová, J. Brožek*

Department of Polymers, University of Chemistry and Technology Prague. Czech Republic
**Corresponding Author's E-mail address: jiri.brozek@vscht.cz*

A common material for the production of book covers is polyvinyl chloride (PVC). Exposure to light and other factors results in loss of thermal stability, colour change, electrical conductivity and ultimately deterioration of mechanical properties[1,2]. In plasticized covers, the low molecular weight plasticizer or lubricant migrates to the surface during degradation. This phenomenon is accompanied by cracking, embrittlement, peeling of the plates and, at the same time, contamination of surrounding objects.
We studied the gradual deterioration of PVC book covers by a number of methodologies - determination of thermal stability, glass transition temperature, colour change, plasticizer loss or thermogravimetric analysis. We evaluated commonly used book covers that have been exposed to many years of natural ageing without quantification of degradation factors. The work included the analyses of samples after a certain period of their artificial (accelerated) ageing. This simulated the ageing of book covers in library conditions over a range of decades.

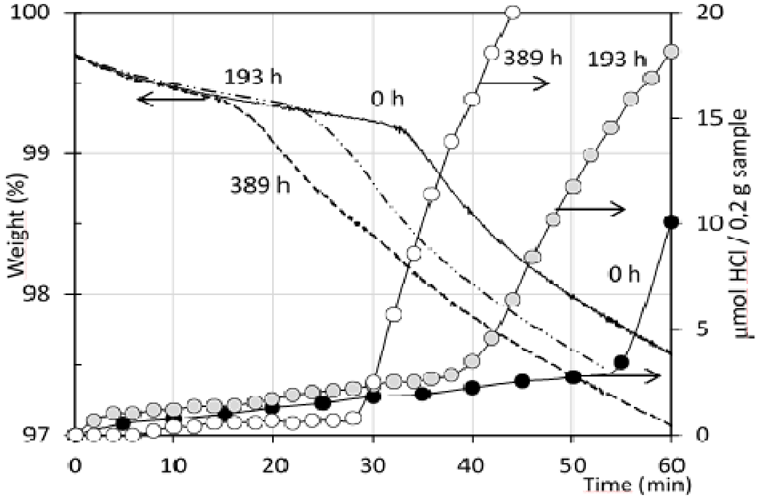

Figure: TGA - ISO mode at 180 °C and dehydrochlorination curves initial (0 h) and artificialy aged (193 and 389 h) samples

TGA is a more sensitive method than potentiometric measurement, hydrochloride loss is indicated earlier and a much smaller sample weight is required for measurement. The disadvantage is that it records the loss of all substances released at 180 °C, so it is only applicable to unplasticized PVC mixtures. In the case of plasticized mixtures, TGA combined with IR spectroscopy is the solution.
Furthermore, it was possible to additionally soften already aged brittle materials on book covers that had lost some of the plasticizer during natural ageing. In this way, they managed to return the covers to the desired mechanical properties – flexibility.

Keywords: book covers, polyvinylchloride, thermal stability, potentiometric titration, TGA

Acknowledgments
This work was supported from Ministry of Culture, Czech Republic, project DG18PO2OVV001 - Synthetic materials in the library collections, programme NAKI II.

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Benchtop NMR vs High Field NMR: Comparison of Chemometric Molecular Weight Analysis of Lignin

R. Burger*[1], S. Lindner[1,2], J. Rumpf[1], X. T. Do[1], M. Schulze[1], Y. Monakhova[2,3]
[1]*Department of Natural Sciences, Bonn-Rhein-Sieg University of Applied Sciences, Rheinbach, Germany*
[2]*Department of Chemistry and Biotechnology, FH Aachen University of Applied Sciences, Jülich, Germany*
[3] *Institute of Chemistry, Saratov State University, Saratov, Russia*
**rene.burger@h-brs.de*

Lignin is a promising renewable biopolymer being investigated worldwide as an environmentally benign substitute of fossil-based aromatic compounds. For its successful implementation into process streams, a quick, easy, and reliable method is needed for the molecular weight determination. A method using ^1H NMR spectra of benchtop as well as conventional NMR systems in combination with simple partial least squares (PLS) regression is presented to determine lignin's molecular weight (M_w and M_n) and polydispersity index (PDI). The PLS regression was calibrated using molecular weights determined by alkaline size exclusion chromatography.

A set of 53 organosolv lignin samples isolated from three different biomasses (*Miscanthus x giganteus*, *Paulownia tomentosa* and *Silphium perfoliatum*) was separated into calibration and external validation set. Validation errors between 5.6 % and 12.9 % were achieved for all parameters on all NMR devices (43, 60, 500 and 600 MHz). Surprisingly, no significant differences in the performance of the benchtop and high-field devices were found.

Furthermore, the calibration transfer between benchtop (43 and 60 MHz) and high-field (600 MHz) NMR was explored using different spectral transfer methods (piecewise direct standardization (PDS), canonical correlation analysis (CCA), transfer via extreme learning machine auto-encoder method (TEAM)). Despite the immense resolution difference between high-field and low-field NMR instruments, the results demonstrate that the calibration transfer from high- to low-field is feasible, achieving validation errors close to the original calibration (down to only 1.2 times higher RMSE). The results introduce new perspectives for applications of benchtop NMR, in general chemometric analysis as well as in transferring existing calibrations from expensive high-field instruments to cheaper benchtop instruments.

Keywords: Lignin, NMR, Benchtop, Chemometrics

Acknowledgments

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Multiscale analysis of thermal degradation of polyamide 6,6 - Influence of temperature on oxygen diffusion-limited oxidation profiles.

M. Pliquet , D. Bourgogne , J.L. Gardette , S. Therias , P.O. Bussiere [*]

Université Clermont Auvergne, CNRS, Clermont Auvergne INP, ICCF, F-63000 Clermont-Ferrand, France
[*]*E-mail : pierre-olivier.bussiere@sigma-clermont.fr*

Aliphatic polyamides are engineering polymers. They can be used in various fields, such as textiles, automotive, and electrical insulation. Certain applications require high-temperature exposure, which can reduce the performance of the material during its service life. The thermal oxidation of polyamides in the bulk is a widely studied process since polyamides are commonly used in applications that require long-term/high-temperature exposure [1,2,3]. Beyond chemical changes, oxygen permeation can also spatially affect the degradation of polymer materials. When the oxygen consumption rate is higher than the oxygen permeation, oxidation then becomes limited by oxygen diffusion (DLO). As a result, an oxidation profile across the material thickness develops and is indicative of heterogeneous oxidation.

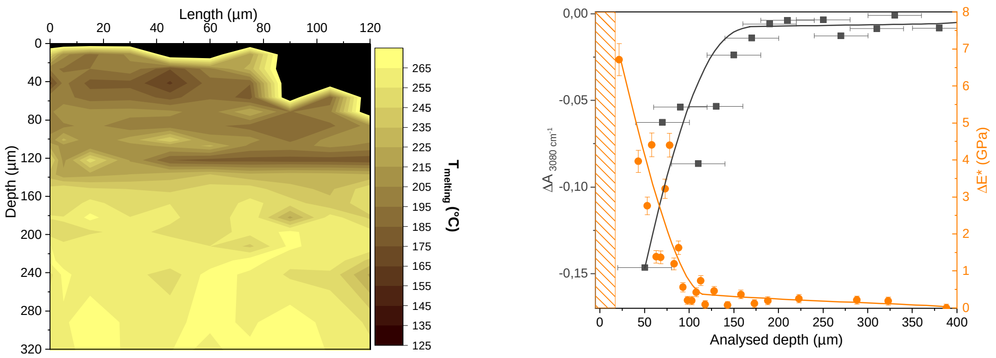

Fig. 1. Left) Melting temperature mapping of samples thermo-oxidised at 180 °C for 197 h. right) Profile measured by micro-FTIR (■) and AFM peak force (▲) of a sample thermo-aged at 180 °C for 197 h

Oxidation profiles of PA 6,6 thick samples were determined using different techniques that characterise the material changes from molecular to macroscopic scales. Recent studies using AFM to characterise the changes in material properties due to ageing have suggested that it can be an efficient tool. In this study, AFM was used to measure thermal and mechanical properties with nanometric precision. The comparison of the chemical structure changes with the thermal and mechanical properties shows a good correlation (Figure1) The main objective was to determine relevant degradation probes to validate the multiscale approach protocol.

Keywords: Polyamide 6,6, Thermo-oxidation, profile, AFM (atomic force microscopy), diffusion-limited oxidation (DLO)

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Polyurethane Cryogenic Insulation for Space Launchers Produced with the Next Generation Blowing Agents

U. Cabulis[1*], V. Yakushin[1], M.Rundans[1,2]

[1]*Latvian State Institute of Wood Chemistry, Riga, Latvia*
[2]*Riga Technical University, Institute of Materials and Surface Technology, Riga, Latvia*
[*]*ugis.cabulis@kki.lv*

Latvian State Institute of Wood Chemistry has more than 40 years' experience in cryogenic insulation and space technologies, starting from Soviet space programme Energia-Buran up to nowadays, when we cooperate with European Space Agency.

Current cryogenic insulation application solution uses rigid polyurethane (PUR) foams with hydro flour carbon gas (HFC) - Solkane 365mfc as a blowing agent. The revised F-Gas Regulation No. 517/2014 bans or restricts use of different F-gases (including Solkane 365mfc) in refrigerators and air conditioners, insulating foams and technical aerosols. The regulation introduces a phase-down mechanism involving gradually declining cap on the total placement of bulk HFCs (in tons of CO_2 equivalent) on the market in the EU. Restrictions are placed on foams that contain HFCs with Global Warming Potential (GWP) of 150 or more. Date of prohibition – 1st January 2023. Current research was focus on replacement of existing foam blowing agent used in cryogenic recipes with blowing agents with low GWP. In current research PUR foams at the first were obtained by hand mixing (pouring) method, after that process was up-scaled by spraying method. Latest information on advances of different low GWP blowing agents shows that there are problems with formulation stability, high price, flammability and plasticisation of PUR polymer matrix. Current research could develop cryogenic sprayed PUR foam formulation with high safety coefficient and low thermal conductivity coefficient. Possible low GWP candidates were:

- Cyclopentane (GWP<11)
- *Ecomate* (Methyl formate & methanol mixture, GWP<1.5)
- *Solstice LBA* (HFO 1233zd, GWP<7)
- *Opteon 1100*, *Formace 1100* (HFO 1366mzz, GWP = 5)

All of the next generation blowing agents can be used to obtain low density PUR foams (with or without additional water in the formulation) but a few of them have significant shortcomings. Further steps focused on development of low density (< 35 kg/m^3) spray foam formulation using *Solstice LBA* as the blowing agent [1]. Optimum concentration of blowing agent as well as suitable catalysts and surfactants impacting foam quality has been studied. As a result, foam material with better thermal and mechanical properties has been selected.

Safety coefficient of the obtained foam material is >3. If cryogenic insulation materials characterizes by safety coefficient above 3, it means, that elongation at break 3 folds or more increase shrinkage at thermal shock. Microstructure of spraying foam in cross sections was not as regular as microstructure of poured foams. Along with regular cells elongated in foam rise direction there are small voids, however they are surrounded by other closed cells and do not form continuous channels. The fine pore structure allowed to obtain a PUR foams with a low coefficient of thermal conductivity (<0.016 W/m·K). The initial values of thermal conductivity coefficient of spraying PUR foams with *Solstice LBA* were significantly lower than values of analogues PUR foams with conventional blowing agents.

Keywords: rigid polyurethane foams, cryogenic insulation, blowing agents

Acknowledgments

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Hierarchically porous polyHIPEs containing hyper-crosslinked resins

Rachele Castaldo[1*], Inna Berezovska[2], Michael S. Silverstein[2], Gennaro Gentile[1]

[1]*Institute for Polymers Composites and Biomaterials, National Research Council of Italy, Pozzuoli, Italy*
[2]*Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa, Israel*
[*]*rachele.castaldo@cnr.it*

Polymers synthesized within high internal phase emulsion (polyHIPEs) and hyper-crosslinked resins (HCLRs) are among the polymers that are investigated the most for their interesting porosities. PolyHIPEs are characterized by a highly macroporous structure generated by the removal of the internal phase, and they have the ability to absorb large quantity of liquids through capillary action [1]. HCLRs, characterized by micro- and mesoporosity created through an extensive crosslinking of the swollen precursor polymer, exhibit very high adsorption capacities for small organic molecules such as aromatic pollutants, from both liquids and gases [2].

In this work, polyHIPEs based on styrene (ST) and divinylbenzene (DVB) that contained up to 20 phr HCLRs that were based on DVB and vinylbenzyl chloride (VBC) were developed for the first time. First, a high surface area DVB/VBC HCLR was obtained and functionalized with amino groups to enhance its hydophilicity and hence its localization at the HIPE's water/oil interface, enhancing the ability of the resulting polyHIPE to adsorb polar substances [3]. The water-in-oil HIPEs containing amino-functionalized HCLRs were obtained using two different strategies: (i) adding the HCLR particles after the HIPE formation, or (ii) dispersing the HCLR particles in the internal phase before HIPE formation. PolyHIPEs containing HCLRs that wer not amino-modified were prepared for comparison.

The resulting polyHIPEs exhibited hierarchical porosities that were characterized by the typical interconnected macroporosities of ST/DVB polyHIPEs and the micro-/mesoporosities of the HCLRs particles (Figure 1a,b). The polyHIPEs that contained the modified HCLR particles were used for the cyclic sorption of organic solvents and volatile organic compounds (VOC) and exhibited an enhanced uptake of polar VOC and aromatic hydrocarbons (Figure 1c,d). In all cases, the HCLR-containing polyHIPEs exhibited very high regenerability.

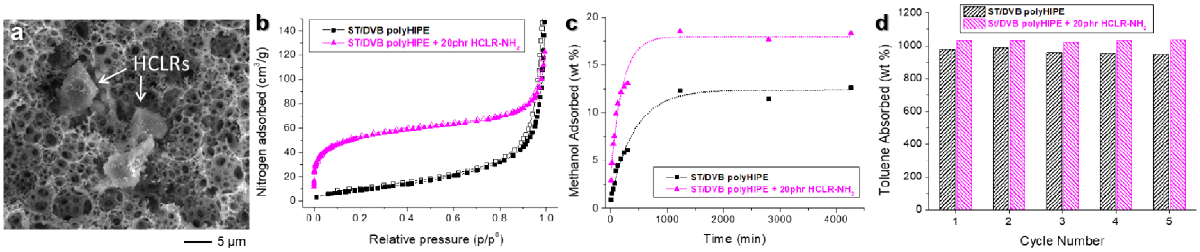

Figure 1. SEM image of ST/DVB polyHIPE containing 20 phr of amino-functionalized HCLR (a), nitrogen adsorption/desorption isotherms (b), methanol kinetic (c) and toluene cyclic (d) sorption of ST/DVB polyHIPE and ST/DVB polyHIPE containing 20 phr of amino-functionalized HCLR.

Keywords: polyHIPEs, hyper-crosslinked resins, absorption, adsorption, regeneration, VOC

Acknowledgments

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nano-FTIR correlation nanoscopy for organic material analysis

Adrian Cernescu

neaspec – attocube systems AG, Haar-Munich, Germany
adrian.cernescu@attocube.com

Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) is a scanning probe approach to optical microscopy and spectroscopy, bypassing the ubiquitous diffraction limit of light to achieve a spatial resolution below 20 nanometers. s-SNOM employs the strong confinement of light at the apex of a sharp metallic atomic force microscopy (AFM) tip to create a nanoscale optical hot-spot. Analyzing the scattered light from the tip enables the extraction of the optical properties of the sample directly below the tip and yields nanoscale resolved images simultaneous to topography. In addition, the technology has been advanced to enable Fourier-Transform Infrared Spectroscopy on the nanoscale (nano-FTIR) using broadband radiation from the visible spectral range to THz frequencies.

Recently, the combined analysis of complex nanoscale material systems by correlating near-field optical data with information obtained by other scanning probe microscopy (SPM)-based measurement methodologies has gained significant interest. For example, the material-characteristic nano-FTIR spectra of a phase-separated polystyrene/low-density polyethylene (PS/LDPE) polymer blend verifies sharp material interfaces by measuring a line profile across a ca. 1 µm sized LDPE island. Near-field reflection/absorption imaging at 1500cm^{-1} of the ca. 50nm thin film allows to selectively highlight the distribution of PS in the blend and simultaneously map the mechanical properties like adhesion of the different materials.

The nano-FTIR spectroscopy enables not only nano-chemical identification and to explore local distribution of polymer blends but it also offers information about local orientation of polymer chains in crystalline organic semiconductors and in polymer monolayers. Various examples of s-SNOM measurements on different polymer samples will be presented.

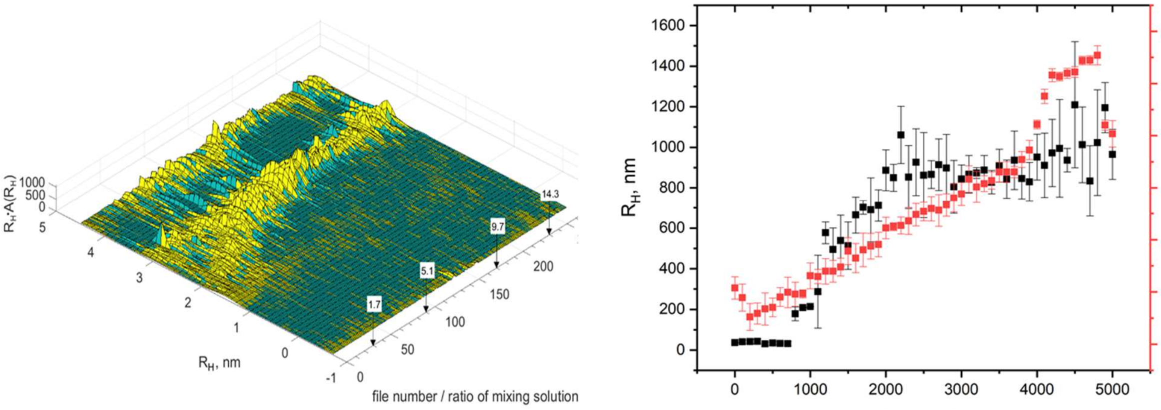
Keywords: nano-FTIR, s-SNOM, organic semiconductors, correlation nanoscopy

Tuned melittin encapsulation and release by multivalent interactions with supramolecular polymer carriers.

H. Zhukouskaya, Z. Cernochova, L. Ctverackova, E. Pavlova, M. Vetrik, P. Černoch,
M. Slouf, M. Filipová, M. Hruby,
J. Panek

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic*

In order to produce a biodegradable biocompatible well-defined nanoencapsulator of polycationic cargos, a series of modified anionic glycogens were synthesized by acylation of oyster glycogen with selected dicarboxylic acid anhydrides, possessing different hydrophobicity (bicyclo[2,2,2]-2,3:5,6-dibenzo-2,5-octadiene-7,8-dicarboxylic, 1,2-cyclohexanedicarboxylic, phthalic and succinic anhydrides). TEM imaging demonstrated that modification of glycogen took place in whole volume of the particles. Selfassembly behavior was studied with DLS as a function of solution temperature and pH. DLS autotitration with model cationic amphiphile cargo – honeybee poison peptide melittin in buffered solution revealed that melittin-modified glycogen polyplex formation occurs in the solution in the ratio 1/3, and survives further increasing of melittin concentration up to 1/9.8 weight ratio. Zeta potential increases from -30 mV to almost 0 mV. This points out a great complex-formation ability of modified glycogens. In vitro experiments on erythrocytes clearly showed that modified glycogens efficiently suppress hemolytic activity of melittin serving as melittin antidotes or may, in opposite use, serve as controlled release carriers. DLS, SLS and TEM characterized the size of resulting complex as 800-900 nm, the molecular weight and density of the particles depend on ionization degree, kind of precursor and its length.[1,2]



**DLS titration
of sample modified glycogen with succinic anhydride (0.1 mg/mL)
with melittin (1.4 mg/mL) at pH 7.4. In 3D scheme the arrows corespond to changing of mass ratio of mixing solutions.**

The authors acknowledge financial support from Czech Science Foundation (grants # 19-10429S and 21-04166S).

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Water vapour permeability of wood-based panels finished with water-borne and solvent-based coating

A. Copak[1*], V. Jirouš-Rajković[2], V. Živković[3], J. Miklečić[4]

[1,2,3,4]*University of Zagreb, Faculty of Forestry and Wood Technology, Zagreb, Croatia*
[*]*acopak@sumfak.unizg.hr*

Abstract- One of the most important factors affecting the application area of wood-based panels is their affinity to water and water vapour. The consequences of uncontrolled moisture flows and moisture accumulation can be severe: mold growth, decay, corrosion, staining, and even structural failure [1]. Affinity to water vapour can be reduced by using a variety of coatings for wood and wood-based panels [2]. In this study, the permeability of coated and uncoated 12 mm thick plywood and particleboard was examined. Plywood is a strong thin wood-based panel consisting of two or more veneers glued together with the grain direction of veneers at a 90˚ angle. Particleboard is manufactured by pressing mixed wood particles with a suitable resin. Particleboard is mainly used in furniture productions and has become popular as a construction material due to its numerous usage possibilities and inexpensive cost [3]. A total of three types of commercial coatings was used and dried in room conditions: transparent one-component water-borne acrylic coating, transparent two-component water-borne polyurethane coating and transparent two-component solvent-based polyurethane coating. Water vapour permeability properties was determined by cup method based on EN ISO 12572:2016. Four samples were made of each type of coated and uncoated panels. Conditioned samples were sealed on the top of the cups with neutral silicone and aluminium rubber seal tape to ensure water vapour loss through the defined test surface area. An initial mass of samples was recorded, and samples were left in laboratory conditions at 23 ± 2 °C and 50 ± 5 % relative humidity. Changes in sample weight were recorded every day for the next 40 days. The results showed a higher water vapour permeability on particleboard samples compared to plywood samples. Moreover, water vapour permeability on particleboard samples was intensive in the first 10 days after which it was equalized. However, water vapour permeability on plywood samples was very small in the first 5 days after which it increases sharply. The water vapour permeability of the water-borne coatings was higher than the water vapour permeability of the solvent-base coating on both types of panels. Also, the water vapour permeability of the polyacrylate coating was higher than the water vapour permeability of the polyurethane coating on both types of panels. The lowest water vapour permeability was recorded on panels finished with two-component solvent-based polyurethane coating, and the highest water vapour permeability was recorded on uncoated panels and then on panels finished with transparent one-component water-borne acrylic coating.

Keywords: water vapour permeability, wood-based panels, water-borne coating, solvent-based coating

Acknowledgments

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Physical-chemical and structural stability of poly(3HB-co-3HV) / (ligno-)cellulosic fibre-based biocomposites over successive dishwashing cycles

E. Doineau*, F. Rol, N. Gontard and H. Angellier-Coussy

JRU IATE 1208, INRAE, Montpellier SupAgro, University of Montpellier, Montpellier, France
Estelle Doineau, e-mail: estelle.doineau@umontpellier.fr

Plastic wastes are one of the causes of current environmental concerns, targeting in particular packaging applications, including single-use packaging such as disposable dishes. In order to minimize the use of resources, it is essential to lengthen the life cycle of packaging materials via several recycling and/or reuse closed loops, before an ultimate composting and/or biodegradation step. Recent European Union decrees go in this direction, e.g., with the article L. 541-10-17 of the Environmental code requiring a 20% reduction target for single-use plastic packaging set for producers, of which at least 50% must be obtained by reuse by 31 December 2025.

In this context, the goal of this work was to assess the impact of successive dishwashing cycles on the structural and physical-chemical stability of PHBV/(ligno-)cellulosic fibre-based biocomposite materials. The effect of fibre composition, morphology, and content was investigated by selecting three types of commercial (ligno-)cellulosic fibres and two filler contents (20 and 40 wt%). For that purpose, PHBV-based films were produced by melt extrusion followed by a thermopressing step. In accordance with the standard NF EN 12875-1, up to 125 dishwashing cycles were carried out. Films having undergone a certain number of cycles in the dishwasher have been characterised under standardised testing conditions. The evolution of the colour, the tensile properties, and the overall migration in two food liquid simulants, i.e., ethanol 50% (vol/vol) and ethanol 95% (vol/vol), was discussed in relation to the structural stability of materials, which was evaluated by changes in sample weight and thickness, thermal transition temperature, and crystallinity assessed by differential scanning calorimetry (DSC), as well as microstructures observed by scanning electron microscopy (SEM).

It was shown that neat PHBV films were very stable, with negligible change in appearance and colour after 125 dishwashing cycles. Regarding mechanical properties, only a slight decrease of rigidity and ductility during the first 5 cycles was noticed, then remaining stable up to 125 dishwashing cycles. Considering OM values, which is the key point to ensure food safety, they remained lower than the overall migration limit of 10 mg.dm^{-2} established by the UE Committee for the two tested food liquid simulants, up to 50 dishwasher cycles. Anyway, the present work highlights that biodegradability and compostability are not incompatible with recycling and reuse processes. The incorporation of increasing amounts of (ligno-)cellulosic fillers negatively impacts the overall stability of PHBV-based materials. Over the 10 first successive dishwashing cycles, biocomposite films became rapidly and obviously less transparent and very brittle, with increased surface rouhghness. The loss in biocomposite performance was ascribed to the degradation of the polymer matrix through hydrolysis reactions, as well as by the swelling of hydrophilic (ligno-)cellulosic fillers, both induced by the sorption of water. High-purity cellulose fibres, with high crystallinity and aspect ratio, should be preferred to limit water sorption and the release of water-soluble components during dishwashing. In the best case, up to only 10 cycles could be applied. Worth to note that to be able to conclude on the possibility to reuse PHBV-based materials as food contact materials, several additional investigations should be carried out. Once the reusability can be fully demonstrated, collection and sorting steps should be established.

Keywords: PHBV; stability; ageing; packaging; dishwasher; biocomposites.

Reference:

Doineau, E.; Rol, F.; Gontard, N.; Angellier-Coussy, H. Physical-Chemical and Structural Stability of Poly(3HB-Co-3HV)/(Ligno-)Cellulosic Fibre-Based Biocomposites over Successive Dishwashing Cycles. *Membranes* **2022**, *12*, 127, doi:10.3390/membranes12020127.

A few exemples of the fruitful encounter between biopolymers and advanced thermal analysis

A. Esposito*, N. Delpouve, L. Delbreilh, E. Dargent

Normandie Univ, UNIROUEN Normandie, INSA Rouen, CNRS, Groupe de Physique des Matériaux, 76000 Rouen, France (antonella.esposito@univ-rouen.fr)

The number of polymers that are partially or entirely based on renewable resources is increasing very fast. Several monomers, synthons and macromolecules are obtained from the biomass with all sort of chemical compositions, atomic arrangements, physical properties and microstructures. Little information is known about novel biopolymers, and often only small samples are availble, because their synthesis is done on a laboratory scale prior to scaling up to the industrial scale. Using techniques such as ThermoGravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) to investigate polymers' thermal properties is widespread. Indeed, thermal analysis offers a wide range of possibilities that are sometime overlooked. The encounter between biopolymers and advanced thermal analysis, e.g. Fast Scanning Calorimetry (FSC), Modulated-Temperature DSC (MT-DSC), Dielectric Relaxation Spectroscopy (DRS), is particularly fruitful. Combining the results obtained with different techniques offers new points of view on the microstructural complexity of semicrystalline polymers, the intimate connection between their crystalline and amorphous phases, their molecular mobility, their glass transition and their relaxation dynamics, allowing to establish relations between chemistry, physics and final properties. As some of these features are time-dependent, this approach also helps understanding why properties change with time, and eventually predicting their evolution. This contribution relates a few examples of the fruitful encounter between biopolymers and advanced thermal analysis techniques, with the support of other techniques such as X-Rays Diffractometry (XRD), Small-Angle X-rays Scattering (SAXS) and Molecular Dynamics Simulations (MDS). **(1)** Polymers are more or less prone to crystallize, and more or less easy to quench. Some applications strictly require the use of semicrystalline polymers, but crystallization's outcomes depend on both the processing and storage conditions. In most cases, a three-phase model should be used to accurately describe the microstructure of semicrystalline polymers. Hoever, the microstructure of cold-crystallized poly (hydroxybutyrate-*co*-hydroxy valerate) (PHBV) [1] is better described by a two-phase model with a *continuum of mobility* [2]. From this point of view, the progressive embrittlement observed upon storage at room temperature was explained by a progressive redistribution of the relaxation times. **(2)** Poly(ethylene 2,5-furandicarboxylate) (2,5-PEF) has been pointed out as an interesting replacement of PET for packaging [3]. The literature reports values of O_2, CO_2, and H_2O permeability reduced by a factor of 11 [4], 19 [5], and 2.8 [6] compared to PET [7]. By investigating the relaxation dynamics in fully amorphous samples of 2,5- and 2,4-PEF (homopolymers obtained with two isomers of furan-dicarboxylic acid), an explanation could be found for the outstanding barrier properties of furan-based polyesters [8]. **(3)** Whenever new biopolymers are synthesized in small batches, and their physical properties are mostly unknown, where to start from? The last exemple shows how FSC helped estimating the equilibrium enthalpy of melting of various polymers [9].

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A new way to switch between LCST und UCST – Multi-responsive transitions of PDMAEMA brushes for switchable surfaces

Patricia Flemming[1,2]*, Alexander S. Münch[1], Andreas Fery[1,2], Petra Uhlmann[1]

[1] *Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany*
[2] *Technische Universität Dresden, 01062 Dresden, Germany*
**flemming@ipfdd.de*

Owing to its multi-responsive behavior upon variation of pH value, ionic strength and temperature, poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) is an attractive candidate for switchable surface coatings. We prepared PDMAEMA "Guiselin" brushes grafted homogenously on silicon substrates using an efficient grafting-to method. These layers were monitored in-situ by an elaborate set of analytical techniques, such as spectroscopic ellipsometry, ATR-FTIR as well as AFM.[1,2,3] While PDMAEMA brushes display a lower critical solution temperature (LCST) in the presence of monovalent ions, it can easily be switched towards an upper critical solution temperature (UCST) thermoresponsiveness via the addition of small quantities of multivalent ions, such as $[Fe(CN)_6]^{3-}$. In-situ FTIR spectroscopy monitors the temperature-dependent electrostatic interactions between polycationic PDMAEMA and $[Fe(CN)_6]^{3-}$ resulting in the unusual UCST behavior of the brushes. Moreover, in-situ AFM exposes the nanostructured surface of pinned PDMAEMA micelles during the UCST transition, whereas a homogenous brush surface was detected both below and above the LCST. By modifying the original grafting protocol, we were able to create end-grafted polymer brushes using a new variant of the grafting-to approach and investigate the LCST and UCST transition as a function of the grafting density. Tuning the thermoresponsive transitions via secondary triggers, like ionic strength or pH-value, provides an excellent approach to tailor surface properties under aqueous conditions, paving the way towards smart coatings for catalysis, drug delivery or sensing.

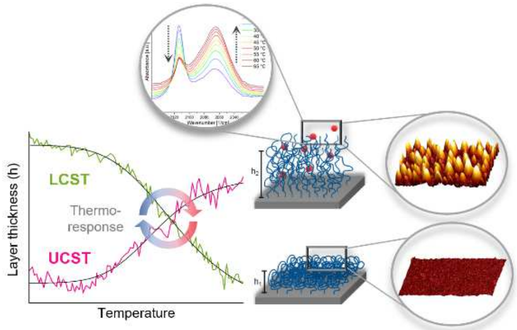

Figure 1. In-situ characterization of the thermo-responsive transitions of PDMAEMA brushes under aqueous conditions.

Keywords: stimuli-responsive polymer brush, upper critical solution temperature (UCST), lower critical solution temperature (LCST), spectroscopic in-situ ellipsometry, pinned micelles

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Development and characterization of novel PP/HGM/PCM syntactic foams for thermal energy storage applications

F. Galvagnini[1,2*], A. Dorigato[1,2], L. Fambri[1,2], A. Pegoretti[1,2]

[1]*Department of Industrial Engineering, University of Trento, Trento, Italy*
[2]*National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy*
[*]*Corresponding Author's e-mail address: francesco.galvagnini@unitn.it*

Syntactic foams (SFs) containing hollow glass microspheres (HGM) in polypropylene (PP) feature a unique combination of low density, high mechanical properties, and low thermal conductivity, which can be tuned according to the specific application [1]. A possible way to improve the versatility of SFs could be that to incorporate thermal energy storage (TES) materials. Among Latent Heat Storage (LHS) systems, Phase Change Materials (PCMs) are the most diffused ones [2,3]. When PCMs are added to syntactic foams, they could limit their abrupt response to temperature change, reducing also the induced thermal stresses. In this work, the microstructural and thermo-mechanical properties of PP/HGM SFs incorporating a microencapsulated phase change material (PCM), having a melting temperature of 57 °C, were comprehensively investigated.

A commercial-grade of PP (Moplen HP456J) was filled with hollow soda-lime-borosilicate glass microspheres HGM (iM16K) having a mean size of 20 µm, and a microencapsulated paraffin PCM (MPCM 57D) having a mean diameter of 40 µm, a melting temperature of 57 °C, and an enthalpy of fusion of 200 J/g. The three constituents were mixed at ten different relative amounts in a melt compounder, working for 5 min at 190 °C, and the resulting materials were then hot pressed at 200 °C for 5 minutes applying a pressure of about 0.5 MPa.

The rheological properties of these foams were strongly affected by the introduction of both the fillers, strongly modifying the processability of the materials at the molten state. As it could be expected, the introduction of HGM reduced significantly both the density and the thermal conductivity values of the resulting materials. Moreover, it was demonstrated that the enthalpy of fusion of the samples was proportional to the PCM concentration. The mechanical properties of these foams were strongly affected by the interfacial ashesion between HGMs and the PP matrix.

This work highlighted that the combination of the two fillers (i.e. PCM microcapsules and HGM) in a PP matrix at different concentrations generated a versatile multifunctional material with tunable thermo-mechanical properties. Therefore, these materials could find large application in the electronics, automotive, refrigeration, and aerospace industries.

Keywords: syntactic foams, polypropylene, glass microspheres, thermal energy storage, phase change materials, thermal properties, mechanical properties.

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Effect of chain orientation on the brittle to ductile transition in Polylactide

S. Xu[1], G. Stoclet[1], J. F. Tahon[1], Isabelle De Waele[2], V. Gaucher[1*]

[1]*Univ. Lille, CNRS UMR 8207 - UMET - Unité Matériaux et Transformations, F-59655 Lille, France*
[2]*Univ. Lille, CNRS, UMR 8516- LASIR- Laboratoire de Spectrochimie Infrarouge et Raman, F-59000 Lille, France*
Corresponding author*: *valerie.gaucher@univ-lille.fr*

Polylactide (PLA) is one of the most promising biopolymers that actually takes part in commercialized biopolymer market. However, its intrinsic brittleness has found to be a major limit to a wider range of applications. Among the various chemical and physical approaches reported in literature aiming at improving the mechanical properties, biaxial stretching is known as an elaboration process that can improve the ductility of some brittle polymers [1]. In this context, the goal of this work is to study the influence of chain orientation on the mechanical behavior of Polylactide (PLA).

While isotropic PLA exhibits as expected a brittle behavior upon uniaxial tension at room temperature, pre-oriented PLA samples display a ductile behaviour with a strain at break exceeding 100%. To better understand the origin of this Brittle to Ductile (B-D) transition, both a crystallizable grade of PLA (C-PLA) and a non-crystallizable grade (NC-PLA) were studied in order to be able to separate the effects induced by macromolecular orientation from the ones due to crystalline phase. Through an in-depth structural characterization of the pre-oriented films, we have demonstrated that it is the macromolecular orientation in the amorphous phase which is the key parameter governing this B-D transition [2]. Additional structural analyses by Small-Angle X-ray Scattering (SAXS) carried out in situ during the stretching of pre-oriented or non-oriented samples, combined with morphological observations, have shown that the B-D transition corresponds to a change in the elementary plasticity mechanisms: crazing, predominant in the case of brittle samples, gradually evolves toward the development of shear bands. Supplementary post-mortem analyses by SAXS have also shown that the macromolecular orientation has no influence on the geometry of the cracks but induces a reduction in the density of cracks formed during stretching. From these analyses, the critical crack nucleation stress (σ_{cr}) as a function of the degree of orientation has been determined. It has thus been shown that the change in deformation mechanisms results from the increase in the crack initiation stress σ_{cr} with the macromolecular orientation while the shear band initiation stress remains unchanged.

Keywords: Molecular orientation, crazing, shear bands

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Towards cell-free enzymatic functionalization: Analytical challenges in understanding the biodegradation of polyethers

M. Geisler[1], A. Kaufmann[1], J. Khan[2], M. Ansorge-Schumacher[2], J. Thiele[1,3*]

[1]*Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany*
[2] *Chair of Molecular Biotechnology, Technische Universität Dresden, Germany*
[*]correspondence: *thiele@ipfdd.de*

Exploiting enzymes to yield polymers with specific modifications has gained significant interest within the last decade,[1] since enzymes may provide a cleaner and safer way in contrast to current practices often requiring harsh conditions or multi-step synthesis strategies. Thereby, enzyme selectivity may provide a better control of the targeted macromolecular structures without the need for wasteful protection/deprotection steps.[2]

Here, we address the enzymatic functionalization of the polymer backbone of polyethylene glycol (PEG), since conventional chemical modification strategies have mostly targeted so far modifications on the polymer's terminal groups. Therefore, we aim to isolate enzymes that may introduce functional groups within the polymer backbone.

To identify suitable enzymes, bacteria cultures originated from the vicinal environment (soil, waste water and laboratory) were isolated in screening series that grow on PEG as a sole carbon source and hence, are putatively able to degrade or modify PEG, respectively. Terminal modifications have previously been reported for PEG up to a molar mass of 6,000 g·mol^{-1}.[1] However, our aim is to yield modifications of PEG with a higher molar mass of 20,000 g·mol^{-1} (PEG-20K), for which a degradation is so far only stated for *Sphingomonad* species[4], but has not been conclusively verified, yet.

Alterations in PEG of the culture media treated by the isolated cultures as well as with cell lysates and potentially expressed extracellular enzyme samples in the supernatant is subsequently characterized by means of matrix-assisted mass spectrometry (MALDI-TOF-MS), size-exclusion chromatography connected to triple detection (SEC-MALS-Visc-dRI) as well as NMR for absolute molar mass and distribution analysis, end or side group identification, and a potential retracing of the enzymatic degradation pathway.

Keywords: polyethylene glycol, size exclusion chromatography, MALDI-TOF MS, enzymatic degradation

Acknowledgments

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The multimode self-assembly behavior in solution of amphiphilic oligo(ethylene glycol)-modified poly(pentafluorostyrene)s

Elisa Guazzelli[1], Matteo Calosi[1], Chiara Pelosi[1], Luca Bernazzani[1], Celia Duce[1], Maria Rosaria Tiné[1], Manfred Kriechbaum[2], Frank Uhlig[2], Giancarlo Galli[1], Elisa Martinelli[1]

[1] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56124 Pisa, Italia.
[2] Institute for Inorganic Chemistry, Graz University of Technology, 8010 Graz, Austria.
elisa.guazzelli@dcci.unipi.it

Amphiphilic tetrafluorostyrene monomers (EFSn) carrying in *para* position an oligoethylene glycol chain with different lengths (n = 3−13) were synthesized and used for the preparation of the corresponding amphiphilic homopolymers (pEFSn-x) by ARGET-ATRP. The self-assembly behavior in water and organic solvents of homopolymers derived therefrom was studied by dynamic light scattering (DLS) and small angle X-ray scattering (SAXS). In particular, DLS measurements on water solutions of the water-soluble homopolymers at room temperature evidenced the presence of nanoassemblies with hydrodynamic radius R_h = 2.5−6 nm, compatible with the formation of unimer micelles. These nanoassemblies were proven to be disrupted by the addition of THF to the water/polymer solution. SAXS measurements revealed that self-folded nanoassemblies were compact globular spheres, with radius of gyration R_g in the range 1.7−2 nm, corresponding to radii of a spherical particle in the range 2−3 nm. The R_g/R_h radius was < 0.5, consistent with a core-shell nanostructure where hydrophilic oligoethylene glycol chain created a hydrated shell, shielding the compact hydrophobic core from the aqueous environment (Figure 1). On heating a cloud point temperature was identified combining light transmittance and nano-differential scanning calorimetry (n-DSC) measurements, indicating the formation of multi-chain microassemblies, which reverted to nanoassemblies on cooling below such a critical temperature. This LCST-type thermoresponsive transition was reversible up to a specific temperature (T_{rev}).

In conclusion, correlations of the single-chain and multi-chain self-assembly behavior with amphiphilic polymer structure (x and n) will be presented and discussed in order to highlight the significance of such chemical parameters in effecting tailored polymer nano-to-micro self-assembling and responsiveness for advanced applications.

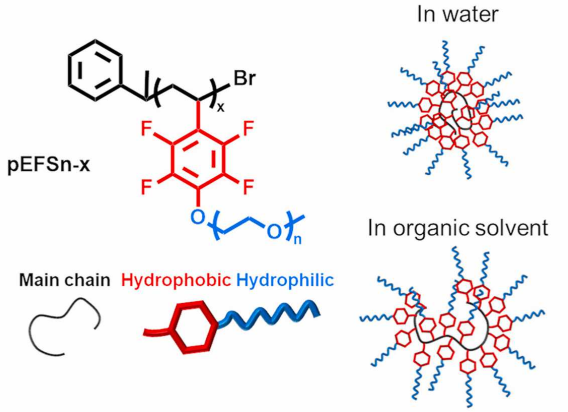

Figure 1. Schematic representation of the unimer micelles formed in water by the amphiphilic homopolymers of this work.

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Thermoresponsive double network hydrogels

L. Hanyková*, V. Ivaniuzhenkov, I. Krakovský, J. Šťastná

Charles University, Faculty of Mathematics and Physics, Prague, Czech Republic
**lenka.hanykova@mff.cuni.cz*

Stimuli-responsive polymer hydrogels are great interest for advanced applications as smart materials, because of the ability to change their properties in response to different external stimuli. Among various stimuli, the temperature is the most extensively exploited in the field of 'smart' polymers due to the important role of temperature in nature.

Temperature response of acrylamide-based double network (DN) hydrogels was studied by a combination of swelling and mechanical measurements, differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR) spectroscopy. A series of DN hydrogels with tightly crosslinked first thermoresponsive network and loosely crosslinked second hydrophilic network was prepared. Temperature response of the studied DN hydrogels was found to be tunable by preparation conditions. DN hydrogels show less intensive changes in deswelling, smaller enthalpy, and entropy changes connected with phase transition and broader temperature interval of the transition than the single network (SN) hydrogels. As follows from NMR relaxation and swelling experiments, collapsed DN hydrogels contain significantly more permanently bound water in comparison with SN hydrogels due to interaction of water with the hydrophilic component. Unlike swelling and DSC experiments, a rather abrupt transition of DN hydrogels was revealed from temperature-dependent NMR spectra. Thermodynamical models of deswelling and NMR behaviour based on the approach of the van't Hoff analysis allow to determine thermodynamical parameters connected with temperature-induced volume transition, such as the standard change of enthalpy and entropy and critical temperatures and characterize the structurally different states of water.

Keywords: thermoresponsive hydrogel, double network, swelling, differential scanning calorimetry, NMR spectroscopy.

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Gaining Insight Into Adhesion in Multi-Layered Polymeric Materials via Interface Imaging

C. Leimhofer[1*], S. Dollberger[1], A. Hammer[2], W. Roland[2,3], A. Kapshammer[4], S. Hild[1]

[1]*Institute of Polymer Science, Johannes Kepler University, Linz, Austria*
[2]*Institute of Polymer Processing and Digital Transformation, Johannes Kepler University, Linz, Austria*
[3]*Pro²Future GmbH, Linz, Austria*
[4]*Institute of Polymer Product Engineering, Johannes Kepler University, Linz, Austria*
[*]*claudia.leimhofer_1@jku.at*

Multi-layered polymeric products have gained significant scientific and industrial importance as they exhibit characteristics superior to those of their individual components. The adhesion at the interfaces between the separate layers is an essential factor as it governs the quality of the overall multilayer structure. For macromolecules, different aspects control adhesion, including the intermolecular interactions, the compatibility of the polymer couple and the degree of interpenetration, i.e. the thickness of the so-called interdiffusion layer [1, 2]. In addition to mechanical characterication of the layer adhesion, microscopic imaging of the interface can provide significant insight into understanding the phenomena surrounding polymer-polymer adhesion.

In this work, a joint approach combining confocal Raman microscopy (CRM) as well as atomic force microscopy (AFM) for interface imaging in co-extruded two-layer sheets is presented. The main focus lies on the assessment of the interdiffusion layer. CRM allows the mapping of the chemical composition with a resolution in the range of 500 nm and is highly suitable for the determination of the interdiffusion layer thickness. The potential of this label-free method in interface analysis is demonstrated for both a highly compatible amorphous system as well as for polypropylene based multi-layered materials. When extending the scope to less compatible polymer pairs or multi-phasic plastics, additional characterization methods are necessary. With a resolution down to a small fraction of the optical diffraction limit, AFM is shown to be an excellent technique for this application.

The combination of CRM and AFM allows a comprehensive analysis as it provides both chemical as well as nano-mechanical properties of the macromolecules in the interface region. These findings can be further correlated to the results of layer adhesion testing and subsequently aid in the development of novel multi-layered products.

Keywords: polymer-polymer interface, polymer characterization, adhesion, interdiffusion

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Viscoelastic relaxation mechanisms in Fe(III)-poly(acrylic acid) hydrogels

A. Lenoch[1,2*], M. Schönhoff[1,2], C. Cramer[1,2]

[1] *Center for Soft Nanoscience, Busso-Peus-Str.10, 48149 Münster, Germany*
[2] *University of Münster, Institut für Physikalische Chemie, Corrensstraße 28/30, 48149 Münster, Germany*
[*] *a.lenoch@wwu.de*

The elasticity of hydrogels based on polymer-transition metal interactions can be flexibly engineered depending on the choice of metal species and polymer ligand. Self-healing is a common property of these materials, as the metal species is highly mobile inside the polymer network and forms reversible bonds. [1] We investigate viscoelastic relaxation phenomena in hydrogels composed of poly(acrylic acid) (PAA) coordinated to Fe(III) with varying concentration of the crosslinking species. The self-healing in these gels was linked to the dissociation of Fe(III)-PAA crosslinks and migration of ferric ions within the polymer matrix [2,3]. Here, we identify different regimes of relaxation and attribute microdynamical models of chain and crosslink dynamics to these. A combination of a generalized Maxwell model and a fractional model is used to describe the complex shear modulus over the whole investigated frequency range. Our rheological results indicate, that dynamics of unentangled chains dominates relaxation at short timescales for all samples, but terminal relaxation of the associative network at longer timescales is drastically altered by the addition of Fe(III). Application of the time-temperature superposition principle allows to distinguish two activation energies for the separate relaxation mechanisms. Thus, an understanding of the interplay of chain and crosslink dynamics is achieved.

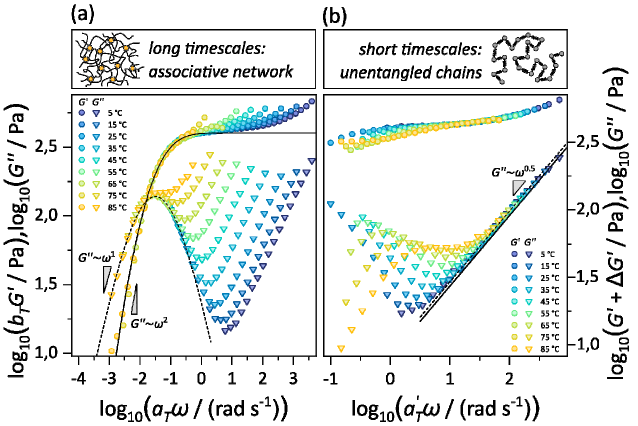

Fig. 1 Superimposed dynamic shear moduli for (a) the low frequency range and the (b) high frequency range, with indicated characteristic scaling according to the Maxwell and a fractional model, respectively.

Keywords: hydrogels, viscoelasticity, rheology, time temperature scaling, gelation

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Molecular motions of statistical copolymers at the interfaces with silica particles

F. Lim[1]*, C. Lorthioir[1]

[1] *Laboratoire de Chimie de la Matière Condensée de Paris, Sorbonne University/CNRS, Paris, France*

Polymer-based composites with silica particles are an important class of polymer materials. In these systems, an improvement of some of the mechanical properties such as the elastic modulus compared to the neat polymer matrix may occur. The dynamics of polymer chains at the interfaces with the filler particles are one of the mechanisms responsible for this enhancement, as shown in recent works on homopolymer-based nanocomposites [1]. To our knowledge, there are only few theoretical studies on nanocomposites composed of statistical copolymers focusing on the description of the interfaces for such systems and attempting to make a link between the polymer dynamics and the mechanical behavior [2]. From an experimental point of view, this question remains to be adressed.

The aim of this work is to describe the local properties of polymer chains at the organic-inorganic interfaces of nanocomposites based on silica nanoparticles and poly(ethylene glycol-*ran*-propylene glycol), P(EG-*ran*-PG), which is composed of hydrophobic units (PG) and hydrophilic units (EG). This description includes the nanocomposite microstructure, the local concentration of PG and EG units as a function of the distance with the nanoparticle surface and also the dynamical behavior of chain segments at the interfaces. The long-term goal of this project is to find some links between these information obtained at the local length scale and the mechanical behavior of these nanocomposites.

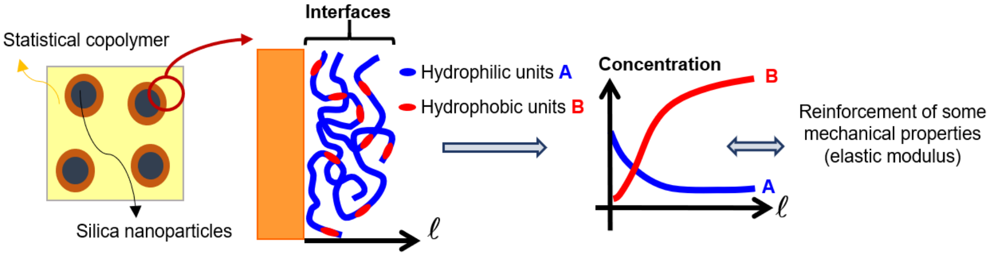

Figure 1 – Some correlations between the interfacial properties and the mechanical behavior of statistical copolymer-based nanocomposites

DSC measurements show that for a silica content above 80 vol%, all the P(EG-*ran*-PG) chains get amorphous and SAXS experiments indicates a similar polymer/silica microstructure for both PEG and P(EG-*ran*-PG)-based nanocomposites. ^{1}H solid-state NMR experiments evidence a more important fraction of immobilized polymer chain segments at the interfaces, the so-called “glassy layer“ [3], for the statistical copolymer-based nanocomposite. A gradient of segmental mobility among the P(EG-*ran*-PG) chains is thus formed with strongly constrained motions close to the silica particles and far away from the nanoparticle surface, polymer chain segments display isotropic reorientational motions. In addition, ^{13}C solid-state NMR measurements have been performed to selectively probe the segmental motions of both EG and PG units. In particular, at 343 K, the ^{1}H-^{13}C dipolar coupling is found to be at least 50 times higher in the case of the nanocomposite with the statistical copolymer chains compared to the one prepared with PEG : this result suggests stronger interactions with the silica surface. These interesting results point out that the presence of PG hydrophobic units increases the interactions between silica nanoparticles and the polymer chain segments. Along this view, one current perspective is to consider P(EG-*ran*-PG) statistical copolymers with varying PG unit content and to investigate the evolution of their segments dynamics.

Keywords: nanocomposites, statistical copolymers, silica nanoparticles, molecular motions, interfaces

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Positron annihilation lifetime spectroscopic analysis of plastic deformation of polypropylene

Cezary Makarewicz[1,2,*], Marta Safandowska[1], Rafał Idczak[3], Artur Różański[1]
[1] *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland*
[2]*The Bio-Med-Chem Doctoral School of the University of Lodz and Lodz Institutes of the Polish Academy of Sciences, Lodz, Poland*
[3]*Institute of Experimental Physics, University of Wrocław, Wroclaw, Poland*
**cezmakar@cbmm.lodz.pl*

The presence of lamellar crystals and amorphous layers determines the properties of semicrystalline polymers and affects the process of their deformation. Although a number of investigations on plastic defomation of such materials, important areas remain poorly understood, especially regarding the role of the amorphous component.

Small angle X-ray scattering (SAXS) technique is usually used to analyze the initial stages of deformation of semicrystalline polymers. However, this technique allows the detection of objects whose size ranges from several to several dozens of nanometers. Meanwhile, the initial size of free volume pores of the amorphous phase remains within 0.1-0.15 nm^3 [1]. One of the most valuable tools enabling the direct analysis of the size/distribution of free volume pores of the amorphous phase and characteristic free spaces of the crystalline component is the positron annihilation lifetime spectroscopy (PALS). Using positronium probes, one can investigate empty spaces with sizes in the range 0.25-16 nm.

PALS was used to track the deformation-induced changes of the structure of the amorphous component of polypropylene. The studies, after appropriate adaptation of the PALS technique in accordance with the methodology presented in the previous work [2], were carried out in the range of local strains (LS) 0-0.20, wherein the yield point was observed at LS=0.10-0.13. Based on the results of the mean o-positronium lifetime (τ_3) in a function of local strain (Fig. 1a), it was indicated that the average size of the free volume pores of the amorphous phase in the studied strain range rather decreased in comparison with the undeformed polypropylene, even after the initiation of the cavitation phenomenon. The observed deformation-induced evolution of the pores dimension had a gradual character/nature, proportional to the observed changes of the thickness of the amorphous layers. It was also shown that the cavitation phenomenon was responsible for the increase of the dispersion of o-positronium lifetime (σ_3, Fig. 1b).

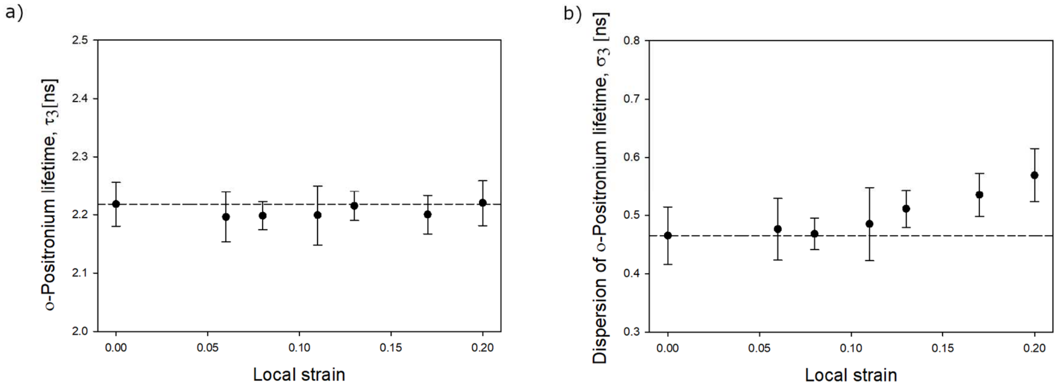

Figure 1. Mean ortho-positronium lifetime (τ_3) (a) and dispersion of ortho-positronium lifetime (σ_3) (b) for polypropylene as a function of local strain. The dashed lines represent the value for undeformed samples.

Acknowledgments

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Study of diffusion-controlled reversible reaction by DRS to model conversion evolution

J. Mangialetto[1]*, M. Wübbenhorst[2], N. Van den Brande[1], B. Van Mele[1]

[1]*Physical Chemistry and Polymer Science (FYSC), Vrije Universiteit Brussel (VUB), Brussels, Belgium*
[2]*Laboratory for Soft Matter and Biophysics, KU Leuven (KUL), Leuven, Belgium*
**Jessica.Mangialetto@vub.be*

Intrinsic thermoreversible networks based on Diels-Alder (DA) cycloaddition are widely used as self-healing materials. DA bonds preferentially break in case of damage and reversibly reform which leads to a repeatable healing cycle and an increased lifetime for many applications, such as sustainable coatings [1]. In that case, mechanical robustness is a requirement to assure thermomechanical stability which implies the necessity of a sufficiently high T_g resulting in a (partially) vitrified network. Forward and retro- DA reaction, as well as self-healing, will thus occur in diffusion-controlled conditions for most application temperatures [2]. The study of diffusion-controlled reversible reactions is lacking in literature as opposed to their irreversible counterparts.

This work will focus on the effect of vitrification on DA reaction kinetics using furan-maleimide network systems. (Non-)isothermal Dielectric Relaxation Spectroscopy (DRS) measurements are performed to follow the vitrification phenomena through the measure of the complex dielectric permittivity ε^* during cure [3] and are compared to the specific heat capacity evolution measured in (non-)isothermal conditions by MTDSC [4].

A mobility factor (MF) based on the DRS isothermal measurements is defined according to a procedure developped for irreversible networks using MTDSC measurements to describe the conversion evolution in diffusion-controlled reaction conditions [5]. Furthermore, the time-temperature-transformation (TTT) and continuous-heating-transformation (CHT) diagrams for reversible thermosets are constructed using a kinetic model and this MF to quantitatively describe these diagrams beyond vitrification [6].

Keywords: reversible thermosets, self-healing, TTT/CHT diagram, DRS, MTDSC, diffusion-controlled reaction

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Electrospun polyamide 6 polymer nanofibers : size effect on the microstructure

T.Missaoui[1], N.Delpouve[1*], Y.Zou[2], D.Papkov[2], Y.Dzenis[2], E.Dargent[1]

[1]Normandie Univ, UNIROUEN Normandie, INSA Rouen, CNRS, Groupe de Physique des Matériaux, 76800 St Etienne du Rouvray, France
[2] Department of Mechanical and Materials Engineering, University of Nebraska Lincoln, Lincoln, Nebraska, 68588-0526, United States
**nicolas.delpouve1@univ-rouen.fr*

Context

Polyamide 6 (PA6) is one the most commonly used aliphatic polyamides as engineering thermoplastics. Its interesting mechanical properties enables it to be applied in various commercial and industrial applications. Recently, a growing interest has been attributed to a new class of this polymer which are polyamide 6 nanofibers, for their distinctive properties. Along with high surface-to-volume ratio, high porosity and lightweight, polymeric nanofibers display compelling mechanical properties, unavailable in their bulk counterparts. This behavior is presumably related to the electrospinning process generating a highly oriented structure.[1] Despite its interest, the characterization of nanofibers is not a straightforward task giving their nanosized structure. Therefore, in this work, a combination of spectroscopic and thermal analysis techniques was used in order to understand the structural behavior of both crystalline and amorphous phases of electrospun polyamide 6 fibers. The aim is to gain more knowledge about the impact of the distinctive morphology of nanofibers on their performances in a way to explore a wider area and specific conditions of applications.

Results

In this work, electrospun PA6 mats with nanofiber diameters ranging from 50 nm to 350 nm were studied in comparison with a PA6 film (110 µm thickness). The microstructure was first investigated by room-temperature X-ray diffraction and infrared spectroscopy. Two crystalline forms were mainly distinguished in consistence with previous studies which showed that α-crystals are formed by extended molecular chains while γ-crystals were formed by pleated chains.[2] Then, the microstructure evolution was monitored by means of high temperature X-ray diffraction. The results underlined that the mat with the smallest nanofiber diameter presents a majority of γ-crystals. Besides, the thinnest nanofibers showed higher thermal stability. Fast scanning calorimetry investigations that allowed heating the samples with extremely high rates, thus hindering the crystalline reorganization, evidenced a shift of the melting to high temperatures with decreasing the nanofiber size. The glass transition temperature, determined by modulated temperature differential scanning calorimetry, increases with decreasing nanofibers diameters, suggesting a higher degree of orientation. These results are in harmony with mechanical properties investigations stating their outstanding improvement with decreasing nanofiber diameters.

Keywords: polyamide 6 , thermal stability, High temperature X-ray diffraction, Fast Scanning Calorimetry

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Polymer characterization on multi-component non alcoholic beer matrix

R.C. Moreno Ravelo*, M. Gastl, T. Becker

Lehrstuhl für Brau- und Getränketechnologie (TUM), Freising, Germany
**rolando.moreno-ravelo@tum.de*

Among the multiple parameters that could be determined from cereal based beverages, the molar mass of polymers is critical for the product´s functionality. However, the same multi-component system may hinder an accurate molar mass determination of molecules present in the matrix. Concerning these products, non alcoholic beer (NAB) have gained relevance among consumers. Thus, this work aims to show a strategy to correctly characterize molar mass of starch and non-starch polysaccharides present on NAB.

NAB contains multipe volatile and non-volatile molecules. Regarding the latter, starch and non-starch polysaccharides are the more predominant. Their concentration and physical characteristics in the final product are dependent on raw materials used and brewing process. Dextrins are product of starch degradation during the mashing process while arabinoxylan and β-glucan are mainly degraded over malting. The physical characteristics of these polysaccharides are key to improve the sensory characteristics of the sample (palate fullness[1]), and its processability (lautering/filtration) respectively[2,3]. Chromatography techniques have been employed to elucidate the distribution and conformation of polymers; exemplary, asymmetrical flow field-flow fractionation (AF4) has been used to fractionate cereal based beverages. Furthermore, when coupled to a multi-angle light scattering (MALS) and differential refractive index (DRI), the absolute molar mass may be obtained[4]. However, since the separation principle is based on hydrodynamic volume, co-elution of molecules with similar size but different characteristics are plausible. Hence, inaccurate characterization of large molecules[5], such as (non-)starch polysaccharides, might be present in NAB. Therefore, an approach to prevent co-elution when analyzing NAB by AF4-MALS-DRI would improve its molar mass determination.

To sum up, the molar mass of starch and non-starch polysaccharides in NAB grant certain functionality highlighting the importance of their correct characterization. However, the same polymers present in the matrix impede an accurate molar mass determination due to AF4 co-elution. Consequently, this work is showing a strategy to circunvent this by using enzymatic degradation. Depending on the (non-)starch polysaccharides to be studied, different enzyme combinations are employed to specifically remove the non-desired polymers from the NAB matrix; hence, improving the molar mass characterization of large molecules by AF4-MALS-DRI. Parameters such as the matrix influence, concentration aggregation, filter size and type, enzymatic innactivation by boiling on NAB matrix will be analyzed. Besides the proposed method, the parameters examined during this work might be extrapolated on other beverage systems for a more accurate polymer characterization.

Keywords: non alcoholic beer, asymmetrical flow field-flow fractionation, molar mass.

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Multi-functional polymer coatings based on zwitterionic phospohrylcholine

Alexander S. Münch[1*], Petra Uhlmann[1]

[1] Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany
**muench@ipfdd.de*

Functional polymer films, like stimuli-responsive polymer brushes, comb-like polymers or cross-linked polymer networks, are a group of smart surface coatings for the design of intelligent interfaces. Such innovative surface coatings have to adopt additional intelligent functions preferentially simultaneously. These films were prepared by a one step “grafting-to” approach of specifically designed and synthesized *co*-polymers allowing the modification of surfaces with preformed and most notably well-defined macromolecules. The formed transparent thin films can adjust and modulate the properties of the interface as a result of the current environmental conditions. As an example for such a system a novel multi-functional coating with simultaneous easy-to-clean, non-fouling as well as anti-fog properties based on *co*-polymers consisting of zwitterionic phosphorylcholine groups (MPC) and benzophenone units (BPO) as anchor and UV cross-linking agent will be presented.[1-3] A set of *co*-polymers with different contents of BPO was synthesized by atom transfer radical polymerisation to investigate the influence of the degree of cross-linking on the performance of the films. To determine an optimal polymer composition and to understand its influence on the easy-to-clean, anti-fouling and anti-fog properties a combined study of infrared and UV-Vis spectroscopy, contact angle as well as in-situ ellipsometry measurements was performed. The study demonstrates that an exactly balanced ratio between thickness of the dry films, degree of swelling, and water contact angle, which can be controlled by tailored polymer chemistry and the amount of the cross-linker, is necessary to create such multi-functional surface coatings with tailored properties.

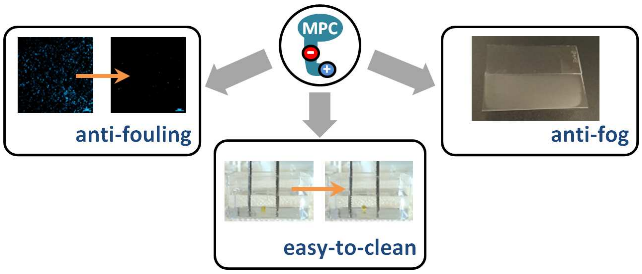

Figure 1. Illustration of anti-fouling easy-to-clean as well as anti-fog performance of a zwitterionic phosphorylcholine coating.

Keywords: phosphorylcholines, functional polymer coating, *co*-polymer, in situ ellipsometry, easy-to-clean, anti-fouling, anti-fog

Acknowledgments

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Effects of PEG on PLLA isothermal crystallization and morphology

Q. Papeloer, S. Demoustier-Champagne, A. M. Jonas
Institute of Condensed Matter and Nanosciences, UCLouvain, Louvain-la-Neuve, Belgium

Poly(L-lactic acid) (PLLA) is a semi-crystalline thermoplastic polymer commonly used for medical applications thanks to its biocompatibility and ease of processing, in particular through 3D printing [1]. For such applications, morphology and mechanical properties are crucial as they define the behaviour of cells toward the material [2]. In turn, these parameters depend on crystallinity, which can be tuned by thermal treatment [3] or by blending with other polymers [4]. In this work, the isothermal crystallization of (partially) miscible physical blends of PLLA and poly(ethylene glycol) (PEG), another biocompatible semi-crystalline polymer, will be studied. The combined effect of PEG blending and isothermal crystallization is expected to broaden the range of accessible morphologies and therefore enlarge the use of PLLA in biomedical applications.

The isothermal crystallization of the blends has been studied by flash Differential Scanning Calorimetry (fDSC), and the semicrystalline morphology was directly observed by Polarised Optical Microscopy (POM). fDSC was used in place of conventional DSC as it allows to quench the PLLA from its melting temperature to the desired crystallization temperature, preventing the PLLA to crystallize during cooling.

The isothermal crystallization of PLLA was found to be perturbed significantly in blends comprising more than 30% PEG, with the emergence of a new PLLA crystal form appearing in the presence of PEG for lower crystallization temperatures below the glass transition temperature of pure PLLA (grey arrows in Fig. 1(a) for a 50/50 PLA/PEG blend). The amount of blended PEG also influences the morphology of PLA spherulites as well as its crystallization temperature on cooling from the melt. For example, a 50/50 PLA/PEG blend starts to crystallize from the melt at 117°C and forms banded spherulites (Fig. 1(b)) whereas a 80/20 PLA/PEG crystallizes at 140°C and forms spherulites exhibiting the standard Maltese crosses (Fig. 1(c)).

These first results reveal the strong effect PEG may have on PLLA crystallization, such as change of crystal form, larger range of crystallization temperature, and different spherulitic morphologies. In the presentation, we will show the complete variety of crystallization behavior and morphologies that the addition of PEG can induce, which should bring new opportunities for using PLLA in biomedical applications.

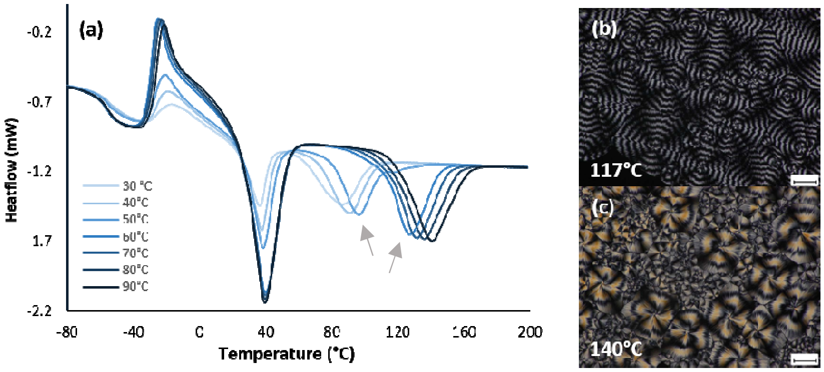

Figure 1 : (a) fDSC heating curves of PLA/PEG 50/50 mixture after isothermal crystallization at the indicated temperatures. Grey arrows point to the two different melting endotherms that emerge depending on crystallization temperature in the presence of PEG. POM images of PLA/PEG 50/50 crystallized at 117°C (b) and PLA/PEG 80/20 crystallized at 140°C (c). Scale bar = 100 µm.

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The fate of microplastics: Release rates of micro- and nanoplastic fragments and dissolved organics

Patrizia Pfohl[1*], Thorsten Hueffer[2], Thilo Hofmann[2], Wendel Wohlleben[1]

[1] *BASF SE, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany*
[2] *Department of Environmental Geosciences, Centre for Microbiology and Environmental Systems Science, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria*
**patrizia-marie.pfohl@basf.com*

Microplastics are ubiquitous in the environment, and fragmentation mechanisms play an important role to understand their fate. [1] For example, nanoplastics < 100 nm are expected to have a potentially higher bioavailability. Insights into fragmentation and degradation mechanisms and rates of microplastics into micro- and nanoplastic fragments and other degradation products are limited.

Here we adapted the ISO22293:2020 NanoRelease protocol [2], originally developed to quantify released fragments from macroplastics under weathering, to simulate UV aging at a beach and abrasion in the surf zone. We assessed the formation of micro- and nanoplastic fragments and other degradation products (Figure 1) from microplastic powders of polyamide (PA-6, PA-12) and thermoplastic polyurethane (TPU) and we developed protocols for a size-selective quantification of the generated degradation products.

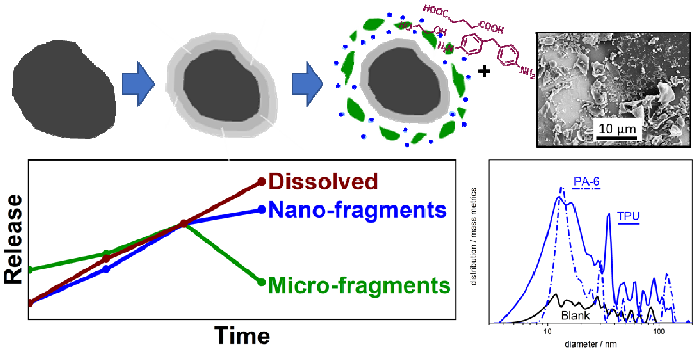

Figure 1: Fragmentation and degradation of microplastics into micro- and nanoplastic fragments and dissolved organics (shape, sizes, concentration).

Since microplastic degradation strongly depends on the chemical composition, the morphological and structural properties of e.g. aged TPU differ from aged PA. Furthermore, TPU ethers vs. esters as well as aromatic vs. aliphatic TPUs show differences in their chemical degradation.

The majority of the polymer powders, except for aliphatic TPUs, showed an increase in carbonyl/hydroxyl groups on the aged surface, changes in morphology (i.e., holes/structures under the surface), and a molar mass reduction with increasing UV dose. With increasing duration of UV irradiation, a larger amount of smaller and also nano-sized fragments was formed. We were able to identify a partial dissociation of aromatic TPUs and PA-6 into water-soluble organic compounds.

The presented results help to better understand the fragmentation of various microplastic types down to nanoplastics and water-soluble organics. The data can be used to validate predicted (micro)plastic degradation processes in mechanistic fragmentation models and to estimate their half-lives.

Keywords: microplastics, fragmentation, degradation, UV aging

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Mutual and Thermal Diffusivities in Polystyrene Melts with Dissolved Nitrogen by Dynamic Light Scattering (DLS)

M. Piszko[1*], T. Schaible,[2] C. Bonten,[2] and A. P. Fröba[1]

[1] *Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP),*
Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen, Germany
[2] *Institut für Kunststofftechnik, University of Stuttgart, 70569 Stuttgart, Germany*
[*] *maximilian.piszko@fau.de*

Thermoplastic foams are used in a broad variety of applications as they offer several advantages, such as comparatively low densities associated with a reduction in component weight. For technical applications, most foam parts are produced by injection molding or extrusion with physical or chemical blowing agents. In such processes, the resulting foam properties are governed by the nucleation and bubble growth behavior, which are both strongly influenced by the thermophysical properties of the blowing-agent-loaded polymer melt. Besides viscosity, solubility, and interfacial tension, especially knowledge on diffusion coefficients in corresponding mixtures is necessary for understanding and characterizing the bubble growth processes during foaming of thermoplastic polymers.

The present contribution demonstrates for the first time the applicability of dynamic light scattering (DLS) for the characterization of molecular mass and thermal transport in binary mixtures consisting of a macromolecular polymer and a dissolved gas by the determination of the mutual or Fick diffusion coefficient D_{11} and the thermal diffusivity a. In comparison to conventional techniques for the study of transport properties, the DLS method is applied in macroscopic thermodynamic equilibrium and does not need any calibration procedure. As model system, a mixture of technical-grade polystyrene and nitrogen was selected. It was evidenced that the obtained experimental signals are associated with hydrodynamic fluctuations. Their analysis allows the determination of a and D_{11} with typical expanded experimental uncertainties ($k = 2$) of (12 and 7)%, respectively. For temperatures T between (423 and 555) K and pressures p between (0.1 and 5.8) MPa, a slightly decreases with increasing p and T. The values for D_{11} tend to decrease as a function of p between about (1 and 5) MPa at given T, but are within combined uncertainties. In contrast, D_{11} shows a significant Arrhenius-like increase as a function of T between about (423 and 555) K. The behavior of D_{11} as a function of T and p is further discussed in connection with the viscosity η, where in this work always an inverse relationship is found. The present experimental data demonstrate that the DLS method allows the accurate determination of a and D_{11} in binary mixtures consisting of polymer melts and dissolved gases. Moreover, the data may further stimulate theoretical and experimental investigations aiming at the improvement of existing or establishing new bubble-growth models allowing an improved prediction of the resulting foam properties.

Keywords: mutual diffusivity, thermal diffusivity, dynamic light scattering, polymer melt, dissolved gas

Epoxy-ionic liquids networks: morphology, molecular mobility and relationships with electrical properties

T. Lefort[1, 2], J. Duchet-Rumeau[1], D. Bachellerie[2], S. Livi[1], F. Jacquier[2], A. Girodet[2] and S. Pruvost[1,2]
[1] Univ. Lyon, INSA Lyon, UMR CNRS 5223, IMP Ingénierie des Matériaux Polymères, F-69621 Villeurbanne, France
[2] SuperGrid Institute SAS- 23, rue Cyprian, BP 1321 - 69611 Villeurbanne, France
*Corresponding Author: *sebastien.pruvost@insa-lyon.fr*

In recent years, ionic liquids (ILs) have attracted great interest in the materials field, due to their low vapor pressure, good chemical and thermal stability, infinite number of cation-anion combinations, high ionic conductivity and ability to dissolve polymers. In addition, their low melting point allows them to be compatible with the polymer process temperature. These characteristics make them attractive in a wide range of fields, such as electrolytes, lubricants, plasticizers and material additives.

Recently, several authors have demonstrated the reactivity of ionic liquids towards epoxy to form new epoxy-based networks. In 2012, the initiation of homopolymerization of an epoxy system by an imidazolium-based IL was demonstrated [2]. A few years later, the same team extended the study to pyridinium- and phosphonium-based ILs and pointed out that they also have the ability to form new epoxy networks without the aid of a conventional hardener [3, 4]. These studies have highlighted the key role of ILs and their impact on the final properties of the material. Indeed, thermal stability, glass transition and hydrophobicity can be increased due to the presence of ILs incorporated in the epoxy network. However, many questions remain open, including the network formation and mechanisms induced by phosphonium-based ILs to the epoxy prepolymer.

The present study proposes to complete the knowledge on these new epoxy-ionic liquid networks, by providing the last building blocks for a complete understanding through molecular mobility [5]. The study of molecular relaxations observed by dielectric spectroscopy as well as characterizations by dynamic mechanical analysis have allowed to finely analyze the epoxy network formed by homopolymerization. Particular attention will be paid to the electrical conductivity and its dependence on the electric field and temperature.

Keywords: epoxy networks, ionic liquid, molecular mobility, electrical properties

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Understanding the morphology of proton-exchange membranes based on functionalized syndiotactic-polystyrene via small-angle neutron scattering

A. Radulescu[1]

[1]*Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science (JCNS) at Heinz Maier-Leibnitz Zentrum (MLZ) , Garching, Germany*
**a.radulescu@fz-juelich.de*

To design new proton exchange membranes (PEM), one should not only consider the polymer molecular architecture, but also understand the microstructure of membranes, such as the crystalline domains, or the water distribution in the conducting regions. The sulfonated syndiotactic polystyrene (s-sPS) in β-form can be a good candidate for PEM in some fuel cell applications, as it presents a high proton conductivity (comparable to NAFION), high chemical and thermo-mechanical stability and a low cost. The preparation of such PEMs should start form the δ-form (clathrate with guest molecules) that allows a homogeneous sulfonation of the amorphous regions and the preservation of the material crystallinity, and can be subsequently transformed into the β-form by annealing at high temperature. We report here a microstructural investigation on s-sPS and s-sPS/fullerene membranes at different hydration levels and temperatures by using the contrast variation small-angle neutron scattering (SANS) technique complemented with XRD, FTIR, UV-Vis and microscopy observations. Uni-axially and as-cast films containing sPS δ-form were functionalized to different degrees, which were determined by neutron activation analysis. The use of uniaxially deformed films and of contrast variation allowed for the identification and characterization of different structural levels with sizes between nm and µm, which form and evolve in both the dry and hydrated states [1]. The scattering length density of the crystalline regions was varied using the guest exchange procedure between toluene isotopologues incorporated into the sPS lattice, while the variation of the scattering properties of the hydrated morphous regions was achieved using different H_2O/D_2O mixtures. A direct understanding of the hydrated regions and conduction paths was possible following the analysis of the relationship between the morphology of hydrated domains as obtained by SANS and the proton conductivity measured in different conditions [2].

Keywords: semicrystalline polymers, proton-exchange membranes, SANS

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Rigid Rodlike Polymers and Rigid Rod Networks : Synthesis, Structure, and Properties

Nikolaus Rennar

University of Applied Sciences Würzburg, Plastics and Rubber Technology
Würzburg, Germany
nikolaus.rennar@t-online.de

Conventional rubber elastic materials consist of flexible polymer chains joined at relatively few junction points to form a three-dimensional network. During deformation a large number of different configuration transitions take place and therefore, the properties of typical elastomers are governed mainly by entropy. Several models quite different in origin try to explain their mechanical and optical properties on theoretical basis. Even the role of fillers and entanglements can be taken into consideration by applying modern physical and mathematical concepts [1]. But only a small number of publications deal with rigid rod networks where the flexible chains have been replaced by rigid rods [2].

Therefore, objective of the present study was to synthesize rigid rodlike polymers and rigid rod networks, to investigate their properties, and to compare these data with theoretical predictions. In a first step, linear polymers with stiff backbone and with specified end-groups were produced by classical polycondensation. In a second step, different types of rigid rod networks were prepared :

- To obtain purely entropic networks, the rods were freely joined with similar topology of crosslinking as in flexible chain networks.
- To get enthalpic networks, rods were connected rigidly.

FTIR spectroscopic measurements as well as TGA, DSC, WAXS analysis, and surface tension experiments were conducted to characterize the uncrosslinked rodlike material. Furthermore, the mechanical and electrical properties of the resulting composite materials were investigated using different test methods and different test conditions (concentration, temperature, frequency, deformation amplitude).

Our studies reveal an initial decomposition of the tested rigid rodlike polymer at about $T > 720$ K in surrounding air atmosphere. DSC thermograms show a first-order transition at $T \approx 620$ K. According to theoretical predictions, the scaling of the shear modulus G with the volume fraction Φ_R of the rods should be different for both types of rigid rod networks :

- $G \sim \Phi_R^{1.5}$ for flexible crosslinks and
- $G \sim \Phi_R^{2.0}$ for frozen crosslinks.

Indeed, the tests indicate that the moduli of both series of composite materials can be described by different scaling laws in accordance with theory [3]. These relationships are quite different from the scaling law of polymer networks consisting of flexible chains. Furthermore, it is demonstrated that a linear polymer with fully conjugated backbone is not a prerequisite for a polymer to become electronically conducting. But the conductivity can be increased tremendously by chemical doping, also in agreement with modern theories [4].

Keywords : rodlike polymers, polymer networks, rubber elasticity, scaling law, electrical conductivity

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Directional Self-Assembly of Polymer-Grafted Nanoparticles

S. Vazirieh Lenjani, C. Rossner[1*]

[1]*Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany.*
[*]*rossner@ipfdd.de*

This presentation will highlight approaches toward nanoparticle patterning through the recently established paradigm of constrained de-wetting in polymer grafted nanoparticles.[1] It will be shown how adaptive polymer ligands can be used to achieve surface patterning through distinct stimuli (like solvent environment, temperature, chemical triggers).[2,3] Building on that, it will be demonstrated how diblock copolymers can be employed to achieve colloidally stable, asymmetrical polymer-coated nanoparticles; and their directional self-assembly into supracolloidal clusters will be discussed (see Figure 1).[3]
Finally, an alternative paradigm for directional nanoparticle self-assembly that does not rely on prior surface patterning with polymer ligands will be discussed. It will be shown that polystyrene-coated gold nanorods can undergo directional tip-to-tip self-assembly, even when they are uniformly coated with a polymer ligand layer.[4] The importance of electrostatic forces for the observed directional colloidal interactions will be discussed.

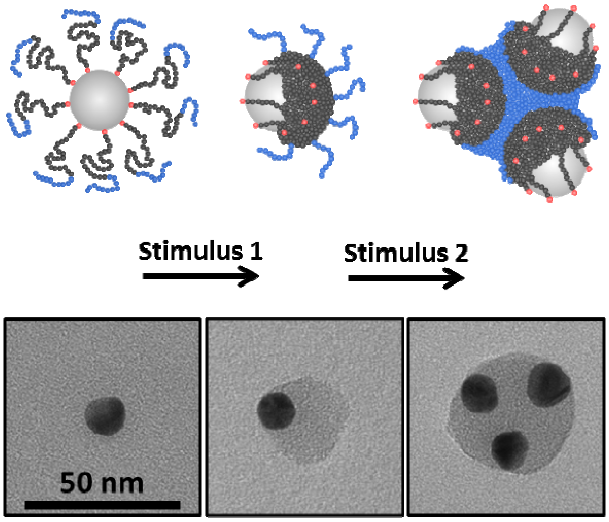

Figure 1. Staged surface patterning and self-assembly of diblock copolymer-grafted nanoparticles, mediated by two orthogonal stimuli.

Keywords: Hairy Nanoparticles, Self-Assembly, Supracolloidal Clusters

Acknowledgments

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Role of polyethylene microstructure in mechanical properties of amorphous regions.

A.Rozanski[1*], M.Polinska[1]
[1]*Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences,*
Sienkiewicza 112, 90-363 Lodz, Poland
[*]*rozanski@cbmm.lodz.pl*

In our recent work[1] a universal method to determine the elastic modulus of interlamellar amorphous phase of semicrystalline polymers was described. The methodological details were presented on the example of high density polyethylene (HDPE). The local deformation of the amorphous component was induced by the introduction of the swelling agent (Fig. 1). The swelling-induced local strain (ε_a) and local stress (σ_a) of the interlamellar amorphous regions were estimated based on the changes of the long period (LP) and the yield stress, respectively. The elastic modulus of the interlamellar amorphous phase of HDPE, determined in accordance with the following equation ($E_a=\sigma_a/\varepsilon_a$), was an order of magnitude higher (≈40 MPa) than the modulus of the bulk rubbery amorphous phase of HDPE (≈3 MPa)[2].

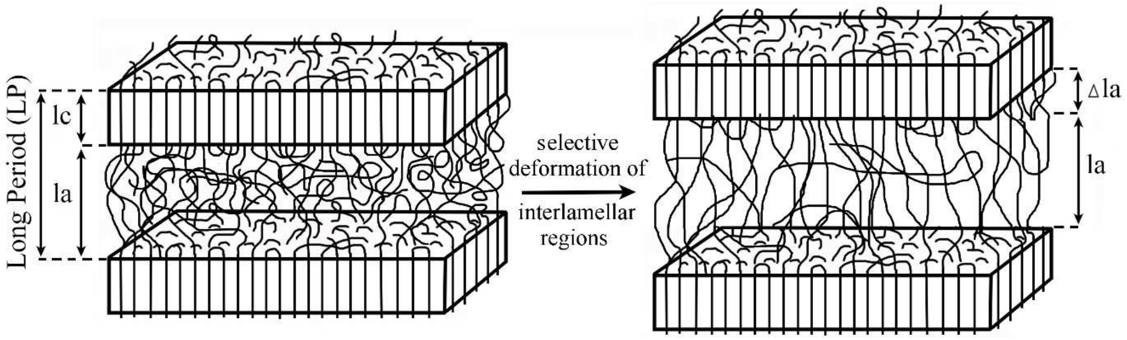

Figure 1. Schematic change of interlamellar distance.

In the current work, a more detailed analysis of the relation between the elastic modulus of the interlamellar amorphous phase and the microstructure of the polymer was carried out. Three different polyethylenes (HDPE, low density polyethylene (LDPE) and ethylene-octane copolymer (EOC)) solidifed under different conditions were analyzed. A linear change of the elastic modulus of the amorphous regions with the thickness of the lamelar crystals was observed. It was shown that with an increase in the crystal thickness, the α relaxation processes of the crystalline component became less "active". This, in turn, induced a gradual decrease in the relaxation ability of the chain's fragments localized in the interlamellar (amorphous) regions and physically connected with the lamellar crystals.

Acknowledgments
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The influence of the furan and maleimide stoichiometry on the thermoreversible Diels-Alder network polymerization

A. Safaei[1*], S. Terryn[1] , B. Vanderborght[1], G. Van Assche[1] and J.Brancart[1]

[1] Vrije Universiteit Brussel, Brussels, Belgium
[*]Corresponding Author: ali.safaei@vub.be

The most studied Diels–Alder (DA) reaction is the cycloaddition of furan, a conjugated electron rich diene, and maleimide, an electron poor dienophile, forming a DA cycloadduct. The reverse process, called the retro Diels-Alder (rDA) reaction, converts the cycloadduct into the starting diene and dienophile. Their sufficiently fast reaction kinetics and high conversion at room temperature [1] make them suitable candidates for thermoresponsive materials, such as, thermoremendable and self-healing polymer networks. These reversible networks have been proven to be valuable in robotics applications [2,3] which can be processed and healed at temperatures between 80 °C and 140 °C due to the thermoreversible crosslinking. DA-polymer networks are synthesized in two steps: (i) furfuryl glycidyl ether (FGE) is irreversibly bonded to Jeffamine (JD400) to yield a furan-functionalized Jeffamine, (ii) the furan groups on the furan-functionalized Jeffamine are reacted with the maleimide groups on a bismaleimide to form DA-crosslinks that form a thermoreversible network. In this study, the thermoreversible Diels-Alder reaction between furan and maleimide functional groups has been studied extensively in the context of self-healing elastomers and thermosets. To elaborate the influence of the stoichiometric ratio between the maleimide and furan reactive groups on the thermomechanical properties and viscoelastic behaviour of formed reversible covalent polymer networks, series of Diels-Alder-based networks with different stoichiometric ratios (r= 1, 0.8, 0.7, 0.6, 0.5, and 0.4) were synthesized. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and dynamic rheology measurements were performed on the reversible polymer networks, to relate the reversible network structure to the material properties and reactivity. In summary, lowering the maleimide-to-furan ratio, creates a deficit of maleimide functional groups, resulting in a decrease in the crosslink density of the system, and a consequent decrease in the glass transition temperature, Young's modulus, and gel transition temperature. The excess of unreacted furan in the system results in faster reaction and healing kinetics and a shift of the reaction equilibrium. Our work illustrated that starting from only two specific monomers, a bismaleimide (DPBM) and a furan functionalized Jeffamines (F400), a wide variety of polymer networks can be synthesized with mechanical properties ranging from very stiff thermoset to a hyperelastic elastomer that can heal at room temperature.

Keywords: Reversible polymer networks; Dynamic covalent bond; self-healing; reaction kinetic simulations

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Changes in the barrier properties of polylactide and its blends as a result of the diversity of amorphous phase microstructure

M. Safandowska[1*], C. Makarewicz[1,2], A. Rozanski[1], R. Idczak[3]

[1] *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland*
[2] *The Bio-Med-Chem Doctoral School of the University of Lodz and Lodz Institutes of the Polish Academy of Sciences, Lodz, Poland*
[3] *Institute of Experimental Physics, University of Wroclaw, Wroclaw, Poland*
[*] *msafan@cbmm.lodz.pl*

The transport properties of polylactide (PLA) materials to different gases and vapors are of paramount importance in assessing their suitability for packaging applications. It is known that gas permeability is significantly affected by any factors that hinder the diffusion of gas molecules. Crystallinity is one of the main factors in reducing polymer permeation. Semicrystalline polylactide is composed of amorphous and crystalline phases. Permeation mostly occurs through the amorphous regions whereas the crystals are known to be almost impermeable [1]. To date, the relationship between the nature of the amorphous phase (content, dynamics, free volume, degree of coupling with the crystalline phase) and gas barrier properties is not completely understood. In a previous work [2] we presented a new way of modification of amorphous regions of PLA by infusing triethyl citrate (TEC) into solidified polymer matrix. In the present study, we focused on determining the influence of a low molecular weight plasticizer (TEC, PEG, Glycerol) on the microstructure of the amorphous phase of polylactide in the context of its transport properties. It was found that the incorporation of small amounts of plasticizer (0.5-1.5 wt.%) into the polylactide matrix greatly reduces the transport properties to oxygen (Fig. 1). On the other hand, a further increase in the modifier content in PLA blends (exceeding 1.5 wt.% for Glycerol, 2.5 wt.% for TEC and 7 wt.% for PEG) led to a deterioration of these properties. Thermal analysis (DMTA and DSC measurements) showed that the plasticizers present in the PLA matrix reduce both the glass transition temperature and the melting point of the crystals, but did not affect the degree of crystallinity (constant value of X_C~33-34%). Therefore, the observed changes in the parameters of O_2 permeability could only be related to the molecular packing density of the PLA amorphous phase. This finding was confirmed by the positron annihilation lifetime spectroscopy, method used to track the average size of the free volume pores of amorphous component. Overall, by selecting the adequate composition of polylactide blends it is possible to obtain materials with appropriate transport properties for application fulfilling the specific requirements.

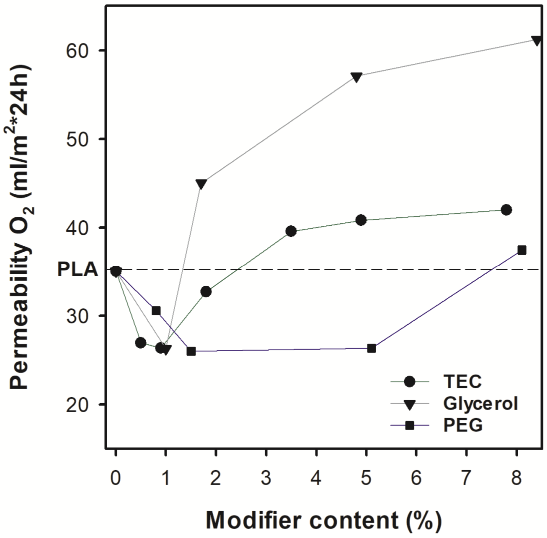

Fig. 1. Oxygen permeability of polylactide.

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Microfluidics fabrication of biomimetic giant polymer vesicles with extremely low size despersity responsive to intracellular imbalances

Vladimir Sincari, Eliézer Jäger, Jiří Pánek, Martin Hruby and Alessandro Jäger*
Institute of Macromolecular Chemistry, Czech Academy of Sciences, 16206 Prague, Czech Republic
**ajager@imc.cas.cz*

Microfluidics technology widenes the prospects of the size-controlled and highly monodisperse production of biomimetic self-assemblies for biomedical research. [1-2]

Herein, PDMS-based microfluidics was used for preparation and characterization of pH-responsive giant polymer vesicles (Ps). Giant Ps are formed from amphiphilic block copolymers by water-in-oil-in-water (W/O/W) double emulsion method with sequential dewetting process. Such synthetic giant Ps are highly attractive as biomimetic material since they possess the cell-like properties including semi-permeable membrane and aqueous core which can serve for cargo entrapment and delivery. [3]

The poly(1,2-butadiene)-*b*-poly(ethylene oxide) and the pH-responsive poly[2-(diisopropylamino) ethyl methacrylate-*b*-poly(ethylene-glycol) synthesized by reversible addition−fragmentation chain-transfer (RAFT) polymerization was utilized for the preparation of giant Ps with extremely narrow size distribution (Figure 1). The presence of the pH-responsive polymer block in giant Ps promotes the physical changes at specific pH, that caused polymeric membrane disruption. This behavior was well-studied by confocal microscopy. The obtained results demonstrated pH-controlled Ps disruption under simulated relevant physiological conditions. Cytotoxicity studies were performed with giant Ps, revealing great biocompatibility, which is important feature for biomedical application. The presented giant Ps could find application in pH-responsive drug and gene delivery, microreactors and as a model of artificial cell studies.

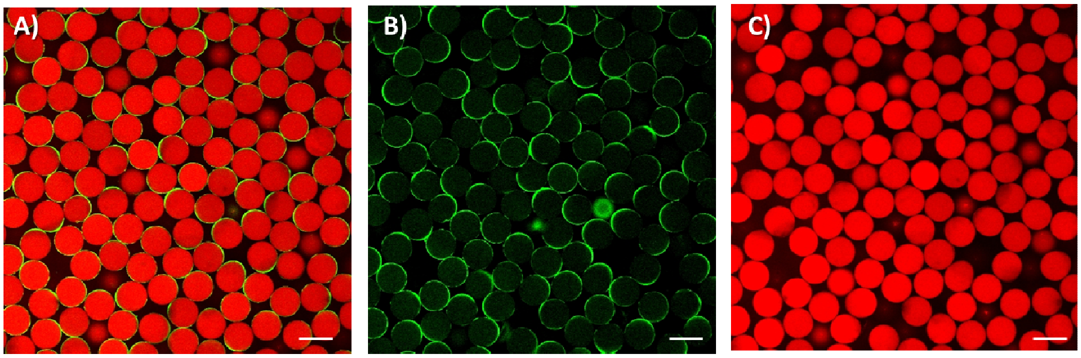

Figure 1. A) Confocal microscopy images of Giant PSs loaded with Nile Red and Calcein after solvent evaporation at cross-channel; B-C) and single channels for each dye; Scale bar 100 µm;

Keywords: microfluidics, PDMS, giant polymer vesicles.

Acknowledgments
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Dewetting of a thin polymer film under shear

K. Kadri[1], J. Peixinho[1], T. Salez[2], G. Miquelard-Garnier[1], C. Sollogoub[1*]

[1]*Laboratoire PIMM, Arts et Métiers, CNRS, Cnam, Hesam Université, 151 boulevard de l'Hôpital, Paris, France*
[2]*Université de Bordeaux, CNRS, LOMA, UMR 5798, F-33405 Talence, France*
[*]*cyrille.sollogoub@lecnam.net*

The objective of this work is to give new insight into the stability of thin polymer films under shear, in order to pave the way to a better control of the nanolayer coextrusion process[1,2]. To do so, a finite-difference numerical scheme for the resolution of the thin film equation was set up taking into account capillary and van der Waals (vdW) forces. This method was validated by comparing the dynamics obtained from an initial harmonic perturbation to established theoretical predictions. With the addition of shear, three regimes have then been evidenced as a function of the shear rate[3]. In the case of low shear rates the rupture is delayed when compared to the no-shear problem, while at higher shear rates it is even suppressed: the perturbed interface recovers its unperturbed state over time. In between these two limiting regimes, a transient one has been identified where shear and vdW forces balance each other, leading to a non-monotonic temporal evolution of the perturbed interface. While a linear analysis is sufficient to describe the rupture time in the absence of shear, the nonlinearities appear to be essential otherwise.

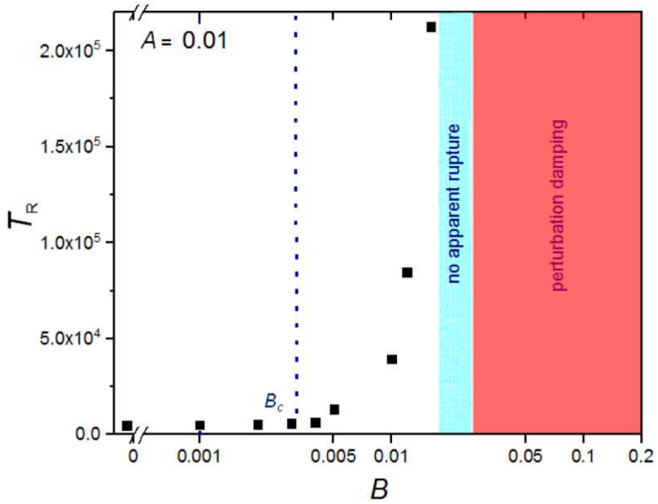

Figure. Dimensionless rupture time TR as a function of the dimensionless applied shear rate B, for a dimensionless Hamaker constant A = 0.01. When TR becomes larger than the total computational time, no rupture is observed, and for large enough B healing of the profile is even observed, as summarized by the colored areas.

Keywords: Thin films, Dewetting, Shear, Nanolayer coextrusion

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The balance of forces in cellulose solubility

Adriana Šturcová[1*], Nikolay Kotov[2], Vladimír Raus[1], Jiří Brus[1], Alexander Zhigunov[1]

[1] *Institute of Macromolecular Chemistry CAS, Heyrovského nám. 2, 162 06 Prague, Czech Republic*
[2]*Department of Chemistry, KTH Royal Institute of Technology, Drottning Kristinas väg 51, SE-100 44 Stockholm, Sweden*
[*] *sturcova@imc.cas.cz*

Despite being studied extensively, the driving forces and the mechanisms underlying dissolution of cellulose are not yet fully understood. Our understanding of cellulose solubility has been hindered for at least two reasons. The first reason is the fact, that cellulose is a polymer and even in amorphous form, polymers do not dissolve instantaneously, the process of polymer dissolution is not fully understood and is considered to be a multi-step process. The second reason, that has hindered our understanding of cellulose solubility, is its highly organized structure resulting from the interplay between the exact conditions of cellulose biosynthesis and physical interactions between the newly synthesized cellulose macromolecules. *E.g.*, cellulose in plant cell walls crystallizes into microfibrils – the microfibrils consist of highly ordered crystalline domains, of less-ordered surface chains, and of amorphous domains. In the crystalline regions, the individual chains are tightly packed as a result of highly cooperative network of intra- and inter-molecular hydrogen bonds and as a result of solvophobic effect (entropic factors). Such highly orchestrated ordering and structural organization does not energetically favour solubility. Treatments involving harsh conditions that are costly and damaging to the environment are necessary to dissolve cellulose.

In the work presented, we compare the structural changes of mixtures composed of cellulose and either of the following two cellulose solvent systems: an organic solvent N,N–dimethylacetamide with addition of lithium chloride salt (DMAc-LiCl) and an ionic liquid 1-butyl-3-methylimidazolium chloride (bmimCl).

It is clear, that both of the above systems are capable of dissolving cellulose without forming covalent bonds with its chains and that the dissolution process in either of them is very sensitive to the content of water. Upon dissolution, the highly co-operative network of cellulose hydrogen bonds is disrupted by both solvent systems and for the ionic liquid, there is also and indirect evidence of stacking between cellulose D-glucose units and ionic liquid aromatic imidazolium rings.[1] By the means of vibrational spectroscopy, X-ray diffraction, and NMR spectroscopy, the structural differences in cellulose chains solubilised by DMAc-LiCl and by bmimCl will be shown in this work.

Following upon our previous work on binary systems of bmimCl with water [2], where we showed the role of capillarity in structural transitions of bmimCl, we follow temperature-induced structural transitions also in binary systems cellulose/bmimCl and in ternary systems cellulose/bmimCl/water. An attempt is made to explain these differences and transitions in terms of rearrangement of hydrogen bonds and as a consequence of hydrodynamic flow, which is pointing to the role of capillarity.

Acknowledgments

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Thermal expansion of free volume in "classic" and regulated dimethacrylates

G. Consolati[1], F. Quasso,[1] E. Yaynik,[1] F. B. Vangosa,[2] O. Šauša,[3,4] K. Ehrmann[5] and H. Švajdlenková[6*]

[1] Department of Aerospace Science and Technology, Politecnico di Milano, via La Masa 34, 20156 Milano, Italy
[2] Department of Chemistry, Materials and Chemical Engineering 'Giulio Natta', Politecnico di Milano, Piazza Leonardo da Vinci 32 – 20133 – Milano Italy
[3] Department of Nuclear Physics, Institute of Physics of SAS, Dúbravská cesta 9, 845 11 Bratislava, Slovakia
[4] Department of Nuclear Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, Ilkovičova 6, 842 15 Bratislava, Slovakia
[5] Institute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9/163 MC, 1060 Vienna, Austria
[6] Department of Synthesis and Characterization of polymers, Polymer Institute of SAS, Dúbravská cesta 9, 845 41 Bratislava, Slovakia
[*]E-mail: helena.svajdlenkova@savba.sk

Dimethacrylate-based resins (poly2M) are widely used in many applications such as protective and decorative coatings, dental medicine, 3D lithography. The main drawback of these materials is that the common mixture of monomers (2M) form inhomogeneous and rather brittle polymer network. Recently, it was revealed that the photopolymerization of 2M via chain transfer agent such as thiol (EDDT) [1] leads to a polymer with more homogeneous network architecture increasing the toughness

In the first PALS studies of cured dimethacrylates, the microstructural characteristics were determined by using spherical approximation for the free volume holes. [2,3]

In this study, the extended knowledge about the real free volume characteristics in "classic" and controlled photocured dimethacrylates by combining the positron annihilation lifetime spectroscopy (PALS) and dilatometry with lattice-hole theory is reported for the first time. It was revealed that both samples have the flattened cylindrical shape of free volume holes at RT, which expand 'anisotropically' in poly2M sample and 'isotropically' in poly2M-co-EDDT resin. Moreover, regulated dithiol-based network structure forms large increased number density of reduced voids resulting to obviously higher void fraction than in poly2M sample. Finally, the NIR spectra of cured samples revealed that the positon of the the overlapping hidden peaks of 1th overtone stretching mode of N-H bonds and increasing relative intensity of the band attributed to "free" N-H groups in the network structure point out the strength and homogeneity of the network structure.

Investigation of relationships between the microstructural free volume characteristics (PALS), the intermolecular H bond interactions (NIR) and material properties can bring valuable knowledge about the key structural factors responsible for the improved material properties.

Keywords: dimethacrylates, free volume, positron annihilation lifetime spectroscopy, dilatometry, lattice-hole theory, Near-infrared spectroscopy

Acknowledgments
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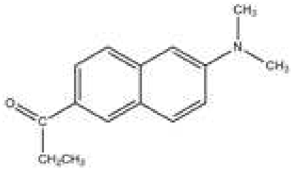
Using fluorescent probes to characterize polymer degradation

E-A Poutougnigni, B. Herve, G. Rapp, J-L Gardette, P-O Bussiere, S. Therias*

Université Clermont Auvergne, CNRS, Clermont Auvergne INP, ICCF, F-63000 Clermont-Ferrand, France
**sandrine.therias@uca.fr*

The aim of this work was to evaluate the potential of 2-dimethylamino-6-propionylnaphthalene (Scheme 1) (denoted Prodan®) as a sensitive fluorophore for monitoring the oxidation of polymers induced by thermal and photochemical oxidation. The emission features of this fluorescent probe are known to be strongly dependent on the polarity of the medium [1].



Scheme 1: Chemical structure of Prodan®

The fluorophore was introduced into polyethylene films (85 µm or 500 µm thick) before and after ageing by soaking in a methanolic solution. The distribution of Prodan® at the surface of PE films was recorded using fluorescence microscopy.

Figure 1 shows the images of Prodan® fluorescence impregnated into unaged and thermooxidized PE film. The images were recorded either at the surface or for the cross-section of a 500 µm thick film.

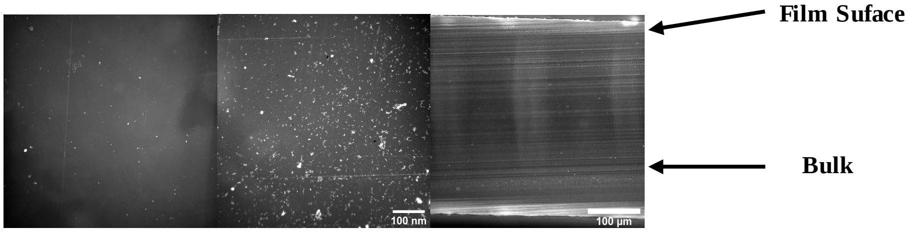


Fig. 1. Fluorescence microscopy images of Prodan® impregnated into a) unaged PE b) 48 h thermooxidized PE film surface and c) 48 h thermooxidized PE film (e=500µm) cross section.

Changes in polarity due to the formation of oxidized products provoked a notable shift of the wavelength at the maximum of fluorescence, which was correlated to the extent of the oxidation measured by infrared spectroscopy. Moreover, the emission intensity of the probe was observed to dramatically increase with the amount of oxidation products. It was observed that there was a good correlation between the wavelength at the emission maximum, the amount of absorbed fluorophore, and the oxidation extent [2].

Keywords: polymers; durability; fluorescence, oxidation, polarity

Acknowledgments

The authors wish to thank Sophie Desset from the CLIC (Clermont Imagerie Confocale) from GReD laboratory at Clermont-Ferrand University (France) for fluorescence microscopy images.

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Repulsive interactions of eco-corona covered microplastic particles quantitatively follow modelling of polymer brushes

Thomas Witzmann[1], Anja F. R. M. Ramsperger[2, 3], Simon Wieland[2, 3], Christian Laforsch[2], Holger Kress[3], Andreas Fery[1, 4] and Günter K. Auernhammer[1]

[1] *Leibniz-Institute of Polymer Research Dresden e.V., Institute of Physical Chemistry and Polymer Physics, Hohe Str. 6, 01069 Dresden, Germany*
[2] *Animal Ecology I and BayCEER, University of Bayreuth, 95447 Bayreuth, Germany*
[3] *Biological Physics Group, University of Bayreuth, 95447 Bayreuth, Germany*
[4] *Physical Chemistry of Polymeric Materials, Technische Universität Dresden, Hohe Str. 6, 01069 Dresden, Germany*

Environmental fate and toxicity of microplastic particles is dominated by their surface properties. In the environment an adsorbed layer of biomolecules and natural organic matter forms the so-called eco-corona [1]. A quantitative description of how this eco-corona changes the particles' colloidal interactions is still missing. Here, we demonstrate with colloidal probe-atomic force microscopy that the formation of the eco-corona on microplastic particles introduces a soft film on the surface which changes the mechanical behaviour. We measure single particle-particle interactions and find a pronounced increase of long-range repulsive interactions upon eco-corona formation. These force distance characteristics follow well the polymer brush model by Alexander and de Gennes. The foundation of the eco-corona interacting like a polymer brush with its surrounding may help understand microplastic transport and aggregation in the environment [2].

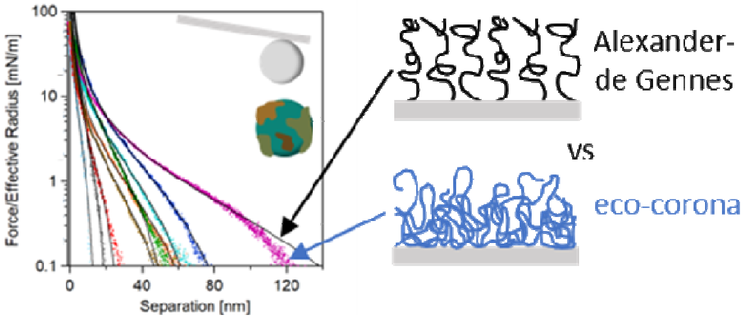

Figure 1. Interaction forces of the eco-corona are well describable by polymer brush theory of Alexander-de Gennes although structure is different as outlined right.

Keywords: eco-corona, interaction force, polymer brush, direct force measurement

Acknowledgments

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PVDF-based terpolymers: from chemistry to crystalline structures and morphologies

S. Zanchi[1*], S. Tencé-Girault[1,2], S. Roland[1]

[1]*Laboratoire PIMM, Arts et Metiers Institute of Technology, CNRS, Cnam, HESAM Universite, Paris, France*
[2]*Arkema, CERDATO, Serquigny, France*
**sara.zanchi@ensam.eu*

Electroactive polymers show a change of properties (size, shape, temperature…) when an electric field is applied [1]. **P(VDF-*ter*-TrFE-*ter*-CTFE)** terpolymers have been particularly studied since the 2000s and exhibit various electroactive properties depending on the comonomer content (%CTFE). For %CTFE=0, copolymers are ferroelectric (FE) and piezoelectric at room temperature (RT) and paraelectric (PE) above the Curie transition. While for %CTFE > 6% terpolymers are **relaxor-ferroelectric** (RFE) and electrostrictive at RT and PE at high temperature. The FE to PE transition is a 1st order crystal-crystal transition while the RFE to PE transition is a continuous crystal-crystal transition [2].

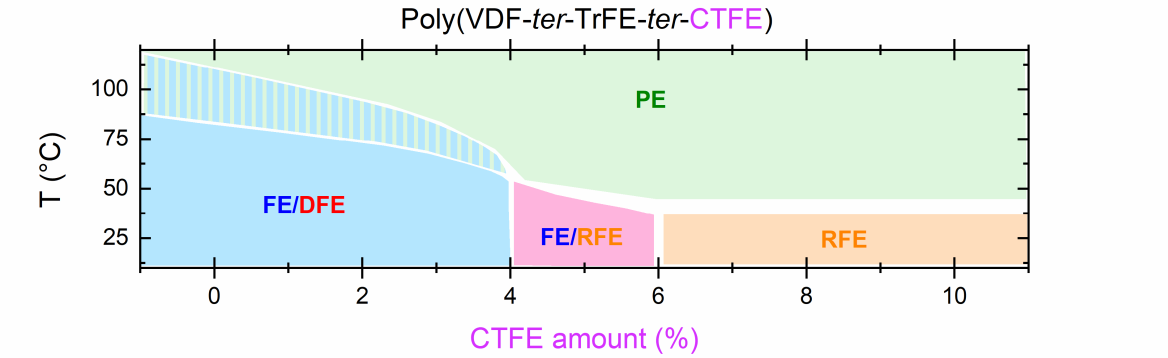

Figure 1 : Temperature versus mol% CTFE phase diagram of annealed poly(VDF-ter-TrFE-ter-CTFE) terpolymers [3].

These terpolymers belong to the family of RFE materials, whose characteristics lie on their peculiar electro-responsiveness (strain proportional to the squared electric field). Thanks to this interesting property, Piezotech® (Arkema) P(VDF-*ter*-TrFE-*ter*-CTFE) terpolymers are increasingly used **in organic printed and flexible electronics, such as actuators**.

The key parameters to take into account are the chemical composition (%CTFE) and the processing conditions, which have a strong impact on the crystalline structure and the morphology, and consequently on the electroactive properties. Recent SAXS (Small Angle X-ray Scattering), WAXS (Wide Angle X-ray Scattering), and AFM (Atomic Force Microscopy) experiments provided very interesting additional information on the evolution of the crystalline lamellae with the chemical composition and crystallization process used.

Keywords: VDF-based copolymers, SAXS-WAXS, AFM

Acknowledgments

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Influence of Gradient Strength on the Elution Behavior of Gradient Copolymers in Different Modes of Liquid Interaction Chromatography

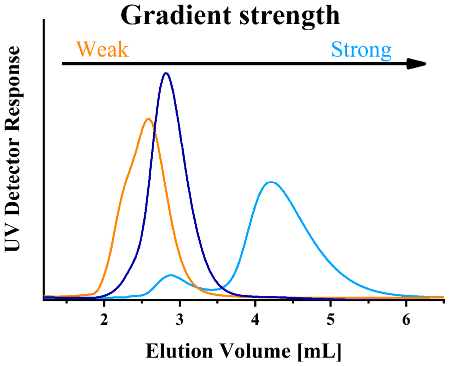
Blaž Zdovc[1*], Heng Li[2], Junpeng Zhao[2], David Pahovnik[1], and Ema Žagar[1]

[1]*Department of Polymer Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, Ljubljana SI-1000, Slovenia*
[2]*Faculty of Materials Science and Engineering, South China University of Technology, 381 Wushan Road, Guangzhou 510641, P. R. China*
[*]*blaz.zdovc@ki.si*

Gradient copolymers exhibit a gradual transition from predominantly A to predominantly B comonomer repeating units along the copolymer chains. This transition is defined by the strength of the gradient or the so-called microstructure, which affects the physical, chemical and mechanical properties of gradient copolymers.

In this contribution, we present the influence of gradient strength on the chromatographic behavior of copolymers in different modes of liquid interaction chromatography. The copolymers consist of poly(propylene oxide) (PPO) and poly(propylene phthalate) (P(POPA)) repeating units and have comparable average chemical composition and molar mass, as well as a narrow molar mass distribution.

The copolymers were separated by liquid chromatography at critical conditions (LCCC) for one of the copolymer constituents and by gradient liquid adsorption chromatography (gLAC). The results show that the gradient copolymers on both stationary phases eluted from the column according to the strength of the gradient, which is consistent with theory.[1] However, the block copolymer eluted from the column slightly before the gradient copolymer with the strongest gradient, which is a consequence of the slightly higher content or the total length of the PPO segments. In addition, the LCCC chromatograms of the gradient copolymer with the strongest gradient and the block copolymer show an additional peak of low intensity, while the gradient copolymers with the weakest and medium gradients show asymmetric chromatographic peaks. These peculiarities are a consequence of the low molar mass species present in the samples, which was confirmed by LCCC×SEC 2D-LC and LCCC/UV-MALS-RI. The influence of gradient strength on the chromatographic behavior of the copolymers was further confirmed by fractionation of the samples and characterization of individual fractions of the copolymers.



LCCC chromatograms of PPO-*g*-P(POPA) gradient copolymers with different gradient strength on PS-DVB reversed stationary phase at critical conditions for P(POPA).

Keywords: Gradient copolymers, microstructure, liquid interaction chromatography

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Using Resin Curing Shrinkage Measurement to Improve Electronic Reliability Prediction

Hossein Akbari [1*], Amandine Battentier[2]

[1]*ETUDES ET PRODUCTIONS SCHLUMBERGER, Clamart, France*
[2]*Schlumberger Technology Corporation, Sugar Land, USA*
[*]*HAkbari@slb.com*

Quantification and understanding of the evolution of chemical shrinkage of thermoset polymers is of crucial importance to model residual strains and stresses [1] . Polymer resins—including different adhesives—are commonly used in the electronic boards. These materials shrink during the curing and create residual stress. Residual-stresses development during manufacturing of composites depends mostly on the shrinkage behaviour of the polymer matrix from the point where stresses cannot be relaxed anymore [2]. Curing cycle and other processing parameters influence resin shrinkage. Electronic board manufacturers often use the resin manufacturer's recommended curing cycle. These curing cycles do not take material shrinkage and residual stress optimization into account. Finite element analysis (FEA) is often used to simulate electronic board reliability. Most simulations consider fully relaxed polymer materials, and we demonstrate that this is the wrong assumption.

In this paper, we evaluate different curing shrinkages and residual stress measurement methods to better understand material behaviour during the curing. We use several curing cycles and measure the impact on resin shrinkage. Chemical shrinkage of the curing resin is a linear function of the degree of cure [3]. We determine degree of cure and measure several critical material properties to find the optimal curing cycle for the application. We then feed shrinkage measurement results into FEA simulation to evaluate the impact of resin optimal curing cycle on overall electronic board reliability.

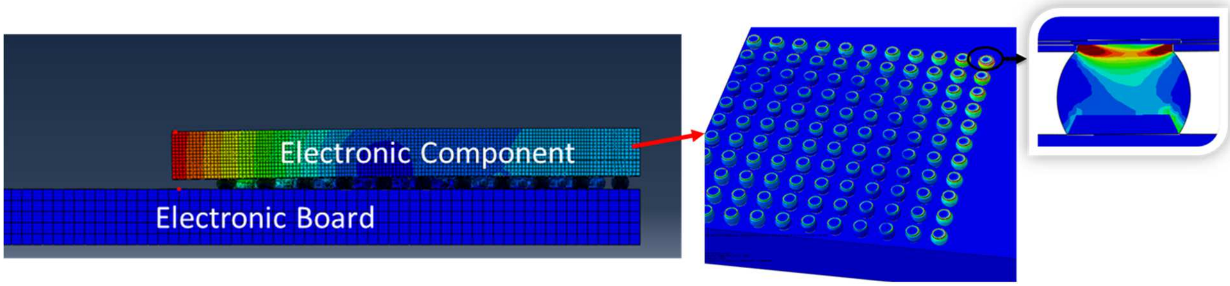

Figure 1: Electronic assembly stress evaluation by FEA

Keywords:
Curing Cycle, Electronics, Finite Element Analysis, Polymer Resin, Reliability, Residual Stress, Shrinkage.

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Liquid-Liquid extraction using hydrophilic & hydrophobic polyHIPE micromixers

H. Barkan-Öztürk[1], A. Menner[1], A. Bismarck[1,2*]

[1]*Polymer and Composite Engineering (PaCE) Group, Institute of Material Chemistry and Research, Faculty of Chemistry, University of Vienna, Währinger Strasse, 42, 1090, Vienna, Austria.*
[2]*Department of Chemical Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, United Kingdom*
[*]*alexander.bismarck@univie.ac.at*

Macroporous polymers produced by emulsion templating, so called polyHIPEs, were fabricated as micromixers to perform continuous liquid-liquid extractions. Micromixers are able to mix fluids through their microscale channels by molecular diffusion in laminar flow. As a result of increasing demand on process intensification units, the design and production of effective micromixers gained importantance in continuous mixing and reactions. In our previous studies,[1], [2] we showed that the interconnected macroporous structure of polyHIPEs can be fabricated as micromixers and advance mixing was achieved through the repeaded splitting and recombination of the fluid flow.

Mass transfer between immiscible liquids happens at their interface. In our polyHIPE micromixers mixing is achieved by emulsification, thus mass transfer can happen in a higher yield than many commercial micromixers, which have limited redirection of fluid compared to our polyHIPE scaffolds. Previously, we found out that the size of droplets created throughout the micromixer was dependent on the pore and pore throat size of the polyHIPE micromixers. We changed the wettability of the micromixer channel by producing polyHIPEs containing both hydrophobic and hydrophilic sections with pore and pore throat diameters of 5-10 µm and ~2 µm, respectively. By changing the wettability of the micromixer channel, we aimed to reverse droplet formation from water-in-oil in hydrophobic to oil-in-water in hydrophilic polyHIPEs, thereby improving mass transfer. The efficiencies of polyHIPE micromixers fabricated using both hydrophilic and hydrophobic polyHIPEs were tested by liquid-liquid extraction of 4-aminoacetophenone from its simulated water and ethanol based reaction medium to ethyl acetate. Extraction efficiency of polyHIPE micromixers increases to 98% using a micromixer produced with both hydrophilic and hydrophobic polyHIPEs, whilst hydrophobic polyHIPE micromixers alone achieved only an efficiency of only 83%.

Keywords: macroporous polymers, micromixers, continuous extraction.

Acknowledgments

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Interpenetrated polymer networks for vat photopolymerization 3D printing

A. Bischoff, B. Fanti, C. Delaite, C. Croutxé-Barghorn, X. Allonas*

Laboratoire de Photochimie et d’Ingénierie Macromoléculaires, Mulhouse, France
**xavier.allonas@uha.fr*

Photopolymerization reaction represents today an important tool in additive manufacturing field, often called 3D printing. Indeed, vat photopolymerization is the corner stone of different technologies such as Stereolithography (SLA), Digital Light Processing (DLP), Continuous Liquid Interface Printing (CLIP) or Liquid Crystal Display (LCD) 3D printing.[1,2] One of the most important effort of research focuses on the development of new materials with enhanced properties. This could be achieved through a fine tuning of the polymer properties[3] and a good control of the photopolymerization process[4,5].

In this study interpenetrated polymer networks have been synthesized through free radical photopolymerization. Butadiene acrylate-based polymer has been introduced in a high Tg acrylate polymer, leading to various material morphologies. Depending on the solubility parameters and the concentration of each component, the degree of interpenetration is shown to vary. Dynamical mechanical analysis was used to evidence the presence of different interphases and atomic force microscopy allowed the imaging of the topology and the mechanical properties. Finally, 3D printing using vat photopolymerization is shown to produce nice final objects with tunable mechanical properties.[6]

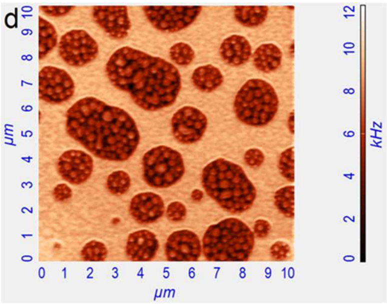

Figure 1: Example of morphology obtained in phase-separated photopolymerized acrylates.[6]

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Quantitative and qualitative determination of antioxidant in aged polyethylene with IR spectroscopy

M.Bredács[1*], E. Kanatschnig[1], A. Frank[1], G. Oreski[1], S. Gergely[2]

[1]Polymer Competence Center Leoben GmbH, Austria, Rosegger Street 12, 8700 Leoben
[2]Department of Applied Biotechnology and Food Science, Budapest University of Technology and Economics, Hungary, Műegyetem rkp. 3, 1111 Budapest
**marton.bredacs@pccl.at*

Lifetime of polyethylene (PE) products in long-term applications are affected strongly by the performance of antioxidants (AO), which protect the product form degradation by preventing oxidative processes. To ensure that the expected lifetime of a PE product will be reached monitoring and comparing the effectivity of AO packages are crucial. Various chromatographic techniques can be used to determine the concentration of active processing and long-term stabilizers, however these tests usually require considerable time and effort. Fast IR spectroscopic tests would be very beneficial for AO development and monitoring the AO consumption in various PE products.

This work focuses on the analysis of AO amount and their consumption in chlorine dioxide (ClO_2), a frequently applied disinfectant in PE pipe systems, aged PE pipe grade via FTIR-ATR and IR-microscopy. Transmission spectra collected form the cross-section of ClO_2 aged sample clearly indicate that the oxidation of the hydroxyl groups of phenolic AO can be monitored. In *Fig. 1* (a) the blue color indicates the loss hydroxyl groups due to the oxidative nature of ClO_2, while green area corresponds to a nonaffected bulk phase. Parallel to this process the increasing amount of quinoidal functional groups originating from the phenolic AO, can be seen in *Fig. 1* (b) signalized by the red area on top. The simultaneous increase of AO degradation product and decrease of active AO molecules represent well that AO degradation products can be studied separately from the PE aging products.

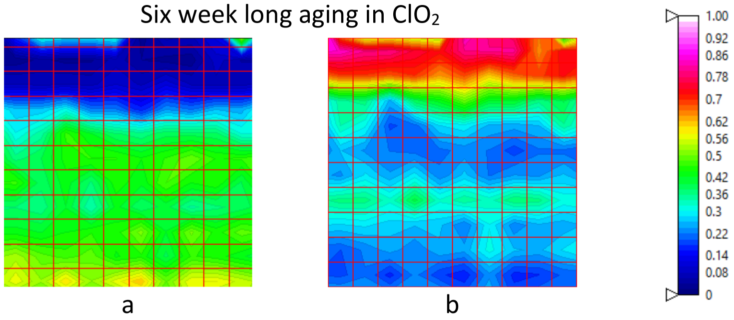

Fig. 1.: Loss of hydroxyl groups between 3700-3630 cm^{-1} (a), and the increment of cyclic ketone groups in the spectral range of 1590-1530 cm^{-1}(b) on the surface of ClO_2 aged PE pipe grade.

Moreover, multivariate data analysis of FTIR-ATR spectra recorded from a model PE mixed with 500, 1000, 1500, 2000 and 5000 ppm of Irganox 1010 – one of the most often used hindered phenolic AO – point out that AO concentration can be predicted. The 0.95 R^2 values of the calibration model based on the 3800-3450cm^{-1} range demonstrate that with FTIR-ATR the amount of active Irganox 1010 can be predicted quantitatively.

The conducted work clearly draws the attention to potential of IR spectroscopic techniques to qualitatively and quantitatively study the concentration of active AO molecules. These fast methods could be very beneficial to investigate AO concentration of PE product in long-term applications and also to aid the development of AO packages.

Keywords: PE aging, antioxidants, IR-microscopy, multivariate data analysis

How to tune thermal conductivity of polymers?

V. Cavallo[1,2*], A. Fina[2], S. Pruvost[1], J.F. Gérard[1]

[1]*Univ. Lyon, INSA Lyon, UMR CNRS 5223, Ingénierie des Matériaux Polymères, Villeurbanne, France*
[2]*Politecnico di Torino – Sede di Alessandria, Dept of Applied Science and Technology, Alessandria, Italy*
**valentina.cavallo@insa-lyon.fr*

Polymers are usually considered as thermal insulators as these ones display a low thermal conductivity, *i.e.* from 0.1 to 0.5 $W.m^{-1}.K^{-1}$. Specific properties of polymers such as their low density, low price, chemical resistance, and ability to sustain large deformations lead to an interest in such types of materials for heat exchangers for low temperature applications [1, 2]. Different ways to improve thermal conductivity in polymers are currently under investigation. For example, Kim et al. have reported a large increase in thermal conductivity of amorphous polymer blends from the substitution of weak Van der Waals interactions by stronger interactions such as hydrogen bonds [3].

In this work, we propose to act on thermal conductivity of amorphous polymers by tuning the nature and number of interactions existing between the macromolecular chains. For such a purpose, poly(methyl methacrylate) PMMA was selected as a reference. In order to gradually introduce intermolecular H-bonds, methyl methacrylate (MMA) monomer was copolymerized with methacrylic acid (MAA) to synthesize MMA-MAA random copolymers. The synthesis proceeded in bulk involved cobalt(II) 2-ethylhexanoate as initiator and led to PMMA homopolymer and PMMA-co-MAA copolymers (up to 70:30 wt.% of MMA:MAA) in a dense and transparent form. Polymers were characterized by ^{1}H-NMR to confirm the MMA:MAA molar ratio, by SEC to determine their molar mass, by DSC and TGA to study their thermal behavior, and by hot disc method to measure their thermal conductivity.

The thermal conductivity slightly increases with increasing the content of methacrylic acid units, *i.e.* from 0.21 $W{\cdot}m^{-1}K^{-1}$ for PMMA to 0.23 $W{\cdot}m^{-1}K^{-1}$ for PMMA-co-MAA 70:30wt%. As expected the thermal conductivity relates with the ratio between the two comonomers. This phenomenon could be explained by the different amount of inter and/or intra molecular chains H-bonds that can be formed.

In order to induce larger differences on thermal conductivity, the acidic functions were neutralized with different salts at various concentrations to introduce ionic interactions, *i.e.* stronger interchain physical bonds.

In a last step, the effect of the same type of interactions will be investigated in heterogeneous materials (polymer/polymer blends, composites, polymer/liquid crystal domains) for which a higher thermoconductive component will be added to the copolymers. For designing of composites, cellulose nanofibers will be considered trying to take advantage by the presence of surface hydroxyl groups. The latter ones could interact with the polar groups of the polymethacrylic polymers eading to larger changes in thermal conductivity.

Keywords: Methacrylate, Copolymers, Thermal conductivity, intra/inter molecular interactions

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Ultrasonic Waves Propagation through Organogel Films

C. Damiani[1,2*], L. Monnier[1], L. Ordronneau[1], N. Berton[2], B. Schmaltz[2], F. Tran-Van[2]

[1]*MODULEUS S.A., Tours, France*
[2]*Laboratoire PCM2E, EA6299, Université de Tours, France*
[*]*claire.damiani@moduleus.com*

Organogels, i.e. a polymeric matrices swollen by a plasticizer, are formulated as thin films for specific ultrasonic applications. In the current study, carboxylate diesters plasticizers are the main constituent of solvent-free organogels (at least 70% by weight) in combination with different matrices. The matrix/plasticizer couple has been selected to reach suitable acoustic attenuation α and acoustic impedance Z, being the product of longitudinal sound propagation u_L with mass density.

In order to study the relation between the chemical structure and the acoustic properties, several carboxylate diesters plasticizers and two matrices are tested. The chemical structure of the plasticizers contains either variations of the central functional group R_1 (aliphatic adipate, sebacate or aromatic trimellitate) or variations of the side functional group R_2 (methyl, ethyl, butyl, isobutyl, isodecyl, 2-bis ethylhexyl, phenyl, butoxy(ethoxy)ethyl). In addition, two matrices named A and B have been separately combined with the plasticizers to form organogels. The matrix A contains electronegative heteroatoms X able to promote H - - -O dipole bonding between carbonyl functional groups from the plasticizers and hydrogen atoms from the matrix (cf. Figure 1), while matrix B is a polyolefin constituted only by hydrocarbonated chains.

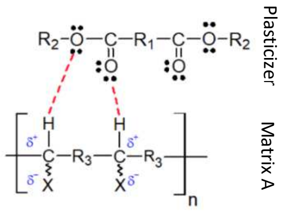

Figure 1: Hydrogen-Oxygen weak bonding between matrix A and carboxylate diester plasticizer

The first objective of our work is to check whether the Rao model is appropriate to correlate u_L and Z values of carboxylate diesters and for each of them corresponding organogels, with their chemical structure and molar concentration [1] [2]. Validating the Rao model would enable forecasting u_L and Z values of matrix A or matrix B based organogels without further test, regardless of the diester plasticizers' concentration or chemical structure. The second purpose of the current study is the assessment of respective contributions on organogels' acoustic attenuation, from pure plasticizers and from plasticizers/matrix interactions by comparing the three following α values ranking, according to changes in plasticizers' chemical structure: pure plasticizers, matrix A organogels and matrix B organogels.

Keywords: Ultrasound, Acoustic attenuation, Acoustic Impedance, Plasticizers, Organogels

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Relaxation features of an epoxy resin towards building applications

B. Quelennec[1], N. Delpouve[1*], R. Delannoy[2], E. Richaud[2], L. Delbreilh[1]

[1] *Normandie Univ, UNIROUEN Normandie, INSA Rouen, CNRS, Groupe de Physique des Matériaux – 76800 St Etienne du Rouvray*
[2] *PIMM, CNAM, CNRS UMR 8006, Arts et Métiers–ParisTech, 151 bd de l'Hôpital, 75013 Paris, France*
**Corresponding Author's: nicolas.delpouve1@univ-rouen.fr*

The addition of epoxy resin helps protecting concrete structures from water infiltration, leading several civil engineering constructions to target one hundred years applications. Nevertheless there is no definitive way to predict the behaviour of an epoxy resin at such a long–time scale, even less the possible interactions between the different aging processes. Indeed, epoxies slowly lose their properties under water uptake, as well as thermo–oxidation and structural relaxation.

The physical aging by structural relaxation occurs in any glass stored below its glass transition temperature. It consists in the minimization of its thermodynamic quantities, such as enthalpy and specific volume, to approach equilibrium. In glassy polymers, this phenomenon can negatively affect the dimensional stability during storage, resulting in the degradation of mechanical and barrier properties, as examples. It is often neglected since it is a long-time process, which makes moreover its study very challenging; however it becomes a concern for any applications targeting durabiliy.

The emergence of fast scanning calorimetry (FSC) provides new glimpses of hope for the depicting of physical aging. During a FSC experiment, a sample with a low mass (about tens to hundreds nanograms), is heated up and cooled down at rates in the order of thousand Kelvins per second. FSC can generate glassy polymers with high level of enthalpy or specific volume [1]. Moreover, since the glass transition is shifted to higher temperatures when increasing the cooling rate, the physical aging can also be investigated at temperatures higher than in standard differential scanning calorimetry. Besides, the structural relaxation can be tracked in accelerated conditions since the ratio surface/volume is significantly increased [2]. All these advantages favor the following of the physical aging in its entirety.

In this study, the relaxation dynamics of two epoxy resins differing by their crosslinking density are compared. The intrinsic mobility of the networks is investigated in the liquid state from dielectric relaxation spectroscopy (DRS) while the study of the physical aging is performed from FSC at various distances from the glass transition. The Tool–Narayanaswamy–Moynihan (TNM) model is employed to analyze the relaxation data. Finally, the impact of combined thermo-oxydation on relaxation kinetics is assessed.

Keywords: Glass transition, calorimetry, physical aging

Acknowledgments

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Radioresistant organic polymers for radiotherapy applications: testing of key properties

Jonáš Divín[1], Hynek Urban[1], Peter Černoch[1], Martin Hrubý[1], Ondřej Ploc[2], Denis Dudáš[3], Jiří Pánek*[1]

[1]*Institute of Macromolecular Chemistry of the CAS, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic,*
[2]Nuclear Physics Institute of the CAS, Hlavní 130, 250 68 Husinec, Czech Republic
[3]*UJP PRAHA a.s., Nad Kamínkou 1345, 156 10 Praha-Zbraslav, Czech Republic*
*panek@imc.cas.cz

The aim of our work is testing a new type of organic polymer material stabilized against degradation by ionizing radiation with prospective use in medical dosimetry. Application requirements include high radiation resistance, water resistance, tissue equivalence and little to no electrical conductivity.

As a final group of stabilised polymers, we tested stabilized polymer based on bisphenol-A-epichlorohydrin epoxy resins hardened by polyfunctional amines, *e.g.* diethylenetriamine, triethylenetetramine or pentaethylenehexaamine. Into the polymer matrix of epoxy resins a stabilizer was covalently bounded, the stabilizer was chosen from group of diapocynin, divanillin quercetin, coumarin, and curcumin combined with CB-A stabilizer 4-amino-2,2,6,6-tetramethylpiperidine.

The key properties of functional samples of the prepared polymers were described. The electrical resistance of the polymer was tested by casting Kelvin's electrodes inside the tested sample, measurements were performed inside a shielded room. Water resistance was measured by weighing the samples before and after storing in stirred water bath for 24 hours. Neither stabilisers nor gamma irradiation of the samples did affect this property in any way. All the tested samples absorbed minimal amounts of liquid, circa 0,2 weight percent. Parallel test of water resistance and long-term functionality of an electronic chip encapsulated into the polymer was done by submerging the capsule into a water and applying of a Co-60 radionuclide beam inside of water phantom PTW MP3 equipped with a positioning system commonly used for clinical measurements. The whole measurement lasted approximately 30 hours. The result showed that the function and response of the electronic chip is stable and gives only a typical static variability of a noise / signal response.

The polymeric materials were also tested for mechanical properties after irradiation with 250 kGy of gamma-rays. Measurements were carried out in accordance with the ISO178:2019 norm with the use of extensometer for accurate deformation measurement. It was shown that after irradiation, the modulus of elasticity and partly the strength of the material increased, however the toughness and bending deformation decreased and the material became slightly more brittle. In summary, the observed results show that selected compositions of the polymers are suitable for the target application.

Acknowledgments

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Determination and characterization of ω-end group functionalities in poly(2-alkyl-2-oxazoline)s using liquid chromatography and mass spectrometry

Nora Engel[1,2,*], Ivo Nischang[1,2], Michael Gottschaldt[1,2], Ulrich S. Schubert[1,2,*]

[1]Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstr. 10, 07743 Jena, Germany
[2]Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany
**nora.engel@uni-jena-de, ulrich.schubert@uni-jena.de*

The analytical investigation of polymers, in particular regarding intended biomedical applications, is becoming increasingly important. Here, we present a liquid chromatography (LC) protocol to precisely characterize poly(2-alkyl-2-oxazoline)s (POx) synthesized by the living cationic ring-opening polymerization (CROP). The growing polymer chains were terminated with potassium phthalimide, followed by hydrazinolysis and polymer ω-end functionalization with bicyclooctyne using the respective *N*-Hydroxysuccinimide (NHS) ester.[1] Additionally to the analytical LC investigation of the observable proton-initated POx (determining the α-end group in side reactions),[2] we focused on the tailored ω-end group which represents a promising strategy for envisaged conjugations in biomedical applications. The synthesized polymers were analyzed in detail by high performance LC on a monolithic, C18-modified silica column with mobile phase gradient elutions comprising binary acetonitrile / water mixtures as the mobile phase. Careful elution fraction collection followed by mass spectrometry (MS) was used in order to erode compositional properties of the polymers, particularly the tailored ω-end group. As a result, side products, e.g., the hydroxy ω-end functional polymers or the post polymerization prepared modifications from the NHS ester coupling were elucidated.

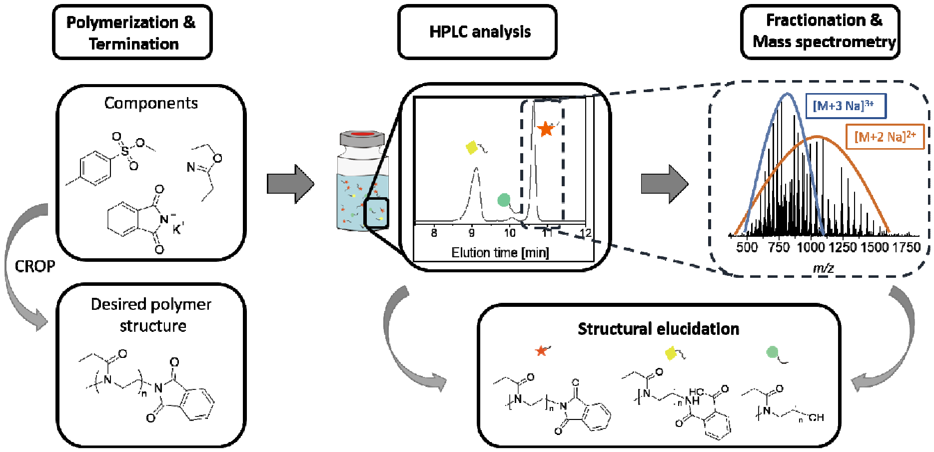

Figure 1: Schematic representation of the workflow starting with the polymerization, developed LC measurement protocols, and subsequent MS measurements in order to elucidate the polymers concerning the ω-end group.

Acknowledgments

The authors acknowledge the Federal Ministry of Education and Research (BMBF) (project: Next-PEG, project number: 13XP5049C), the Thüringer Aufbaubank (project number: 081220/265) and PolyTarget (SFB 1278 - project number: 316213987, project Z01) for funding.

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Quantification of Molecular Weight Discrimination in *Grafting to* Reactions from Ultrathin Polymer Films by MALDI

Riccardo Chiarcos[1], Diego Antonioli[1], Viviana Ospina[1], Michele Laus[1], Michele Perego[2], Valentina Gianotti[3*]

[1] *Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Universitá del Piemonte Orientale "A. Avogadro", Viale T. Michel 11, 15121 Alessandria, Italy*
[2] *Laboratorio MDM, IMM-CNR, Via C. Olivetti 2, 20864 Agrate Brianza, Italy*
[3]*Dipartimento per lo Sviluppo Sostenibile e la Transizione Ecologica (DISSTE), Università del Piemonte Orientale "A. Avogadro", Piazza S. Eusebio 5, 13100 Vercelli, Italy*
**valentina.gianotti@uniupo.it*

Very recently some hints of discrimination by molecular weight[1], occurring during the *grafting to* process from solution, were reported. For example, a distortion of the molecular weight distribution during the *grafting to* reaction of hydroxy terminated polymethylmethacrylates dissolved in toluene was described[2], with shorter chains being preferentially attached. So far, to the best of our knowledge no data have been reported in the literature about molecular weight discrimination effect in *grafting to* process from melt.

In the present study, a reliable and rugged method was developed to quantify the molecular weight discrimination that can occur in *grafting to* reactions via indirect MALDI-TOF quantification of the molecular weight of grafted chains by comparing the characteristics of the polymeric material before the grafting reaction with those of the unreacted material recovered after grafting.

Two polystyrene samples with different molecular weight and narrow molecular weight distributions were employed to prepare (Figure 1) model blends that were grafted to a silicon wafer and an analytical method was developed and validated to assess and quantify the modification of the molecular weight distribution that takes place during the *grafting to* process.

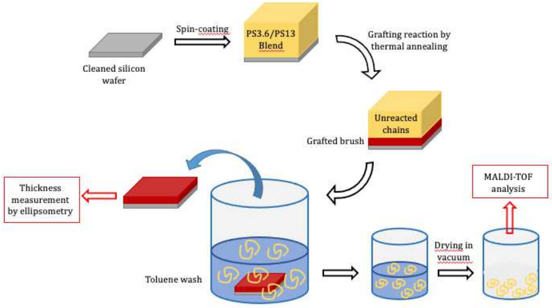

Figure 1. Scheme of the grafting to process and sample preparation.

Furthermore, to evaluate the accuracy a further experiment was carried out by comparing the new optimized MALDI-TOF method and direct measurements with TGA-GC-MS on a model blend containing deuterated and hydrogenated polystyrene samples with the appropriate molecular weights and distributions.

The optimized method was applied on samples obtained by thermal induced *grafting to* reaction from ultrathin polymer films and, for the first time, to our knowledge, an enrichment effect occurred in ultrathin grafted layer obtained from melt was evidenced.

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Realization of a new efficient material for optical limitation: Polyvinylcarbazole (PVK)

M. Guerchoux[1]*, O. Muller[1], J. Caillieaudeaux[1,2], S. Braun[1], M. Dandois[1], A-S. Schuller[2], C. Delaite[2], L. Merlat[1]

[1] French-German Research Institute of Saint-Louis (ISL), Saint-Louis, France
[2] Laboratoire de Photochimie et d'Ingénierie Macromoléculaires (LPIM), Mulhouse, France
**morgane.guerchoux@isl.eu*

Since the development of increasingly compact laser sources emitting short intense radiations, it has become essential to develop suited protection means. For this purpose, polymer-based optical filters with passive optical limiting properties have been developed. Due to their nonlinear properties, they have the ability to self-activate when the incident laser threat exceeds a certain intensity level. This allows to limit the laser aggression and to protect the targeted optical systems (detectors, photoreceptors, even the human eye).

The optical limiting filters are based on guest-host systems composed of a polymer matrix and nanomaterial loads (i.e.: nanoparticles, dyes…) [1] both of which can contribute to the nonlinear optical properties of the filter. The matrix employed is the polyvinylcarbazole (PVK) which is a thermoplastic polymer. It has a high Tg, around 220 °C and was chosen for its intrinsic nonlinear optical properties (nonlinear third-order susceptibility $\chi^{(3)}$) [2], it has never been produced as a bulk optical filter before.

PVK is obtained from a radical polymerization in bulk associated with an initiator. Different synthesis were carried out by modifying some parameters, such as the quantity of initiator, the temperature, the reaction time or even the addition of nanomaterials in order to obtain a filter (Figure 1) meeting the specifications, i.e.: a product without bubbles, transparent in the visible and the near infra-red (T>70%).

Samples were characterized analytically by means of DSC and ^{1}H NMR showing presence of residual monomer. Their optical limiting properties were assessed on an optical bench in order to determine their overall performance (nonlinear threshold, global attenuation). The results appeared to be better than those obtained with a conventional PMMA-based optical limiting filter.

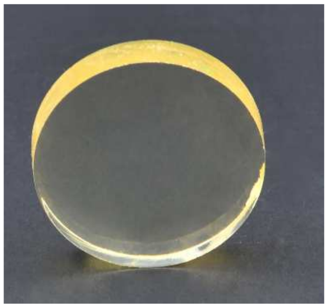

Figure 1 : Optical limiting filter in PVK

Keywords: Polyvinylcarbazole, radical polymerization, optical filter, optical limitation, nonlinear properties

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Ageing Timescales of Amorphous Polymers during Laser Sintering

M. Hamid[1*], P. Van Puyvelde[1], B. Goderis[1]

[1]*KU Leuven, Leuven, Belgium*
[*]*mouna.hamid@kuleuven.be*

The additive manufacturing of amorphous polymer powders by Laser Sintering (LS) remains a challenge. The sintered material typically experiences multiple heating/cooling cycles and ages an extended time at a high temperature close to the glass transition temperature, T_g, prior to being cooled down to ambient conditions. This ageing involves a segmental relaxation at small length scale, which can drastically change the properties of the sintered material and increase the brittleness in particular. Needless to say, ageing must be avoided. Therefore, extensive research is needed to map the timescales of ageing at different processing conditions and to define the conditions at which ageing is repressed the most. One of the most relevant processing parameters is the powder bed temperature. Generally, the bed temperature for LS of amorphous materials is chosen just below T_g. [1] Above T_g, the powder will agglomerate, inducing caking. Too far below T_g may cause part warpage. Hence, there seems to be an optimal temperaure. However, in defining this optimimum temperature, ageing effects need to be considered as well. Furthermore, as the susceptability to ageing also depends on the initial conditon of the polymer, the cooling rate at which this ageing temperature is reached also counts. In LS, cooling rates after the laser passages are rather fast and a function of the powder bed temperature and the temperature of newly deposited powder layers on top of the sintered matter. Therefore, ageing at a wide range of temperatures under T_g was investigated over periods from 10^{-3} to 10^5 s. These temperaures were approached at LS relevant rates from 10^{-1} to 10^5 °C/s. The amorphous material used was polystyrene Dynoseeds TS-20 and the ageing experiments were performed with a Fast Scanning Chip Calorimeter (FSC, Flash DSC). This high-end DSC technique operates at ultra-high scanning rates and allows studying (fast) ageing phenomena via the subsequent heating runs. On top of that, FSC is ideal to mimic the processing conditions of LS, the high cooling rates in particualr. The latter is impossible to achieve with conventional DSC. The obtained relaxation times show a deviation to the well-known Vogel-Fulcher-Tammann (VFT) theory, describing the temperature dependency of relaxation around T_g. [2] This deviation increases with decreasing ageing temperature.

The relaxation timescales of the polydisperse, high molecular weight Dynoseeds TS-20 are compared to the ones of monodisperse polystyrene standards of various molecular weights.

Keywords: Laser Sintering, amorphous materials, physical ageing

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Poly(*N,N´*-diethylacrylamide)-based multiresponsive hydrogels with double network structure

V. Ivaniuzhenkov*, L. Hanyková, I. Krakovský, J. Šťastná

Charles University, Faculty of Mathematics and Physics, Prague, Czech Republic
**iva.vladon@gmail.com*

Multi-sensitive polymer hydrogels which can undergo distinct physical changes towards a fine environmental alterations show appealing application potential in targeted controlled release, biosensors and actuators, soft robotics, and intelligent switches.

We studied behavior of double-network (DN) based hydrogels in dependence on temperature and solvent (water/acetone) composition. For the synthesis of DN structure were used poly(*N,N´*-diethylacrylamide) (PDEAAm) as a temperature-sensitive component and polyacrylamide (PAAm) as a component that is sensitive to the water/acetone composition. We used the following combinations with different molar ratios of components for the preparation of DN hydrogels: heteropolymer combination (PDEAAm/PAAm), reverse combination (PAAm/PDEAAm) and homopolymer combination (PDEAAm/PDEAAm). The effect of various network compositions and reverse sequences in the preparation procedure of the network on the volume phase transition was examined using various experimental techniques. As the main method, we used NMR spectroscopy to measure temperature and solvent composition dependences of integrated intensities in high-resolution NMR spectra. NMR relaxation can provide information on the behavior of water during the temperature-induced phase transition and it was shown that especially measurements of spin-spin relaxation times T_2 of water are useful to detect bound water molecules with restricted mobility. From a macroscopic point of view, we carried out differential scanning calorimetry (DSC), swelling experiments and static mechanical analysis (SMA). DSC allows determining the transition temperatures and enthalpies. Elastic properties of hydrogels with two temperatures under collapse and after heating above collapse was detected by SMA. Swelling and deswelling behavior of hydrogels was investigated by the volume (diameter of samples) and weight measurements in dependence on temperature and various solvent composition. The knowledge of how the phase transition depends on the DN composition and preparation can be useful in the design of new responsive materials.

Keywords: multiresponsive hydrogel, double network, poly(*N,N´*-diethylacrylamide), swelling, differential scanning calorimetry, NMR spectroscopy, elasticity.

Acknowledgments

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Damping properties of 3D printed structures

D. Jaška[1*], S. Zenzingerová[1], V. Chalupa[2], R. Čermák[1], P. Sáha[3], M. Staněk[2], T. Martinek[4], O. Vojta[3], E. Klabalová[5]

[1]*Department of Polymer Engineering, Faculty of Technology, Tomas Bata University in Zlin, Vavreckova 5669, 760 01 Zlin, Czech Republic*
[2]*Department of Production Engineering, Faculty of Technology, Tomas Bata University in Zlin, Vavreckova 5669, 760 01 Zlin, Czech Republic*
[3]*University institute, Tomas Bata University in Zlin, Nad Ovcirnou 3685, 760 01 Zlin, Czech Republic*
[4]*Department of Electronics and Measurements, Faculty of Applied Informatics*
[5]*Doplnit*

This work aimed to find out which of the flexible materials has the best damping properties, i.e. whether the material behaves elastically or plastically and after how many cycles plastic deformation occurs. The damping properties were investigated on samples printed from flexible polymeric materials with an open structure called Gyroid. Elastomeric polymers thermoplastic elastomer (TPE), thermoplastic polyurethane (TPU) and polyether block amide (PEBA) were used for this study. Cylindrical test specimens with different percentages of infill (15, 20, 25 %) were printed on the 3D FDM printer with 0.4 mm nozzle. The damping properties were tested on a standard bursting device in the cyclic compressive stress mode with a frequency 0.5 Hz. It has been found that different materials with the same infill reach the maximum deformation value during a different number of loading cycles. The energy required to compress a material by one millimetre differs from other materials with the same infill. The samples with the lowest damping value show the highest dynamic stiffness.

Keywords: damping, thermoplastic elastomer, 3D printing

Acknowledgments
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Effectiveness of p-phenylenediamine antioxidants through their coordination ability towards selected transition metals

I. Jelemenská[1*], M. Breza[1]

[1]*Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology STU in Bratislava, Slovakia*
[*]*ingrid.jelemenska@stuba.sk*

Interaction energies, metal atom charges and electron density Laplacians at bond critical points of metal - nitrogen bonds in [Aox center dot center dot center dot M](2+) complexes of a series of p-phenylenediamine antioxidants (Aox) with selected transition metals M(II) in various spin states were evaluated in order to predict the antioxidant effectiveness through their coordination ability [1, 2]. All the above M2+ dications exhibit similar trends of antioxidant effectiveness relation vs. interaction energies and nitrogen-to-metal electron density transfer. The only problem is in their ability of metal - nitrogen bonding because they are strongly attracted by neighboring aromatic rings. Only copper atoms are bonded exclusively to nitrogens in all the systems under study [3].

Keywords: B3LYP functional, geometry optimization, population

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Foaming of PLA cellulose composites : effect of fibres on the solidification and crystallisation behaviour

Villamil-Jiménez J.[1,2]*, Le Moigne N.[1*], Sauceau M.[2], Sescousse R.[2], Bénézet J-C.[1] , Espitalier F.[2]

[1] *Polymers Composites and Hybrids (PCH), IMT Mines Ales, 30100 Ales, France.*
[2] *Centre RAPSODEE, IMT Mines Albi, Université de Toulouse, 81013 Albi, France.*
[*]*jennifer.villamil_jimenez@mines-albi.fr*, *nicolas.le-moigne@mines-ales.fr*

In many industrial fields, the development of porous and light polymer composite structures is of great interest because of their several advantages compared to a massive solid of the same chemical nature. Batch foaming of polymers is a process carried out normally in an autoclave. The samples are saturated in a pressurised vessel, and their foaming is achieved by inducing an instability into the system, which can be sudden drop in pressure or by a raise in temperature.

Polylactic acid (PLA) is a well-known and commercially available biopolymer that can be produced from different sources. Its different characteristics generated a great deal of interest in various industrial fields as in the foaming one. PLA's crystallisation kinetics is reported to be slow and can be enhanced by using different solid additives (filler) as crystal-nucleating agents [1-2]. It is known that crystallisation kinetics of polymers can influence different polymer shaping processes such as injection, moulding, foaming, etc and, that additives can modify the crystallisation kinetics of the polymers; but it is not reported in literature whether the shape and dimension of the additives matter and, consequently there is not information about their effect on processes like foaming.

This works aims to understand the effect of the filler content and aspect ratio (length/diameter) on PLA's solidification and crystallisation kinetics. Cellulose fibres (Rettenmaier France) of different aspect ratios (2 and 5) were compounded with PLA by extrusion at 5, 20 and 30 %wt, then injected into discs. Solidification and crystallization kinetics of the materials were evaluated through polarized optical microscopy with hot-stage (POM), isothermal DSC and oscillatory shear rheology (at an angular frequency of 1 rad/s). In all tests, pure PLA and composite samples were heated up to melting and then cooled to the desired isothermal crystallization temperature, ranging from 80 to 120 °C.

In general, crystallisation induction (time to observe the first crystals) and half crystallisation times were reduced with increasing fibre content but also when increasing their aspect ratio. Crystallisation rate constant, increased with both, content and aspect ratio. Studying the evolution of the viscosity of the samples with time at a certain temperature, in general it was shown that after a first plateau corresponding to the beginning of the isotherm, a rise in viscosity attributed to the solidification of the polymer occurred. A second rise in viscosity corresponding to the crystallisation of the sample was observed depending on crystallisation conditions.

This work shows that fibre content and aspect ratio are two important parameters in the solidifcation and crystallisation behaviour of PLA-cellulose composites. This result emphasizes that we can choose between two different additives or even master the crystallisation kinetics of PLA not only by chemical interactions between additives and PLA, but by just changing the aspect ratio of filler. This opens interesting perspectives for the development of bio-based materials and allows us to go one step further in the understanding of composites shaping processes dependent on crystallisation like foaming. An interesting question lies now on the table: can we master the foaming of PLA composites by changing the aspect ratio of the fillers to obtain materials with suitable functional properties?

Keywords: PLA, composites, solidification cystallisation, cellulose fibre.

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Thermoresponsive transition and peculiar antiplasticization in poloxamer-based polyurethane elastomers

Izabela Łukaszewska*, Konstantinos N. Raftopoulos, Artur Bukowczan, Edyta Hebda, and Krzysztof Pielichowski

Department of Chemistry and Technology of Polymers, Cracow University of Technology, Kraków, Poland
Izabela.lukaszewska@doktorant.pk.edu.pl

Research on thermoresponsive polymers focuses mainly on their behaviour in aqueous solutions. Less attention is paid to dimensionaly stable materials, although this is of interest for applications such as topical (e.g. ocular, transdermal, and mucosal) drug delivery [1].

Poloxamers i.e. triblock copolymers of the PEO-PPO-PEO type are quite common thermoresponsive polymers [2]. In this work we employ them as soft segments in polyurethane elastomers, with soft poloxamer content ranging between 40 and 70 wt%. The hard segments consist of isophorone diisocyanate and butanediol and provide the desired dimensional stability, for hard segment content over 30 wt%.

The materials were equilibrated at varying environmental relative humidity (*rh*) ranging from 0 to 98%. At each relative humidity the amount of absorbed water was measured, and the thermal transitions of the materials were monitored by differential scanning calorimetry (DSC).

It was found that the materials exhibit a reversible order-disorder transition when immersed in water, as well as when exposed to 98% environmental humidity. This transition is visible as clouding, and as a complex asymmetric endothermic event in DSC heating curves. The phenomenon is reversible upon cooling, with negligible hysterisis.

At lower humidities, a peculiar antiplasticization event was observed: with increasing relative humidity and despite the increasing amount of absorbed water, the glass transition temperature of the materials increases instead of dropping. Two mechanisms may contribute to this behaviour. The first is a gradual dissolution of the hard domains into the soft phase, and the second is that water molecules may form “bridges” between hydration sites of adjacent chains, thus restricting mobility.

The materials are quite hydrophilic, absorbing 5-10% of water when exposed to *rh* 98%, with the highest absorption observed for the material with 60 wt% of poloxamer. The degree of microphase separation seems to play a strog role on the water absorption capacity of the elastomers. The region *rh* 0-60 % can be descibed adequately with the Brunauer-Emmett-Teller (BET) equation [3].

Keywords: poloxamers, polyurethane, differential scanning calorimetry, water

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Composition effects on the thermal properties of non-isocyanate polyurethanes

Izabela Łukaszewska*, Piotr Stachak, Artur Bukowczan, Edyta Hebda, Konstantinos N. Raftopoulos, and Krzysztof Pielichowski

Department of Chemistry and Technology of Polymers, Cracow University of Technology, Kraków, Poland
Izabela.lukaszewska@doktorant.pk.edu.pl

Polyurethanes (PUs) have become one of the most commonly used polymers in industry due to their versatility. Since it is possible to tailor their properties by selecting appropriate raw materials, PUs have found application in many fields (automotive, furnishing, textiles, coatings, construction, etc.) [1]. However, using isocyanates as one of the main PU components brings growing concerns about the potential harm to human health and environemt. Thus, alternative routes of synthesis have been developed to obtain non-isocyanate polyurethanes (NIPU) [2].

In polyurethanes, the thermal properties are mainly driven by the hydrogen bonding between urethane groups and other polar components in the chain. In this work we study a series of non-isocyanate polyurethanes with varying amount of polar groups along their contour. The flexible component is a PPO-based oligomeric bifunctional cyclic carbonate. The amine component is a combination of two amines, a short carbon chain one (diaminobutane, DAB), and the second a longer one bearing secondary amine groups along its contour (triethylenotetraamine, TETA). The TETA content in the amine component varied between 0 and 100%.

The materials were characterized by Fourier transform infrared spectroscopy (FTIR) to confirm their structure. FTIR was also applied to monitor reaction progress. Thermal stability of obtained materials was monitored by thermogravimetry (TG), and glass transition temperature (T_g) was studied by differential scanning calorimetry (DSC).

It is interesting to note that the thermal degradation onset did not vary between inert and oxidative atmosphere except for high TETA contents (>70 wt%), reflecting a sensitivity of TETA to oxidating decomposition. DSC analysis of materials stored in a room conditions showed glass temperature (T_g) values increasing with TETA content from -2 °C (TETA content 0%) to 25 °C (100%). This trend is attributed to the higher amount of hydrogen bonds, which restricts mobility.

Since obtained materials are expected to be highly hydrophillic due to hydroxyl groups formed alongside of urethane groups during aminolysis of cyclic carbonate ring, influence of relative humidity on glass transition temperature was investigated. Materials conditioned over phosphorus pentoxide were considered as dry materials (rh=0%) and constituted a poinf of reference for further studies. The glass transition temperature showed the same trend as the ambient materials. It was found out that even slight increase in relative humidity (rh=8%) results in significant plasticization, reducing T_g by up to 9 °C [3]. The effect was more prominent for higher TETA content materials.

Keywords: non-isocyanate polyurethanes, NIPU, glass transition, differential scanning calorimetry, water

Acknowledgments

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Polyelectrolytes based on poly(2-Nonyl-2-Oxazoline-co-2-Dec-9’-enyl-2-Oxazoline): conductivity, ion diffusion, thermal and electrochemical stability

A. Mahun[1,2*], S. Abbrent[1], J. Brus[1], L. Kobera[1]

[1]*Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Heyrovskeho nam. 2, 162 06 Prague 6, Czech Republic*
[2]*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 8, 128 40 Prague 2, Czech Republic*
[*]*mahun@imc.cas.cz*

Today’s lithium-ion batteries (LIBs), found in a large variety of the electronic devices and electric vehicles, still suffer from safety and insufficient durubility issues [1]. Electrolytes are the key components of batteries and their further improvement is crucial for the development of new high-energetic and safe LIBs. Usage of polymeric electrolytes which also act as separators, can provide the answer to solving the above-mentioned issues of conventional LIBs [2]. Gel polymer electrolytes (GPEs), comprising a polymer matrix plastisized with a solution containing Li salt and/or additional low-molecular weight compounds, are deemed good candidates for potential practical use in LIBs because of their sufficient mechanical stability and relatively high ionic conductivity [3].

Current work covers synthesis and characterization of new GPEs based on poly(2-Nonyl-2-Oxazoline-*co*-2-Dec-9’-enyl-2-Oxazoline) copolymers. A series of samples was synthesized by cationic ring-opening polymerization (CROP) of the respective 2-Oxazolines with different ratio of the co-monomers (Figure 1 (a)), and their further crosslinking and swelling in 1M solution of LiTFSI salt in propylene carbonate. Structures of the electrolytes were investigated by ^{1}H, ^{7}Li, ^{13}C and ^{19}F NMR spectroscopy. The samples were investigated in terms of ionic conductivity measurements using electrochemical impedance spectroscopy. Thermal stability and glass transition temperature of the samples were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Pulse-field gradient (PFG) NMR spectroscopy was used for probing the ionic diffusion at various temperatures (Figure 1 (b)) as well as for evaluation of Li^+ transference number, theoretical conductivity and degree of salt dissociation. Finally, lithium striping-plating experiment and cyclic voltammetry were used for evaluation of the electrochemical stability of the chosen samples. Promising samples possessing relatively high conductivity (~10^{-4} S/cm at 25 °C) and good stability were obtained within this research.

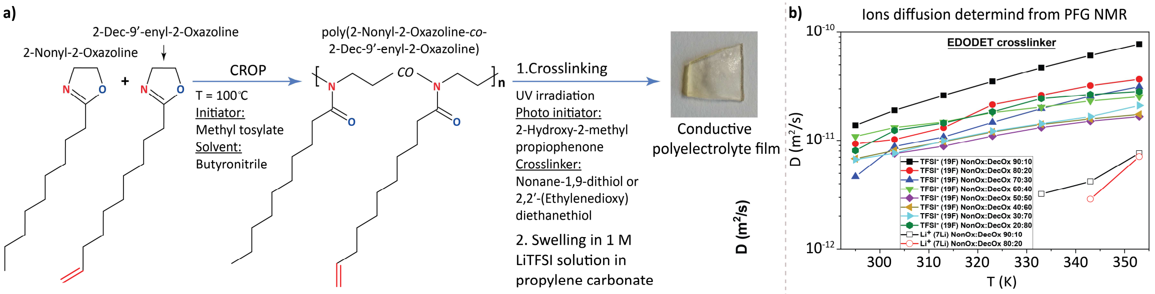

Figure 1. Simplified scheme of polyelectrolyte samples preparation (a) and temperature dependence of the self-diffusion coefficients of Li^+ cation (empty points) and $TFSI^-$ anion (solid points) obtained by PFG NMR for the polyelectrolytes with 2,2’-(Ethylenedioxy)diethanethiol (EDODET) crosslinker (b).

Keywords: Lithium ion-batteries, Polyelectrolytes, PFG NMR, poly(2-Oxazolines)

Acknowledgments

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Effect of the multilayer coextrusion process on lamellar thickness distribution of ethylene-vinyl alcohol copolymers by SSA

G. Mallamaci[1*], C. Sollogoub[1], M. Gervais[1], A. Guinault[1]

[1]*Laboratoire PIMM, CNRS, Arts et Métiers Institute of Technology, Cnam, HESAM Université, 75013 Paris, France*

*Gianmarco.mallamaci@ensam.eu

Ethylene-vinyl alcohol (EVOH) copolymers are a class of materials commercially obtained by saponification reaction of ethylene-vinyl acetate (EVA) copolymers. It has been previously demonstrated that the OH groups of these copolymers act as interstitial defects and due to the free radicalization nature of EVAs, EVOH copolymers possess a certain degree of short-chain branching [1].
In the proposed study, the effect of the multilayer coextrusion process on the mean lamellar thickness distributions of EVOH copolymers was evaluated through self-nucleation/annealing protocol (SSA). This particular thermal fractionation technique developed by Müller et al. [2], based on the existence of defects in the main polymer chain, consists of a series of melting and re-crystallization cycles at different temperatures, interspersed with isothermal steps, allowing self-nucleation and annealing of the crystals (Fig. 1). SSA analysis coupled with other microscopy techniques showed that multilayer coextrusion process has an impact on the ability to form crystals with the same dimensions.

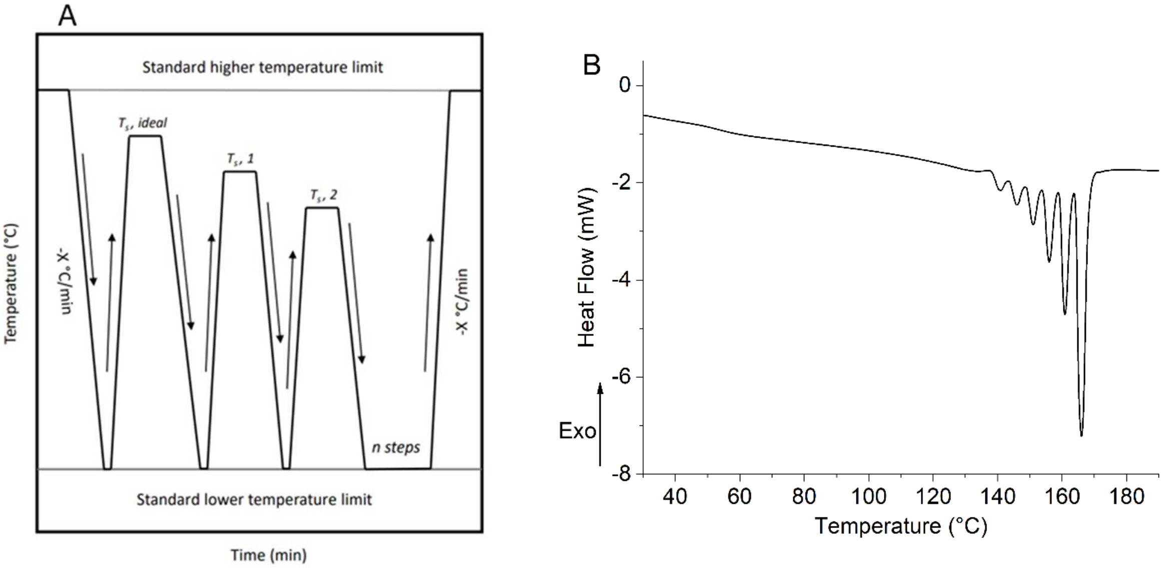

Figure 1. A: Schematic representation of SSA thermal protocol. Heating and cooling cycles are performed at a constant scanning rate. B: DSC heating scan after SSA fractionation.

Keywords: EVOH, multilayer coextrusion, SSA.

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Ionic liquids : New plasticizers for PVC

Charlotte Michelin*, GERARD Jean-François, LIVI Sébastien, DUCHET-RUMEAU Jannick

IMP Ingénierie des Matériaux Polymères – UMR CNRS 5223, Université de Lyon – INSA Lyon, F-69621
Villeurbanne Cedex – France
**charlotte.michelin@insa-lyon.*

PVC is one of the most used polymers with an excellent performance/cost ratio. The plastisol is the formulation corresponding to mixture of a suspension of PVC powder into a liquid plasticizer with various additives (flame retardant, light stabilizer, pigments, etc.). Plastisol is initially a more or less viscous liquid which is transformed into a homogenous solid under the effect of heating. The most widely used plasticizers usually are esters derived from phtalic acid. These plasticizers with a low molecular weight can migrate from PVC causing environmental and health problems. New alternatives must be found to respect new norms of legislation. In particular, a new class of small molecules called ionic liquids (ILs) has recently emerged as an interesting alternative. An ionic liquid is a association of cations and anions with a melting temperature close to ambient temperature. They display many advantages of being fire-resistant[1], almost no-volatiles[2], and good solvents. Moreover, several studies have shown that plasticization by ionic liquids is possible on a large number of polymers including PVC. In fact, the low quantity of ionic liquid in a matrix can change mechanical properties (Young's modulus et elongation at break) and thermal properties (lower glass transition) [3,4,5,6]. The aim of this study focused on the formulation of PVC with ionic liquids is to propose an alternative to current plasticizers with the same thermal and mechanical performances and using a smaller quantity of plasticizers. The second point is that, according to the anion and cation that compose the ionic liquid, they are able to act as flame retardant in addition to be a plasticizer. Ionic liquid appear like a magic additive answering to several functions, fire-retardant and plasticizing effect.

This poster will present the study of the behaviour of PVC formulations with ionic liquids compared to a conventionnal formula. For this, the thermal properties (glass transition temperature, degradation temperature,...) were studied by DSC, ATG, etc. But also mechanical properties in order to determine the viscoelastic behaviour as well as the α and β transition. Finally, the study of these properties will enable us to identify and understand the behaviour of the plasticizer and gelling process associated.

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Progress in Polymers Charactrerisation by Advanced Analysis of Fluorescence Correlation Spectroscopy

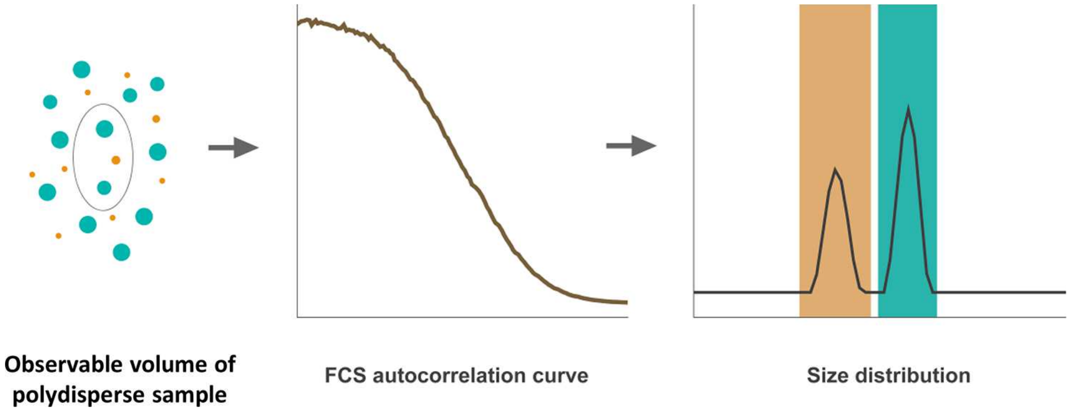
Jiří Pánek*, Petr Štěpánek, Peter Černoch, Martin Hrubý

Institute of Macromolecular Chemistry of the CAS, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic, panek@imc.cas.cz

Fluorescence correlation spectroscopy (FCS) provides most commonly values of diffusion coefficients of fluorescently labeled species, mainly biopolymers in solutions. A newly developed procedure for the determination of diffusion coefficient distributions applicable to polydisperse polymers or nanoparticles [1], based on the CONTIN algorithm, is described and tested on both simulated FCS correlation functions and real experimental data. Good resolution of bimodal distributions is observed and it is quantitatively established how the resolution depends on the level of experimental noise. Effects of incorrect calibration of the focal volume on the obtained diffusion coefficient and its distribution are also described for single-focus FCS.

Computational simulations were used for a study of three types of situations that are most representative in polymers characterisation: i) bimodal distributions of diffusion times with three levels of random noise ε typical for experimental data; ii) a bimodal distribution of diffusion times with two fixed diffusion times $\tau_{D,1}$ and $\tau_{D,2}$, and varied amplitude A_1 of $\tau_{D,1}$ in the range from 2 % to 98 %; iii) FCS correlation functions with variable width at several values of noise in the range 0% to 7 %.

It was shown that the newly implemented technique makes FCS analysis more accessible for interdisciplinary fields, since distributions of diffusion times can be obtained with the same ease as in dynamic light scattering. The resolution power of the method depends on the experimental noise that is on typical setups larger than in dynamic light scattering due to lower light intensity levels. For practical applications of the method it has to be kept in mind that the molecular brightness of the fluorescent label depends on its environment and changes after binding to a polymer or nanoparticle, which has to be taken into account when considering quantitatively the amplitudes of the peaks in the distribution function.



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Radiation resistant organic polymers for radiotherapy applications

Hynek Řeháček[1], Hynek Urban[1], Peter Černoch[1], Martin Hrubý[1], Ondřej Ploc[2], Denis Dudáš[3], Jiří Pánek*[1]

[1]*Institute of Macromolecular Chemistry of the CAS, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic,*
[2]*Nuclear Physics Institute of the CAS, Hlavní 130, 250 68 Husinec-Řež, Czech Republic*
[3]UJP PRAHA a.s., Nad Kamínkou 1345, 156 10 Praha-Zbraslav, Czech Republic
**panek@imc.cas.cz*

Polymers are widely used as materials with a broad range of possible properties. If their composition and structure is chosen properly, these materials can also withstand high doses of ionizing radiation without considerable decrease in either mechanic or thermic stability, and therefore they can be used for specific applications. We designed and tested polymers usable as construction parts for detectors of ionizing radiation. In this application, both radiation and water resistance of the polymers are particularly important, since the detector or detector arrays are submerged in water during calibration procedures.

Among others, we tested stabilized polymer based on bisphenol-A-epichlorohydrin epoxy resins hardened by polyfunctional amines, *e.g.* diethylenetriamine, triethylenetetramine or pentaethylenehexaamine. Into the polymer matrix of epoxy resins a stabilizer was covalently bounded, the stabilizer was chosen from group of diapocynin, divanillin quercetin, coumarin, and curcumin combined with CB-A stabilizer 4-amino-2,2,6,6-tetramethylpiperidine.

A change of material properties is caused mostly by alternation of chemical structure of the polymer. Radiation can destroy the bonds in macromolecular chains and hence shorten their length, which has major impact on not only to strength but also for flexibility. On the other hand, if components, their ratios and process of manufacture are chosen properly, the radiation can initiate further lengthening of the chains by creating radicals at correct places in the chain and improve the mechanical endurance.

Bond strength between stabilizers and monomeric units also plays an important role in overall performance of the material because of possible creation of a weak spot in the chain, therefore their choice is very important and varies for each type of monomer used. In our contribution we discuss possible choices and assess which compounds fit to the requirements of the target application.

Acknowledgments

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Analysis of the water uptake kinetics of an epoxy coating by means of dielectric measurements in immersion at various temperatures

A. Roggero[1,2,*], N. Caussé[2], N. Pébère[2], E. Dantras[3]

[1] *Université de Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, UCBL, INSA, UJM, Villeurbanne, France*
[2] *Université de Toulouse, CIRIMAT, UPS/INPT/CNRS, ENSIACET, Toulouse, France*
[3] *Université de Toulouse, CIRIMAT, Physique des Polymères, Université Paul Sabatier, Toulouse, France*
[*]*aurelien.roggero@insa-lyon.fr*

The main strategy to protect metallic structures against corrosion in operational conditions involves the deposition of a polymer coating on the exposed surfaces. To a certain extent, such coatings act as a barrier against the sorption of water molecules. Electrochemical impedance spectroscopy (EIS) have been long used to monitor the water sorption in polymer coatings at room temperature, by means of mixing laws of the dielectric permittivities of the polymer and water (*e.g.* Brasher-Kingsbury, linear [1]). However, such measurements are rarely performed at elevated temperatures, although it is known that diffusion is a thermally activated process. One objective of this study was to analyze the temperature activation of water sorption in an epoxy coating by means of a temperature controlled EIS test bench developped in the laboratory (between 20 and 80 °C) [2]. The water uptake was monitored via the increase in the real dielectric permittivity, in the high frequency region (Figure 1).

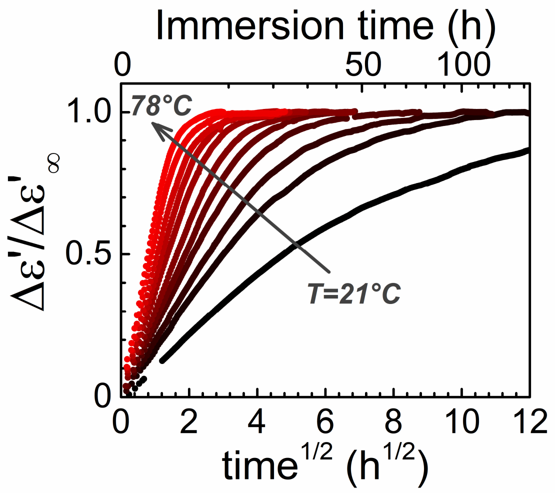

Figure 1 – Relative increase in dielectric permittivity as a result of water ingress at various temperatures.

The analysis of the sorption kinetics showed little impact of the glass transition on the coefficient of diffusion. It displayed a monotonous Arrhenius dependence over the entire temperature range, embodying T_g, with an activation energy (50 kJ/mol) consistent with the literature based on gravimetric measurements. By fitting the sorption curves of Figure 1 with stretched exponentials (KWW functions), we showed that the proper Fickian behavior was obtained only at temperatures above the dry T_g of the epoxy coating. This was ascribed to the progressive plasticization of the epoxy network during the sorption experiment, introducing an heterogeneity of diffusion pathways for water molecules [3].

While this technique eliminates the need to remove the sample from immersion to monitor the water uptake (the case of gravimetric measurements), the mixing laws generally used to calculate the volume fraction of absorbed water rest on very debatable assumptions (*e.g.* water does not interact with the polymer) which will be discussed.

Keywords: glass transition, plasticization, water interaction, impedance spectroscopy

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The influence of hydrophobicity balance in novel glycerol-containing poly(meth)acrylates on their phase transition properties

A. Schweigerdt[1*], M. Weinhart[1, 2]

[1]*Freie Universität, Berlin, Germany*
[2]*Leibniz Universität, Hannover, Germany*
[*]*a.schweigerdt@fu-berlin.de*

Polymers exhibiting thermoresponsive behavior belong to the class of smart materials.[1] Of particular interest for the biomedical field are thermoresponsive polymers with a lower critical solution temperature (LCST) in aqueous solutions. Immobilized on surfaces, such polymers can be employed to culture and harvest cell sheets non-invasively simply by temperature control of the environment.[2]
The key for LCST behavior is the balancing of hydrophobic and hydrophilic groups in the polymer structure, either by monomer design or by copolymerization. Studies with thermoresponsive poly(oxazolines) or poly((meth)acrylates) with ethylene oxide side chains tuned the polymers' phase transition by expanding either the hydrophobic substituents on the oxazoline unit or the hydrophilic segments of the ethylene oxide side chain, thereby also altering the molecular formula.[3] To adress this issue and be able to study differences in thermoresponsive properties solely based on balancing of hydrophobic groups while keeping the molecuar formula constant we synthesized novel thermoresponsive glycerol containing poly((meth)acrylates) based on monomers with identical molecular formula. When shifting the hydrophobicity from the backbone of a polymethacrylate (PMA) to the side chain of a polyacrylate (PA), we observed a lowering of the cloud point temperature by more than 12 °C as well as a significant change in the sharpness of the phase transition. Also a distinct dependence of the transition on the concentration and molecular weight was observed, as shown in Figure 1. Temperature dependent DLS and NMR measurements give further insights into the aggregation behavior and conformational changes during the temperature induced dehydration.[4] The resulting structure-property relationship allows for the rational design of LCST type polymers with tailored thermoresponsive properties for the envisioned application.

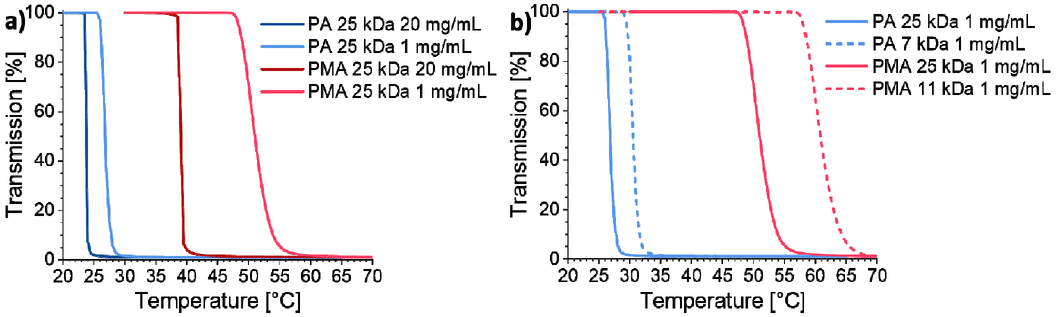

Figure 1. Concentration (a) and molecular weight (b) dependence of the phase transition (blue for polyacrylate (PA), red for polymethacrylate (PMA)) determined by turbidimetry measurements upon heating.

Keywords: LCST type polymer, micro/macroscopic phase transition, structure property relationship

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Insight into chemical composition and molar mass distribution of highly branched amorphous polyethylene copolymer using preparative temperature rising elution fractionation and advanced analytical techniques

Mawande Sigwinta[1], Anthony Ndiripo[1,2,3], Jan Merna[4], Albert van Reneen[1], Albena Lederer[1,2]

[1]*Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag, X1, Matieland, 7602, South Africa, msigwinta@sun.ac.za*
[2]*Center Macromolecular Structure Analysis, Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany*
[3]*Department of Applied Chemistry, National University of Science and Technology, Box AC 939, Ascot, Bulawayo, Zimbabwe*
[4]*Department of Polymers, University of Chemistry and Technology Prague, A, Technická 5, Dejvice, 166 28 Praha 6, Czechia*

Chain walking polyethylene (CWPE) exhibits novel molecular structure topology with special properties that are of interest for potential new applications.[1,2] Furthermore, late-transition catalysts tolerate incorporation of polar functional groups to the end-groups or in-chain, which further expand the applications of CWPE.[3,4]Due to the molecular complexity of these polymers, it is imperitive to establish structure-property relationships that are relevant to their application. At present, the full potential of these materials has not been explored due to limited information on their molecular structure. Classical polyolefin characterization techniques are based on crystallization-based fractionation techniques, which are not adequate for the separation and characterization of non-crystalline polymers such as hyperbranched PE.[1,5] Herein, we propose the use of preparative temperature rising elution frationation at sub-ambient conditions (pTREF-sA) using solvent/non-solvent eluent mixtures as an alternative method to the crystallization-based methods. Furthermore, advanced column-based techniques including high-temperature interaction chromatography (HT-IC) in solvent gradient (SG) and temperature gradient (TG) mode, two-dimensional high-temperature liquid chromatography (2D-HT-LC), multiple detector size exclusion chromatography (SEC) are employed to gain detailed information about the molecular structure of hyperbranched CWPE.

Keywords: Chain walking polyethylene, hyperbranched polyethylene, preparative temperature rising elution fractionation, high-temperature interaction chromatography, multiple detector size exclusion chromatography.

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Kinetic Peculiarities of Co-curing Reaction of Cyanate Ester Resin with Benzoxazine

O. Starostenko[1*], O. Grygorieva [1], D. Shulzhenko[1], A. Fainleib[1], D. Grande[2]

[1]*Institute of Macromolecular Chemistry of the NAS of Ukraine, Kyiv, Ukraine*
[2]*Institut de Chimie et des Matériaux Paris-Est, CNRS-UPEC, Thiais, France*
[*]*starostenko.o.m@nas.gov.ua*

In this work, the kinetic peculiarities of dicyanate ester of bisphenol E (DCBE) polycyclotrimerization in the presence of bisphenol A-based benzoxazine (BOA) with varying proportions (*i.e.*, 0, 2, 5, 10, and 25 wt.%) were investigated by DSC.

It is well known that cyanate ester resins during high temperature polymerization transform to densely cured polycyanurate (PCN) networks and benzoxazines form polybenzoxazine (PBA) networks through reaction of polymerization with oxazine cycle opening. The copolymerization of DCBE and BOA is possible as well *via* reaction of cyanate groups of DCBE with phenolic groups of PBA, thus affording PCN/PBA hybrid thermosets. *Figure 1a* shows DSC thermograms for neat DCBE, and all the mixtures of different compositions. It is seen that introduction of BOA into DCBE leads to shifting the polymerization exotherm maximum, *i.e.* the curing temperature peak, toward much lower temperatures from 260 °C for individual DCBE to 180 °C for the mixture with 25 wt.% BOA. Interestingly, for the materials containing 5 and 10 wt.% BOA, two exothermic peaks on DSC thermograms are detected. We suppose that the first exothermic peak (at 206 and 193 °C, correspondingly) is due to the co-reaction between DCBE and BOA, and the second exothermic peak (at 219 and 214 °C, respectively) is due to DCBE self-polymerization. For the BOA 25 wt.% system, the DSC thermogram shows three peaks, where the third peak at 250 °C is due to BOA self-polymerization. *Fig.* 1*b* depicts the temperature dependence of DCBE conversion values for individual DCBE and all the mixtures studied. One can see that, with increasing BOA contents, the induction period of DCBE conversion decreases, and the reaction occurs faster. We conclude that the thermal polycyclotrimerization of DCBE is catalyzed by the phenolic groups of BOA mostly at the early stages of polymerization.

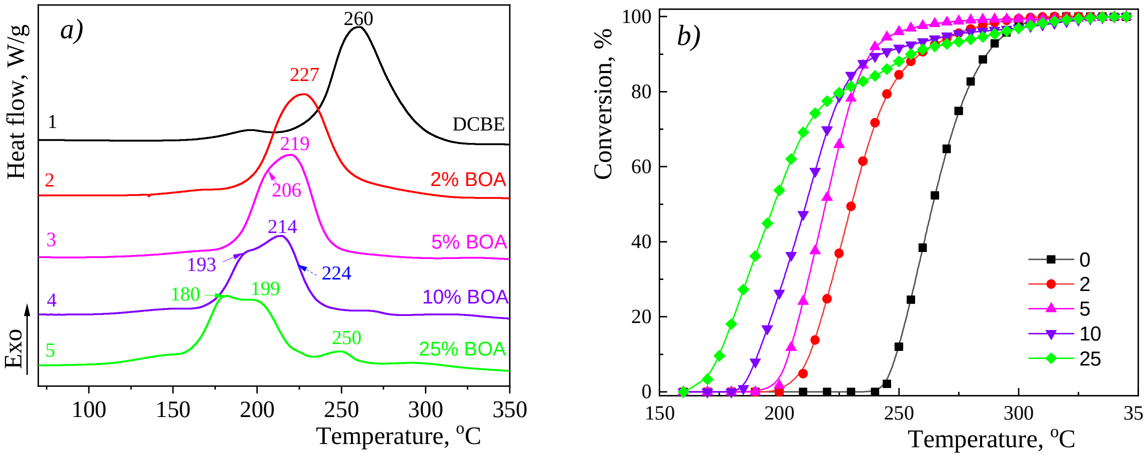

Fig.1. DSC thermograms (a) and temperature dependence of conversion (b) for neat DCBE and DCBE/BOA mixtures (BOA mass content is indicated in the plot)

Keywords: cyanate ester resin, benzoxazine, co-curing, hybrid thermosets

Acknowledgments

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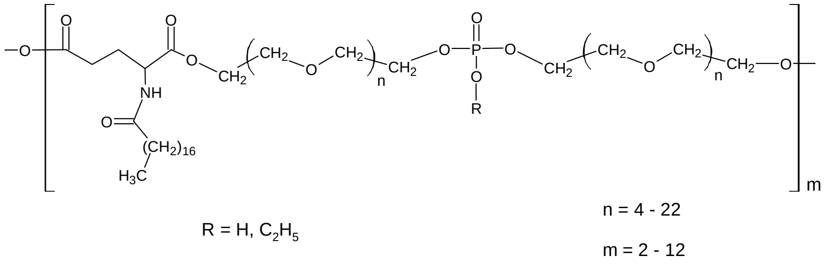
Study of the particle distribution of the dispersed phase of phosphorus-containing polyesters

A. Stasiuk[1], V. Lyakh[1], I. Dron[1], D. Ostapiv[2], V. Samaryk[1]

[1]*Lviv Polytechnic National University, Lviv, Ukraine*
[2] *Institute of Animal Biology NAAS, Lviv, Ukraine*
anna.v.stasiuk@lpnu.ua

The introduction of phosphate groups into the polymer chain of the pseudo-poly(amino acid)s of polyester type are promising materials for biomedical applications. Due to pentavalent phosphorus atom which is an excellent option for further modification or binding to the low molecular weight therapeutic drugs or proteins [1]. There are a number of publications [2-3] that discuss the synthesis and research of different types of pseudo-poly(amino acid)s. The most convenient method of obtaining phosphorus-containing pseudo-poly(amino acid)s of the polyester type is the interaction of N-derivatives of dicarboxylic α-amino acids with diols of the polyoxyethylene series by the Steglich reaction. For this purpose, polyoxyethylene glycols with an ethyl phosphate group were previously synthesized.



R = H, C_2H_5

n = 4 - 22

m = 2 - 12

Fig. 1 General structure of phosphorus-containing pseudo-poly(amino acid)s of the polyester type

Phosphorus-containing pseudo-poly(amino acid)s of the polyester type show surface activity and are capable of forming pseudo-micelles due to the presence of hydrophilic and lipophilic fragments in the structure. Studies have shown that the character of the distribution is basically the same as for the pseudo-poly(amino acid)s of polyester type, without the phosphate group. The introduction of the ethyl phosphate group into the hydrophilic fragment of polyoxyethylene glycol slightly weakens the stabilization and disrupts the formation of the structural-mechanical barrier. At a concentration of polyphosphates of 0.5%, the particles of the dispersed phase of polyesters with ethyl phosphate group are formed with a size of 150÷300 nm. The formation of a hydroxyl group in the phosphate fragment significantly increases the stabilization ability, and the particle size distribution, which is obtained on the same polymer, forms particles with a much smaller size of the dispersed phase - 60-80 nm. The aqueous dispersions of the obtained polymers are able to solubilize significant amounts of water-insoluble organic compounds and are non-toxic.

Keywords: phosphorus-containing polyesters, pseudo-poly(amino acid)s, Steglich reaction, drug delivery

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Preparation and characterization of surface adherent polydopamine films on various substrates

Jan Svoboda[1*], Martin Král[2], Marcela Dendisová[2], Pavel Matějka[2] and Ognen Pop-Georgievski[1]

[1]*Department of Chemistry and Physics of Surfaces and Interfaces, Institute of Macromolecular Chemistry, Czech Academy of Sciences, 162 06 Prague 6, Czech Republic*
[2]*Department of Physical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology, 166 28 Prague 6, Czech Republic*
[*]*svoboda@imc.cas.cz*

Polydopamine (PDA), also known as synthetic melanin, is widely used as a biomimetic anchoring layer for the modification of various solid substrates. PDA is utilized for a wide range of biomedical, sensing and tribological applications, even though the polymer's precise covalent structure has not been completely revealed yet. Even more, it is not evident to which extent the chemical nature of the substrate, on which the layer is formed, influences and predetermines the covalent structure of resulting PDA. The growth of PDA layer was studied using various surface sensitive techniques such as spectroscopic ellipsometry, atomic force microscopy and X-ray photoelectron spectroscopy. We supplemented grazing angle attenuated total reflection FTIR spectroscopy and scattering-type scanning near field optical microscopy in the infrared region and Fourier-transform infrared nanospectroscopy with multivariate statistical analysis to further gain analytical power. We have particularly focused on the effects of polymerization time and substrate on the PDA structure. We found notable differences in the chemical composition of PDA formed on gold and on surfaces terminated with oxides/reactive hydroxides such as silicon and N-dopped-TiO_2 in the early stages of the layer formation. At the later stages of layer formation, a merely unified chemical structure was observed independently on the type of substrate. [1]

Acknowledgments
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Polyimide Materials for Enantioselective Membranes

P. Sysel[1*], M. Kašová[1], M. Kohout[2], J. Žádný[3], P. Izák[3]

[1]*Department of Polymers, University of Chemistry and Technology Prague, Czech Republic*
[2]*Department of Organic Chemistry, University of Chemistry and Technology Prague, Czech Republic*
[3]*Institute of Chemical Process Fundamentals of the AS CR, Czech Republic*
**Petr.Sysel@vscht.cz*

The separation of components from their mixtures by using membranes is becoming increasingly important both in practice and in research. These are mostly procedures that are beneficial from the economic and ecological point of view. Processes handling large quantities of raw material (e.g. natural gas purification) and disproportionately smaller quantities (e.g. separation of enantiomers from racemic mixtures) are under consideration. The isolation of enantiomers represents a significant challenge in a number of industries, e.g. in the pharmaceutical industry [1].

A key prerequisite for the satisfactory operation of any membrane separation process is, of course, finding a suitable membrane. The membrane must not only exhibit an acceptable relationship between permeability and separation capacity, but also be resistant to all influences at all times during its operation. Although membranes can also be metallic or ceramic, a decisive proportion of them are currently polymer-based. A significant proportion of polymer membranes are those prepared from polyimides. These are versatile polymers up to temperatures of around 200 °C for which very favourable separation characteristics have been found, so far especially for gaseous media [2].

In this work, the focus was on the preparation and characterization of polyimides that could potentially be used for the separation of enantiomers from racemic mixtures. Procedures in which the relevant selector is incorporated into the main chain of a linear polyimide as one of the monomers (diamine) or as a termination agent (monofunctional carboxyl compound) of a highly branched polyimide have been used. In particular, in this phase of the research, the conditions for the preparation of the respective polyimides were optimized to maintain the optical activity of the components in the final product. Furthermore, the problem of limited self-supporting properties of flat, homogeneous membranes (tens of µm thick) prepared from the above specified products was addressed. The optical activity of the final products was evaluated by polarimetry and circular dichroism methods.

Keywords: polyimides, optical activity, polarimetry, circular dichroism

Acknowledgments

The support of the Grant Agency of the Czech Republic (project GA20-06264S) is acknowledged.

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The influence of photo and thermooxidative ageing on NBR/PVC blends cracks

Clara Thoral[1,2*], Gérald Soulagnet[2], Pierre-Olivier Bussière[1], Sandrine Therias[1]

[1]*Université Clermont Auvergne, CNRS, Clermont Auvergne INP, ICCF, F-63000 Clermont-Ferrand, France*
[2]*Trelleborg Industrie SAS, ZI La Combaude, Rue de Chantemerle, F-63050 Clermont-Ferrand, France*
[*]*E-mail : clara.thoral@sigma-clermont.fr*

Blends of Nitrile butadiene Rubber/Poly(vinyl chloride) are commonly used for the fabrication of hoses conveying fluids, such as fuel for the automobile sector. This particular application calls for NBR due to its good resistance to oils and solvents. To improve the mechanicals properties, NBR is blended with PVC, this will bring both higher thermal resistance and stifness [1]. However, as the majority of insaturated polymers, the presence of double bonds in the backbone of the NBR (found in butadiene units) makes it particularly sensitive to thermo- and photoageing [2,3]. This study has been conducted in collaboration between Trelleborg Industrie SAS and the Institute of Chemistry of Clermont-Ferrand.
Indeed, NBR/PVC hoses have shown a loss of their usual properties during its lifespan, leadind sometimes to cracks occurance on the surface during lifetime. The aim of this work is to perform a multiscale study of the materials under thermo- and photoageing conditions in order to determine the main contributor involving cracks formation. The results obtained show significant differences between the effect of photooxidation exposure, occuring only at the extreme surface of NBR/PVC blends and leading to micro-cracking under stress, and thermooxidation which tends to make the whole material brittle.

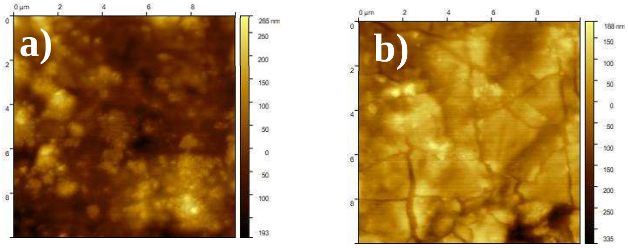

Figure 1. AFM images of a NBR/PVC (66/33 %wt) blend a) at 0h and b) after100h of irradiation

To reach this objective, different characterisation techniques have been investigated at molecular scale, exhibiting modifications corresponding to the formation of oxidation products monitored by infrared spectroscopy. At macromolecular scale where crosslinking was followed by Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal (DMTA) analyses. As we can see in Figure 1, Atomic Force Microscopy (AFM) was used to follow not only the polymer modulus but also cracks formation at the surface during ageing. This approach allows us to explain how the crosslinking mechanism, taking place in both photo- and thermoageing, can initiate cracking effects in one case and of a material breaking in the second.

Keywords: NBR/PVC, photoageing, thermoageing, cracks

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Nanoscale infrared spectroscopy and imaging - Characterizing polymeric systems at the surfaces -

M. Unger[1*], A. Roy[2], Q. Hu[2]

[1] *Bruker Nano Surfaces and Metrology, 76187 Karlsruhe, Germany*
[2] *Bruker Nano Surfaces and Metrology, Santa Barbara, CA 93117, USA*
[*]*miriam.unger@bruker.com*

One method of nanoscale infrared spectroscopy and imaging, atomic force microscope based infrared spectroscopy (AFM-IR) directly detects IR radiation absorbed by the sample using the AFM probe tip to sense thermal expansion. This thermal expansion depends primarily on the absorption coefficient of the sample and is largely independent of other optical properties of the AFM tip and the sample.

Over the last years, we have developed two major improvements in the photothermal AFM-IR technique and introduced (1) resonance enhanced version of AFM-IR and (2) Tapping photothermal-based AFM-IR spectroscopy and imaging. Recently, building on our knowledge in photothermal AFM-IR, we have invented the surface sensitive AFM-IR mode. This mode allows to chemically analyze sample surfaces with a high degree of surface sensitivity by measuring IR spectra and/or images of the top of the sample surfaces.

This presentation will describe the underlying technology of the new surface sensitive AFM-IR mode. Additionally, we will discuss the differences between traditional resonance enhanced AFM-IR vs surface sensitive AFM-IR and will also highlight numerous polymer applications (multilayer films, nano-phase separation of polymer blends etc.).

Keywords: Photothermal AFM-IR, Surface Sensitivity, nanoscale IR spectroscopy and imaging, nanoIR

Synthesis and characterization of bisimidazole-based ionenes for high pressure gas storage applications.

F. Wanghofer[1*], E. Kanatschnig[1], A. Wolfberger[1], M. Wolfahrt[1], E. Rossegger[1], S. Schlögl[1]

[1]*Polymer Competence Center Leoben GmbH, 8700 Leoben, Austria*
[*]*florian.wanghofer@pccl.at*

Ionenes are ionic polymers with main chain ionic moieties in their repeating units, in contrast to polyelectrolytes, which commonly have the ionic moieties as pending groups (Fig. 1). Ionic polymers are used in membrane materials due to their improved permeability and selectivity towards CO_2. The permselectivity of a material is inversely proportional to the permeability of a material [1], therefore, membrane materials can provide a significant gas barrier against H_2 in CO_2/H_2 separation membranes [2]. This property could potentially be exploited for use in type IV hydrogen pressure vessels, which consist of a thermoplastic liner that acts as the gas barrier and a composite overwrap that ensures the stability of the high pressure vessel. Inspired by the reports of the low gas permeability [2,3] of ionenes and their versatile synthesis [4], ionenes based on bisimidazole monomers were synthesized and characterized. The properties of the ionenes are altered by changing the anion and through spacer molecule variation with the goal to achieve a melt-processable material with low barrier properties and transition temperatures above 100 °C while maintaining the thermal and mechanical specifications for type IV pressure vessels. In the presented work, four imidazole-based polymers were synthesized. An anion exchange from Br^- or Cl^- to BF_4^-, *p*-toluenesulfonate, dicyanamide and Tf_2N^- was performed and the impact on the thermal properties was investigated. A clear improvement of the thermal stability could be achieved, with an increase of the onset temperature of degradation in the range of 50 °C to 80 °C. For the investigated polymers, glass transition values in the range of −30 °C to 162 °C were achieved.

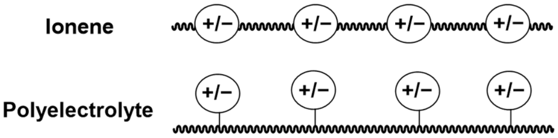

Figure 1: Schematic representation of ionenes and polyelectrolytes. Adapted from [5].

Acknowledgments

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Synthesis and electrical study on novel bipyridine-centered PDMS-PMMA copolymers

A. Wrzesińska[1,2], H. Komber[2], A. Wypych-Puszkarz[1], I. Bobowska[1], J.Ulanski[1], B. Voit[2], F. Böhme[2]

[1]*Department of Molecular Physics, Faculty of Chemistry, Lodz University of Technology, Lodz, Poland*
[2]*2Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany*
**angelika.wrzesinska@edu.p.lodz.pl*

There is a high need for innovative dielectric materials with elevated value of dielectric permittivity (k) for flexible electronic devices i.e. organic field effects transistors (OFETs) [1][2]. The main purpose of this work was an elaboration of new solid-state dielectric polymers and to study their molecular dynamics, structural, and electrical properties. For this reason, a series of novel dielectric bipyridine-centered PDMS (0.9 eq.) - PMMA (0.1 eq.) copolymers (Figure (a)) was synthesized, following the description in the work of Bao et al. [3]. The created new dielectrics exhibit elevated k value ~4.5 vs. ~2–3 for common polymers used in OFETs, and at the same time, they do not show thermal transitions at the operating temperatures of mentioned device (Figure (b)). Implementation of the described materials as insulation layers for elastic electronics can be the breakthrough for the development of flexible electronics.

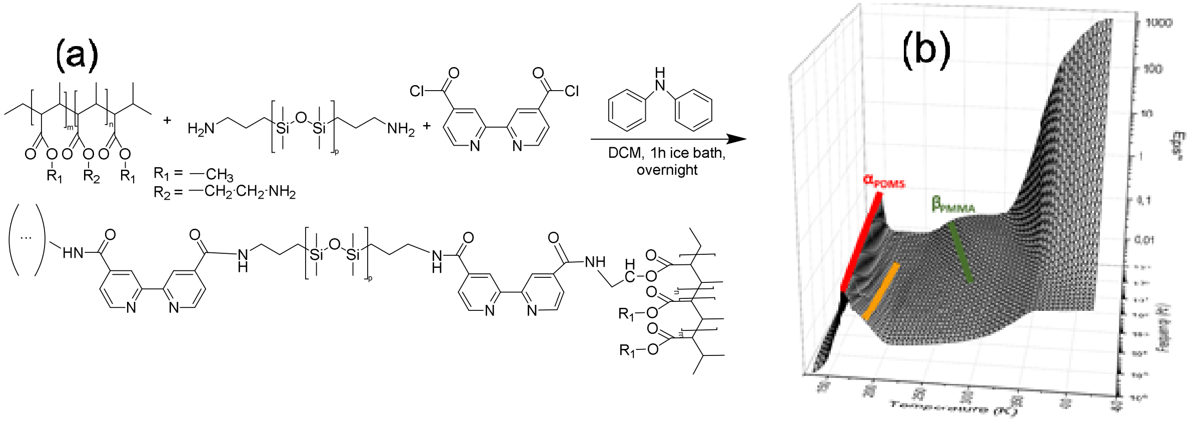

Figure (a) Synthesis scheme and, (b) Frequency-temperature dependences of imaginary part of dielectric permittivity (eps") for bipyridine-centered PDMS-PMMA copolymers (the solid lines, drawn as a guide for eyes, indicate the detected relaxation processes).

Acknowledgments

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Different Entangled Networks in Weakly-entangled Polyethylene Melt

Huaqin Yang[1*], Dario Romano[2,1], Sanjay Rastogi[2,1]

[1] *Maastricht University, Faculty of Science and Engineering (AMIBM), Geleen, The Netherlands*
[2] *King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering, Thuwal, Kingdom of Saudi Arabia*
* huaqin.yang@maastrichtuniversity.nl; dario.romano@kaust.edu.sa; sanjay.rastogi@kaust.edu.sa

With the advances in the synthesis of crystals having reduced number of entanglement in their non-crystalline region, entanglements formation in un-equilibrated polymer melt and its characterization has been a new subject of study.[1] So far, most of the studies are limited to UHMWPE (having $M_w > 1.0$ million g/mol) where the chain dynamic is extraordinarily slow. For this reason, a series of low entangled PEs with molecular weight ranging from 0.2 to 1.0 million g/mol have been synthesized under controlled synthesis conditions. Similar to UHMWPE,[2] even for these low molar mass PEs, rheological studies coupled with DSC isothermal crystallization experiments, revealed the retention of the melt heterogeneity having difference in topological constraints. During rheological measurements, in the low molar mass PEs, two crossover points are observed from the oscillatory frequency measurements where normally only one crossover point is accessible in UHMWPE. The high-frequency crossover point is related to the polymer chain length representing the classic tube renewal time. The low-frequency crossover point is associated with the heterogeneity of the polymer melt and is found to be dependent on melting of the crystals. Polymer melt heterogeneity (as extracted in Figure 1) consists of unentangled (non-woven entanglement, equivalent to non-concatenated rings) and entangled melt (woven entanglement). With longer time in the melt, the low-frequency crossover point shifts horizontally to higher frequency region and vertically to higher moduli (G' and G") values, while the high-frequency crossover point remains unchanged. This transformation from unentangled (non-woven entanglement) to entangled melt (woven entanglement) appears to be limited by the polymer chain length. Possible effect of chain branch or degradation have been excluded by means of FT-IR and liquid-state ^{13}C NMR characterization.

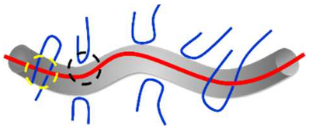

Figure 1. The schematic showing heterogeneity in the topological constraints. The virtual tube represents a test chain in red surrounded by woven (yellow circle) and non-woven (black circle) entanglements, where the non-woven entanglements are equivalent to that foreseen in non-concatenated rings.

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The effect of accelerated and natural aging on the properties on Poly-1-butene extrudates

S. Zenzingerová[1], Michal Kudláček[1], David Jaška[1], Lubomír Beníček[1*], Jana Navrátilová[1], Lenka Gajzlerová[1], Roman Čermák[1]

[1]*Department of Polymer Engineering, Faculty of Technology, Tomas Bata University in Zlin, Vavreckova 5669, 760 01 Zlin, Czech Republic*
[*]*benicek@utb.cz*

Isotactic poly(1-butene) (PB-1) has many valuable properties that differs it from the common polyolefins (Marigo, 2000).

The degradation process of PB-1 is not fully defined. The process is assumed to be the same as with isotactic polypropylene due to the presence of tercial carbon in the main chain (Grossetete, 2002; Grause, 2020).

The effect of photodegradation in isotactic poly(1-butene) has been investigated using infrared spectroscopy, degradation analysis (carbonyl and yellow index) and mechanical properties. Specimens prepared by compression molding were artificially aged by UV irradiation from 0 to 100 hours and then compared to specimens naturally aged from 0 to 102 days. Chemism of extrudate degradation was studied. Mechanical properties of specimens were compared to the surface analysis. The acceleration index was defined from carbonyl index to correlate the changes induced by artificial and natural ageing. The correlation between carbonyl index and yellow index measurement was defined, and it is possible to substitute the carbonyl index measurements with yellow index measurement. The yellow index measurement can approximate with only a few days difference the stage of degradation of the measured material.

Due to the comparison of naturally aged samples and artificially aged samples, it can be said that artificial ageing is 44 times faster than natural ageing.

Changes in supermolecular structure were not observed. Even though supermolecular changes were not observed, mechanical properties changed with the level of degradation, thus, the cause of these changes was deemed to be structural changes, such as cracks.

Keywords: isotactic poly(1-butene), tensile properties, infrared spectroscopy, surface changes, weathering

Acknowledgments

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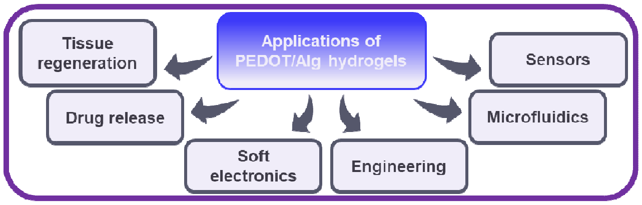
Electroconductive PEDOT/Alginate Hydrogels: A New Concept in Soft Materials for Biomedicine and Engineering

Carlos Alemán[1,2,*], Samuele Colombi,[1,*] Lorena P. Macor,[1,3] Anna Puiggalí-Jou,[1] and Jose García-Torres[4,*]

[1] Departament d'Enginyeria Química and Barcelona Research Center in Multiscale Science and Engineering, EEBE, Universitat Politècnica de Catalunya, C/ Eduard Maristany, 10-14, 08019, Barcelona, Spain
[2] Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute of Science and Technology, Baldiri Reixac 10-12, 08028 Barcelona Spain
[3] IITEMA-CONICET, Departamento de Química, Facultad de Ciencias Exactas Físico-Químicas y Naturales, Universidad Nacional de Río Cuarto, Agencia Postal Nro. 3, X5804BYA Río Cuarto, Córdoba, Argentina
[4] Biomaterials, Biomechanics and Tissue Engineering Group, Department of Materials Science and Engineering, Universitat Politècnica de Catalunya (UPC), 08019, Barcelona, Spain
carlos.aleman@upc.edu

Hydrogels made individually of poly(3,4-ethylenedioxythiophene) (PEDOT), a well known and very stable conducting polymer, or alginate (Alg), a natural, edible, biocompatible, biodegradable, biostable and hydrophylic hetero-polysaccharide extracted from brown algae, have been shown to present some restrictions in terms of applicability. In order to enhance and extend the applicability of PEDOT- and Alg-based hydrogels, as well as to overcome their individual limitations, our group has developed a new type of hydrogels by combining such two components (PEDOT/Alg hydrogels). Thus, the utilization of PEDOT:Alg have been proposed for biomedicine (*e.g.* tissue regeneration, drug release and biosensors),[1,2] microfluidics,[3] soft electronics[4] and energy[5] (Scheme 1). In this work, we disclose the advantages and disadvantages of PEDOT/Alg hydrogels, as a new class of materials, with respect to other hydrogels. Remarkable importance has been given to the discussion of aspects related to the shortcomings in the simultaneous exploitation of the properties of the two components.



Scheme 1. Proposed applications for PEDOT/Alg hydrogels

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Determining the surface tack of medical gloves

Siavash Amirosanloo[1], Boris Maroh[1], Raimund Schaller[2], Reza Beglari[2], Armin Holzner[2], Sandra Schlögl[1,*]

[1]*Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, 8700 Leoben, Austria*
[2]*Semperit Technische Produkte GmbH, Triester Bundesstrasse 26, 2632 Wimpassing, Austria*
**Corresponding author: sandra.schloegl@pccl.at*

Medical gloves are prepared by a coagulant dipping process and have been already introduced at the end of the 19th century to protect the hands of operating room personnel from noxious antiseptics such as carbolic acid.[1] Whilst there are several standardised methods for the quality control of gloves, there is a lack in methods for quantifying their surface related properties. However, surface properties are crucial for the industrial production of disposable medical gloves. In particular, untreated gloves obtained from diene-rubber latices suffer from an inherently high surface tack, which compromises on their processability at the dipping line. Tacky gloves stick to porcelain formers, used in the dipping process, and are easily teared during stripping. Moreover, they suffer from poor donning properties, as the insides of the gloves pack together during storage. If gloves with high surface tack are densely packed in dispenser boxes right after the production, they strongly adhere to each other, which makes it difficult to separate them during use.
Advancing from empirical testing, herein, we aim at the development of a measurement set-up similar to a probe tack test in order to quantify the surface tack properties of thin elastomer films and to distinguish between small tack forces. The effect of selected measurement parameters such as haul-off speed, compression time and force on the surface tack values of thin elastomer films was studied in detail. Additionally, the established test set-up was used to quantify surface tack of medical gloves as a function of selected lubricants and post-treatment procedures (e.g. washing). The results revealed that the method offers a good reproducibility, a low deviation of the surface tack values and provides a convenient way to easily and reliably evaluate the surface tack properties of medical gloves in contact with each other.

Acknowledgments
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Rheology, Polymer Processing, and Additive Manufacturing

Advanced combined rheometer setups to in-situ correlate molecular dynamics with mechanical properties

C. Fengler[1], K.F. Ratzsch[2], J. Lacayo-Pineda[3], S. Nie[1], M. Wilhelm[1,*]

[1]*Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*
[2]*Bruker BioSpin GmbH, Ettlingen, Germany*
[3]*Continental Reifen Deutschland GmbH, Hannover, Germany*
[*]*manfred.wilhelm@kit.edu*

Molecular understanding of mechanical properties over a broad length and time scale is crucial to develop advanced materials. Our research aims to design unique combined rheometer setups that can monitor in-situ molecular observables, such as molecular dynamics or chemical functional groups, that are correlated to macroscopic mechanical responses. These combined experimental setups overcome the experimental challenges associated with offline measurements and facilitate the understanding of structure-property relationships. Recently, we developed a unique combination of rheology and low-field time domain ^{1}H NMR (TD-NMR) by implementing a compact 25 MHz NMR magnet into a DHR-3 rheometer.[1] This RheoNMR device can quantify segmental motion of polymer chains via transverse relaxation times (T_2) while simultaneously performing advanced rheological protocols. We used this device in rubber science to test whether varying vulcanization procedures of natural rubbers impact the nanostructure of the polysulfidic crosslinks.[2] At a same elastic shear modulus of 0.2 MPa, we find that rubbers produced by efficient vulcanization (i.e., high ratio of accelerator to sulfur) exhibit approximately 50 % higher transverse relaxation rates compared to conventional vulcanization procedures (i.e., low ratio of accelerator to sulfur), indicating that during efficient vulcanization predominantly rigid mono-sulfidic crosslinks are formed. The formation of this rigid nanostructure has to be considered for applications where fracture resistance is essential. The RheoNMR device was further used in hydrogel synthesis to study the impact of crosslinker concentration (*DC*) during the aqueous crosslinking copolymerization of acrylic acid and *N*,*N*'-methylenebis(acrylamide).[3] The inverse correlation of the elastic shear modulus with T_2 relaxation times reveals a pronounced molecular rigidity for higher *DC* at early gelation times, suggesting the formation of inelastic, rigid domains such as crosslinking clusters, which reduce the overall crosslinking efficiency. A further outlook and applications of other unique rheometer combinations with dielectrics and infrared spectrometry (IR) will be demonstrated as well.[4,5]

Keywords: rheology, NMR, rubber, hydrogel

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Material and process optimisation for 3D printable polypropylene-based materials

G. Bernagozzi[1], D. Battegazzore[1], R. Arrigo[1], A. Frache[1*]

[1]*Department of Applied Science and Technology, Polytechnic of Turin, Alessandria, Italy*
[*]*alberto.frache@polito.it*

Among all the 3D printing techniques for polymers processing, Fused Deposition Modelling (FDM) is the most used and the most developed in the global production system, being simple and economic in terms of both materials and tools [1]. However, the limiting factor for additive manufacturing processes for polymer-based systems is the poor variety of available material [2]. The aim of this work is the development of a deep knowledge about polypropylene (PP), one of the most studied and commercialised polymer, focusing on its fundamental characteristics in order to be suitable for FDM. In the first part of this work, PP-based compounds containing different amounts of talc, calcium carbonate or an organomodified montmorillonite have been formulated using a twin-screw extruder and characterized, aiming at optimizing the thermal and rheological properties of the materials. In particular, the introduction of the different types of fillers allowed reducing the melting entalphy of the PP-based systems, hence minimizing the typical high volumetric shrinkage of PP and, consequently, the severe warpage usually observed in 3D-printed manufacts based on semi-crystalline polymers. As far as the rheological behavior of the investigated materials is concerned, the results of small amplitude oscillatory shear measurements pointed out that the presence of all used fillers caused the disappearance of the Newtonian behavior exhibited by unfilled PP at low frequencies, with the occurrence of a yield-stress behavior which is progressively more pronounced as the amount of fillers increases. Furthermore, all investigated composites shown a marked shear thinning behavior at high frequencies. It is known from the literature that the typical Newtonian behavior of unfilled polymers represents an issue for an optimal 3D-printing process, as during the not printing extruder movements or when it temporarily stops, the absence of a yield stress behaviour cause material oozing. Another zero-shear condition is obviously when the material is deposited, when it is still in the semisolid state. In this case, a high value of yield stress coupled with a strong shear thinning behavior would assure the material to keep its shape without drooping [3]. Therefore, the introduction of the different fillers allowed properly modifying the rheological behavior of PP, helping in ensuring an effective printability of the materials.

In the second part of the work, a step-by-step optimisation of the process parameters has been conducted, outlining some general rules and suggestions to fulfil the FDM filament requirements and to improve the details resolution of a 3D printed little model.

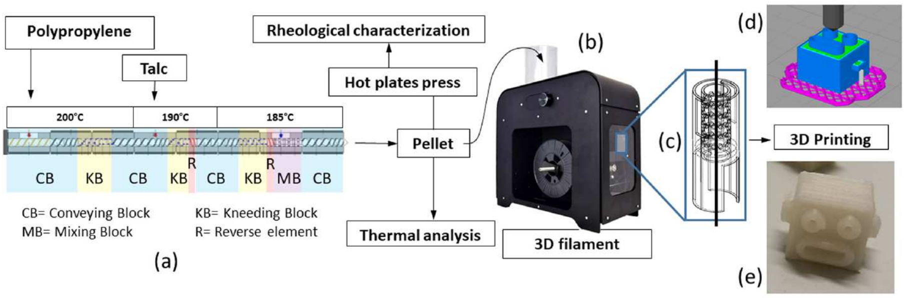

Fig. 1. Working Scheme for the optimization of printable PP/Talc composites: (a) Twin screw compounding process details; (b) Filament making machine; (c) Homemade 3D printed airflow deviator; (d) 3D Printing software design project; (e) Final 3D printed object.

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How the 3D-printing technology can revolutionize the conception of Polymeric Materials with Adaptive Properties ?

J. Odent[1], J.-M.. Raquez[1*]

[1] *Laboratory of Polymeric and Composite Materials (LPCM), Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons - UMONS, Place du Parc 20, B-7000 Mons, Belgium*
[*] *jean-marie.raquez@umons.ac.be*

Slowly yet steadily, additive manufacturing technologies have become a major player in the fabrication of polymeric devices with controlled architectures such as personalized prototypes, soft electronics, sensors and actuators as well as tissue and biomedical engineering[1, 2]. Based on a layer by layer fabrication, with resolution in the range of micro- to nanometers per layer, the computer-assisted printing significantly speeds up the development of custom 3D devices without actually inflating the costs. Despite the irrefutable progress made around 3D printing, the technique still suffers from rigid and static properties of the printed parts and lack of fabrication approaches controlling the material anisotropy[3]. In light of these limitations, a breakthrough strategy towards designing anisotropy-encoded structures using commercial stereolithography technology is reported by means of controlling either the specific surface area to volume ratio, the crosslinking density or the chemical composition of discrete layers during fabrication[4]. The key element here is the time, where the actuation, the sensing and the programmability are directly embedded into the material structure and occur in desired time frames. More precisely, we address the challenge of building more complex 3D objects with elevated adaptive properties towards the 3D-printing of *e.g.* multi-responsive actuators[4, 5], piezoionic touch sensors and rapid responsive visible indicators. This work represents a flexible platform for designing more advanced 3D-printed polymeric materials beyond the present study that would promote new potential applications.

Keywords: 3D-printing, mutliresponsive materials, stereolithography, free-radical polymerization

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Can the initially low entangled non-woven melt ever form woven entanglement?

Sanjay Rastogi and Dario Romano

Division of Physical Science and Engineering
King Abdullah University of Science and Technology (KAUST)
Thuwal 23955; Saudi Arabia
e-mail: sanjay.rastogi@kaust.edu.sa and Dario.romano@kaust.edu.sa

Physical entanglement are the foundation of polymer science that influences the viscoelastic response of a polymer melt, its crystallization, and the resultant mechanical properties. Making judicious choice of a catalytic system it is now possible to tailor the entangled state of polymer during polymerization. In a semi-crystalline polymer, entanglement formed during polymerization are heterogeneously distributed; while the crystalline region is free of entanglement the physical contact points between the neighboring chains is localized in the non-crystalline region. The abstract nature of these topological constraints remain elusive, and their density in the non-crystalline region is found to be strongly dependent on the chosen catalytic system and the polymerization condition. On melting of the semi-crystalline polymer, the heterogeneously distributed entanglement get homogeneously distributed. In this presentation, we will demonstrate the strong influence of polymerization condition on the melt state having everlasting memory effect that challenges the desired formation of woven entangled network in low as well as high molar masses of linear chains. The paper will also address morphological variations in the solid state along with the topological constraints.

Keywords: entanglement, chain dynamics, non-equilibrium melt, crystallization, melting kinetics, mechanical properties

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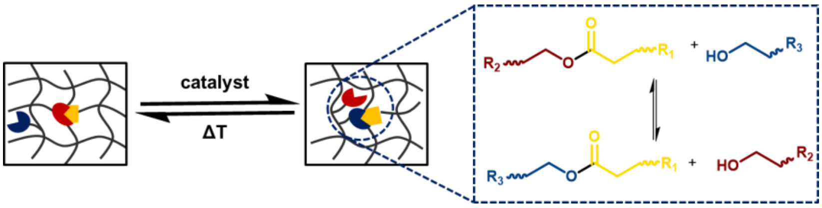
Dynamic exchange reactions in 3D-printable photopolymers

E. Rossegger[1], R. Höller[1], D. Reisinger[1], K. Moazzen[1] and S. Schlögl[1]

[1]*Polymer Competence Center Leoben GmbH, Leoben, Austria*
**elisabeth.rossegger@pccl.at*

Commonly used photosensitive resins for DLP (=digital light processing) 3D-printing techniques feature fast curing rates, low viscosity, high resolution and tunable mechanical properties. Once printed, they perform like classic thermosets and reprocessing, re-cycling or malleability is no longer possible. Via the introduction of dynamic covalent bonds into photopolymers, these shortcomings can be overcome by topology rearrangements, which are activated upon an external stimulus. These so-called covalent adaptable networks (=CANs) rely on bond exchange reactions above the topological freezing temperature (Tv) of the network. An outstanding example are thermo-activated transesterification reactions between carboxylic ester linkages and free hydroxyl groups, in the presence of a suitable catalyst.



Schematic representation of dynamic transesterification reactions

However, classic transesterification catalysts are characterized by poor solubility and compromise on the curing rate and pot life of photopolymers. Herein, a mono-functional methacrylate phosphate was studied as new transesterification catalyst, which enables the DLP 3D printing of thiol-acrylate- and acrylate-based vitrimeric systems for the manufacture of soft-robotic actuators. Once photocured, the dynamic networks were able to rapidly undergo thermally activated rearrangement reactions. Triple shape memory and self-healing of the 3D printed objects were successfully performed, even of networks with glass transition temperatures above room temperature.[1] Advancing from traditional initiators for thermally induced bond exchange reactions, photolatent transesterification catalysts can be introduced to spatiotemporally control topology rearrangements. The utilization of photoacid generators as latent transesterification catalysts results in the local formation of Brønsted acids upon UV exposure, which can efficiently activate thermo-triggered transesterification reactions. By using a dual-wavelength 3D printer (operating at 405 and 365 nm) the prototyping of soft active devices, which undergo locally controlled topology rearrangements at increased temperatures is realizable.[2]

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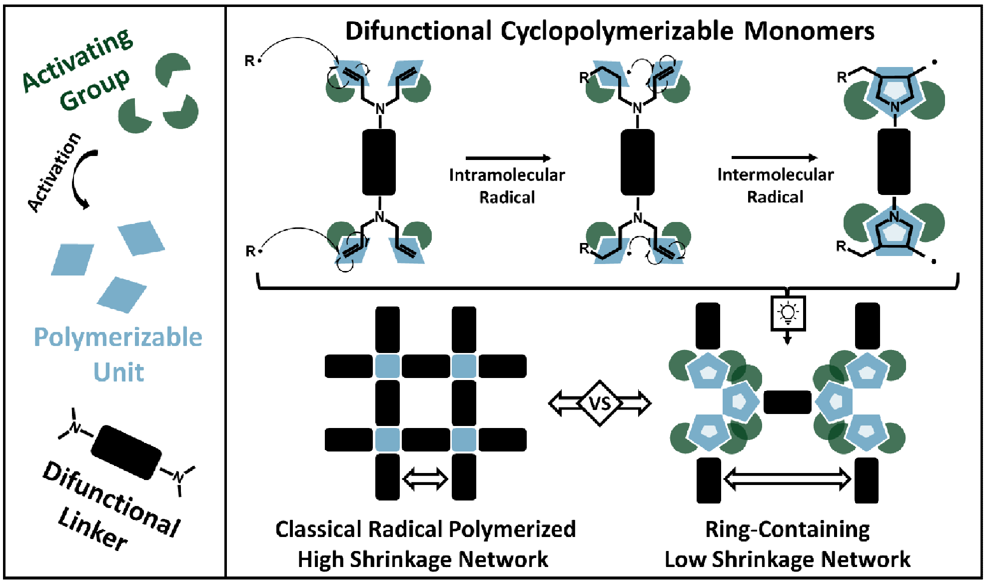
Low Shrinkage Networks of Difunctional Cyclopolymerizable Monomers via photo-induced Radical Polymerization

Larissa Alena Ruppitsch[1*], Gernot Peer[1], Katharina Ehrmann[1], Thomas Koch[2], and Robert Liska.[1]

[1]*Institute of Applied Synthetic Chemistry, University of Technology Vienna, Austria*
[2] *Institute of Material Science and Technology, University of Technology Vienna, Austria*
[*]*larissa.ruppitsch@tuwien.ac.at*

Cyclopolymerizable monomers (CPM) consisting of non-conjugated dienes can form polymer networks with cyclic structures in their backbones. This cyclization is performed in a two-step mechanism alternating in an intra- and intermolecular way upon light initiation, and it is caused by the lack of homopolymerization behavior of the corresponding monoene monomers.[1,2] These ring-containing networks may exhibit a reduced shrinkage than those formed during classical radical photo-induced homopolymerization.[3]



Reduced shrinkage of photopolymerized networks *via* cyclopolymerization of difunctional monomers

This study focuses on difunctional CPMs based on allyl-moieties as a primary motif widely used in state-of-the-art coating applications. The synthetic strategy of novel diamine-linked difunctional 1,6-diene CPMs with various double bond activation (allyl-, methacryloyl-, and ester-activated allyl-moieties) is presented. These novel compounds reveal their enhanced properties during reactivity and mechanical studies *via* photo-DSC, photorheology, DMTA, and tensile testing. Herein, not only improved reactivities (up to 60%) and amplified mechanical properties could be demonstrated but also a significant shrinkage reduction (up to 40%) compared to the corresponding monoene compounds. This enhanced behavior highlights the influence of double bond activation accompanied by the formation of cyclic units in the polymer backbone upon photo-induced cyclopolymerization.

Keywords: shrinkage reduction, radical photo-polymerization, cyclopolymerization, difunctional monomers, mechanical analysis

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Additive manufacturing (AM) of rubber parts based on low viscous compounds using Fused-Filament-Fabrication (FFF)

F. Schneider[1*], B. Klie[2], U. Giese[2]

[1,2]*Deutsches Institut fuer Kautschuktechnologie e. V. (DIK*
Eupenerstr. 33, 30519 Hannover, Germany)
*Fritjof.Schneider@DIKautschuk.de

The additive manufacturing of carbon black- or silica-filled curable rubber compounds is a new branch of technology that has become increasingly important in recent years. Based on the classic FFF-process, 3D printers have been developed and set up [2,3,5] at DIK depending on the dosage form of the rubber compound (e.g. as a high-viscosity filament or granulate or as a low-viscosity paste), which enable the dosage of this class of materials using AM [4,6-8].
This presentation deals with material investigations to transfer a conventionaly high-viscous EPDM-based rubber compound into a low viscous rubber paste to allow additive manufacturing of sulfur-crosslinkable compounds in the "direct-printing" process [1]. Solvents in different concentrations are used to reduce the viscosity of the compound to be able to print the material using the machinery setup described in [5]. The biggest challenges concern the supply of a homogeneous mixture, which requires a homogeneous absorption of the solvent. This is necessary for a high-quality and stable printing process. After printing individual layers, it becomes evident to remove the solvent from the printed rubber part before vulcanization, as the low boiling temperatures of solvent components below the vulcanization temperature (app. 160-180°C) of the printeded rubber part can lead to undesirable bubble formation. For this purpose, appropriate printing strategies must be developed to enable early evaporation of the solvent already during the printing process.

Keywords: 3D-Printing, Additive Manufacturing, Rapid Prototyping, process chain, low viscous compounds, solvents

Acknowledgments

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Mittelstand

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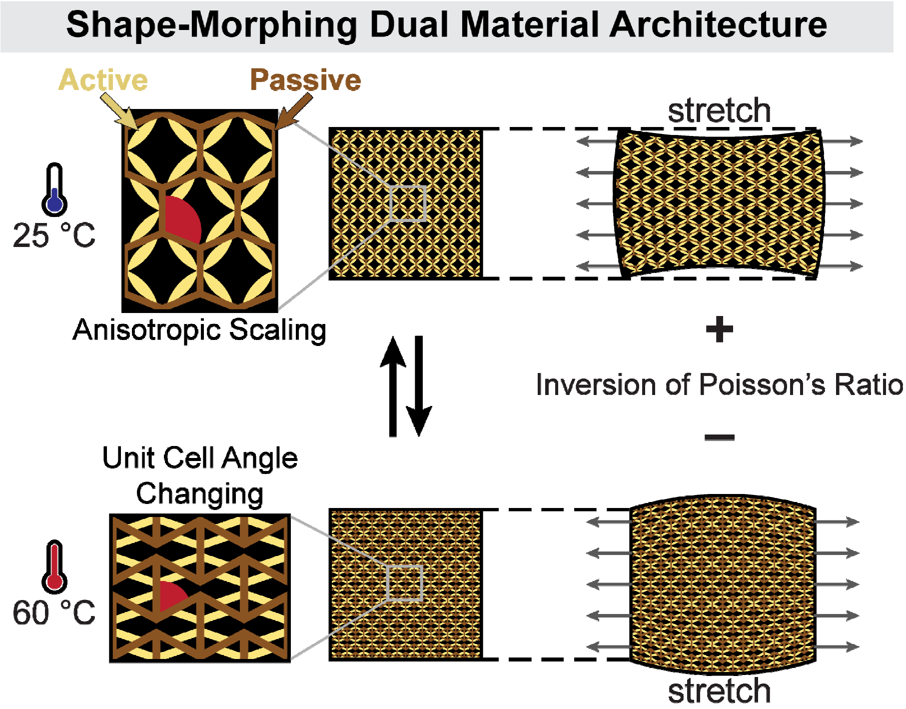
Programmable Auxeticity in Hydrogel Metamaterials via Shape-Morphing Unit Cells

O. Skarsetz[1], V. Slesarenko[2*], A. Walther[1,2*]

[1]*Department of Chemistry, Johannes Gutenberg University Mainz, Mainz, Germany*
[2]*Cluster of Excellence livMatS @ FIT—Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg, Freiburg im Breisgau, Germany*
[*]*viacheslav.slesarenko@livmats.uni-freiburg.de*
[*]*andreas.walther@uni-mainz.de*

Shape morphing mechanical metamaterials are architectured materials consisting of stimuli-responsive in combination with passive materials where structural reconfiguration with tunable response to applied mechanical forces is achieved through basic kinematic motion. However, metamaterial reconfiguration is mostly limited to bending or buckling motion. Herein, we show shape morphing of a hydrogel metamaterial architecture via one dimensional elongation of actuating struts to achieve programmable auxeticity. The directly attached actuating struts exhibit forces onto the passive re-entrant architecture resulting in change of unit cell angle. Via thermal control, the unit cell angle can be precisely programmed from 68° to 107° which results in negative, zero or positive Poisson's ratio under applied tensile strain. This concept of shape morphing hydrogel metamaterials via the addition of actuating struts into otherwise passive architectures extends the toolbox of structural reconfiguration. It can be readily extended to other architectures as well as soft robotic applications where Finite-Element-Method simulation predicts the reconfiguration and response to applied mechanical forces.



Keywords: Mechanical Metamaterials, Shape Morphing, Auxetics, Hydrogel Metamaterials

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This work was supported by the Carl Zeiss Research Cluster on "Interactive and Programmable Materials" (IPROM). Andreas Walther acknowledges generous support from the Gutenberg Research College.

3D Printing of Propargyl Ether Derivatives Based on Dual-cure Chemistry

K. Sommer[1*], T. Griesser[1], S. Müller[1]

[1]*Montanuniversitaet Leoben, Leoben, Austria*
[*]*katharina.sommer@unileoben.ac.at*

In recent years, dual-cure chemistry has been exploited to develop interpenetrating networks (IPNs) that enhance thermo-mechanical properties of photo-curable resins.[1] In this contribution the photo-induced polymerization of (meth)acrylates was utilized to build up the desired 3D structure within the additive manufacturing (AM) process, while a thermally triggered reaction allows the enhancement of the network properties in a subsequent annealing step. This strategy combines advantages of traditional UV curable monomers with high-performance thermosets.[2]

Propargyl-terminated derivatives of bisphenol A were investigated as thermo-curable building blocks in a photosensitive resin with the aim to increase the thermo-mechanical properties of the formed photopolymers. It is well reported that aromatic bispropargyl-ethers undergo a thermal polymerization reaction due to the formation of cross-linked bischromenes. These networks provide excellent thermostability, low moisture uptake, and high strength.[3]

After the successful synthesis of the aromatic propargylether derivatives, these compounds were introduced in an acrylate based resin. The good printability of various formulations containing different amounts of the thermo-curable building block was demonstrated. The obtained IPNs provide enhanced thermo-mechanical properties making these resins suitable for the AM of functional 3D parts for high performance applications.

Keywords: dual-cure chemistry, 3D printing, photopolymerization

Acknowledgments
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Development of dynamic polymer nanocomposite to reach homogenous mechanical properties in FDM

V. Tran[1,2*], L. Rozes[1], S. Delalande[2], A. Forré[2] L. Nicole[1], F. Szmytka[3]

[1] *Sorbonne Université, CNRS, Laboratoire de Chimie de la Matière Condensée de Paris, LCMCP, Paris, France*
[2]*Stellantis Research Center, Velizy, France*
[3] *Institute for Mechanical Sciences and Industrial Applications (IMSIA-UME), CNRS, ENSTA Paris, Institut Polytechnique de Paris, Palaiseau, France*
[*]*viviane.tran@sorbonne-universite.fr*

3D printing or additive manufacturing is a process of fabrication that enables the conversion of computer design into tangible 3D object by a layer-by-layer printing. One of the main drawbacks of this technique is the anisotropy of the mechanical properties caused by the weak interlayer bonds between printed layers.[1]

Covalent adaptable network (CAN) is polymer bonded with reversible covalent crosslinkers.[2] Vitrimer is a new class of polymer among the CAN polymers in which crosslinking between the covalent network is reversible owing to an associative mechanism bond exchange. [3] (Fig1a) Thus, the network behaves like a thermoset/elastomer at room temperature but at higher temperature it behaves like a thermoplastic. Polymer nanocomposites, made by the crosslink of organic macromolecules by an inorganic component, can lead to 3D permanent network with a vitrimer behavior. Therefore, such dynamic polymer nanocomposites may be a way to create more interlayer bonds between two printed layers. By activating the bond exchange with the rise of temperature, topology of the network can rearrange in all the material and more particulary it may rearrange to create new interlayer bonds (Fig.1b). Moreover following an associative mechanism, there is no loss of the dimensional stability upon reheating the printed object. This presentation will highlight a reversible metal-ligand bond nanocomposite polyurethan system printed with Fused Deposition Modeling (FDM) technique, a promising material to decrease the anisotropy of 3D-printed objects which can be demonstrated by traction and adhesion tests.

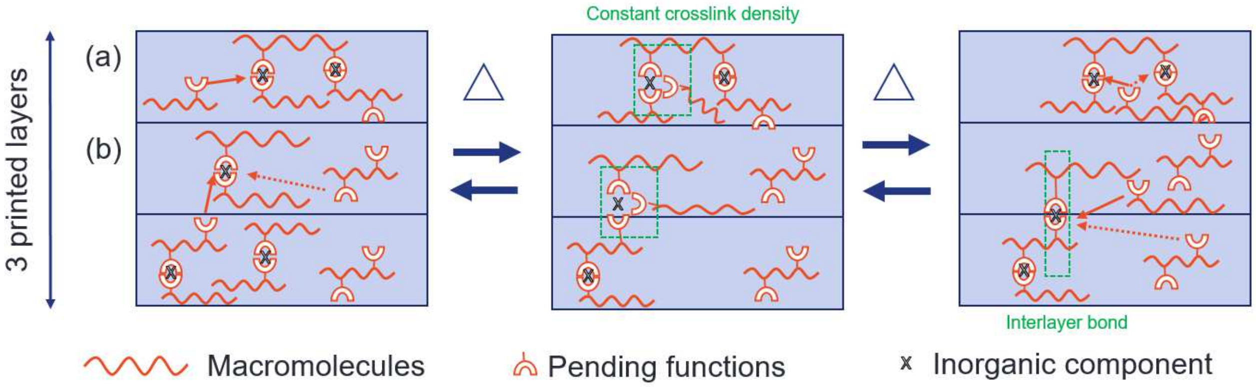

Figure 1: Bond exchange mechanism in a associative Covalent Adaptable Network applied in 3D-printed object, (a) in a layer, (b) between two layers.

Keywords: Vitrimer, Dynamic covalent polymer networks, Nanocomposite polymer, 3D printing, Anisotropy, CAN

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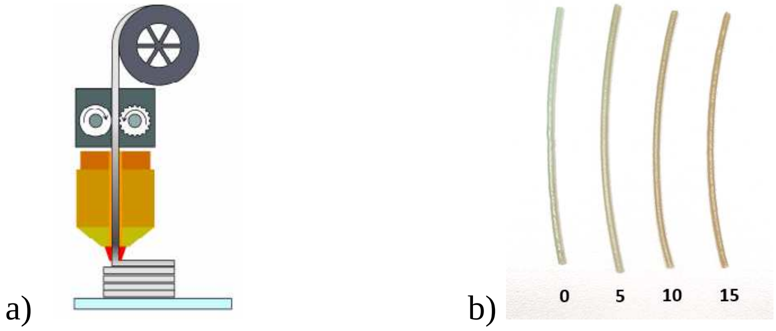
Integrative material characterization of crystalline nanocellulose reinforced filaments for fused-filament fabrication

H. Weingrill[1], M. Walluch[1*], J. Gonzalez-Gutierrez[2]

[1]*Anton Paar GmbH, Graz, Austria*
[2]*Chair of Polymer Processing, Montanuniversitaet Leoben, Austria*
[*]*matthias.walluch@anton-paar.com*

In terms of sustainability, the interest in green materials and green technology gets more and more important and gains more and more significance. The increased interest in this material class and the desire to use it in an even broader range of applications is leading to numerous different material combinations and manufacturing techniques coming into the focus of the scientific community. One example is crystalline nanocellulose (CNC), which can be used as a reinforcing fiber for various polymers. Due to its low density combined with high stiffness, this type of fiber has a very high specific modulus of around 90 MPa/(kg.m^3)[1]. During the 3D printing process using fused filament fabrication (FFF), the material is subjected to high loads both mechanically and thermally. When designing products or analyzing and modeling components manufactured in this way, these stresses must be taken into account.



a) Schematic of fused filament fabrication (FFF)[2] b) Filaments with filler contents of CNC in vol% in a recycled polypropylene matrix.

In this work, different amounts of CNC fibers (up to 15 vol%) were used as reinforcement for a recycled 3D printing grade polypropylene. To achieve maximum adhesion between fiber and matrix [3] essential for the reinforcement effect, an aleic-acid-anhydride based compatibilizer was used for fiber coating. In addition to their shrinkage behavior, the bio-composite materials used were investigated in terms of their dynamic mechanical properties, as well as their shear rheological behavior. The rheological measurements showed - against expectations - a viscosity decrease with increasing filler content in the compound. This effect occurred together with a change in the sample color, and can be attributed to a degradation of the compatibilizer. This assumption could be confirmed by differential scanning calorimetry (DSC).
Therefore, a tailor-made aging process, which imitates the thermal material stress during processing by FFF, was integrated into the DMA measurement procedure for the analysis of the filaments. This procedure enables a reliable material characterization, which allows a prediction of the component properties of the 3D printed product.

Keywords: (optional, Calibri, 11 pt.) keyword 1, keyword 2, keyword 3…

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Photo-chemically induced polycondensation of a pure phenolic resin for additive manufacturing[1]

Raffael Wolff[1], Katharina Ehrmann[1], Patrick Knaack[1], Konstanze Seidler[2], Christian Gorsche[2], Thomas Koch[3], Jürgen Stampfl[3] and Robert Liska[1*]

[1]Institute of Applied Synthetic Chemistry, Vienna University of Technology, 1060 Vienna, Austria
[2]Cubicure GmbH, Gutheil-Schodergasse 17, Tech Park Vienna, 1230 Vienna, Austria
[3]Institute of Materials Science and Technology, Vienna University of Technology, 1060 Vienna, Austria
**Email: robert.liska@tuwien.ac.at*

Bakelite© or phenoplasts are considered the first synthetic polymers in the world. These resins, produced by polycondensation, have always been known for their chemical resistance, excellent flame resistance and thermal stability. Therefore, they are still used today in space and aviation as well as in the automotive industry. Originally, pressure and temperature are required for processing and limited the production of phenoplasts to compression and injection molding. However, with the invention of lithography and 3D printing, new processing possibilities emerged. Previous work in this area has focused on thin-layer photoresists or parts that can only be printed using other polymers as matrix. Here we report a direct 3D printing method, without binders or matrix polymers, using hot lithography, a stereolithography-based 3D printing technology at elevated temperatures. Formulations could be presented that are stable under the selected conditions and yet reactive enough for the printing process. In addition to the onium-salt based photoacidgenerators (PAG), novolaks and curing agents (CA) are required to obtain a solid thermoset. Novolaks are temperature-stable, non-self-condensing phenolic resins that can only form a network with the help of a CA, usually based on formaldehyde. The most satisfactory results were achieved with a self-prepared CA. In simultaneous thermal analysis and photo-DSC experiments we investigated suitable conditions for the UV-induced polycondensation of the phenolic resins.

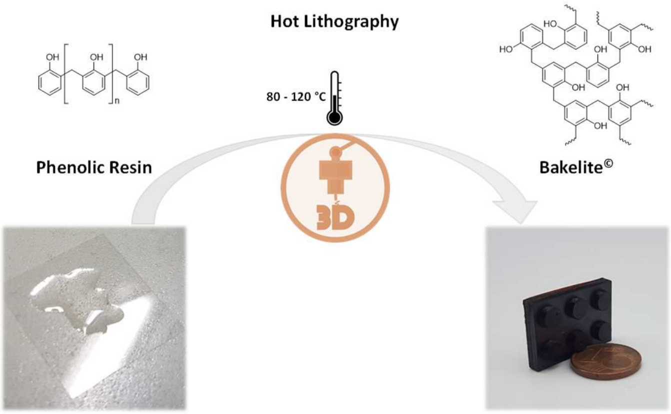

Figure 1: Schematic procedure of this work.

Direct 3D printing with Hot Lithography and post-curing gave bubble-free specimens for mechanical characterization, thus a simple production of complicated structures could be achieved without the conventional complex injection molding. Furthermore it is the first bulk polycondensation process using this technique and moreover the first time that 3D printing of pure Bakelite could be reported.

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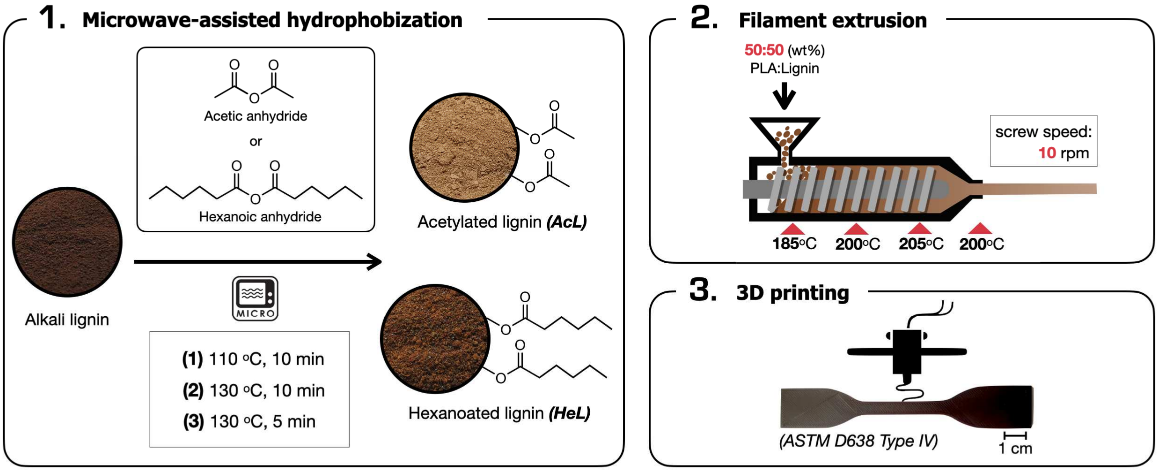
Fused filament fabrication 3D printing of biobased blends with microwave hydrophobized alkali lignin

Jenevieve Yao[1], Karin Odelius[1], Minna Hakkarainen[1*]

[1]*Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden*
[*]*minna@kth.se*

Lignin is a plant-derived polymer that constitutes up to 20-35 wt% of wood, and it is the most abundant natural source of aromatics. In industry, technical lignin is generated in large scales by the pulping industry as an underutilized sidestream, typically combusted for energy production. Efforts to valorize this byproduct in high-value material applications have grown in both research and industry, although the inherent properties of lignin pose some challenges. For instance, the hydrophilic nature of technical lignin results in its aggregation propensity and poor compatibility in polymer blends and non-polar matrices. Its incorporation in blends and composites is thus limited to small amounts, and even then it is typically accompanied by a severe deterioration of mechanical properties. In this study,[1] we demonstrate a microwave-assisted approach for the hydrophobization of alkali lignin *via* esterification. This strategy yields lignin ester derivatives through a fast reaction of 10 minutes as well as high efficiency, reaching greater than 90% substitution of aliphatic and phenolic hydroxyl groups. This enabled the successful melt-extrusion of blends of polylactide (PLA) with up to 50 wt% hydrophobized alkali lignin into filaments having tight dimensional tolerance suitable for fused filament fabrication (FFF) 3D printing. Despite the relatively high amount of lignin at 50 wt%, the resulting 3D printed materials retained the mechanical properties of neat PLA, and at 10-30 wt% loading levels, the inclusion of lignin resulted to a slight improvement in tensile properties. Further demonstrating the beneficial effects of hydrophobized alkali lignin in polymer blends, the materials exhibited both UV-shielding and antioxidant activity, demonstrating up to three times the UV absorbance of neat PLA, scavenging up to 55% of DPPH (2,2-diphenyl-1-picrylhydrazyl) free radical, and increasing oxidation induction temperature (OIT) of the 3D printed materials by up to 40 °C.



Schematic illustration of the steps involved in 3D printing of PLA/hydrophobized lignin blends.

Keywords: Fused filament fabrication, alkali lignin, microwave-assisted hydrophobization

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Long-Chain Branched Poly(Butylene Succinate-co-Terephthalate) Copolyesters: effect of chain extension strategies on melt strength properties

T. Dadouche[1], M. Yousfi[1,2*], C. Samuel[1*], M-F. Lacrampe[1]

[1]*IMT Nord Europe, Institut Mines-Télécom, Université de Lille, Centre for Materials and Processes, F-59000 Lille France*
[2]*Univ Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon1, INSA Lyon, Université Jean Monnet, F-69621 Villeurbanne, France*

[*]*Corresponding Author(s): mohamed.yousfi@insa-lyon.fr; cedric.samuel@imt-nord-europe.fr*

Highly-biobased poly(butylene succinate-co-terephthalate) (PBST) with processing temperatures close to commodity polymers (160 – 180°C) and long-chain branched (LCB) architectures are here prepared by various strategies. Their rheological properties are specifically investigated, in particular their melt strength behaviors. A two-step synthesis route was first proposed starting from linear PBST produced by polycondensation followed by reactive extrusion with Joncryl® at concentrations up to 2 wt-%. A one-step synthesis route was also developed using glycerol at a low concentration (0.5 wt-%) introduced directly during PBST polycondensation. For PBSTs synthesized by the two-step route, a concentration of Joncryl® close to 2 wt-% is required to significantly improve their melt strength properties with the appearance of a significant strain hardening phenomenon. However, PBSTs synthesized by a one-step route display also high melt strength properties with an outstanding strain hardening phenomenon which were attributed to an efficient branching effect of glycerol during polycondensation without any additional post-treatments by reactive extrusion. Furthermore, deeper investigations were performed by dynamic rheology and GPC. The latter showed a significant change in the distribution of molar masses of Long-Chain Branched PBSTs according to the synthesis strategy used.

This work provides an effective approach to improve the melt strength of highly-biobased aliphatic-aromatic copolyesters (theoretical biobased content up to 85% for PBST) which can reduce or even eliminate extrusion defects instabilities during melt processing. This may strengthen and expand the industrial implementation of these polymers into packaging and other durable advanced applications.

Keywords: Melt polycondensation, elongational rheology, long chain branching, thermal stability.

Rheology and (additive) manufacturing of covalent adaptable networks

J. Ayestarán, H. Sardón, I. Calafel, R. Aguirresarobe

[1]*POLYMAT and University of the Basque Country, Donostia-San Sebastián, Spain*
[*]*roberto.hernandez@ehu.eus*

Traditional thermostes are an important part of the polymer industry, due to their the enhanced performance in terms of mechanical and thermal properties in comparison with the thermoplastic counterparts. However, due to their cross-linked network structure, they present several drawbacks in terms of manufacturing and recyclability. Indeed, once the polymer network is formed, it is not possible to melt or solubilize the material without degrading the structure.

Recently, a new concept has been stablished in order to overcome these limitations. This concept is based on the incorporation of active elements capable to undergo reversible or "dynamic" reactions upon stimulation. [1,2] This new class of materials, known as dynamic polymer networks or covalent adaptable networks (CANs), can potentially merge the most appealing characteristics of two worlds: The enhanced performance of thermosets and the processability and recyclability of thermoplastics.

In terms of actuation mechanism, CANs can be divided into 2 main groups (associative and dissociative) and a combination of both. [1–3] These mechanism, affect the rheological behavior, as well as the manufacturing possibilities of the CANs. In this work, we discuss the rheological implications of introducing dynamic structures into polymers. Additionally, we will see how to take advantage of these rheological features to produce 3D parts.

Keywords: Covalent adaptable networks, vitrimers, 3D printing, rheology

Acknowledgments

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Polymer-Metal joining improved by laser microstructuring

K.Bula [1*], B.Korzeniewski[1], Ł. Bernat[1]

[1]*Institute of Materials Technology, Poznan University of Technology, Poznan, Poland*
[*]*Corresponding Author karol.bula@put.poznan.pl*

Joining of metal parts with polymers by using overmolding technique is still the most versatile method to manufacture bimaterial hybrid elements in a large production scale. One of the significant advantage of the overmolding method is that the materials coupling is make in the same production step, as wel as in the same tool. On the other hand lack adhesion of metals to polymers enforce to additional pre-processing step which involve metal surface structurisation [1-3]. In the presented work the microstructurisation of aluminum plates (AL 6061) as well as austenitic steel (316) was used to enhance the micromechanical adhesion to polyamide 6 filled with 30% of glass fibers. For metal surface patterning the diode laser, with the maximum force of 30 W, working in pulse mode was used. Selected laser scanning speeds (50, 100, 200, 300 mm/s) and distances between groooves (400, 800 µm) were chosen. Before overmolding the metallic inserts were cleaned with ultrasonic bath and then scanned with roughness tester to evaluate actual surface parameters. For observation of laser engraved traces in metallic surfaces the Nikon Eclipse MA200 reflecting microscope with motorised stage was used (Fig. 1). Overmolding process was realised in one-side joints, two-sided joints and finally in sandvich like structure, where the metallic plates were as the outer layers. Injection molding was conducted using the ENGEL injection molding machine with 20 tons of clamping force, with the barrel temperature of 240 – 250 °C, mold temperature 80 °C, injection speed of 90 mm/s. Obtained lap joints were shear tested using a Zwick/Roell Z010 testing machine with the test speed of 2 mm/min, accorting to ISO 4587 standard. The tensile test results showed that the grooves formed onto the metallic surfaces by the laser worked at the moderate speed (200 mm/s) gives the highest shear force during shearing of the metal-polyamide 6 GF 30 two-sided joints. Moreover, this kind of joint revealed almost two times higher elongation at break, which is most expected feature in such connections.

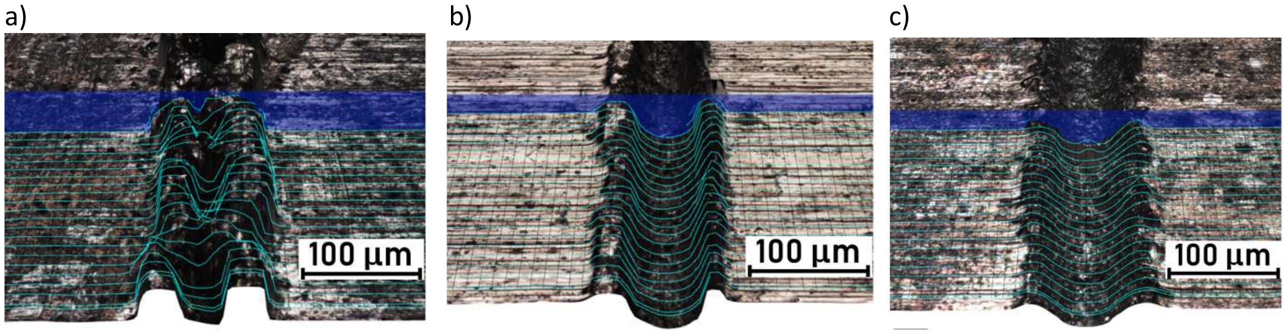

Fig. 1. 3D microscopic pictures of grooves on Al 6061 surface engaraved at the laser speed: a) 50 mm/s, b) 200 mm.s, c) 300 mm/s.

Keywords: hybrid joints, polymer-metal composites, laser microstrructuring

Acknowledgments
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Present and Future of extrusion-based 3D printing of flexible PVC

I. Calafel[1], R. Aguirresarobe[1], B. Pascual[2], I. Conde[2], M. Tierno[2], A. Santamaria[1].

[1]POLYMAT and Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizabal, 3, 20018, Donostia-San Sebastian, Spain
[2]ERCROS S.A., Innovation and Technology Department, Chlorine Derivatives Division, Diagonal 595, 08014, Barcelona (Spain)
**itxaso.calafel@ehu.eus*

Polyvinyl chloride, PVC, is on the most wordwidely used materials due to its properties, durability and versatility. The possibility of copolimerization with diverse comonomers and/or incorporation of assorted additives makes it certainly suitable in innumerable applications related to construction, health, electronics, automotive, etc[1]. Recently, as a result of new and complex technological interests, new processing techniques have emerged. Concretely, additive manufacturing, known as 3D printing, has been positioned as one of the most promising one due to the potential for transforming different kind of materials into customized complex prototipes in a reasonable low proccesing time and cost[2]. However, as far as fused deposition modeling (FDM) is concerned, the most common materials are the polylactic acid (PLA), poly(acrylonitrile-butadiene-styrene) (ABS), Nylons, thermoplastic polyuretante (TPU), etc, that is, engineering thermoplastics or even composites with appropiate physico-chemical properties to be printed layer-by-layer from melting state. Nevertheless, multiple studies have demostrated that PVC could also be considered one of the leading candidates because of its excelent printability by different extrusión-based 3D printing techniques. In this sense, rheology has certainly consolidated itself as a powerfull tool capable of predicting the likelihood of filament buckling, nozzle clogging and the correct welding between deposited layers[3].

Thus, this work explores some of the most remarkable findings regarding the printability of flexible PVC formulations from a rheological point of view. The following cases are explored: a) Plasticised PVC formulations[4]; b) Polyvinyl chloride-butyl acrylate random copolymers, PVC/PBA[5]; c) Polyvinyl chloride-butyl acrylate block copolymers, PVC/PBA/PVC[6] and d) PVC with chemical blowing agents: printability of foams.

Keywords: flexible PVC, 3D printing, rheology

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Development of Polypropylene Composites through Fused Deposition Modeling: the Effect of Carbon-Based fillers on Material Properties

Francesco Casamento[1*], E. Padovano[1], S. Pappalardo[1], A. Frache[1], C. Badini[1]

[1]*Department of Applied Science and Technology, Politecnico di Torino, Turin, Italy*

Fused Deposition Modeling (FDM) is the most widespread technology amongst Additive Manufacturing processes for polymeric materials due to its flexibility and cost-effectiveness. One of the challenges of research is to increase the available materials for FDM, as there are still few polymers which are optimized for this technique. Polypropylene (PP) is widely used in a wide range of fields, but its application in FDM is still limited due to some issues, such as warping and lack of adhesion, related to the intrinsic properties of this material [1].

The main goal of this work is the development of PP composites reinforced with carbon-based fillers, namely Carbon Fibers (CF) and Carbon Nanotubes (CNTs), in the quantities of 15% wt. and 2.25% wt. respectively. Starting from pellets, the first steps were related to the production of filaments and the development of a viable FDM process. The study then deeply characterized the obtained materials in terms of their thermo-physical, chemical, compositional, mechanical, and electrical properties, and analyzed the effect of the addition of the carbon-based fillers on these properties.

To produce the filaments, a single-screw extruder was used. The combination of a set of parameters, including screw speed, the temperatures of the heating zones and the fan speed, allowed to produce filaments having circular section and diameter requested by FDM process. To overcome the previously cited limits in the processing of PP through FDM , the materials were printed by applying a rough PP slab on the printing bed and the bed temperature was set to high values to mitigate warping. The distance between the nozzle and the plate was adjusted in order to avoid welding, but also to ensure good adhesion with the first layer. In this way, the applied process parameters provided the development of a viable 3D-printing process.

DSC, XRD and FTIR analyses showed that the matrix was made from a blend of polypropylene and high density polyethylene (HDPE). TG analyses showed the presence of a filling mineral phase, which was identified as talc. The degree of crystallinity of PP was equal to 74%. The addition of CNTs brought to an increase in crystallinity, and an anticipated crystallization of the PP phase. Conversely, the introduction of CF caused a significant decrease of crystallinity degree and anticipated the crystallization of the HDPE phase. The thermal stability of the PP/CNTs composite was improved in inert atmosphere but worsened in oxidizing atmosphere compared to the matrix; the PP/CF composite, on the contrary, showed the opposite behavior.

Tensile tests were carried out for each material; specimens were printed with a flat arrangement and with a printing pattern of ± 45 °. PP showed values of elastic modulus and tensile strength equal to 0.72 GPa and 13.6 MPa respectively. The addition of CNTs brought to an increase of 25% of the elastic modulus, while the tensile strength did not show a significant variation. Conversely, the addition of CF caused a significant increase in elastic modulus, which resulted almost 4 times higher than the matrix, while the tensile strength was 29% higher than the matrix.

The electrical conductivity of PP/CNTs composites was shown to be dependant on the manufacturing technique. Specimens obtained from compression molding of the pellets showed values of resistivity of $8.7 \cdot 10^{-1}$ Ω·m; this value was significantly increased when testing the electrical resistivity of the filament, which was equal to $9.7 \cdot 10^{3}$ Ω·m, while FDM specimens showed insulating behavior. This was explained by supposing agglomeration phenomena of the CNTs occurring during processing, which would be confirmed by the only little increase of mechanical properties.

Keywords: Additive Manufacturing, Fused Deposition Modeling, Polymers, Composite Materials

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The effect of temperature and particle size on the rheological properties of particulate crosslinked gelatin-methacryloyl gels

Tess De Maeseneer[1], Lana Van Damme[2], Rodrigo de Oliveira Silva[3], Dimitrios Sakellariou[3], Sandra Van Vlierberghe[2], Ruth Cardinaels[1], and Paula Moldenaers[1*]

[1]*Soft Matter, Rheology and Technology, Department of Chemical Engineering, KU Leuven, 3001 Heverlee, Belgium*
[2]*Centre for Membrane Separations, Adsorption, Catalysis and Spectroscopy for Sustainable Solutions (cMACS), KU Leuven, 3001 Heverlee, Belgium*
[3]*Polymer Chemistry & Biomaterials Group – Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Ghent University, 9000 Ghent, Belgium*
[*]*paula.moldenaers@kuleuven.be*

Crosslinked gelatin-methacryloyl is an excellent candidate for tissue engineering purposes due to its excellent biocompatibility and easily tunable mechanical properties. It is a chemically modified natural polymer that undergoes UV-induced crosslinking in the presence of a photo-initiator. The latter induces chemical crosslinks in addition to the physical crosslinks inherent to gelatin. These physical crosslinks are present below a temperature of 35 °C as single α-helices or triple helices depending on the chain conformation and thermal preparation conditions. A triple helix consists of three individual helices which are all in trans-conformation, whereas an α-helix can be in trans- or cis-conformation. To design a stable scaffold material that maintains its mechanical properties inside the human body, rheological characterization at physiological conditions is of great importance. Here, crosslinked gelatin-methacryloyl is used in powder form of which the powder particles swell upon addition of water. The rheological properties of three distinct gel materials, which are chemically identical but differ in crosslinking degree and particle characteristics, are studied at temperatures ranging from just below room temperature to elevated temperatures encountered inside the human body. The absolute values of the elastic moduli are related to the swell behaviour of the particles which is particle size dependent. This swell behavior has been investigated by laser diffraction and light microscopy at multiple temperatures. Furthermore, the gels show a decrease in modulus at elevated temperature related to the loss of physical crosslinks. Upon cooling, the modulus of certain gels is not restored (see Figure 1). The (ir)reversibility of the reduced modulus can be correlated to the swell behaviour of the particles and conformation of the gelatin chains. The latter has been characterized as a function of temperature by circular dichroism, FTIR-spectroscopy, Raman microspectroscopy and NMR-spectroscopy.

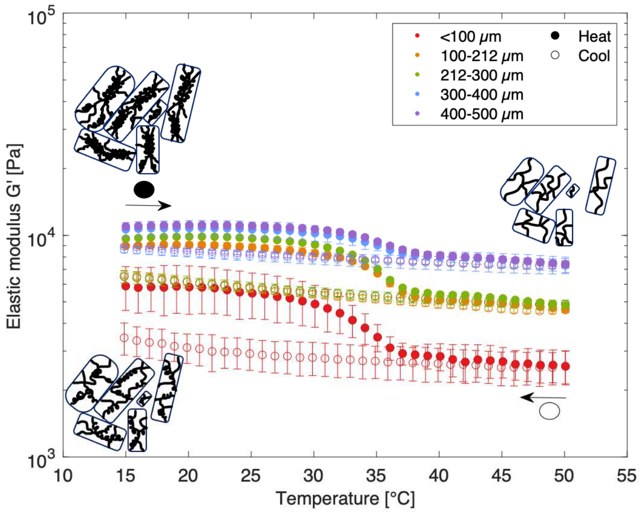

Figure 1: Irreversible reduction in elastic modulus as a function of temperature which is correlated to the swell behaviour of the gel particles and conformation of the gelatin chains.

Effect of shear and elongation on the stability of thin multilayer polymer films

A. Dmochowska[1], J. Peixinho[1], C. Sollogoub[1], G. Miquelard-Garnier[1*]

[1]*Laboratoire PIMM, CNRS, Arts et Métiers Institute of Technology, Cnam, HESAM Université, 75013 Paris, France*
[*]*guillaume.miquelardgarnier@lecnam.net*

Multilayer polymeric films can find applications in packaging, functional coatings, etc. During processing, interfacial instabilities may occur, preventing the successful production of the multilayer structure [1]. Controlling these instabilities is even more crucial when the targeted thickness layer is in nanoscale. Hence, there is a need for a deeper understanding of the underlying physical phenomena. An example of one of the processes allowing the design of such films is multilayer coextrusion. Recent studies have evidenced the existence of a critical thickness below which the layers spontaneously break-up during the processing of two immiscible polymers [2,3]. It was hypothesized that such break-ups are due to capillary waves amplified by attractive long-range interactions between adjacent layers, i.e. a dewetting mechanism.

During processing, shear and elongation of the polymer flows commonly occur – shear along the screw elements and elongation at the die in extrusion. In the proposed study, the effects of both shear and elongation on the stability of nanolayers were evaluated in multilayers of two well-known amorphous polymers: polystyrene (PS) and poly(methyl methacrylate) (PMMA). First, the dewetting dynamics of a PS ultra-thin layer embedded in between two thicker PMMA layers was observed at different shear rates, by using a shearing hotstage under an optical microscope. The growth velocity of dewetting holes clearly increased with the shear rate and seemed to be related to the shear-thinning behaviour of the PMMA. Next, the effect of elongation was studied by quantifying extensional behaviour of multilayer films with different layer thicknesses and number of interfaces.

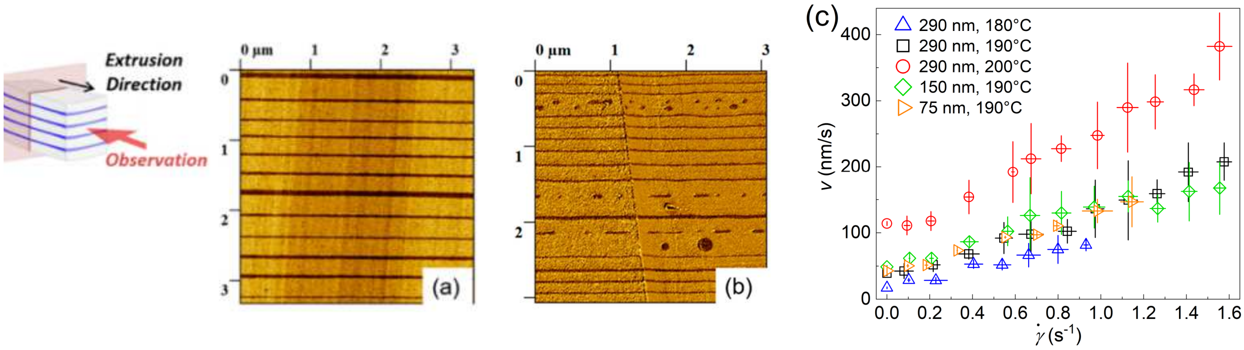

Figure 1. PMMA/PS nanolayered film imaged by atomic force microscope [2] with continuous layers (a) and broken layers of PS (b); (c) Differences in dewetting dynamics with increasing shear rate for different temperatures and PS film thicknesses.

Keywords: thin films, polymer films, shear flow, extensional rheology, dewetting

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Evaluating the dispersion of macrocycle-functionalized carbon nanotube-polyethylene composites using melt rheology

Matthew D. Eaton[1*], Marisol Rivas Caramés[1], Alicia Naranjo Chacón[1], Marta González Sánchez[1], Emilio M. Pérez[1]

[1]*IMDEA Nanociencia, Ciudad Universitaria de Cantoblanco, C/Faraday 9, E28049 Madrid, Spain.*
[*]*matthew.eaton@imdea.org*

One of the major issues in developing high-performance thermoplastic-carbon nanontube (CNT) composites is the tendency for CNTs to agglomerate during composite fabrication [1]. Chemical functionalization of CNTs have been significantly explored to improve the dispersion and mechanical reinforcement of composites [2]. Recent success in the development of mechanically-interlocked carbon nanotubes (MINTs), that consist of circular organic molecules wrapped around the carbon nanotube, has shown improved mechanical strength vs. as-produced carbon nanotubes [3]. The organic macrocycle can be easily modified with a variety of functional groups that improve chemical compatibility with polymer matrices.

However, the development of high performance composites is hindered by mainly two challenges, **1**) the energy intensive challenge of processing the functionalized carbon nanotubes with solvents and the subsequent removal of the solvent, and **2**) the time-consuming and intensive process of preparing polymer composite samples of different MINT formulations and testing them for mechanical properties. As such, a quick, informative method of dispersion and mechanical reinforcement is necessary to evaluate different potential formulations. Recent work has been focused in optimizing techniques to synthesize MINTs using minimal solvent, but difficulties persist in making composites of similar mechanical properties to their solution based counterparts.

Melt rheology has been used to evaluate the dispersion of CNT-polymer composites before, and provides the benefit of requiring small amounts of composite sample that don't have the processing effects of solid state samples. However, the melt rheology of CNT-polymer composites can be complicated and hard to understand, which can make it difficult to extract meaningful conclusions from rheology data[4]. In this talk, we will discuss how the rheometer can be used to evaluate the dispersion of polymer-MINT composites, and demonstrate how the data can be used to draw relationships with bulk tensile mechanical properties using low-density polyethylene as a model system.

Keywords: Polymer, composites, carbon nanotubes, rheology, mechanical properties

Acknowledgments

José Hobson and Jimena de La Vega of IMDEA Materiales for help with microcompounding, and Dr. Juan Pedro Fernandez Blazquez for rheology discussions. Funding from Nanocore, Inc. (Copenhagen, Denmark)

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Interfacial rheology for probing reaction at polymer/polymer interface: Effect of temperature and molecular weight on the interfacial properties

Y. EL Omari[1*], M. Yousfi[1], J. Duchet-Rumeau[1] and A. Maazouz[1,2]

[1]*Univ Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon1, INSA Lyon, Université Jean Monnet, F-69621 Villeurbanne, France*
[2]*Hassan II Academy of Science and Technology, Rabat, Morocco*
[*]Corresponding author(s): younes.el-omari@insa-lyon.fr

This work provides an effective rheological approach to study the interfacial reaction of polymer systems encountered in different fields, including reactive extrusion and multilayer reactive polymers, which allows a better control of the manufacturing processes and the resulting functional properties. Nowadays, studying reactive multiphase polymer systems is a subject of extending interest in the industrial and academic communities. Interfacial rheology is a powerful tool to probe in a direct manner reactive polymer interfaces and investigate *in-situ* the reaction/diffusion phenomena. In the present work, polymer/polymer interfaces resulting from reactive molten polymers have been assessed. Polydimethylsiloxane trimethyl siloxy terminated, Polydimethylsiloxane Aminopropyl terminated, and Polyethylene grafted maleic anhydride (PE-g-MA) were chosen. Firstly, the chemical reaction at the interface between different polymers was followed by different techniques such as dynamic rheology, FTIR spectroscopy, DSC and the developed morphology by Scanning Electron Microscopy. Then, the interfacial reaction has been revealed by the interfacial shear rheology using a homemade developed biconical setup [1]. Secondly, the oscillating drop method was used to examine *in-situ* the chemical reaction degree between the subphases. The effect of molecular weight and temperature on the interfacial reaction kinetics was highlighted. Finally, the measured interfacial viscoelastic modulus was compared to the interfacial modulus calculated from indirect modelling methods [2].

Keywords: Interfacial shear rheology, bicone, oscillating drop, Interface, interphase, reaction, diffusion

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Fast visible-light photopolymerization in the presence of MWCNTs: Towards 3D printing conducting nanocomposites

Antonela Gallastegui[1*], Antonio Dominguez Alfaro[1,2], Nuria Alegret[2], Maurizio Prato[2,3,4], María L. Gómez[5], David Mecerreyes[1,5]

[1] POLYMAT, University of the Basque Country UPV/EHU, Donostia-San Sebastian, Spain
[2] Center for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA), Donostia-San Sebastián, Spain
[3] Department of Chemical and Pharmaceutical Sciences, INSTM unit of Trieste, University of Trieste, Trieste, Italy
[4] Instituto de Investigaciones en Tecnologías Energéticas y Materiales Avanzados (IITEMA), Río Cuarto, Argentina
[5] IKERBASQUE, Basque Foundation for Science, Bilbao, Spain
*antonela.gallastegui@polymat.eu; antob.gallastegui@gmail.com

A new photoinitiator system (PIS) based on Riboflavin (Rf), triethanolamine (TEA) and multiwalled carbon nanobutes (MWCNTs) is presented for visible light induced photopolymerization of acrylic monomers. Using this PIS, photopolymerization of acrylamide and other acrylic monomer was quantitative in seconds (see Figure 1a). The intervention mechanism of CNTs in the PIS was studied deeply, proposing a surface interaction of MWCNTs with Rf which favors the radical generation and the initiation step. As a result, polyacrylamide/MWCNT hydrogel nanocomposites could be obtained with varying amounts of CNTs showing excellent mechanical, thermal and electrical properties. The presence of the MWCNTs influences negatively the swelling properties of the hydrogel, however, significantly improves its mechanical properties (young modulus values) and electric conductivity. The new PIS was tested for 3D printing in a LCD 3D printer. Due to the fast polymerizations, 3D printed objects based on the conductive poly-acrylamide/CNT nanocomposites could be manufactured in minutes, as observed in Figure 1b.

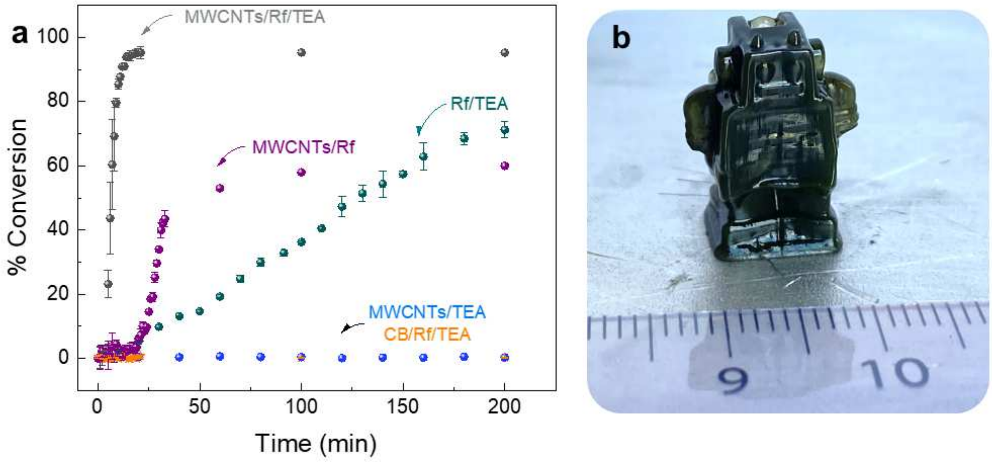

Figure 1. Photopolymerization kinetics given by % acrylamide monomer conversion vs irradiation time (min) of different photoinitiator systems (PIS) (a); picture of a printed 3D object (b).

Keywords: CNTs, Visible-light Photopolymerization, Hydrogels, LCD 3D printing

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Rheological investigation of thermo reversible CNT composites via Diels-Alder chemistry

Jie Guo, Franceco Picchioni, Ranjita K.Bose*

Department of Chemical Engineering, Product Technology, University of Groningen,
Nijenborgh 4, 9747 AG, Groningen, The Netherlands
**r.k.bose@rug.nl*

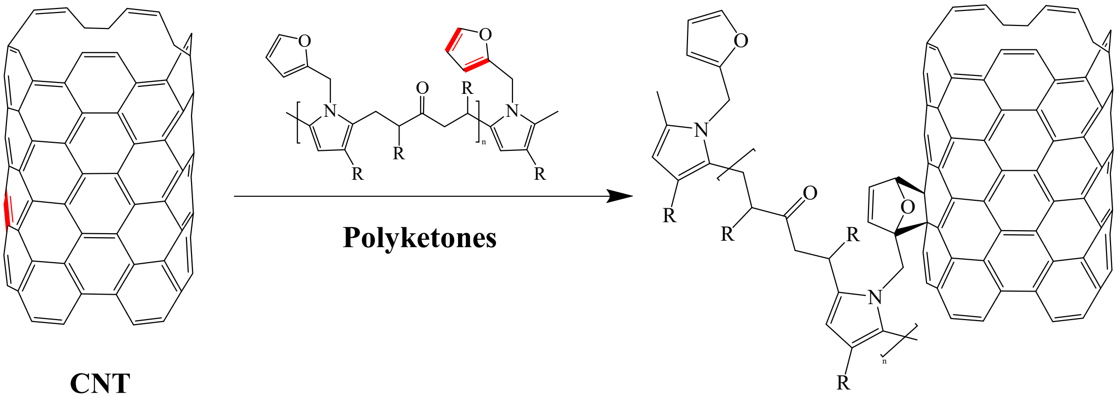

Figure 1 Scheme of direct Diels-Alder on CNT with furan functionalized polyketones

Carbon nanotubes (CNTs) are one of the various nanofillers that can be used to improve the thermal and conductive properties of nanocomposites. In this study, CNTs were employed as a reactive filler with the role of dienophile in the Diels-Alder (DA) reaction[1,2]. The polymer matrix was prepared by functionalizing polyketones with furfurylamine to attach furan groups on the polymer chain. These furan groups act as the diene in the DA reaction. The functionaliztion of CNTs through DA was confirmed successfully by elemental analysis and thermogravimetric analysis. Rheological tests were performed to evaluate the reversible thermal behavior of the composites. By comparing control samples without the DA reaction, the composites demonstrated obvious dynamic temperature dependent behavior which indicates the DA reaction between CNTs and furan-pendant polyketones. The results showed good reversibility between 50°C and 120°C. Different CNTs weight percentages also have a significant effect on the composites with better reversibility at higher percentage. However, the composites became irreversible at temperatures above 160°C. It is speculated that a secondary reaction occurs between the DA adducts and the unreacted diene groups. This reaction is irreversible and therefore the materials become stiffer. The self-healing effect was investigated by both thermal treatment and external conductive tests. This direct Diels-Alder approach on CNTs provides the possibility of broader and easier application of CNTs in thermally responsive polymer composites.

Keywords: CNT, Diels-Alder, rheology , reversibility

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Viscoelastic behaviour of novel thermoplastic elastomer blends for fused filament fabrication (FFF)

A. Harlay[1], A. Regazzi[2*], J.-C. Quantin[2], M. Batistella[1], S. Blanquer[3], J.-J Robin[3], J.-M. Lopez-Cuesta[1]

[1]*Polymers Composites and Hybrids (PCH), IMT Mines Ales, Ales, France*
[2]*LMGC, IMT Mines Ales, Univ Montpellier, CNRS, Ales, France*
[3] *ICGM, Univ Montpellier, Montpelier*
[*]*arnaud.regazzi@mines-ales.fr*

Despite the increasing range of elastomeric materials available for 3D printing, polymers currently in use cannot meet some specific requirements in relation to the increasing portfolio of applications using additive manufacturing. In particular, a design of thermoplastic elastomers based on polymer blends leading to a limited shrinkage and showing an important flexibility could attract interest. Hence, various formulations of non-compatibilized and compatibilized EPDM/PA12 were compounded in a twin-screw extruder and then processed as filaments using a single-screw extruder in order to be manufactured by fused filament fabrication (FFF).

Rheological measurements carried out in oscillatory shear mode using paralel plate geometry showed a decrease in viscosity with increasing both PA12 content and temperature. As expected, the relaxation times of PA12 rich blends are shorter than those of EPDM due to the smaller molecular weight of PA12. The phase inversion was observed for formulations in the range of 50 to 60 phr of PA12 as confirmed by Han's diagram (Fig 1.A). Surprisingly, Cole-Cole's (Fig 1.B) and Han's diagrams revealed a quite homogeneous structure at with less than 30 phr of PA12 in correlation with the SEM images of cryofractured FFF filaments (Fig 1.C). The Cross-WLF model was sucessfully used over the processing temperature range to confirm the time-temperature superposition principle of EPDM, PA12 and blend formulations. All these data contributed to a better understanding of the material-process relationship and allowed the most relevant formulation for FFF to be selected. Hence, an assessment of the printability of PA12/EPDM blends can be performed thanks to the better understanding of the polymer flow into the hot end as well as the anticipation of filament buckling[1].

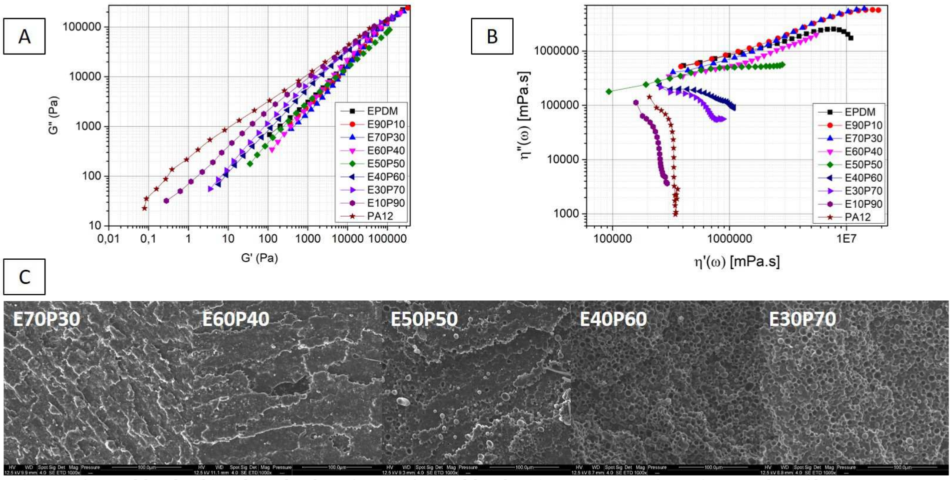

Figure 1: (a) Han plot of EPDM/PA12 blends, (b) Cole-Cole plot of EPDM/PA12 blends, (c) SEM image of cryofractured 3D filament

Keywords: polymer blends, EPDM, PA12, viscoelastic behavior, FFF, 3D printing

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Micro and Nano Porous Polymers obtained through Supercritical-CO_2 Continuous or Disontinuous Processes

M. Haurat[1*], Y. Anguy[2], M. Sauceau[3], F. Baillon[3], L. Le Barbenchon[2], A. Kusiak[2], M. Dumon[1]

[1]*LCPO laboratoire de chimie des polymères organiques -UMR* CNRS *5629 Université de Bordeaux, France*
[2]*I2M institut de mécanique et ingénierie -UMR* CNRS *5295 Université de Bordeaux, France*
[3]*Centre RAPSODEE, UMR* CNRS *5302, IMT Mines Albi, Université de Toulouse, France*

Generally speaking, foams belong to porous materials. The word foam is often used to name low-density materials (irrespective of the pore size) and is related to the production process. In the broad field of porous materials, one of the ultimate challenge is to reduce both specific mass (e.g. < 0.1 g.cm^{-3}) and cell size (e.g. average pore diameter < 80 nm typically). These polymer materials may be competitors of organic meso porous aerogels, but with much less fragile behaviors and easier fabrication procedures. We try to address this challenge via formulations of structured polymers (thanks to block copolymers) and two foaming processes (extrusion or batch).

Indeed, mass gain is the first concern both from a technical and a societal point of view and-presents many additional properties (thermal insulation, shock absorption, filtration, catalysis, optical or acoustical properties, etc).

Continuous (i.e. extrusion, injection) processes or discontinuous processes (i.e. batch) will be presented to elaborate cellular polymer foams, in the micro to nano* cellular range, i.e. pores lower than 1 micrometer (1 μm), through foaming in a supercritical fluid (here $scCO_2$). Such a cellular range is very favorable to enhance thermal insulation and some mechanical properties.

Moreover, $scCO_2$ polymer foams are good candidates to *generate multifunctional lightweight materials* (e.g. with introduction of CNT carbon nano tubes) to exhibit cumulative properties such as a low thermal conductivity and a high electrical conductivity, or a good compromise of rigidity vs. toughness.

The talk will describe how to control a continuous or a discontinuous process for innovative, (nano)structured cellular porous materials, responding to the challenge of mass reduction (density lowering) **and** a homogeneous lowering of pore sizes in nanometric ranges* of cellular polymers.

These features of very light, very small pores and easy-to-do cellular polymers are hardly not achievable if a single technical or commodity polymer is used (whatever the polymer or the process).

We'll give a scan of the parameters influencing size and density through saturation by supercritical fluid CO_2 followed by expansion. We explain how to control micro and nano porosities in the case of amorphous polymers. PMMA is a case study for the intended talk, where the polymer is expanded either in batch or extrusion. We present the role of T (temperature), P (CO_2 pressure), PDR (pressure drop rate) and nanostructuration by BCP (block copolymer), introduction of CNT (carbon nanotube). We will finally present some thermal and mechanical properties.

*According to **IUPAC**, *mesoporous* stands for pores between 2 and 50 nm while *macroporous* have pores above 50 nm, and *microporous* below 2 nm.

In the **domain of polymer foams**, literature describes micro foams as cells around in the μm range and nano foams in a range averagely below 100 nm.

This work was supported by the Agence Nationale de la Recherche (ANR, France) [AAPG PRCE 2018 CE06 0030, 2019]; ANR is gratefully acknowledged.

Investigation of the reaction kinetics of PBT and PET in presence of an epoxy-based chain extender using a micro-compounder

A. Himmelsbach[1], Y. Akdevelioğlu[2], M. Nofar[2], H. Ruckdäschel[1*]

[1]*Department of Polymer Engineering, University of Bayreuth, Bayreuth, Germany*
[2] *Metallurgical and Materials Engineering, Department Faculty of Chemical and Metallurgical Engineering, Istanbul Technical University, Maslak, Istanbul, Turkey*
[*]*ruckdaeschel@uni-bayreuth.de*

Unmodified polyesters such as polybutylene terephthalate (PBT) and polyethylene terephthalate (PET) have relatively low molecular weight, resulting in poor mechanical and rheological properties.[1,2] It is well known that the low melt strength of polyesters is detrimental to foam formation. To increase the molecular weight and viscosity, chemical modifications are carried out by adding chain extenders in the reactive extrusion process.[1,3,4] This modifier can result in increased molecular weight (branching and/or crosslinking) and altered rheological properties (increased shear viscosity and melt strength).[2] Chain extenders are multifunctional additives that can react with the terminal functional groups of the polyester (i.e., hydroxyl and carboxyl groups). The reaction between the carboxyl and epoxide groups is more preferable than that with the hydroxyl group. It is also known that the time required to complete the reaction decreases dramatically as the reaction temperature increases.[1] Both polymers, PBT and PET, have a quite similar chemical structure. The difference between the two polymers is two methylene groups in the repeating unit. As a result, PBT has better chain mobility, which is reflected, among other things, in its crystallization behavior. [5]

In this work, we address the question of whether this difference in chain mobility has a significant effect on reactivity. Therefore, the kinetics of the reaction of polybutylene terephthalate with a multifunctional epoxy-based chain extender (CE) was studied using a micro-compounder. 15 g of pre-dried PBT was mixed with 1 wt% CE and extruded at 100 rpm at various temperatures between 260 °C and 280 °C. The force required to hold the screws in position was recorded and evaluated over 10 minutes.

In addition, the reactivity of the two polymers and their blends as a function of composition was also investigated at 280, 285 and 290 °C.

It could be shown that the reaction between PBT and the epoxy-based CE follows the quasi-1. order reaction kinetic. An activation energy of 1849 J/mol could be found between 260 °C and 280 °C. The molecular weight of the two unmodified polymers was quite similar. Thus, the difference in reactivity should result from the difference in the chemical structure. It could be shown that reaction between PBT and CE is slightly preferable. This phenomenon becomes less evident with increasing reaction temperature.

Keywords: PET/PBT blend, Joncryl chain extender, Reaction kinetic, Reactive extrusion

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Digital Materials - Photopolymers with increased toughness

B. Koch[1,2*], A. Hochwallner[1], T. Theuer[1], T. Koch[1], R. Liska[2], J. Stampfl[1]

[1]*Institute of Materials Science and Technology, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria*
[2]*Institute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria*
[*]*bettina.koch@tuwien.ac.at*

Most photopolymers, produced by lithography-based additive manufacturing technologies (L-AMTs), yield brittle materials limiting the field of application. For this reason, a lot of effort is put into the development of strategies to increase the toughness of these materials. Well known approaches are for example changes in the polymer architecture, the addition of rubber additives or chain transfer agents and the fabrication of interpenetrating polymer networks (IPNs).[1] This work is focused on the local modification of photocurable resins. By selective addition of a secondary material to the layers of a primary material the photopolymer and its properties can be modified locally by inkjet printing. The obtained composite material can be referred to as digital material since the product is either modified by the secondary material or unmodified.

This strategy is based on natural toughening mechanism of nacre or glass sponges. The brick-and-mortar structure or the alternating hard and soft phases lead to crack deflection and branching or crack propagation can be stopped in the soft layer called shielding effect.[2, 3] Fratzl et al. figured out that an effective shielding effect can be observed if the difference in elastic moduli of soft and hard phase is factor 5 or higher.[4] By printing the primary hard matrix material by a lithography-based AMT-printer and adding a soft ink as secondary material by an inkjet-printer, fracture toughening of the digital material should be achieved.

The hard matrix material should provide a high elastic modulus as well as a high tensile strength and a high glass transition temperature T_g. The soft ink should have a T_g lower than room temperature to guarantee a low elastic modulus and subsequently a significant difference compared to the matrix material. Furthermore, a high elongation at break is preferable and the viscosity has to be very low (< 20 mPa*s) to be processable by inkjet printing. Digital materials consisting of suitable matrix and ink materials were characterized regarding the quality of the printed structures by laser scanning microscopy (LSM) and nanoindentation measurements and the effect on the fracture toughness was determined by tensile tests.

Keywords: digital materials, L-AMT, inkjet, photopolymers, toughening

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Toward Lithium-ion thermoplastic Battery: development of electrically conductive nanocomposites filaments for FDM 3D printing technology

M. Louati[1*], V. Boudeville[2,3,4], S. Grugeon[2,3], S. Panier[2,4], L. Dupont[2,3], E. Leneveu[5], G. Ales[5], C. Campagne[1] and A. Cayla[1]

[1] Univ. Lille, ENSAIT, ULR 2461 – GEMTEX – Génie et Matériaux Textiles, F-59000 Lille, France
[2]Laboratoire de Réactivité et Chimie des Solides, CNRS UMR 7314, Université de Picardie Jules Verne, 33 rue Saint Leu, 80039 Amiens, France
[3]Réseau sur le Stockage Electrochimique de l'Energie, CNRS RS2E FR3459, France
[4]Laboratoire des Technologies Innovantes, LTI-EA 3899, Université de Picardie Jules Verne, 80025 Amiens, France
[5]Nanovia, ZA Saint Paul, 22540 Louargat, France
**Corresponding author: maroua.louati@ensait.fr*

The booming demand for the miniaturization of electronic devices and the growing need of consumers for energy-storage devices with free form geometries and challenging performances (long-cycle-life, high-specific energy...) are some of reasons for conducting the global market towards the next generation of lithium-ion batteries with customized geometric structures suitable for a variety of applications such as aerospace electronics, micro-electromechanical systems, etc. The adopted strategy for the fabrication of these batteries is based on the use of 3D printing technologies.[1-3] Among the 3D-printing techniques, Thermoplastic Material Extrusion (TME), also commonly called Fused Deposition Modeling (FDM) presents a promising route to prepare the lithium-ion battery within the final 3D printed object. The development of printable and electrically conductive polymer composite monofilaments corresponding to electrodes and current collectors is one of the key conditions for realization of a fully printed battery.

For this purpose, the present work is focused on the development of printable and electrically conductive polymer composite (CPC) monofilament for the current collector based on propylene thermoplastic elastomer matrix (denoted PBE). The incorporation of carbon nanofillers in the PBE matrix may reduce its viscosity and therefore its melt processability. To avoid this problem, our strategy is based on preparing hybrid fillers systems containing a blend of two kinds of nanofillers: multi-walled carbon nanotubes (denoted CNT) and/or nanocarbon black (denoted KB). The hybrid nanocomposites characterizations are mainly based on their rheological, mechanical and electrical properties. Once the 3D printed parts are produced, the electrical conduction results will be discussed depending on the type of the applied filler. Besides, the impact of the implementation process by FDM is highlighted.

Keywords: melt process, monofilament, polyolefin matrix, synergy carbon nanofillers, conductive polymer composites, 3D printing and fused deposition modeling.

Acknowledgements
The authors want to express their gratitude to National Research Agency (ANR) for the support given to the current IODA project.

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Layer breakup in multilayered PC/ABS blends: causes and consequences

Xavier Mackré-Delannoy[1]*, Matthieu Gervais[1], Anne Grandmontagne[1], Alain Guinault[1], Bruno Fayolle[1], Cyrille Sollogoub[1]

[1]*Laboratoire des Procédés et Ingénierie en Mécanique et Matériaux, Arts et Métiers Sciences et Technologies, CNRS, CNAM, HESAM, 151 bd de l'hôpital, 75013 Paris,*
**xavier.mackre@ensam.eu*

Multilayer coextrusion enables the fabrication of films with up to several thousands layers, with an individual layer thickness ranging down to nanometric scale. Such films may be used in packaging application (80%)[1] because of the large increase in barrier properties observed in the case of some semi-cristalline polymers [2]. Furthermore some authors also report increases in mechanical properties or changes in deformation mechanisms [3]. Aiming to upgrade polymers from Waste Electrical and Electronic Equipements (WEEE), the benefits of this original processing method on PC/ABS blends are studied here.

Multilayered films with up to 2049 alternating layers were fabricated from PC (Trinseo, Calibre 201-22) and ABS (LG chemical, HF 380) with 80 and 20 wt.% composition respectively. The films were then characterized by optical, electronic and atomic force microscopes, while mechanical properties were assessed by tensile tests, DMA and impact strength.

AFM analysis, as presented in Figure a, puts in evidence homogeneous and regular layers for thicknesses larger than 600 nm. Figure b points out the layer distortion due to the butadiene nodules and ultimate layer breakups when decreasing the layer thickness. Macroscopic properties seem to be affected by these phenomena as shown in Figure c. A drop in elongation at break is oberved for nominal thicknesses below 1000 nm. Possible relationships between microscopic irregularities in layers and macroscopic embrittlement will be discussed.

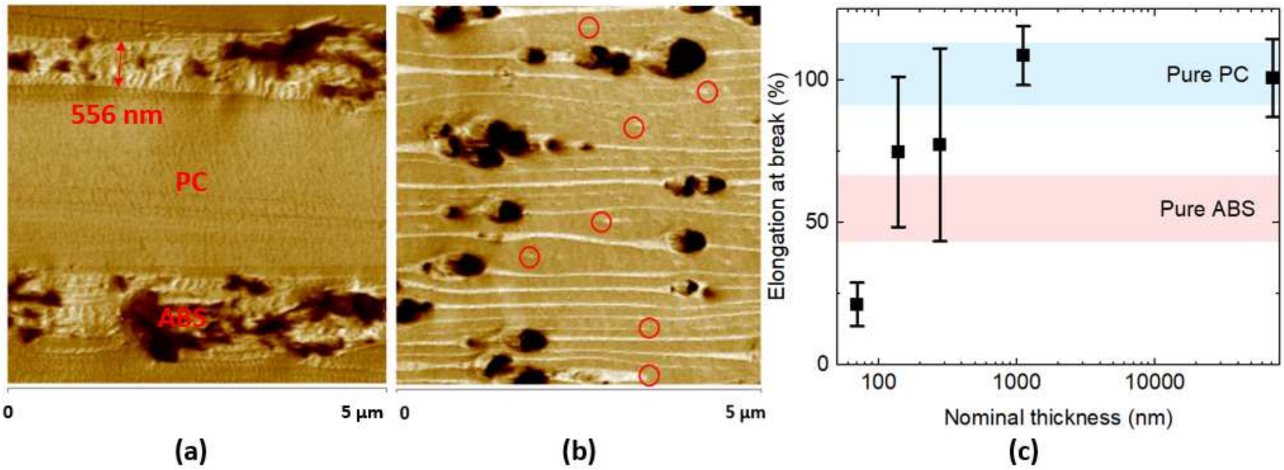

Figure : (a)AFM image of layers of nominal thickness 555nm (b) AFM image of layers of nominal thickness 35nm, red circles show broken layers (c) Elongation at break versus nominal layer thickness

Keywords: Multilayered coextrusion, PC, ABS, Layer breakup, upgrading, recycling

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Effect of self-nucleation on the crystallization kinetics and part microstructure of a SLS-compatible polypropylene material

T. Maulet[1,2]*, J. Gimenez[2], F. Demé[2], C. Barrès[3], R. Fulchiron[1]

[1]Univ Lyon, Université Lyon 1, CNRS UMR5223, IMP, F-69622, Lyon, France
[2]Setup Performance SAS, F-38290, Frontonas, France
[3]Univ Lyon, INSA Lyon, CNRS, IMP UMR 5223, F-69621, Villeurbanne, France
**thomas.maulet@setuperformance.com*

Selective laser sintering (SLS) of thermoplastic polymers is an additive manufacturing (AM) technique experiencing a remarkable growth in the recent years. Nowadays the most widely used materials are polyamides (PA12, PA11…) but massively available SLS-compatible polyolefins powders like polypropylene (PP) recently arrived on the market. In-depth understanding of the melting and coalescence behavior as well as of the crystallization is a key aspect to control parts microstructure and properties. Specifically, degree of crystallinity, crystalline microstructure and degree of particle melt (*i.e.* fraction of unmolten grains) have major influence on final parts properties [1] but such investigations on PP in the SLS context are still seldom [2].

The aim of the present work is to account for self-nucleation effect in the crystallization step during the building stage. More specifically, isothermal and non-isothermal crystallization kinetics of a propylene-ethylene random copolymer were studied by DSC. Sintered parts microstructure was thoroughly investigated via polarized light optical microscopy (POM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and wide-angle X-rays diffraction (WAXD) experiments. This brought to light the importance of considering the significant nucleating effect of the solidification of the subjacent layer during the building stage. Indeed, crystallization from a self-nucleation molten state revealed to be a condition for half-crystallization times to be consistent with experimental observations. Evidence of the presence of these germs was given thanks to microscopic and WAXD techniques. Alternate patterns of very fine microstructured, oriented transcrystalline and isotropic spherulitic regions every 100 µm (*i.e.* the layer thickness during printing) have been highlighted.

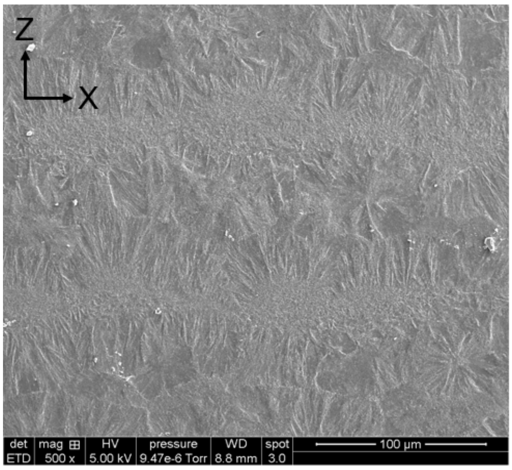

Figure 1 : SEM picture of a part cross-section prepared by chemical etching

Keywords: Additive manufacturing, selective laser sintering, polypropylene, microstructure.

Acknowledgments

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DLP 3D printing parameters prediction of a photosensitive resin: from photochemistry to photopolymerization

B. Metral, M. B. Hamouda, C. Croutxé-Barghorn, C. Ley, X. Allonas*

Laboratoire de Photochimie et d'Ingénierie Macromoléculaires, Mulhouse, France
**xavier.allonas@uha.fr*

Vat photopolymerization is a constantly evolving 3D printing field, with new technological improvements emerging every decade[1,2]. Since their early beginnings, these photosensitive techniques have used the so called Jacobs' law, established as soon as 1992[3], allowing to predict the behavior of any resin during the printing process:

$$\text{(1)} \quad \mathrm{Cd} = \mathrm{Dp}.\ln\left(\frac{\mathrm{E}}{\mathrm{E_c}}\right)$$

where Cd is the cure depth of the photopolymerized film (in µm), Dp is the penetration depth of light into the photopolymerizable resin (in µm), E is the incident energy dose (product of the irradiance by the exposure time in mJ/cm²) and Ec is the critical energy needed to polymerize the resin up to its gelation threshold (in mJ/cm²).

However, recent works have demonstrated deviations from this equation, leading to the construction of new models[4-7]. In this work, a simpler and faster way to empirically determine the Ec parameter is proposed using Real-Time Fourier-Transformed Infrared Spectroscopy (RT-FTIR). For the first time, a link between the maximum rate of photopolymerization obtained by RT-FTIR and the critical energy for gelation Ec obtained with Jacobs experiments is established. A simple equation allows the determination of a predicted Ec from conversion curves. Futhermore, using the rate of initiation and the rate of polymerization, critical energy can also be correlated to the quantum yield of radical formation. Therefore, the role of molecular photochemistry during printing can be evidenced via prediction of the Ec parameter.

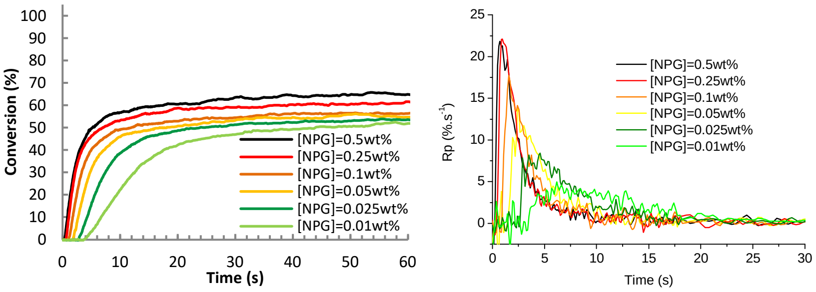

Figure 1: Photopolymerization curves (left) and rates of polymerization (right) of various studied formulations obtained by RT-FTIR

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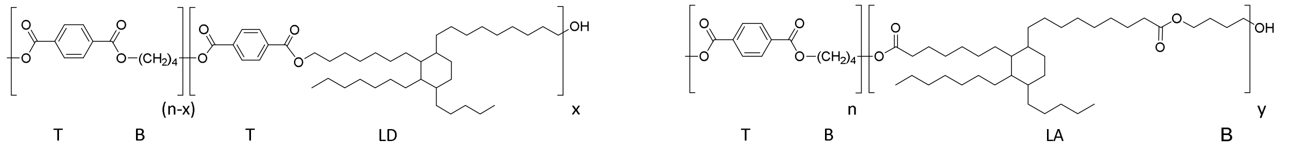
Design of polyesters for temperature-resistant particle foams and determination of structure-property-processing relationships

C. Mielke[1,2*], J. Kuhnigk[3], D. Pospiech[1], H. Komber[1], A. Lederer[1,4], R. Boldt[1]

[1]*Leibniz-Institut für Polymerforschung Dresden e.V., Germany*
[2]*Technische Universität Dresden, Organic Chemistry of Polymers*
[3]*Universität Bayreuth, Polymer Engineering, Germany*
[4]*Stellenbosch University, Department Chemistry and Polymer Science, South Africa*
**mielke@ipfdd.de*

Poly(butylene terephthalate) (PBT) is very challenging in extrusion foaming in regard to achieve a high expansion and a homogeneous cell morphology.[1,2] This is due to its unfavorable rheological behavior (low melt strength, absence of strain hardening). In this study, the chemical structure of PBT is modified by copolycondensation with biobased monomers (dilinoleic acid, LA/dilinoleic diol, LD) with defined, short side chains in order to alter the rheological properties to improve extrusion foaming. The terpolyesters are prepared by transesterification (melt polycondensation). Detailed chemical characterization by NMR spectroscopy and size exclusion chromatography demonstrates the random chain structure of the terpolyesters and the generation of polymers with high relative molar masses. In addition, the intrinsic viscosities were determined and an analysis was carried out using static and dynamic light scattering. The results show that the short-chain branches change the shape of the polymer coil and the general behavior in solution.



Series P(T-LD-B)

Series P(T-LA-B)

Figure 1. Chemical structure of terpolyesters based on short-chain branched comonomers (T: terephthaloyl; B: 1,4-butanediyl; LD: dilinoleic diol; LA: dilinoleic acid).

The incorporation of both types of dilinoleic derivatives results in an increase of solubility, a reduction of glass transition temperatures and a reduced crystallinity. Most importantly, the rheological behavior is altered, especially the elongational rheology toward strain hardening. The comparison with terpolyesters with linear comonomers without side chains as control polyesters demonstrates that the strain hardening[3] occurs only after incorporation of side chains.

Keywords: PBT, branching, rheology, strain hardening, crystallinity, light scattering.

Acknowledgments

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Static collector design in electrospinning: Highly-aligned electrospun fibers using a corrugated geometry

G. Papaparaskeva[1*], P. Papagiorgis[2], G. Itskos[2], and T. Krasia-Christoforou[1]

[1] *Department of Mechanical and Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus*
[2]*Department of Physics, University of Cyprus, Nicosia, Cyprus*
[*]*Corresponding Authors' E-mail address: papaparaskeva.georgia@ucy.ac.cy, krasia@ucy.ac.cy*

Electrospinning technology is a well-established technique for processing polymer, ceramic and composite materials. It is extensively utilized both academically and industrially for the production of electrospun fibrous membranes exhibiting high interest in multiple fieldssuch as biomedicine, catalysis, energy, filtration, sensing, and so on.[1] Electrospun fibers have constantly attracted high interest due to their outstanding morphological and multi-functional structural features including fiber configuration, porosity, high surface-to-volume ratio, micro-, nano- and subnanometer diameters[2], unique physicochemical characteristics and so on.[3] Fiber alignment has been considered of utmost importance in optoelectronics, sensing, tissue engineering, as well as energy-related applications, since oriented fibrous morphologies may result to a significant enhancement in materials properties. Various approaches[4] have been implemented towards the electrospinning equipment with the aim to achieve aligned electrospun fibers. Our recent work[5] has focused on an innovative, very simple and cost-effective design concept for obtaining highly-aligned electrospun fibers, using a static metallic collector having a corrugated geometry (without movable parts and complex configurations) in a conventional electrospinning setup. Highly aligned electrospun fibers based on three polymer systems exhibiting different physicochemical characteristics were produced successfully: Polyvinylpyrrolidone (PVP) (insulating), poly(3-hexylthiophene-2,5-diyl) (P3HT)-rich polymer blend (semiconducting), and poly(4-vinylpyridine-co-butylmethacrylate) (P4VPBuMA) (polyelectrolyte). The successful fiber alignment is due to the inhomogeneous electric field profile generated in the presence of the corrugated static collector, compared to the corresponding electric field profile produced when the standard flat static collector is used. The electric field profile differences existing between the corrugated and the conventional flat static collectors were investigated by means of finite element analysis. Quantification of fiber alignment for all polymer systems performed with a Fourier transform method on different deposition sites of the corrugated collector, demonstrated an exceptionally high degree of alignment (up to 95%) after a prolonged electrospinning time. In contrast, randomly oriented electrospun fibers were deposited on the typical flat collector. The generation of highly aligned fibers is atributed to the inhomogeneous electric field profile produced when introducing the corrugated static collector compared to that corresponding to the typical flat static collector. Finally, electro-optical characterization perfomed on the P3HT-rich fibers (aligned and randomly oriented) demonstrated that the aligned P3HT-rich electrospun fibers exhibited superior electrical properties compared to the randomly oriented fiber analogues.

Keywords: electrospinning, aligned fibers, corrugated static collector, polyvinylpyrrolidone, poly(4-vinylpyridine-co-butylmethacrylate), poly(3-hexylthiophene-2,5-diyl)

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Fabrication of superparamagnetic electrospun fibrous adsorbents and their evaluation in ofloxacin removal from aqueous media

P.Ch. Papaphilippou,[1,2*] O. Marinica,[3] E. Tanasă,[4] F. Mpekris,[1] T. Stylianopoulos,[1] L. Vekas,[5] T. Krasia-Christoforou[1*]

[1]*Department of Mechanical and Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus.*
[2]*Department of Life Sciences, School of Science, European University Cyprus, Nicosia, Cyprus.*
[3] *Research Center for Engineering of Systems with Complex Fluids, Politehnica University Timisoara, Timisoara, Romania.*
[4] *Politehnica University of Bucharest, Bucharest, Romania.*
[5] *Center for Fundamental and Advanced Technical Research, Romania Academy, Timisoara, Romania.*
[*]*Corresponding Authors' E-mail addresses: krasia@ucy.ac.cy, papaphilippou.petri@ucy.ac.cy*

Through many decades, humanity is facing a major problem of water contamination with subsequent high risks in human health and quality of life. During the last years there is an increased interest on the protection and purification of contaminated urban wastewater [1]. Herein, microfibrous crosslinked membranes generated by electrospinning were evaluated as adsorbents for ofloxacin, which is a well-known antibiotic drug. Electrospinning is a low-cost method that is used in the production of fibrous materials with fiber diameters ranging between a few nanometers up to a few micrometers [2]. Consequently, such materials are characterized by high surface-to-volume ratios rendering them appropriate in various applications including water remediation [3, 4]. Random copolymers consisting of hydrophobic methyl methacrylate (MMA) and hydrophilic/pH-responsive 2-diethylamino ethyl methacrylate (DEAEMA) moieties, were synthesized by conventional free radical polymerization and upon blending with polyvinylpyrrolidone (PVP) in an appropriate solvent followed by electrospinning, cylindrical, bead-free microfibrous polymer membranes were obtained. The latter were thermally crosslinked to yield water-insoluble microfibrous membrane adsorbents. This was followed by a post-treatment step, resulting to the anchoring of iron oxide nanoparticles onto the fibers' surfaces. Information on the morphological characteristics and magnetic properties of the aforementioned membranes were obtained by electron microscopy and vibrational sample magnetometry (VSM), respectively, while mechanical testing under tensile stress was also performed. These materials were evaluated as adsorbents for the removal of ofloxacin from wastewater by measuring the optical density (OD) of ofloxacin by UV-vis spectrophotometry. The obtained results suggested that such fibrous nanocomposites may act as effective adsorbents for the removal of antibiotics from aqueous media while their adsorption efficiency is further enhanced upon introducing magnetic nanoparticles onto the fibers' surfaces.

Acknowledgements

This work has been funded by the University of Cyprus and the Grant "New Researchers" supporting Dr. P. Papaphilippou.

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Hot-lithography 3D printing of biobased epoxy resins

L. Pezzana[1], R. Wolff [2], G. Melilli[3], N. Guigo[3], N. Sbirrazzuoli[3], R. Liska[2], M. Sangermano[1*]

[1]*Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino,*
C.so Duca degli Abruzzi 24, 10129, Torino, Italy
[2]*Institute of Applied Synthetic Chemistry, Technische Universität Wien, Getreidemarkt 9/163*
MC, 1060, Vienna, Austria
[3]*Laboratory of Experimental Thermodynamics, UMR-CNRS-139,*
University of Nice-Sophia Antipolis, 06108, Nice, France

[*]*Corresponding Author's lorenzo.pezzana@polito.it*

UV-induced cationic polymerization of multifunctional epoxides has found many industrial applications, from coatings to electronics. The exploiting of UV-curing allowed to reduce time and energy cost with respect to the traditional thermal-curing. The UV-curing of liquid resin to form thermoset cut the production of VOCs due to the fact that the presence of solvent can be avoided. Furthermore the cationic process is not inhibit by oxygen leading to better workability with respect with other photocuring process that involve radical process (e.g. acrylates). However, one limitation can be notice in the lack of large variety of reactive monomers to undergo UV-curing. Considering the epoxy field the most used are the fossil based (bisphenol A derivatives). The actual concern of climate change and limitation of fossil resource are leading to synthesize and to industrially develop new bio-based monomers to substitute the commercial available fossil ones.

In this view, we investigated the use of two biobased epoxy monomers in hot-lithography 3D printing [1]. The hot-lithography permitted to print at elevated temperature exploiting the UV-light emitted from a laser source. The high printing temperature increased the reactivity of epoxy monomers and decreased the viscosity of the formulations. Taking advantage from these features, we successfully printed two different biobased epoxy resins: furandimethanol diglycidyl ether (FDE) and resorcinol diglycidyl ether (RDE). The FDE was synthetized starting from 2,5-furandimethanol, a derivative of cellulose [2]. Moreover, the 1,4-cyclohexandimethanol diglycidyl ether (CDE) was used to compare the result with a fossil-base monomer.

The formulations were prepared using the p-(Octyloxyphenyl)phenyl iodonium hexafluoroantimonate as photoinitiator. The photocuring process was fully characterized by means of real-time NIR/photorheology and photo-DSC analysis. The thermo-mechanical properties of the final thermosets were investigated by DMTA and tensile test. Finally, the 3D printing of complex shapes was carried out in order to demonstrate the possibility to obtain complex shapes self-standing.

Keywords: bio-based monomers, cationic UV-curing, photopolymerization, epoxy, furan, hot-litography, 3D printing

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The dependence of the crystallization kinetics of PA12 on the thermal history in the laser sintering process

Charlotte Poisson[1*], Bart Goderis[2] and Peter Van Puyvelde[1]

[1] Department of Chemical Engineering, KU Leuven, Celestijnenlaan 200J box 2424, 3000 Leuven, Belgium
[2] Department of Chemistry, KU Leuven, Celestijnenlaan 200F box 2404, 3000 Leuven, Belgium
** charlotte.poisson@kuleuven.be*

During laser sintering (LS), 90 % of the polyamide 12 (PA12) powder remains un-sintered in the build, as it only acts as a support material for the printed parts. However, the reuse rate of the un-sintered PA12 for LS purposes is limited to 50 %. This low recyclability of this powder is a consequence of powder ageing, as it resides for a long time at an elevated temperature of 175 °C in the build. Powder ageing leads to a reduced coalescence and solidifation rate, as the chemical and physical properties of PA12 change during LS. Apart from ageing of the un-sintered powder, the sintered powder is subject to severe temperature differences caused by the repeated process of the laser passing by, the deposition of a new powder layer and the printing of subsequent layers. The temperature profile to which a printed part is exposed influences its final characteristics such as crystallinity and mechanical properties.

To date, the temperature profiles that both un-sintered and sintered powder experience during the sintering and cooling step of LS and their effect on the crystallization kinetics of PA12 are still under debate. In literature, the maximum values for the heating rate obtained by the laser vary between hundreds and thousands of degrees per second. In addition, for the maximum temperature measured during LS, variations between 190 °C and 240 °C are reported dependent on the laser powder and scan speed.[1,2] In order to both increase the reuse rate of PA12 and to produce high-quality parts, it is necessary to know the applied temperature profiles during LS.

As a first step, this research aims to determine the temperature profiles that act on PA12 during LS, using thermocouples in the build and infrared cameras at the top. This allows to measure the real-life temperatures and the heating and cooling rates inside an LS device. As a second step, fast scanning calorimetry is used to unravel the dependence of the crystallization kinetics of PA12 on these temperature profiles. This research demonstrates that the crystallization kinetics of PA12 are influenced by the induced thermal history during LS. The results show that not only post-condensation is playing a role in the end properties of PA12, but self-nucleation and the entanglement degree of the polymer as well. From fast scanning calorimetry, the co-existence and interplay of these effects are seen to influence the crystallization kinetics of PA12 when thermal cycling gives rise to dynamic and isothermal crystallization, as is the case during LS.

Keywords: laser sintering, polyamide 12, temperature profile, crystallization kinetics

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Thermal and mechanical properties of bonded Nd-Fe-B magnets

Janez Slapnik[1], Irena Pulko[1], Rebeka Rudolf[2], Ivan Anžel[2], Mihael Brunčko[2,*]

[1]*Faculty of Polymer Technology, Ozare 19, 2380 Slovenj Gradec, Slovenia*
[2] *University of Maribor, Faculty of Mechanical Engineering, Smetanova ulica 17, 2000 Maribor, Slovenia*
[*]*mihael.bruncko@um.si (presenting author: irena.pulko@ftpo.eu)*

Bonded magnets are composite materials consisting of a polymer matrix and magnetic particles. Today, the highest demand for bonded magnets is in the automotive, aerospace, and consumer electronics industries, with annual growth rates exceeding 10%.[1-3] Industrial production of bonded magmets generally uses injection moulding, but three-dimensional printing processes are an alternative for small batches and for products with complex geometry.

In this study, highly filled (90%) composite filaments for fused filament fabrication were prepared with thermoplastic matrix (polymamide and polyurethane based) and Nd-Fe-B magnetic particles. It is known that magnetic particles can affect the decomposition of polymers. It was found that magnetic particles accelerate the decomposition of thermoplastic polyurethane, while the polyamide matrix remains more or less unchanged (see Figure 1). The operating temperature range of the prepared bonded magnets was determined by dynamic mechanical analysis. It was found that the storage modulus at room temperature was much higher for polyamide (6340 MPa) than for thermoplastic polyurethane (1410 MPa). With increasing temperature, the deviation was much smaller; at 140 °C, the difference was 1100 MPa. However, both bonded Nd-Fe-B magnets have excellent magnetic properties (remanence: 382 mT for the PA -based bonded magnets and 532 mT for the TPU-based bonded magnets) and have been used for the fabrication of magnets by fused filament fabrication.

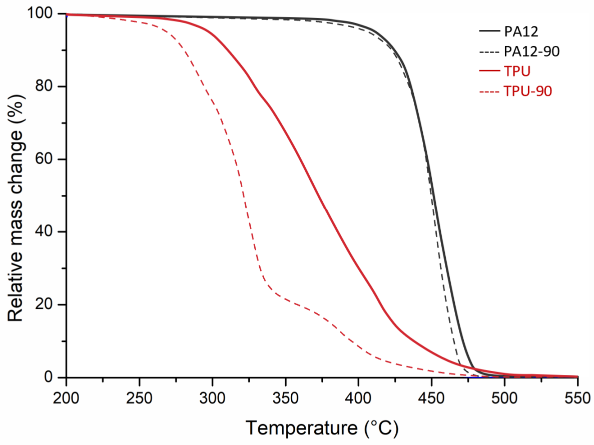

Figure 1: TGA diagrams

Keywords: bonded magnets, Nd-Fe-B, thermoplastic polyurethane, polyamide

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Design and Fabrication of a Microfluidic Device by 3D Printing for Biomedical Application

I.C. Radu[1], C. Zaharia[1], M.I. Necolau[1], E. Vasile[2], A.M. Vadureanu[1]

[1]*University Politehnica of Bucharest, Advanced Polymer Materials Group, Bucharest, Romania*
[2]*University Politehnica of Bucharest, Bucharest, Romania*
[*]*Corresponding Author's E-mail address: radu.ionucristian@gmail.com*

Keywords: microchannel, polyvinyl alcohol, 3D printing, microfluidic device, organ-on-a chip

Introduction: Microfluidics is an important domain that studies the behaviour of fluids through microchannels, but also an interesting technology for the fabrication of miniatuarized devices having chambers and tunnels where very small volume of fluids flow. A microfluidic chip is a set of microchannels etched or molded into a material such as polydimethylsiloxane, silicon, ceramicsm or metal. This network of microchannels embedded into the microfluidic chip is connected to the outer environment by inputs and outputs penetrated within the chip. The liquids are injected and removed though these holes from the microfluidic chip: through tubing, syringe adapters or simple holes in the chip with external active systems (pressure controller, syringe-pump or peristaltic pump) or passive ways (hydrostatic pressure). These microfluidic systems could be used to develop an organ-on-a-chip platform that contains continuously perfused chambers occupied by living cells to simulate tissue and organ morphology and function. Organ-on-a chip platforms have shown application potential in various biomedical fields: liver, kidney, heart, brain, blood vessel, lung, intestion, and human tumors [1]. **Experimental:** A new concept of microfluidic device was designed using 3D printing technology as a powerful manufacturing tool. The microfluidic device is composed of parts obtained by Fused Deposition Modeling 3D printing. The device contains cylindrical microchannels assembled into a specific pattern and an external shell. Both the assembled microchannels and the shell have an entry and an exit from where the fluids go inside and outside. The two parts of the microfluidic device (microchannels and shell) communicate through the microchannel walls. The microchannels are desiged with CAD and CAM software. Furthermore, they are 3D printed with polyvinyl alcohol (PVA) and crosslinked with glutaraldehyde in various conditions. Before crosslinking, they are thermally treated in special conditions (one and three days at 50 °C). The crosslinking medium contains glutaraldehyde (25% w/v) and nitric acid (0.1M) in which the 3D printed PVA microchannels are immersed for 3 and 24 hours. Finally, the crosslinked microchannels are subjected to the following succesive steps: drying, purification by dialysis, and drying. The dried-crosslinked microchannels are stable enough to be assembled into a specific pattern. The microchannles assembly is embedded into the external shell. The microfluidic properties are highlighted by microchannel walls permeability. In this regard, various tracer molecules (salts, drugs) are used to study the communication between the external shell and internal microchannels. **Results and discussion:** The morphological investigation by micro-CT revealed the complex structure of the entire microfluidic device. The microchannel internal space was rebuilt to reveal the internal geometry. The crosslinking ability of the PVA microchannels was assessed by Fourier Transform Infrared Spectroscopy with Attenuated total reflectance and swelling measurements. Dynamic mechanical analysis, differential scanning calorimetry and X-Ray diffraction were perfomed to check the influence of the thermal treatment on the crosslinking process and PVA thermal transitions and crystallinity. The thermal treatment positively influenced the crosslinking process and modified the characteristic temperatures of PVA. The microfluidic mesurements revealed the microchannel walls permeability for several tracers in specific flowing conditions (different flow ratio and pressure between the external shell and internal assembled microchannels). **Conclusions:** In conclusion, we reported the development of a new structural concept for a microfluidic device based on 3D printing technology. The PVA microchannels were computer aided designed, 3D printed, crosslinked and assembled to manufacture a microfluidic channel system. The PVA microchannels showed good water mechanical stability and permeability for tracers. This new device can be used to develop an organ-on-a-chip platform for cancer management in the near future studies. ***Acknowledgements:*** *"This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2020-1448, within PNCDI III".* **References:** [1] Ding, C.; Chen, X.; Kang, Q.; Yan, X. Biomedical Application of Functional Materials in Organ-on-a-Chip, *Frontiers in Bioengineering and Biotechnology* **2020**, *8*, article 823.

One-Component Cationic Photoinitiators for 3D Printing Applications

Joanna Ortyl[1,2,3*], Filip Petko[1,2], Andrzej Świerzy[1,2], Jan Sosin [1], Jakub Strzała[1], Bartosz Oksiuta[1], Jakub Szymański[1], Paweł Niezgoda[1,3], Mariusz Galek [1,2]

[1]Cracow University of Technology, Faculty of Chemical Engineering and Technology,
Laboratory of Photochemistry and Optical Spectroscopy,
Warszawska 24, 31-155 Cracow, Poland,
[2]Photo HiTech Ltd., Bobrzyńskiego 14, 30-348 Kraków, Poland
[3]Photo4ChemLtd., Lea 114, 30-133 Kraków, Poland
[*]*Corresponding Author's:* jortyl@pk.edu.pl

Recently, cationic photopolymerization meets with growing interest, finding new applications in such areas as microelectronics, dentistry, and especially in 3D printing. These new applications create demand for new efficient photoinitiators.

One of the most active cationic photoinitiators is diaryliodonium salts which are characterized by good thermal stability, excellent solubility in monomers as well as low toxicity too. However, most of the commercially available diaryliodonium photoinitiators have poor absorption properties above 300nm which makes them inactive under common Light Emitted Diodes (LEDs) irradiation (especially maximum emission located at 365nm and 405nm). A very promising approach to overcome this drawback is to replace one of the aryl rings with a more efficient chromophore like coumarin which improves absorption in the near-UV region significantly. This approach allows the iodonium salt to be photolyzed efficiently using LED emitting at 365nm and thereby generates superacid which initiates the polymerization process of such monomers as epoxides, vinyl ethers, oxetanes, and glycidyl ethers.

Here, we present a group of new one-component iodonium photoinitiators in which one of the aryl rings was replaced by efficient chromophores based on benzylidene scaffold. These chromophores containing extended conjugated bond system (double bond) and D-π-A structure exhibit push-pull effect which red-shifts absorption of their iodonium salts significantly and make them active under 365nm LED and in some cases under 405nm LED irradiation. Use of an easily modifiable scaffold allowed to preparation 14 new iodonium salts with different properties which makes the possibility for analyzed effects of each modification on iodonium salt photoinitiating properties.

The photochemical activity of presented new iodonium photoinitiators was investigated in terms of the efficiency of photolysis (steady-state photolysis) and quantum efficiency of superacid generation. Their photoinitiating properties were analyzed by performing a photopolymerization test using the real-time FT-IR technique. Photopolymerization process of 25µm thick coatings containing epoxide or vinyl ether monomers and tested iodonium salt (in 1% wt. concentration) was analyzed. Most efficient photoinitiators were used in 3D printing application tests with epoxide and oxetane monomers. They allow to obtain prints with desired spatial resolution under 365nm LED irradiation. Some of the chromophores used in presented iodonium salts exhibit an increase of fluorescence intensity in course of coating irradiation. This effect can be used for the photopolymerization process online monitoring. Therefore such designed compounds can be used as fluorescent sensors what is their additional advantage.

Acknowledgments

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Improving the properties of post-consumer recyclate with natural Zeolite

B. Purgleitner[1*], T. Gruber[2], C. Burgstaller[1]

[1]*Transfercenter für Kunststofftechnik GmbH, Wels, Austria*
[2]*Lithos Natural GmbH, Ennsdorf, Austria*
[*]*bianca.purgleitner@tckt.at*

Zeolites have a complex crystaline structure on wich substances can acculuIate or chemical rections can take place. They are used in chemical industry for the drying and adsorption of gases, for ion echange or as catalysts [1]. While artificial zeolite has well known and defined properties, natural zeolite (Klinoptiolith) has an unknown potential as adsoption material. Natural zeolite has a good availability, economic and ecological advantages and can adsorb substances, wherby it can be used as a carrier material for sensitive additives or for odor adsorption in recycled polymers [2]. The challenge of natural zeolite is its variability and less specified behaviour, thus extensive investigations with natural zeolite are important to use its full potential. When post-consumer polymer-recyclate has to be processed, bad odour is an issue for the operater at the processing machine as well as for the end user of the final product. To enhance applicability of recycling materials, the reduction of bad smell is essential.

In this study we investigated the influence of a special milled natural zeolite (LithoFill MM) on the smell behaviour and material properties of two post-consumer recyclates. Therefore, a PP/PE (Dipolen S) and a polypropylen (Purpolen PP) post-consumer recyclate was mixed with different amounts of finely ground natural zeolite. The total carbon emissions were measured by means of a headspace gas chromatography and sensory smell tests were performed with the compounded granules. Furthermore, test specimens were produced and characterised for their mechanical properties (tensile test and charpy impact test). For the investigation of the rheological behaviour, melt flow index was measured from the compounded granules.

The mechanical and rheological results showed, that using up to 10 weight percent of natural zeolite has a negligibly impact on tensile properties and flow behaviour, whereas total carbon emissions at 120°C are clearly reduced when natural zeolite is added (figure 1). This finding was approved by the performed smell tests, where the majority of the test persons found the granules with natural zeolite to smell less unpleasant than the recyclate granules without natural zeolite.

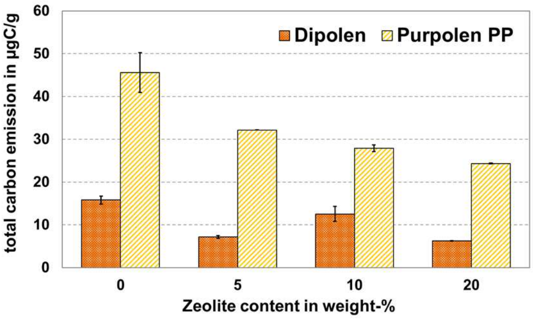

Figure 1: Total carbon emission versus natural zeolith content in weight-% in two different post-consumer recyclates.

Keywords: zeolite, post-consumer recyclate, smell reduction

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Modulation of the Network Connectivity in Vitrimers

A. Quinteros-Sedano, N. J. Van Zee*, R. Nicolaÿ*

Chimie Moléculaire, Macromoléculaire, Matériaux, ESPCI Paris, Université PSL, CNRS, 75005 Paris, France.
**E-mail address : nathan.van-zee@espci.psl.eu and renaud.nicolay@espci.psl.eu*

Vitrimers are permanent chemical networks incorporating dynamic covalent bonds that undergo degenerate exchange reactions [1]. These exchange reactions allow vitrimers to behave like a viscoelastic liquid under processing conditions, while the associative nature of the exchange mechanism ensures a constant average crosslinking density across all temperatures [2]. Our laboratory recently developed vitrimers relying on boronic ester metathesis that exhibit highly desirable features, such as compatibility with polar and apolar polymer matrices, improved thermomechanical properties and adhesion, or healing capacity [3 and 4]. Nevertheless, improving the processability of vitrimers remains an important challenge. Indeed, the high viscosity caused by the temperature-independent network connectivity can preclude in some cases the use of typical techniques used in the processing of thermoplastics, such as extrusion and injection molding. To address this issue, we propose to use small molecules to modulate the network connectivity and rheological behavior of vitrimers at high temperatures. Vitrimers with different loads of additive were characterized by dynamic mechanical analysis and rheology, giving insight into the complexities of these systems (Figure 1). This approach is an innovative and promising way to improve processability of vitrimers and render them more industrially relevant as a promising next-generation material for recycling and upcycling applications.

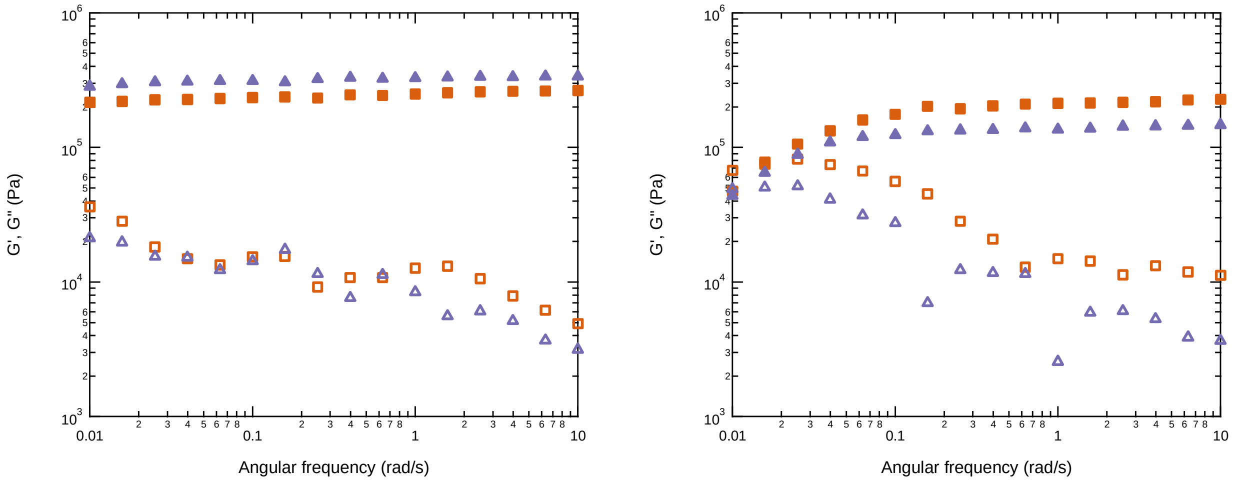

Figure 1. Frequency sweep test of : polybutadiene-based vitrimer with (triangles) and without (squares) reactive additive at 140 °C (left), and at 220 °C (right). Filled symbols (G'), and open symbols (G'').

Keywords: Vitrimers, dynamic covalent chemistry, boronic esters, processability.

Acknowledgments

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Advancing photocurable resin formulations for dual-wavelength digital light processing 3D printing

N. Šebalj[1], I. Cazin[1], M. Fleisch[1], M. Berer[1], M. Sangermano[2], S. Schlögl[1*]

[1]*Polymer Competence Center Leoben, Leoben, Austria*
[2]*Department of Applied Science and Technology, Politecnico di Torino, Torino, Italy*
[*]*sandra.schloegl@pccl.at*

Additive manufacturing has gained increased attraction over the last decade as it allows the successive building of 3D objects without molds and heavy machining. Among the various additive manufacturing techniques, vat photopolymerization benefits from a fast and precise production of objects with a high level of complexity in their designed shapes.[1] Vat photopolymerization 3D printing relies on the local solidification of a resin formulation by light exposure and is typically limited to the printing of a single material. Currently, research is focused on the additive manufacturing of objects with heterogeneous properties by exploiting multi-material 3D printing. With respect to vat photopolymerization 3D printing of multi-material objects, a promising approach is the use of orthogonal photoreactions for wavelength selective controlling the network properties and related (thermo)mechanical performance.[2]

In previous work, we optimized hybrid acrylate-epoxy resins (Figure 1) for dual-wavelength digital light processing (DLP) 3D printing, employing two different light engines, which operated at 405 and 365 nm.[3] At visible light irradiation, we selectively activated a long-wavelength absorbing radical photoinitiator and cured the acrylate component. Upon UV exposure, a radical curing as well as a cationic ring opening process of the epoxy component was initiated yielding an interpenetrating network with higher crosslink density and stiffness. For full conversion of the epoxy based monomers, a thermal post-baking step had to be carried out. Herein, we set up a library of dual curable resin formulations to cover a broad range of material properties, which can be realized by DLP printing using two different wavelengths.

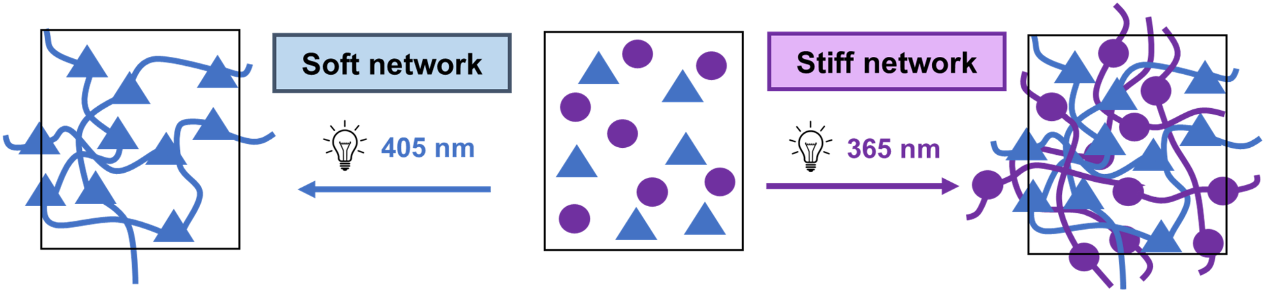

Figure 1. **Representation of a dual-curing system**

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Structure-property relationships of thiol–acrylate based vitrimers: From liquid resins to additive manufacturing of self-healable devices

Usman Shaukat[1], Elisabeth Rossegger[1], Sandra Schlögl[1,*]

[1]Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, 8700 Leoben, Austria
**Corresponding author: sandra.schloegl@pccl.at*

Vitrimers based on thiol-acrylate monomers offer the combined advantages of dynamic covalent chemistry along with the outstanding traits of "click" reactions including homogenous network properties and reduced shrinkage stress. The limited storage stability of thiol-acrylate based vitrimers can be improved by the addition of an acidic organic phosphate, which acts as a stabilizer and catalyzes dynamic transesterification reactions at elevated temperature. Sufficiently high exchange reaction rates induce topological rearrangements and a corresponding macroscopic reflow of the material, paving the way towards photopolymers that are reprocessable, malleable, mendable and have shape-memory properties. Herein, selected thiol and acrylate monomers are comprehensively studied for the development of 3D-printable vitrimers. Thiol crosslinkers with varying functionality and number of ester moieties are reacted with mono- and di-functional acrylates having hydroxy groups in their structure. The crosslinking degree of the vitrimers was increased by adding tri- and tetra-functional acrylates to the resin formulations. In a systematic way, the impact of monomer structure, network architecture and crosslinking degree, on the mechanical, thermal, curing and dynamic nature of the vitrimers was analyzed. The results clearly revealed that a higher number of ester and hydroxy moieties in the formulations leads to faster exchange reactions, which enables the additive manufacturing of self-healable soft active devices with adequate flexibility and healing efficiency [1].

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Rheology of a lubricated polyethylene melt: wall slip and flow instabilities

Z. Starý[*], M. Nevoralová, A. Rakitina

[1]*Institute of Macromolecular Chemistry CAS, Prague, Czechia*
[*]*stary@imc.cas.cz*

Production of polymer products by extrusion such as tubes, films, fibres or profiles is governed to a large extent by flow behaviour of processed polymer melt. The main limitation of the production rate is the onset of flow instabilities manifested by melt fracture phenomena, such as sharkskin, stick-slip and gross melt fracture. These effects occur when the shear stress at the wall exceeds a critical value [1]. Another phenomenon so called melt rupture is related to the instability of the elongational flow when the melt enters the die. In order to postpone the onset of these effects to higher throughputs different types of processing aids or lubricants are used. In general these compounds act at the wall-polymer interface, decrease the wall shear stress and promote wall slip [2].
In this contribution the complex effect of stearate-based processing aid on wall slip and flow instabilities of polyethylene melt in both shear and elongational flow is investigated using high-pressure capillary rheometry.

Keywords: rheology, wall slip, processing aids

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Mechanical, thermal and rheological properties of e-beam crosslinked ethylene octene copolymer

Rajesh Theravalappil[1*], Petr Svoboda[2]

[1]*Center for Refining and Advanced Chemicals, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia. *e-mail: rajesh@kfupm.edu.sa*
[2]*Department of Polymer Engineering, Faculty of Technology, Tomas Bata University in Zlin, Vavreckova 275, 76001, Zlin, Czech Republic.*

Abstract- Ethylene-octene copolymer (EOC) with high octene content (45 wt.%) was crosslinked via electron beam irradiation at different dosages (30, 60, 90, and 120 kGy). Effect of irradiation dosage on thermal and mechanical properties was studied. When compared to low density polyethylene, EOC exhibited higher degree of crosslinking reflected in increased gel content, higher elastic modulus (G'), and lower tanδ obtained by rheology measurement at 150 °C. Crosslinking caused improvement in high temperature creep and also in elastic properties at room and elevated temperatures. Differential scanning calorimetry revealed that e-beam irradiation has caused a gradual reduction in crystallinity and a presence of a fraction with higher melting temperature. In the case of EOC, as the extent of crosslinking increased, stress at break showed an increasing trend whereas irradiation dosage had an inverse effect on elongation at break which could be aroused from the formation of crosslink networks. Radiation dosage has positive effect on thermal stability estimated by thermogravimetric analysis. After 30 min of thermal degradation at 220 °C, slightly higher C=O peak for crosslinked sample was found by Fourier transform infrared spectroscopy while for room temperature samples no C=O peak was detected.

Keywords: Ethylene octene copolymer, e-beam irradiation, crosslinking, mechanical properties, rheology

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Intergrating Flame Retardancy and Weathering Resistance in Halogen Free PP compounds intended for outdoor cable protection conduits

A.D. Porfyris[1], C. Gkountela[1], C. Politidis[2], G. Messaritakis[3], P. Orfanoudakis[3], S. Pavlidou[4], D.M. Korres[1], A. Kyritsis[2], S.N. Vouyiouka[1,*]

[1]Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens 15780, Greece.
[2]Dielectrics Group, School of Applied Mathematical and Physical Sciences, National Technical University of Athens, Zographou Campus, Athens 15780, Greece.
[3]EMM. KOUVIDIS S.A. VIOPA Tylissos 71500, Heraklion, Crete, Greece.
[4] MIRTEC S.A., Thiva Branch, 72nd km of Athens-Lamia National Road, 34100, Chalkida, Greece.
[*]Corresponding Author: S.N. Vouyiouka mvuyiuka@central.ntua.gr

Cable protection conduits (EN 61386) are typically manufactured from PVC, which exhibits flame retardant (FR) behavior due to the inherent chlorine[1]. Nevertheless, due to the increasingly demanding safety regulations for cables and conduits in most european countries regarding halogen content, smoke density and corrosiveness of released gases (EN 50642, EN 61034-2, EN 60754-2), PP is rising as a viable alternative[2]. However, PP requires halogen free additivation for flame retardancy in order to comply with the aforementioned standards. Furthermore, when it comes to outdoor electrical installations, additional UV and heat stabilization is needed, so as to incease the life cycle performance of these materials[4]. The reasearch challenge that arises is to combine FR and UV functionalities at concentrations below 30 wt.% and without any antagonistic effect[3]. For this purpose 4 different FR/UV PP compounds were developed (FR1-FR4), consisting of different commercial organo-phosphorous FRs and several commercial light stabilizers such as hindered amines (HALS) or N-alkoxy hindered amine (NOR-HAS). The oxygenation level of the organo-phosphorous compounds determines the FR mechanism[4], therefore in FR1, FR2 where a phosphate and a char forming agent (CFA) is used, flame retardancy occurs mainly in the condensed phase *via* char formation. Additionally, an aminoether HALS or a NOR-HAS compound is added for UV stabilization, resulting in total loading in the range of 20-25wt%. On the contrary, in FR3 and FR4, where a phosphonate or a phosphinate are used as FRs, along with the NOR-HAS compound for UV stabilization, self-extinguishing occurs in the gaseous phase, and the loading level is reduced to 5-11wt%. The developed halogen free FR/UV compounds were monitored prior to and after accelerated weathering by means of UL94, mechanical and thermal properties (DSC, TGA) and MFR. Their overall performance rendered these compounds as promising candidates for the manufacture of conduits for outdoor applications.

Keywords: polypropylene, flame retardants, halogen free, weathering.

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Photopolymer formulations for projection µ-stereolithography-based 3D printing of hydrogel microstructures as swellable functional elements

N. Weigel[1], J. Thiele[1]*

[1]*Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany*
**thiele@ipfdd.de*

Digital light processing (DLP)-based 3D printing, also known as projection micro-stereolithography (PµSL) enables precise and monolithic manufacturing of 3D objects exhibiting micro-structured surfaces or objects with complex internal structures, e.g., microfluidic devices.[1] In this process, a liquid layer of photopolymer resin with a defined thickness is illuminated by an UV light projector in a defined pixel pattern and polymerized on a movable building platform. By stacking up several layers in this manner, the as-designed 3D object is eventually built.[2] To apply and integrate hydrogel materials in 3D-printed microfluidic devices, we require control over the swelling behavior of those functional elements.

On this account, we studied novel hydrogel-based materials consisting of 4-hydroxybutyl acrylate (HBA), poly(ethylene glycol) methyl ether methacrylate (PEGMEMA, Mn = 500 g mol^{-1} and 900 g mol^{-1}), poly(ethylene glycol) diacrylate (PEGDA, Mn = 575 g mol^{-1} and 700 g mol^{-1}), lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP) as photoinitiator well as tartrazine[3] as photoabsorber and processed them *via* PµSL. We screened the swelling degrees of 3D-printed discs made of eight different resin compositions dependent on a variety of parameters, e.g., molar mass of monomer and cross-linker. Additionally, we explored the achievable resolution for an examplary resin formulation to be approx. 70 µm for straight internal channel structures and approx. 50 µm for straight surface-located channels.

For further studies, we applied these materials as swellable elements in 3D-printed microfluidic devices made of the commercially available resin Perfatory® R11. First, we studied the swelling behavior and dimensional channel changes under different confinement conditions and explored the utilization of the hydrogel materials as time-dependent latching elements in 3D-printed microchannels. Second, 3D-printed pyramid- and cylinder-like geometries of the hydrogel materials were applied in chambers with the same geometry to visualize the time-dependent closure of these chambers.

With the presented study, we expand the catalogue of applicable hydrogel-based resin formulations for PµSL exhibiting tunable swelling degree from 13% to 86% and illustrate their utility in 3D-printed microfluidics. Furthermore, with optimization of post processing procedures these materials are potential candidates for high-resolved and soft cell culturing platforms.[4]

Keywords: Hydrogel, 3D printing, Digital Light Processing, Stereolithography, Photopolymerization, Microfluidics

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Storage stable formulations for cationic frontal polymerization

David Wottawa[1*], Moritz Mitterbauer[1], Patrick Knaack[1] and Robert Liska[1]

[1] *Institute of Applied Synthetic Chemistry (IAS), Vienna University of Technology, Vienna, Austria*
[*]*david.wottawa@tuwien.ac.at*

Frontal polymerization is a unique polymerization technique, which requires only one initial stimulus to cure bulk samples. Therefore, this process is extremely energy efficient, since no large furnaces are needed. Since ready-to-use formulations can be premixed and stored, it is not necessary to add any curing agents to trigger polymerization. Frontal polymerization is a self sustaining curing process, which can be achieved through the combination of certain ingredients in one formulation. The basic requirements are at least a thermal initiator, which triggers polymerization and a monomer that releases heat during curing. An initial stimulus is given in order to trigger the reaction, thereby heat is generated, which decomposes the thermal initiator to start the chain reaction. The use of thermal acid generators (TAG) as cationic initiators proves to be unfavorable, as TAG based formulations tend to gel after a short storage time. Therefore, a circuitous route must be taken. It is known that photoacid generators (PAG) used for cationic photopolymerization, especially iodonium and azonium-based ones, are able to oxidize free radicals to form initiating cations. Therefore, the combination of radical thermal initiators (RTI) and PAG's could be used to promote cationic frontal polymerization. Nevertheless, storage stability is limited, especially in the case of reactive mixtures. The aim of this work was to develop and characterize systems that undergo cationic frontal polymerization and exhibit improved storage stability. For this purpose, ready-to-use formulations were prepared and investigated with regard to their ability to induce frontal polymerization and their storage stability. The polymerization experiments were conducted in a PTFE mold equipped with thermocouples and a ruler. The tests were recorded to evaluate the front temperature and the front velocity, which are the most important parameters for frontal polymerization. In addition, the storage stability of the formulations at elevated temperatures was evaluated on the basis of viscosity.

Chemical Modification of Recycled PET (R-PET) and R-PET/PBT Blends and Enhancements in their Corresponding Rheological Properties

Yonca Alkan Göksu[1], Merve Güçlü[1], Burcu Özdemir[1], Mohammadreza Nofar[1]*

[1]*Sustainable & Green Plastics Laboratory, Metallurgical & Materials Engineering Department, Faculty of Chemical and Metallurgical Engineering, Istanbul Technical University, Istanbul, Turkey*
**Corresponding Author's E-mail address : nofar@itu.edu.tr*

The global demand for single-use plastics is gradually rising. Along with this increase in consumption, polymer wastes have become a global concern. The amount of global plastic waste is expected to grow from 260 million tons/year in 2016 to 460 million tons/year by 2030 [1]. Poly(ethylene terephthalate) (PET) composes the majority among those single-use plastics, especially in packaging applications of beverage bottles. Hence, accumulation of its waste in both soil and marine environments is enormous and it is imperative to provide efficient recycling routes immediately. Among several recycling routes, melt reprocessing is a practical and widely applied method to recycle PET due to its low cost and little adverse environmental impact [2]. However, during melt reprocessing of PET, chemical, mechanical, thermal, and oxidative degradations could occur. These result in reduced molecular weight and viscosity of PET, which ultimately suppress its processability [3]. In order to overcome these drawbacks, chemically selective chain extenders (CE) could be incorporated during melt reprocessing. Depending on the chemical nature of the chain extender, linear or branched macromolecular chains with improved mechanical and thermal properties could be obtained. Among them, Joncryl ADR is a well-known commercial multifunctional chain extender that is frequently used to enhance melt properties of recycled PET (R-PET) [4]. The carboxylic acid (-COOH) and hydroxyl (-OH) end groups of R-PET react with the epoxide functionalities available on the chain extender and different R-PET chains are connected each other to form branched/network structures. In this study, the thermal stabilization and rheological properties of R-PET with the addition of Joncryl ADR and melt blending with PBT were investigated. The time sweep rheological experiments revealed that upon the addition of 0.4 and 0.8 wt% CE, the complex viscosity of R-PET considerably increased due to the induced branched structure. The synergistic effects of melt blending of R-PET with PBT at different compositions with or without 0.2 wt% CE on the thermal stability and rheological properties of the samples were also examined. The addition of 0.2 wt% CE resulted in enhanced rheological properties of the blends. Therefore, the processability and the final properties of a product containing post-consumer PET (R-PET) could be improved.

Keywords: PET, Joncryl, Chain Extension

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Devloppement new polymer composite materials for 3D printing

H. Askanian[1*], Nicola Schiavone[1], Vincent Verney[1]

[1] *CNRS, Clermont Auvergne INP, ICCF, Université Clermont Auvergne,Clermont-Ferrand, France*
[*] *haroutioun.askanian@sigma-clermont.fr*

An eco-friendly solution to produce new material for the material extrusion process is to use quarry waste as filler for biopolymer composites. A fine fraction of pozzolan waste was developed as a filler for polymer composites. In this study, the optimization of the formulations and processing parameters of composites produced from bio-based polyethylene, polylactic acid (PLA) with pozzolan and destined for 3D printing technology was performed. The results showed that the presence of the pozzolan acted as a reinforcement for the composite material and improved the cohesion between the layers of the 3D printed objects. Furthermore, the optimization of the process conditions made it possible to print pieces of complex geometry..

Keywords: 3D printing, bio-based polyethylene composite, PLA composites, X-ray tomography

Anti-adhesive coating comprising visibility-on-demand. A smart approach for quality control

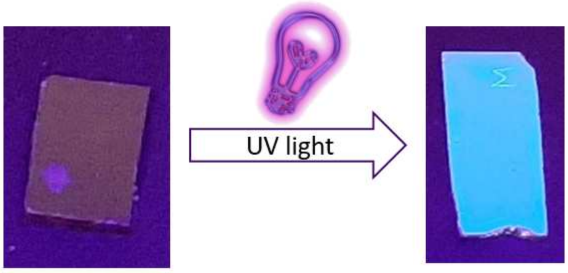
Christine Bandl [1*], Wolfgang Kern [1,2], Matthias Müller [1], Nina Krempl [3]

[1]Chair in Chemistry of Polymeric Materials, University of Leoben, Otto Glöckel-Straße 2, A-8700 Leoben
[2]Polymer Competence Center Leoben GmbH, Roseggerstraße 12, A-8700 Leoben
[3]Chair of Polymerprocessing, University of Leoben, Otto Glöckel-Straße 2, A-8700 Leoben
[*]E-mail: christine.bandl@unileoben.ac.at

There is a wide application field for anti-adhesive and hydrophobic coatings ranging from self-cleaning surfaces over anti-graffiti coatings, separation layers for adhesive tapes and labels to demolding aids in the production of polymers. In our previous studies we developed an anti-adhesive coating based on perfluorinated organaosilanes, which was proven suitable as a covalently bound/long term demolding aid in the field of polymer processing. [1, 2] Since the coating is transparent and in the nanometer scale, the arising demand for a temporary quality control was answered by the incorporation of a fluorescent marker molecule enabling visibility-on-demand. For this purpose, 1,8-naphthalimide-N-propyltriethoxysilane (NIPTES) was synthesized and deposited together with the silanes of the anti-adhesive formulation in a sol-gel process (hydrolysis and condensation).

The coated substrates were investigated with regard to their surface energy by contact angle measurements, while different spectroscopic techniques such as XPS, FTIR, UV-Vis and fluorescence spectroscopy were used to study their surface composition and optical properties. The anti-adhesive effect of the coating was investigated by means of injection molding experiments, monitoring the static friction coefficient and the related demolding force over repeated production cycles. Moreover, abrasion and wear of the coating throughout injection molding was followed by UV-induced fluorescence.

The incorporation of NIPTES as a fluorescent marker represents a straightforward method for a temporary quality control of the applied anti-adhesive coating. Information about the presence and homogeneity of the entire coated area can quickly be assessed by the convenient use of a UV-lamp.



Visibility-on-demand property of the anti-adhesive organosilane layer utilizing UV-induced fluorescence

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Bioemulsifying ability of fucose-rich exopolysaccharide FucoPol on physical stability of O/W emulsions: Textural and Rheological analysis

S. Baptista[1,2,3], J.R. Pereira[1,2], C.Gil[1,2], C.A.V. Torres[1,2], M.A.M. Reis[1,2], F.Freitas[1,2]

[1] *Associate Laboratory i4HB - Institute for Health and Bioeconomy, School of Science and Technology, NOVA University Lisbon, Caparica, Portugal;*
[2] *UCIBIO – Applied Molecular Biosciences Unit, Department of Chemistry, School of Science and Technology, NOVA University Lisbon, 2819-516 Caparica, Portugal*
[3] *73100, Lda. Edifício Arcis, Rua Ivone Silva, 6, 4º piso, 1050-124 Lisboa, Portugal*

Current sustainability concerns demand the utilization of biobased raw materials. In the cosmetic industry, polysaccharides are being incrementally used as rheology modifiers in skin-care products, which can increase the spreading properties of products and enhance their sensorial profile[1,2]. In this study, the bacterial exopolysaccharide FucoPol was used to form and stabilize emulsions at different oil/water (O/W) ratios with four different oils generally used in cosmetic applications. Response surface methodology (RSM) was used for defining the optimal ingredients (FucoPol, olive oil and α-tocopherol) concentration for emulsion development. The structural and mechanical attributes of the obtained emulsions were assessed using rheological and texture analysis, demonstrating that FucoPol can be used as a natural emulsifier, acting as a potential alternative to other emulsifiers. FucoPol high performance with olive oil was supported by an effective impact on the physicochemical and structural characteristics of the emulsions, mainly on their emulsification stability.

Keywords: Exopolysaccharide; FucoPol; Response surface methodology; O/W emulsions; rheology.

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Development of 3D printable formulations containing carbon nanotubes with enhanced electrical conductivity

A. Bonessa [1*], F.Iervolino[1], R. Suriano[1], M. Levi[1]

[1] *Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Square Leonardo Da Vinci 32, 20133, Milan, Italy;*
[*]*aurora.bonessa@polimi.it*

Since the discovery of carbon nanotubes (CNTs) in the early 90s, the scientific community has been investigating methods to fully exploit their properties like aspect ratio, mechanical strength, electrical and thermal conductivity. Concerning electrical properties, one interesting CNTs application field regards their use as conductive fillers in composite materials for Micro Electro Mechanical Systems *(MEMSs)* [1].

In our study, a new resin formulation containing multi-walled carbon nanotubes (MWCNTs) was developed and compared to a commercial one, to fabricate 3D printed conductive structures via stereolithography (SL). Stereolithography exploits a photosensitive resin and a UV laser to print complex shapes with high resolution, good accuracy, costumization and flexibility. Nowaday, the continuous expansion of the resin market for SL has prompted many companies and research groups to develop new types of filled resins using nano- or composite materials [2].

The electrical, thermal and mechanical properties of our composites containing both pristine CNTs and those functionalized with NH_2 groups were measured and compared varying filler concentrations (0.25%, 0.5%, 0.75% w/w). The increasing of the filler content implies the conductive fillers particles start to contact each other, and form a continuous path which makes the free electrons travel easily and conduct the electricity (Table 1). These conductive composite materials have lightweight, resistance to corrosion, and can be easily adapted to meet the needs of specific applications like accelerometers, pressure and gyro sensors [3] replacing other conventional materials based on silicon.

Table 1. Comparison between the conductivity values of our nanocomposites containing MWCNTs-NH_2 in three different weight percentages (0.25 wt%, 0.50 wt%, 0.75 wt%)

MWCNTs-NH_2	**Conductivity [S/cm]**
0.25 wt%	$3\ 10^{-4} \pm 0.003$
0.50 wt%	$6\ 10^{-3} \pm 0.005$
0.75 wt%	$9\ 10^{-3} \pm 0.004$

Keywords: additive manufacturing, 3D conductive polymers, carbon nanotubes, stereolithography

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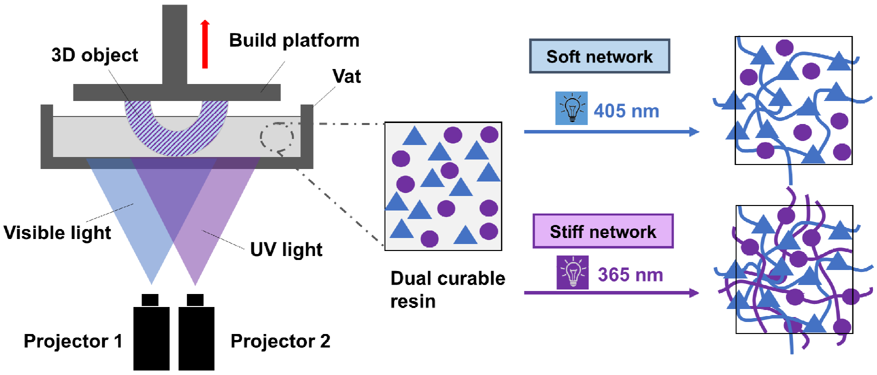
Spatially controlling the mechanical properties of 3D printed objects by dual-wavelength digital light processing

I. Cazin[1], M. O. Gleirscher[1], M. Fleisch[1], M. Berer[1], M. Sangermano[2], S. Schlögl[1*]

[1]Polymer Competence Center Leoben GmbH, Leoben, Austria
[2]Department of Applied Science and Technology, Politecnico di Torino, Torino, Italy
[*]sandra.schloegl@pccl.at

To date, the 3D printing of polymers with heterogeneous and locally controlled material properties is still a challenging area in additive manufacturing.[1] In terms of digital light processing (DLP) 3D printing, the fabrication of multi-material objects typically relies on an automatic material exchange of different resin vats. However, along with the high complexity of the printing equipment, this technique suffers from a low build speed and often yields 3D printed objects with week interlayer adhesion across the various material interfaces. Herein, we use chemo-selective wavelengths to fabricate objects with multi-material properties by dual-wavelength DLP 3D printing employing a single vat. The photopolymers' stiffness and flexibility are conveniently controlled by two photoreactions working at two different wavelengths. In particular, a dual photocurable resin is applied containing multi-functional acrylates, which are cured by a radical induced chain growth reaction at 405 nm, and bi-functional epoxy monomers, which additionally undergo cationic curing upon UV exposure (365 nm). FT-IR experiments confirm the wavelength selective network formation whilst dynamic mechanical analysis and tensile tests give evidence of the distinctive difference of the related mechanical properties. By being able to produce soft ($E'_{(25°C)}$ = 15 MPa) and stiff ($E'_{(25°C)}$ = 1.98 GPa) networks with a single resin vat, we demonstrate the efficient fabrication of 3D structures with locally controlled mechanical properties using a dual-wavelength 3D printer operating at 405 and 365 nm. In contrast to previous work in this field, we were able to significantly expand the range of mechanical properties by appropriate selection of the acrylic components and to drastically accelerate the build speed by changing the cationic photoinitiator and using a customized DLP printer with high intensity LED sources.



Schematic representation of the dual-wavelength DLP printer and the wavelength selective formation of soft and stiff domains.

Acknowledgments

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Shear-induced crystal nucleation of poly (L-lactic acid)

Mengxue Du[1], Katalee Jariyavidyanont[*1], Regine Boldt[2], Muhammad Tariq[3], Matthieu Fischer[2], Yvonne Spörer[2], Ines Kühnert[2], René Androsch[*1]

[1] *Interdisciplinary Center for Transfer-oriented Research in Natural Sciences, Martin Luther University Halle-Wittenberg, 06099 Halle/Saale, Germany*
[2] *Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany*
[3] *Institute of Physics, Martin Luther University Halle-Wittenberg, 06099 Halle/Saale, Germany*
[*] *rene.androsch@iw.uni-halle.de, katalee.jariyavidyanont@iw.uni-halle.de*

As widely known, shear, evident in polymer melt-processing, has a significant influence on polymer crystallization, structure and eventually properties. Therefore, the evaluation of the effect of shearing the melt on crystal nucleation is an indispensable task for understanding the relationship between processing, structure, and properties of products.

In this work, the concept of specific work of flow has been applied for analysis of critical shearing conditions for formation of crystal nuclei in poly (L-lactic acid) (PLLA).[1,2] The critical specific works of flow, above which shear-induced nucleation occurs, for PLLA with the molar mass of 120 kDa is around 25 kPa.

For proving the concept, the role of shearing the melt in short-cycle-time-PLLA processing on the number of crystal nuclei in fully amorphous injection-molded test bars was estimated by evaluation of the kinetics of cold-crystallization by differential scanning calorimetry (DSC). It was found that the cold-crystallization kinetics in the skin is faster than in the core of the component related to higher shear rates, estimated by simulation as shown in Figure 1.

This study demonstrates that knowledge about the crystallization kinetics of the sheared melt of PLLA can be used to predict structure formation in industrial processing.

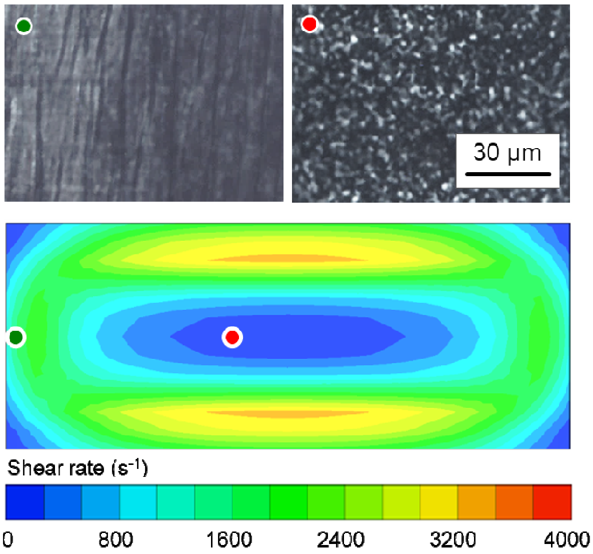

Figure 1. Polarized-light optical microscopy (POM) micrographs of the skin and core-region, taken after cold-crystallization at 90 °C for 400 s (top). Shear-rate distribution in the cross section of the injection-molded test bar after completion of form-filling (bottom).

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3D printed sound absorber panels

N. Gama[1], G. Pinheiro[2], I. Cardoso[3], R. Ribeiro[3], P. Pinto[3], V. Freitas[4] and A. Ferreira[1]

[1]*CICECO/ESTGA and University of Aveiro, Aveiro, Portugal*
[2]*Communication and Art department of University of Aveiro, Aveiro, Portugal*
[3]*Amplitude Acoustics - Acústica E Vibração, Lda, Maia, Portugal*
[3]*Lightenjin Iluminação, Águeda, Portugal*
[*]*nuno.gama@ua.pt*

Additive manufacturing, which is commonly known as 3-dimensional (3D) printing, is a material processing method that uses computer-aided design (CAD) to create 3D prototypes or batch parts [1,2]. This technique has gained popularity, due to its advantages, such as the capability to produce objects with high geometrical complexity or high customization [1, 3]. Aiming the enhancement of the environmental sound quality, the study of the acoustic properties of sound absorbing panels is widely performed [4]. In this context, the fine tuning of the panel geometry can result in significant sound absorption improvements. In that sense, following our interest in the design of noise reduction systems, 3D printing was used to create panels with enhanced sound absorption performance. In this work, different materials were used to produce the panels, as well as different geometries were tested, as shown in Figure 1.

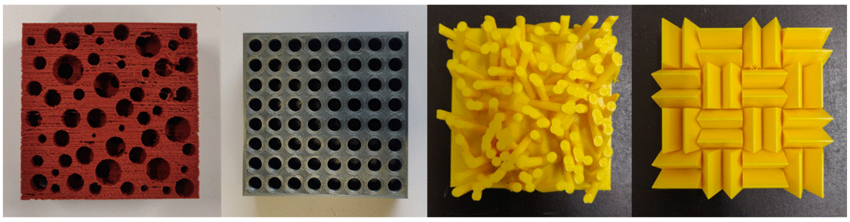

Figure 1 – 3D printed model prototypes of sound absorbers

The noise reduction coefficient (NRC) of the ensuing panels were measured using a microflow in-situ absorption set-up. It was obtained NRC values between 0.40-0.50, depending on the geometry and material used. Furthermore, it was observed that the panel's sound absorption coefficient (α) is frequency dependent, with peaks influenced, among others, by the surface finishings, openings and texture. From the results, it was observed that the sound absorption properties of the 3D printed panels can be tuned, accordingly to the specifications intended. Overall, it was concluded that the 3D printed panels presented suitable performance to be used as sound absorbers for open-space offices.

Keywords: 3D printing, 3D models, Noise Reduction Coefficient (NRC), Sound absorption.

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Development of novel immobilized TEMPO catalysts for selective alcohol oxidation using 3D printing

H. Grotian genannt Klages[1], K. M. Zentel[1], G. A. Luinstra[1*]

[1]*Institute for Technical and Macromolecular Chemistry, University of Hamburg, Hamburg, Germany*
[*]*luinstra@chemie.uni-hamburg.de*

Oxidation of alcohols to aldehydes is a standard, but not trivial reaction in organic chemistry. Regular oxidation agents tend to be unselective also because of the required harsh conditions. In particular, the unintended oxidation to carboxylic acid takes place easily.[1] The use of TEMPO (2,2,6,6-tetramethyl piperidinyloxyl) as catalyst, however, may circumvent some of the problems because of its good selectivity at comparatively mild conditions.
A further advantage can arise when a catalyst is immobilized onto a polymer matrix that is integrated into a continuous reaction setup.[2,3] Such a setup could be easily achieved with 3D printing technology. It enables the preparation of adapted fixed-bed catalysts and of a suitable reactor. The approach in the context of selective alcohol oxidation consists of an immobilized TEMPO catalyst in a designed reactor. It allows an easy scale-up and stepwise optimization of the reactor geometry during development.

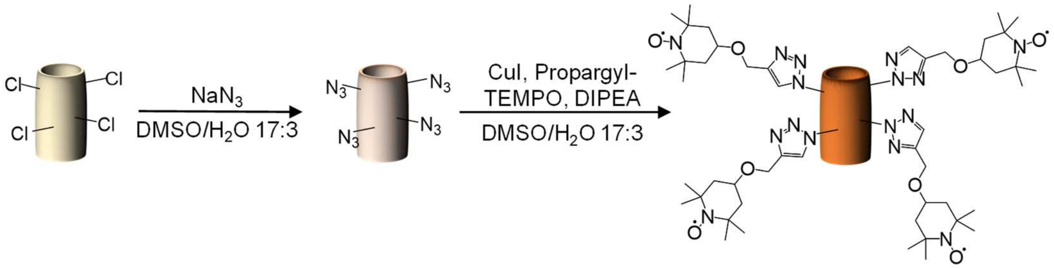

Figure 1. Representation of the surface reaction of a PVC-based and 3D-printed continuous flow reactor with TEMPO using click chemistry.

Thus a commercially available PVC filament was taken as matrix material for a dedicated 3D-printed catalytic reactor. Using azide substitution and click chemistry, the surface was functionalized with TEMPO (**Figure 1**). Analysis by energy dispersive X-ray spectroscopy showed that the amount of chlorine on the surface decreased significantly, while the amounts of nitrogen and oxygen increased. Catalytic oxidation of benzyl alcohol to benzaldehyde was successful in the set up. The reaction time could be significantly lowered over comparable former efforts[4], allowing to perform the reaction in flow in a tube reactor of acceptable length. Flow properties in a fixed-bed reactor were also simulated using Comsol, giving hints for good mixing and thus how efficient oxidation may be achieved.

Keywords: 3D-printing, surface functionalization, heterogeneous catalysis, selective oxidation

Acknowledgments

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Novel Biodegradable ABA-triblock Copolymers for Synthesis of 3D Printable Inorganic/Organic hybrids

Haffsah Iqbal[1], Athanasios Skandalis[1], David R. Sory[2], Yu-Chien Lin[1], Theoni K. Georgiou[1], Julian R. Jones[1, *]

[1]*Department of Materials, Imperial College London, London, UK*
[2]*Faculty of Medicine, National Heart & Lung Institute, Imperial College London, London, UK*
[*]*julian.r.jones@imperial.ac.uk*

Introduction

Organic-inorganic class II hybrids have synergistic properties of their components while acting as a single-phase material. Biodegradable silica/poly(ε-caprolactone) (PCL) hybrids have been prepared, in which hydroxyl groups at either end of the PCL polymer chains were modified with a triethoxysilyl group (TEOS) [1], but mechanical properties were not optimal. Poly[(methyl methacrylate)-*co*-(3-(trimethoxysilyl) propyl methacrylate)]-SiO_2 hybrids have been investigated in bone regenerating biomaterials because of their promising mechanical properties, but biodegradation has been limited [2]. The aim here was the synthesis of ABA biodegradable copolymers containing with PCL as the biodegradable entity along with methyl methacrylate (MMA) and 3-(trimethoxysilyl) propyl methacrylate (TMSPMA) as comonomers. The polymer-TEOS hybrid system was optimized as ink for the preparation of 3D-printed scaffolds. The effect of polymer molar mass (MM) on the mechanical strength and degradation was investigated.

Experiment Methods

The ABA-type biodegradable triblock copolymers used in this study were synthesized by a combination of ROP and RAFT polymerization methodologies. The MMs and compositions of all the resulting copolymers and their precursors werecharacterized by GPC and ^{1}H-NMR, respectively. At first, the PCL-diol was synthesized by ROP and converted to a RAFT agent via an esterification reaction. Following, the PCL-based CTA was introduced as a macro-RAFT agent for the synthesis of the final copolymers. The copolymers were then used as the organic phase for the preparation of 3D-printed (extrusion printing) class II glass-polymer hybrid scaffolds *via* the sol-gel method [2]. The scaffolds were characterized for mechanical properties, morphology (SEM, microCT), biodegradability and *in vitro* toxicity.

Results And Discussion

P(MMA-*co*-TMSPMA)-*b*-PCL-*b*-P(MMA-*co*-TMSPMA) well-defined triblock copolymers with MMs ranging from 14000-27000 g.mol^{-1}were successfully synthesized as confirmed by GPC and NMR. The copolymers were later utilized as hybrid sol ink for direct extrusion printing. Gelation time of the hybrid ink increases as MM increases. SEM imaging of the 3D-printed scaffolds showed a well interconnected pore channel structure. The qualitative pore inter-connectivity was confirmed *via* microCT. Uniaxial compression and cyclic loading measurements of 3D-printed scaffolds exhibited promising mechanical properties of 7-9Mpa, which is within the range of those of the trabecular bone. *In vitro* bioactivity of the hybrid showed that material is biocompatible.

Conclusions

A novel, biodegradable hybrid ink containing P(MMA-*co*-TMSPMA)-*b*-PCL-*b*-P(MMA-*co*-TMSPMA) triblock copolymers as the organic phase was successfully prepared. Direct ink writing led to the construction of 3D printed scaffolds with interconnected porous structures with pore size of 250-300 µm. Optimal printability was observed with polymers with MM around 15000 to 17000 g.mol^{-1}. The porosity and mechanical properties of the scaffolds were within the range of the trabecular bone. *In vitro* studies showed bone regeneration ability of the scaffolds. Based on these results, material shows promising properties for the potential use for bone regeneration application.

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Analytical methods for characterisation of isotactic polypropylene with varying flow properties

D. Kaineder[1,2*], S. Hild[2]

[1]*Competence Center CHASE GmbH, Linz, Austria*
[2]*Johannes Kepler University- Institute of Polymer Science, Linz, Austria*
**dominik.kaineder@chasecenter.at*

Polymer processing companies tend to rely on simple-to-use methods, such as the melt flow index (MFI), for initial assessment for incoming material, may it be recycling material or virgin polymers. MFI measurements are defined as gram per ten minutes melt flowing through a capillary at a defined temperature and standardized weight as pressuring force [1]. Yet, MFI analyses provide just a single value to characterise the structure-viscous behaviour, which may be inadequate for determining the whole spectrum of flow properties. This is one reason why, although often attempted, the correlation to “zero-viscosity” and therefore the average molar mass can be less than reliable. Still, while more elaborate methods are known and acknowledged, the MFI continues to be routinely utilized in this field. This is due to its economically beneficial advantages in cost and measurement time, including in applications where there is good reason to query the validity and reliability of this measurand.

In this work, the melt flow index of various isotactic polypropylene (i-PP) samples is shown to be incapable of reliably predicting the flow characteristics of a structure-viscous fluid in an extrusion process. More accurate and complex methods must therefore be used for the characterisation of the viscosity and elasticity of a polymer melt, as well as determining the molar mass and distributions, which concern the relevant shear rates for extrusion of i-PP. This work shows that gel permeation chromatography (GPC) and plate-to-plate rheometry yield strongly correlated results, even though the two measurement approaches are fully independent. On the contrary the correlation to the measured MFIs is very weak, matching the findings in polymer processing practice [2,3]. We were thus able to clearly and reproducibly distinguish different polypropylene samples with similar or even equal melt flow indices. Even products declared as “identical” by the manufacturer, as demonstrated by identical, warranted MFIs, could be proven to vary significantly with regards to molar mass and flow properties over shear-rate, both of which are highly relevant for extrusion processing.

Concluding the arguments presented, due to the inadequacies of the MFI, investment in measurements geared towards increasingly comprehensive methods such as rheometry may prove to be beneficial, even for processing enterprises. Alternatively, a different method for initial material assessment should be taken into account as priority objective.

Keywords: melt flow index, polymer processing, molar mass, rheometry

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Ultra-peelable thermal crosslinked urethane adhesive with linear and multi-arm additives to improve wettability

Misol Kim[1], Hanki Cho[2], Hyunjee Yoo[2], Jaseung Koo[1*]

[1]*Department of Organic Applied Materials Engineering, Chungnam National University, Daejeon, Korea*
[2]*R&D Center, O-Flex Co Ltd., Daejeon, Korea*
[*]*jkoo@cnu.ac.kr*

A temporary protection film (TPF) was required for surface protection during cell cutting and laser lift off during the organic light emitting diode (OLED) manufacturing process. The TPF should attach to the uneven surface and be easily removed after the protection role is finished. An urethane resin previously used for TPF was difficult to attach on uneven substrates due to poor wettability. In this study, we designed TPFs to improve wettability by adding two additives with different structures to the urethane resin. Simultaneously, the amount of adhesion and cohesion failure induced by additives should be kept to a minimum. The urethane resin with diisocyanate and linear or multi-arm additives was coated on base films and exposed to heat treatment. After that, the TPFs were laminated with silicon release film and aged. We analysis adhesive physical properties with surface energy (SE), rheological test and 180° peel test. The SE of TPF was measured by the contact angles of the solvents of four different polarities and calculated by the OWEN-WENDT equation.[1,2] The additives containing hydroxyl groups increased wettability by forming secondary bond with the main chain.[3] Since the multi-arm additives had more entanglement points and lower diffusion than linear additives in main chain, the multi-arm additives showed 3 times lower peel strength and higher cohesion than linear additives in physical properties test.[4,5] Clear debonding properties were observed from scanning electron microscope (SEM), time-of-flight secondary ion mass spectrometry (TOF-SIMS) and SE on the substrate after the TPF film was removed. In the 2D TOF-SIMS and SEM image, multi-arm additives with urethane observed less distribution of residues and $C_2H_5O^+$/ Si^+ ratio than linear additives. We found that multi-arm additives with urethane resins had good wetting, low peel strength and clear debonding properties. For this reason, TPFs with multi-arm additives could be applied to prevent contiminations for OLED encapsulation layer.

Keywords: Urethane, thermal crosslinked adhesive, additive, wettability, debonding

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Supramolecular Hydrogels Cross-linked by Cyclodextrin

S.N. Kirmic Cosgun[1*], D. Ceylan Tuncaboylu[2]

[1]Department of Biotechnology, Institute of Health Sciences, Bezmialem Vakif University, Istanbul, Turkey
[1]Department of Pharmaceutical Biotechnology, Faculty of Pharmacy, Bezmialem Vakif University, Turkey
[*]skirmic@hotmail.com

Cyclodextrins (CD), often depicted as truncated cone-like structures, have a polar outer surface and relatively nonpolar inner cavity due to the ether-like oxygens and the hydrocarbon frame. This unique structure allows them to form inclusion complexes with various types of low molecular weight compounds as well as polymer chains. α-CD-based inclusion complexation with poly(ethylene glycol) (PEG) to yield supramolecular assemblies was first reported by Harada et al. in 1990 [1]. CD based supramolecular gels have been constructed through a variety of non-covalent interactions related to dimensional fit between the interior cavity of the CD and the cross-sectional area of the polymer. These complexes are called pseudopolyrotaxane (PPR) where the CD molecules can be rethreaded of the polymer chain when immersed into the water. CD gels based on the PPR systems usually possess poor stability due to the sol-gel transformation that is caused by the dethreading of CDs from polymer chains under certain conditions.

In this study, CD molecules were used as crosslinking domains that hold PEG and poly(N-vinylpyrrolidone) (PVP) chains in a physical network structure [2]. Unlike the literature studies, the presence of PVP and thus the additional secondary forces have been strengthened the interactions in the physically crosslinked CD/PVP/PEG networks. Only the physical interactions are responsible during the formation of inclusion complexes between CD and PEG and then the self-assembly of the complexes in the presence of PVP that supports the structure. The molecular weight of the PEG chains, the feed ratios of the reaction components, and the size of the CD units were found to be important to determine the properties of the final networks and to obtain insoluble networks with a self-healing ability. The synergistic effect of physical and chemical crosslinking by adding poly(ethylene glycol) dimethacrylate (PEGDMA) to the system was also investigated at varying concentrations.

Keywords: Hydrogel, Cyclodextrin, Poly(ethylene glycol), Poly(*N*-vinylpyrrolidone), Self-healing

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Influence of the microstructure on the electrical properties of 3D printed PLA/PCL/GNP composites

N.-A. Masarra[1*], J.-C. Quantin[2], M. Batistella[1], R. El Hage[3], M.F. Pucci[2], R. Ravel [1], J.-M. Lopez-Cuesta[1]

[1]*Polymers Composites and Hybrids (PCH), IMT Mines Ales, Ales, France*
[2]*LMGC, IMT Mines Ales, Univ Montpellier, CNRS, Ales, France*
[3]*Laboratory of Physical Chemistry of Materials (LCPM), PR2N-EDST, Faculty of Sciences II, Campus Fanar, Lebanese University, Jdeideh P.O. Box 90656, Lebanon*
[*]*nour-alhoda.masarra@mines-ales.fr*

Conductive fillers such as graphene are able to increase the electrical conductivity in polymer composite systems. Beyond a certain concentration called the electrical percolation threshold, graphene particles can form interconnected 3D percolated network and thus leading to a sudden rise in the conductivity of the composites [1].

In this context, this work aims to highlight for the first time the differences in terms of the microstructure of polymer blend composite systems based on polylactic acid (PLA 2003D, Nature Works) and polycaprolactone (PCL Capa^{TM} 6800 , Perstorp) that are filled with 10 wt.% of graphene nanoplatelets (GNP-Grade M5, XG Sciences) and their influence on the electrical properties. The polymer composites were prepared using the melt blending technique via a mini twin-screw extruder. The polymer proportions were varied (the percentage of PLA was increased from 30 wt.% to 80 wt.% in the polymer total weight percentage). 3D printing and compression moulding techniques were used to manufacture the samples for the conductivity tests and the microstructural analysis by scanning electron microscopy (SEM).

The SEM image (Figure 1.a) is related to PLA30/PCL70/10 wt.% GNP compression moulded composite in which the PLA nodules (brighter phase) are dispersed in the PCL (darker phase) that contains all the GNPs. The same sea-island morphology was obatined for the 3D printed sample. And from the electrical conductivity measurement tests, this formulation showed inferior electrical performance as compared to PLA60/PCL40/10 wt.% GNP composite (Figure 1.b). The latter possesses superior conductivity due to the presence of a co-continuous structure of PLA and PCL phases in addition to the selective localization of the graphene in the PCL phase. This phenomenon is related to the existence of a double percolation threshold that exists in the case of immiscible polymer blend composites which contain filler whose preference is to one polymer phase rather than the other [2].

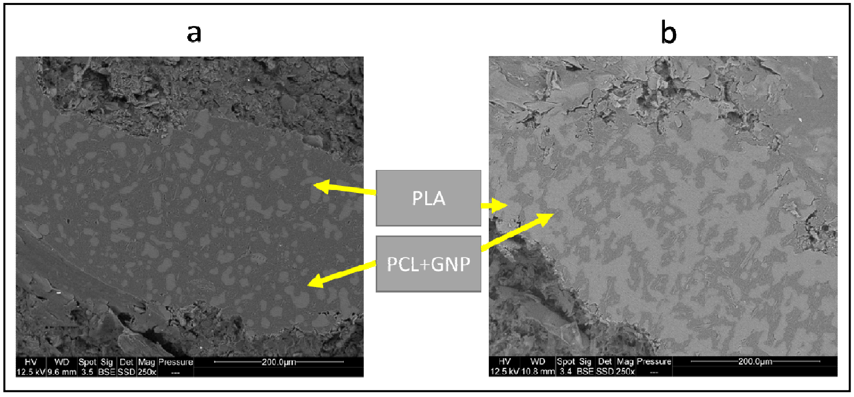

Figure 1. SEM images of PLA30/PCL70/10 wt.% GNP (a) and PLA60/PCL40/10 wt.% GNP (b) composites (Back scattered electrons (BSE) were used to obtain better contrast between the PLA and PCL)

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Salicylic acid based monofunctional reactive diluents with low volatility for radiation curable formulations

Markus Kury[1], Florian Mayer[1], Katharina Ehrmann[1], György Attila Harakaly[1], Christian Gorsche[1], Robert Liska[1]

[1]*Institute of Applied Synthetic Chemistry, Technische Universität Wien, Vienna, Austria*
[*]*robert.liska@tuwien.ac.at*

The importance of UV curable formulations has increased in the last decades, due to fast curing speeds, solvent free conditions, and the obtained highly crosslinked and hard photopolymers. Commercial UV resins are usually a composition of multifunctional vinyl oligomers, additives, photoinitiators and reactive diluents. Reactive diluents function as thinners, to lower the viscosity and increase the processability. A problem which occurs in many monofunctional reactive diluents like isobornyl (meth)acrylate or benzyl (meth)acrylate is their high volatility, even at room temperature. This can lead to a change in resin composition while processing, but can also lead to unpleasant odours or potential health risks. As a replacement, a new group of reactive diluents based on salicylate (meth)acrylates, are proposed. Therefore, thinners based on salicylate are synthesized, polymerized and characterized. The characterization took place in respect to their volatility, viscosity, thermal stability, as well as their photoreactivity and thermomechanical properties of the homopolymers. Furthermore, their function as thinners for a highly viscous difunctional polyester urethane methacrylate is shown with 30 wt% of a cycloaliphatically and an aromatically substituted salicylate methacrylate. The glass transition temperatures of 110 °C and 126 °C of the diluted polymers are in the same range as the undiluted resin.

Keywords: low volatility, photopolymerization, radiation curing, reactive diluent, salicylate (meth) Acrylate

Recycled Thermoplastic Elastomer Composites with Magnetic Properties

A. Munteanu[1*], M. Cvek[1], M. Sedlacik[1]

[1]*Centre of Polymer Systems, Tomas Bata University, Zlín, Czech Republic*
[*]*munteanu@utb.cz*

Recently, the climactic change and the enviromenal polution have led to strict policies regarding $C0_2$ emisions and the usage of plastics. As a result, enviromental-friendly materials such as biodegradable and recycled products are constantly emerging. We present a unique type of a magnetorheological elastomer (MRE) composed of thermoplastic elastomers (TPE) and Carbonyl Iron (CI) particles. Both the MREs and the pure matrix can be recycled multiple times while maintainting their mechanical properties. The preparation and reprocessing of the TPE elastomers is performed using injection molding. Subsequently, the samples are subjected to three recyclation cycles under the same conditions. Unlike typical recycling during which only one third of the material is usually reused, in this study the whole samples are recycled. The recycled matrices preserved their mechanical properties which were evaluated by means of rheology and tensile tests. In addition, a degradation and an oxidation study revealed that the elastomers were slightly degrated but stable and almost identical to the initial samples. The latter conclution was obtained using reliable methods such as, whiteness index, FTIR spectroscopy, GPC, DSC, and lastly melt rheology. Similar elastomers were synthesized with the addition of CI particles which were embeded in the matrix in various concentrations. These matrices were also recycled three times and evaluated essentially as the pure elastomer. These MREs showed enhanced mechanical properties in comparison with the pure matrix. Moreover, the degradation was significantly reduced compared to pure TPE matrix which was atributed to the covalent bonds between the matrix and the CI particles. Furthermore, these matrices preserve the typical features of an MRE.[1] When exposed to an external magnetic field, the stiffness of these elastomers is reversably enhanced (thus controlled) according to the intensity of the field. Lastly, the piezoresistive properties of the MREs are superior to the pure and are retained after recyclation.

To conclude, the elastomers in this study can easily compete with the comercial TPE even after multiple recyclation cycles while retaining the magnetic properties of a typical MRE.[2] It is important for such materials to pave the way for advanced applications which can be used in an enviromental-friendly way.

Keywords: thermoplastic polyurethane, recycling, magnetorheology, carbonyl iron.

Acknowledgments

The authors wish to thank the Internal Grant Agency of Tomas Bata University in Zlín (project no. IGA/CPS/2022/004) for its financial support. The authors also gratefully acknowledge project DKRVO (RP/CPS/2022/007) supported by the Ministry of Education, Youth and Sports of the Czech Republic.

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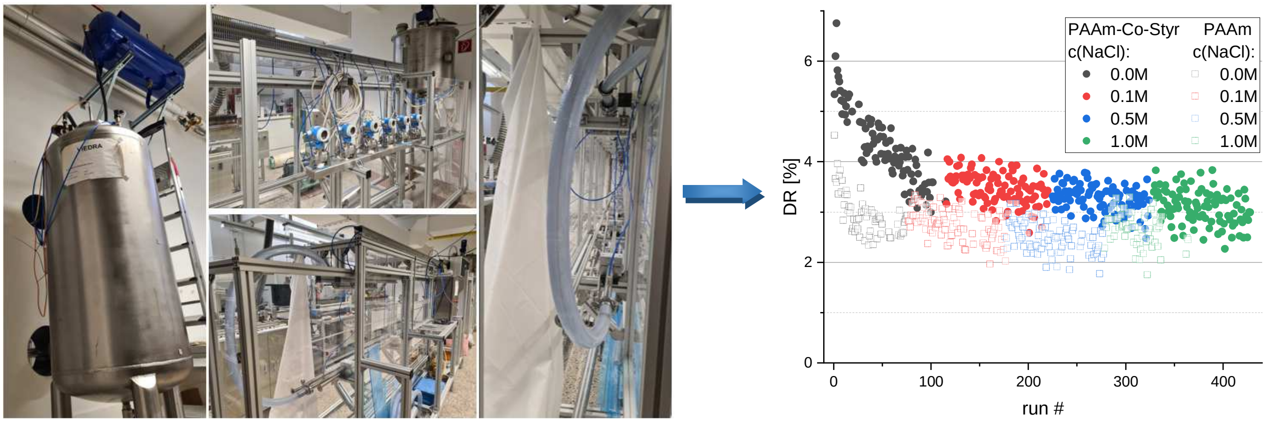
Can associating hydrophobically modified copolymers find their application as drag reducing agents in water flows?

Emina Muratspahic[1], Hans Werner Müller[1*], Lukas Brandfellner[1], Alexander Bismarck[1]

[1] *Institute of Materials Chemistry and Research, University of Vienna, Währinger Straße 42, 1090 Vienna, Austria*

* *e-mail: hans.werner.mueller@univie.ac.at*

Fluid flow in pipes faces turbulence thus enhancing drag and leading to a significant dissipation of the input energy driving the flow. Polymeric agents in 100 wppm concentrations are commonly added to the fluid to reduce drag.[1] Large economic benefits for fluid transportation systems in industry, agriculture and infrastructure are achieved by the drag reduction. Nevertheless, there are still severe limitations in the use of polymeric drag reducing agents as the mechanical stress in the fluid's velocity shear breaks them up.[2] When degraded, polymers lose their potential as drag reducing agents. To overcome this issue we produced hydrophobically modified polymers of acrylamide (poly(acrylamide-co-styrene)) forming ultra-high molecular weight associations. These associations provide weak links and are reversible meaning that they protect the polymer backbone and allow for "self-healing" through the recovery of hydrophobic interactions.



Drag reducing properties of poly(acrylamide-co-styrene) and commercial polyacrylamide (M_w ~ 1.3 * 10^6 g/mol) examined in a pilot-scale flow facility

Micellar polymerisation has been employed to obtain water soluble poly(acrylamide-co-styrene) with hydrophobe content of up to 4 mol%. Successful styrene incorporation was confirmed and the amount of hydrophobic moieties was determined by NMR and elemental analyses. The copolymer microstructure was modified by varying the hydrophobic blocks' length. The molecular weight of the synthesised materials has been determined by triple detection gel permeation chromatography to be in the range of 0.4 to 1.8 *10^6 g/mol. In dilute aqueous salt solutions the association capability of the synthesised polymers has been verified by multi angle static light scattering. Drag reducing properties of hydrophobically modified polymers have been tested in a pilot-scale flow facility and found to be higher than those for commercial polyacrylamide of the same molecular weight (~1.3 * 10^6 g/mol). Nevertheless, improvements are still to be made. A focus will be on increasing molecular weight of the backbone while retaining associating properties as well as water solubility of synthesised polymers. Moreover, recovery potential after shear stress will be examined.

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Reactivable photo-polymers for 3D additive fabrication

Hoai Nam Nguyen[1*], Jean Louis Clément[1], Didier Gigmes[1]

[1] *Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire, UMR 7273, Marseille 13397 France*

3D Printing that can manufacture objects with sizes ranging from a few microns to centimeters has significantly lowered the barrier-of-entry in terms of cost, time andyyyyyyyyyyyyyyyy accessibility to micro-fabricated intricate shapes and sophisticated devices, in various fundamental research domains such as lab-on-chip systems[1], organ-on-a-chip engineering[2] and microfluidic devices[3]. However, the main limitation of 3D laser printing (3DP-UV and Two-Photon Stereolithography, TPS) by photo-polymerization is that the surface chemistry of an object is imposed by the selected monomer (photoresist). A monomer which, for ex. confers specific mechanical properties, will not offer distinct surface properties (polarity, texturing, biocompatibility, etc.). Therefore, 3D objects with chemically functionalized surfaces are still untenable as there are no simple techniques for surface modifications at a located place (structural and chemical patterning).

In that context, Photo-Sensitive Alkoxyamines used in Nitroxide Mediated Photo-Polymerization (NMP2, Photo-RDRP) are the more versatile photo-initiator/controller to take advantage of the reactivatable character of the surface chains to decorate preformed 3D objects by various functionalities (chemical structure and architecture) by simple light activation.

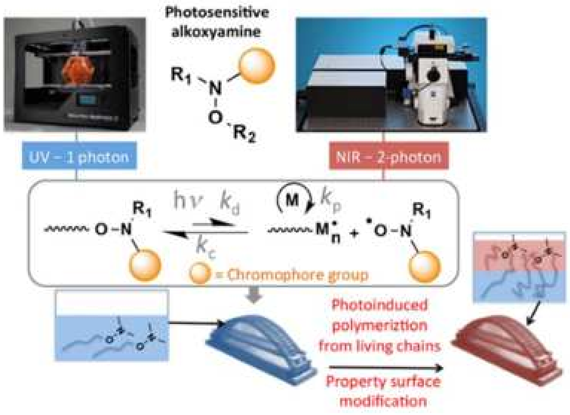

***Figure 1**: Overview of 3D-CustomSurf project*

Keywords: Photo-Sensitive Alkoxyamines, Nitroxide Mediated Photo-Polymerization (NMP2), 3D printing, Additive manufacturing.

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Polymers for Sustainable Development: Biobased and Degradable Polymers, Recycling

Plastic circulation – myths and facts

S. Hvilsted

Hvilsted Consult, Hørsholm, Denmark and
Technical University of Denmark, Kgs Lyngby
soren@hvilstedconsult.dk

”One Word: Plastics” – “there is a great future”. Plastic is nowadays the most versatile, imperative, and unavoidable material class. However, due to the low price of virgin fossil-based polymers and ease of fabrication of various plastic objects of all kinds the common use also generates an appreciable amount of waste especially from the households. 29 Mtons of plastic waste was collected in Europe in 2018 (1) corresponding to an average of 34 kg from every European. It has been estimated that of this plastic waste 32% was sent for recycling, 43% was incinerated and 25% was landfilled (1). Incineration is for environmental reasons not acceptable although the gained energy could replace energy, heating and cooling needs based on oil, gas, or coal, however, it will inevitably lead to the undesirable CO_2 emission affecting the global temperature rise and thus ultimately causing dramatic climate changes. Landfilling is also strongly unacceptable since this is resulting in permanent carbon capture due to the extremely slow degradation of most of the fossil-based polymers in mixed soil. The EU Packaging Directive (2) encourage “the prevention of packaging waste, and promote the reuse, recycling and other forms of packaging waste, instead of its final disposal” with the following specific targets for recycling of plastic packaging of at least 50% in 2025 and 55% in 2030.

From a Danish perspective only an estimated 16% of the 360 ktons (corresponding to >60 kg from every Dane) of the plastic waste collected in 2018 was reused. The reasons for the very low plastic circularity are many but mainly economical. Also, technical reasons like polymer incompatibility, unknown and undesirable impurities or additives, and partial polymer degradation upon reprocessing play important roles. For these reasons the physical reuse of plastic waste is still rather limited and not foreseen to increase substantially in the future. Alternatively, chemical recycling by thermal degradation or catalyzed pyrolysis to either monomers or valuable low boiling hydrocarbon fractions seem to be the future feasible solution. This, however, requires effective collecting and sorting systems and massive investments based on technologies that are still not fully developed.

Keywords: plastic waste collection, plastic incineration, plastic landfilling, physical and chemical recycling

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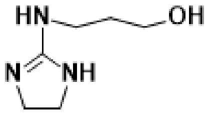
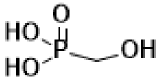
Cyclic Esters Polymerization with Initiator and Catalyst in the same Molecule

S. Penczek*, J. Pretula, K. Kaluzynski, P. Lewinski
Centre of Molecular and Macromolecular Studies of Polish Academy of Sciences, Lodz, Poland
*spenczek@cbmm.lodz.pl

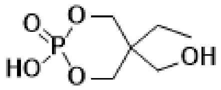
Polylactide (PLA) and poly(Ɛ-caprolactone) (PCL) are both biocompatible and biodegradable. In addition, PLA is biobased. These polymers are mostly prepared by ring-opening polymerization (ROP) of the corresponding cyclic monomers. There are several catalytic systems, including particularly important organocatalysts, used in polymerization of lactide (LA) and Ɛ–caprolactone (CL). In both basic and acidic catalytic systems initiators and catalysts are used separately. As initiators the most often are used alcohols Many of the suggested systems are highly sophisticated and multicomponent. Further application of the resulting polymers requires purification of the final product: removal of the used catalyst. We introduced initiator and catalyst in one molecules, thus, both are imbedded in the polymer via the initiator side and polymers do not require purification. For these compounds we coined the expression INICAT. Examples of some INICATs used in our work are shown below:



3-[(4,5-dihydro-1H-imidazol-2-yl)amino)] propanol [1]

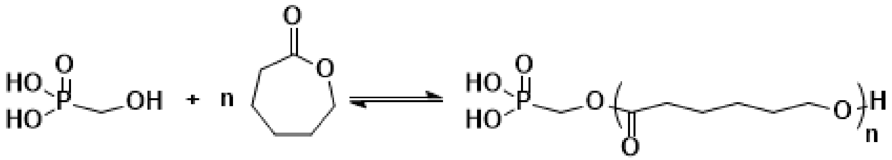


hydroxymethylphosphonic acid [2]



5-ethyl-2-hydroxy-5-hydroxymethyl-1,3,2-dioxaphosphorinane-2-oxide [3]

Particularly rewarding is polymerization with cationic INICATs (CINICATs), like shown above derivatives of phosphonic or phosphoric acids. Polymerization of CL [2] or LA [3] proceeds as living/controlled, according to the activated monomer mechanism [4] and the acidic end-groups, as shown below, can be used for the subsequent functionalization.



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Diversification of Discarded Polyesters to High Value Segmented Thermoplastic Copolyesters

A. Karanastasis,[1] V. Safin,[1] L. M. Pitet[1]*

[1]*Advanced Functional Polymers (AFP) Lab, Institute for Materials Research (IMO), Hasselt University, Hasselt, Belgium*
**louis.pitet@uhasselt.be*

Thermoplastic copolyester elastomers (TPC) are found in countless products, from cable insulation to airducts to phone cases. The wide range of suitable products derives from the extremely versatile chemical makeup employed to tailor the properties. Nearly all of these materials, however, have one common ingredient – polybutylene terephthalate. In particular, the terephthalate unit has a relatively large carbon output during production, especially compared with common (poly)olefins. Production of virgin terephthalic acid is an energy intensive process, and essentially all TPCs are manufactured from virgin raw materials. This continues despite the fact that millions of tons of terephthalates are discarded every year in the form of PET bottles and polyester fabric. We have been investigating the transformation of discarded polyesters into TPCs by chemically harvesting the terephthalate units. By repurposing discarded materials, we are working toward dramatic reduction in CO_2 output associated with this industry, and contributing to a circular plastic economy.

This work encompasses the chemical transformation of polyester waste to high-value TPCs by way of a one-step transesterification depolymerization/repolymerization with diol exchange (Figure 1). We employ a custom built melt reactor to produce 100 g batches, wherein we observe quantitative diol exchange. The final materials are molecularly and mechanically comparable to commercial counterparts. This shows a diverse set of materials can be accessed by reutilizing polyester waste streams.

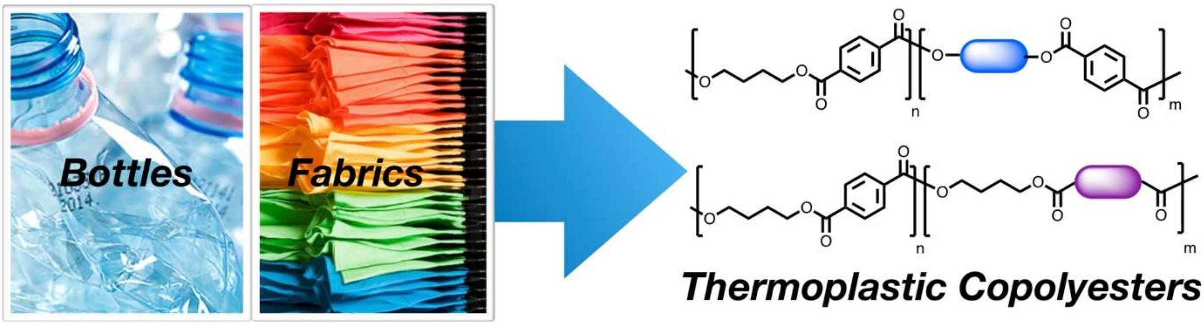

Figure 1. Chemical upcycling via transesterification of polyester waste to produce thermoplastic copolyesters with various structures and diverse mechanical properties.

Keywords: Polymer recycling; upcycling; thermoplastic copolyesters

Photopolymerization of bio-renewable monomers and oligomers

M. Sangermano[1*], L. Pezzana[1], C. Noè[1], M. Hakkarainen[2],
G. Melilli[3], N. Guigo[3], N. Sbirrazzuoli[3]

[1]*Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia,*
C.so Duca degli Abruzzi 24, 10129, Torino, Italy
[2]*Department of Fibre and Polymer Technology, KTH Royal Institute of Technology,*
Teknikringen 56-58, 10044 Stockholm, Sweden
[3]*Eco-Friendly Materials and Polymers TeamInstitute of Chemistry of Nice (ICN) – UMR CNRS 7272*
University Côte d'Azur (UCA), 28 avenue Valrose, 06108 Nice Cedex 2, FRANCE
[*]*Corresponding Author's marco.sangermano@polito.it*

UV-induced polymerization of multifunctional monomers has found many industrial applications, mainly in the production of films, inks and coatings on a variety of substrates including paper, metal and wood. Moreover, it has been demonstrated to be useful for more high-tech applications such as coating of optical fibers and fabrication of printed circuit boards. Part of the reason for the growing importance of UV-curing techniques, both in industrial and academic research, is a peculiar characteristic that induces fast transformation of a liquid monomer into a solid polymeric film having distinctive physical-chemical and mechanical properties. This polymerization technique can be considered environmentally friendly owing to the solvent-free methodology and is usually carried out at room temperature, thus conferring energy-saving advantages.

Within this frame, we reported in literature different strategies in the direction of exploiting bio-renewable materials in UV-Curable formulations to achieve coatings, composites or 3D-printed hydrogels.

Bio-based epoxy monomers were investigated in cationic UV-Curing[1], where bioderived furanic precursors, the furfuryl alcohol and the 2,5-furandimethanol were functionalized with epoxy groups and the synthesized monomers were used in the cationic UV-curing process to obtain crosslinked coatings.

Fully bio-based epoxy composites were achieved via "green" and fast frontal photopolymerization technique. Two different natural fiber fabrics made of cellulose and flax fibers are selected as reinforcing agents for a biobased epoxy resin deriving from vanillin alcohol. The thermo-mechanical properties of the composites increase as the fibre content increases confirming a good adhesion between the matrix and the fibre fabrics[2].

Finally, Starch[3] were exploited for light processable hydrogels fabrication by utilizing maize starch as raw material. To render starch light processable, it was gelatinized and methacrylated by a simple reaction with methacrylic anhydride. The methacrylated starch was then evaluated for its photocuring reactivity and 3D printability by digital light processing (DLP). Hydrogels with good mechanical properties and biocompatibility were obtained by direct curing from an aqueous solution containing lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP) as a photo-initiator.

Keywords: biorenewable monomers, photopolymerization, epoxy composites, starch hydrogels

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Microwave-assisted chemical recycling of polyurethanes and polyamides

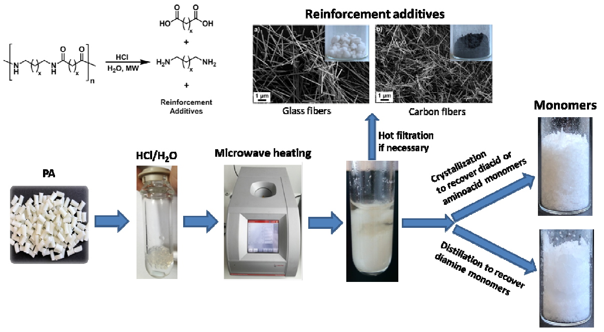
E. Žagar*, U. Češarek, M. Grdadolnik, D. Pahovnik

Department of Polymer Chemistry and Technology, National Institute of Chemistry, Ljubljana, Slovenia
**ema.zagar@ki.si*

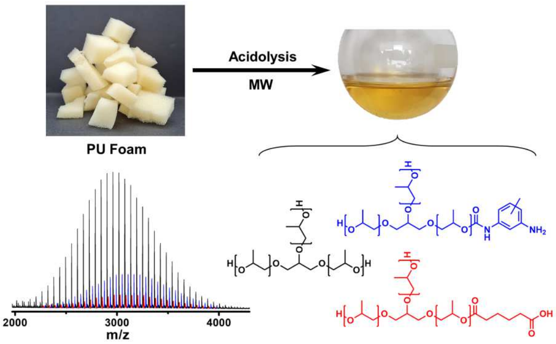
Plastic materials are key components of almost every technology today. The production of plastics consumes substantial feedstock resources and after their service life, they represent a waste that has become a growing environmental problem in terms of inadequate circular economy, environmental pollution and related climate change. The reuse of post-consumer sorted polymers by mechanical recycling is hampered by the deteriorated performance of the materials. Therefore, chemical recycling of polymers, especially those that encounter difficulties in reprocessing and those with cross-linked structure, provides an alternative that maintains the high-performance of polymer materials made from recycled feedstock.

We have developed an efficient process for the chemical recycling of short- and long-chain aliphatic polyamides (PA66, PA11, PA12 and PA1010) [1,2]. For each polyamide type, we have determined the optimal experimental conditions under which they are completely degraded to the constituent monomers by microwave-assisted acid-catalyzed hydrolysis. The advantages of our chemical recycling method compared to known methods are the rapid (several minutes) and efficient conversion of the aliphatic polyamides into monomers as the only degradation product, which greatly simplifies the procedures for isolation and purification of the recovered monomers and reinforcing additives (glass fibers, carbon fibers) in the case of composites. The secondary raw materials obtained by this process are of comparable quality to commercially available chemicals used in polyamide production.

Moreover, a highly efficient microwave-assisted acidolysis and aminolysis of polyurethane foams (PUFs) will be presented [3]. Here, we studied the influence of experimental conditions, such as reaction temperature, time, and ype and amount of degradation reagent, on polyol functionality, molecular weight characteristics, the presence of side products, and the degree of degradation of the remaining PUF hard segments. The recycled polyols were used for the synthesis of flexible PUFs. The morphology and mechanical properties of the PUFs show that the degree of functionalization of the polyol by the carboxyl and/or amine end groups, originating from esterification side reaction and incomplete urethane group degradation, significantly affects the quality and performance of the flexible PUFs prepared from the recycled polyols.



Chemical recycling of aliphatic polyamides (PA66, PA1010, PA11, PA12).



Structural properties of recycled polyols from flexyble PU foams.

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Fungal chitin-glucan complex: an exciting natural polymer blend

M. Jones[1], A. Bismarck[2*]

[1] *Institute of Materials Science and Technology, Faculty of Mechanical and Industrial Engineering, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria*
[2]*Polymer and Composite Engineering (PaCE) group, Institute for Materials Chemistry and Research, Faculty of Chemistry, University of Vienna, Währinger Straße 42, 1090 Vienna, Austria.*
[*]*alexander.bismarck@univie.ac.at*

Greener alternatives to synthetic polymers are constantly being investigated and sought after. You will have heard about cellulose but also nanofibrillated cellulose, an exciting material strong and stiff extracted from cell walls of plants. Chitin has, however, been largely overshadowed by cellulose when discussing the materials aspects of the nanosized components. [1] Chitin is a natural polysaccharide that gives structural support to crustacean shells, insect exoskeletons, and fungal cell walls. Like cellulose, chitin resides in nanosized structural elements that can be isolated as nanofibers and nanocrystals by various top-down approaches, targeted at disintegrating the native construct. The structural element in fungal cell walls is chitin linked with glucan. These fibres were covalently linked, forming a ready-made nanocomposite, that could be potentially useful for the development of a single-sourced renewable reinforcement combining the strength of chitin and the toughness of glucan. The chitin-glucan material we will be talking about was extracted from common mushrooms (Agaricus bisporus) and tree bracket fungi (Daedaleopsis confragosa). As control material we used animal chitin extracted from crab shells (Cancer pagurus). We developed a mild extraction process to preserve the quality of the chitin-glucan present within the fungal source. Initially we will compare fungal- with animal chitin and than explore potential applications as films, membranes and leather alternatives for this type of material. We will show that in the case of fungal derived chitins the physical and mechanical properties do depend on its chemical composition.

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Influence of H bonds on synthesis and properties of biobased polymers

S. Caillol[1*]

[1]*ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France*
[*]*sylvain.caillol@enscm.fr*

The observation and influence of hydrogen bonds in epoxy-system curing and material properties is crucial. Hence, epoxy-amine systems are widely used polymers for various industrial applications, such as composites, adhesives, paints and coatings due to their high thermal and mechanical properties. The reactivity of epoxy-amine system is crucial for both academic and industrial communities and is dramatically influenced by H bonds. In addition, the ring opening reaction of epoxy system yields hydroxyl groups, which can form hydrogen bonds and thus influence the curing kinetic and the material properties [1]. Those formed hydroxyl groups have also an influence on the properties of cured materials due to their H bond sites. In polyhydroxyurethanes, the most promising route to non-isocyanate polyurethanes, the use of H bonds exert also a very important influence, both on reactivity of polymerization and final properties of material [2,3]. New biobased β-hydroxy amines have also been synthesized in order to exhibit enhanced reactivity in both epoxy [4]and hydroxyurethane polymers [5].

Additionally, we have focused our studies on the synthesis of novel biobased monomers designed for free radical polymerization which could increase the biomass carbon content and pursuing to equal or improve he performance of existing polymers from non-renewable sources. For instance, poly(alkyl)methacrylate (PMAs) have known a significant widespread since the beginning of the 20th century in various applications and more especially as viscosity modifier additives for mineral oils. However, except some patents reporting the synthesis of acrylic acid from glycerol, the majority of common PMAs are originated from petroleum resources. Therefore, the objective of our work was to synthesize monomers from fatty acids bearing reactive function through radical process and evaluate the resulting methacrylate polymers as viscosity modifiers in various oils such as mineral or vegetable oils. H bonds have also exhibited crucial influence on the solubility properties of plant oil-based PMAs on both mineral and vegetable oils to allow the synthesis of viscosity index improvers [6].

Keywords: biobased polymers; polyhydroxyurethanes;poly(methacrylate); vegetable oils

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Bio-Based Non-Isocyanate Synthesis by Reactive Extrusion

V. Salvado, F. Magliozzi, H. Cramail, E. Grau*

[1]*LCPO, Unviersité de Bordeaux, CNRS, Bordeaux INP, Bordeaux, France*

Polyurethanes (PUs) are specialty polymers found in many markets, such as coatings, paints, elastomers, adhesives and, of course, foams. Nonetheless, the current industrial pathway for the synthesis of conventional polyurethanes involves the use of toxic isocyanates to react with polyols.
The combination of fossil resources price variations together with environmental and health concerns pushes scientists to develop green chemistry strategies in the course of polymer synthesis. To that purpose, the development of bio-based monomers and the use of safe chemicals and processes are two main challenges that we tried to tackle in this study.
Indeed, among the routes to non-isocyanate PUs, the polyaddition between a bis-cyclic carbonate (bisCC) and a polyamine, leading to polyhydroxyurethanes, PHUs, bearing pendant hydroxyl groups linked to the polymer skeleton, is quite promising. Nevertheless, this pathway still presents some limitations such as a rather low reaction kinetics and the low PHUs' molecular weight generally obtained. [1,2,3]
Herein, the improvements brought by the reactive extrusion, in comparison to bulk conditions, with respect to PHU synthesis were investigated (Fig 1).
The efficiency and main features of this process towards PHUs synthesis, was investigated with different BisCC/diamines systems. The PHUs so-formed were characterized according to the conversion ratios, molar masses, thermal properties and the reaction time needed to reach those values. A comparison with bulk conditions will be presented.

Finally some unique properties of these PHUs will be highlighted.

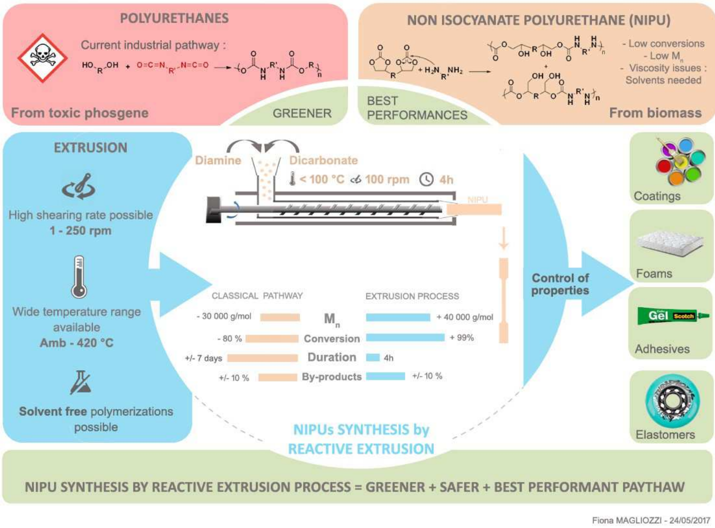

Fig. 1: Graphical abstract summarizing the purpose of the study

Keywords: (optional, Calibri, 11 pt.) NIPU, Reactive Extrusion, Green Chemistry

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Shining light on poly(ethylene glycol): a new backbone modification and crosslinking strategy towards water erasable polymer materials

H.A. Houck[1]*

[1]*The Institute of Advanced Study and Department of Chemistry, University of Warwick, CV4 7AL Coventry, United Kingdom*
**Hannes.Houck@warwick.ac.uk*

The implementation of stimuli-responsive bonds into 3D network assemblies is a key concept to design adaptive materials that can reshape and degrade. Here, a new platform technology is presented that enables the covalent modification, crosslinking and 3D laser printing of commodity poly(ethylene glycol) (PEG), whilst installing water-degradable sites along the polyether backbone (see Figure 1).[1]
Specifically, a straightforward but unique initiator-free photoresist is introduced that allows for the tailored fabrication of PEG materials that can be readily erased by water, even without the need for acidic or basic additives. Rather than photo-induced polymerisation, this new class of photoresist operates through the backbone crosslinking of PEG when irradiated in the presence of a bivalent triazolinedione. Hence, macroscopic gels are obtained upon visible LED irradiation (λ > 515 nm) that are stable in organic media but rapidly degrade upon the addition of water. Photoinduced curing is also applicable to multiphoton laser lithography (λ > 700 nm), thereby providing access to 3D printed microstructures that vanish when immersed in water at 37 °C. Moreover, PEG-based materials with varying crosslinking densities can be accessed simply by adapting the applied laser writing power, thereby allowing for tunable – and biologically relevant – hydrolysis kinetics.

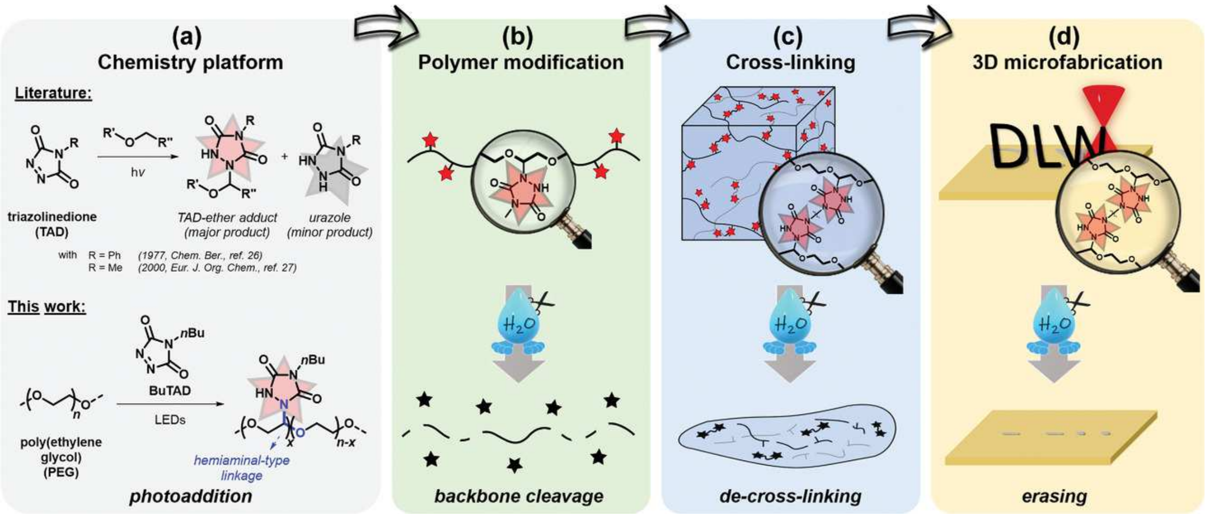

Figure 1: Chemistry platform technology enabling the facile design of poly(ethylene glycol)-based macromolecules, gels and 3D printed objects that can be cleaved, de-crosslinked and erased, simply by water.

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Design of biobased (co)polymers and nanoparticles through emulsion polymerization of biosourced monomers in green solvent

Mauricio Balarezo, Fanny Coumes, François Stoffelbach

Polymer Chemistry team (ECP), Parisian Institute of Molecular Chemistry (IPCM)
Sorbonne University, Campus Pierre et Marie Curie
4 Place Jussieu, 75005 PARIS
fanny.coumes@sorbonne-universite.fr

From a global point of view, the development of greener processes and the use of “greener” building blocks are one of the main challenges that synthetic chemists must address to solve current environmental and economic issues. Polymers represent an important class of materials widely used in industrial applications. Nevertheless, synthetic polymers are essentially based on petrosourced monomers. To achieve sustainable chemistry, several teams are currently investigating the synthesis of biosourced polymers.[1–3] In our group, we combine the use of the polymerization induced-self-assembly (PISA) technique and reversible-deactivation radical polymerization (RDRP) in green solvents (ultimately in water) to engineer nanoparticles (NPs) based on new **biobased amphiphilic copolymers**. While the RDRP -such as the reversible addition-fragmentation chain transfer (RAFT) polymerization - allows the preparation of defined polymers in a controlled fashion[4], the PISA approach, proceeding in heterogeneous potentially “green” conditions, relying on the use of a hydrophilic macromolecular control agent to promote the emulsion polymerization of hydrophobic monomers, leads to the formation of amphiphilic block copolymers that self-assemble into self-stabilized nanoparticles (NPs), avoiding the use of any free surfactant in the medium.[5–7]

In this work, hydrophobic and hydrophilic biobased radically polymerizable monomers were either purchased or designed from **biosourced precursors**. Then, a hydrophilic biobased reactive block, namely a macro-RAFT agent, was used in the PISA approach to generate completely biosourced NPs. The polymerization conditions were varied (molar mass of macroRAFT, DP targeted, pH) in order to achieve the *in-situ* formation of stable NPs. The molar mass of the amphiphilic diblock copolymer was assessed by size-exclusion chromatography (SEC), while the shape and size of the final NPs were determined by means of dynamic light scattering (DLS), small-angle X-ray scattering experiments (SAXS) and cryogenic transmission electronic microscopy (cryo-TEM) as illustrated on Figure 1.

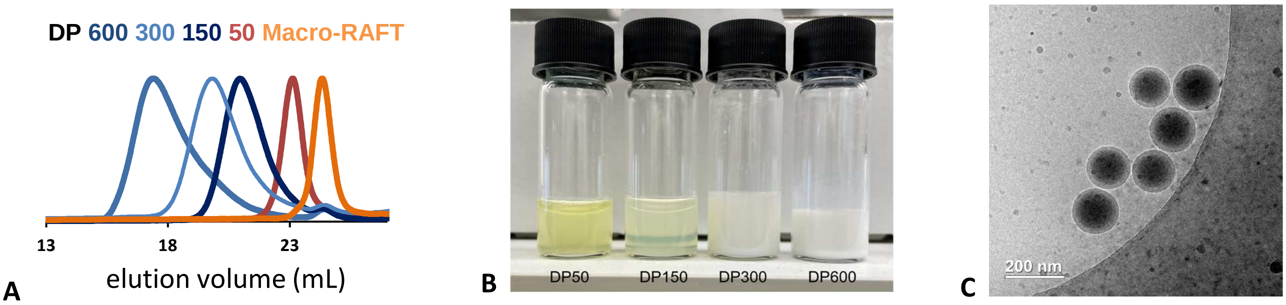

Figure 1: (A) Size-exclusion chromatography profiles (in THF), (B) visual aspects of the NPs in water; (C) Cryo-TEM image of NPs in water DP 600

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Fast relaxing siloxane-based fiber-reinforced vitrimer composite

Tapas Debsharma[1*], Virginia Amfilochiou[2], Ola Wróblewska[1], Ives De Baere[2], Wim Van Paepegem[2] and Filip Du Prez[1]
[1]Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium
[2]Department of Materials Science and Engineering, Ghent University, Ghent, Belgium
**Tapas.Debsharma@UGent.be*

Thermoset-based fiber-reinforced composites are typically dominated in high-value lightweight structural applications such as the aerospace industry, wind power industry, and many more.[1] The three-dimensionally crosslinked permanent network structures of thermosets give composites their structural strength but at the same time make them difficult to recycle. Consequently, such highly engineered materials become waste after their primary use, only to be buried or incinerated.[2] One such example is glass-fiber reinforced composite (FRC)-based wind turbine blades that are decommissioned well before their usable lifetime purely due to economic reasons.[3] Being able to change the shape of FRCs for a desired second application would extend their usable lifetime. Vitrimers,[4] owing to their dynamic covalent bonds, can be reshaped by heating. Thus, FRCs produced with vitrimers (instead of a standard thermoset) can in principle be thermoformed, give a second life to composites.

Different dynamic covalent chemistries[5] have been explored in the vitrimer field. Siloxanes[6] are a type of dynamic covalent bond in the presence of a suitable catalyst. In this work, a new type of siloxane exchange mechanism was discovered which led to the fastest siloxane exchange currently known in the literature. Using this siloxane dynamic exchange mechanism, a fiber reinforced vitrimer composite was prepared and was then successfully thermoformed.

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Prospects and challenges of the mechanical recycling of Polyhydroxybutyrate-co-valerate for food packaging applications

Dedieu Isabelle[1*], Aouf Chahinez[1], Peyron Stéphane[2]

[1]*INRAE, Montpellier, France*
[2]*Université de Montpellier, Montpellier, France*
[*]*isabelle.dedieu@inrae.fr*

Polyhydroxyalkanoates (PHAs) are gaining increasing interest in the biopolymer market due to their promising properties such as biodegradability in natural madia, biocompatibility and vesatility of processing.. PHAs offer potential sustainable substitutes for oil-based thermoplastics, particularly in the packaging sector which represents 40% of plastic demand. However, their high production costs, mainly due to the high raw material prices, is still limiting their industrialization. Mechanical recycling, a thermo-mechanical eco-friendly process is able to reduce PHA's cost, by extending the material life. For food contact applications, beyound the reprocessing (reshaping) of the material, it is mandatory to go through a decontamination step that guarentees the safety of the recyclates. [1]. Multi-reprocessing of PHA does not appear to affect its properties [2, 3]. However the decontamination efficiency of PHA, and its impact on the properties of recyclates , has never been evaluated so far.
The objective of this work is to study the opportunities and limitations of potential mechanical recycling of PHA for food contact application. reprocessing and decontamination steps were studied separately, in order to evaluate their respective impacts on the recycled polymer quality. First, decontamination was performed at different time/temperature couples, using a wide rage of polar and non-polar surrogates. The decontamination efficiency was compared to food safety assessment.

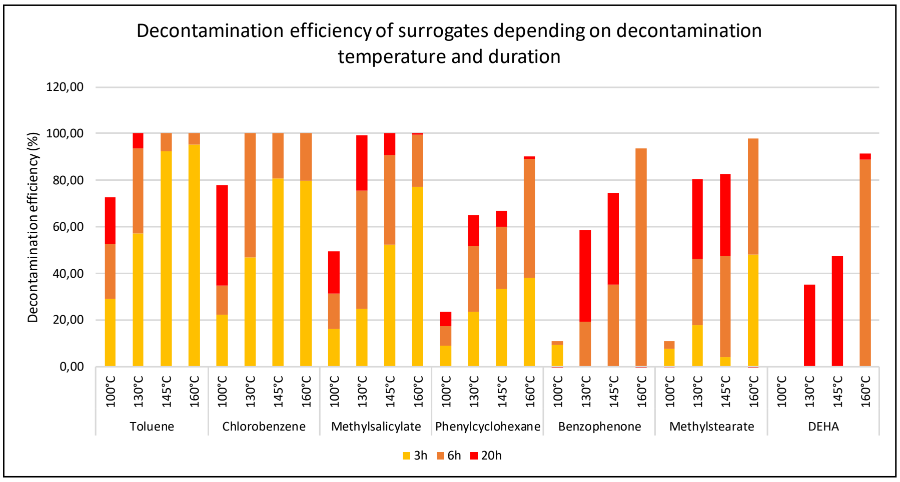

Figure 1 – Decontamination efficiency of PHA surrogates, depending on time and temperature.

Then, the impact of the decontamination thermal treatment on the polymer structure and chemical degradation was evaluated. Both recyclates safety and quality were assessed and confronted with regulation for food contact materials.

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Chemical recycling of tires waste: Radical devulcanization reaction to recover functionalized rubber

J.N. Noël[1], A.C. Gaumont[1], J.F. Pilard[2], I. Dez[1*]

[1] *Normandie Université; UNICAEN; ENSICAEN; Laboratoire de Chimie Moléculaire et Thioorganique ; CNRS; 6 boulevard du Maréchal Juin, 14050 Caen, France.*
[2]*LUNAM Université, Institut des Molécules et des Matériaux du Mans (IMMM), Equipe Méthodologie et Synthèse des Polymères, UMR CNRS 6283, Université du Maine, Avenue Olivier Messiaen, 72085 Le Mans, Cedex 9, France.*
[*]*isabelle.dez@ensicaen.fr*

Due to the large amount of polymer production, the chemical recycling of polymers waste, is of major importance. This process consists in the conversion of polymer waste into monomers or reactive functional polymers and in their use for the development of new high value polymers. In this regard, the recycling of waste tires, is still a challenge [1]. The major part of the tire being composed of a mix of different natural rubbers, such as polyisoprene (PI), or artificial rubbers, such as polybutadiene (PB) or styrene–butadiene rubber, whose proportions depend on their use, the devulcanization consisting in breaking C–S and/or S–S bonds to lead to rubber polymers that can be used as feedstocks, is the ideal recycling process [2]. The chemical devulcanization process requires the use of chemical agents: Diphenyl disulfide and benzoyl peroxide are the most used chemical agents. The later agent affords to reach 57% devulcanization rate of model sulfur cross-linked natural rubber [3 Sabzekar]. Based on this work, we extended the radical process directly on waste tires, using various functionalized peroxide derivatives as devulcanizing agents (figure 1) [4 Dez] to afford the recovery, in a good yield of functionalized rubber with well-defined architectures having $\overline{Mn}$ values between 3100 and 11,200 g·mol^{-1} and low dispersities Đ between 1.1 and 2. Moreover, this devulcanization process affords not only the recovery of rubber from the waste tire but also the functionalization of the residual waste tire aggregates.

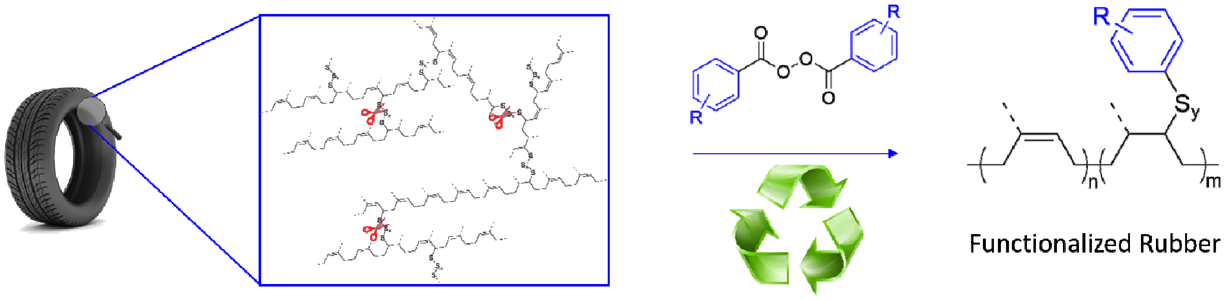

Figure 1: Radical devulcanization process of tire waste.

Keywords: devulcanization, waste tires, rubber recovery, functional polymers, radical reaction

Acknowledgments

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Investigating the Antioxidant Activity of Kraft Lignin Fractions Obtained via Solvent Extraction

X. T. Do*, Q. D. Vu, J. Rumpf, R. Burger, M. Schulze

Bonn-Rhein-Sieg University of Applied Sciences, Rheinbach, Germany
**xuan-tung.do@h-brs.de*

Lignin is the second most abundant biopolymer on earth. It makes up almost a third of wooden plants in terms of mass. The main source of technical lignins is the pulp and paper industry. Worldwide around 100-150 million tonnes per year are produced as a waste product. [1,2] However, this waste product has great potential to be used other than being incinerated for energy production. Among other things, its natural antioxidant activity can be exploited and utilised in, e.g., active packaging materials for perishable products. [3]

In this study, the antioxidant activity of eight solvent extracted lignins was investigated using the DPPH assay and Folin-Ciocalteu (FC) assay. The lignins were extracted from kraft lignin by a multi-step extraction process involving the use of acetone, ethanol, and diethyl ether (see figure 1). [4] Additionally, size exclusion chromatography (SEC) was performed to investigate correlations between molar weight and antioxidant activity.

The results show that the extraction process yields eight lignin fractions with a high degree of reproducibility in terms of molar weight (RSD < 8 %, N = 6). Antioxidant activity determined by DPPH assay does not show any correlation with molar weight ($R^2 = 0.248$, RSD < 18 %, N = 6), while antioxidant activity determined by FC assay shows high correlation ($R^2 = 0.965$, RSD < 9 %, N = 2). The FC assay seems to be sensitive to reactive species with low molecular weight, while the DPPH assays' reaction seems to be independent of the lignin molecular weight.

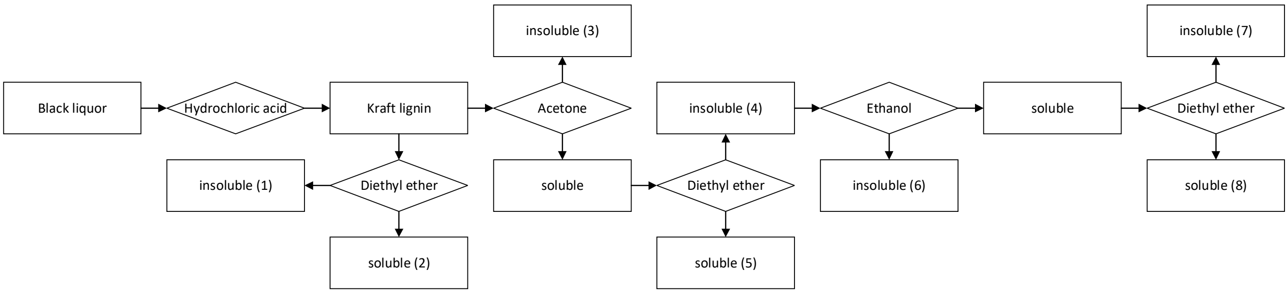

Figure 1: Flow chart of the multi-step solvent extraction process.

Keywords: Lignin, solvent extraction, antioxidant activity

Acknowledgments

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NIR Organic Dyes as Innovative Tools for Reprocessing/Recycling of Plastics: Benefits of the Photothermal Activation in the Near-Infrared Range

V. Launay[1,2], Aurore Caron[1,2], Guillaume Noirbent[3], Frédéric Dumur[3], Didier Gigmes[3], Jacques Lalevée[1,2]

[1]*Université de Haute-Alsace, CNRS, IS2M UMR 7361, Mulhouse, France*
[2]*Université de Strasbourg, Strasbourg, France*
[3]*Aix Marseille Univ, CNRS, ICR UMR 7273, F-13397 Marseille, France*
**frederic.dumur@univ-amu.fr*

The use of plastic is widespread and worldwide. The global plastic production has increased up to more than 4000% between 1960 and 2013. Due to the low cost and the high versatility of plastics, the global plastic production will continue to grow in the future. Unfortunately, the reprocessing, recycling, and recovering of plastics cannot match this huge consumption which engenders high environmental problematics. Notably, plastic reprocessing or recycling is still underexploited. Parallel to this, self-healing of polymers constitutes an efficient strategy to improve the lifetime of polymers and to reduce their maintenance costs, notably by the healing of cracks.

Recently, photoinduced thermal polymerization upon Near-InfraRed (NIR) light has been reported in the literature as an efficient tool for polymer synthesis. By an efficient light-to-heat conversion, decomposition of thermal initiators could be obtained. However, this efficient light-to heat conversion can also be advantageously used for reprocessing, reshaping, recycling, and self-healing.[1] To get this result, several parameters have to be studied such as the wavelength of the NIR irradiation, the irradiance of the NIR light source, the choice of the NIR dye and the heater concentration.

In this presentation, an overview of the recent advances concerning the use of NIR dyes for reprocessing, reshaping, recycling, and self-healing of polymers will be presented.

Keywords: NIR Dyes, photopolymerization, recycling, reprocessing, self-healing

Acknowledgments
Aix Marseille University and the Centre National de la Recherche Scientifique (CNRS) are acknowledged for financial support.

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Levulinic Acid-based Ketal–Esters: a step forward in the transition from plasticizers to bioplasticizers

Davide Morselli[1,]*, Micaela Degli Esposti[1], Simona Braccini[2], Federica Chiellini[2], Paola Fabbri[1,]*

[1] Dep. of Civil Chemical, Environmental and Materials Engineering, Università di Bologna, Via Terracini 28, Bologna, Italy
[2] Dep. of Chemistry and Industrial Chemistry, Università di Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy
***** *davide.morselli6@unibo.it;* ******p.fabbri@unibo.it*

Plasticizers are the most used polymer additives and approx. 65% of them are phthalic anhydride derivatives (known as phthalates). Conventional plasticizers do not meet the requirements in terms of renewability, biodegradability and cytotoxicity that nowadays are required,[1] especially if they are compounded with biopolymers. The existing "green plasticizers" have costs, plasticization performance and versatility towards different polymers that are not comparable to phthalates, or their production process is not sustainable from an environmental point of view. In this study novel bioplasticizers (Figure 1) are synthesized starting from bio-based levulinic acid by a three-steps selective synthesis.[2]

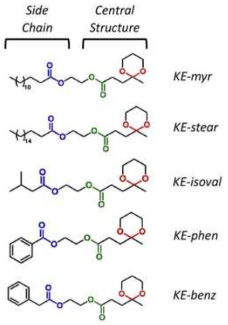

Figure 1. The new five syntehsized ketal-diester plasticizers.

The plasticization effect of the synthesized bioplasticizers has been tested on PHB as model semicrystalline biopolyester characterized by very challenging thermal and mechanical properties, which typically limit its processability and commercial diffusion [3]. In particular, the bioplasticizers showed remarkable miscibility with PHB, low leaching and remarkable plasticization effect. Specifically, the typical stiffness, glass transition and melting temperatures are reduced (Figure 2), comparably with the performance of the best commercially available "green plasticizers". It is noteworthy that the observed effects result in an expansion of the processability thermal window, in which PHB can be processed without thermal degradation. Moreover, the bioplasticizers do not significantly affect the typical biodegradability and biocompatibility of PHB, showing their promising properties as bioplasticizers for technological applications in the food packaging or biomedical field.

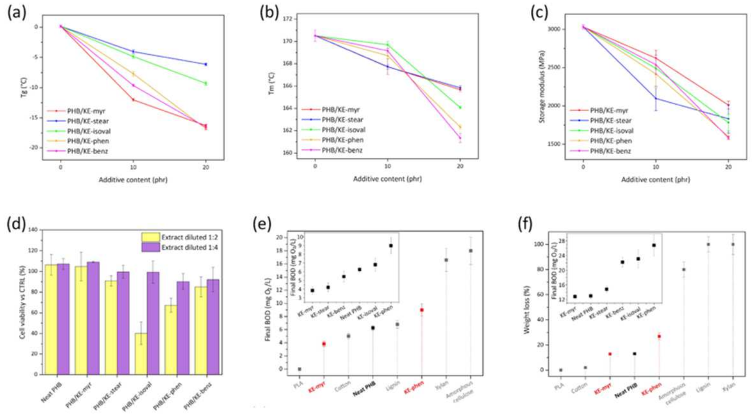

Figure 2. *(a) Glass transition temperature (T_g), (b) melting temperature (Tm) and storage modulus (E') as a function of the additive content. (c) Cell viability (from mouse embryo fibroblasts Balb/3T3 clone A31) after 24 h of incubation. In yellow extract diluted 1:2 and in purple extract diluted 1:4. (e) BOD_{30} values of KE-myr, KE-phen, and neat PHB in comparison to other biopolymers. The inset shows the BOD_{30} values of all KE samples and neat PHB. (f) Weight losses after 30 days immersed in seawater of KE-myr, KE-phen, and neat PHB in comparison to other biopolymers. The inset shows the weight losses after 30 days immersed in seawater of all KE samples and neat PHB.*

Keywords: bioplasticizers; ketal-esters; PHAs; mechanical properties; thermal properties

Acknowledgments

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Fully renewable photocrosslinkable polymers from the rapidly emerging cellulose-derived levoglucosenone platform molecule

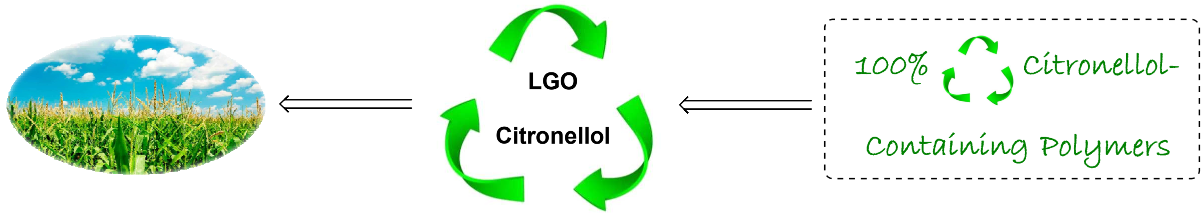
Sami Fadlallah,* Mattia Annateli, Aihemaiti Kayishaer, Louis Mouterde, Aurélien A. M. Peru, Yasmine Werghi, Quentin Carboué, Michel Lopez, Fabio Aricò,* Florent Allais*

[1]*URD Agro-Biotechnologies Industrielles (ABI), CEBB, AgroParisTech, 3 rue des Rouges-Terres, 51110 Pomacle.*

[2]*Department of Environmental Science, Informatics and Statistics, University Ca'Foscari of Venice, Via Torino155, 30172 Venezia Mestre, Italy.*

*sami.fadlallah@agroparistech.fr, florent.allais@agroparistech.fr, fabio.arico@unive.it

Levoglucosenone (LGO) is a biomass-derived molecule that is prepared through the acid-catalyzed pyrolysis of cellulosic waste on a multi-ton/year scale.[1] Special considerations were recently given to the synthesis of renewable monomers and polymers starting from LGO that served not only as a versatile and highly tunable platform thanks to the presence of readily reactive functional moieties such as an α,β-conjugated ketone and a ketal. Herein, we introduce the one-pot two-step synthesis of a new citronellol-containing five-membered lactone (HBO-citro) from LGO.[2] Two kinds of monomers having either three or two reactive hydoxy groups (Triol-citro and Lactol-citro) were then prepared from HBO-citro by a fine-tuning of the experimental conditions. Branched citronellol-containing renewable polyesters with low glass transition temperature (T_g) ranging from -20 °C to -42 °C were prepared from the novel monomers. To assess the biodegradability of the obtained polymers, a commercial lipase from *Thermomyces lanuginosus* (Lipopan® 50 BG) was used. An impact of the polymer structure as well as of the co-monomer chain length on the enzyme accessibility and degradation profile was observed. Indeed, a higher degradation profile was found for the polyesters prepared using co-monomers (acyl chlorides) having longer chains, likely due to the decreased steric hindrance around the ester bonds which allowed enhanced accessibility of the enzyme. Other renewable polymers, such as hydroxy-functionalized polycarbonates, were also prepared from Triol-citro.[3] These functional LGO-derived polymers are not only fully biobased with a branched structure, but also bear citronellol side chains that were successfully crosslinked upon ultraviolet irradiation to further control the polymer properties.



Keywords: Levoglucosenone, citronellol, oxa-Michael addition, Baeyer-Villiger oxidation, branched polymers, renewable materials, sustainability, biodegradation.

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Biodegradability of polymers – Laboratory scale vs. field scale test

N. Wild[1], M. Feuchter[1], P. A. Schindler[2], A. Poczi[2], I. C. Gebeshuber[3], M. Vasiljevic[3], M. MacQueen[4], H. Pamminger[5], A. Brandstätter[6]

[1]Montanuniversitaet Leoben, Institute of materials science and testing of polymers, Leoben, Austria
[2] Fraunhofer Austria Research GmbH, Production and Supply Chain Management, Vienna, Austria
[3] Vienna University of Technology, Institute of Applied Physics, Vienna, Austria
[4]AN-COR-TEK Ltd., Vienna, Austria
[5] Pamminger Verpackungstechnik Ges.m.b.H., Linz, Austria
[6]Lenzing Plastics GmbH & Co KG., Lenzing, Austria
**nadine.wild@unileoben.ac.at*

Recent studies showed that in Austria the amount of contaminations in composting plants is an increasing problem. Nearly half of the pollutions are plastic bags, films and other packaging [1]. In order to decrease the impurities, the use of biodegradable polymer packaging is repeatedly discussed. Biodegradable polymers should not influence the composting process negatively, biodegrade within the composting process and leave no harmful residues behind. To verify that, standards for laboratory tests are available (e.g. EN ISO 14855-2). But as on composting plants the temperature and the humidity differ during the biodegradation it is essential to assure the comparability of laboratory and field scale tests.
Therefore, common used biodegradable polymers (PHBH, PLA, PBAT) were chosen and a laboratory test (based on EN ISO 14855-2) as well as a field scale test were performed. The polymers were processed to films with a thickness of 70 µm for these tests. For the laboratory test an amount of 100 g compost was used (see Figure 1), whereas for the field scale test a compost pile with 20 t was available (see Figure 2). To implement the material into the compost pile mesh bags (mesh 0,2 mm) were used. Every two weeks samples from the laboratory and the field scale test were collected to investigate physical parameters of the polymers by FTIR, Raman, DSC and microscope.

Figure 1: Laboratory scale test

Figure 2: Field scale test

Depending on the environment of the tests (laboratory, field scale) the analyses showed differences regarding the biodegradation of the polymers. Noticeable is that even after a period of six weeks in the composting plant as well as in the laboratory test still polymer residues with grain sizes above 2 mm are detectable for some of the tested polymers. Although the results of the measurements showed differences between the initial and the biodegraded films, which lead to the conclusion that degradation has happened, the aim should be that no residues of the polymers are left in the compost.

Acknowledgments
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Percolation threshold and degradation kinetics in PLA/hemp green composites

L. Vitiello[1], S. C. Carroccio[2], G. Filippone[1*]

[1] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, p.le Tecchio 80, 80125 Naples, Italy
[2] Institute for Polymers, Composites and Biomaterials, National Reseacrh Council of Italy, via Gaifami 18, 95126 Catania, Italy
[*]gfilippo@unina.it

Many plastics are biodegradable, which means that they will break down into carbon dioxide, water, and a few other elements, but the time needed to complete the process can be very long [1]. The challenge is shortening this time as much as possible while preserving the plastics properties. In the present study, this goal is pursued by exploiting the inherent pro-degradation ability of natural fibers. The latter convey water and microorganisms within a host biopolymeric matrix. If susceptible to hydrolysis, the polymer molecular weight decreases and the chains can be "digested" by the microorganisms [2]. For such a mechanism may occur fast, the natural fibers should pervade the matrix, possibly touching each other forming continuous paths across the material. Therefore, the role of fiber content and, in particular, of the percolation theshold is crucial. Aiming at investigating this aspect, we prepared a series of green composites made of poly(lactic acid) (PLA) filled with various amounts (0-30 vol.%) of hemp shives (HS). The materials, compounded using a batch mixer operating at 180°C and at mixing rate of 60 rpm, were hot compacted using a hydraulic press in the form of plates. The fibers were conditioned at 25°C and 80% RH before compounding. The fiber percolation threshold was assessed by exploitin a two-phase viscoelastic model [3]. Originally proposed for polymer nanocomposites, the two-phase model proved to be effective also for the green composites used in the present study. Hydrolytic degradation tests were performed by immersing the samples in 50 mL of natural water at 45°C for 7 weeks. The progress of degradation was estimated by evaluating changes in the viscoelastic properties of the samples using dynamic mechanical thermal analyser (DMTA) in single cantilever geometry. Temperature sweep tests were performed from ambient temperature down to 170°C at 2°C/min with a frequency of 1 Hz and amplitude of 0.02 mm. Among the various possible descriptors that have been related to the change in PLA molecular weihgt [4], the best correlation was found with the rubbery plateau modulus, E'_r. The latter decreases over immersion time in water for all samples, but the rate at which this happens exhibits a clear discontinuity across the filler percolation threshold. The latter was identified at 13.8 vol.% through rheological analysis. Such an estimate is in line with theoretical predictions and was also supported with dielectric spectroscopic analyses. Unlike these methods, the exploitation of the two-phase model is much easier. We are currently running soil burial tests to highlight the relevance of a correct estimation of the filler percolation threshold in green composites, whose ability to biodegrade in reasonable times is too often taken for granted while being far from being proved.

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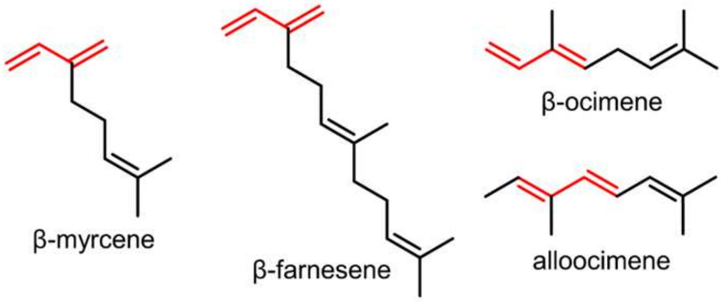
Terpenes as Valuable Bio-Based Monomer Source for New Materials

Holger Frey*, Axel H. E, Müller, Dominik Fuchs, George Floudas, Christian Wahlen

Department of Chemistry, Johannes Gutenberg University, Duesbergweg 10-14, 55128 Mainz, Germany
*hfrey@uni-mainz.de

Biomass-derived polymers possess vast potential for material science and industry in the next decades. Decreasing fossil resources and increasing environmental awareness increase the demand for sustainable feedstock-based alternatives. In addition to natural rubber (*cis*-1,4-polyisoprene), the class of terpenes offers a large variety of renewable monomers, like the 1,3-diene monomers β-myrcene and β-farnesene as well as related structures, such as ocimene (Figure 1). Living anionic polymerization of bio-based 1,3-diene monomers enables the synthesis of well-defined, high molecular weight block- and copolymers with unique control over molecular weights, polymer architecture and polydiene microstructure. The resulting materials are tested for a variety of applications. For instance, polyfarnesene has been introduced as an additive in tire mixtures to replace fossil resource-based rubbery building blocks in styrenic thermoplastic elastomers. In addition, the unsaturated nature of polymyrcene and polyfarnesene enables functionalization by a variety of postmodification reactions, which can result e.g., in improved interaction with functional fillers, but also polar thermoplastic rubbers. (End-)functionalized polyterpenes are promising candidates as precursors for the synthesis of fully bio-based thermoplastic elastomers. In the talk an overview of recent developments regarding the anionic and oxyanionic polymerization of terpene-based monomers will be given and the considerable potential the resulting polymer architectures for material science and a more sustainable future will be discussed.



Keywords: terpene monomers, farnesene, myrcene, glycidyl ethers.

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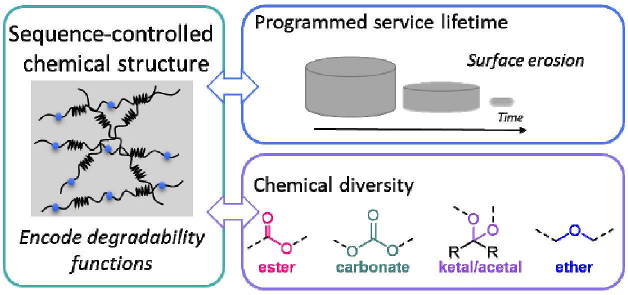
Design strategies to program the service lifetime of degradable polymers: from bulk degradation to surface erosion

Tiziana Fuoco

Department of Fibre and Polymer Technology, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, Teknikringen 56-58, SE 100-44 Stockholm, Sweden.
tiziana@kth.se

Aliphatic polyesters have a leading position among degradable polymers. Their ability to degrade by abiotic hydrolysis accounts for their use in biomedical applications for the last decades. Today, this ability is valued outside the biomedical field as an opportunity to meet sustainability challenges.[1]
Despite being considered degradable, their degradability is however a controversial matter and their degradation behaviour is in most cases unpredictable. A long temporal gap (even decades) can occur between the loss of mechanical integrity, i.e., the service life of the material, and its complete erosion. As a consequence, brittle and crystalline domains persist for several years without having any function and being harmful to the environment. This behaviour is typical of polyesters and it is a consequence of the slower hydrolysis of the ester bonds than the water penetration in the polymeric matrix that leads to a bulk degradation mechanism. Contrary to bulk degradation, surface erosion ensures longer retention of the polymer properties, a faster erosion rate and a more predictable and programmable degradation profile. Surface erosion cannot be achieved for the currently available polyesters because of the intrinsic reactivity of the ester cleavable bonds.[2]
Design strategies are presented to tackle the limited scope of the degradation behaviour of polyesters and to **reach a balance between degradability and performance**. Such purpose is crucial to truly advance the applications scope of these polymers towards sustainable alternatives. Green, versatile, and simple synthetic strategies were developed: A precise and *a priori* design of the primary structure plus the controlled positioning of purposely identified degradability functions enabled polyesters' **surface erosion** to be unlocked.[3,4] Sequence-controlled ester acetal copolymers exhibited a predictable degradation profile and surface erosion under hydrolytic conditions.[3]
While, the precise enchainment of, besides ester, carbonate and ether bonds pave the way to different degradation pathways that are triggered by the environmental conditions and lead to surface erosion.[4]



Keywords: sequence-controlled copolymers, degradability functions, surface erosion.

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Alditols-based polyesters: structural and synthetic investigations towards fully biobased and biodegradable materials

S. Gazzotti[1,2*], M.A. Ortenzi[1,2], A. Silvani[1,2], C.A. Pagnacco[3], M. Hakkarainen[4]

[1] *CRC Materiali Polimerici "LaMPo", Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy.*
[2] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy.*
[3] *Donostia International Physics Center (DIPC), Paseo Manuel Lardizábal 4, 20018 San Sebastián, Spain.*
[4] *Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56, 100 44 Stockholm, Sweden.*
**stefano.gazzotti@unimi.it*

As the field of polymeric materials is going through a profound revolution driven by the need of more environmentally friendly solutions, the development of new biobased and biodegradable materials is currently one of the hottest topics in the field of materials science. From one side, academic and industrial research is oriented towards the investigation of possible biobased alternatives to already existing monomers and polymers. The use of monomers coming from renewable sources makes the resulting materials more sustainable, although these materials can either be biodegradable or not.[1] To this regard, alongside renewability, biodegradability is anyway one of the most seeked properties of new materials since a biodegradable material is less likely to accumulate in the environment. One of the main hurdles linked to biodegradable materials is often given by their poor mechanical and thermal properties. These problems are usually difficult to address as they come directly from the chemical nature of the monomers, which can prevent these polymers to be widely employed at industrial level for certain applications. Within this context, a material that has the potential to couple renewable nature, biodegradability and chemical versatility to modulate final properties appears valuable.[2]

Here we aimed to develop new renewable and biodegradable polyesters based on alditols. One of the main difficulties regarding the use of carbohydrates as monomers comes from their multifunctional character, which makes the polymerization reaction difficult to control, also preventing the formation of high molecular weight products. A protection-deprotection strategy of the starting monomer was therefore developed, in order to confer the final material tunable properties and the versatility that is usually lacking in this kind of systems. Mannitol and sorbitol were chosen as model alditols and protected as diisopropylidene and dibenzylidene derivatives through high yield, one step procedures. These difunctional monomers were employed for the synthesis of polyesters, in combination with biobased sebacic acid. The polymerization reaction was optimized and resulted in the formation of high molecular weight products with good control over the macromolecular architecture, as opposed to the previous literature reports on mannitol and sorbitol sebacate polyesters.[3] Indeed, the protection of the starting alditols as bifunctional diols resulted in the formation of highly ordered, linear polymers. Their properties were investigated, demonstrating the strong influence that the protecting group can have on the final thermal and mechanical properties of the material. A selective removal of the protecting group while preserving the macromolecular structure of the polymer was performed and resulted in a dramatic increase of the wettability of the material. Finally, degradation tests were performed, pointing out good degradability features in different conditions.

Keywords: Polyester, Biobased, Biodegradable, Tunable properties

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New gentle and environmentally friendly processes for the production of microparticles and fibers from the milk protein casein

R. Gebhardt[1*]

[1]*Soft Matter Process Engineering, Aachener Verfahrenstechnik, (SMP.AVT), RWTH-Aachen, Aachen, Germany*
[*]*ronald.gebhardt@avt.rwth-aachen.de*

In this presentation we will talk about two processes we have established to produce higher aggregated casein materials in detail casein microparticles and fibers. Both are a promising material for new innovative foods, tissue engineering or controlled release of drugs. Since caseine is a renewable raw material, the functional products made from it are an environmentally friendly alternative to petroleum-based plastics. Caseins can be simplified as block copolymers to explain their adsorption behavior and assembly. In this modeling approach, the caseins consist of alternating clusters of phosphoseryl-residues interacting with colloidal calcium phosphate and hydrophobic blocks through which caseins are interconnected. In cow's milk, four types of casein (α_{S1}-, α_{S2}-, β- and κ-casein) together with calcium phosphate form spherical association colloids which are historically referred to as casein micelles. The crucial step for the new structure formation processes shown here is the weakening of the colloidal stability of the micelles, which is caused by a κ-casein surface layer. This salted brush provides steric stability and is either compressed as in microparticle production or enzymatically degraded as in casein fibers. During compression, casein micelles first associate into aggregates due to volume exclusion of added pectin and then become even more compacted during subsequent film drying. After pectin hydrolysis, the casein microparticles can be extracted from the film matrix and resuspended. The microparticles produced in this way have a superporous inner structure and show from pH 8 onward, a two-stage swelling behavior, which proceeds all the faster the higher the pH value is [1]. While the pH value influences both swelling steps, calcium exclusively influences the first swelling step. This is demonstrated by swelling experiments on microparticles from which calcium was removed on the one hand by using a low-esterified pectin and on the other hand by adding the strong calcium-chelating agent citrate. However, at the end of the swelling process, untreated microparticles irreversibly disintegrate. We inserted covalent cross-links into the microparticles using transglutaminase transforming them into microgels. As a result, they swell to a stable equilibrium value and successive swelling and de-swelling cycles can be carried out without decomposition occurring. Furthermore, we report on a new environmentally friendly wet-spinning process for the production of casein fibers, which does not require the use of harmful chemicals. The starting material is enzymatically destabilized casein micelles, which are available in the non-aggregated state in the cold and are thus injectable. We will present the underlying temperature-dependent aggregation process, which we have investigated for the first time using single particle tracking [2]. For fiber formation we realize this under flowing conditions in a two-substance nozzle. The resulting fibers have a network structure which is stretched in the fiber direction [3]. We will show the influence of calcium, the type of solvent as well as subsequently inserted chemical cross-links on the swelling behavior and mechanical stability of the fiber. Both aggregated casein structures (particles and fibers) could be used in the future as bulding blocks of higher organized structures such as artificial tissues. The pH-dependent swelling behavior could be exploited to protect encapsulated bioactive substances during passage through the stomach and then release them in a controlled manner in the intestine.

Keywords: casein, microparticles, fibres

Acknowledgments

We are grateful for the experimental contributions of Jann Schulte and Sebastian Thill (both from SMP.AVT).

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Elucidating the structure-property relations and crystallization kinetics of polyhydroxyalkanoate biopolymers

H. Geeraert[1*], R. Verhelle[1], E. Peeters[2], N. Van den Brande[1]

[1] *Research Group of Microbiology, Department of Bioengineering Sciences, Vrije Universiteit Brussel, Brussels, Belgium*
[2] *Research Group of Physical Chemistry and Polymer Science, Department of Materials and Chemistry, Vrije Universiteit Brussel, Brussels, Belgium*
[*] *hannelore.geeraert@vub.be*

Polyhydroxyalkanoates (PHAs) are biocompatible polymers produced through biosynthesis, potentially from renewable feedstocks. Fundamental knowledge on the structure-property relations of PHAs is still lacking, especially for less common copolymers such as poly(3-hydroxybutyrate-co-4-hydroxybutyrate), which is a very promising material for high value-added applications in the biomedical industry. A systematic study on P(3HB-co-4HB) is thus needed, although this is complicated due to the lack of commercial sample availability [1]. Therefore, shake-flask fermentation by *Cupriavidus sp.* USMAA2-4 was performed to produce P(3HB-co-4HB) samples with varying structural properties. By varying the synthesis conditions, including the carbon sources fed to the bacterial cultures, samples with varying 4HB molar fraction were obtained. Extensive thermomechanical analysis of these samples was performed and the crystallization kinetics of P(3HB-co-4HB) were studied by differential scanning calorimetry (DSC). The experimentally observed crystallization kinetics were modelled with an adapted Haudin-Chenot numerical model [2]. This model accurately describes the crystallization kinetics of P(3HB-co-4HB) with varying composition over a large temperature range. Slow crystallization is known to be an issue for the industrial melt processing of PHA materials, e.g. injection molding, where rapid polymer crystallization is critical. Characterization of the crystallization as function of time and temperature is therefore crucial to acquire fundamental understanding of the relation between structure, processing and properties. This project is the first to explore the variation of the kinetic and physical crystallization parameters, obtained through numerical modelling of experimentally observed crystallization kinetics, with P(3HB-co-4HB) composition.

Keywords: polyhydroxyalkanoates, microbial biosynthesis, structure-property relations

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Nature-inspired Circular-economy Recycling (NaCRe) for Proteins: Proof of Concept

S. Giaveri[1,2], A.M. Schmitt[1,3], L. Roset Julià[1], V. Scamarcio[1], A. Murello[1], S. Cheng[2], L. Menin[4], D. Ortiz[4], L. Patiny[4], S. Bolisetty[5], R. Mezzenga[5,6], S.J. Maerkl[2*], F. Stellacci[1,2*]

[1]*Institute of Materials, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland*
[2]*Institute of Bioengineering, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland*
[3]*Faculty of Chemistry, University of Strasbourg, CNRS, Strasbourg, France*
[4]*Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland*
[5]*Institute of Food, Nutrition and Health, ETH Zurich, Zürich, Switzerland*
[6]*Department of Materials, ETH Zurich, Zürich, Switzerland*
**sebastian.maerkl@epfl.ch, *francesco.stellacci@epfl.ch*

Every year the planet is loaded with billion tons of synthetic polymer-based materials, commonly named plastics. A sustainable production, use, and disposal of such materials is one of the greatest challenges that humanity has to face.

Natural polymers, such as proteins, are more abundant than man-made ones, yet they do not accumulate into the environment. The key for protein sustainability lies on the circularity in the materials' use. Proteins are sequence-defined natural polymers. Indeed living organisms "recycle" mixtures of proteins by digesting (i.e., depolymerizing) them into their amino acid building blocks, and reassembling the so achieved monomers into arbitrarily different sequences, that is the proteins of need at the time of synthesis. This process breaks a common recycling paradigm where a material is recycled into itself.

In this study we show that complex mixtures of (up to >30) peptides and/or proteins are recycled into fluorescent, and bioactive proteins, outside any living organism. We named this approach to recycling Nature-inspired Circular-economy Recycling (NaCRe) [1].

In detail, we initially established NaCRe depolymerizing short peptides (magainin II, glucagon, and somatostatin 28) into their constitutive bluilding blocks by using thermolysin endoprotease and leucine aminopeptidase. The so obtained amino acids were used as the sole source of monomers for producing fluorescent proteins (mScarlet-i, GFP), by using an amino acid-free cell-free transcription-translation (TX-TL) system[1]. We then performed multiple cycles of NaCRe by recycling mixtures of low and high molecular weight proteins (glucagon, β-lactoglobulin A, and silk fibroin) into fluorescent (mScarlet-i, GFP), and bioactive (catechol 2,3-dioxygenase) proteins[1]. Finally, we demonstrated that NaCRe is not limited to the functionalities present in the 20 proteinogenic monomers by recycling non-proteinogenic amino acids[1].

By NaCRe, unseparated mixtures of polymers are recycled into new polymers, not necessarily related to the parent ones. NaCRe is based on sequence-defined polymers, reversibly cleavable backbone bonds, and polymerization reactions starting from unseparated mixtures of monomers. This work highlights an advantage of sequence-defined polymers that is their ability to be recycled in a way that is compatible with the principles of a circular economy.

Keywords: recycling, sequence-defined polymers, protein-based materials, sustainability.

Acknowledgments

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Sustainable modification of lignin by reactive extrusion for the fabrication of green, recyclable biocomposites

A. Avella,[1] C. Gioia,[2*] M. Ruda,[3] T. Roulin,[3] C. Carrick,[3] G. Lo Re,[1,4*]

[1]*Department of Industrial and Materials Science, Chalmers University of Technology, 41296 Gothenburg, Sweden.*
[2]*Department of Civil, Chemical, Environmental, and Materials Engineering, University of Bologna, 40131 Bologna, Italy.*
[3]*Lignin Industries AB, 74171 Knivsta, Sweden.*
[4]*Wallenberg Wood Science Centre (WWSC), Chalmers University of Technology, 41296 Gothenburg, Sweden.*
**claudio.gioia2@unibo.it* ; **giadal@chalmers.se*

As packaging constitutes more than 40 % of the annual plastic production and waste, novel sustainable alternatives are needed to shift from environmentally costly materials. The responsible design of new-concept packaging materials needs to combine feedstocks from natural resources able to confer a sustainable carbon footprint, along with benign end-of-life perspectives such as recyclability and biodegradability. To achieve such purposes and to confer desired performances, biosourced lignocellulosic derivatives can be effectively exploited.

In this work, biomaterials based on lignin and biodegradable poly(butylene adipate-co-terephthalate) (PBAT) were developed, maximizing the renewable content while preserving their processability for film blowing. In a first step, the plasticization of lignin was designed by reactive extrusion with a bio-sourced fatty acid to obtain a thermoplastic compound (Renol). Thermal analysis showed a tuneable reduction of raw lignin glass transition temperature as a function of fatty acid content. Lignin functionalization was further confirmed by infrared and nuclear magnetic resonance spectroscopies, which unraveled the reaction mechanism of the fatty acid grafting onto lignin. A series of biomaterials were fabricated by melt blending of PBAT with Renol, reaching a lignin content up to 80 wt.%. Compared to raw lignin/PBAT reference, Renol provided the biomaterials with larger deformability and toughness, thus enabling film blowing up to 35 wt.% lignin content with the potential for packaging applications. To provide end-of-life strategies of the film blown biomaterials, their mechanically recycling was successfully carried out after aging for a year of the blown films in room conditions, indicating a concrete possibility for the Renol-based biomaterial circularity. This research enabled the scaling-up of the reactive extrusion of Renol from a lab- to pilot-scale with a running production rate of 350 kg/h, providing the front product of the Swedish company Lignin Industries.

Figure 1: General approach for lignin plasticization via reactive extrusion, blending with PBAT, film blowing, followed by films recycling.

Keywords: Lignin modification, Lignin characterization, Reactive extrusion, Film blowing, Recycle.

Self-Reinforcement of Tough Polylactide Monofilaments towards materials with programmed degradability

Christina Schippers[1], Larisa A. Tsarkova[1,2], Jochen S. Gutmann[1,2*]

[1]*German Textile Research Center North-West, Krefeld, Germany*
[2]*Universität Duisburg-Essen and CENIDE, Duisburg, Germany*

Bio-based semicrystalline polylactide (PLA) has a growing value as a substitute for fossil-based polyesters in technical applications and as a biocompatible material in medicine. Poor toughness is generally recognized as a limitation for the expansion of PLA usage in the applications that require elastic-plastic deformations at high stress levels. An identified research challenge is to develop new insights and approaches to guide the mechanical properties of PLA to a level that will make it suitable for industrial usage as well as to programm its degradation rate with regards to the particular environmental/application conditions. Presented research reveals that under certain environmental aging conditions melt-spun highly crystalline PLA monofilaments demonstrate a long-term preservation of the toughness, outlasting the hydrolytic degradation [1]. Environmentally triggered structural changes and hydrolytic degradation of the monofilaments have been evaluated by analysis of their crystalline structure, thermal and mechanical properties as well as their long-term relaxation behavior using a self-developed model (Figure 1). The mechanism behind the observed durability of PLA material is presumably attributed to the relaxation of the confined amorphous phase presumably as a result of local chain scission.

A self-developed model was elaborated to predict the long-term mechanical behavior of the fibers. New model is based on the well-known Maxwell model and assumes a mean relaxation time in combination with a relaxation coefficient and allows to derive master curve from one measurement series at a single strain by fitting the data to the model equation [2]. The proposed model turned to be extremely sensitive in revealing changes in the mechanical performance of the treated polymer samples.

Presented results offer possible design strategies toward tough neat PLA materials for sustainable technologies [3].

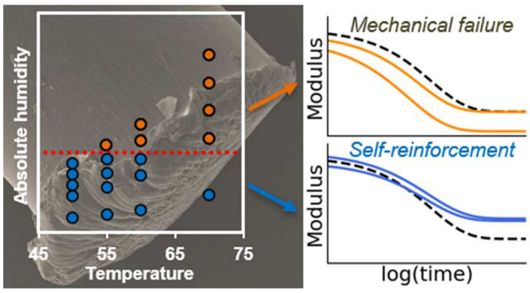

Figure 1. Left panel: SEM immage of the fibre edge and the diagram of the mechanical stability (blue dots) or chemical degradation (orange dots) vs the treatment temperature and absolute humidity.
Write panel: Examples of model relaxation curves of pristine (dashed line) and treated PLA fibers [1].

Keywords: polylactide fibers, degradation, self-reinforcement, life-time prediction

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Internal catalysis on the opposite side of the fence in non-isocyanate polyurethane covalent adaptable networks

Aitor Hernández[1], Hannes Houck[1], Marc Guerre[2], Haritz Sardon[3,4] and Filip E. Du Prez[1]*

[1] Polymer Chemistry Research Group, Center of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Faculty of Science, Ghent University, Ghent, Belgium.
[2] Laboratoire des IMRCP Université de Toulouse CNRS UMR5623 Université Paul Sabatier, Toulouse, France
[3] POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, San Sebastian, Spain
[4] Ikerbasque, Basque Foundation for Science, Bilbao, Spain
**Filip.DuPrez@Ugent.be*

We developed a novel methodology to provide non-isocyanate polyurethane-based covalent adaptable networks (CANs)[1], with embedded tertiary amines that serve as internal catalytic moieties for the dynamic bond exchange processes. For the CAN design, multifunctional N-substituted 8-membered cyclic carbonates, which can be ring-opened by macromolecular amines, were used. Several model reactions were conducted to investigate transcarbamoylation bond exchange reactions at elevated temperatures and assess the influence of catalytic moieties within the urethane structure. This led to the design of a non-isocyanate PU CAN[2] wherein the position of the internal catalyst was changed with respect to previous reported polyhydroxyurethane CANs,[3] while maintaining close proximity to the dynamic carbamate linkages.

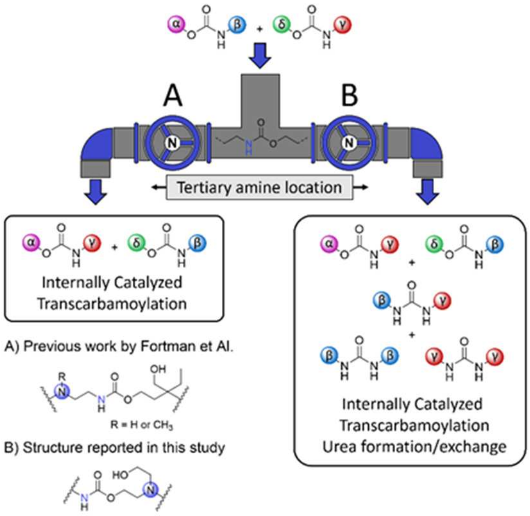

Fig 1. Left (structure A, previous work): previously reported tertiary amine internally catalyzed dynamic urethane exchanges. Right (structure B, this work) internally catalyzed reactions on the urethane structures reported in this study.

This positioning change of the tertiary amines resulted in an internal catalytic effect on the dynamic exchange reactions, hence providing a better understanding of their role as internal catalysts during the reprocessing of PU networks.

Acknowledgments *This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant agreement No 860911.*

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Design of novel Fenton- and laccase-based materials for the degradation of organic trace pollutants in water

C. Horn[1,2*], D. Pospiech[1], P. J. Allertz[3], R. Hommel[4], K. Licha[5]

[1]*Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany*
[2]*Organic Chemistry of Polymers, Technische Universität Dresden, Dresden, Germany*
[3]*Faculty of Natural Science, Brandenburg University of Technology, Senftenberg, Germany*
[4]*IFN Forschungs-und Technologiezentrum GmbH, Tröglitz-Elsteraue, Germany*
[5]*FEW Chemicals GmbH, Bitterfeld-Wolfen, Germany*
[*]*horn-christoph@ipfdd.de*

Growing population, globalization and modern life style have led to a dramatic increase in the consumption of pharmaceuticals, personal care products and pesticides in industry, agriculture and everyone's household. The increasing pollution of surface water with persistent organic trace pollutants (POPs), for instance the analgesic diclofenac or the polymer base material bisphenol A have become currently a major challenge. Conventional wastewater treatments such as ozonation and activated carbon adsorption do not remove these persistent substances sufficiently. Therefore, advanced catalytic materials for a more flexible treatment are required.[1] The aim of the BMBF-funded collaboration project CeraFe$^+$ is to develop new materials for pollution elimination. Here, a combination of new heterogeneous Fenton catalysts in Fenton process and enzymatic degradation in a two-stage, modular system is developed and will be presented. In case of high pollution concentration, a heterogeneous Fenton process is used in the first stage. It is considered to be one of the most efficient and advanced oxidation processes and enables the oxidative degradation of several organic substances by adding the readily available hydrogen peroxide (H_2O_2).[2] A low-cost heterogeneous Fe_2O_3/SiO_x-based Fenton catalysts prepared by sol-gel process with improved properties such as reduced iron leaching is presented. Moreover, the iron compounds are embedded into a thermoplastic polymer matrix, resulting in almost no iron leaching and a typical heterogeneous linear degradation according to a pseudo-zero order kinetics model of Reactive Black 5 as model pollution compound.[3]

For the degradation of trace pollutants in low concentrations, enzymes are employed in the second stage. Particularly oxidoreductases such as laccase (Lac) are capable of targeting a wide range of pollutants. Here, the design of hydrogels with immobilized Lac and a new way of tethering Lac covalently to a hydrogel will be presented. For this purpose, in a first step, Lac is modified by itaconic anhydride leading to an increase in enzyme activity compared to the native enzyme. In a second step, the hydrogel is smoothly polymerized by UV radiation. In order to increase the mechanical stability, the hydrogel is coated onto porous Al_2O_3-ceramics. The hydrogel-coated ceramics are intensively studied with respect to the degradability of various model trace substances.[4] Furthermore, the combination of both systems in a modular system is studied and represents a unique new way of removing trace pollutants from wastewater by a modular system.

***Acknowledgement**: Financial support by BMBF (project CeraFe+, KMU_Innovativ, project number 13XP5065D) is gratefully acknowledged.*

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Tailoring the properties of bioplastics by addition of thermoplastic starch with selected plasticizers

I. Chodak*, H. Peidayesh, K Mosnáčková

Polymer Institute of the Slovak Academy of Sciences, Bratislava, Slovakia
upolchiv@savba.sk

Starch, an inexpensive and abundantly available material, is considered to be fully sustainable plastics. Frequently it is applied as thermoplastic starch (TPS) prepared by mixing the starch with a plasticizer and processing at high shear stress to break the hydrogen bonds between starch macromolecules and substitute it by weaker starch – plasticizer hydrogen bonds. Generally, nowadays almost all TPS commercial grades contain glycerol as plasticizer.

In the presentation, we investigated tailoring the TPS properties by selection of several factors affecting the physical properties of TPS. Among these, the most interesting options are the plant origin of a particular starch, chemical composition of plasticizers (besides glycerol as the most frequently used plasticizer, number of other species are applied) as well as the plasticizer amount. The energy of hydrogen bonds between starch and various plasticizers is decreasing in order urea > formamid > acetamid > polyols. If applying plasticizers containing hydroxyls (glycols or polyols), TPS containing plasticizers with higher molecular weight is stronger and more brittle, with higher tensile strength and Young's modulus, as well as higher Tg.

Addition of TPS to biodegradable compostable bioplastics is a useful application of TPS aimed to a decrease of price compromising certain deterioration of physical, especially mechanical properties. However, it was shown that the degree of worsening depends significantly on the properties of the TPS, therefore application of TPS with higher tensile strength or lower moisture absorbance may lead to lowering the negative effect of the TPS presence in the mixture if TPS with appropriate physical parameters is used. In the presentation several features mentioned above will be discussed in detail and various factors will be compared, including the mode of TPS preparation. The effect is demonstrated also on properties of various biopolymer / TPS mixtures.

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Bio-based poly(ester-*alt*-thioether)s synthesized by ring-opening copolymerizations of eugenol/vanillin/syringaldehyde-based epoxides and *N*-acetyl homocysteine thiolactone

N.Illy[1*], B. Quienne[2], S. Le Luyer[1], S. Caillol[2] and P. Guégan[1]

[1]Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, Equipe Chimie des Polymères, 4 place Jussieu, F-75005 Paris, France
[2]ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France.
[*] *nicolas.illy@sorbonne-universite.fr*

Lignin is the second most abundant natural polymer: its depolymerization is the biggest natural source of aromatic compounds, including commercially-available eugenol, vanillin and syringaldehyde.[1] Our group recently reported the synthesis of well-defined poly(ester-*alt*-thioether)s by organo-catalyzed anionic ring-opening copolymerization of γ-thiolactone and various epoxides under mild conditions.[2,3] The obtained poly(ester-*alt*-thioether)s are very promising materials due to the presence in each repeating units of both cleavable ester groups and oxidable thioether groups.

In this work, the organo-catalyzed alternating ring-opening copolymerizations of bio-based epoxides, derived from eugenol (EGE), vanillin (VGE) and syringaldehyde (SGE), were carried out with renewable N-acetyl homocysteine thiolactone (NHTL). The polymerization process is organo-catalyzed and atom-economical, it occurs in the presence of moisture and air at moderate temperatures from readily accessible monomers. Well-defined alternating poly(ester-*alt*-thioether)s were obtained with number-average molar masses M_n up to 11 kg mol^{-1}. The prepared copolymers display perfect poly(ester-*alt*-sulfide) alternating structures for all epoxide monomers as evidenced by ^{1}H, ^{13}C, COSY, HSQC, ^{1}H-^{15}N NMR and MALDI–TOF mass spectrometry. The thermal properties were determined by TGA and DSC. In addition, the use of eugenol and vanilin monomers allows the preparation of multi-functional poly(ester-alt-thioether) bearing allyl or aldehyde groups in each repeating unit, respectively. Thus, poly(NHTL-*alt*-EGE), poly(NHTL-*alt*-VGE) and poly(NHTL-*alt*-SGE) scaffolds are reactive platforms that could be post-functionalized using a wide range of mild chemical reactions.

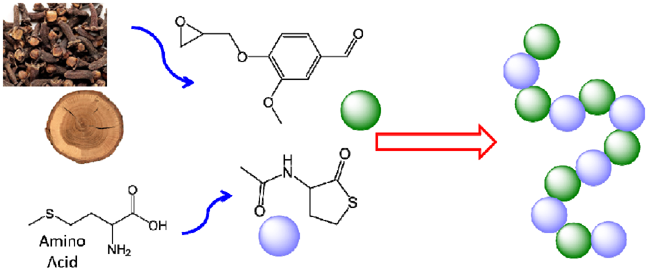

Figure 1. Anionic ring-opening polymerization of biobased aromatic epoxides with renewble N-acetyl homocysteine thiolactone.

Keywords: Anionic ring-opening copolymerization, alternating copolymer, eugenol, vanilin, bio-based polymers.

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High-throughput Synthesis and Reprocessing of Vitrimer-Thermoplastic Blends

L. M. A. Joosten[1,2], P. Cassagnau[1], D. Montarnal[2*], E. Drockenmuller[1*]

[1] *Univ Lyon, Université Lyon 1, CNRS, Ingénierie des Matériaux Polymères, UMR 5223,*
F-69003, Lyon, France
[2]*Univ Lyon, CPE Lyon, CNRS, Catalyse, Polymérisation, Procédés et Matériaux, UMR 5128,*
F-69003, Lyon, France
[*]*damien.montarnal@univ-lyon1.fr*
[*]*eric.drockenmuller@univ-lyon1.fr*

Cross-linked polymers are used in a wide range of high performance applications. While they have an outstanding performance, their recyclability is inherently limited to methods that are cost- and energy-intensive and often not desirable in terms of sustainability [1].
Recently, a new class of materials called covalent adaptable networks (CANs), were introduced [2]. CANs contain dynamic bonds controlled by exchange reactions that are activated by triggers such as temperature. The bond exchange mechanisms can be classified in dissociative and associative reactions. In dissociative networks a cross-link is broken before it is reformed, whereas in associative networks, also referred to as vitrimers, the bonds are reshuffled *via* reversible exchange reactions without compromising network integrity [3]. Even in absence of depolymerization, the fast bond reshuffling induces stress relaxation and allow the material to flow and be reshaped. Hence, vitrimers might be key elements in the future recycling of cross-linked materials, and in the necessary shift in the high performance materials sector to a more sustainable and circular economy. Numerous researches have been reported on various exchange reaction chemistries, as well as on the reprocessability of the thereby created vitrimers [4]. In order to allow the implementation of vitrimer production at industrial level, the upscalability of the process needs to be considered already in the design of the material. For example, exchange reactions are often either too slow at processing temperatures to allow the flow of fully cross-linked vitrimers in high-throughput processing devices such as extruders, or too fast to provide satisfactory creep resistance at service temperatures.
In order to bridge the gap between high-throughtput processability and performance during application we have synthesized vitrimer-thermoplastic blends by reactive extrusion, using commercially available low cost building blocks. The mechanical performance of these vitrimer-thermoplastic blends is governed by the morphology resulting from the reactive processing, which can be controlled by carefully selecting the formulation (*i.e.* chemical nature and composition) and processing parameters. We will present the thermomechanical properties of these new materials and high shear rheology demonstrating excellent (re)processability.

Keywords: vitrimers, covalent adaptable networks, reactive processing, polymer blends

Acknowledgments

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Investigation of the degradation of PVC and polymeric additives in commercial PVC compositions during multiple re-extrusion cycles – the first step towards improving repetitive PVC recyclability

M. Kaczorowski*, W. Thielemans

[1]*Sustainable Materials Lab, Department of Chemical Engineering, KU Leuven, Campus Kulak Kortrijk, Kortrijk, Belgium*
marcin.kaczorowski@kuleuven.be

Poly(vinyl chloride) (PVC) has been used commercially for almost 100 years, and still remains one of the most important polymers. Large-scale production and widespread application of PVC make it imperative to develop PVC compositions that could be recycled multiple times to decrease their environmental impact and guarantee multiple life-cycles for the same polymer. These PVC compositions must be stable not only during use, but also during processing. To achieve this, low molecular weight modifiers such as phthalates have been replaced with polymeric additives that are much less prone to leakage and degradation. Nevertheless, in order to improve stability and recyclability of PVC compositions, an in-depth study of their recycling behavior and the change in properties during reprocessing is required.

In this study, commercial PVC blends containing high molecular weight acrylic copolymer (several MDa) were investigated. Such polymer additives are used as process aids. To simulate 8 recycling steps, the PVC compositions were extruded up to 8 times and degradation of PVC and acrylic copolymer was studied using several experimental techniques including SEC-MALS, NMR, UV-VIS, TGA and rheological measurements. To characterize the PVC and acrylic copolymer additive in more detail, an extraction procedure was developed to separate them. Initial results suggested that PVC remains fairly stable during the reprocessing. Although an increase in double bond concentration was detected by UV-Vis, NMR and TGA results showed that it was not significant, which means that the degree of dehydrochlorination remains very low. On the other hand, a substantial decrease in the molecular weight of the acrylic copolymer was detected with SEC-MALS, which suggests that this processing aid is susceptible to chain scission (Fig. 1). The degradation of the modifier is likely responsible for the change in the rheological properties of the entire composition detected during capillary rheometer measurements. The results of these studies clearly show that in order to improve the recyclability of the tested PVC compositions, there is a need to develop new additives with better stability.

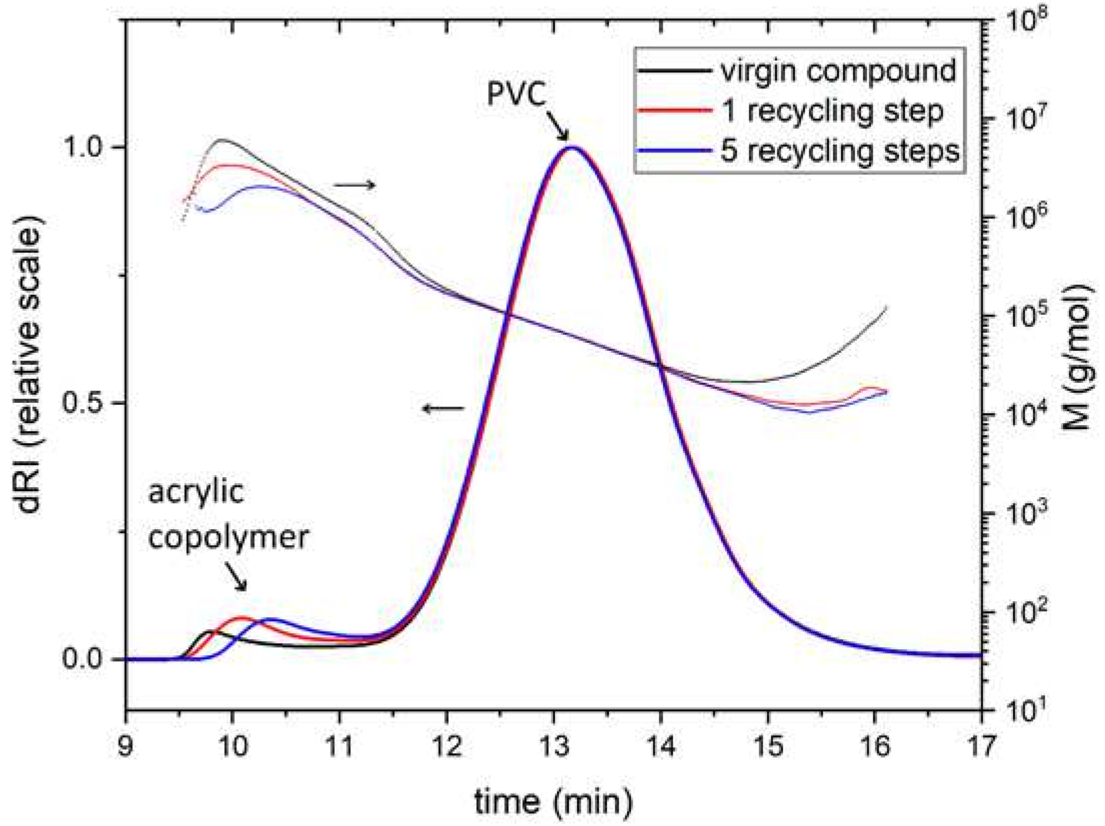

Fig. 1 Chromatograms and number-average molar masses of virgin and reprocessed PVC compositions.

Keywords: recycling, PVC, size exclusion chromatography, degradation

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Tall oil fatty acids based thermoset foams obtained using Michael addition reaction

M. Kirpluks[1]*, R. Pomilovskis[1], A. Fridrihsone[1]

[1]*Polymer Laboratory, Latvian State Institute of Wood Chemistry, Riga, Latvia*
mikelis.kirpluks@kki.lv)

The Michael addition reaction is a versatile synthesis type for linking electron-poor olefins to a wide range of nucleophiles. Michael addition reaction can create a variety of linear, graft, dendric, highly cross-linked and hyperbranched polymer networks [1]. Moreover, this chemical reaction can be used to obtain different type of materials, such as rigid foams, flexible foams and elastomers. The reaction between acrylates and active methylene group of β-ketoesters is quick and system cures at room temperature after mixing in the presence of strong base catalysts.

The renewable materials have been proven as a viable alternative for petrochemical products in polymer production. Tall oil-based materials have a further advantage as they are produced from second-generation bio-based feedstock as tall oil which is a side-stream product of cellulose manufacture [2]. In present study tall oil fatty acids have been valorised for Michael donor monomer synthesis and synthesised monomers have been used for different elastomer and rigid foam production.

Michael donor monomers have been obtained from tall oil fatty acid based polyols via transesterification reaction of polyol -OH groups with t-butyl acetoacetate ester. A thermoset material has been obtained by crosslinking the high functionality monomers with different acrylates. To obtain a foamed polymer structure a physical blowing agent was added to the formulation. Obtained material cured at room temperature. Proposed process could be viable alternative for common foamed thermoset polymers, such as rigid polyurethane foams that are applied as thermal insulation material in civil engineering and appliance industries. Physical and thermal properties of the developed polymers were studied using DMA, DSC, TGA, TMA and universal strength testing machines. The approximate chemical structure and containing functional groups of the developed polymer were determined using FTIR spectroscopy.

Keywords: polymer foams, tall oil, bio-based polymer

Acknowledgments
The Latvian Council of Science, project High bio-based content thermoset polymer foam development from plant origin oils (Bio-Mer), project No. lzp-2020/1-0385.

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Follow the format below for this purpose:

[1] Mather, B.D.; Viswanathan, K.; Miller, K.M.; Long, T.E. Michael addition reactions in macromolecular design for emerging technologies, *Prog. Polym. Sci.* **2006**, 31, 487–531. https://doi.org/10.1016/j.progpolymsci.2006.03.001.

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Glass fiber and powder filled polylactic acid composites - physical and structural properties

Teodoro Klaser[1*], Luka Pavić[1], Željko Skoko[2], Ana Šantić[1]

[1] *Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia*
[2]*Department of physics, Faculty of science, Bijenička cesta 32, 10000 Zagreb, Croatia*
[*]*tklaser@irb.hr*

An effective solution to the negative environmental impact of synthetic polymers includes their replacement with biopolymers (such as starch, cellulose, chitosan, zein or gelatin) derived from renewable resources. While biopolymers offer many advantages in terms of production and performance, but their unfavourable property is mainly related to their poor mechanical characteristics. To overcome this drawback and produce an environmentally friendly polymer with superior physiochemical properties, various composites with different combinations of matrix biopolymers and fillers have been developed in the last decade.

One of the most studied types of biopolymers is polylactic acid (PLA), a versatile biodegradable material derived from natural resources. PLA has great potential to replace traditional petroleum-based polymers, however, its brittleness and low thermal resistance still pose some limit from the applicative point of view. On the other hand, a glass-filled polymer is a mouldable composite material whose properties are enhanced by the addition of short glass fibres in a matrix of a polymer material. It is used to fabricate a wide range of structural components by injection or compression moulding.

In this study, PLA composites with different contents and types of glasses: bioglass, phosphate-based glasses containing various modifiers (alkali oxides and transition metal oxide) and glass waste from Kelteks company, in a form of glass fiber (GF) and glass powder (PG), were prepared with the aim to tailor their thermal, structural, mechanical and electric properties. The results of our thorough characterization of these materials using differential scanning calorimetry (DSC), X-ray diffraction, microscopy techniques, IR spectroscopy and impedance spectroscopy show that these novel PLA-GF and PLA-PG composites cover a wide range of physical properties.

Acknowledgments

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Photo-active chitosan-based hybrid films

R. Fernandez[1], S. Bonardd[2], J. Gutierrez[1], A. Tercjak[1], G. Kortaberria[1*]
[1]*University of the Basque Country, Donostia, Spain*
[2]*Universidad de la Laguna, La Laguna, Spain*
[*]*galder.cortaberria@ehu.eus*

Biodegradable films for food packaging have received increasing attention from the industry in recent years [1, 2]. Due to its extraordinary properties, chitosan has demonstrated to be an exceptional candidate for that kind of applications. In this study, chitosan-based films modified with an azopolymer and silver nanoparticles were prepared by solvent-casting. The quality and homogeneity of the samples was satisfactory and films with thicknesses of the order of 25 µm and of various sizes, with diameters ranging from 5 to 15 cm, were obtained. The developed hybrid films were characterized by several experimental techniques including: atomic force microscopy, attenuated total reflectance-Fourier transformed infrared spectroscopy, thermogravimetric analysis, ultraviolet–visible spectroscopy and water contact angle measurements. In addition, the mechanical properties of the samples were investigated. Specifically, the tensile strength and the elastic modulus were enhanced in the films modified with azopolymer and silver nanoparticles. Moreover, the developed films showed reversible induced birefringence properties, indicating that they could be used for optical storage applications.

Keywords: chitosan, azopolymer, silver nanoparticles, films

Acknowledgments

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Open porous magnetic microspheres as adsorbents

Stanko Kramer[1], Janja Stergar[2,3], Mitja Kolar[4], Irena Ban[2],Peter Krajnc[1]*

[1]*PolyOrgLab, Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova ulica 17, 2000 Maribor, Slovenia*
[2]*Laboratory of Inorganic Chemistry, Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova ulica 17, 2000 Maribor, Slovenia*
[3]*Faculty of Medicine, University of Maribor, Taborska ulica 8, 2000 Maribor, Slovenia*
[4]*Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna Pot 113, 1000 Ljubljana, Slovenia*
*stanko.kramer@um.si , *peter.krajnc@um.si*

The growth of the human population and the ever-increasing demand of food and different electronics (technological goods) severly impacts the environment [1]. Both agriculture and the electronics industry produce numerous compounds which are harmful for the environment. These compounds range from different pesticides and fertilisers to heavy metals and rare earth elements which are all necessary for our modern lives. However, these compounds severely impact the environment and human health [2]. Therefore, their removal from the environment should be of utmost importance. These substances can be removed through adsorption on different sorbents. A promising adsorbent are polymers as they can be produced from various monomers and be functionalised with various functional groups to enable the adsorption of specific compounds [3,4]. Additionally, introducing porosity into these polymers further enhances their adsorptive capabilities. One method that can be used to produce porous polymers is emulsion templating of high internal phase emulsions (HIPEs). HIPEs have an internal phase volume of at least 74.05% and after the polymerisation polyHIPEs are produced [5]. The monomers trimethylolpropane tris(3-mercaptopropionate) (TMPTMP) and trimethylolpropane triacrylate (TMPTA) were used in our case. The monomers were polymerised with LED light via thiol-ene click chemistry which generated porous magnetic microspheres. The incorporation of the MNPs enables the delivery of the microspheres to a target area and their subsequent removal by using a magnet. By combining all of these methods it is possible to remove pollutants from wastewater in a fairly simple and straightforward way.

Keywords: PolyHIPE, multiple emulsions, thiol-ene, magnetic nanoparticles, adsorption

Acknowledgments
This research was funded by the Slovenian Research Agency (Javna agencija za raziskovalno dejavnost Republike Slovenije; grant number P2-0006).

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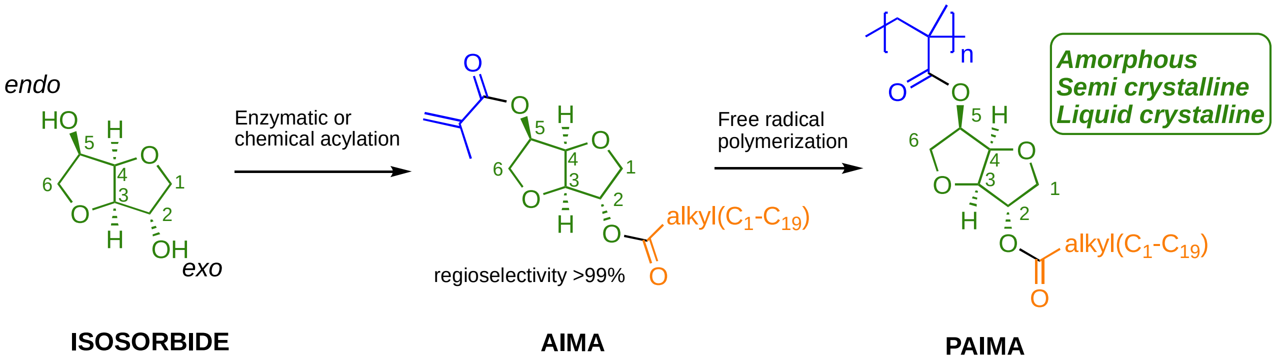
Poly(alkanoyl isosorbide methacrylate)s: From Amorphous to Semicrystalline and Liquid Crystalline Biobased Materials[1]

Siim Laanesoo[1], O. Bonjour[2], J. Parve[3], L. Matt[1], O. Parve[3] L. Vares[1] and P. Jannasch[1,2]
[1] *Institute of Technology, University of Tartu, Tartu 50411, Estonia*
[2] *Department of Chemistry, Lund University, Lund 221 00, Sweden*
[3] *Department of Chemistry and Biotechnology, Tallinn University of Technology, Tallinn 19086, Estonia*
**siim.laanesoo@ut.ee*



Rising environmental concerns have made it urgent to replace today's fossil-based polymeric materials by more sustainable alternatives.

Isosorbide, produced from a biomass in a commercial scale, is considered as a potential building block to replace fossil based counterparts in many applications. Structurally, isosorbide is a chiral bicyclic compound with two non-equivalent secondary hydroxyl groups, which can be modified in a regioselective manner.

In this work, we present a highly regioselective (>99%) synthesis of isosorbide monomethacrylate monomers (AIMAs) with different pendant linear alkanoyl chains (lengths from C2 to C20). The essentially complete regioselectivity is achieved by using a biocatalytic acylation developed by us.[2] Next, these isosorbide monomethacrylates were polymerized by conventional free radical polymerization to afford a series of 12 poly(alkanoyl isosorbide methacrylate)s (PAIMAs).

The polymers were thoroughly characterized by NMR spectroscopy, size-exclusion chromatography, optical microscopy, melt rheology, and thermal analysis. We discovered that the polymer properties are readily tunable by adjusting the length of the pendant alkanoyl chain. Depending on the chain length and regiochemistry, the PAIMAs formed either fully amorphous, semi crystalline or liquid crystalline materials. Consequently, this family of isosorbide polymethacrylates with tunable properties potentially presents biobased alternatives in various applications.

Keywords: biobased polymers, isosorbide, polymethacrylates

Acknowledgements

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For a sustaiNable and EuropeaN valUe chain of PHA-based mateRials for high-volume consumer products (NENU2PHAR project)

Carole Lainé[1*], Pierre Lemechko[2], Stéphane Bruzaud[1]

[1]*Université de Bretagne-Sud, Institut de Recherche Dupuy de Lôme, UMR CNRS 6027, 56321 Lorient, France*
[2] Institut Régional des Matériaux Avancés (IRMA), 2 allée Copernic, 56270 Ploemeur, France
**Carole.laine@univ-ubs.fr / www.irdl.fr*

Bio-based biodegradable plastics clearly offer a valuable alternative to non-biodegradable, petroleum-based plastics. Nevertheless, high costs and low yields associated with their production, together with their dependence on sugar or oilseed feedstock, are significant obstacles which still remain to be tackled.

The goal of NENU2PHAR is to set up a new European value chain of PHA-based bio-plastic products from a sustainable non-food bio-source with an acceptable end of life. To reach such ambitious target the NENU2PHAR project will have 5 main objectives (Fig. 1)

The presentation will summarize how NENU2PHAR consortium (www.nenu2phar.eu) will develop a PHAs stream integrated in a circular economy concept, from the production to the biodegradability or recyclability of plastic products to new compounds. Special focus on PHA fermentation using micro-algae as substrate , eco-friendly PHA extraction routes and innovative PHA-based formulation will be given.

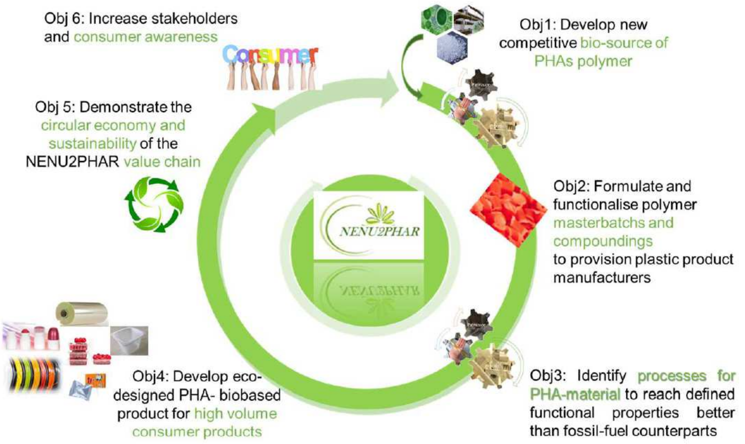

Figure 1 NENU2PHAR concept based on a new PHA value chain on circular economy

Keywords: polyhydroxyalcanoates, micro-algae, biobased plastic, sustainable polymer, biodegradability

Acknowledgments *This project has received funding from the Bio Based Industries Joint Undertaking (JU) under grant agreement N 887474. The JU receives support from the European Union's Horizon 2020 research and innovation programme and the Bio based Industries Consortium.*

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Scalable, biodegradable dextrin-based elastomers for triboelectric nanogenerators

Xiaohong Lan, Wenjian Li, Chongnan Ye, Laura Boetje, Jur van Dijken, Albert Woortman, Katja Loos

Macromolecular Chemistry & New Polymeric Materials, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747AG, Groningen, The Netherlands

x.lan@rug.nl

Elastomeric materials have attracted tremendous attention for soft electronics because of their high stretchability, light weight, and low cost. Although elastomer-based smart life holds the promise of enriching the lives of humans, it produces electronic waste (e-waste). In the field of triboelectric nanogenerators (TENGs), severe wear and degradation driven by inevitable friction are ubiquitous, posing significant durability and sustainability concerns. [1,2] However, no reported materials can achieve good stretchability, scalability, as well as biodegradability simultaneously. Here we show for the first time, a supersoft elastic transparent material (ASSET) synthesized from dextrin with good scalability (20 g scale), stretchability (250%), and biodegradability (up to 80%) (Figure 1). Dextrins are a group of low-molecular-weight carbohydrates produced by the hydrolysis of starch. They bear three hydroxyl groups in one repeating unit and are therefore a suitable building block for aliphatic polyesters. In this work, we synthesized a dextrin-based elastomer by a three-step reaction, and the effect of side chains on the properties of the network were experimentally investigated. In the first step, a dextrin ester (DE) with amphiphilic properties was synthesized by introducing 10-undecenoic acid to the hydroxyl groups in dextrin. Owing to its amphiphilic properties, the DE can be dissolved in almost all kinds of lactones, and acts as an initiator for the ring-opening polymerization of lactone, making the whole process solvent-free. Finally, ASSET was formed by crosslinking this polylactone grafted dextrin ester (DE-CV) with PEG dicarboxylic acid. Based on ASSET, a soft triboelectric nanogenerators (TENGs) that enables tactile sensing was fabricated. The sustainable, ASSET-based TENGs could function well in vertical contact-separation modes, with excellent electrical potential as high as 50 V, and a high cyclability of 1000. Upscaling to 20 g experiments verified the practical industrial applications and support for a sustainable plastic circular economy. This material is a step towards soft, sustainable robotic and electronic systems, and the tunability of the elastomer facilitates the further improvement of electrical outputs, benefiting numerous applications of human-interactive triboelectrification.

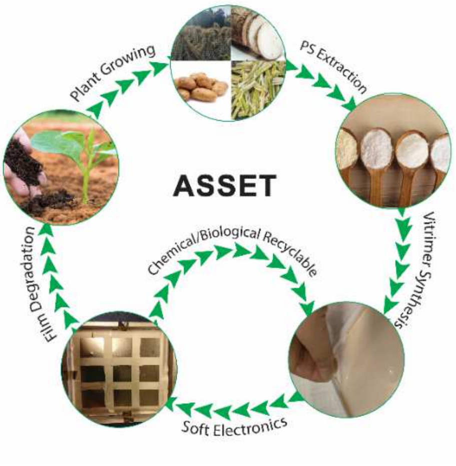

Figure 1 A schematic demonstration of how ASSET is produced and recycled

Keywords: dextrin, elastomers, biodegradable, caprolactone, TENG

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Straightforward preparation of micron-sized polyester particles through the use of block copolymers generated by transesterification *in situ*.

Jeppe Madsen[1*], Anders E. Daugaard[1]

[1]*Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark*
**pjma@kt.dtu.dk*

Block copolymers are commonly used to stabilise particles in a wide range of applications.[1], [2] However, although block copolymers can typically be tailored to stabilise particles of most polymers, their synthesis can be complicated and labour-intensive. This can limit their use as stabilisers compared to for example commercially available detergents.
Here we exploit a one-pot procedure that uses a transesterification reaction between an alcohol-terminated stabilising poly(ethylene oxide) block and a range of commodity main-chain polyesters and a polycarbonate to generate a mixture of block copolymers and homopolymers (see scheme 1).[3]

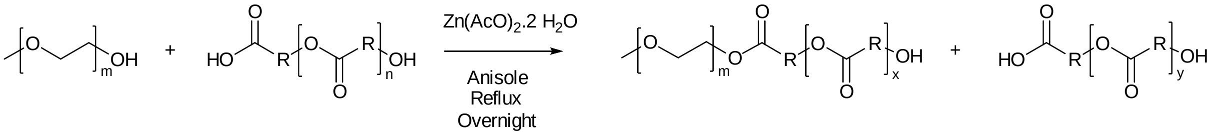

Figure 1: Transesterification between polymeric alcohol and polyester

Subsequent dispersion of the polymer solution into water followed leads to formation of well-defined droplets that retain their size after removal of the solvent and are easily re-dispersed (see Figure 2).
The versatility of the reaction allows easy formation of well-defined micron-sized particles of a range of commonly used polymers. The approach can be expanded to prepare fluorescently labeled particles through the use of fluorescent alcohols or carboxylic acids. These particles are currently being evaluated as model particles for microplastics to evaluate their fate in biological environments.

Polymer	Diameter (dry) / µm
Polyethylene terephthalate, PETG	2,7 ± 0,60
Polycaprolactone, PCl	2,7 ± 0,80
Polycarbonate, PC	5,9 ± 3,4
Polylactic Acid, PLL	3,0 ± 1,5

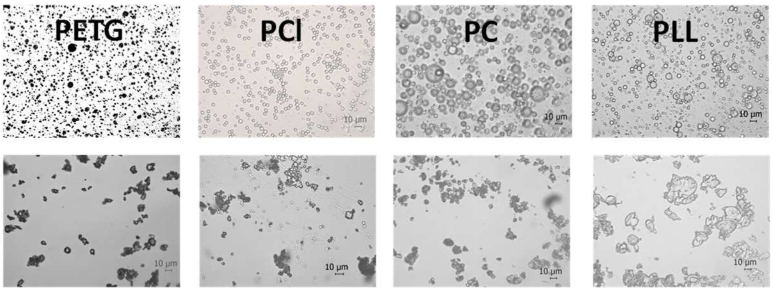

Figure 2: Table: Particle diameter after drying determined by microscopy. Microscopy images of : Top row: As-dispersed particles. Bottom row: Dried particles

Keywords: block copolymers, polyesters, micrometer particles

Acknowledgments
Innovation Fund Denmark is acknowledged for funding

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Polyamide recovery and recycling from textiles through selective dissolution with calcium chloride/ethanol/water mixtures

A.P. Manian*, F. Krägeloh, P. Mayer, A. Mahmud-Ali, T. Bechtold, T. Pham

Research Institute of Textile Chemistry/Physics, University of Innsbruck, Dornbirn, Austria
**avinash.manian@uibk.ac.at*

Calcium chloride/ethanol/water (CEW) mixtures act as polyamide solvents [1], and do not exert a deleterious effect on other textile fibers such as wool, cellulose and polyurethane. Thus, the CEW mixture is potentially a solvent for selective dissolution and recovery of polyamide from fiber blends [2]. The dissolved polyamide may be precipitated with addition of water. We report on investigations of the CEW system for recovery of polyamide 6,6 fibers from blends with cellulose fibers. The effects of component proportions in the CEW mixture, the presence of cellulose, and the solvent-to-fiber mass ratio were examined on the extent of polyamide recovery. The recovered polyamide was investigated for presence of solvent residues, and their thermal behavior was analyzed to assess suitability for respinning into fibers for textile use. The load-elongation profiles of the cellulose fibers were measured to determine if there was any fiber deterioration. The results of these investigations will be presented, alongwith issues to be addressed in the ongoing research as well in the textile sector as a whole for improving recyclability and thereby circularity.

Keywords: recycling, polyamide, dissolution, circularity

Acknowledgments

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Water Treatment facilitated with Renewable Polymer Nanofibrils

A. Mautner[1*]

[1]*Polymer and Composite Engineering (PaCE) group, Institute of Materials Chemistry and Research, Faculty of Chemistry, University of Vienna, Währinger Straße 42, 1090 Vienna, Austria*
[*]*andreas.mautner@univie.ac.at*

Safe and clean potable water is one of the most precious commodities on this planet, responsible and necessary for all living organisms, with its significance constantly increasing. This was also acknowledged by the UN Sustainable Development Goals putting clean water and sanitation among the most important issues humankind faces. Cleaning water is frequently performed with polymer materials, for instance in membranes or adsorbents, that exhibit high efficiency combined with easy processes. However, best performing materials are commonly based on non-renewable, non-biodegradable resources. Hence, regeneration operations are essential but often connected to high resource as well as energy demands and hence challenging. Furthermore, at the end of their use, disposal of saturated or exhausted materials constitutes a vast issue. Thus, technologies for water remediation, e.g. adsorbents or membrane and filter processes, being based on renewable materials, in particular nanofibrillar polysaccharides (NFPS), for instance cellulose nanomaterials [1] or chitin nanofibrils [2, 3], would also address another Sustainable Development Goal, responsible consumption and production.

In recent years, the interest in using NFPS in the domain of water treatment has seen a tremendous development. NFPS were initially proposed as adsorbent materials but are also appplicable in membrane and filter set-ups. In particular the use of nanopapers made from nanofbrillar materials for ultra- or nanofiltration as well as adsorptive filtration was demonstrated to be a compelling approach. However, several challenges surfaced that obstructed the wide-spread use of NFPS in such applications, in particular on large scale. Whereas costs of NFPS have steadily decreased, technical issues such as dewatering of NFPS as well as low permeance and adsorption capacities are still problematic. In terms of size-exclusion filtration, the performance of NFPS membranes and filters is still limited due to irregularities in the NFPS network established.

Many of those obstacles have succesfully been tackled by various approaches. For instance, thin active filtration layers of NFPS are very effective in terms of water permeance but also allow for high adsorption capacities in case of adsorbent membranes and filters. Such architectures were recently established already on pre-industrial scale. Furthermore, highly porous structures or the use of functionalized NFPS were found to be highly effective. Membrane fouling, which is an important issue in filtration applications, has also been demonstrated to be mitigated with the use of certain types of NFPS and antimicrobial membranes been established.

Keywords: water treatment, nanocellulose, fungal chitin

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Bio-based photocurable piezo- and thermoresistive sensing materials based on acrylated epoxidized soybean oil

C. Mendes-Felipe[1,2,*], P. Costa[3], I. Roppolo[2,4], M. Sangermano[2], S. Lanceros-Mendez[1,5]

[1]*BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain*
[2]*Dipartimento di Scienza Applicata e Tecnologia (DISAT), Politecnico di Torino, 10129, Torino, Italy*
[3]*Center of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal*
[4]*Center for Sustainable Future Technologies, Istituto Italiano di Tecnologia,10144 Torino, Italy*
[5]*Ikerbasque, Basque Foundation for Science, 48009 Bilbao, Spain*
[*]*cristian.mendes@bcmaterials.net*

Bio-based photocurable polymers are increasingly demanded as environmentally friendly materials for advanced applications. In fact, the consumption of non-renewable energy and the carbon dioxide emission can be reduced through the use of natural-based materials, being bio-based thermoplastics widely available but bio-based thermosets still limited, representing thus an interesting challenge for materials research. In this scope, vegetable oils, terpenes and carbohydrates are among the most used monomers for the manufacture of bio-plastics [1]. In particular, oils obtained from vegetables are the most important renewable feedstock employed in the synthesis of photocurable bio-based materials and soybean oil stands out as it is one of the vegetable oils with largest global production volumes, most economical prices for large-scale use, presents good mechanical properties, low curing time in the presence of photoinitiator and high thermal stability [2,3].

Together with functional fillers, these bio-based photocurable polymers can represent a next step for the generation of functional and active smart materials. Among fillers, carbon-based materials are particularly suitable for developing multifunctional sensing materials, as they present thermal stability, low toxicity, flexibility and high electrical and thermal conductivities. Polymer-based composites containing carbonaceous materials have been widely used in applications such as temperature, humidity, pressure or deformation sensors [4]. However, there are not cases in which carbon-based fillers have been combined with photocurable bio-based resins in order to obtain sensing materials with improved sustainability, addressing therefore, both the functional and environmental needs of current society.

In this way, this work reports on acrylated epoxidized soybean oil (AESO) mixed with different amounts of reduced graphene oxide (rGO) up to 6 wt.% in order to obtain UV-curable piezoresistive and thermoresistive materials. It is shown that the addition of rGO to AESO hinders the curing process, but maintains always high double bond conversions. The filler dispersion along the composites characterized by scanning electron microscopy together with the crosslinking degree measured with dynamic mechanical analysis (DMA) proved to be key factors on the interesesting mechanical, electrical and both piezo- and thermo-resistive behaviors obtained. The UV-curable composites with piezoresistive and thermoresistive responses suitable for applications thus obtained, are characterized by gauge factors around 26 for deformations up to 2% and maximum thermoresistive sensitivity of S = 0.43, giving similar values to the ones obtained for petroleum-based materials.

Keywords: Bio-based resins, Reduced graphene oxide, Polymer composites, UV-curing, Piezoresistive

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Influence of polyolefin cross-contaminations on fracture resistance

M. Messiha[1*], A. Frank[1], J. Hinszica[1], M. Bredács[1], G. Oreski[1], G. Pinter[2]

[1]*Polymer Competence Center Leoben GmbH, Leoben, Austria*
[2]*Montanuniversitaet, Leoben, Austria*
[*]*mario.messiha@pccl.at*

Polyethylene (PE) and Polypropylene (PP) are regarded as the most popular plastics of our time [1,2]. While conquering large fields of the plastic market, particularly in the field of single use plastics, such as packaging, or long-term structural applications, such as pipe systems, the increasing production of those polymers and the sub-sequential enormous amount of waste generates an aspiration for recycling. This, however, has raised serious discussions throughout the globe evoking recommendations for or against the use of post-consumer or post-industrial recycled plastics (also known as non-virgin materials). Implementing a non-virgin material in a pipe system is usually performed via blending approaches or in form of sandwich structures. In spite of extensive studies concerning fracture mechanical lifetime prediction of PE and PP pipes, the influences of non-virgins on lifetime relevant properties of virgin materials, such as the Slow Crack Growth (SCG) resistance, have not been fully investigated. Therefore, a comprehensive study was conducted by examining the influence of different polyolefin cross contaminations on the SCG performance. Blends of virgin PE pipe grades (PE100 and PE80) with different contents of homo- and block-copolymer PP (PP B and PP H), a blow molding PE HD, and a recycled first-generation PE HD pipe were manufactured and analyzed with the cyclic Crack Round Bar (CRB) test. Results demonstrate the negative impact of an already small amount of polymeric impurity, which leads to a significant reduction of the SCG resistance. Already 5% cross-contamination evokes a dramatic decrease of SCG resistances of up to 40 %, where the highest reduction is caused by blending with PP B. Furthermore, the importance of determining the highest possible non-virgin material content in polyolefin pipes, which leads to no significant lifetime reduction, is highlighted. Striving for more circular economy, as has been set out by the European Union [1], the use of a maximum amount of recycled materials in pipe applications without altering the lifetime would significantly contribute to the global plastic waste problem.

Keywords: *slow crack growth, cracked round bar test, recycling, circular economy*

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Functional polymers from renewable monomer Tulipalin A

J. Mosnáček[1,2*], F. Pippig[1], J. Kollár[1], M. Danko[1], D. Moravčíková[1], S. Lenka[1]

[1]*Polymer Institute, Slovak Academy of Sciences, Dubravska cesta 9, 845 41 Bratislava, Slovakia*
[2]*Centre for Advanced Materials Application, Slovak Academy of Sciences, Dubravska cesta 9, 845 11, Bratislava, Slovakia*
[*]*jaroslav.mosnacek@savba.sk*

Recently, a possibility of using natural products to replace petroleum-based raw materials in large commodity markets, such as plastics, fibers, and fuels, has been broadly studied. For example, several compounds containing an α-methylene-γ-butyrolactone moiety were found and isolated from various plants. The simplest member of these butyrolactones, α-methylene-γ-butyrolactone (MBL), know also as a Tulipalin A, found in tulips, is the most studied monomer and has already successfully been polymerized by various radical polymerizations.

Tulipalin A was used also as a monomer for the preparation of particles via heterogeneous polymerization process. According to experimental conditions nearly monodisperse polymer particles of 0.15 to 0.65 µm were produced and pendant lactone ring could be used for particles surface postfunctionalization.

Hydrogels, based on 4-hydroxy-2-methylenebutanoate, prepared from Tulipalin A, were synthesized by free radical aqueous polymerization [1,2]. Hydrogels showed equilibrium degree of swelling in the range $2\times10^3 - 7\times10^4$ % in distilled water. Water absorption capacity and viscoelastic properties, including G´ and G´´ were significantly influenced by monomers ratio and crosslinker content.

Tulipalin A was used as a comonomer with CL in ROP under various feed ratios in order to prepare functional copolyesters containing pendant double bonds in their structure. $Al(OiPr)_3$ was used as a cheap and commonly available catalyst for anionic ROP [3]. Upto 25 mol% MBL units allowed incorporation of high content of double bonds into the copolyester chain, while their post-functionalization is possible by either thermal or photochemical thiol-ene reactions.

Poly(amido amines) were succesfully prepared by polyadition of Tulipalin A with diamines. The polymerization is based on combination of Michael reaction of amine with double bond of the Tulipalin A together with lactone ring opening by amine under formation of amide in main chain and pendant hydroxyethyl groups.

Keywords: superabsorbent hydrogels, polymeric particles, polyesters, poly(amido amine)s

Acknowledgments

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New eco-friendly composites fully obtained by the recycling of exhausted coffee capsules: thermo-mechanical characterization, life cycle assestment (LCA) and cost-analysis

A. Nanni[1*], M. Colonna[1], G. Liberati[1], A. Bonoli[1], M. Messori[2,3]

[1] *Department of Civil, Chemical, Environmental and Material Engineering, University of Bologna, Via U. Terracini 28, 40131, Bologna, Italy*
[2] *INSTM, National Consortium of Material Science and Technology, Via Giuseppe Giusti 9, 50121, Firenze, Italy*
[3] *Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Torino, Italy*
[*] *Corresponding Author's E-mail address: alessandro.nanni18@unibo.it*

Exhausted plastic capsules, typically formed by a shell-case made of polypropylene (PP), a protective film in PP and polyesters, a bottom paper filter and spent coffee grounds (SGC), are nowadays destined to landfill or incineration since the selective recovery of each component would require expensive treatments.

In the first part of this study, a simple and industrially feasible sorting step has been adopted to separate approximately 93% of the SGC from the rest of the capsules without using water or solvents. Separated SGC have been subsequently melt mixed in different percentages (10% and 20% wt.) with the same empty grinded capsules by the means of a laboratory internal mixer obtaining new composites formed by the different parts of the same waste. The compounded pellets have been injected moulded and obtained samples have been compared with pristine neat PP and recycled neat PP in terms of thermo-mechanical properties (TGA, DSC, tensile test, DMTA, creep and recovery strain tests), physical-chemical properties (FT-IR and water uptake tests), morphology (SEM) and rheological behaviour (MFR) to evaluate the SGC filler effect and to determine the degradative contributes due both to lifetime and to the recycling process. In addition, two coupling agents - 3-aminopropyltriethoxy-silane (SIL) and maleic anhydride grafted PP (PPgMA) - have been also tested at 2%wt. and several micro-mechanics models have been fitted on experimental data. Results have shown the SGC ability to improve the tensile (+4-24%) and storage moduli (+20-50%) as well as the creep resistance (+3-14%) and the creep recovery (+4-7%) of the recyled capsules in a way almost proportional to the SGC loading. In parallel, the use of 20%wt. of SGC particles has counterbalanced and restored the loss of processability of the recycled capsules due to degradation and the MFR values (11 g/10') of the 20SGC-based formulations have been similar to those of pristine neat PP (9 g/10'). Among all the tested formulations, EP 20SGC 2PPgMA sample has exhibithed the best overall results in terms of both mechanical properties and melt processability [1].

In the second part of the work, the EP 20SGC 2PPgMA sample has been fabricated using a twin-screw extruder to evaluate the scalability of the proposed formulation and the effect of virgin PP (10 and 20%wt.) on the processability and on the final properties has been also considered. Extruded pellets have been injected moulded to obtain new recycled coffee-based capsules shells, in perfect accordance with the principles of the circular economy.

Finally, in the third part of the work, the LCA analysis (performed with the software SimaPro) and the cost-analysis (performed with the software SuperPro Designer) of the processes involved for the recycling of the coffee capsules and for the fabrication of the SGC-based composites have shown that the presented system could represent a cost-effective, eco-friendly and industrially feasible solution.

Keywords: Recycling, Bio-composites, Thermo-mechanical properties, Scaling-up, Life Cycle Assessment

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Bio-based vitrimers from poly(butylene succinate): A kinetics study of vitrimerization reactions in the melt

C. Panagiotopoulos, D. M. Korres and S. Vouyiouka*

Laboratory of Polymer Technology, School of Chemical Engineering,
National Technical University of Athens, Zographou Campus, 157 80 Athens, Greece
*mvuyiuka@central.ntua.gr

Vitrimers, pioneered by Leibler and co-workers in 2011, constitute a very new subcategory of dynamic crosslinked macromolecular structures (cited also as recyclable thermosets), that bridge the gap between thermosets and thermoplastics, since they combine ideally the processability and malleability of thermoplastics with the dimensional stability and robust mechanical properties of thermosets [1,2]. The dynamic covalent bonds present in vitrimers can undergo *associative* rapid exchange reactions upon heat or stress stimuli, permitting network topological rearrangements and rendering the relevant materials smart ones. The current study investigates an efficient, solvent-free method to synthesize bio-based vitrimers using a commercial bio-based and bio-degradable polyester, poly(butylene succinate), PBS. PBS was chosen since succinate polyesters can be produced from bio-based succinic acid and are considered promising alternatives to polyolefins [3]. A two-step process was followed; the first step involved the preparation of the prepolymers by melt mixing PBS with the crosslinker (diglycidyl ether of bisphenol A, DGEBA or glycerol) and the transesterification catalyst (Zinc(II) acetylacetonate hydrate, $Zn(acac)_2$) in an internal mixer. The second step (vitrimerization) comprised crosslinking reactions of the homogenous mixtures in the melt state at different temperatures (150, 160 and 170 ˚C), resulting in the formation of a dynamic crosslinked network, with epoxy or glycerol moieties serving as the crosslinkers. By tuning the crosslinker content (0 − 10% mol with respect to PBS repeating unit) and the ratio of Zinc(II) catalyst to crosslinker (0 to 1), tailor-made vitrimers were prepared with high insolubility (gel fraction up to 86 %). The chemical reactions scheme was constructed and the kinetics were studied by monitoring changes in end group (COOH, OH, epoxy) and backbone linkages (ester, ether moities) concentrations via ATR-FTIR analysis. The apparent reaction rate constants and Arrhenius parameters were calculated for each vitrimerization reaction. The overall kinetics study was performed under different synthesis conditions, i.e. reaction temperature and time, molar ratio of crosslinker and catalyst, while determing the rate-controlling steps and variables.

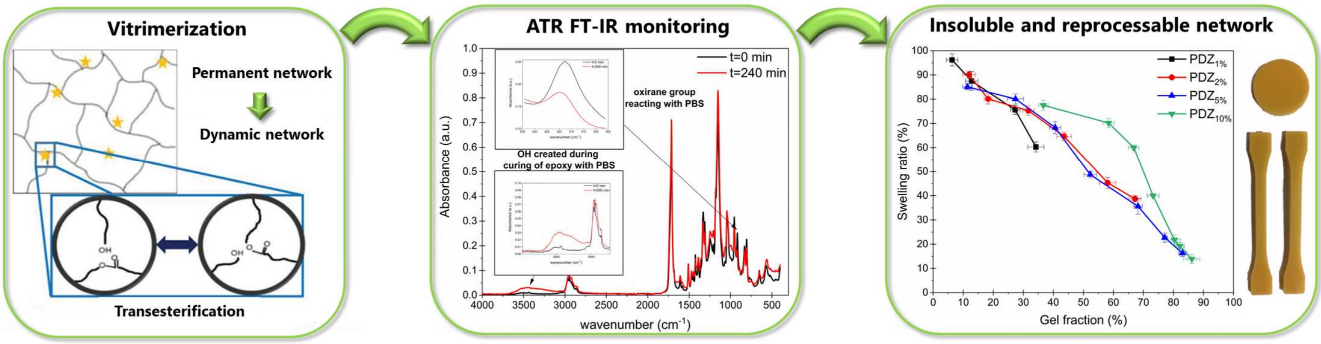

Figure. Overview of synthesis and kinetics study via ATR-FTIR for PBS-based vitrimers

Keywords: poly(butylene succinate), epoxy-based vitrimers, polyesters, crosslinking, recycling

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Biodegradable microencapsulation system for essential oils using a cellulose acetate shell

Joana F. Parente, Vânia I. Sousa, Carlos J. Tavares*

Centre of Physics of the Universities of Minho and Porto, Campus of Azurém, 4804-533 Guimarães, Portugal
**ctavares@fisica.uminho.pt*

Environmentally friendly alternatives have aroused wide interest in scientific and industrial development. Biodegradable polymeric materials have been the most promising solution for microencapsulation systems allowing the sustained, controlled and delayed release. Many industrial sectors have a high interest in microencapsulation associated with the controlled diffusion of compounds [1,2]. This process allows the optimization of products performance, as it promotes the stability of encapsulated active compounds, preserving their chemical and physical properties for a longer period. Furthermore, this phenomenon facilitates their handling, due to the absence of direct contact with the encapsulated active compounds [3,4]. Essential oils are unstable and highly susceptible to changes caused by external factors (light, temperature, oxygen and humidity) [5]. As the high volatility and reactivity of these compounds represent challenges for their application, microencapsulation emerges as an alternative to maintain the functional and biological characteristics of these compounds and to control their release [6]. Cellulose Acetate (CA) microcapsules were developed and allowed the encapsulation of several essential oils (citronella, eucalyptus, cajeput, lemon) with antimicrobial and anti-repellent properties. The morphological characterization of CA microcapsules show that they have a spherical shape and a smooth structure (Figure 1). Thermal analysis allowed to conclude that these microencapsulation systems have a high thermal stability. Applications for these microcapsules are being studied in different matrices to be included in different industries such as textile, automobile and agrochemical sectors.

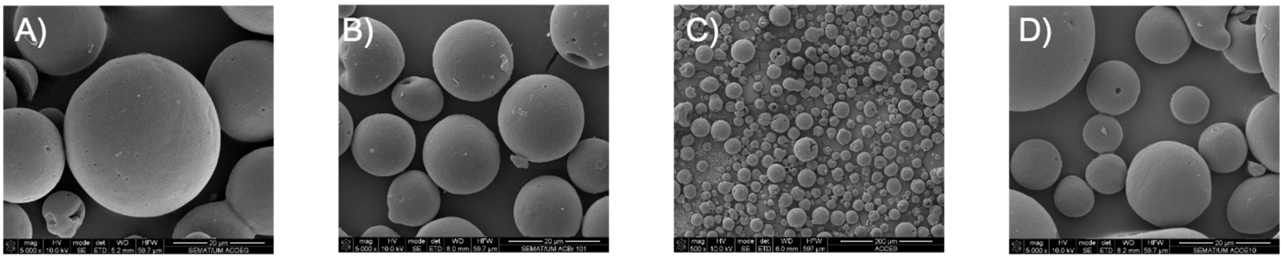

Figure 1: Scanning electron microscopy micrograpts of cellulose acetate microcapsules containing essential oils: A) Eucalyptus, B) Citronella, C) Lemon and D) Cajeput.

Keywords: biodegradable microcapsules, microencapsulation, biodegradable polymers, essential oils, controlled release

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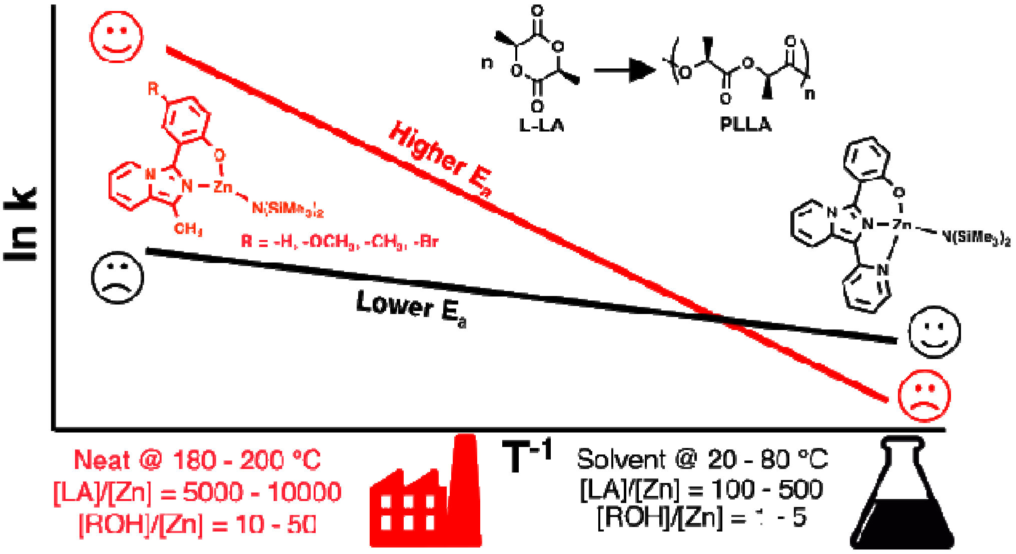
New Zn(II) Catalysts for the ROP and the Upcycling of L-Lactide: Mild Laboratory and Industrial Conditions Make a Difference

M. C. D'Alterio,[1] I. D'Auria,[1] L. Gaeta,[1] C. Tedesco,[1] S. Brenna,[2] C. Pellecchia[1,*]
[1] *Dipartimento di Chimica e Biologia "A. Zambelli", Università di Salerno, Fisciano (SA), Italy*
[2] *Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, Como, Italy*
[*] *cpellecchia@unisa.it*

Poly(lactic acid) (PLA) is one of the best candidates as a sustainable plastic material for a circular economy [1], being biodegradable, bio-based, recyclable and displaying good thermal and mechanical properties. The industrial production of PLA is mainly based on the Ring Opening Polymerization (ROP) of L-lactide (L-LA) promoted by Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) in a continuous solvent-free process operating at temperatures between 180-200 °C, above the melting point of the resulting isotactic polymer [2].

Despite the huge efforts in the research of alternative catalysts based on less toxic metals, resulting in a plethora of highly active catalysts under laboratory mild conditions, very few candidates can compete with $Sn(Oct)_2$ under industrially-relevant conditions.



We report a family of new Zn(II) complexes (see figure above), bearing variously substituted monoanionic $[N,O^-]$ (Imidazol[1,5-*a*]pyrid-3-yl)phenol ligands, as catalysts for the ROP of L-LA under both mild (20°C, solvent) and industrially relevant (190 °C, in the melt, technical grade unpurified monomer, very low catalyst loading) conditions.

Interestingly, the best performing catalyst under mild conditions is the worst performing under harsh conditions, and, on the contrary, the less active catalysts under mild conditions compete well with $Sn(Oct)_2$ under industrially-relevant conditions. Kinetic and DFT mechanistic investigations shed light on the non-trivial role of the 2-pyridine substituent in the catalytic performances at different temperatures.

Preliminary depolymerization tests on commercial PLLA samples suggested that the new catalysts can also be suitable candidate for chemical recycling of PLA under mild conditions [3].

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Polybenzoxazines: a chemical platform to elaborate bio-based degradable and recyclable vitrimers

A. Adjaoud[1,2], L. Puchot[1], P. Verge[1]*

[1] *Luxembourg Institute of Science and Technology, Esch-sur-Alzette, Luxembourg*
[2] *University of Luxembourg, Esch-sur-Alzette, Luxembourg*

Over the past few decades, the apogee of industrialization has led to a compelling increase in the consumption of thermosets worldwide, resulting in an abundant source of wastes which cannot be recycled or repaired. To address this issue, reversible dissociative or associative bonds have been inserted within the chemical structure of thermosets to create covalent adaptable networks (CANs), enabling self-healability or recyclability. In 2011, Leibler and co-workers successfully introduced dynamic covalent bonds in thermoset polymer networks and developed the first "vitrimer", combining the antithetical properties of a thermoplastic and a thermoset [1]. At service temperatures, vitrimers behave like a traditional thermoset with high mechanical properties, chemical resistance, and insolubility. At higher temperatures, they display the fluidity and the reprocessing ability of a thermoplastic. Among the different strategies and methodologies used to conceive vitrimers, the dynamic transesterification reaction (TER) occurring between ester bonds and aliphatic OH is the most representative chemistry for vitrimers. Catalysts are required to trigger the dynamic exchanges. They can be either external (the most common is zinc acetate) or internal. The latter is generally achieved by introducing tertiary amines in the chemical structure of the vitrimers. [2][3]

Among the different chemical structures suitable to combine the specifications of traditional thermosets to recyclability, healability and degradability, polybenzoxazines (PBZ) have recently shown their significance. PBZ are monocomponent thermosets constituted by an abundant number of tertiary amines, suitable to design vitrimers relying on TER. They are also a promising alternative to phenolic and epoxy resins due to their unique mechanical and thermal properties, such as a high glass transition temperature, near-zero shrinkage upon polymerization, and high char yield polymers. [4]

This presentation will illustrate the strategies to conceive degradable, self-healable and recyclable polybenzoxazine vitrimers from bio-based materials such as polyethylene glycol, isosorbide, lignin-like materials, with high thermal and mechanical properties (figure 1). [5][6]

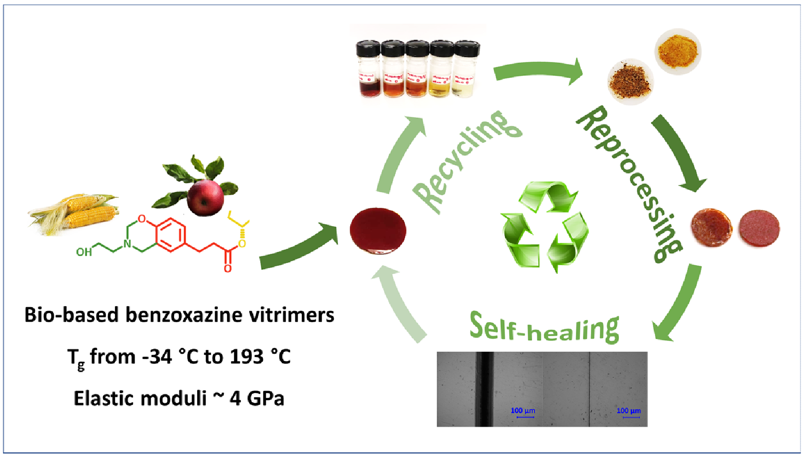

Figure 1. Schematic representation illustrating Polybenzoxazines and their properties

Keywords: Vitrimers, Polybenzoxazines, degradable, recyclable, biobased

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Synthesis of Sugar-Based Polymers From Reactive Natural Low Transition Temperature Mixtures

Gabriel Duaux, Etienne Fleury, Daniel Portinha*

Université de Lyon CNRS, UMR 5223, INSA Lyon, IMP@INSA Villeurbanne F-69621, France
*Daniel.portinha@insa-lyon.fr

Deep Eutectic Solvents (DES) [1] or Low Transition Temperature Mixtures (LTTM) [2], have appeared as a new class of solvents obtained by mixing two or more substances, which form mixtures with melting point or glass transition temperature much lower than that of their individual components. Like ionic liquids, many of such solvents have numerous attractive physicochemical properties (chemical and thermal stability, non-flammability, low volatility high electrical conductivity etc..) and in the field of polymers, present the potential of replacing conventional organic compounds as solvents, plasticizers, additives etc. Moreover, similarly to functional ionic liquids, some DES/LTTM have been designed such as one over their components act as a monomer (DEMs : Deep Eutectic Monomers) [3], opening the scope for a large variety of novel possible uses of these renamed Deep Eutectic Systems. More recently, combinations of agro-based, natural, metabolites or renewable components have appeared and been named Natural DES (NaDES) [4] or LTTM (NaLTTM) [2], which undoubtedly represent a very interesting family of raw materials to be developed in the framework of green chemistry. So far, the academic and industrial uses of NaDES have mainly concerned the extraction of molecules of interest for food, pharmaceuticals, and cosmetics or as solvent for organic synthesis. In this communication, the synthesis of carbohydrate polymers from Natural Low Transition Temperature Monomer Mixtures (NaLTTMM) made of functional natural polyols and organic acids will be presented [5]. The preparation process and physicochemical properties (viscosity, transition temperature, pH etc) of the mixtures will first be presented. Then their polymerization will be discussed, in particular as a function of the reaction temperature that is always lower than the melting points of monomers taken separately. Structural parameters of the polymer (chemical bonds type, molecular weight, topology etc) can be adjusted by operation conditions and careful selection of the starting raw materials [6], which will be discussed during this communication.

Keywords: Natural Low transition temperature mixture ; Polymerization ; crosslinking

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Carbonaceous Porous Materials Arising from Emulsion Templating of Kraft Black Liquor

R. Poupart[1,2,3], A. Foulet[1], J.-L. Bobet[2], R. Backov[3], H. Deleuze[1*]

[1]*Institut des Sciences Moléculaires UMR 5255, Université de Bordeaux, Talence, France*
[2]*Institut de Chimie de la Matière Condensée de Bordeaux UMR 5026, Université de Bordeaux, Pessac, France*
[3]*Centre de Recherche Paul Pascal UMR 5031, Université de Bordeaux, Pessac, France*
[*]*herve.deleuze@u-bordeaux.fr*

Kraft black liquor is a cheap by-product of paper industry mainly composed of an alkaline solution of lignin and hemicellulose fragments. This solution has been succesfully emulsified in presence of a chlorinated solvent (*i.e.* 1,2-dichloroethane) as well as epichlorohydrin (as a crosslinker) to give materials with a porosity up to 70 %v of the total volume.[1] Different method of emulsification have been tried. On the one hand, a conventional stirred reactor with an anchor-type impeller. On the second hand, a “laboratory-made” two-syringes emulsification device has been used to shear the emulsion.[2] Both materials have been calcinated in an oven to give porous carbonaceous foams (CarboHIPE), with a total specific area up to 1000 $m^2.g^{-1}$.[3] Such specific area could be increased by the presence of metallic nanoparticles at the surface. With these particles, these carbon-based materials could be used in catalysis or hydrogen storage.

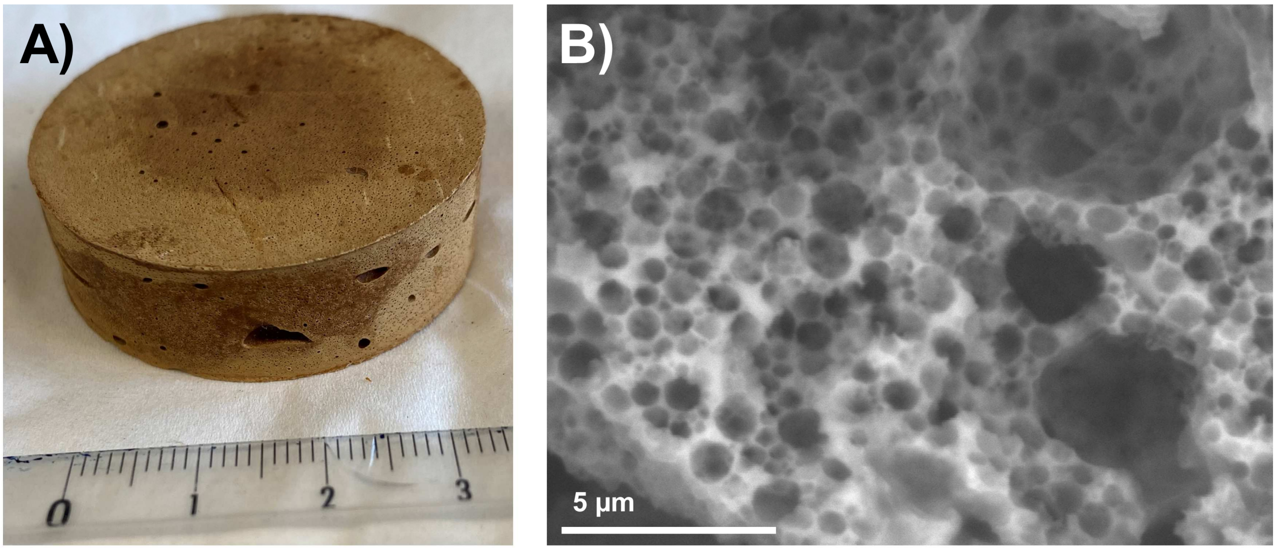

Figure 1: A) Photography of a Kraft black liquor-based HIPE sample (ruler in centimeter) & B) SEM picture of the sample porosity

Keywords: Emulsion templating, Porous material, Kraft black liquor, Polymers

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Effect of calcium carbonate nanoparticles on the soil burial degradation of polybutyleneadipate-*co*-butylenetherephthalate films

Marco Rapisarda[1], Maria Chiara Mistretta[2], Michelangelo Scopelliti[3], Melania Leanza[1], Francesco Paolo La Mantia[2,4], Paola Rizzarelli[1]

[1] *Istituto per i Polimeri, Compositi e Biomateriali, Consiglio Nazionale delle Ricerche, Via Paolo Gaifami 18, 95126 Catania, Italy*
[2] *Dipartimento di Ingegneria, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy*
[3] *Dipartimento di Fisica e Chimica - Emilio Segrè, Università degli Studi di Palermo, Viale delle Scienze 17, 90128 Palermo, Italy*
[4] *INSTM, Via Giusti 9, 55100 Firenze, Italy*
*marco.rapisarda@ipcb.cnr.it

A polybutyleneadipate-*co*-butylenetherephthalate (PBAT) sample, commercially known as Ecoflex®, was processed via melt extrusion with calcium carbonate ($CaCO_3$) nanoparticles (average diameter = 70 nm, specific surface area = 17 m^2/g) coated with a hydrophobic coating made of a mixture of calcium stearate and calcium palmitate. Blown films (average thickness = 40 µm) of PBAT and two composites with a filler content of 2 wt% (PBAT-2%) and 5 wt% (PBAT-5%) were prepared and degradation test in soil up to 180 days carried out. Additionally, biodegradation test according to ISO 14851 was carried out. The effect of the addition of $CaCO_3$ nanoparticles on soil burial degradation was assessed by surface wettability and scanning electron microscopy (SEM). Weight loss measurements were used to follow biodegradation in soil. Attenuated Total Reflection-Fourier Transform Infra-Red (ATR-FTIR) and X-ray Photo electron Spectroscopy (XPS) analyses highlighted chemical modifications induced by soil degradation. $CaCO_3$ nanoparticles decreased surface wettability and discouraged the disintegration in soil of the PBAT-2% and PBAT-5% film samples. SEM showed no significant changes on the morphology of the materials with the addition of $CaCO_3$ nanoparticles. Interestingly, SEM imagines after soil degradation highlighted in the PBAT-2% and PBAT-5% films selective zones of disintegration. In agreement with the literature, XPS showed an increasing peak area C1s ratio of C-O to C=O with degradation time. Moreover, carbonyl index determined by ATR-FTIR for virgin PBAT was unchanged, while in nanocomposites it increased after the soil burial test. In fact, the addition of $CaCO_3$ nanoparticles leads to a rise in the area of the carbonyl zone due to the presence of the carbonate group. Overall, the results revealed that polymer films after biodegradation in soil have a higher carbonate content than initial samples.

Keywords: biodegradable polymers; soil burial test; Ecoflex®; poly(butyleneadipate-*co*-butyleneterephtalate); polyethylene; calcium carbonate; nanoparticles; polymer degradation

Acknowledgments

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Study of the Structure and Antioxidant Activity of Organosolv Lignins from Various Biomasses

J. Rumpf*[1], R. Burger[1], X. T. Do[1], M. Schulze[1]

[1]*Bonn-Rhein-Sieg University of Applied Sciences, von-Liebig-Str. 20, 53359 Rheinbach, Germany*
**jessica.rumpf@h-brs.de*

Lignin is a complex biopolymer found in plant cell walls and the largest source of aromatics on earth. [1] Its heteropolymeric structure mainly consists of three different monomers (monolignols), that are randomly crosslinked, whereby the ratio of monolignols and the nature and number of linkages depend on the biomass origin and isolation procedure. [2] It carries a variety of functional groups, whereby especially phenolic hydroxyl and methoxy groups possess various biological activities, like antioxidant, antimicrobial, antimutagenic. [3] Thus, lignins are promising candidates to replace synthetic antioxidants, even though it is difficult to assign these properties to just one specific structural element due to its molar complexity.
In this study, the structure and antioxidant activity of organosolv lignins from the three low-input crops *Miscanthus x giganteus*, *Paulownia tomentosa* and *Silphium perfoliatum*, respectively, were examined and compared to organosolv lignins from beech wood and wheat straw, and an industrial kraft lignin. Organosolv pulping was carried out in an ethanol/water mixture at 170 °C for 90 minutes in triplicate. [2]
For structural analysis, monolignol ratios were identified via HSQC NMR, which differ significantly between the different biomasses. Grass lignins from miscanthus and wheat straw are composed of all three monolignols, while hardwood lignins are made up of only S und G units, and softwood lignins are exclusively comprised of G units, as expected. [2] The silphium lignin resembles paulownia and other hardwood-based lignins and therefore clearly differs from grass-derived lignins.
The antioxidant activity was measured via DPPH assay and ferric ion reducing antioxidant potential (FRAP) assay as Trolox Equivalent Antioxidative Capacity (TEAC) value, while the total phenolic content (TPC) was determined via Folin-Ciocalteu (FC) assay. The kraft lignin shows a significantly higher TEAC and TPC than all organosolv lignins. Comparing the different biomasses, lignins from beech wood and miscanthus show highest TEAC values using the FRAP assay, while silphium lignin possesses the lowest TEAC. Using the DPPH assay, only small differences between the different lignins could be observed, with paulownia lignin showing the highest TEAC value and wheat straw lignin showing the lowest one. When these TEAC values are compared to the TPC of each lignin, as phenolic groups influence the antioxidant activity, a good correlation between FRAP and FC assay results can be observed with $R^2 > 0.95$, while between DPPH and FC assay a correlation of only $R^2 = 0.60$ is found, which might be due to the different reaction mechanisms of the assays [4].

Keywords: lignin, low-input crops, antioxidant activity, HSQC NMR

Acknowledgments

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Rigid spirocyclic diols derived from citric acid and the preparation of chemically recyclable polymers

Rauno Sedrik[1*], O. Bonjour[2], S. Laanesoo[1], I. Liblikas[1], T. Pehk[3], P. Jannasch[1,2], L. Vares[1]

[1]Institute of Technology, University of Tartu, Nooruse 1, Tartu 50411, Estonia
[2]Department of Chemistry, Lund University, Box 124, Lund 221 00, Sweden
[3]Laboratory of Chemical Physics, National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, Tallinn 12618, Estonia
**rauno.sedrik@ut.ee*

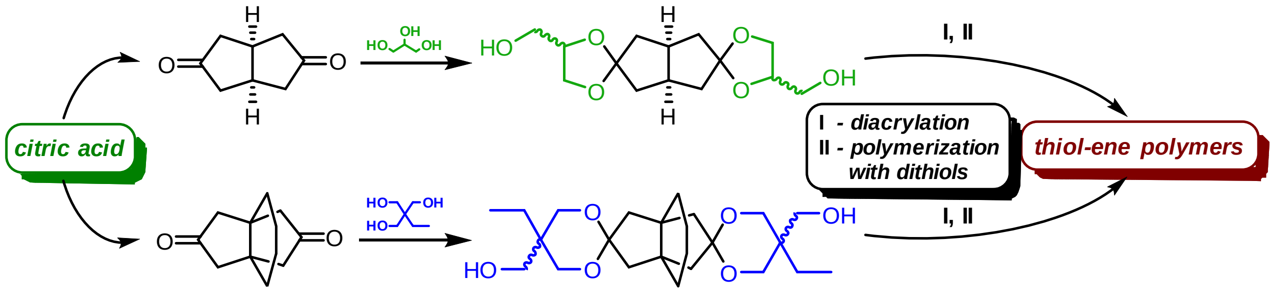

Fig. 1. *Synthesis path of novel bio-based spirocyclic diols derived from citric acid and their conversion into thiol-ene polymers.*

Diols belong to the most versatile building blocks in polymer chemistry. In addition to the direct use as monomers in condensation polymerizations, they can be readily converted into corresponding di(meth)acrylates, divinyl derivatives, diallyl derivatives, diepoxides and other building blocks, for the preparation of a wide variety of different polymers. However, developing *rigid* diols from bio-based sources, needed for high-performance bio-based polymers, has proven to be a challenging task. One way to induce stiffness is to introduce cyclic acetal or ketal units into the diols by reacting aldehyde or ketone groups with suitable triols [1].

In this work citric acid, a widely used platform chemical derived from biomass, has been efficiently converted into structurally rigid di- and tricyclic diketones. Next, spirocyclic diols were produced in cycloketalization reactions using glycerol and trimethylolpropane (TMP), respectively, as triol building blocks (Fig.1). The utility of these spirodiols has been demonstrated in the preparation of a range of thiol-ene polymers, which are obtained in the polymerization of the corresponding di(meth)acrylate esters with various dithiols. Furthermore, the presence of the hydrolytically cleavable ketal functionality opens prospects for the chemical recycling of these materials.

We envision that the two new spirocyclic diols have the potential to become valuable bio-based building blocks in various applications where stiff diols, or derivatives thereof, are required.

Keywords: rigid bio-based diols, bio-based polymers, chemical recycling

Acknowledgements

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Understanding the phase separation and crystallization in thermoplastic elastomers based on recycled pet

Amruta Sharma[1*]; Ir. Gijs de Kort[1]; Jacek Walkowiak[1]; Gerard Werumeus Buning[1]; Jules Harings[1]; Sanjay Rastogi[2*]

[1]Aachen-Maastricht Institute for Biobased Materials, Maastricht University, Geleen, Netherlands
[2]King Abdullah University of Science and Technology, Thuwal, Saudi Arabia
*amruta.sharma@maastrichtuniversity.nl; sanjay.rastogi@kaust.edu.sa;

Polyethylene terephthalate (PET) is among the most widely used packaging material, globally generating millions of tons of waste per year. This has fueled to development of economically viable recycling process to dispose the large volume of waste. Using recycled PET stream as a feedstock in combination with readily available bio-based materials to manufacture thermoplastic elastomers with high value and performance via circular upcycling approach provide a better alternative. Thermoplastic elastomers (TPE's) with semi-crystalline hard and amorphous soft segments sequences exhibit biphasic morphological structures at room temperature. Although, there have been various studies on structure and properties of TPE's in literature, complexities in the microstructure consisting of hard phase, mixed phase and soft phase and their implications on the phase separation behavior is still an open question. Understanding the phase separation phenomenon in correlation with the crystallization kinetics of the hard phase is critical for developing robust structure-property link in these materials. Further complexity is added by the co-monomers present in the recycled PET, which then become part of backbone of TPE molecule. This alters the structure formation upon cooling from the melt.

Here, we aim to systematically explore the influence of co-monomers, block length of soft and hard segments and their composition on the phase separation and crystallization phenomenon. We perform in situ experiments to study the structure development of these materials using tools like small angle and wide angle X ray scattering, optical microscopy etc. Rheology along with thermal analysis are used as an indirect probe to the structural evolution during spinodal decomposition phase separation and crystallization. Finally, we relate above-mentioned parameters with the evolution of the microstructure.

Keywords: thermoplastic elastomers, recycled PET, phase separation, crystallization

***Acknowledgments**: Iris Hilker, (DSM), Richard Ensinck (DSM)*

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Properties degradation of PLA-based compounds in marine environment

L. Conzatti, C. D'Arrigo, G. Luciano, R. Utzeri, M. Vignolo, P. Stagnaro*

Istituto di Scienze e Tecnologie Chimiche "Giulio Natta" SCITEC - CNR, Genoa, Italy
**paola.stagnaro@scitec.cnr.it*

For some time now, due to environmental concerns, limited petrochemical resources and the demand for new property profiles, bioplastics have increasingly attracted the attention not only of the research community and the industrial sector, but also of the general public and of policy makers. Particularly focused are the bio-based polyesters, such as poly(lactic acid) (PLA), polyhydroxyalcanoates, poly(butylene succinate), developed in the past 30 years [1]. Among these, PLA appears the most feasible alternative to petrochemical-based polyesters, due also to its appreciable rate of degradation under industrial composting conditions [2]. However, even though PLA degrades approximately 20 times faster than high-density polyethylene on land, the two polymers behave surprisingly similar in the marine environment [3].

Within the framework of BIOPLASTICS EUROPE project [4], aimed at developing and implementing sustainable strategies and solutions for bio-based plastic production and use, as well as at preserving land and sea environmental quality in Europe through approaches focused on circular innovation, different compounds based on PLA and produced by consortium partners were chosen as promising candidates for sustainable short-to-medium-term applications, such as cutlery, rigid packaging, agricultural mulch films.

In this work, on field degradation tests were carried out on three PLA-based compounds immersed in the Mediterranean Sea. Temperature and other relevant water parameters were monitored throughout the exposure period (1 year) carried out in tanks with circulating sea water (Fig. 1). Samples aspect and weight, as well as their tensile properties (ISO 527-1÷5), thermal behaviour (DSC, TGA), spectroscopic (ATR-FTIR) and morphological (SEM) features were evaluated at different collection times (1, 3, 6, 12 months), and compared to those of the as-received samples.

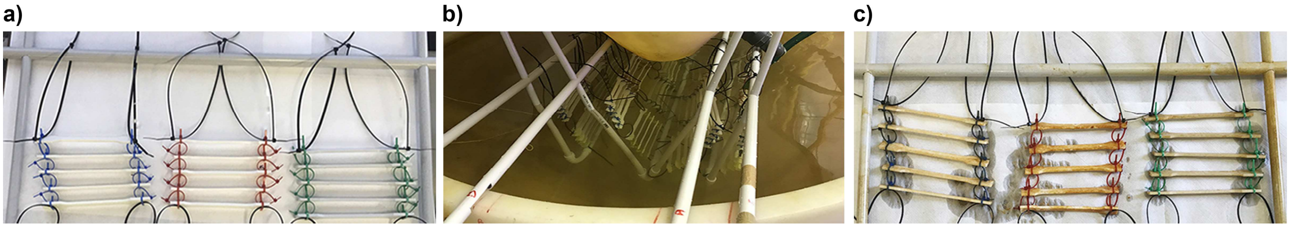

Figure 1: *a) Dog-bone shape samples before immersion; b) tank with circulating sea water; c) samples recovered after 12 months immersion.*

Keywords: Bio-based and degradable polymers, on field degradation, sustainability, circular innovation.

Acknowledgments

BIO-PLASTICS EUROPE project funded by H2020 research and innovation programme (GA No. 860407). Arctic Biomaterials Oy LTD (Finland) and NaturePlast sas (France) kindly supplied PLA-based compounds. IBF-CNR kindly made available the marine labs in Camogli (Genoa, Italy).

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Bio-polyester/Elastomer Compounds: Characterization, Bio-degradation and Applications

Carina Frank[1,2,] Anita Emmerstorfer-Augustin[1], Franz Stelzer[1,2,*]

[1] *ACIB Austrian Center of Industrial Biotechnology, Austria)*
[2]*Institute for Chemistry and Technology of Materials, Graz University of Technology*
[*]*franz.stelzer@tugraz.at*

Carelessly disposed plastic waste and "Microplastics" are part of the most concerning environmental pollution. In its smallest version as "Fine Dust" it is already found almost ubiquitously, with the largest partition as abrasion product from car tires. Furthermore, there is a strong trend away from fossil ressources towards biobased materials. So it is desirable to replace as much this by biodegradable biobased polymeric materials. As a consequence we investigate blends of biobased biodegradable polyester (polyhydroxyalkanoates, PHAs) and natural rubber NR), both from fully natural ressources.

PHAs have already been used since years as fully biobased and biodegradable thermoplastc materials, but with some technological drawbacks, such as hig crystallinity with a narrow thermal processing window, quite fast recrystallization leading to a still low commercial availability and high prices. So improvement of impact resistance and increase of flexibility is one important goal of actual research in this field.

We carried out investigations on blends of various PHAs and commercial PHA compounds blended with natural rubber (NR). These PHA/NR blends can be processed as thermoplastic materials but also be crosslinked to form flexible rubbery workpieces. Characterization methods applied were SEC, thermal methods (DSC; TG), mechanical testing (see Diagram 1) and rheology, spectroscopic methods (IR, NMR), optical and electron microscopy.

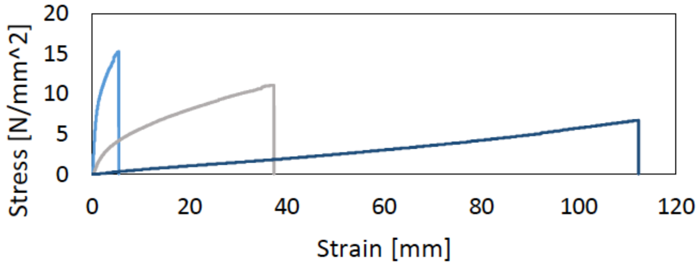

Diagram 1: Mechanical testing of blends with 20, 50 and 80 % of rubber

In addition, we investigated the bio-degradability of these compounds. For this, in vitro methods were developed applying various PHA-depolymerases, esterases and lipases. In order to investigate the influence of the elastomeric blend compound and crosslinking on biodegradability a pH dependent assay was established to monitor the degradation. Fluorescein was used to visualize the pH change.

Keywords: Bio-polyester, natural rubber, biodegradable, PHA blend, characterization

Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 860407. BIO-PLASTICS EUROPE project website: www.bioplasticseurope.eu; we thank NaturePlast® for providing us the PHA samples.

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Morphological and structural characterization of microplastics collected from the Axios river

E. Tarani[1]*, N.M. Ainali[2,3], D. Kalaronis[2,3], D.A. Lambropoulou[3], D.N. Bikiaris[2], K. Chrissafis[1]

[1]*Laboratory of Advanced Materials & Devices, Physics Department, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece*
[2]*Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece*
[3]*Laboratory of Environmental Pollution Control, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece*
**etarani@physics.auth.gr*

In Pollution of microplastics (tiny polymer fragments with a diameter of less than 5 mm) has been identified as one of the most serious environmental problems in recent years, resulting from the degradation of plastics through various physicochemical processes. Despite the increase in studies on this field, it is a common assumption of researchers that research is still in its early stages, with a lot of unresolved questions that need to be answered. In this work, microplastics were collected from the Axios river which is the second longest river in Greece, and the second-longest river in the Balkans in order to evaluate some of the most widely used polymers covering a variety of applications in modern everyday life. The structural and morphological characterization of the selected microplastics were studied with the help of Infrared Spectroscopy with Fourier transform (FT-IR), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). Additionally, Pyrolysis - Gas Chromatography/Mass Spectrometry (Py-GC/MS) was employed for the thermal characterization and dynamic study of polymeric materials. The complementary use of these techniques provides conclusive and convincing results from the studies being carried out on microplastics and their ever-increasing abundance in the environment.

Keywords: microplastics, Axios river, FTIR, XRD, SEM, Py-GC/MS

Main-chain photocleavable inorganic polymers

Ian Teasdale*

Johannes Kepler University*, Linz, Austria*
ian.teasdale@jku.at

Despite the pervasiveness of polymers in our society and the level of complexity achieved, the vast majority are based solely on combinations of carbon, nitrogen and oxygen. Expanding this to metals and p-block elements can open the door to mechanical and chemical properties that go above and beyond those achievable with organic polymers [1]. Despite these exciting prospects, in particular within the context of a booming field in dynamic, functional and smart polymers, the field of inorganic polymer chemistry is brimming with untapped potential. Herein we present the molecular design, synthesis and stimuli responsive properties of novel families of macromolecules based on inorganic polymer chains. We have developed a number of inorganic polymer families incorporating particular boron [2], phosphorus [3] and transition metals [4] which can debond-on-demand [5], in some cases reversibly [6], leading to selectively degradable and/or self-healable materials (Figure 1). The polymers are selectively cleavable in responsive to oxidation, pH and light, Herein we focus on those responsive to light in the visible and near infrared regions [2,6].

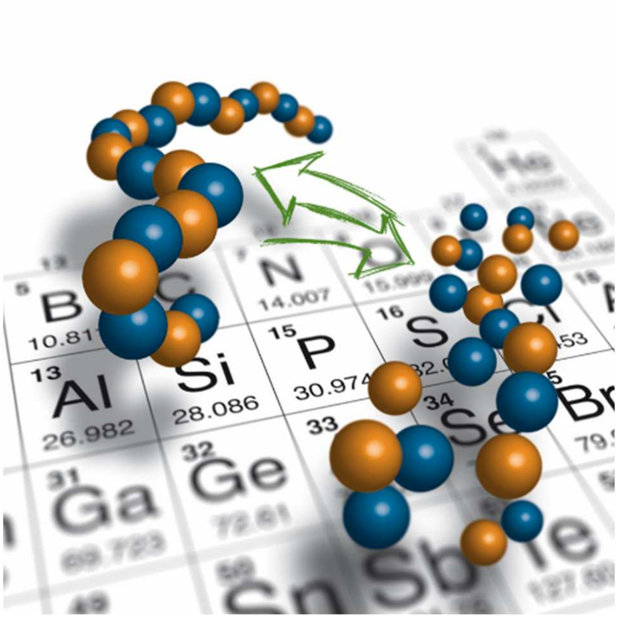

Figure 1: Concept of main-chain cleavable inorganic polymers

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Valorization of Coffee Silverskin in Green Particulate Composites based on PLA and PBS

L. Sisti[1], G. Totaro[1*], A. Rosato[1], N. Bozzi Cionci[2], D. Di Gioia[2], L. Barbieri[3], A. Saccani[1]

[1]*Dept. of Civil, Chemical, Environmental and Material Engineering, University of Bologna, Bologna, Italy*
[2]*Dept. of Agro-food Sciences and Technologies, University of Bologna, Bologna, Italy*
[3]*Dept. of Engineering "Enzo Ferrari", University of Modena, Modena, Italy*
[*]*Corresponding Author's mail: grazia.totaro@unibo.it*

Food waste valorization, considered as energy and/or chemicals source, via biorefinery or biotechnology, gained great attention in recent years, because of the fast depletion of primary resources, increased waste generation and landfilling worldwide [1].

Coffee is one important, widespread source of by-products and waste (i.e. coffee pulp, coffee husks, silver skin, spent coffee, etc.). It has been investigated in different forms either as a source of antioxidant and valuable chemicals and as a filler in composites. Silver skin (SSK) for example, which is the integument surrounding the coffee beans, constitutes about the 3 wt% of the original treated product and after the roasting process, it becomes a by-product [2].

The valorization of SSK, up to now just sent to damping, is here investigated through the preparation of particulate biocomposites based on poly(lactic acid) (PLA) and poly(butylene succinate) (PBS), two of the most common aliphatic biodegradable polyesters, commercially available. In the current research a characterization of the polyphenols content and antioxidant activity of SSK, the tensile properties and dynamic mechanical response of the biocomposites together with their stability toward photo oxidation have been reported.

This approach has a high potential as to what concerns the application of renewable polymers, because some properties (i.e durability) can be improved, the amount of polymer matrix (presently more expensive than oil-derived materials) can be reduced, and the waste damping can be avoided [3].

Keywords: coffee silver skin, green composite, PLA and PBS, recycling, UV degradation

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Preparation and characterization of new biobased flexible Non-Isocyanate PolyUrethane (NIPU) foams

V.Valette*, L.Lecamp, N.Kébir

Normandie Université, INSA Rouen Normandie, Laboratoire PBS, UMR CNRS 6270 & FR 3038, Avenue de l'Université, 76801 Saint Etienne du Rouvray, France
*vincent.valette@univ-rouen.fr

Polyurethanes (PUs) foams are versatile materials which find their application in automobile, construction, packaging and so on.[1 -2] Their importance in the polymer materials market is still significant and the global PU foam market is expected to reach 12.74 million tons by 2024.[3] Since 1947, PUs foams have been produced from the polyaddition of di- polyol on di- polyisocyanates and the CO_2 generated insitu through the reaction of added water with isocyanates. From rigid to flexible, a large panel of PUs foams has thus been proposed. In recent years, the concerns about sustainable chemistry and health have oriented researches towards replacement of polyisocyanates, which most of them are toxic and CMR, by less or non-toxic substitues. In addition, isocyanates are produced from phosgene that is highly toxic. Therefore, in order to find an alternative to isocyanates, the synthesis of Non-Isocyanate PolyUrethanes (NIPUs) has become an important field of research. Nowadays, the few examples of NIPU foams in the litterature are mainly obtained by polyaddition of di- polyamines onto di- polycyclocarbonates leading to poly(hydroxyurethane) (PHU).[4-5-6] However, due to low reactivity of the cyclocarbonates used, the foam elaboration process requires high temperatures and/or reaction times in order to crosslink the material (from 200°C during 30 min to room temperature during 3 days).

In this work, we propose a new approach to obtain NIPU foams. Indeed, amino-telechelic dicarbamates were synthesized from bio-based molecules and then crosslinked with a bio-based polyepoxide. As the reactivity of the epoxy groups towards the amine groups is higher than that of the cyclocarbonate groups, NIPU foams can be obtained more quickly and at a lower temperature compared to the above-mentioned process. In addition, this pathway allows for a wider choice of monomers, thus increasing the diversity of properties and applications of NIPU foams. More specifically, in this study, different amino-telechelic dicarbamates were synthesised, formulated, foamed and characterised. Poly(methylhydroxysiloxane) (PMHS) was used as a blowing agent as it showed effective behaviour in epoxy-amine foaming.[7]

Keywords: Non-Isocyanate PolyUrethane, foam, bio-based.

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A Biobased Photoinduced Self-Healing Thermoset Coating

Daniela Vuluga*, Laurence Lecamp*, Ludovic Geelhand de Merxem

Normandie Univ, INSA Rouen, UNIROUEN, CNRS, PBS, 76000 Rouen, France
daniela.vuluga@insa-rouen.fr

The need to find alternatives to the non-renewable resources used in polymer chemistry has gradually become obvious. In this context, vegetable oils can be considered as a very interesting option: in addition to the renewable aspect, their low cost is an important argument. These are mostly composed of triglycerides, *i.e.* esterification products of glycerol with mostly unsaturated fatty acids -that represent 95% of the total weight of triglycerides- and their composition is characteristic of each vegetable oil. Many studies have been conducted on such oils to develop new materials[1,2] but few products are available on the market. Moreover, bio-based raw materials are rarely usable directly after harvesting or extraction, and long processes are often required to transform them into molecular building blocks. In this context, highly unsaturated oils are an exception since their native form has been used directly in coatings for a very long time, or after chemical modification (epoxidation, maleinisation, acrylation ...).[3] Unfortunately, these materials have a major drawback: they exhibit high crosslinking, so that they are difficult to process or modify once they have been damaged.

On another hand, self-repairing materials are a class of intelligent materials that have the ability to repair damages caused by mechanical wear and tear over time. In this context, disulfide compounds appear as an attractive repair system. Indeed, the homolytic cleavage of the S-S bond occurs naturally at room temperature and the resulting thiyl radicals can then be involved in metathesis reactions with other disulfide bridges.[4,5] However, this exchange reaction is very slow in materials in solid state.

In this work, we report a thermoset material based on vegetable oil that can self-repair after surface damage by dynamic exchange of disulfide bridges by means of a relatively low temperature process involving UV radiation.[6]

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A green route towards poly(aspartic acid)-based polyampholytes

S. Vynnytska[1*], S. Van Vlierberghe[2], K. Bernaerts[1],

[1] *Sustainable Polymer Synthesis group, Maastricht, the Netherlands*
[2] *Polymer Chemistry and Biomaterials Group, Ghent, Belgium*
[*]s.vynnytska@maastrichtuniversity.nl

During the last decades, there has been continuously growing interest for “smart” adaptive materials, such as polyampholytes.[1] Such copolymers carry positive and negative charges on separate monomeric repetitive units. This makes polyampholytes stimuli-responsive. Indeed, they can demonstrate both polyelectrolyte and antipolyelectrolyte behavior depending on solution pH, copolymer composition, and the presence of low molecular weight electrolyte.[2] Such copolymers find their application as dispersants, anti-fouling coatings, hydrogels and antifreeze materials. Nowadays, the majority of polyampholytes are synthesized via free radical polymerization of (meth)acrylic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), 2-(dimethylamino)ethyl methacrylate (DMA) or acrylamide, which are not biobased nor biodegradable. In order to contribute to the sustainable world, it is important to have a polymeric backbone, which is biobased, biodegradable, biocompatible and non-toxic. Poly(aspartic acid) and its precursor polysuccinimide fully meet this requirement.[3]

In this work, polyampholytes were synthesized with pendant carboxylate groups and quaternary ammonium groups. The starting backbone, polysuccinimide (PSI), was synthesized via polycondensation of biobased L-aspartic acid. Polysuccinimide was partly modified via ring-opening reaction with cationic (carboxymethyl)trimethylammonium chloride hydrazide (Girard’s reagent T) and afterwards the remaining succinimide rings were hydrolyzed into aspartic acid units. Traditionally, PSI is modified with amine-containing reagents in high boiling polar solvents like DMF and DMSO. We developed a more sustainable procedure using water as a green solvent under hydrothermal conditions in the microwave. The reaction conditions were optimized with regard to reaction time, temperature and pH in order to tune the degree of substitution from 4 to 46%. The obtained amphoteric polymers were characterized by ^{1}H NMR, FTIR spectroscopy, dynamic light scattering and zeta potential measurements. The copolymers were tested as a dispersant and anti-fouling biomedical coatings. As a result, in this work, biobased and biodegradable polyampholyte copolymers were obtained with tuneable composition via a green synthesis route and a proof-of-principle for their application potential was delivered.

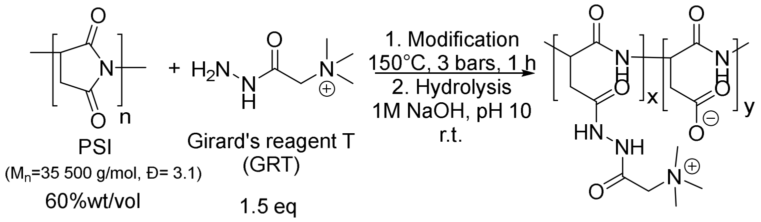

Figure 1. Synthesis of polyampholyte copolymer

Acknowledgments

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The undiscovered potential of thermosetting polycondensation resins

O. Weichold, F. Weitenhagen

Insitute of Building Materials Research, RWTH Aachen University, 52062 Aachen, Germany
** E-mail: weichold@ibac.rwth-aachen.de*

With increasing demand for stronger, lighter, and more durable composite materials, thermosetting polymers play a critical role as base for load-bearing matrices, fibre coatings, and adhesives.[1] The most prominient examples for reinforced composites are epoxy and formaldehyde resins, unsaturated polyesters, and vinyl ester resins, which exhibit high reactivities and excellent materials properties. All these resins are of the polyaddition type, which means that all atoms of the starting materials are incorporated into the final product. However, their main source is petrochemical feedstock and the desired high reactivity comes at the cost of an equally high toxicity and environmental hazard.

On the other hand, nature produces a vast amount of substances every second without using highly reactive functional groups such as epoxy or isocyanate. All of these reactions proceed close to or slightly above ambient temperature and quite a number of these are condensation reactions, which produce small molecules such as water as byproduct. Thus, it seems that natural building blocks would not be suitable for making thermoset resins. However, the growing need for materials with low environmental impact as well as the vast amount of natural or bio-based multifunctional molecules merits a closer look.

As part of our work on bio-based building materials, we are investigating methods for the preparation of thermosetting polycondensation resins based on natural or bio-based polyacids and polyols.[2] These liberate one molecule of water per per newly formed linkage in the polymer. This can be used to generate rigid or elasic foams depending on the used monomer and functionality. With careful control of the reaction conditions, the type of catalyst, and potential additives such as cellulose or shredded feathers, foaming can be avoided and hard or rubber elastic but compact materials can be obtained. The contribution will present our latest results on the correlation between reactants, reaction conditions, and materials properties to synthesize suitable building materials.

Figure 1. Citric acid/glycrol foam with a density of 0.26 g·cm^{-3} (left) and solid cube from the same polymer mixture containing 20 wt% of recycled cellulose with a density of 0.89 g·cm^{-3} and a compressive strength of 23 N·mm^{-2} (right). Sample size 4 × 4 × 4 cm^3.

Keywords: Sustainability, contruction materials, foams

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Multi-purpose lignin-based benzoxazines: from hydrophobic coatings to catalyst-free vitrimers

A. Adjaoud[1,2], L. Puchot[1], P. Verge[1]*

[1] *Luxembourg Institute of Science and Technology, Esch-sur-Alzette, Luxembourg*
[2] *University of Luxembourg, Esch-sur-Alzette, Luxembourg*

The meaningful concept of circular economy has prompted the scientific community to change the way of designing materials toward biobased and recyclable polymers. Lignin, the second largest natural polymer produced on Earth, epitomized the main source of phenolic compounds for the preparation of bio-derived functional materials. Lignin can be incorporated as mechanical fillers for composites; employed as UV-barrier, antioxidant, or antimicrobial agents; or even used as a matrix in a wide range of value-added materials such as phenol-formaldehyde (PF) resins, polyurethane foam, and more recently as smart materials[1]. Polybenzoxazines (PBZs) emerged as a promising alternative to phenolic and epoxy resins thanks to their competitive features such as superior mechanical properties and thermal stability[2]. For the past two decades, the exceptional versatility of their chemical structure is at the root of the explosive growth of research works on the design of benzoxazine from renewable resources. As unmodified lignin meets few commercial applications, we have reported a promising green and eco-friendly approach to increase the reactivity of lignin[3]. In this study, technical soda lignin was esterified in solvent-free condition with phloretic acid, a naturally occurring compound extracted from the leaves of apple trees. This sustainable synthetic route grants technical lignin with ester bonds and an increased number of phenolic reactive sites. Therefore, this enriched platform of *ortho*-free phenolic rings was employed for the catalyst-free design of a series of lignin-based benzoxazines (LBZs). The properties of the biobased resins can be easily tuned depending on the amine used to close the benzoxazine ring. The nature of the amine side group has a strong influence on the mechanical strength, thermal stability, solubility, or surface interaction of the resultant LBZs. Biobased amines synthons such as long-alkyl chain stearylamine confer hydrophobicity to LBZs coatings, while furfurylamine-based LBZs generate high-T_g materials. Amino-alcohol derivatives grant recyclability to cross-linked lignin-vitrimers thanks to dynamic transesterification exchanges, joining the recent but growing family of lignin-based vitrimers[4, 5]. This presentation will illustrate the scope of applications of these monocomponent and fully biobased LBZs (Fig. 1).

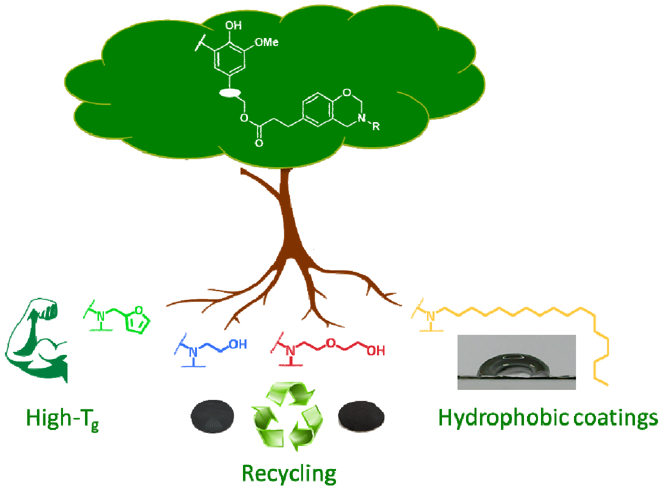

Fig. 1 *Multi-purpose applications of lignin-based benzoxazines*

Keywords: Lignin, Polybenzoxazines, Thermoset, Vitrimers, Biobased

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Grafted PLA/pecan nutshell biocomposites: Effect of ball milling and thermal annealing on thermomechanical properties and biodegradation

S. Agustin-Salazar[1*], M. Ricciulli[2], V. Ambrogi[2], P. Cerruti[3], Gennaro Scarinzi[1]

[1]*Institute for Polymers, Composites and Biomaterials (IPCB-CNR), Pozzuoli (Na), Italy*
[2]*Chemical, Materials and Production Engineering (DICMAPI), Naples, Italy*
[1,3]*Institute for Polymers, Composites and Biomaterials (IPCB-CNR), Lecco, Italy*
[*]*sarai.agustin@ipcb.cnr.it*

The use of lignocellulosic-rich biowaste as reinforcing filler in biodegradable polymers represents a sustainable option to obtain bio-based materials to be used for several applications (structural, household, packaging, etc.) [1]. In this work, polylactic acid (PLA) was first chemically modified with with itaconic anhidride (from here, MPLA), then MPLA/pecan (*Carya illinoinensis*) nutshell (PNS) biocomposites were prepared and characterized. In this respect, the effect of two environmentally friendly physical treatments, namely ball-milling of the filler and thermal annealing on biocomposites, were assessed, along with their biodegradation in soil [2,3]. Even though grafting occurred at low percentage, it was enough to improve crystallinity and performance of the polymer. PNS enhanced the thermal stability, the viscoelastic response, and the crystallinity of the polymer. Furthermore, filler ball-milling also increased the melt fluidity of the biocomposites, potentially improving melt proccessing. Even with 50 wt.% of filler, all biocomposites displayed mechanical properties comparable to the plain matrix. Moreover, thermal annealing dramatically increased the mechanical and thermomechanical properties of all materials. In particular, heat deflection temperature of the biocomposites dramatically increased, up to 60 ◦C with respect to the non-annealed samples (Fig. 1). Finally, PNS promoted the swelling of PLA under burial, favoring its biodegradation. These results highlight the potential of combining natural fillers and environmentally benign physico-chemical treatments to tailor the properties of PLA biocomposites, especially for those applications which require a stiff and lightweight material with low deformability.

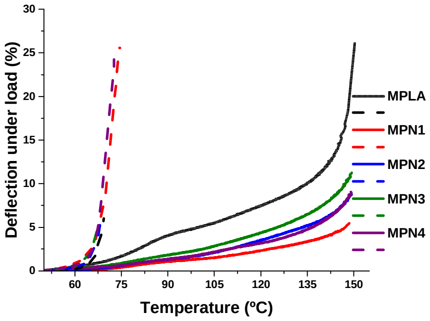

Figure 1. Deflection under load of MPLA and its biocomposites as a function of temperature, before (dash lines) and after (solid lines) annealing.

Keywords: Grafting, polylactic acid (PLA), Pecan nutshell (PNS), Biocomposites, Lignocellulosic materials, Ball-milling, Thermal annealing

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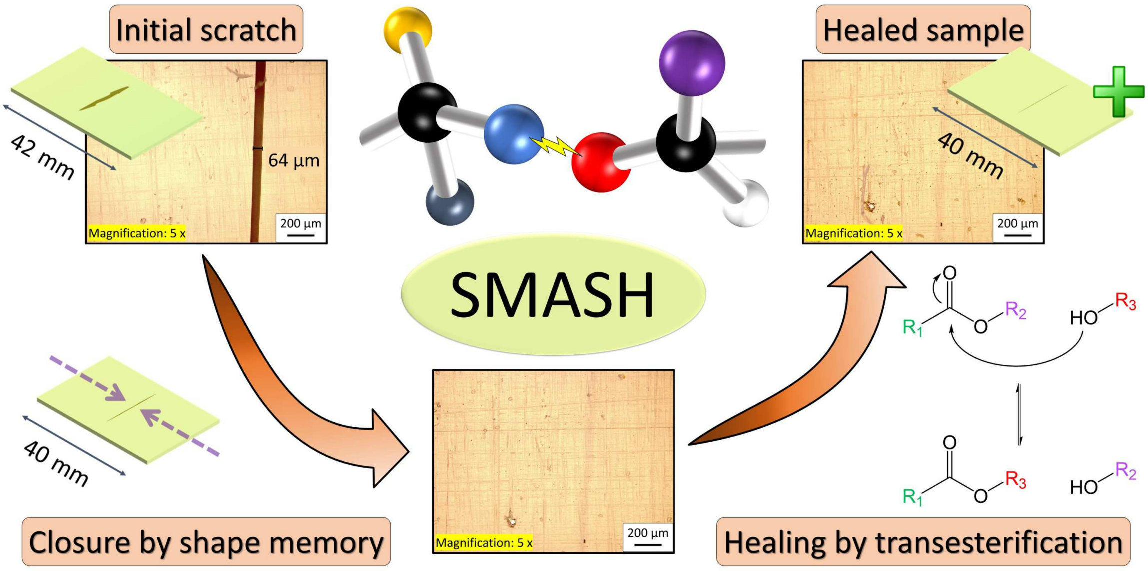
Enhancing the self-healing performance of thiol-acrylate dynamic networks by introducing shape memory-assisted scratch closure

Walter Alabiso,[1] Tiago Hron,[2] David Reisinger,[1] Daniel Bautista,[1] Sandra Schlögl[1,*]

[1] *Polymer Competence Center Leoben GmbH, Roseggerstraße 12, 8700 Leoben, Austria*
[2] *Montanuniversität Leoben, Otto Glöckel-Straße 2/IV, 8700 Leoben, Austria*
** Correspondence: sandra.schloegl@pccl.at, Tel: +43 3842 402 2354*

Self-healing polymers are tremendously attractive due to their ability to repair macroscopic damage and defects, thus opening doors to sustainable and reliable functional polymers. In this scope, vitrimers are in the spotlight, as dynamic polymer networks exhibiting unique properties such as self-healing ability, recyclability and malleability [1]. The possibility of intrinsically healing macroscopic damage on the molecular scale repeatedly is undoubtedly appealing, although it would strongly benefit from an additional driving force bringing the surfaces of larger defects together. Herein, we present a study on the synergistic combination of physical and chemical healing of a thiol-acrylate vitrimeric photopolymer based on thermo-activated transesterification by pursuing a close-then-heal approach [2]. By following shape-memory assisted self-healing (SMASH), we used the shape-memory properties of thiol-acrylate photopolymers to physically close a scratch, whilst chemical healing was obtained via thermo-activated dynamic exchange reactions of the –OH groups and ester moieties available in the network. We prepared formulations with varying thiol content and characterised their mechanical, chemical, and shape memory properties and healing efficiency. We provide a comprehensive picture of the role of physical recoil, bond exchanges and network mobility on self-healing efficiency as well as its limitations. By appropriate network design, defects with a size of 50–150 µm can be rapidly closed, and healing efficiency up to 90% can be reached in terms of ultimate tensile strength, thus demonstrating the potential of SMASH for vitrimers.



Graphical Abstract: Schematic illustrating the concept of Shape Memory-Assisted Self-Healing (SMASH)

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Furan-based Bio-epoxy Resins: from biomass to applications

V. Ambrogi[1,2*], P. Cerruti[2], G.Gentile[2], A.Marotta[1], N. Faggio[1,2,] A. Mija[3]

[1]*Department of Chemical, Materials and Production Engineering, University of Naples, Naples, Italy*
[2]*Insitute for Polymers, Composites and Biomaterials, CNR, Pozzuoli (NA), Italy*
[3]*Laboratoire de Physique de la Matière Condensée (LPMC) CNRS – UMR 7336, Université Nice Sophia Antipolis, Nice, France*
[*]*Corresponding Author's E-mail address: ambrogi@unina.it*

Epoxy resins are covalently cross-linked networks with high dimensional stability, excellent mechanical resistance and chemical inertia over a broad range of temperatures. Due to these outstanding properties epoxies are the preferred materials for numerous applications, ranging from structural composites to adhesives. Since they have a pivotal role in several industrial fields, the improvement of their sustainability is becoming a crucial challenge, as traditional production protocols are in conflict with the recent principles of green chemistry, being the precursors used oil-based and frequently toxic. This is the case, for example, of the DGEBA, whose use is now limited due to its disruptive endocrine activity and adverse impact on human health [1]. Therefore, to address this problem, a strong effort has recently been made to introduce new platform molecules of biological origin for the production of epoxy resins [2]. In particular, molecules derived from vegetable oils, lignin and cellulose have been used to produced new epoxy resins with a variety of features, achievable for different applications. Among the most promising alternatives to BPA, precursors derived from cellulose and sugars have received a huge interest, as they are prone to a variety of modification processes that allow the production of compunds of different chemical structure from linear, cyclic to aromatic [3]. Herein, the eco-design, production and potential applications of furan-based epoxy resins is discussed. Furan molecule is an appropriate alternative building block, not only for its aromatic nature, but also for its environmentally-safety, and its easy availability. Furan derivatives can be easily obtained from vegetal biomass and efficiently modified to get a plethora of monomers and curing agents for the production of epoxy thermosets. In this work, a comprehensive overview on the recent synthetic approaches based on the use of furan biorenewable precursors for epoxy resins is provided [3]. Among the different alternatives, 2,5-dihydroxy methyl furandiol (BHMF) has been selected as starting compound for the synthesis of the corresponding diepoxy monomer the 2,5-bis[(2-oxiranylmethoxy)methyl] furan (BOMF). First, an ex-ante life cycle assessment (LCA) study on the production of the bio-sourced monomer is presented, which includes the pre-treatment of lignocellulosic biomass, the glucose production, its isomerization to fructose, and the subsequent dehydration to 5-(hydroxymethyl) furfural (HMF), which is the main green chemical platform used for the production of BOMF. Then, the synthesis of BOMF/anhydride resins is discussed, considering the influence of the nature of anhydride and catalyst, and the anhydride-to-epoxy content ratio on the curing behaviour, as well as on the physico-chemical and mechanical properties of the final products. The use of furan-based epoxy resins as coatings for metal substrates is also provided, demonstrating the potential of this class of bio-based resins for industrial applications [4].

Keywords: furan-based compounds, bio-based epoxy, sustainabile polymers

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Biodegradation of natural and vulcanized rubber

R. Andler[1*]

[1]*Escuela de Ingeniería en Biotecnología, Universidad Católica del Maule, Talca, Chile*
[*]*randler@ucm.cl*

Over the last years, the increasing global rubber production has become a serious environmental problem. According to the International Rubber Study Group, the total rubber production in the year 2017 reached 28,600,000 metric tons. In this scenario, recycling of rubber materials is necessary and biodegradation of rubber could be an environmentally friendly alternative. Several bacterial species have been described to cleave the backbone of poly(*cis*-1,4-isoprene), one of the main constituents of rubber. Recently, the actinomycete *Gordonia polyisoprenivorans* strain VH2 was cultivated with poly(*cis*-1,4-isoprene) rubber particles as sole carbon and energy source in fermenter scale[1]. Using genetic tools, the rubber degrading strains can be modified to form products of interest. In this matter, rubber waste could be suitable as C-source for the synthesis of high valuable products. However, slow growth of bacteria makes the process not suitable in large scale in terms of productivity and further investigations are needed. As an alternative, rubber cleaving enzymes can be incubated in the presence of poly(*cis*-1,4-isoprene) rubber to achieve faster degradation rates. The following enzymes: RoxA, RoxB and Latex clearing protein (Lcp) have been described as catalyzers of the polymer[2]. Lcp has been produced and partially purified using simple and cost-effective purification processes. Recently, Lcp was tested for biotechnological degradation approaches in the presence of solid particles of poly(*cis*-1,4-isoprene)[3]. Different strategies, including *in vivo* and *in vitro* processes, can be implemented to achieve partial or total degradation of the polymer. As a result, conformational changes on the surface of the polymer are detected and oligo(*cis*-1,4-isoprene) molecules of different molecular weights are formed.

A sustainable alternative for the treatment of vulcanised rubber is the use of microorganisms that can biotransform polymers and aromatic compounds and then assimilate and mineralise some of the degradation products. Vulcanised rubber materials present great resistance to biodegradation due to the presence of highly hydrophobic cross-linked structures that are provided by the additives they contain and the vulcanisation process itself. Rubber waste can be treated by chemical, mechanical and biological processes. However, as a result of the high degradation resistance of rubber materials, no clean and efficient processes have been established to date. One of the reasons that vulcanized rubber is difficult to degrade is due to the presence of disulfide bridges, which link the rubber molecules together in a strong bond. Consequently, a first desulfurization step is essential for improving the overall degradation process[4]. The integrative analysis of the biodegradation process, supported by genetic and bioinformatics tools, allowed a deeper analysis of the biodeterioration of vulcanised rubber. It is expected that this type of analysis can be used to find more efficient biotechnological solutions in the future.

Keywords: Biodegradable polymer, in vitro degradation, latex clearing protein, rubber biodegradation**,** biodesulfurization

Acknowledgments
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GREEN POLYMERS from sustainable raw materials and additives

Elaine Armelin[1,2]*

[1] *IMEM-BRT – Innovation in Materials and Molecular Engineering-Biomedical Regenerative Therapies, Dpt. of Chemical Engineering, Universitat Politècnica de Catalunya (UPC), C/ d'Eduard Maristany, 10-14, Building I, 2nd floor, 08019 - Barcelona (Spain).*
[2] *Barcelona Research Centre for Multiscale Science and Engineering, Universitat Politècnica de Catalunya (UPC), C/ d'Eduard Maristany, 10-14, Building I, basement, 08019 - Barcelona (Spain).*
**Corresponding Authors: elaine.armelin@upc.edu (Twitter: @ElaineArmelin)*

Sustainability play an increasingly important role in the chemical supply chain since there is a strong motivation to move from petroleum sourced raw materials to bio-sourced ones due to future regulations and environmental concerns. Consequently, to address the aforementioned challenges, academics and industry have been joining efforts in the past decades. In Europe, some rules and regulations had a great impact on research and developments of new materials. One example is the exponential growth of waterborne coatings formulations to replace solvent-borne systems, since 2004.[1] The objective was to reduce VOC footprint (from organic solvents) in certain paints, varnishes and vehicle refinishing products.

In this work, we will show some polymers developed in our Group that are prepared from sustainable and eco-friendly alternatives to synthetic polymers. The first is a limonene derived epoxy thermoset with suitable properties for adhesive and coatings applications. The excellent mechanical stress-strain behaviour, adhesion force and gel content achieved, demonstrated that the novel bio-based product is workable for such abovementioned areas.[2-4] The bi-component epoxy thermoset (2K formulation) developed can be cured at high temperature, being suitable for enamel coatings, as well as for powder coatings formulations. For such approach we only used synthetic hardeners but efforts to replace than by eco-friendly curing agents are ongoing.

In a second example, we have used diacrylate monomers obtained from succinic acid, malic acid and tartaric acid (natural sources), for the preparation of 3D-printed photocurable resins. The crosslinking of such compounds with poly(ethylenglycol diacrylate) (PEG-DA), with low molecular weight (250 g.mol^{-1}), *i.e.* liquid resins necessary for stereolithography (SLA) processes; resulted in biodegradable prototypes with much higher decomposition rates than the homopolymer counter-part.

As well-known, plastic field involves several other compounds, such as fillers, plasticizers, colorants, among others; which are many times necessary for the final polymer application. Therefore, not only the polymer science should move to a good sustainable direction but also the polymer additives market should do. In this third example, a free-brominated flame retardant organic additive was developed for the modification of expanded polystyrene plastics (EPS), used in construction area. The new additive is also free from aromatic compounds.

Keywords: *poly(limonene carbonate)epoxy, photocurable polymers, fire retardant additives, coatings, adhesives.*

Acknowledgments

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Enhancement of gas barrier properties and durability of Poly(butylene succinate-co-butylene adipate)-based nanocomposites for food packaging applications

H. Askanian[1*], A. E. Delorme[1], Tanja Radusin[2], Petri Myllytie[2], Vincent Verney[1]

[1] *Université Clermont Auvergne, CNRS, SIGMA Clermont, ICCF, F-63000 CLERMONT-FERRAND, France*
[2]*Norner Research, Asdalstrand 291 NO-3962 STATHELLE, Norway*
[*]*haroutioun.askanian@sigma-clermont.fr*

In this study, we investigate the properties of nanocomposites based on biodegradable PBSA which is food contact grade (complying to EU10/2011). We adopt the approach of mixing LDH fillers into PBSA to improve the overall durability and gas barrier properties of the nanocomposites. The commercially available SORBACID® 911 is our choice of filler due to its low-cost and also because it is listed as an acceptable material in the "Plastic Food Contact Materials" report (Regulation (EU) 10/2011). Moreover, considering that SORBACID® 911 is used on industrial scale as an acid scavenger for PVC materials it presents an appropriate scalability for food packaging applications. The properties of PBSA-LDH based nanocomposites were investigated by rheological, tensile testing, thermogravimetric and optical methods, which demonstrate that the PBSA-LDH combination form compatible polymer composites with good dispersion. The addition of SORBACID® 911 fillers enhanced the gas barrier properties, in particular, the water vapour barrier, rendering the nanocomposites competitors to conventional plastic films used for food packaging [1]. Furthermore, the photo-durability of the PBSA-LDH nanocomposites is examined through accelerated photoaging and compared to natural weathering. The results demonstrate improved resistance to photodegradation and weathering compared to pristine PBSA, and the resistance towards both photoaging and weathering increases with the LDH concentration in the PBSA matrix. With the improved gas barrier properties together with increased durability of PBSA with added SORBACID® 911 we demonstrate a realistic opportunity for transitioning from non-biodegradable to biodegradable food-packaging.

Keywords: Biodegradable polymers, food packaging, Layered Double Hydroxides, Nanocomposites, Poly(butylene succinate-co-butylene adipate)

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High performance recycled CFRP composites based on reused carbon fabrics through sustainable mild solvolysis route

W. Ballout[1*], N. Sallem-Idrissi[a], M. Sclavons[1], C. Doneux[2], C. Bailly[1], T. Pardoen[2] and P. Van Velthem[1]

[1]Institute of Condensed Matter and Nanosciences - Bio & Soft Matter (IMCN/BSMA), UCLouvain, 1 Place Croix du Sud, box: L7.04.02, 1348 Louvain-la-Neuve, Belgium
[2]Institute of Mechanics, Materials and Civil Engineering, UCLouvain, Place Sainte Barbe 2, 1348 Louvain-La-Neuve, Belgium

**wael.ballout@uclouvain.be*

A novel environmentally friendly recycling method is developed for large carbon-fibers reinforced-polymers composite panels whose efficiency is demonstrated through a proof-of-concept fabrication of a new composite part based on recycled fibers. The recycling process relies on formic acid as separation reagent at room temperature and atmospheric pressure with efficient recycling potential of the separating agent. Electron microscopy and thermal analysis indicate that the recycled fibers are covered by a thin layer of about 10wt.% of residual resin, alternating with few small particles, as compared to the smooth virgin fibers. The recycled composites show promising shear strength and compression after impact strength, with up to 93% retention of performance depending on the property as compared to the reference. The recycled carbon fibers can thus be reused for structural applications requiring moderate to high performances. The loss of properties is attributed to a lower adhesion between fresh epoxy resin and recycled carbon fibers due to the absence of sizing, partly compensated by a good interface between fresh and residual cured epoxy thanks to mechanical anchoring as well as chemical reactions. The room temperature and atmospheric pressure operating conditions combined to the recyclability of the forming acid contribute to the sustainability of the entire approach.

Keywords: Recycling, Solvolysis, CFRP, catbon fabrics.

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Recycled plastic content quantified through aggregation-induced emission: ReCon^2

T. Bennett[1,2], Z. Schyns[1,2], M. Shaver[1,2*]

[1] *Department of Materials, School of Natural Sciences, University of Manchester*
[2] *Sustainable Materials Innovation Hub, Henry Royce Institute, University of Manchester, Manchester, M13 9BL, United Kingdom*
[*] *michael.shaver@manchester.ac.uk*

The linearity of the plastics economy is problematic and polluting. To encourage recycling and decrease diversion to landfill, new legislation within the EU and UK will tax products made with less than 30% recycled plastic [1,2]. At present, quantitative determination of recycled content is elusive and existing methods inconsistent. We present a fluorescence-based analytical technique to determine recycled content in packaging plastics. Bathochromic shifts resulting from aggregation of a non-toxic fluorescent dye in three commodity plastics (high-density polyethylene, polypropylene and poly(ethylene terephthalate)) at extremely low loadings were used to quantify simulated recycled contents as low as 10 wt%. Linear correlations were found between recycled content and three fluorescence-based properties: emission, lifetime, and resulting colour. We demonstrate how this multi-branched verification system is completely independent of sample dimensions and processing conditions, has little effect on polymer properties, and is inexpensive and highly compatible with existing recycling infrastructure (Fig. 1). This technology has recently been patented and is in the process of being spun-out though the University of Manchester under the name "ReCon^2", short for "Reconnaissance of Recycled Content".

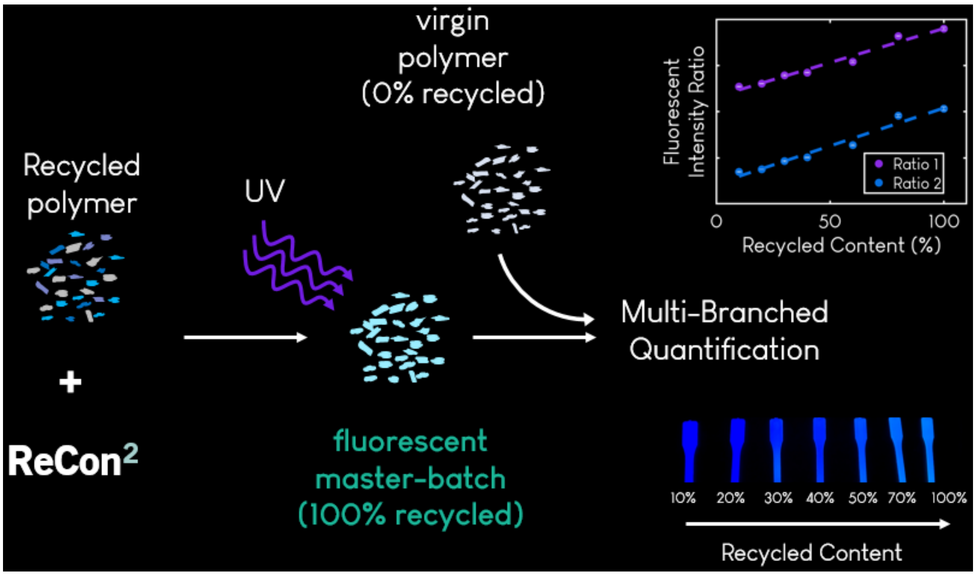

Fig. 1. Graphic representation of proposed recycled content fluorescence marking technique, now being spun-out as "ReCon^2".

Keywords: Recycling, Fluorescence, Plastic Packaging, Polymers, Circular Economy

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We thank the Henry Royce Institute for Advanced Materials and the Sustainable Materials Innovation Hub for facilities and equipment access, funded through the European Regional Development Fund (OC15R19P).

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Reciclyng of rigid PVC foam under glycolisis conditions

M. Calosi[1], M. Renon[2], S. Buoso[3], V. Mazzanti[4], F. Mollica[4], A. Massi[1], M. Bertoldo[1,3*]

[1]*Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Ferrara, Italy*
[2]*Department of Quality & Environment, DIAB Spa, Longarone (BL), Italy*
[3]*Institute of Organic Synthesis and Photoreactivity–Italian National Research Council, Bologna, Italy,*
[4] *Department of Engineering, University of Ferrara, Ferrara, Italy*
[*]*monica.bertoldo@unife.it*

Rigid PVC foam is one of the main core materials used in wind turbine blade construction thanks to its excellent strength-to-weight ratios, low cost, and good chemical resistance properties.[1] Despite its name, rigid PVC foam is actually a semi-interpenetrating hybrid of PVC, polyurethane and polyurea. It is made by reacting isocyanates and acidic anhydrides in the presence of PVC.[2]

The main current end-of-life options for decommissioned wind blades are landfilling and incineration, with only a minority of the material being mechanically recycled into low-value filler.[3-4] Investigations into the chemical recycling of wind blades have thus far focused on high-temperature and high-pressure solvolysis of the entire blade, the core being treated together with the glass fiber reinforced polymer shell and have not thus far resulted in viable industrial processes due to energy costs and the low purity of the resulting materials.[4] To our knowledge the chemical recycling of PVC foam by itself has not been investigated before.

Here we report a recycling strategy to effectively depolymerize the isocyanate-derived crosslinked portion of the foam, preserving the PVC fraction from an extended degradation. The process is accomplished by glycolysis in the presence of potassium acetate or dibutyltin dilaurate (DBTL) as catalyst and thermal stabilisers. Ethylen glycol (EG), 1,4 butanediol (BD), diethylene glycol (DEG), dipropylene glycol (DPG) and polyethylene glycol with average molecular weight of 600 Da (PEG600) were tested to investigate the effect of the glycol structure on the process efficency as well as on the degradation of the PVC. The reaction time and temperature were varied from 8 min to 180 min and from 155 °C to 200 °C, respectively. Heavy depolymerization of the crosslinked fraction was accomplished by processing at T ≥165 °C for not less than 30 min. The disentangled PVC fraction, recovered after extraction with methanol, was characterized by DSC, FT-IR spectroscopy, solubility test in THF, elemental and rheological analyses. The recovered solid showed a solubility in THF strongly dependent on processing time, with the value affected by both crosslinked fraction residua and degradation processes. The maximum was 90-95% after processing at 175°C for 30 min in DEG or DPG. The complex viscosity by rotational rheometry at 170°C and 100 rad/s of the so recovered PVC was about 500 Pa s suggesting the possibility of processing it by injection moulding in conventional machines.

The process cost, as well as the enviromental impact of the proposed process in perspective may be reduced by also exploiting the fraction soluble in methanol. Indeed, NMR, FT-IR and hydroxyl groups titration showed it is composed of hydroxyl-ended olygourethane and oligoureas that will be tested for polyuretane preparation.

Keywords: rigid PVC, chemical recycling, glycolisis
Acknowledgments: *DIAB Spa for funding.*

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Synthesis of smart polymeric flocculants for microalgae harvesting by RAFT polymerisation

Valentin Beyer[1], Jonas Blockx[1], Wim Thielemans[1*]

[1] *Sustainable Materials Lab, Department of Chemical Engineering, KU Leuven Campus Kulak, Kortrijk, Etienne Sabbelaan 53, Kortrijk 8500, Belgium*
[*] *wim.thielemans@kuleuven.be*

Microalgae are a promising CO_2-fixing feedstock which is gaining growing attention for the production of biofuel, the extraction of valuable fatty acids, and other high value chemicals. Despite the great potential of microalgae, their production and especially the isolation of the biomass remains economically unsustainable due to the high energy cost for harvesting. Since microalgae carry an overall negative surface charge, sedimentation can be induced by addition of cationic flocculants, which is a common harvesting technique. The presented work will investigate the structural impact of polymeric flocculants by assessing different macromolecular architectures, namely linear, branched, and core-crosslinked polymers. RAFT copolymerisation of commercially available 2-(dimethylamino)ethyl methacrylate (DMAEMA), the quaternised [2-(Acryloyloxy)ethyl]trimethylammonium chloride, and a dimethacrylate crosslinker is demonstrated to be a suitable technique for the synthesis of all three target architectures with different compositions. The polymer library is thoroughly analysed in order to confirm their absolute structure, molecular weight and solution properties. Furthermore, the results of flocculation tests on fresh- and salt water algae under various conditions are presented and a relationship between polymer architecture and flocculation efficiency is assessed.

Keywords: RAFT polymerisation, pH responsive, thermoresponsive, core-crosslinking, microalgae harvesting

Thermal stabilisation during processing: Impact of blending PHA with polyphenols

Bonnenfant Chloë[1], Aouf Chahinez[1], Gontard Nathalie[1]

[1]*INRAe Montpellier, 2 place Pierre Viala, 34060 Montpellier*
chloe.bonnenfant@umontpellier.fr

Given the huge impact of plastic pollution today, the scientific community needs to address this problem by developing new alternatives to the usual oil-based-plastic. To cope with the issues of fragmentation and persistence of conventional plastics in environment, bio-based and biodegradables polymers such as polyhydroxyalkanoates (PHAs), seems to be one of these alternatives. However, PHAs suffer from thermal instability which hinders their take-up in the plastics market[1].
The purpose of our research is to study the effect of polyphenols as thermal stabilizers for a food packaging material produced from polyhydroxyalkanoates (PHAs) during its whole life cycle (processing, using, mechanical recycling and biodegradation). This communication will focus on the first part: the effect of polyphenols on polymer processing.
Quercetin and Gallic Acid are the polyphenols that have been chosen to evaluate the thermal stabilization of a polyhydroxyalkanoate[2]: the PHBV, during the processing steps (fig1). Several analytical and imaging techniques were employed to assess the impact of polyphenols on the polymer thermal and structural behavior during extrusion, namely TGA, DSC, SEC and fluorescent microscopy.
The study has revealed that the stabilization effect is dependent on the percentage and the chemical structure of the polyphenols added in the matrix.. Special attention to polyphenol/PHBV interactions and their role on the thermal degradation mechanism of the polymer allowed to determine the polyphenol structure and optimal amount leading to stabilization.

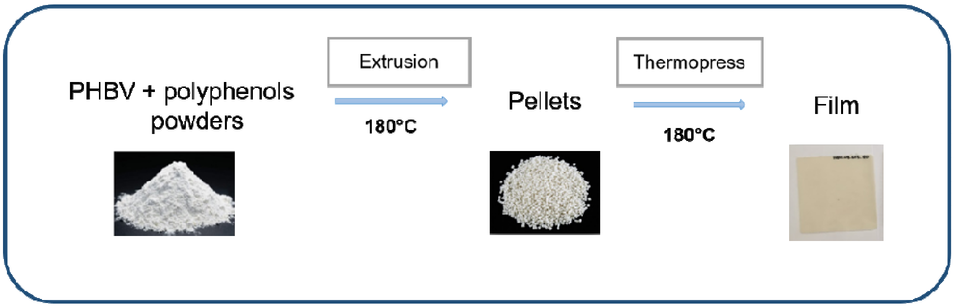

Figure 1: Processing procedure to produce PHBV/polyphenols blend films from powders

Keywords: Polymer, Polyphenols, Biodegradable, Stability, Process

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Reprocessable polylactide-based dynamic networks

K. Borska[1], M. Bednarek[2*], Andrzej Pawlak[2], Miroslav Mrlik[3], Josef Osicka[3], Danila Gorgol[3]

[1] *Polymer Institute, Slovak Academy of Sciences, Dubravska Cesta 9, 845 41 Bratislava, Slovakia*
[2] *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-362, Lodz, Poland*
[3] *Centre of Polymer Systems, Tomas Bata University in Zlin, Trida Tomase Bati 5678, 6760 01 Zlín, Czech Republic*
[*] *bednarek@cbmm.lodz.pl*

Polylactide (PLA) is biocompatible and biodegradable polymer obtained from renewable resources and used in different applications. To improve PLA thermal properties and introduce shape stability, the multifuncional hydroxyl-terminated PLA (star PLA) could be coupled by diisocyanate and the poly(ester-urethane) network is formed. The disadvantege of such networks is they cannot be reshaped or reprocessed. To solve this problem, the concept of “dynamic polymer networks” was created [1,2], according to which the networks are able to rearrange their structure due to the presence of linkages undergoing dissociative or associative exchange reactions under appropriate stimuli.

In the present contribution, poly(ester-urethane) networks with incorporated additional low molecular weight diols containing weak covalent bonds susceptible to thermal dissociation were obtained (Figure 1). As additional diols, able to reversible dissociation, disulfide [3] or tetraphenylethane groups were used. Analogous networks without “reversible” bonds were synthesised for comparison.

Thermal, mechanical, and rheological properties of obtained networks with different reversible bonds density were studied together with their ability to be reprocessed. Some samples containing dynamic bonds were suitable candidates for reprocessing by 3D printing technique.

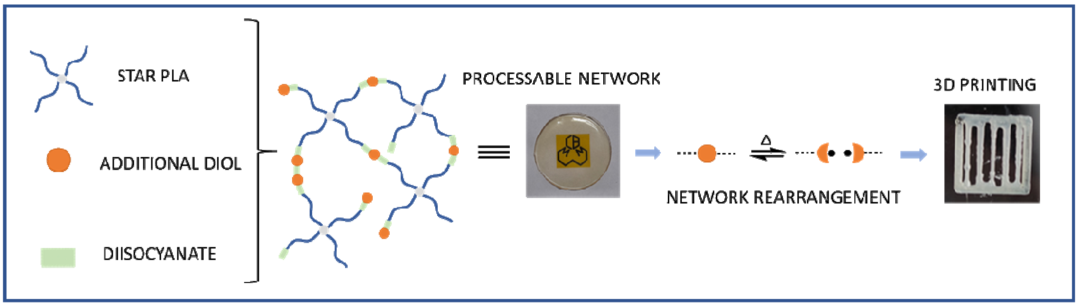

Figure 1: Network synthesis and reprocessing.

Acknowledgments

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Advanced data processing to improve the mechanical recycling of post-consumed plastic waste

M.Bredács[1*], C. Barretta[1], J. Geier[1], G. Koinig[2], K. Friedrich[2], D. Vollprecht[2], G.Oreski[1], S. Gergely[3]

[1]Polymer Competence Center Leoben GmbH, Austria, Rosegger Street 12, 8700 Leoben
[2]Chair of Waste Processing Technology and Waste Management, Montanuniversitaet Leoben, Austria
[3]Department of Applied Biotechnology and Food Science, Budapest University of Technology and Economics, Hungary, Műegyetem rkp. 3, 1111 Budapest
**marton.bredacs@pccl.at*

Several initiatives are aiming to increase the recycling of plastic products in order to achieve a circular economy. The European Plastic Alliance Declaration set the objective of 10 million tons of recycled plastic per year to be accomplished by 2025 [1]. Current state-of-the-art NIR hyperspectral imaging based plastic sorting lines can separate various polymer types, however the separation of one polymer class based on material properties such as density and melt flow rate is not feasible nowadays. These material properties determine the possible reprocessing and consequently the quality of the recycled product. Despite the intensive research concerning the improvement of mechanical sorting several challenges have not been solved yet.

Multivariate data and principal component analyses (PCA) [2] are frequently used in spectroscopic data evaluation allowing to uncover hidden spectral information and predict various material properties such as density [3]. Furthermore, PCA is an excellent tool to classify high amount of spectral data. In this study the main focus was put on the improvement of NIR data collection and analysis in order to increase the sorting degree. One major goal was the separation of polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) into various subclasses based on their material properties. The PCA results clearly indicate that PE, PP and PET products made of various polymer grades can be differentiated allowing a higher degree of sorting. Differentiation between (low density) LDPE grades, copolymer and homopolymer PP as well as PET materials based on their molecular weight is possible with advanced data processing of NIR spectra. Moreover, different classes of acrylnitril-butadien-styrol, and polystyrene were determined highlighting the importance of data processing.

Such results are of high importance in the quality improvement of recycled polymer fractions. Accurate material identification and separation of post-consumed plastic waste would mean a significant step toward circular plastic products and supporting the objective of the European Plastic Alliance Declaration.

Keywords: Mechanical recycling, NIR spectroscopy, multivariate data analysis

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Closing the polymer loop for aliphatic polyesters

L. Cederholm[1*], J. Wohlert[1], P. Olsén[1], M. Hakkarainen[1], K. Odelius[1]

[1]*Wallenberg Wood Science Center, WWSC, Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56-58, 100 44 Stockholm (Sweden)*
[*]*lced@kth.se*

A circular polymer economy is vital for realizing a sustainable use of plastics in our society. Closing the polymer loop via chemical recycling to monomer (CRM), where the original monomer is regenerated from polymer waste, is a promising strategy to reduce the need of virgin polymers to a minimum. Independent of the feedstock origin (fossil or biobased), this is an important design criterion for new polymeric materials. To meet the requirements of circularity as well as material properties, the library of recyclable polymers must be extended, and to achieve that we have to understand what dictates the recyclability and learn how to control it.

The equilibrium between monomer and polymer and, hence, the reversibility of a polymerization (**Figure 1**) is governed by the thermodynamics of polymerization. Ring-opening polymerization (ROP) of heterocyclic monomers is often highlighted as a promising polymerization technique to achieve CRM. [1] The ROP equilibrium is controlled by specific monomer features, like ring-size and substituents, but also by external factors, like temperature and concentration. It is this interplay between monomer properties and the surrounding environment that determines the equilibrium which can help us to close the polymer loop. We have previously demonstrated how the thermodynamic stability of the inherently recyclable poly(δ-decalactone) can be improved to better meet material property requirements. [2] Now, we can also present a strategy for polymers with a high ceiling temperature. This strategy enables recycling directly back to the original cyclic monomers with high conversion and high selectivity.

Figure 1. To achieve a circular polymer economy, we must understand the thermodynamic features that dictates the reversibility of a polymerization reaction and learn how to control them.

Keywords: chemical recycling to monomer, aliphatic polyester, thermodynamics

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Pecan Nutshell (PNS)-Based Functional And High-Performance Compounds

Sarai Agustin-Salazar[1], Andrea Panaro[1], Gennaro Scarinzi[1], Federica Moccia[2], Rita Argenziano[2], Lucia Panzella[2], Alessandra Napolitano[2], Anna Calarco[3], Ilenia De Luca[3], Francesca Di Cristo[4], Anna Valentino[3], Veronica Ambrogi[5], Paolo Aprea[5], Pierfrancesco Cerruti[1,*]

[1]*Institute for Polymers, Composites and Biomaterials (IPCB-CNR), Pozzuoli (Na), Italy*
[2]*Department of Chemical Sciences, University of Naples Federico II, Naples, Italy*
[3]*Research Institute on Terrestrial Ecosystems (IRET-CNR), Naples, Italy*
[4]*Elleva Pharma s.r.l. via P. Castellino, 111 – 80131 Naples, Italy;*
[5]*Department of Chemical, Materials and Production Engineering, University of Naples Federico II, Naples, Italy*
**cerruti@ipcb.cnr.it*

Lignocellulosic agri-food wastes represent an attractive source of highly added value bioactive molecules as well as cheap fillers for the preparation of low-cost biocomposites [1]. In addition, their use limits landfilling and incineration, also relieving the environmental burden relative to these practices. In the last few years, pecan nutshell (PNS) has been reported as a source of highly valuable antioxidant and antimicrobial phenolic compounds [2], as well as of fillers able to modify mechanical and rheological properties of polymer biocomposites [3]. Herein, we report the results concerning the use of PNS-derived phenolic compounds as active agents for the development of active packaging, as well as AgNP-based photocatalytic and antibacterial devices. Morever, we also document the potential of PNS as a source of sustainable filler to develop cost-effective polylactic acid (PLA) biocomposites with tailored mechanical properties. These materials could be used when stiff, light, and low deformable products are required, including structural, household, and packaging applications.

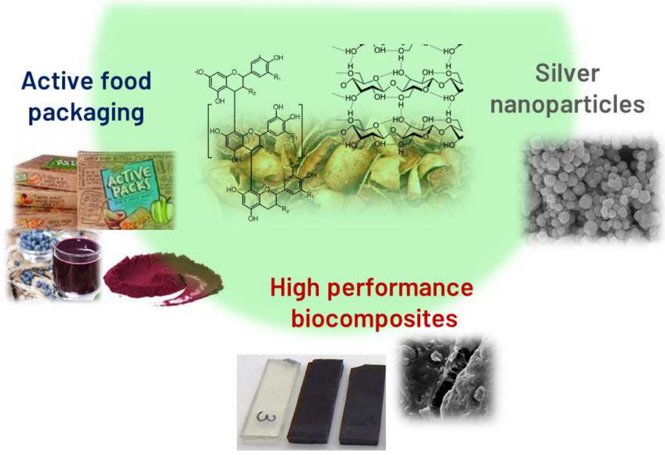

Figure 1. Pecan nut shell as a sustainable source of multifunctional compounds for active packaging, nanoparticles, and biocomposites.

Keywords: pecan nutshell, active packaging, sustainability, antimicrobial, nanoparticles, polylactic acid, biocomposites

Acknowledgments

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Cascade (dithio)carbonate ring opening reactions for self-blowing Polyhydroxythiourethane foams[1]

Guilhem Coste[1], Claire Negrell[1], Sylvain Caillol[1]*
[1] *ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France*
*sylvain.caillol@enscm.fr

Polyurethane (PU) foams are nowadays common polymers used in various domains such as insulation or mattresses. Due to the growing concern about the environmental impact of isocyanates, greener routes are actively studied. Polyhydroxyurethanes (PHU) have been developed in order to produce isocyanate-free polyurethane thermosets.[2] Nevertheless, to replace PU foams, a gas production is required in order to blow the foam. Thus, different routes have been developed to blow PHU; such as the reaction amine-polymethylhydroxysiloxane or the use of low boiling point liquids.[3,4] Such strategies suffer from different drawbacks (flammable gases or/and the price of the blowing agent). In this work, we present a new strategy based on the Pearson reaction e.g. between thiol and cyclic carbonate to produce carbon dioxide.[5] Despite the interest of such reaction it requires the use of stinking thiols which might induce toxicity problem. In this work, we present a new strategy in order to produce carbon dioxide through a cascade reaction. Indeed the gas production is induced by the formation of thiol in situ from the ring opening of dithiocarbonate monomers by an amine. Owing to this original way of blowing, different foams have been synthesized and characterized in order to determine the influence of different additives on morphologies and properties.

Keywords: Polyhydroxyurethane, NIPU, foam, blawing agent

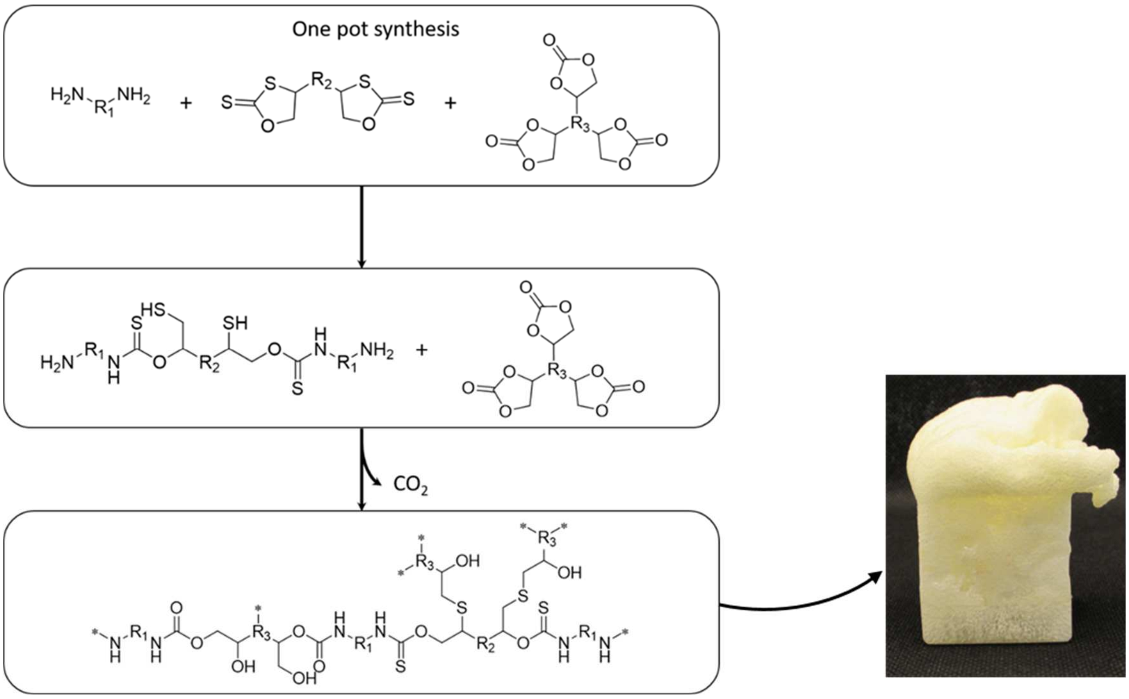

Figure 1: NIPU foam synthesized from dithiocarbonate and cylic carbonate

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FDCA-based copolyesters modulate the properties of PLA-based blends

Z. Terzopoulou[1,2*], A. Zamboulis[1], L. Papadopoulos[1], D. Bikiaris[1], G. Papageorgiou[2]

[1]*Laboratory of Chemistry and Technology of Polymers and Dyes, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece*
[2]*Department of Chemistry, University of Ioannina, P.O. Box 1186, GR-45110 Ioannina, Greece*
*****terzoe@gmail.com*

Poly(lactic acid) (PLA) is currently the most frequently used biobased thermoplastic polyester. It is compostable, processable but also brittle. The properties of polymers often need tuning to obtain final products with the desirable characteristics for specific applications. Polymer blending has attracted considerable interest as an easy and cost-effective method of fabricating materials for a wide range of applications. Therefore, PLA blends with both biodegradable and non-biodegradable polymers have been investigated for many applications. Biobased polymers derived from 2,5-furan dicarboxylic acid (2,5-FDCA), a promising monomer produced by the oxidation of hydroxymethylfurfural, are in the forefront of both academic and industrial research towards this goal [1]. In this work, biobased and biodegradable copolymers poly(butylene 2,5-furan dicarboxylate-co-adipate) (PBF-co-PBAd) with different comonomer ratios were synthesized and blended with PLA, to produce fully biobased blends and examine their physicochemical properties.

PBF, PBAd and PBF-co-PBAd copolymers were synthesized with the transesterification and melt polycondensation method with Titanium(IV) butoxide catalyst. The copolymers were prepared in three different molar ratios; 25/75, 50/50 and 75/25. Afterwards, each hopolymer and copolymer was blended with 70 wt% PLA by melt compounding at 190 °C and 35 rpm for 5 min. Intrinsic viscosity [η] was measured with an Uhbelode viscometer. The chemical structures and comonomer ratios were confirmed with NMR spectroscopy. Thermal transitions and thermal stability were examined with Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA), respectively. Mechanical properties were studied with nanoidentation. The compatibility of the blends was evaluated with Scanning Electron Microscopy (SEM) and DSC. Finally, reactive blending was tested as a means to improve the compatibility of the polymer blends.

Keywords: biobased polymers; blends; FDCA; poly(lactic acid)

Acknowledgments

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Lignin-based reversible elastomers: Combining bio-aromatics with Diels-Alder chemistry

M. Thys[1,2*], J. Brancart[1], G. Van Assche[1], R. Vendamme[2], N. Van den Brande[1]

[1]*Physical Chemistry and Polymer Science (FYSC), Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050 Brussels, Belgium*
[2]*Flemisch Institute for Technological Research (VITO), Boeretang 200, 2400 Mol, Belgium*
[*]*marlies.thys@vub.be / marlies.thys@vito.be*

In recent years, the biopolymer industry has been growing intensively which is mainly due to the increasing production capacity of a variety of aliphatic bio-based polymers such as polylactic acid.[1] In contrast, the development of bio-aromatic polymers from sustainable resources is lagging behind. As a biogenic by-product of the paper and pulp industry, lignin is a promising aromatic resource that could provide for interesting properties when integrated into polymer resins or composites. However, these materials are often limited in their recycling possibilities which restrict the development of highly sustainable materials. These limitations can be mediated by the incorporation of reversible covalent bonds.

Therefore, this work aims to develop lignin-based reversible networks based on the thermo-reversible furan-maleimide Diels-Alder (DA) reaction.[2] An EMK (ethyl methyl ketone) extracted Kraft lignin was modified with furan moieties and integrated into an optimized Diels-Alder formulation based on a furan-modified polyether (F5000) and 1,1'-(methylenedi-4,1-phenylene)bismaleimide (DPBM). Increasing amounts of lignin were added to tune the mechanical properties of the obtained elastomers (Fig. 1). The integration of lignin significantly improved the thermal properties as measured by thermogravimetric analysis (TGA). In addition, differential scanning calorimetry (DSC) indicated, besides the glass transitions (T_g), the reversibility of the DA reaction. The obtained networks were analyzed using different (thermo)mechanical techniques such as dynamic mechanical analysis, rheology, and tensile testing. The networks showed a substantial improvement in the mechanical properties going from a Young's modulus of 13 MPa for the reference network up to 425 MPa for a 29 wt% lignin-containing network. Moreover, their healing capacity and processing opportunities were repeatedly tested and showed promising recycling and end-of-life options.

Figure 1. **Developed DA-networks, from left to right: the reference network without lignin, lignin networks with increasing lignin content of 17 wt%, 22 wt%, and 29 wt% respectively.**

Acknowledgments

The authors would like to thank Innventia Institute for providing Lignoboost KL, Brigitte Lamers from the Meijers research group at Tu/e for measuring the SAXS spectra, and The Research Foundation Flanders for the Ph.D. fellowship of M.T. (1SA8620N) and for the Junior postdoctoral fellowship of J.B. (12W4719N)

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Enzymatic degradation of the most common aliphatic biopolyesters

A. Romano[1], A. Rosato[1], G. Totaro[1*], A. Celli[1], G. Zanaroli[1], L. Sisti[1]

[1]*Dept. of Civil, Chemical, Environmental and Material Engineering, University of Bologna, Bologna, Italy*
[*]*Corresponding Author's mail: grazia.totaro@unibo.it*

The constant increase of the plastic production over the world has become a serious problem, since most conventional plastic materials come from fossil resources and are not biodegradable. This causes significant plastics accumulation in the environment, whose end-life must be managed. An effective and eco-friendly approach to solve such problem is the use of biodegradable materials. Biopolymers such as poly(butylene succinate) (PBS), poly(butylene succinate-*co*-adipate) (PBSA), poly(caprolactone) (PCL), poly(lactic acid) (PLA) and poly(propylene carbonate) (PPC) are among the most promising biodegradable commercial polyesters thanks to their high susceptibility to hydrolytic enzymes and to many microorganisms naturally occurring in the environment [1-2]. The current study is an investigation of the degradation ability of several hydrolytic enzymes belonging to different subclasses (i.e. lipase, esterase, proteinase, etc.) against some common aliphatic commercial polyesters. A deeper elucidation on the degradative ability and the mechanism of hydrolytic biodegradation can be useful for the management of biodegradable plastic wastes, the bioremediation of plastic-polluted environments, as well as the design of innovative biodegradable plastic materials. The end-of-life of biopolymers indeed, should also be addressed in view of a circular economy concept.

The enzyme screening was first carried out by investigating the capacity of fully degrading the target polymers in 24 h, then weight loss measurements of selected polyesters and target enzymes were performed. Solid residues after enzyme degradation were characterized by proton nuclear magnetic resonance (^{1}H NMR), gel permeation chromatography (GPC), infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC) and thermogravimetry (TGA). Liquid fractions were studied via GPC, ^{1}H NMR and high-performance liquid chromatography (HPLC). This, in order to understand molecular and chemical modifications induced at the surface and/or in the bulk of polymer materials over time. The results showed that the enzymatic degradation occurred homogenously from the surface through an erosion mechanism. Cleaving action mode for each enzyme towards the selected polyesters (endo- and/or exo-type) is also proposed.

Keywords: Aliphatic biopolyesters, Enzymatic degradation, Endo/exo-type action mode

Acknowledgments

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Stabilization of PLA with natural polyphenols extracts: towards fully bio-based polymers formulations

L. Valero*, F. Delor-Jestin, H. Askanian

Université Clermont Auvergne, Clermont Auvergne INP, CNRS, ICCF, F-63000 CLERMONT-FERRAND, FRANCE
**luna.valero@sigma-clermont.fr*

The development of natural additives are increasingly investigated in the plastic field, and particularly for biopolymers. A major challenge is to substitute synthetic additives, including stabilizing agents, with greener chemicals. Throughout their lifecycle, polymers are subject to degradation, such as thermo- and photo-degradation, leading to the deterioration of their properties. Stabilizers are used to prevent and/or slow down the degradation kinetics and control the durability of polymer materials. Recently, bio-sourced antioxidants, like polyphenols, have shown promising stabilizing effects in hindering polymers degradation and aging [1]. As part of the European project H2020 SEALIVE*, this work aimed to design fully bio-based plastic formulations, by incorporating polyphenols extracts from biomass valorization for the thermal and photo-stabilization of poly(lactic acid) (PLA).

As a first step, the extraction of polyphenols from vegetal matrices (agri-food by-products, industrial residues, wild plants) and their characterization allowed an initial evaluation of the extracts' potential as antioxidant additives (*figure 1*). As a second step, thermal and photo stabilization studies were conducted on PLA formulated with the polyphenols exhibiting high antioxidant activities. The stabilizing efficiency of the extracts was evaluated using rheological analysis to assess the kinetics and mechanisms of degradation of the polymer matrix. The stabilization of PLA was firstly analyzed in terms of the thermomechanical degradation occurring during processing at high temperatures (*figure 2*). Then, the service-life durability of PLA was investigated through thermal and photo-aging studies in accelerated conditions. The results demonstrated that different polyphenols extracts successfully delay PLA degradation and constitute very promising natural stabilizers.

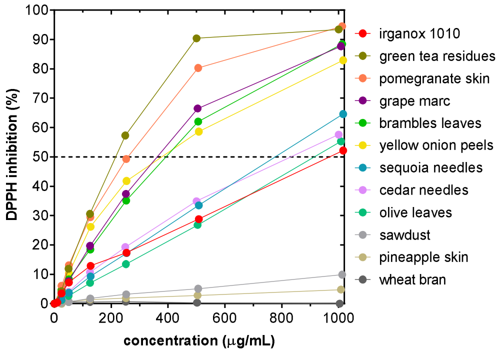

Figure 1: antioxidant activity of natural polyphenols extracts.

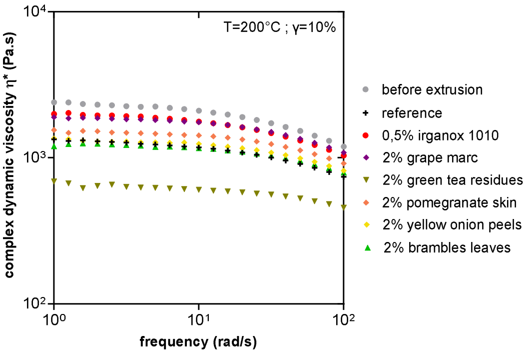

Figure 2: impact of the processing on PLA materials.

Keywords: poly(lactic acid) (PLA), degradation, natural antioxidants, polyphenols, durability

Acknowledgments

* *SEALIVE project "Strategies of circular Economy and Advanced bio-based solutions to keep our Lands and seas alIVE from plastics contamination"* https://sealive.eu/

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 862910 (SEALIVE). This output reflects only the author's view and the European Union cannot be held responsible for any use that may be made of the information contained therein.

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Synthesis of biobased benzoxazines for anticorrosion application on Magnesium

Louis Van Renterghem, Romain Tavernier, Leïla Bonnaud, Roya Malekkhouyan, Marjorie Olivier, Jean-Marie Raquez

Materia Nova Research Center, Avenue N. Copernic 3, 7000 Mons, Belgium.
University of Mons (UMons), Place du Parc 23, 7000 Mons, Belgium.
louis.vanrenterghem@umons.ac.be; Romain.tavernier@umons.ac.be ;
Leila.bonnaud@materianova.be; Roya.MALEKKHOUYAN@umons.ac.be;
marjorie.olivier@umons.ac.be; *jean-marie.raquez@umons.ac.be;*

The growing demand for lightweight materials in the automotive, aeronautic, electronics and construction industries has lead to a renewed interest for magnesium alloys due to their low density, high strength-to-weight ratio and easy recyclability. However, the weak resistance of magnesium alloys to salt water, moisture and acids limits their use in many applications[1]. Various protections have been considered to prevent the degradation of magnesium but most of them include toxic hexavalent chromium compounds[2]. A more environment friendly alternative consists in the use of protective organic coating. Interestingly, thermosetting benzoxazine resins exhibit good thermal, anti-corrosion and alkaline resistance and thus appear as promising candidates[3]. In addition, such resin precursors can be readily obtained via a solvent free process from renewable phenolic and amine compounds[44]. Recently, we also demonstrated that the incorporation of additional dynamic exchangeable covalent groups, such as carbamate, within the resin network leads to healable and recyclable materials[5].
In this frame, this research focus on the use of ester and hydroxyl functions also known to undergo dynamic exchangeable bonds to develop innovative benzoxazine structures for coatings exhibiting self-healing and enhanced adhesion on magnesium substrates. Finally, the reduction of VOC emissions upon coating application is also considered thanks to the use of a dry process.

Keywords : benzoxazines ; anti-corrosion ; magnesium

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Enzymatic synthesis of tannin-based polymers

M. Vera[1*], N. Li[2], C. Silva[2], B. F. Urbano[1]

[1]*University of Concepción, Concepción, Chile*
[2]*University of Minho, Braga, Portugal*
[*]*mylevera@udec.cl*

The use of polymeric materials obtained through biologically based renewable resources emerges as a response to the current problem related to fossil-based plolymers. Tannins are the second most abundant natural source of phenolic compounds after lignin. These plant secondary metabolites are an important biobased resource with the potential to replace many of the fossil-based materials[1]. These polyphenolic compounds are among the most abundant bio(macro)molecules in nature, have a low cost and are chemically versatile[2,3]. In this work we report the synthesis of tannin-based polymers obtained by enzymatic polymerization. Tannin-based polyphenols were synthesized using the enzyme *Myceliophthora thermophila* laccase as a biocatalyst and condensed tannins extracted from the bark of Pinus Radita (Figure 1). Polymerization was carried out in the presence of oxygen and was followed by UV-Vis, phenol content analysis, rheometry, and gel permeation chromatography (GPC). During the polymerization, a decrease in the content of phenols and an increase in viscosity were observed. In addition, the resulting polymers showed a high antioxidant capacity and improved thermal properties. This work proposes an ecological route to obtain bio-based polyphenols with a wide potential in various applications at the industrial level.

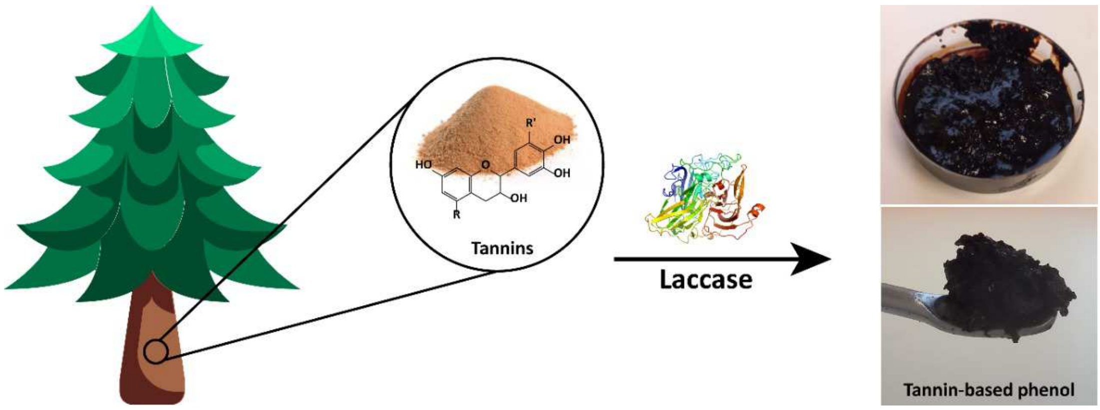

Figure 1. Schematic process of obtaining tannin-based polyphenols by enzymatic synthesis.

Keywords: Tannins, laccase polymerization, *Myceliophthora thermophila* laccase, green polymer synthesis, bio-based plastics.

Acknowledgments

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Conductive lignin derived polyurethane foam and PEDOT: PSS coating

Fernanda Rosa Vieira[1*], Sílvia Soreto[2], Luís Cadillon Costa[2], Ana Barros- Timmons[1], Dmitry V. Evtuguin[1] and Paula C. O. R. Pinto[3]

[1]*Department of Chemistry, CICECO-Institute of Materials, University of Aveiro, Aveiro, Portugal*
[2]*I3N and Department of Physics, University of Aveiro, Aveiro, Portugal*
[3]*RAIZ, Forest and Paper Research, Aveiro, Portugal*
[*]*fernanda.rvieira@ua.pt*

The growing interest in the complete or at least partial replacement of petroleum-derived polymers with renewable ones is a common trend towards zero-cabon and sustainable economy. Among the polymers from renewable resources, lignin is a natural aromatic polyol, second in natural abundance after cellulose, which is particularly attractive for the development of a new generation of polyurethanes upon being oxyalkylated[1]. Polyurethane (PU) foams, due to their porous structure are well known as lightweight insulating materials. However, PU foams have been also explored as sensors in robotic and wearable systems[2,3] using a conductive polymer as poly (3,4-ethylene dioxythiophene): polystyrene sulfonate (PEDOT: PSS), nanofillers as carbon nanotubes (CNTs), and other conductive fillers to enhance the electrical conductivity, an essential property to develop electronic devices[4].

The present study aimed at developing conductive bio-based polyurethane foams derived from oxyalkylated lignin upon homogeneously coating them with PEDOT: PSS (PDT). The effect of conducting nanomaterials in the formulation such as MWCNTs, was also evaluated. Figure 1 illustrates the strategy followed. The DC electrical conductivity of the ensuing coated foams increased 10 orders of magnitude from 10^{-15} to 10^{-5} S/m, showing the potential of these composite foams to be used as bio-based materials in electronic devices.

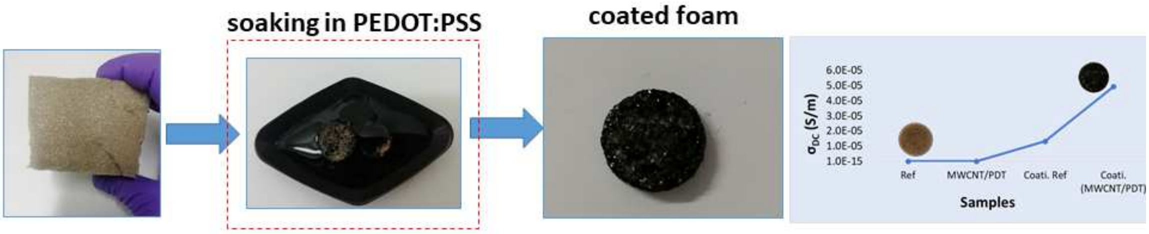

Figure 1. Strategy followed to prepare conductive PUFs derived from lignin.

Keywords: lignin, bio-based polyurethane, PEDOT: PSS, conductive polymer, electrical conductivity, electronic devices

Acknowledgments

This work was carried out under the Project Inpactus—innovative products and technologies from eucalyptus, Project N° 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 n° 246/AXIS II/2017 and CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, and I3N projects UIDB/50025/2020 and UIDP/50025/2020, financed by national funds through the FCT/MEC (PIDDAC).

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Dynamic polyurethane thermosets: triggering associative exchange reactions by visible light

G. Vozzolo[1], F. Elizalde[1], Daniele Mantione[1] L. Irusta[1], H. Sardon[1]

[1] *Faculty of Chemistry, Basque Country University UPV/EHU, 20018 San Sebastián (Spain).*

Email: giulia.vozzolo@ehu.eus

Classic thermosets are permanently crosslinked materials suitable for a wide variety of applications, anyway they cannot be reprocessed, reshaped and recycled. In order to overcome this limitation, adding dynamic crosslinks into the polymer networks can be an alternative for these materials to exhibit malleability and faster stress relaxation when the dynamic crosslinks are activated [1]. To speed up the dynamicity of these materials one of the leading strategies is the introduction of catalysts in combination with high temperatures. [2] This strategy has been applied in polyurethanes, one of the most widely used class of polymers in the thermoset market. Recently it has been demonstrated that the dynamic behavior of polyurethanes is highly dependent on the nature of the catalyst used, the ratio urethane/free alcohol group into the network and the nature of the isocyanate (aromatic vs aliphatic). It has been demonstrated that the stress relaxation of the aromatic polyurethane networks is way faster if a strong acid like paratoluensulfonic acid (PTSA) was added into the polymer. [3] However this strong acid is permanently present into the network, eventually leading to permanent deformation. Photoacids that undergo proton dissociation upon irradiation avoid the permanent presence of a strong acid into the system. Metastable photoacids (mPAHs) are able to reversibly change the pH of a solution upon irradiation with appropriate wavelength, usually UV or even visible light. [4][5]

Herein we explored the use of reversible photoacids as catalysts that trigger faster transcarbamoylation exchange reactions into crosslinked polyurethane networks; the acid release is triggered by visible light; the release of an acid species into the network catalyzes a faster exchange reaction of the urethane bonds in presence of free alcohol groups. Polyurethane crosslinked films with 5% mol of two different photoacids were prepared and stress-relaxation measurements at 120ºC were carried out in order to investigate the dynamicity of the urethane bonds before and after irradiation. Polyurethane crosslinked films without any catalyst and with 2% mol of PTSA were prepared in order to compare the results obtained with the photoacids with these control samples. Overall, immediately irradiated materials showed faster stress relaxation times than films irradiated several days before, confirming the activation of the dynamic covalent chemistry by acidic catalysis within the polyurethane network.

Acknowledgments

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Acid catalyzed Lignin-Resorcinol-Formaldehyde Aerogels: Influence of Solvents on Particle Morphology

P. Weidmann[1], R. S. A. Meyer[1 *], I. Smirnova[2], G. A. Luinstra [1]

[1] *Institute for Technical and Macromolecular Chemistry, University of Hamburg, Hamburg, Germany*
[2] *Institute for Thermal Separation Processes, Hamburg University of Technology, Eißendorfer Straße 38, 21073 Hamburg, Germany*
[*] *robert.meyer@chemie.uni-hamburg.de*

Lignin is the second most abundant biopolymer on earth but rarely used as source of aromatic thermo-sets.[1] Its chemical structure and properties make lignin potentially a natural substitute for oil-based phenolics. It could be utilized as a component in coatings and adhesives.[2] Lignin can also partly replace resorcinol in the synthesis of organic aerogels. The reaction of resorcinol and formaldehyde is mostly alkaline catalyzed,[3] however, the acid catalyzed polycondensation gives material with promising properties and allows to shorten gelation times.[4, 5]

Here a report is given on the preparation of mechanically stable gels from an acid catalyzed polycondensation of a mixture of 40 *wt*% resorcinol and 60 *wt*% lignin and the appropriate amount of formaldehyde. Gels formed within a few minutes. The morphology of the gels is reminiscent of the usual interconnected beads, partly with a substantial amount of “clunky” agglomerates. The application of a mixture of solvent and non-solvent for lignin in the gelling reaction led to different bead sizes, ranging from about 200 nm to 2 µm (Figure 1).

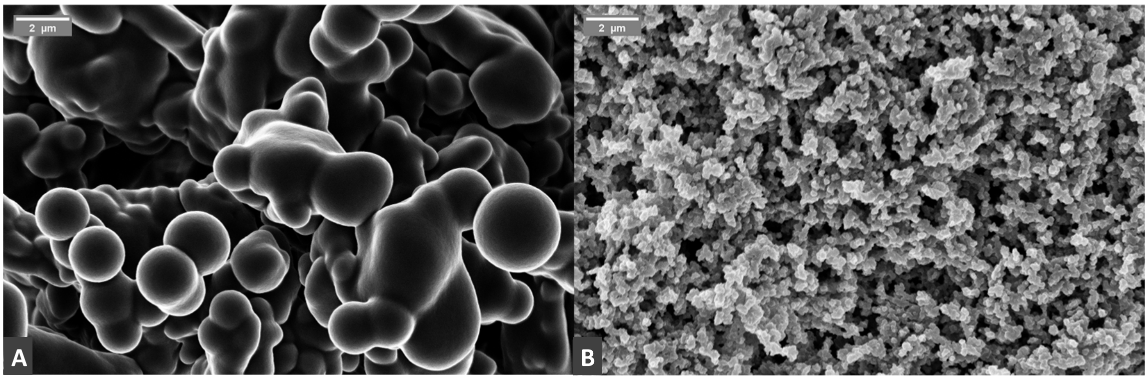

Figure 1: SEM images of aerogels formed via gelation in A) acetone/water (60/40) and B) ethanol/water (50/50).

Gels with larger bead sizes showed very low shrinkage. Drying under ambient conditions was found possible instead of using supercritical CO_2, offering the possibility for an easy and cost-efficient scale up. Aerogels up to a size of 15x15x4 cm were produced with densities of 0.2 g/cm^3 and porosities of 85 %. Compression testing gave a Young’s modulus up to 1.2 MPa for a gel prepared in acetone/water.

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Stretchable and durable inverse vulcanized polymers with chemical and thermal recycling

Peiyao Yan[1*], Wei Zhao[1], Samuel J. Tonkin[2], Justin M. Chalker[2], Tara L. Schiller[3] Tom Hasell[1*]

[1]*Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD (UK);*
[2]*Institute for Nanoscale Science and Technology, College of Science and Engineering, Flinders University Bedford Park, South Australia 5042, Australia;*
[3]*WMG, University of Warwick, Coventry CV4 7AL, UK.*
[*]*Tom Hasell: t0m@liverpool.ac.uk*
[*]*Peiyao Yan: Peiyao.Yan@liverpool.ac.uk*

Inverse vulcanized polymer materials have received considerable attention as a way to use sulfur, an industrial by-product, as starting material for synthesis. The resulting high-sulfur content polymers have also been investigated because their properties give rise to promising applications like infrared imaging, energy storage, and heavy metal capture due to their unique structure. However, synthesis of a flexible sulfur polymer network which shows good mechanical properties combining high strength, high elongation, and high toughness is still a significant challenge. Moreover, further exploration of the properties of sulfur polymers to better understand the relationship between the polymers' structure with their performance is still needed. Here, a range of crosslinked sulfur polymers with high tensile elongation and toughness, and without losing high strength were successfully synthesized. The obtained crosslinked sulfur polymers show high solvent tolerance in most organic solvents but are demonstrated to be chemically de-crosslinked in polar solvents dimethylformamide, dimethylacetamide and N-methyl-2-pyrrolidone and can be re-crosslinked after removing the solvent due to the high sulfur ranks present in the polymer network. Despite the significantly improved mechanical properties, highly efficient thermal recycling performance typical of inverse vulcanized polymers was retained. Flexibility and durability, combined with chemical and thermal recycling, could open a new door for wider applications of inverse vulcanized polymers.

This work is published on the journal 'Chemistry of Materials', and this work is an extended work from our previous work (Yan, Peiyao, et al. "Inverse vulcanized polymers with shape memory, enhanced mechanical properties, and vitrimer behavior." Angewandte Chemie International Edition 59.32 (2020): 13371-13378.) Based on our published work, I would like to give a presentation on the interesting functions of inverse vulcanized polymers and how to make stroger inverse vulcanized polymers.

Novel biobased poly(ethylene furanoate-*co*-ethylene vanillate) copolymers

Evangelia Balla[1], Lazaros Papadopoulos[1], Nina-Maria Ainali[1], Maria-Eirini Grigora[2], Dimitrios Tzetzis[2], Alexandra Zamboulis[1*], Dimitrios N. Bikiaris[1*]

[1]*Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece*
[2]*School of Science and Technology, International Hellenic University, N. Moudania, Greece*
**azampouli@auth.gr, dbic@chem.auth.gr*

During the last decades, public awareness regarding environmental issues is steadily rising. To respond to consumers' demand for greener products, and due to steadily dwindling fossil fuel resources, renewable resources are being investigated as sources for raw materials. Indeed, efforts are being made to exploit natural feedstock, such as cellulose and lignin, for the production of biobased monomers for the synthesis of more sustainable polymers [1]. In this context, poly(ethylene furanoate) (PEF), the most prominent member of the family of furanic polyesters, is currently considered as a potential substitute of poly(ethylene terephthalate) (PET) in some applications.

Biobased vanillin, isolated from lignin, is already commercially available [2]. Vanillic acid or 4-hydroxy-3-methoxybenzoic acid, obtained by vanillin oxidation, has recently regained attention due to its bifunctional aromatic structure. Poly(ethylene vanillate) (PEV) was thus synthesized and studied, exhibiting promising characteristics [3,4]. In the present work, the copolymerization of PEF with PEV, will be presented. Poly(ethylene furanoate-co-ethylene vanillate) copolymers (PEFV) were prepared by two-step melt polycondensation. The copolymers were structurally characterized by nuclear magnetic resonance spectroscopy and infra-red spectroscopy, while their thermal behavior and thermal stability was studied by differential scanning calorimetry and thermogravimetric analysis. Finally, their mechanical properties were evaluated by nanoindentation.

Acknowledgements

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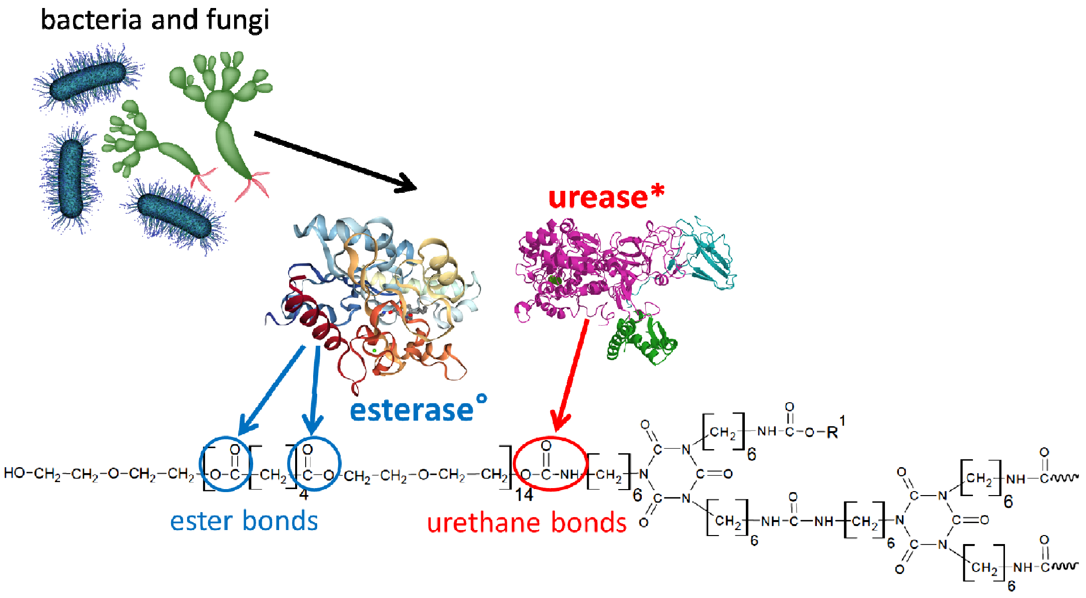
Non-hazardeous polyurethane foam for environmental applications: study of its abiotic and microbial degradation

Olga Trhlíková[1], Věra Vlčková[1,2], Sabina Abbrent[1], Kateřina Valešová[3], Lívia Kanizsová[1], Kateřina Skleničková[1], Aleksandra Paruzel[1], Sonia Bujok[1], Zuzana Walterová[1], Petra Innemanová[3]. Martin Halecký[2*], Hynek Beneš[1*]

[1] *Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic*
[2] *Department of Biotechnology, Faculty of Food and Biochemical Technology, University of Chemistry and Technology Prague, Czech Republic*
[3] *Faculty of Science, Charles University, Prague, Czech Republic*
[*] *martin.halecky@vscht.cz (M. Halecký), benesh@imc.cas.cz (H.Benes)*

Polyurethane (PUR) foams are currently in high demand not only in traditional applications but also in biotechnological and environmentally-oriented processes in which they can reach the open environment. Newly designed PUR foams with degradation-on-demand features are highly desirable but their (bio)degradation behaviour has to be thoroughly understood. Herein, we have studied abiotic and microbial degradation of fully aliphatic PUR foam, developed as a biomass carrier for biofiltration. The progress of abiotic hydrolysis shows complete degradation of soft polyol segments and partial cleavage of hard isocyanate-derived segments. Regarding microbial in-vitro degradations, they show much higher activity for fungus Fusarium solani than for bacterium Pseudomonas sp. Finally, biodegradation of the PUR foam in soil reveals that 77% of the soft segments are mineralized after 6 months, reaching final mineralization of 43%. The results demonstrate that a non-hazardous and sustainable PUR foam can be successfully prepared for applications requiring material bioactivity (biorecycling, etc.).



Keywords: Biodegradation, Hydrolysis, Mass spectrometry, NMR spectroscopy, Polyurethane

Acknowledgments

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Development of PISA vitrimer latexes

M. Beaugendre[1], S. Wang[2], M. Lansalot[2], F. D'Agosto[2], R. Nicolaÿ[1], C. Soulié-Ziakovic[1]

[1]*Chimie Moléculaire, Macromoléculaire, Matériaux (C3M), ESPCI Paris PSL, Paris, France*
[2]*Catalyse, Polymérisation, Procédés et Matériaux (CP2M), CPE Lyon, Lyon, France*
Contact information : corinne.soulie@espci.psl.eu

In order to comply with the 2010 European directive imposing a threshold of volatile organic compounds (VOCs) in products such as paints, aqueous film-forming have been developed. These latexes are dispersions of polymer particles synthesized in emulsion and stabilized by surfactants.
But, the surfactant molecules can detach from the surface of the polymer particles. As a result, the polymer particles are no longer sufficiently stabilized in the aqueous phase and may sediment. [1]
To address the long-term stability of the latexes, we used the PISA (Polymerization Induced Self Assembly) method which relies on a hydrophilic macroRAFT agent (methacrylic acid) from which hydrophobic polymer particles are grown. [1]
When drying, i.e. when water evaporates, the polymer particles coalesce and form a continuous film whose optical and mechanical properties depend directly on the composition of the (co)polymer (MMA and BA). [1,2] However, these coatings are not recyclable and/or repairable.
To respond to the durability of the films, covalent dynamic crosslinks have been implemented within the systems: latexes containing benzaldehyde monomers were crosslinked with di amines. Resulting imine crosslinks can exchange while the network is maintained (associative mechanism). In addition, imine bonds can also be fully hydrolyzed under acidic conditions, allowing films to be dissolved.
The resulting films are transparent, flexible and swell in solvents without dissolving. Their thermomechanical, studied as a function of the imine crosslink density, depend mostly on the hydrophilic block. Indeed, the methacrylic acid polymer is neutralized at the end of the latex synthesis and forms a thin hydrophilic continuous phase by electrostatic interactions (T_g 50°C). [1]

Keywords: Vitrimers, latex, PISA, imines, recyclability

Acknowledgments

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Preparation and application for coating purposes of biodegradable polyesters water-based dispersions

G. Belletti[1,2*], S. Buoso[2], V. Castelvetro[3], O. Bortolini[1], M. Bertoldo[2]

[1]*Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari 46, 44121 Ferrara (Italy)*
[2]*Institute of Organic Synthesis and Photoreactivity, National Research Council; Via P. Gobetti 101, 40129 Bologna (Italy)*
[3]*Department of Chemistry and Industrial Chemistry, University of Pisa, via G. Moruzzi, 2, Pisa, Italy*

The water-based polyester coatings have gained significant interest during time, indeed they have been considered a valid alternative to the commonly used solvent-borne coating systems due to their safety in application [1]. For this reason, water dispersions are gaining ground in many fields of application where the consumers safety is of utmost importance such as paints, adhesives, inks and the food packaging sector [2]. Besides, due to the current resource depletion, biodegradable polyester have emerged as a promising alternative for the replacement of their fossil-based counterparts [3].

Herein, an effective and innovative methodology for the preparation of water-based dispersions of biodegradable polyesters for coating purposes is presented [4]. The procedure involves two steps: in the first one, an oil-in water emulsion is obtained by mixing a solution of the chosen polyester in the proper organic solvent with a water phase containing surfactant and stabilizer. Different homogenization methods as well as oil/water phase ratio, surfactant and stabilizer combinations were examined. In the second step, the quantitative evaporation of the organic solvent provides stable water dispersions. The organic solvent recovered can be properly recycled to lower the process's environmental impact. Biodegradable polyester dispersions with polymer contents around 20 % and biobased content higher than 85 % are obtained. Particle size was in the 200 nm or 500 nm range, depending on the chosen substrate and preparation conditions. Furthermore, the film forming ability of formulations developed was studied by identifying the temperature which allows the formation of continuous and homogenous polymeric film. The identified temperatures were observed to be related to the glass transition or melting temperature of the polyester.

In order to coat the formulation onto porous-substrate, such as paper, the viscosity of the formulation was increased by the addition of thickeners. Several polysaccharides were tested and suitable rheology control was achieved with xanthan gum [5]: the thickened dispersions were successfully coated on paper. The barrier to liquid water was increased up to 50% with respect to the uncoated paper, the exact effect depending on the coating composition and morphology.

Keywords: waterborne dispersions, biodegradable polyesters, film formation.

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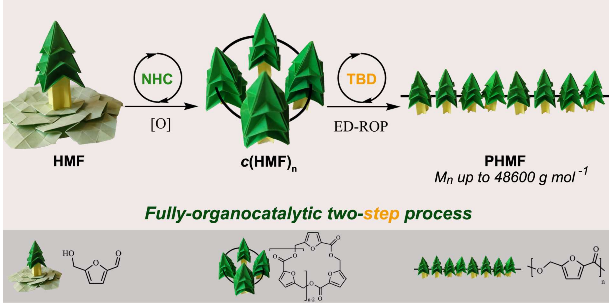
Organocatalytic Synthesis of Poly(hydroxymethylfuroate) via Ring-Opening Polymerization of HMF-Based Cyclic Oligoesters

D. Ragno[1], G. Di Carmine[1], M. Vannini[2], O. Bortolini[3], D. Perrone[3], S. Buoso[4], M. Bertoldo*[1],
A. Massi[1]

[1] *Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Ferrara, Italy.*
[2] *Department of Civil, Chemical, Environmental, and Materials Engineering, University of Bologna, Bologna, Italy.*
[3] *Department of Environmental and Prevention Sciences, University of Ferrara, Ferrara, Italy*
[4] *Institute of Organic Synthesis and Photoreactivity - Italian National Research Council, Bologna, Italy*

**monica.bertoldo@unife.it*

The synthesis of hydroxymethylfuroate macrocyclic oligoesters ***c*(HMF)$_n$** promoted by an N-heterocyclic carbene (NHC) organocatalyst[1] is herein presented together with the subsequent organocatalytic, entropically-driven ring-opening polymerization (ED-ROP)[2] leading to the fully furan-based poly(hydroxymethylfuroate) (**PHMF**). The target macrocycles (mostly trimer and tetramer species) have been obtained directly from the platform chemical **HMF** (77% isolated yield) under high dilution conditions using a quinone as the external oxidant and the green solvent Me-THF. The ED-ROP of ***c*(HMF)$_n$** has been optimized at 160 °C (melt condensation technique) with the couple triazabicyclodecene (TBD)/n-octanol (1:1) as catalyst/initiator of the polymerization process in the presence of commercial antioxidants Irganox 1010 (0.1% w/w) and Irgafos 126 (0.3% w/w) to suppress degradation side reactions. Under these conditions, the bio-based **PHMF** (poly-HMF) was obtained as a color-free polymer with number-average molecular weight up to 48600 g mol^{-1} and dispersity between 1.5 and 1.9 as determined by NMR and GPC analyses. The thermal behavior of the novel furan-based polyester **PHMF** was investigated (TGA and DSC analyses) observing a good thermal stability (onset temperature of degradation ~310°C) and a semicrystalline structure with melting temperature above 160°C when processed from solvent, thus making **PHMF** a promising material for processing as others commercial polyesters.[3]



Keywords: furan-based polymers • organocatalysis • platform chemicals • renewable resources • ring-opening polymerization

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Covalent adaptable networks: thermo-reversible crosslinked rubber prepared via melt blending and its nanocomposites

F. Cantamessa [1], G. Damonte [2], O. Monticelli [2], R. Arrigo [1], A. Fina [1,] *

[1] *Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Alessandria, Italy*
[2] *Dipartimento di Chimica e Chimica Industriale, Università di Genova, Genova, Italy*
**alberto.fina@polito.it*

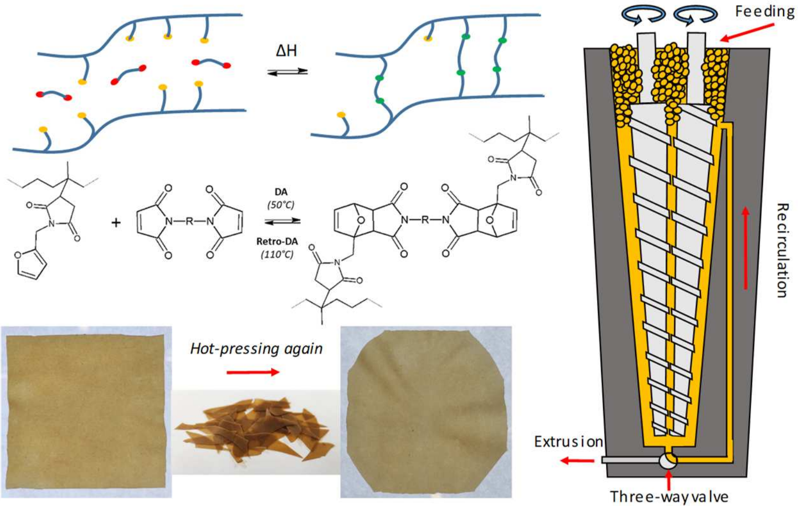

Figure 2

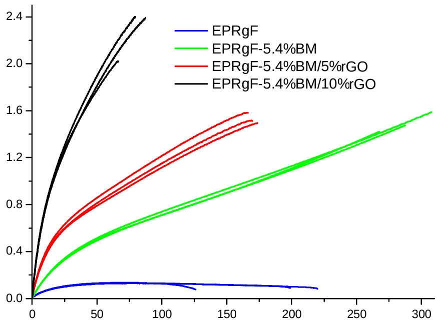

Figure 1

Covalent adaptable networks [1] represent an interesting route to solve the long-standing problem of thermosets non-reprocessability. Indeed, polymers containing reversible or exchangeable crosslinks may deliver mechanical and chemical stability while retaining reprocessability in the molten state. In this work, an ethylene-propylene-based rubber with a thermally reversible crosslinking, based on the well-known Diels-Alder (DA) reaction [2], was prepared for the first time via melt processing (Figure 1), thus without the use of solvent, paving the way to sustainable and industrially viable applications. The process was carried out in two melt blending steps. First, the commercial ethylene-propylene rubber grafted with maleic anhydride (EPRgMA) was functionalized with furan groups, as proven by FT-IR and ^{1}H NMR spectroscopy. Subsequently, the resulting furan grafted rubber (EPRgF) was crosslinked with different amounts of bismaleimide (BM) in a lab scale extruder. Crosslinking was investigated by FT-IR spectroscopy and solubility tests at room temperature. Mechanical reinforcement of the rubber carried by crosslinking was investigated by tensile tests on hot-pressed films. The thermal reversibility character of the crosslinking was confirmed by solubilization test near retro-DA activation temperature, resulting in the full dissolution of the network, and further proved by multiple re-moulding via hot-pressing to obtain new fully homogenous films (Figure 1). In the second part of this research work, the rubber was added with two different amounts (5 and 10 wt%) of reduced graphene oxide (rGO) to prepare nanocomposites. SEM and rheology measures were addressed to evaluate the distribution and dispersion of the filler. Mechanical reinforcement was investigated by tensile tests, evidencing significantly higher stiffness and resistance (Figure 2). Furthermore, inclusion of dispersed rGO enhanced thermal conductivity, up to 125% increase at 10% rGO, thus opening for applications in the field of thermally efficient and highly flexible devices, including wearable and flexible electronics.

Acknowledgments

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Synthesis of new innovative biopolymers from saccharide sources

A. Cappitti1*, D. Martella2, C. Parmeggiani1, C. Matassini1, A. Salvini1

[1]*Department of Chemistry “Ugo Schiff” University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (Italy)*
[2] *Istituto Nazionale di Ricerca Metrologica (INRiM), Strada delle Cacce 91, 10135 Torino (Italy)*

In recent years, thanks to the raise of public attention towards the environment, the exploitation of biomasses for the production of fuels and chemicals has assumed a central role in the modern chemical industry. Biopolymers, obtainable from biomasses are, therefore, an alternative to petroleum-based polymers, which makes it possible to limit the use of fossil raw materials,. In this scenario, the use of biopolymers has therefore increased considerably, with applications in the most various fields, from medical to packaging, from adhesives to the conservation of cultural heritage.

In this research several saccharides, obtainable from lignocellulosic biomasses, have been used as starting material and versatile building block to produce innovative biopolymers with a structure containing polar and reactive groups capable of influencing the application behavior. Their applications span from different technological and biomedical application, from adesive to multivalent drugs.

In particular α,α’-trehalose and α-D-glucose are used as feedstock in order to obtain new monomers for the following copolymerization in dependence of their application. The synthetic methodology involved the functionalization of trehalose and glucose through a transesterification reaction using ethyl methacrylate and potassium carbonate as catalyst for the reaction.

Then, the monomers were used for the synthesis both vinyl acetate or ethyl methacrylate copolymers, always through radical copolymerization reaction. These biopolymers will be performed in accordance with the requirements of low environmental impact which can be employed for new formulation of adhesives or in the field of cultural heritage.

Saccharide monomers have been also copolymerized with monomers obtained from iminosugars, molecules able to act as glycosidase inhibitor and then potential drugs for many metabolic desease. The obtained glycopolymers owe their activity to the multivalent effect that characterizes the interactions of carbohydrates with their receptors.

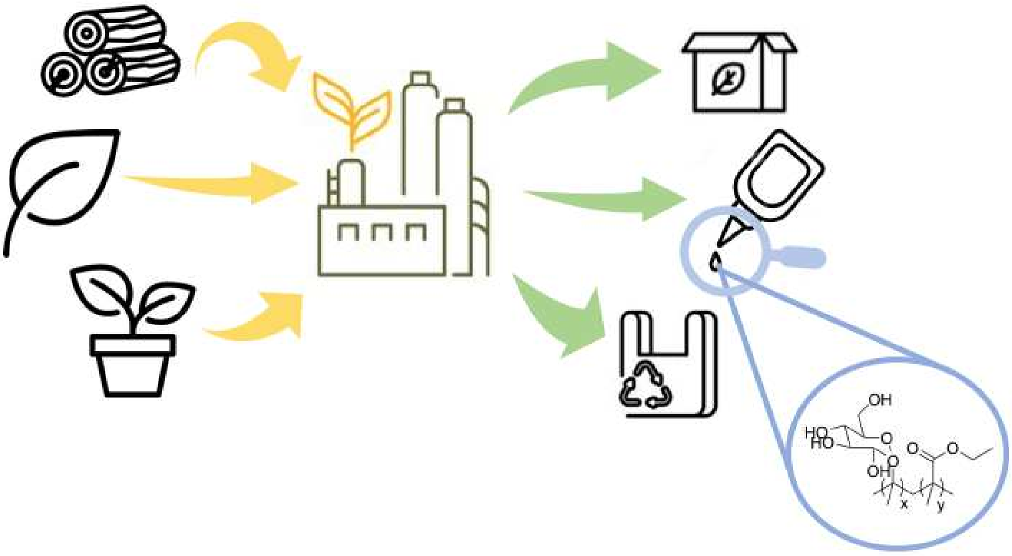

Figure 1: From biomass to innovative materials

Valorization of multilayer plastic waste

A. Cavuquila[1*], C. Maganinho[1], G. A. Carreira[2], I. Portugal[1], C. M. Silva[1], A. Timmons[1].

[1] CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal
[2]i9green, Av. D. José Alves Correia da Silva, Edifício Vela Sul 2º D, Rotunda Sul, Cova da Iria, 2495-402 Fátima, Portugal
[*]Email: anareth@ua.pt

Plastics are indispensable to ensure our lifestyle and are currently produced on a large scale. Since its discovery, more than 9 billion tonnes of plastics have been produced. Consumer environmetal awareness has driven the plastics industry to collect and recycle plastics. In Europe, more than 29 million tonnes of plastic waste were collected in 2020 with over one third being sent to recycling facilities, 40 % for energy recovery, and 23 % sent to landfill. A significant part is lost in the environment [1].
Plastic packaging is the plastic waste category which raises more concern given its abundance in municipal solid waste and the low lifetime use. Among this, the food multilayer plastic packaging category is particularly worrisome because conventional mechanical recycling technologies can not recycle these residues. Although other approaches have been explored, such as selective dissolution-precipitation techniques, thermal and catalytic pyrolysis, and compatibilization, scientfic effort is still needed to develop economically feasible processes [2].
The present work addresses strategies for the chemical valorization of polymer-based multilayer packaging to recover valuable products with focus on the selective dissolution-precipitation of mixed plastic waste. Extensive chemical and structural characterization results of the starting material and of the isolated polymers collected under different conditions will be presented and discussed.

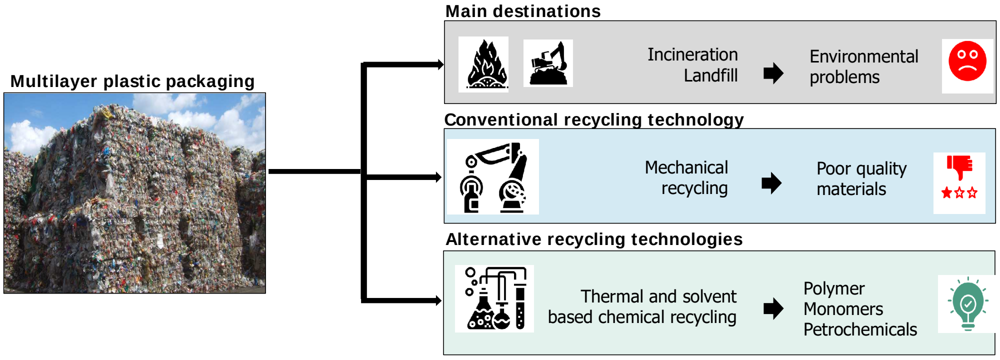

Figure 1. Alternatives for the recycling of multilayer plastic packaging.

Keywords: plastic recycling, multilayer packaging, dissolution-precipitation, circular economy.

Acknowledgment

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Microwave assisted extraction from citrus waste as source of pectin and bioactive compounds

G. Dal Poggetto[1*], D. Zannini[1], M. Monteforte[1], G. Santagata[1], B. Immirzi[1]

[1]*Institute for Polymers, Composite and Biomaterials IPCB-CNR, Pozzuoli, Italy*
giovanni.dalpoggetto@ipcb.cnr.it

The industrial processing of citrus lead to the accumulation of large amounts of by-products composed of peel, seeds and pulp. This material is disposed as solid waste or used as animal feed, but the copiousness of interesting compounds in waste fraction highlight the possibility of utilizing it as a low-priced source of different biomolecules and biopolymers, in particular pectin. In literature several methods to extract pectin from plant matrix are described[1;2].
Microwave Assisted Extraction (MAE) is a green technique employed as complementary method to extract carbohydrates, polysaccharides and other molecules of biological interest from vegetable sources, offering some advantages like faster heating to extract bioactive materials from matrix, reduced equipment size, reduced thermal gradients and increase in extract yield.
In this work we focused on MAE of citrus waste, as capable source of pectin and bioactive compounds, investigating several parameters (controlled temperature/power, different extracting agents e.g.) in order to maximize yields and composition of extracted compounds and compare it with traditional glass-based extracion methods.
On one side extracted pectins were studied in terms of yield, thermogravimetric analysis, molecular weights (through gel permeation chromatography) and methylation degree (MD) (through titration method). Last two aspects play an important role for gelation behavior in prospective of different applications ranging from food packaging to particles capable to release molecules of biological interest. On the other side evaluation of bioactive compounds (narangine, hesperidine e.g.) in terms of yield and antioxidant activity was estimated.
Among several MAE parameters tested, preliminary results evidenced a very challenging result as a high pectin yield (22%w/w) was obtained; moreover, by changing the extracting agent, it was possible to obtain pectin with different MD.

Keywords: Polysaccharides; Pectin; Microwave Assisted Extraction; Antioxidant

Acknowledgments
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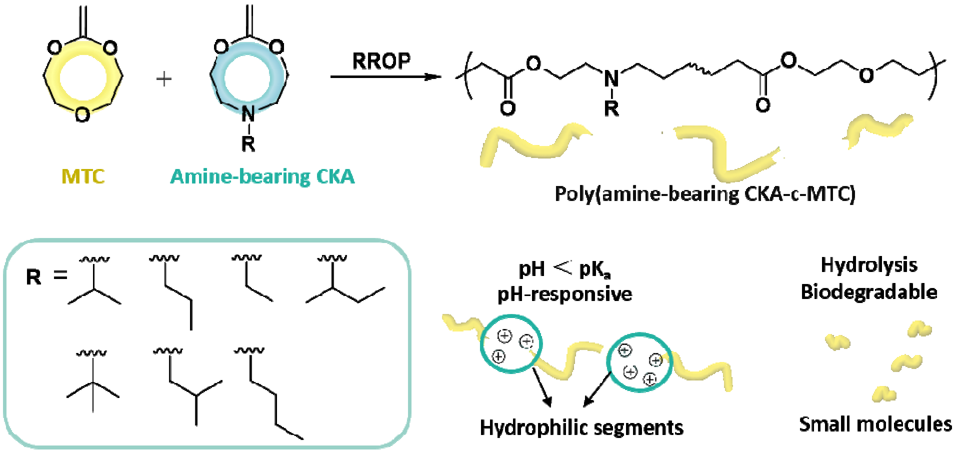
Radical Ring-Opening Polymerization of Amine-bearing Cyclic Ketene Acetals: A route towards smart and biodegradable Poly(β-aminoesters)

Yiyi Deng[1, 2], Anaïs Frezel[1, 2], Jens Gaitzsch[1*], Brigitte Voit[1, 2*]

[1] *Leibniz-Institut für Polymerforschung Dresden e. V., Hohe Straße 6, 01069, Dresden, Germany*
[2] *Lehrstuhl Organische Chemie der Polymere, Technische Universität Dresden, 01062 Dresden, Germany*
[*] *voit@ipfdd.de, gaitzsch@ipfdd.de*

Poly(ester)s are highly attractive materials for the biomedical field, since they can be hydrolyzed into small molecules. However, their range of potential applications are restricted due to the lack of responsive groups. To address this issue, radical ring-opening polymerization (RROP) of amine-bearing cyclic ketene acetals (CKAs) is regarded as an ideal route for the synthesis of smart biodegradable polymers, namely poly(β-aminoesters)[1]. Protonating the tertiary amine has been shown to yield a change in solubility and thus a responsive, i.e. smart, behavior. This notion has encouraged us to vary the side chains of the tertiary amine of CKAs through the reported intermediated carbonate method[2, 3], aiming to investigate the effect on the responsive properties of resulting polyesters. Additionally, nanoparticles with inherent pH sensitivity and biodegradability were obtained by self-assembly of these polyesters[1]. We believe that copolymerization of those novel CKAs with conventional CKAs, such as 2-methylene1,3,6-trioxocane (MTC), will result in smart Poly(amine-bearing CKA-c-MTC) copolymers thanks to the unique structure of poly(β-aminoesters). In this way the smart properties of polyesters can be modulated. Moreover, the cleavable ester units in the backbone promise the polymers will be susceptible to enzymatic degradation. Herein, we will show that this method can simplify the synthetic route towards functional polyesters and open new opportunities for smart biodegradable and biocompatible materials.

Keywords: Cyclic ketene acetals; radical ring-opening polymerization; pH-responsive; biodegradable.



Scheme 1. RROP copolymerization of MTC and amine-bearing CKAs with various side groups to yield pH-responsive and biodegradable Poly(amine-bearing CKA-c-MTC) copolymers.

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Debonding on Demand of Epoxy resins

J. Ecker[1*], K. Ehrmann[1], J. Stampfl[2], and R. Liska[1]

[1] *Institute of Applied Synthetic Chemistry, Technische Universität Wien, 1060 Vienna, Austria*
[2]*Institute of Materials Science and Technology, Technische Universität Wien, 1060 Vienna, Austria*
[*]*jakob.ecker@tuwien.ac.at*

Crosslinked polymers, in particular based on epoxy monomers, are well known for their good mechanical properties and resistance against heat, moisture, and chemicals. Thus, these polymers are desired products in industry and economy. Above all, their capability to be cured by cationic photopolymerization makes them suitable for photocurable materials. This offers the advantages of solvent-free curing conditions, low production and energy costs, and probably further applications in the field of 3D printing. This already widely acclaimed research field gains much importance due to its easier and cheaper accessibility for the market in the last decades. [1]

However, crosslinke7d polymers cannot be recycled, and incorporated components cannot be reutilized. Due to the polymer's glassy nature, adhesive properties and thermal stability, it is not possible to regain embedded parts, such as electronic devices or rare earth elements, out of these polymers.

Debonding on Demand (DoD) offers a new way to overcome this drawback by integrating labile crosslinkers into the network, which can be degraded by an external stimulus, such as heat. Through this stimulus, it is possible to debond the crosslinked network at suitable temperatures to rescue valuable components from the polymer matrix.

Therefore we synthesized a cationically curable and thermally cleavable photopolymer network. Thus formulations with different reactive diluents have been investigated. Furthermore, the synthesized polymers were then tested with respect to their (photo)chemical and (thermo)mechanical behaviour. To test the crosslinker's ability for DoD, debonding experiments have been performed compared to commercially available non-labile crosslinker systems.

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Creating an efficient recycling system and bioconversion process for waste tetra pak packaging materials

Anabel Itohowo Ekere[1*], Brian Johnston[1], Fideline Tchuenbou-Magaia[2], David Townrow[1], Szymon Wojciechowski[3], Adam A. Marek[3], Jan Zawadiak[3], Khadar Duale[4], Magdalena Zięba[4], Wanda Sikorska[4], Grażyna Adamus[4], Marek Kowalczuk[4,] and Iza Radecka[1,]

[1]*School of Science, Faculty of Science and Engineering, University of Wolverhampton, Wolverhampton WV1 1LY, UK; I.A.Jonah@wlv.ac.uk (A.I.E); B.Johnston@wlv.ac.uk (B.J.); D.Townrow@wlv.ac.uk (D.T.)*
[2]*School of Engineering, Computing, and Mathematical Sciences, Faculty of Science and Engineering, University of Wolverhampton, Wolverhampton WV1 1LY, UK; F.Tchuenbou-Magaia@wlv.ac.uk (F.T.M)*
[3]*Department of Chemical Organic Technology and Petrochemistry, Silesian University of Technology, Gliwice 44-100, Poland; szymonwoj@gmail.com (S.W.); adam.a.marek@polsl.pl (A.M.); jan.zawadiak@polsl.pl (J.Z.)*
4Centre of Polymer and Carbon Materials Polish Academy of Sciences, 34 M. Curie-Sklodowska St., 41-800 Zabrze, Poland; mzieba@cmpw-pan.edu.pl (M.Z.); wanda.sikorska@cmpw-pan.edu.pl (W.S.); kduale@cmpw-pan.edu.pl (K.D.); grazyna.adamus@cmpw-pan.edu.pl (G.A.)

This research proposes a novel recycling method for waste Tetra Pak packaging materials. The polyethylene (PE-T) component of waste Tetra Pak packaging material was separated from other components via solvent techniques [1] to obtain a purified PE material, that was further oxidized to obtain oxidized tetra pak (TPPEOX). PE-T and TPPEOX were individually investigated for their potential as a sustainable carbon source for bacterial synthesis of polyhydroxyalkanaotes (PHA) by *Cupriavidus necator H16*. Nitrogen rich tryptone soy broth medium (TSB) or nitrogen limited basal salt medium (BSM) was supplemented with either PE-T or TPPEOX, inoculated with *C.necator* and incubated at 30°C for 48 hours. *C. necator* cell growth was monitored using viable cell count. Results obtained from this analysis demonstrated that *C. necator* was able to utilise PE-T and TPPEOX in either TSB or BSM for both cell growth and synthesis of PHA, although no PHA was synthesized when BSM was supplemented with PE-T. The highest PHA yield of 40% was observed in TSB supplemented with TPPEOX. Significantly lower PHA production was seen in control cultures cultivated in TSB only (1.5 % PHA of CDW) regardless of carbon sources present in TSB in the form of peptone and glucose. The synthesized PHA biopolymer was extracted from dry cell biomass using chloroform, and characterized using Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared Spectroscopy (FTIR), Electrospray Tandem Mass Spectrometry (ESI-MS/MS) and Gel Permeation Chromatography (GPC). PHA characterization by ESI-MS/MS revealed that PHA produced by *C. necator* in TSB with both PE-T and TPPEOX contained 3-hydroxybutyrate, 3-hydroxyvalerate and 3-hydroxyhexanoate co-monomeric units. Thus, this study demonstrates the synergistic enhancement of recycling PE from waste Tetra Pak packaging material via solvent separation method and directing its use for the biosynthesis of high-value biodegradable PHA.

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The influence of three types of plant oil as antimicrobial agents in retarding the biodegradation of PHB

Ahmad Fayyazbakhsh, Dagmar Šašinková, Vendula Krátká, Marek Koutný

The environmental engineering department, faculty of technology, Tomas Bata University in Zlin, Zlin, Czech Republic

Polyhydroxybutyrate (PHB) is a biodegradable polyester that belongs to Polyhydroxyalkanoates (PHA)[1] and is favorable due to its high degradability compared to other biopolyesters. On the other hand, its high biodegradability sometimes limits its use. In this regard, retarding its biodegradation would reprsent a true value. In this experimental study, different types of plant oils were blended with PHB as the antimicrobial potential of some plant oils has been proved [2,3]. The selected plant oils have an antimicrobial activity that can inhibit microorganisms living in the soil. The results show that the blending of these additives could retard the biodegradation of the polymer with different efficiency. The strongest effect was observed for green tangerine with almost 22% retardation, while the two other additives (cocoa and tree's pyrolysis) retarded the biodegradation only by about 5% after 216 days. SEM images complemented the results of biodegradation. For the biodegradation test, a mass spectrometer HPR-40 DSA (HIDEN Analytical, 2020, UK) was used to assess the polymer samples' carbon content. Scanning electron microscopy (Phenom Pro Desktop SEM, Thermo Fisher Scientific, Waltham, MA, USA) was implemented to observe surface changes in various films in high vacuum mode at an acceleration voltage of 10 kV.

Keyword:

Polyhudroxybutyrate, Biodegradation, Polymer, Plant oil, Microorganisms

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Functional Polyesters from Radical Ring-Opening Polymerisation

F. Mehner[1], Y. Deng[1], J. Folini[2], P. Welsch[2], J. Gaitzsch[1*]

[1]*Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany*
[2]*University of Basel, Mattenstrasse 24 – BPR 1096, 4058 Basel, Switzerland*
[*]*gaitzsch@ipfdd.de*

Aliphatic polyesters hold a great potential as green polymers of the future since they are inherently hydrolysable and in many cases biodegradable as enzmes like esterase catalyse the hydrolysis. Radical Ring-Opening Polymerisation (RROP) of cyclic ketene acetals (CKAs) is a potent tool to synthesise new polyesters as it allows for non-responsive polyesers as well as responsive amine-bearing polyesters. [1], [2]
In order update RROP, we have first updated and widened the synthetic routes to obtain the CKAs. By introducing a cobalt catalyst, we were able reduce reaction temperatures form over 100 °C to RT, which greatly saves energy during the synthesis. We also developed a new pathway via an intermediate carbonate to enable previously unknown amine-bearing CKAs. Following our initial efforts, the range of amine bearing CKAs has now been broadend considerably to cover an array of side chains. Similar to methacrylates, the nature of these side chains influence the pKa of the resulting polymers. (Figure 1a) [2]
When polymerising CKAs, a number of side reactions have to be considered. The CKA 2-methylene-1,3-dioxepane (MDO), for example, polymerises into a structure that appears to be equal to poly(caprolactone) (PCL). However, during the polymerisation the ring can remain closed (ring-retaining reaction) and if the ring opens, side reactions that lead to branched polyesters need to be considered. The branching reactions are typical for free radical polymerisations and heavily influence the macroscopic properties of the final polymer, e.g. the melting temperature, which correlates linearly with the branching density. This semi-crystallinity then significantly lenghtens the half-life of the polymer in the presence of enyzmes as it degrades slower than comparable different polyesters from RROP. [3]
Altogether, the nature of the monomer, the degree of side reactions and also the way the the polymerisation is run, impact the several functions of polymer, affecting pH responsiveness, crystallinity and also their biodegradability.

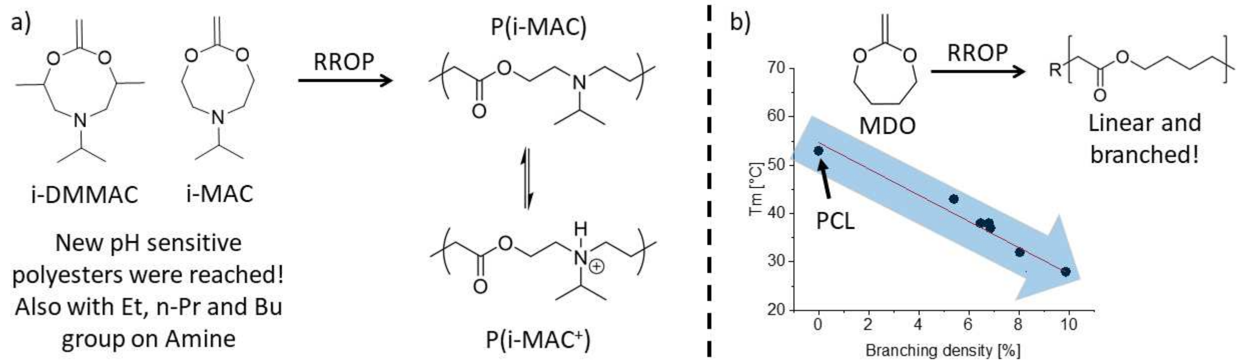

Figure 1: a) Chemical structure of the amine-bearing CKAs (here i-DMMAC and i-MAC) and their corresponding pH sensitive polyesters from RROP. b) The CKA „MDO" gets polymerised and in addition to the shown linear structure (equal to PCL), some branched structures occur. The amount of the branched structures determine the melting peak.

Keywords: Polyesters; branching; radical ring-opening polymerization; pH-responsive; biodegradable.

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Architectural coating for potencial NO_X abatement made of recycled high-density polyethylene and TiO_2 nanoparticles

D. Gavilanes[1*], A. Carbonnel[2], R. Balart[3] and P.A. Zapata[1]

[1]*Departamento de Ciencias del Ambiente, Facultad de Química y Biología, Universidad de Santiago de Chile (USACH), Grupo Polímeros, Santiago, Chile.*
[2]*Laboratorio de Exploración de Materiales Arquitectónicos Ambientales, Facultad de Arquitectura, Universidad de Santiago de Chile (USACH), Santiago, Chile.*
[3]*Instituto de Tecnología de Materiales (ITM), Universitat Politècnica de València (UPV), Plaza Ferrándiz y Carbonell 1, 03801 Alcoy, España*
[*]*dgavilanes.ruiz@gmail.com*

Supporting TiO_2-based photocatalysts over construction materials such as ceramic tiles, blocks and concrete is gaining importance among the strategies to tackle air pollution (e.g., NO_X abatement) [1]. More interesting is that plastic waste can also work as a supporting material, which allows addressing another environmental issue regarding waste management. In this context, a synergistic effect can be achieved by creating an architectural photocatalytic coating made of recycled high-density polyethylene (rHDPE) and TiO_2 nanoparticles. Nevertheless, current methodologies for TiO_2 impregnation over the supportive material are not completely developed. For instance, it was found that nanoparticles were embedded in the rHDPE structure when 8wt%-TiO_2 nanocomposites were prepared by extrusion (rHDPE/ex nanocomposites). This is terrible news as the photocatalyst may not be adequately exposed to UV radiation, reducing abatement efficiency. The significance of this work lies in improving the nanoparticle dispersion in the supportive material surface. It can be attained by a plasma pre-treatment over the polymer surface before TiO_2 impregnation [2]. Then, the nanoparticles were incorporated into the modified surface by immersion (rHDPE/in nanocomposites). Remarkably, it was demonstrated a uniform distribution of the nanoparticles on the modified surface, which offers a suitable interaction between the photocatalyst and the NO_X molecules. In terms of mechanical properties, the tensile modulus (E), the tensile strength at yield (σ_Y), the elongation at break (ε_b) are shown in Table 1, as well as the primary thermal parameters obtained from DSC and TGA analysis. Both nanocomposites reflected similar mechanical and thermal properties, except for the ε_b, which decreased to 23,01±2,35% for rHDPE/ex due to compatibility issues between TiO_2 nanoparticles and the polymer matrix.

Table 1. Mechanical and thermal properties

	Tensile test			*DSC test*		*TGA test*
Nanocomposites	*E (MPa)*	σ_y *(MPa)*	ε_b *(%)*	T_m *(°C)*	T_c *(°C)*	T_{deg} *(°C)*
rHDPE/ex	454,29±42,29	20,16±0,58	23,01±2,35	130,47	117,94	455,25
rHDPE/in	438,97±33,66	19,50±0,64	887,34±49,21	130,15	116,82	450,68

On the other hand, contact angles were measured to determine the surface hydrophobicity. An outstanding reduction of the contact angle was identified in the rHDPE/in nanocomposite as it decreased from 93° to 20°, reaching a hydrophilic surface that stimulates the nanoparticle-polymer matrix compatibility. Finally, the NO_X degradation was measured to assess the potential applications of these nanocomposites, which were 0.54% and 8.36% for rHDPE/ex and rHDPE/in, respectively. Consequently, these findings suggest these novel plasma-modified nanocomposites represent a promising approach for sustainable construction materials towards in-situ air pollution abatement.

Keywords: Recycled HDPE, NPs TiO_2, NO_x abatement.

Acknowledgments

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1,3-Dioxolan-4-Ones as powerful tool for the synthesis of functionalized PLA-based materials with tailored properties

S. Gazzotti[1,2*], M.A. Ortenzi[1,2], A. Silvani[1,2]

[1] *CRC Materiali Polimerici "LaMPo", Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy.*
[2] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy.*
[*] *stefano.gazzotti@unimi.it*

Within the pursue of environmentally friendly alternatives to oil-derived plastics, polylactic acid (PLA) has emerged as one of the best candidates, thanks to a winning combination of green nature and good processability properties. In addition, PLA is biocompatible and its degradation byproducts are harmless in vivo. On the other side of the coin, however, drawbacks such as poor toughness and poor thermal stability strongly limit its industrial applicability. For this reason, PLA-related research is usually aimed at improving its lacking properties, while preserving its good features. Compared to other strategies, the synthesis of highly functionalized PLA-based materials, endowed with tailored properties, is scarcely investigated, due to a reduced monomer scope. On a general level, when targeting modified PLA-based materials, functionalized α-hydroxy acids are usually easily accessible. However, direct polymerization of lactic acid and α-hydroxy acids in general is scarcely efficient. For this reason, on an industrial level lactide (i.e. the cyclic dimer of lactic acid) is employed, but the synthesis of modified lactides is extremely difficult to achieve, despite being extensively studied. Given these premises, the study of alternative monomeric systems that could guarantee good reactivity and high functionalization possibilities appears intriguing. Within this field, 1,3-dioxolan-4-ones (DOXs) appeared as promising candidates.[1] DOXs synthesis is straightforward and their high reactivity is ensured by the release of a small molecule (i.e. a ketone or aldehyde) during the polymerization, providing a strong driving force for the reaction. Albeit being promising monomeric systems for the synthesis of functionalized PLA-based materials, their chemistry has been scarcely investigated. For this reason, different DOX monomers bearing different substituents have been synthesized and both homo- and copolymerized, to yield PLA-based materials with variegated properties.

Organocatalyzed, solvent-free polymerization of lactic acid-derived DOX was optimized and the conditions applied to an eugenol-functionalized monomer (EuDOX) to yield a biobased, recyclable thermoset.[2] Naturally occurring phenols as cardanol and carvacrol were employed as substituents for the synthesis of CardDOX and CarvDOX monomers respectively, which were successfully copolymerized with L-lactide yielding PLA based materials with tunable thermal properties.[3]

Styrene bearing DOX monomer (StyDOX) was successfully synthesized and exploited for the synthesis of polystyrene-polylactic acid copolymers, preventing phase separation phenomena and promoting self-assembly behavior. Finally, benzophenone-functionalized DOX (PhenDOX) was copolymerized with L-lactide, allowing to get light-sensitive PLA based copolymers.

These different examples were useful to scratch the surface of this innovative chemistry, showing its potential. Further studies will be carried out, aimed not only at the study of new substituents, but also at an optimization of the homo- and copolymerization conditions in order to expand even more the concept of functionalized PLA derivatives with tailored properties.

Keywords: PLA, DOX, Copolymerization, Solvent-free

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Improving the detection of film-covered plastic packaging for mechanical recycling

J. Geier[1*], C. Barretta[1], G. Koinig[2], M. Bredács[1], D. Vollprecht[2], G. Oreski[1]

[1]*Polymer Competence Center Leoben GmbH, Leoben, Austria*
[2]*Chair of Waste Processing Technology and Waste Management, Montanuniversitaet Leoben, Austria*
[*]*jutta.geier@pccl.at*

The European Union is striving for a more circular economy and has set the objective to increase the recycling rate of plastic packaging waste (currently 34 w% in Austria) to 55 w% by 2030 [1, 2]. To achieve this aim, current challenges in the recycling of packaging material must be overcome. One of these challenges is the correct sorting of multi-material components (e.g. multilayer films, sleeve-covered bottles). The core layers of such components are often not detected by conventional sorting methods. Therefore, they are prone to missorting, leading to either the loss of valuable material or contamination of recycling streams and thus lower recyclate qualities.

This work investigates the sorting of a typical class of such multi-materials, namely plastic packages covered with film-labels or sleeves. Four different containers (bottles and cups) made of different polymers were combined with three different sleeves (see Table 1). The goal was to determine whether the packaging materials under the films are detectable and thus sortable, and how their sorting could be improved. For this purpose, an initial characterisation of the chemical structure of the individual components was carried out by means of FTIR spectroscopy and NIR spectroscopy. The combined materials (container with sleeve) were also measured using NIR spectroscopy. In order to imitate industrial scale sorting conditions, additional measurements were performed on a lab-scale NIR sorter. For both NIR techniques used on the combined materials, an optimised measuring method was applied in addition to the commonly used reflectance measurements. Multivariate data analysis was used to determine whether it is possible to detect the different plastics underneath the films.

The investigation showed that the quality of the classification into the different materials depends on the type of sleeve. With the adapted measuring method, an improvement of the classification was achieved. However, to obtain a more comprehensive overview of the influence of sleeves, further measurements on a wider variety of material combinations should be carried out. Further data on more material combinations can also help to create a database. This database could then be implemented in sorting lines and help to separate multi-material components from mono-materials and sort multi-material packages into the different subclasses of material combinations.

Table 1: Investigated material combinations (PET – polyethylene terephthalate, HDPE – high-density polyethylene, PP – polypropylene, OPS – oriented polystyrene, LDPE – low-density polyethylene).

	PET sleeve	**OPS sleeve**	**LDPE sleeve**
PET bottle	x	x	x
HDPE bottle	x	x	x
HDPE bottle, opaque	x	x	x
PP cup	x	x	

Keywords: plastic recycling, circular economy, multilayers, NIR spectroscopy, multivariate data analysis

Acknowledgments

The work described was carried out within the project “Multilayer Detection” funded by the ”Zukunftsfond Steiermark” program of the Austrian region of Styria (project number 1314).

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A contribution to the circular economy concept: biocomposites based on fully valorized agro-industrial residues

M. Vannini, C. Gioia*, S. Bianchi, G. Totaro L. Sisti, P. Marchese, A. Celli
Department of Civil, Chemical, Environmental, and Materials Engineering, University of Bologna, Italy
**claudio.gioia2@unibo.it*

The increasingly pressing demand of civil society to move towards the circular economy model drives the scientific community to explore new routes to fully valorise wastes and by-products in order to achieve the zero-waste objective. From this perspective, the agro-industrial residues can be considered a potential source of valuable products, which could find application in different fields.

Within the H2020 PROLIFIC project, a cascading approach based on green and innovative processing technologies has been designed to recover significant amounts of value-added compounds from industrial residues of legumes (seeds of peas, beans and chickpeas), fungi (cuttings and mycelia of different species), and coffee (silver skin residue and not compliant roasted seeds). The protein extraction has been performed by using environmentally friendly aqueous extraction (EFAE), enzyme-assisted (EAE), ultrasound-assisted (UAE), and microwave-assisted (MAE) extractions. The resultant residues have been further exploited by using supercritical CO_2 extraction (SFE-CO_2), subcritical water extraction (SWE), and alkali extraction to recover polyphenols, caffeine, and fibres (Figure 1). The described extraction sequence produces an ultimate fibrous waste, which can be further valorised. In fact, it is well-known the use of natural fibre residues as filler in polymeric matrices to prepare bio-composites, characterized by decreased costs and retained mechanical properties[1,2].

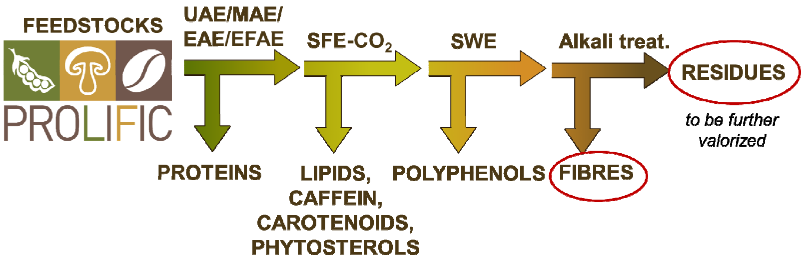

Figure 1: Designed biocascading approach for a complete and PROLIFIC valorization of agro-residues

New composites based on biodegradable and bio-sourced polymers have been successfully prepared by melt-mixing, using the extracted residues in different ratios, without any additional additive. All the materials are characterized by high thermal stability: indeed, the temperatures of thermal degradation result higher than the polymer processing temperatures. The tensile tests show an increment in the Young modulus and a decrement in both the strength and the elongation at break consistent with filler loadings. However, for a reduced amount of filler, the overall properties of the matrix have been retained. Up-scaling of the best formulations are in progress. Then, the results demonstrate that also the ultimate agro-residues, after the extraction of high-value molecules, can be successfully exploited to produce biocomposites for packaging applications at reduced costs.

The work leading to these results has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No. 790157.

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Suberinic acid modification and further use in bio-polyol synthesis

Daniela Godina*, R. Makars, J. Rizhikovs, A. Paze, A. Abolins, M. Kirpluks

Laboratory of Biorefinery, Latvian State Institute of Wood Chemistry, Riga, Latvia
**daniela.godina@kki.lv*

Depolymerized suberinic acids (SA) can be considered as an alternative material to obtain bio-polyols that can be further used in polymeric material production.

Isolated and fractionated birch outer bark from AS Latvijas Finieris plywood factory (Latvia) was used in these experiments. Prior to use the birch outer bark was extracted with ethanol to remove extractives (triterpenoids, phenolic compounds etc.). Based on our previous work [1], the main goal of this research was to modify SA isolation process by separating tannins from the reaction mixture to obtaine lower amount of oligomeric fractions. For the tannin separation we used two methods – SA filtrate acidification with HNO_3 to pH7 and addition of $FeCl_3$ to produce Fe-tannin complexes that can be easily separated by filtration.

In order to determine the chemical properties of obtained SA samples total phenolic content (TPC), acid number, saponification number, epoxy groups and hydroxyl number were determined. Three instrumental methods were used – DSC, FTIR, SEC-RID. After the obtained data the optimal SA isolation conditions were selected and with obtained SA sample bio-polyol synthesis was performed via esterification reaction with diethylene glycol (DEG) and triethanolamine (TEA). The obtained bio-polyol samples were characterised using previously described methods.

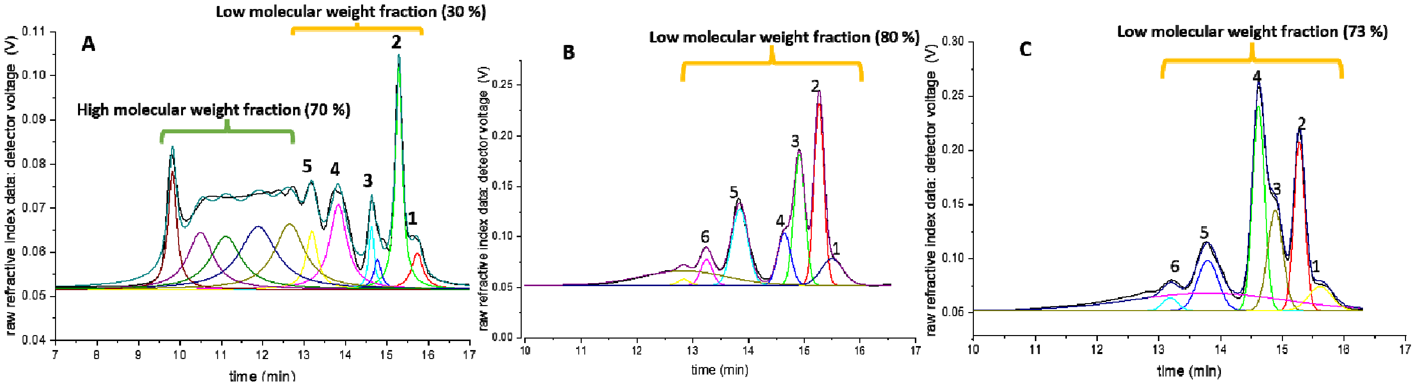

Figure 1. SEC-RID chromatograms of unmodified SA sample (A), acidified SA sample (B) and SA sample modified with $FeCl_3$ (C)

From the obtained data (Figure 1) it can be observed that additional SA modification significantly lowers the amount of high molecular weight fraction in SA samples. These modified SA samples are more perspective feedstock for bio-polyol obtaining. The obtained bio-polyols from modified SA samples have higher functional group content and have lower viscosity than bio-polyols obtained from unmodified SA samples. This is vital for further processing to obtaine regid polyurethane foams from these SA samples.

Keywords: birch outer bark; suberinic acids; high functionality polyols; polyurethane materials

Acknowledgments

This research was funded by ERDF project No. 1.1.1.1/19/A/089 "Birch bark as a valuable renewable raw material for producing formaldehyde-free particle boards and suberinic acids polyols for the development of polyurethanes".

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Piperazine-based biodegradable polyesters with tunable hydrophilicity

Shubhra Goel*, Josemon Jacob

Department of Materials Science and Engineering, Indian Institute of Technology, New Delhi-110016, India
**Email: shbhr.goel@gmail.com*

Environmental concerns over the usage of commodity plastics have prompted researchers to seek more sustainable and biodegradable polymers. Various materials have been developed to obtain polymers that are less harmful to the environment. Hydrolyzable linkages in polymeric backbones such as amides, esters, and urethanes, are vulnerable to breakdown by hydrolytic enzymes or microbes. Among them, aliphatic polyester-based polymers have received the immense attention due to their susceptibility to hydrolytic scission and combined features of biodegradability and biocompatibility[1]. The functional groups are introduced to increase the polymer hydrophilicity, allowing water molecules to attack the labile bonds, hence increasing the biodegradability of the polyester[2]. Due to the possibility of crosslinking caused by pendant functionalities, cationic aliphatic polyesters with charged units distributed throughout the main chain have emerged as an exciting field of current research[3]. Among the different cationic units, nitrogen-containing piperazine-based heterocycle organic compounds have drawn considerable attention for their distinct physiochemical and biological features. Moreover, upon quaternization, the piperazine moiety may easily impart stimuli-responsive pH sensitivity to polymers[4,5].

Taking these characteristics into account, the current study develops a novel family of biodegradable aliphatic pH-responsive polyesters with tunable hydrophilicity based on piperazine moiety. Polycondensation of dimethyl 2,2'-(piperazin-1,4-diyl)diacetate with a series of alkane diols (C4 to C10) resulted in the formation of aliphatic polyesters with a high thermal stability up to 340 °C. The resultant polyesters are found to be highly crystalline (~47-55%) as determined by XRD, and moderately hydrophilic, with a water contact angle of 63° - 72°. Protonation or an N-alkylation approach was used to tune crystallinity and hydrophilicity for biodegradability enhancement. Zeta potential tests were carried out to determine the pH responsiveness of the polyesters. Furthermore, hydrolytic and microbial degradation demonstrated that quaternized polyesters degrade more rapidly, establishing their importance as a novel class of biodegradable polyesters.

Keywords: piperazine, biodegradable polyester, pH-responsive, microbial degradation

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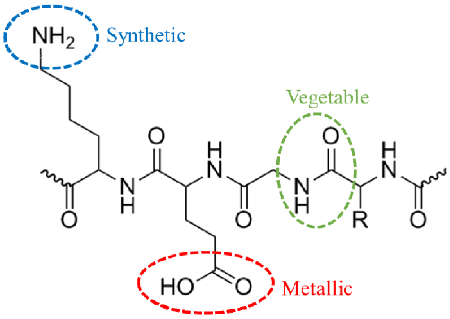
Sustainable leather : Cyclocarbonates in leather tanning

V. Gonnot[1*], D. Vuluga-Legros[1], F. Burel[1], Stéphane Marcotte[2], Ghislain Rabodon[2]

[1]*INSA de Rouen, Saint-Etienne du Rouveray, France*
[2]*Hermès, Paris, France*
[*]*Vincent.gonnot@insa-rouen.fr*

The skin is a putrescible material. Its transformation into a sustainable and functionnal material passes through a stabilization stage against thermal and enzymatic degradation called tanning. The resulting leather can be used in various sectors such as apparel, shoes, or automotive industry. The collagen, main constituent of hides, is cross-linked during the stabilization process. The different tanning methods are linked to the reactive functions carried by the collagen molecule. Three main types of systems according to the targeted function are found:

Tanning	**Targeted site on collagen**	**Amino acid involved**
Metallic	Carboxylic acid	Aspartic and glutamic acid
Synthetic	Amine	Lysine and hydroxylysine
Vegetable	Hydrogen Bond	All



Today, mineral tanning, more precisely with $Cr_2(SO_4)_3$, represents more than 90% of the tanning in the world [1]. This method has the advantage to lead to a rapid process with excellent mechanical properties and good stability over time for the leather. However, it is the object of more and more distrust. Indeed, Cr III can, under certain conditions, oxidize into hexavalent Cr VI classified as a skin sensitizing substance. This has pushed tanners to find alternatives to reduce or eliminate chromium from the tanning process.

In this context, cyclocarbonates are a very interesting class of molecule as potential cross linking agent. They can be synthesized from biobased epoxy and captured CO_2, which participates in the valorisation of this gas considered as a waste and responsible for global warming. Few articles exist on the ability of cyclocarbonates to react with amines in water [2][3][4]. First, a multifonctional cyclocarbonate was successfully synthesized with biobased and hydrophylic epoxy. Unfortunately the cyclocarbonate agent was not soluble in water. Nevertheless, the biphasic reaction between cyclocarbonate in dichloromethane and a diamine in water led to the formation of a urethane film in a few hours at room temperature. A simulation of the tanning process could be done with these agents on collagen powder.

Keywords: Tanning, collagen, cyclocarbonate

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Recycling of Flexible Polyurethane Foams by Acidolysis

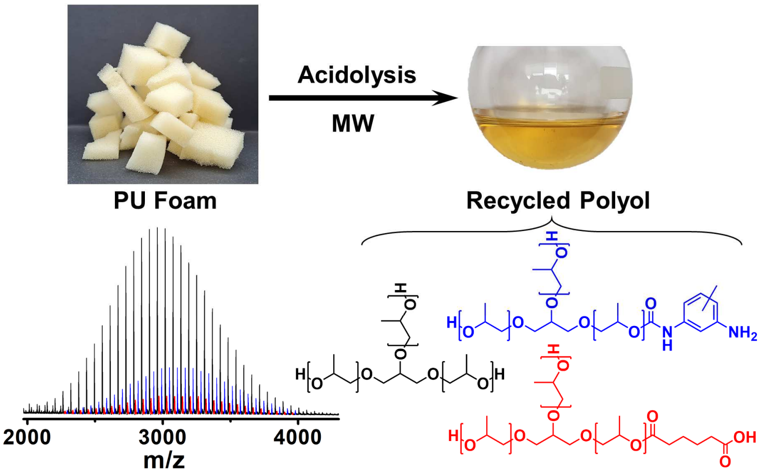
M. Grdadolnik[1*], A. Drinčić[1], A. Oreški[1], O. Can Onder[1], P. Utroša[1], D. Pahovnik[1], and Ema Žagar[1]

[1]*Department of Polymer Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, Ljubljana 1000-SI*
[*]*maja.grdadolnik@ki.si*

Polyurethane foams (PUFs) account for a large portion of total PU production and consumption, and therefore generate an increasing amount of waste that requires efficient and sustainable management. Since PUFs are thermoset polymers with a cross-linked structure, chemical degradation methods such as glycolysis and acidolysis prove to be the most suitable options for their recycling.

Here, we present a cost- and energy-efficient acidolysis of flexible PUFs with adipic acid (AA) using microwaves as a heating source [1]. The obtained degradation products were analyzed by MALDI-TOF MS, NMR, SEC coupled to a multidetection system, and FT-IR to evaluate the effects of reaction temperature, time, and amount of AA degradation reagent on molecular weight characteristics, polyol functionality, presence of side products, and degree of degradation of the remaining PUF hard segments. Then, different amounts of the purified recycled polyols were used for the synthesis of new flexible PUFs.

The results show that microwave heating significantly shortens the reaction time compared to conventional heating of the reaction mixtures. Nevertheless, even with an increase in reaction temperature, time, or amount of AA, we could not achieve complete degradation of the urethane groups. Moreover, the increased amount of AA led to a higher degree of esterification of the hydroxyl groups of the polyol by AA, resulting in a polyol with a higher content of carboxyl end groups. The morphology and mechanical properties of the newly synthesized PUFs were strongly influenced by the degree of functionalization of the polyol by the carboxyl groups.



The reaction conditions of the acidolysis of polyurethane foams determine the end-group functionality of the recycled polyol, which affects the synthesis and properties of the newly synthesized polyurethane foams.

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DOI: 10.1021/acssuschemeng.1c07911

Humidity-Sensitive Bilayer Actuator Derived from Cellulose Nanofibrils and Reduced Graphene Oxide

Frédéric Héraly[1*], Jiayin Yuan[1*]

[1] *Department of Materials and Environmental Chemistry, Stockholm University. Svante Arrheniusväg 16C, Stockholm 106 91, Sweden*
**Jiayin.Yuan@mmk.su.se*

Bilayer actuators, traditionally consisting of two laminated materials, are the most common types of soft or hybrid actuators. Herein, a nanomaterial-based organic–inorganic humidity-sensitive bilayer actuator composed of TEMPO-oxidized cellulose nanofibrils (TCNF-Na^+) and reduced graphene oxide (rGO) sheets is presented. The hybrid actuator displays a large humidity-driven locomotion with an atypical fast unbending. Cationic exchange of the anionically charged TCNF-Na^+ and control of the layer thickness is used to tune and dictate the locomotion and actuator's response to humidity variations. Assembly of a self-oscillating electrical circuit, that includes a conductive rGO layer, displays autonomous on-and-off lighting in response to actuation-driven alternating electrical heating.

Keywords: bilayer actuators, cellulose nanofibrils, humidity sensors, reducedgraphene oxide, smart materials

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Catalyst Design for the Synthesis of Polyesters: Chemo-, Regio- and Stereo-Selective?

M. Hirschmann[1*], T. Fuoco[1]

[1]*Royal Institue of Technology (KTH), Stockholm, Sweden*
**maxhi@kth.se*

One polyester is a commodity polymer, which is used for plastic bottles. Other polyesters are bio-compatible and bio-degradable; properties that enable a broad variety of applications including their usage in biomedicine.[1] Most of these polyesters are produced with petrochemicals, although, biomass feedstocks are known. Dialcohols, diacids, and hydroxy acids (or lactones) constitute this biomass feedstock. The ring-opening alternating polymerization (ROAP) further increases the available biomass feedstock of polyesters by epoxides and anhydrides.[2]

Naturally abundant epoxides and anhydrides can possess complex molecular structures that pave the way to multiple polyesters with a broad range of properties on the one hand, but, which lead to many synthetical challenges on the other hand. We seek an ideal polymerization that follows green chemistry principles [no (harmful) solvent, low temperature, non-toxic catalyst, etc.] and has a broad functional-group tolerance. The catalytic routes used for such polymerizations further shall be *chemo-selective* (to prevent side-reactions and ether formation), *regio-selective* (in case of asymmetric monomers), and *stereo-selective* (to control the tacticity of the polyester, c.f. Figure 1).[3]

The presented work focuses on catalyst designs that follow green chemistry principles and that can achieve chemo-, regio- and stereo-selectivity. Ultimately, the goal is to synthesize polyesters with a controlled structure.

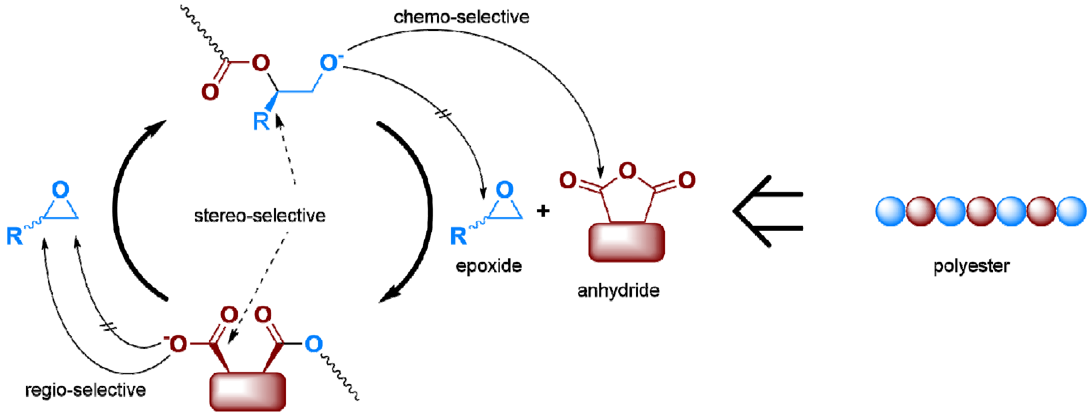

Figure 1: The ring-opening alternating polymerization (ROAP, or copolymerization: ROcoP) of epoxides and anhydrides requires a chemo-, regio- and stereo-selective mechanism to obtain polyesters with controllable properties.

Keywords: ring-opening alternating polymerization (ROAP), ring-opening copolymerization (ROcoP), organocatalysis, green chemistry

Acknowledgments

The Swedish Research Council for Sustainable Development (FORMAS) (Early carrier reserach grant n. 2020-00910) is acknowledged for financial support.

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Equipment for polymer coating the fabric

Serhiy Horiashchenko[1], Ievgeniia Golinka[2]

[1]*Khmelnitskiy national university, Khmelnitskiy, Ukraine*
[21]*Khmelnitskiy national university, Khmelnitskiy, Ukraine*

Development of this method and the method of spraying viscous liquids was related to the need to make more economical and cheaper spray systems. In the master's thesis examined the structure and design of the device for dyeing leather upper parts. We have determined the main physical and chemical attributes of disperse systems that can be put on textile materials on the basis of mathematical modeling of the influence of characteristics of the surface and capillary-porous structure of the materials on the technological processing parameters. Also we have created the program for the choice of the optimal conditions depending on the characteristics of the coating, mono- or multilayers, their durability, elasticity, adhesion strength [1, 2].
Model was developed sprayer polymers and dispersion modeling conducted flare polymer. (Fig.1). The device (Fig.2) for implementing of the new technology consists of the module for preparation of polymers, the module for heating and supply of air, dispenser, nozzle, module for the control and measurement [3]. The use of polymers as liquid at the temperature up to 250^{0}C [4].
For experimental studies selected products from imitation leather and fabric. The penetration depth in capillary-porous objects characterizes the strength of the adhesive bond strength. The penetration depth depends от diameters of the capillaries and pores in the fabric that create a total area of adhesive contact with the surface detail of the surface structure(Fig.3) .

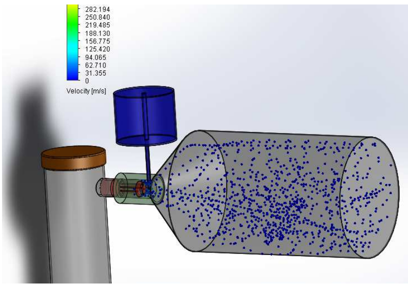

Fig. 1 The virtual model

Fig. 2 The equipment for polymer coating

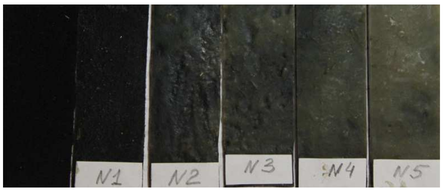

Fig 3. Resault of coating

This device, unlike the analogs involves the coating of the polymeric films outdoors, which allows the application of paint, adhesive and duplicating substances for the various apparel garments. Besides, we can use nanoparticles as additives to polymers and production of the composite dispersions with the help of the elaborated device.

Keywords: polymer coating, equipment

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From vegetable oil to coatings: hydrophobic UV curable bio-based coatings for different substrates

I. Husic[1*], A.R. Mahendran[1], C. Jocham[1], H. Lammer[1]

[1]*WOOD K Plus - Competence Center for Wood Composites and Wood Chemistry, Altenberger Strasse 69, A-4040 Linz, Austria*
i.husic@wood-kplus.at

Significant efforts are being made in scientific community to replace petrochemicals with bio-based materials. In that aspect, vegetable oils show a good potential for bio-based coatings. In our previous work [1] we developed UV curable coatings based on acrylated epoxidized linseed oil (AELO) for wood applications. In this work, we continue to develop new AELO hydrophobic UV curable coatings for various substrates such as paper, wood, and aluminum with a special emphasis on exploring the efficiency of different diluents [2] and hydrophobic additives in our formulations [3].

Epoxidized linseed oil (ELO) was used as a precursor for the synthesis of AELO resin as a monomer for UV polymerization using acrylic acid. Isosorbide methacrylate (IM) was synthesized in the lab and used as a diluent. In UV curable formulations, 1-hydroxycyclohexyl phenyl ketone or Irgacure 184 (I184) was used as a photoinitiator, isobornyl acrylate (IBA) and IM were added to AELO as diluents, and hexadecyltrimethoxysilane (HDTMS), 3-(trimethoxysilyl)propylacrylate (TMSPA), and hexamethyldisiloxane (HMD) as hydrophobic additives. The formulations were coated to the surface of wood, paper, and aluminum substrates (layer thickness was 30, 60, 90, and 120 µm) and UV cured at the wavelength of 180-450 nm. In separate experiments, aluminum and paper were plasma-activated before coating. The consumption of acrylate group double bonds during UV polymerization was monitored by FT-IR spectroscopy, and hydrophobic properties of the AELO coatings were characterized by contact angle (CA) measurements. Mechanical properties of the coatings were examined with cross cut tests.

A high degree of conversion of acrylate double bonds was observed by FT-IR analysis. The AELO coatings on aluminum substrates with isosorbide methacrylate as a diluent and HDTMS as a hydrophobic additive showed the lowest surface energy (about 14 mN/m) and the highest contact angle (CA) values (about 108 °). CA values were not significantly affected by the layer thickness of the coatings on the substrate. A better adhesion of the coatings on the substrate was observed for paper and wood than for aluminum substrates. Cross cut test results indicated that the mechanical properties of the coatings still needed to be improved.

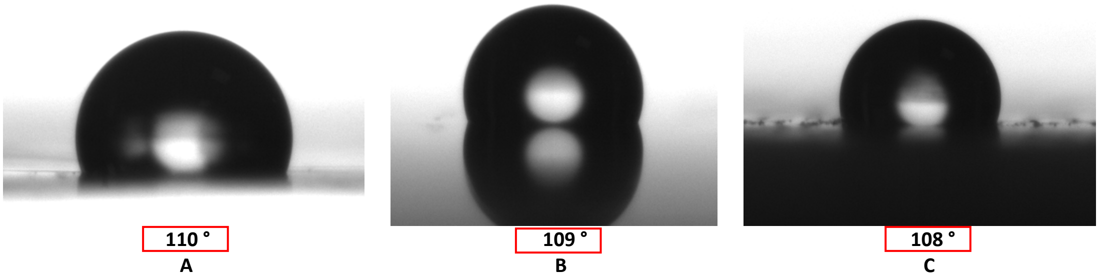

Figure 1. Contact angle of the AELO coatings on paper (A), aluminum (B), and wood (C) substrates.

Keywords: UV curable coatings, acrylated vegetable oil, renewable diluents, hydrophobic additives, contact angle

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From polyisoprene to waste tires: synthesis of telechelic elastomers through olefin metathesis

Charles Jambou[1,*], Jean-Philippe Faure[2], Flavien Geisler[3], Frédéric Loup[3], Rémi Perrin[4], Jean-François Pilard[5], Christine Robach[4], Annie-Claude Gaumont[1], Isabelle Dez[1]

[1]Normandie-Université, UNICAEN, ENSICAEN, CNRS, Laboratoire de Chimie Moléculaire et Thioorganique (LCMT), 6 boulevard du Maréchal Juin, 14050 Caen, France
[2]Aliapur, 71 cours Albert Thomas, 69003 Lyon, France
[3]EIFFAGE Infrastructures, Centre d'Etudes et de Recherche, 8 Rue du Dauphiné, 69964 Corbas, France
[4]SOPREMA, 14 rue de Saint Nazaire, 67025 Strasbourg, France
[5]Institut des Molécules et des Matériaux du Mans (IMMM), Université du Maine, Avenue Olivier Messiaen, 72085 Le Mans, Cedex 9, France
[*]charles.jambou@ensicaen.fr

The challenge of polymer waste recycling is of a great concern in today's society. In the case of the tires waste, which represent millions of tons of valuable materials generated each year, they are mostly used as alternative fuel in the cement industry to replace coal. As an alternative, several chemical ways to recycle tires waste emerged during the 20th century like pyrolysis, devulcanization and depolymerization. The depolymerization, which includes biodegradation, photodegradation and chemical degradation (mainly through oxidative reaction), lead to the formation of telechelic polymers. But these processes are limited by various side-reactions resulting in a low control over the depolymerization and the structure of the polymer obtained.

Recently, one of us reported a process relying on ruthenium catalyzed olefin metathesis[1], allowing simultaneously to decrease the molecular mass of the polyolefin and to functionalize it with a functionalized alkene as chain transfer agent (CTA). Using a wide variety of CTA, the reaction allows to reach a very good control over the structure of the polymer (molecular weight, dispersity and functionalization rate).

In the frame of our study, we reported the use of a CTA bearing diethylphosphonate functions to generate phosphorylated telechelic polymers which have been growing interest in a variety of applications such as dental adhesives, flame retardants and ligands in various organic-inorganic framework and hybrid materials[2]. After an optimization of the reaction on polyisoprene, the process was extended on ground tires waste and afford, on one hand, the synthesis of telechelic phosphorated oligomers and on the other hand, the functionalization of residual aggregates of tire waste.

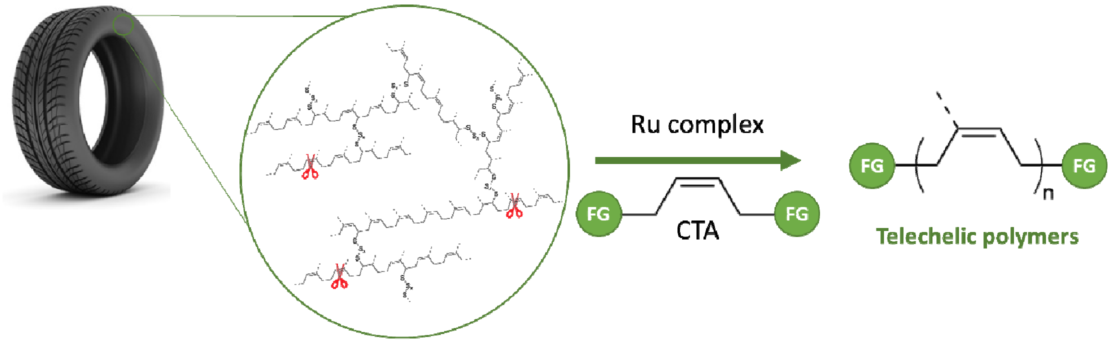

Figure 1 : Synthesis of telechelic polymer from waste tires by olefin metathesis

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A New Class of Fully Bio-Based Elastomer prepared *via* RAFT-Mediated Miniemulsion Polymerization

Uddhab Kalita[1], Nikhil K. Singha[1,2*]

[1] *Rubber Technology Centre, Indian Institute of Technology, Kharagpur, 721302, India*
[2] *School of Nanoscience and Technology, Indian Institute of Technology, Kharagpur, 721302, India*
**nks8888@yahoo.com/nks@rtc.iitkgp.ac.in*

Abstract: Elastomers are one of the most widely used polymers in the modern world. They are employed in different fields of applications ranging from automotive, flexible electronic devices, footwear, building-construction, and adhesives to biomedical applications. Nevertheless, synthetic elastomers which are part of most of these applications are in fact derived from petroleum-based resources. However, the diminution of petro-based resources has encouraged the use of renewable or bio-based resources for the production of elastomers. Herein, we report a fully bio-based elastomer synthesized using a terpene monomer and a glyco-monomer. RAFT-mediated miniemulsion polymerization technique was used to copolymerize these two monomers. Well controlled molecular weights and narrow dispersity (Đ) of the copolymers were observed. The terpene part in the prepared copolymer contributes to the elastomeric property, whereas the glyco part contributes to the strength of the copolymer. The copolymer elastomer prepared using the combo of these two monomers essentially replicates the emulsion styrene-butadiene rubbers (SBR). This newly prepared bio-based elastomer displayed remarkable mechanical properties as well as good recyclability. The samples prepared showed good film-forming ability and transparency. Excellent biocompatibility of the prepared elastomer was also realized *via* MTT assay. The prepared elastomer therefore can be engaged for potential biomedical applications such as for manufacture of catheter pipes, patches, etc.

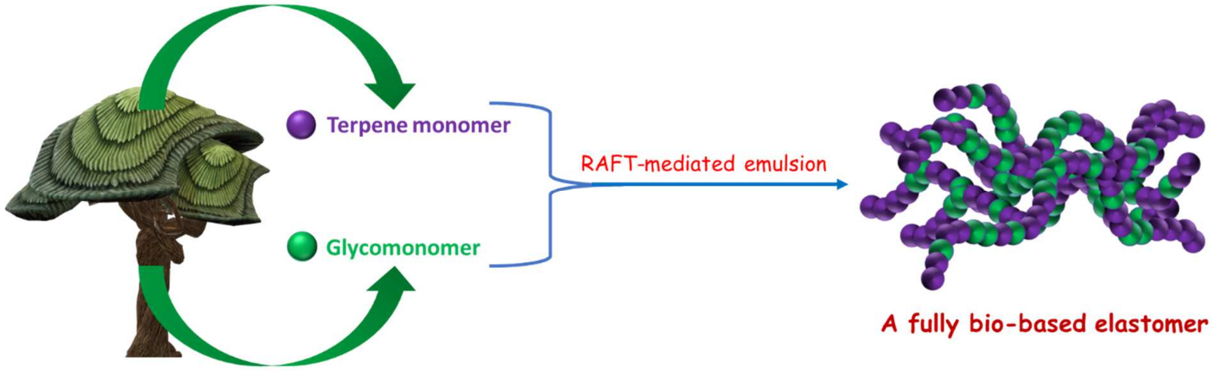

Figure: Graphical representation of a fully bio-based elastomer synthesized via RAFT-mediated emulsion polymerization

Keywords: Bio-based elastomer, terpene, glycomonomer, RAFT polymerization, emulsion polymerization

Recyclable Polyurethane elastomers via dynamic covalent chemistries

Hiba Kassem[1, 2]*, Lucie Imbernon[1], Lucas Stricker[2], Filip E. Du Prez[2], Bart Haelterman[1]

[1] *Recticel, Damstraat 2, Industriezone 7,9230 Wetteren, Belgium*
[2] *Polymer Chemistry Research Group, Center of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Krijgslaan 281 S4-bis, Ghent B-9000, Belgium*
**Hiba.kassem@ugent.be*

Besides their outstanding mechanical, durability and insulation properties, polyurethane (PU) thermosets are resilient in diverse environments[1], [2]. Owing to these features, PUs are currently versatile materials used in a broad range of applications such as coatings, automotive, foams…[3]. However, the simultaneous high production and consumption of PUs generates a significant volume of accumulated waste that ends up either being landfilled or grinded and incinerated, by that representing a classical linear economy[4].

A much more promising approach would be to create inherent recyclable PU-thermosets by introducing dynamic covalent bonds in their polymer architecture. Various dynamic chemistries have been developed in recent years and depending on their nature, the dynamic bond exchange is usually triggered by an external stimulus such as heat or light[5], [6]. Those so-called covalent adaptable networks (CANs) hold good mechanical properties, yet at the same time they possess a decent level of malleability when exposed to stimuli. This feature allows their reprocessability and recyclability, therefore obtaining a balance between thermoset and thermoplastic properties[1].

The aim of this work is to introduce dynamic covalent chemistries in industrial relevant PU thermoset materials, allowing these materials to be recycled and reshaped. Additionally, this study will show how PU thermosets can be transformed from materials generating large volumes of wastes, into sustainable materials that can be recycled and transformed into valuable products at their "end-life".

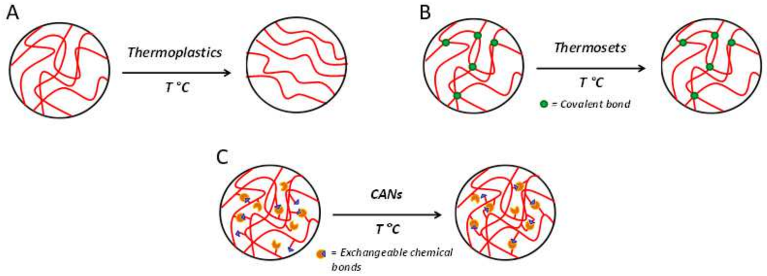

Fig 1: Schematic illustration of the behavior of A) thermoplastics, B) thermosets and C) CANs upon heating.

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Introduction of Isosorbide into high performance Oxazolidinone-based thermoplastics from renewable resources

P. Klein[1], M. Reiher[1], M. Wang[1], C. Over[1], M. Glaßner[1], S. Westhues[2], S. Yogendra[2], S. Movahhed[2], K. Laemmerhold[2], A. Wolf[2], C. Gürtler[2], W. Leitner[1]

[1]*RWTH-Aachen University, Worringer Weg 2, 52074 Aachen*
[2]*Covestro Deutschland AG, Kaiser-Wilhelm-Allee 60, 51373 Leverkusen*

Polyoxazolidinones (pOXA) obtained from the reaction of bisisocyanates and bisepoxides show remarkable characteristics in terms of thermal stability, high glass transition temperature as well as chemical resistance.[1] Therefore, they have high potential in advanced materials e.g. thermoplastics. In the last decade, CAT Catalytic Center Aachen and Covestro have made considerable improvements in precise, side product free pOXA synthesis by the choice of monomers and catalyst design[2], thus allowing pOXA to be tailored for specific applications.

Economical and ecological interests have to fit very well for the launch of a new product, therefore recyclability and availlability of renewable resources need to be taken into consideration.[3] While Covestro is developing a biobased route to Methylene diphenyl diisocyanate (MDI) from biobased Anilin[4], the introduction of the sugar-based material isosorbide diglycidylether (ISDGE) into polyoxazolidinone thermoplastics will allow an access towards fully biobased pOXA high-performance materials (Figure 1 a).[5]

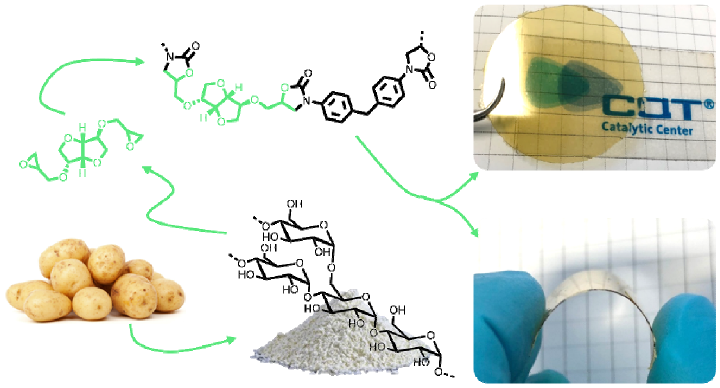

Figure 1: High-performance thermoplastic obtained from ISDGE and 4,4-MDI.

A facile monomer/polymer synthetic pathway and detailed characterization by spectroscopic, thermal and mechanical methods opens access to remarkably stable and highly pure thermoplastics. Outstanding thermal properties alongside precisely tunable and high molecular weights of up to 20-30 kg/mol allowed highly flexible and transparent films to be manufactured.

Keywords: Biobased materials, renewable resources, thermoplastics.

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The competition between hydrolysis and ring-opening polymerization of MDO in water. Who makes the race?

B. R. Kordes[1], L. Ascherl[1], C. Rüdinger[1], S. Agarwal[2], T. Melchin[1*]

[1]*Wacker Chemie AG, Munich, Germany*
[2]*University of Bayreuth, Bayreuth, Germany*
[*]*timo.melchin@wacker.com*

Cyclic ketene acetals, such as its most common representative 2-Methylene-1,3-dioxepane (MDO), are known to introduce biodegradable breakpoints in otherwise undegradable polymers via a ring-opening mechanism.[1] For solution and bulk polymerizations, these properties have been intensively studied. However, there are hardly any examples for the use of cyclic ketene acetals in emulsion polymerization.[2] This is because these monomers are sensitive to hydrolysis and react with water to form undesirable by-products unable to undergo a polymerization.

In this kinetic study, the hydrolysis of MDO was investigated as a function of pH, concentration, solvent and temperature. A deeper understanding of the hydrolysis kinetics of MDO can clarify whether emulsion polymerization of MDO is possible which would than lead to biodegradable dispersions.

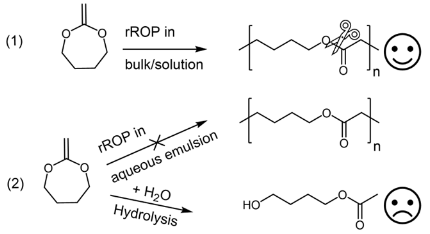

Figure 1: (1) The radical-ring-opening polymerization (rROP) of MDO leads to biodegradable breaking points, (2) Emulsion polymerization of MDO leads to hydrolysis forming the undesired 4-hydroxy-1,4-butanediol.

For this study, MDO-water emulsions were tracked using an online IR instrument, and MDO-water solutions were tracked by NMR spectroscopy. A clear temperature and pH dependence was observed. At pH values below 7, a pseudo-first-order reaction order could be identified, while above pH 7 an autocatalytic mechanism occurs.

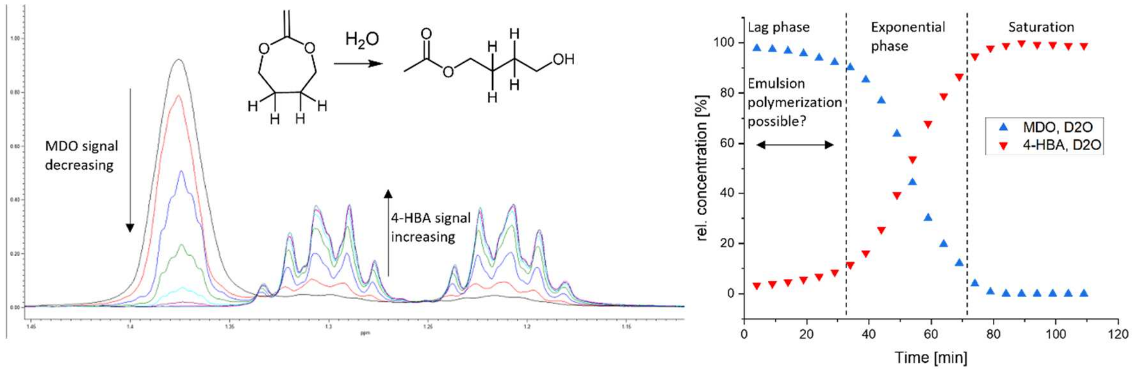

Figure 2: Left: Superimposed ^{1}H-NMR spectra of the kinetic measurement, right: Evaluated kinetics experiment for the case pH 7, 25 °C, MDO:D_2O = 1:100.

Keywords: Biodegradable dispersions, hydrolysis kinetics, radical-ring-opening polymerization, MDO

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Use of solid product of biomass pyrolysis for grafted PHB and its biodegradation

Vendula Krátká[1], Dagmar Šašinková[1], Ahmad Fayyazbakhsh[1], Markéta Julinová[1], Marek Koutný[1], Alena Kalendová[2]

[1]*Department of Environmental Protection Engineering, Faculty of Technology, Tomas Bata University in Zlín, Nad Ovčírnou 3685, 760 01 Zlín, Czech Republic*
[2]*Department of Polymer Engineering, Faculty of Technology, Tomas Bata University in Zlín, Vavrečkova 275, 760 01 Zlín, Czech Republic*

The application of solid product of biomass pyrolysis (SPB) as a filler in polymers can be viewed as a sustainable approach that incorporates agricultural waste based value-added material and simultaneously expands the possibilities of use bio-waste in a smart way. The main aim of this work was to investigate the biodegradation of the PHB filled by the SPB. In this experimental study, PHB (poly-3-hydroxy butyrate) was filled by SPB, grafted by maleic anhydride (MA) and 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane. The foils characterization was performed by X-ray difraction analysis (XRD), scanning electron microscopy (SEM), optical microscopy and FTIR.

Biodegradation was studied in the soil environment, with 54 % humidity and 25 °C and took more than 200 days. Level of biodegradation was evaluated by the production of carbon dioxide, measured by a mass spectrometer, scanning electron microscopy and fluorescence microscopy. Samples were observed before the biodegradation and also during the biodegradation process. These analysis confirmed that the SPB changed the morphological structure of the grafted PHB, and thus affected the biodegradation.

Keyword:

Biodegradation, biomass pyrolysis, polyhydroxybutyrate, polymer

Acknowledgments

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Synthesis and characterization of eco-friendly thermoplastic composites based on recycled polyethylene terephthalate reinforced with banana fibers

Martial KUETE[1, 2, 3], Pascal Van Velthem[1], Wael Ballout [a], Thomas Pardoen[3], Maurice Ndikontar Kor[2], Christian Bailly[1*]

[1]Institute of condensed Matter and Nanosciences – Bio &Soft Matter (IMCN/BSMA), UClouvain, 1348, Louvain-la-Neuve, Belgium
[2]Institute of Mechanics, Materials and Civil Engineering, UClouvain, 2 Place Sainte Barbe, 1348 Louvain-la-Neuve, Belgium
[3]Macromolecular Chemistry Unit, Applied Chemistry Laboratory, Faculty of Science, University of Yaoundé I, Yaoundé, Cameroon
***Corresponding Author:** Christian Bailly, Institute of condensed Matter and Nanosciences – Bio & Soft Matter (IMCN/BSMA), UClouvain, 1348, Louvain-la-Neuve, Belgium
Email: christian.bailly@uclouvain.be

Nowadays, polyethyleneterephthalate (PET) recycling becomes very important, since worldwide PET wastes increase rapidly, in particular in developing countries. Incorporation of bio-sourced aliphatic chain and natural fibers could be reduced their environmental impact and produced the add value product from their waste. Saturated co-polyesters (ScP) are first prepared from recycled polyethylene terephthalate (PET) and next melt blended banana fibers (BF) (5 to 20%wt) obtained from banana pseudo-stem to produce bio-composite materials in environmentally friendly conditions. Chemical recycling of PET takes place by glycolysis of ground PET with 1.3-propanediol to produce co-oligomers, which are next reacted with succinic anhydride and solid-state polymerized (SSP) to yield suitable ScP compositions. An FTIR method is used to quantify the concentration of chain-ends (hydroxyle and acid values) in order to estimate the number average molecular weight (Mn) of the ScP. The results show a huge reduction of chain-ends concentration in the ScP compared to PET co-oligomers. Moreover, the melting temperature (Tm) and the glass transition (Tg) of ScP is lower than those of starting PET even if their Mn value are similar. The observed high storage storage modulus of injection-molded BF-ScP composites seems to be related to the strong orientation of the fibers in the tensile direction, to their high aspect ratio and the excellent matrix/fibers cohesion.

Keywords: Recycling, glycolysis, PET, succinic anhydride, saturated polyester

The use of fillers derived from coal combustion products in the technology of polyurethane materials

M. Kuźnia[1*], B. Zygmunt-Kowalska[1], K. Pielichowska[2]

[1]*AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Department of Heat Engineering and Environment Protection, Mickiewicza 30 Av., 30-059 Krakow, Poland*
[2]*AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Biomaterials and Composites, Mickiewicza 30 Av., 30-059 Krakow, Poland*
([*] kuznia@agh.edu.pl)

Coal fly ash is a waste material having great potential as modifier in rigid polyurethane (PUR) technology. Addition of fly ash can improve mechanical and thermal properties of manufactured polyurethane composites. In developing countries, hard coal is still the main fuel used in power plants and combined heat and power plants. However, coal combustion generates large amounts of solid waste, including fly ash, which is produced in Poland by several million tons per year. According to the guidelines of the European Union, the Member Countries should operate in accordance with the principle of Circular Economy. Due to the properties of fly ash, they can be used as a filler in materials science, improving the properties of the produced materials and reducing the amount of petrochemicals. In earlier works, researchers performed analyzes using conventional fly ash [1-2], fluidized fly ash [3] and microspheres in the amount of 0%, 5%, 10%, 15% and 20% of the filler in relation to the total weight of the finished material. The research results showed that the most optimal amount of filler is the addition of 10%. The paper presents a comparison of selected parameters of the manufactured rigid polyurethane composites with the addition of 10% of various fillers. The following analyzes were carried out: thermal analysis, flammability of materials, gross calorific value, thermal conductivity, mechanical strength, microscopic analysis of the structure of PUR cells and analysis of the elemental composition of the produced PUR materials. The test results show that the manufactured PUR composites can be widely used as an insulating material in building industry. The use of modifiers improved the selected parameters of PUR composites as compared to the unmodified PUR foam.

Keywords: coal fly ash, microspheres, PUR composite, PUR modification

Acknowledgments
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Copper ions removal from wastewaters with polymeric adsorbent materials

D.G. Trikkaliotis[1], A.C. Mitropoulos[1], D.N. Bikiaris[2], D.A. Lambropoulou[2], G.Z. Kyzas[1,*]

[1]*Department of Chemistry, International Hellenic University, Kavala, Greece*
[2]*Department of Chemistry, Aristole University of Thessaloniki, Greece*
[*]*kyzas@chem.ihu.gr*

A major public and environmental issue is the presence of heavy metals (Cu, Ni, Zn, Pb, Cr, Cd, Co, As, Fe) in industrial effluents. Indicative conventional methods for the removal of heavy metal ions from polluted water are ion exchange, membrane filtration, reverse osmosis, flotation, sedimentation and adsorption where the latter is preferred due to simplicity, effectiveness, fast response, no secondary pollutants such as toxic sludge, and lower costs in the whole process of preparation [1]. Polymer blends have enhanced properties than their individual components (synergistic effect) possessing advantages such as low(er) cost, enhanced mechanical and chemical properties, improved porosity and high(er) efficiency of metal ion removal. Chitosan is considered to be an excellent metal-ligand binding agent and can easily form stable complexes with many metal ions due to (i) its abundancy of hydroxyl (−OH) and amino ($-NH_2$) groups on its chain backbone, and the general hydrophilicity and metal location of the polymer functional groups and their concerted chelating binding action that can be directed at the metal cations. In this study, a Cs/PVA/PEG blend in bead form was used as novel adsorbent for Cu(II) ions removal from aqueous solutions. The selection of copper ions as model pollutant in the present work is based on the fact that Cu^{2+} can be found in high concentrations because it is usually used in many industrial sectors like metal finishing, electroplating, plastics, and etching. The influence of pH, temperature, contact time and initial copper ion concentration were studied. Adsorption data were fitted by Langmuir-Freunldich isotherm model. The composite's morphology and properties were evaluated by SEM, XRD and FTIR characterization techniques.

The beads' diameter was found ~665 μm and the thickness of the surface was ~20 μm. The characteristic squamous structure of Cs was visible as well as the plenty black holes, which are related to PVA and PEG macroporous effect. The beads retain the morphological characteristics after the Cu(II) adsorption, but present a decrease in diameter ~3.6% and cracking, which may be attributed to the adsorption conditions (pH, agitation, temperature). The effect of pH on the adsorption of Cu(II) onto the Cs/PVA/PEG beads was studied within the range of 2-5 (±0.05). The point of zero charge (PZC) was found equal to 3.5. The maximum removal of Cu(II) was obtained at pH 5 for 1 g/L of adsorbent dose. At low pH values the concentration of H^+ is high, leading to competition with Cu(II) to attach with the functional groups. On the contrary, increment of pH increase the number of negatively charged active sites boosting the copper adsorption. Precipitation of Cu(II) ions as $Cu(OH)_2$ occurs for $pH>6$. The maximum adsorption was observed equal to 99.99% for initial copper ion concentration of 25 mg/L at pH 5, temperature 45 °C, 5 h as contact time and 1 g/L of adsorbent dose. The fitted maximum theoretical adsorption capacity was found to be 45 mg/g (L-F model). Also, the following proposed mechanism can be assumed based on FTIR spectroscopy.

Keywords: Chitosan, Poly(vinyl alcohol), Poly(ethylene glycol), Adsorption, Copper ions, Characterizations

Acknowledgments

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Influence of needle punch desity for properties of recycled PET nonwoven fabrics

Jae Min Lee[1], Jeong Jin Park[1], Ji Beom Choi[1], Seung Goo Lee*[1]

[1]*Department of Organic Materials Engineering, Chungnam National University, Daejeon 34134, Korea*
**lsgoo@cnu.ac.kr*

As environmental pollution accelerates, regulations related to the use of recycled polyethylene terephtalate(PET) are being strengthened. Accordingly, researches related to PET recycling are being actively conducted, and in particular, efforts to process the recycled PET into a nonwoven fabrics and use it as wheel guard materials are continuing. In this study, a nonwoven fabrics was manufactured using recycled PET staple fiber and recycled low melting point(LM) PET staple fiber for a wheel guard material. Recycled LM PET staple fiber is a sheath-core type fiber using partially recycled PET. The sheath part is made of low-melting PET and the core part is made of regular PET, which acts as a thermal binder. Recycled PET staple fiber and recycled LM PET staple fiber were mixed in a mass ratio of 6:4, and carding and needle punching were performed. Recycled PET nonwoven fabrics was manufactured by processing the recycled PET nonwoven fabrics with different needle punching densities and thermal bonding conditions. The purpose of this study is to improve the physical properties of recycled PET nonwoven fabrics by analyzing the characteristics of nonwoven fabrics according to needle punch density. Finally, the mechanical properties of the recycled PET nonwoven fabrics were analyzed using a universal testing machine, and the charicteristics of the nonwoven fabrics such as the porosity and air permeability were evaluated.

Keywords: Recycled PET, nonwoven fabrics, needle punched fabrics, needle punch density

Acknowledgments

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Synthesis of Ultrahigh Molecular Weight PLAs Using a Phenoxy-Imine Al(III) Complex Catalyst

Feijie Li[1,2*], Sanjay Rastogi[1,2*], Dario Romano[1,2*]

[1] Aachen-Maastricht Institute for Biobased Material(AMIBM) and Maastricht University, Faculty of Science and Engineering, Department of Biobased Materials,Geleen 6167 RD, The Netherlands
[2] King Abdullah University of Science and Technology, Thuwal 23955, The Kingdom of Saudi Arabia
[*]Corresponding Author: feijie.li@kaust.edu.sa; dario.romano@kaust.edu.sa; sanjay.rastogi@kaust.edu.sa

Polylactide (PLA) has become a very important polymer because of its favorable biodegradablilty, biocompatibility and bioresorbable properties. It is considered to be used as possible candidate to replace polyethylene in the packing applications.[1] However, one of the main shortcomings of PLA is its brittleness in nature and relatively poor mechanical properties, which often limits its further application.[1] It is generally accepted for polymeric materials that some mechanical properties of oriented structures can be improved as the molecular weight of PLA increases. At present, ring-opening polymerization (ROP) of lactides is the preferred method over classic polyaddition of lactic acid to obtain high molecular weights. However, the monomer purity is probable the most critical aspect for achieving high molecular weights. The present literature mainly focuses on the synthesis of relatively low molecular weights (in the order of 10^3–10^5 g/mol); while only limited works tackle the synthesis of ultrahigh molecular weight (UHMW) PLA. Indubitably, tin octanoate (or tin (II) 2-ethylhexanoate) is the most commonly employed catalyst for the large scale production of PLA; but trans-esterification tendency of the tin octanoate and its severe cytotoxic to almost all kinds of living cells, question the use of tin for the synthesis of PLA.[2] Therefore, efficient, less toxic, and environmentally friendly alternatives to tin catalysts are eagerly sought. Herein, we report L- and D-lactide polymerization kinetics using phenoxy-imine ligands of the type $Me_2Al[O\text{-}2\text{-}tert\text{-}Bu\text{-}6\text{-}(C_6F_5N{=}CH)C_6H_3]$ in the presence of n-butanol and benzyl alcohol by ring-opening polymerization into polylactide. Effects of initiator concentration, catalyst concentration, polymerization temperature and time on the molecular weight of poly-L-lactide are also investigated. Purification and drying of the lactides are found to significantly influence the polymerization kinetics and the final molecular weight achieved. Ultrahigh molecular weight poly(L-lactic acid) PLLA (M_w = 1.4 × 10^6 g/mol with Đ = 1.8) and ultrahigh molecular weight poly(D-lactic acid) PDLA (M_w = 1.3 × 10^6 g/mol with Đ = 2.0) are obtained when polymerization are performed with a molar ratio of monomer to catalyst (LA/Al) of 8000 for 72 h at 120 °C in the presence of benzyl alcohol with conversions of 96 and 91%, respectively. We report for the first time the synthesis of ultrahigh molecular weight poly-L- and D-lactide using the $Me_2Al[O\text{-}2\text{-}tert\text{-}Bu\text{-}6\text{-}(C_6F_5{=}CH)C_6H_3]$ catalyst.[3] The identified catalyst is found to be suitable for the synthesis of a broad range of molecular weights. The resulting polymers have been characterized by DSC and MALDI-TOF-MS proving the synthesis of mainly linear as well as partialy macrocyclic structures.

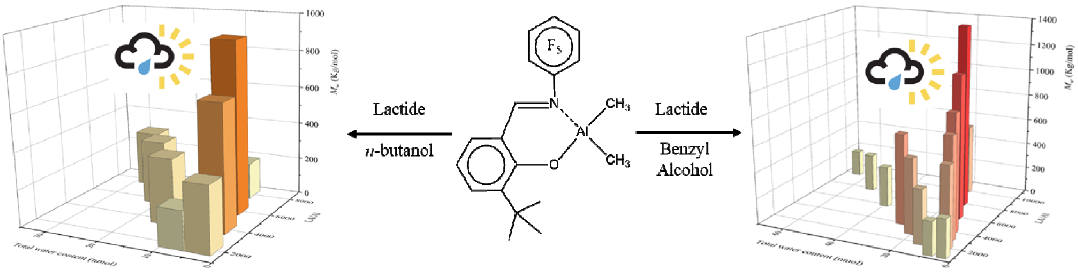

Figure 1. Summary of the molecular characteristics (M_w) and total water content as a function of LA/Al molar ratio using 3x_LA and 6x_LA for 1B (left) and BA (right).

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Tailoring PLA Properties by Reactive Extrusion

B. Liedl[1*], C. Burgstaller[1]

[1] *Transfercenter für Kunststofftechnik GmbH, Wels, Austria*
[*] *barbara.liedl@tckt.at*

Driven by the need of a substitution for petrochemical polymers, the development of environmentally friendly polymers is progressing inexorably. Bio-based and bio-degradable polymers have their advantages in terms of sustainability and waste reduction, but they still lack indispensable properties for widespread use as packaging materials and consumer goods.[1,2] Of all known biopolymers, a significant attention is paid to polylactic acid (PLA), a bio-degradable and bio-based polyester made from lactic acid, which in turn can be obtained from natural glucose or starch containing resources.[2]

Much effort has been made to overcome the brittleness of PLA[2]. The approach we pursue is to positively influence the PLA properties by conventional and reactive extrusion with biobased additives. PLA was blended with 5 and 10 wt.% of three different bio-based plasticisers (based on fatty acids and liquid polyester molecules) by extrusion in a conventional twin-screw extruder. Blends with the same composition were produced with the addition of 0.5 wt.% of coupling agent by reactive extrusion. Mechanical tests were carried out on universal test specimens obtained by injection moulding. The extent of the tailoring of the PLA properties was evaluated by thermal and mechanical characterisation.

The blending of PLA with biobased compatibilisers appears to effectively lowering T_g by up to a third and increasing crystallinity of the blends. As to be expected, the melt flow rate of the blends is increased and mechanical properties such as E-modulus, yield stress, yield strain, and stress at break suffer. However, the drawback of declining mechanical properties can be overcome by reactive extrusion of PLA and plasticisers with the coupling agent. Depending on the type of plasticiser, a strong reduction of the melt flow rate is achieved, which indicates effective coupling of the reactive partners. The main results demonstrate that the lowering of the mechanical properties of PLA/plasticiser blends can be prevented or attenuated by reactive extrusion with a coupling agent. The elasticity was kept high despite the coupling, and notched impact strength was even enhanced by a factor of 1.5 – 3.4 compared to neat PLA.

The biobased additives we used were efficient plasticisers as reducing the brittleness of PLA. Observation of the flowability of the blends shows the effectiveness of the reaction with the coupling agent and improved mechanical properties compared to non-reactive PLA/plasticiser blends.

Acknowledgments

The authors are grateful to Sarah Wimmer for carrying out part of the lab work.

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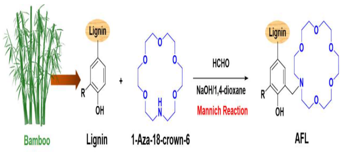
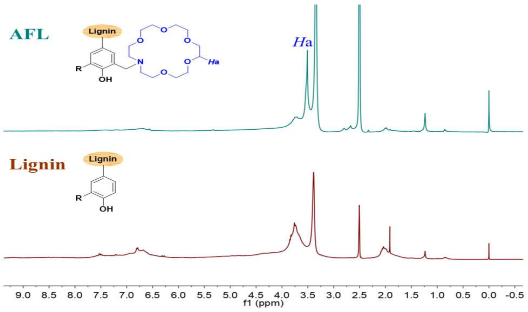
Lignin-based biosorbent for application in selective removal of Pb(II)

Z. S. Liu[1,*] and C. Jin[2]
[1]*National Center for Agricultural Utilization Research, Agricultural Research Service, U. S. Department of Agriculture, 1815 N. University Street, Peoria, Illinois 61604, United States*
[2]*Institute of Chemical Industry of Forest Products, CAF; National Engineering Lab. for Biomass Chemical Utilization Jiangsu Province, Nanjing 210042, China*
**Kevin.liu@usda.gov*

A novel 1-Aza-18-crown-6 functionalized lignin-based adsorbent (AFL) has been prepared through Mannich reaction in a one-step process. Characterizations of the AFL were carried out by Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, elemental analysis and X-ray photoelectron spectroscopy. The AFL was observed to display enhanced adsorption capacity ($Q_{\max}$ = 91.4 mg/g) and superior selectivity toward Pb(II) ions, due to a display of crown ether units and their interaction with metal ions. This AFL could be regenerated by desorption of Pb(II) ions and remained at over 80% adsorption efficiency after four adsorption-desorption cycles. Therefore, the AFL displays acceptable adsorption performance and can serve as a bioresource-based and recyclable adsorbent material, portending a new expectation in the application for water purification engineering.

Scheme 1 shows the synthesis of 1-Aza-18-crown-6 functionalized lignin (AFL) and Fig. 1 shows the ^{1}H-NMR spectra of lignig and AFL samples. Table 1. shows the comparison of the maximum Pb(II) adsorption capacities to various reported adsorbents.





Scheme 1. Synthesis of 1-Aza-18-crown-6 functionalized lignin (AFL). Fig. 1 ^{1}H NMR (400 MHz, DMSO-d_6) spectra of lignin (bottom) and AFL (top).

Table 1. Comparison of the maximum Pb(II) adsorption capacities by various reported adsorbents.

Adsorbent	Experiment condition		Adsorption capacity ($Q_{\max}$, mg/g)
	pH	*T* (K)	
AFL	6	298	91.4
Porous lignin-based sphere	5	303.2	31.8
Lignin xanthate resin	5	303	63.9
Amine functionalized lignin	6	298	69.4
Lignin-based bio-adsorbent	5	298	130.2
Functionalized lignin	-	298	123
Modified sugarcane bagasse	5-5.5	298	122.4
Modified cellulose	-[a]	296	71.9
Amino functionalized graphene	6	313	28.0
Modified magnetic chitosan	5	298	76.9
Activated carbon	5.7	291	13.1
Silica gel	5-6	-	82.6
Biochar	5	298	82.5

[a] Not available.

Towards the development of performant eco-friendly formulations. Physico Chemical challenges of the deposition of bio-based polycations.

Eduardo Guzman[1], Lionel Bureau[2], Fabien Leonforte[3], Ramón G. Rubio[1], Gustavo S. Luengo[3]

[1] *Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid*
[2]*Universit´e Grenoble Alpes, CNRS, LIPhy, 38000, Grenoble, France*
[3]*L'Oréal Research and Innovation, 93600 Aulnay-Sous-Bois, France*

Polymer-surfactant systems have many technological and industrial applications such as: fabrication of functional materials and coatings, personal care and pharmaceutical products, food science, paints, anti-icing liquids, tertiary oil recovery, and paper industry. Mixtures containing polymers and surfactants are especially important on the development of formulations for shampoos and hair conditioners.

We have studied the self-assembly in solution of a natural polymers (chitosan) as well as biosurfactants (rhamnolipids) in binary mixtures comparing the results with classical petrochemical ingredients as surfactant sodium laureth sulfate (SLES) or poly(diallyl- dimethyl-ammonium chloride (PDADMAC) . The combination is of particular interest in formulation. In particular, we have also studied binary mixtures formed with sugar-based rhamnolipids (RL) and alkylpolyglucoside (APG). The reason being in this case that glycolipid biosurfactants provide good physico-chemical properties and can be considered potential good substitutes of synthetic surfactants, with a better environmental impact and lower toxicity.

Dynamic Light Scattering (DLS) and turbidimetry measurements, together with electrophoretic mobility measurements, have been used for characterizing the polyelectrolyte ? surfactant complexation in bulk.

The adsorption of such mixtures onto solid surfaces mimicking the negative surface charge of damaged hair has been followed by two complementary techniques: Ellipsometry and Dissipative Quartz Crystal Microbalance (D-QCM). The combined information has provided important insights on the conditioning effects and lubrication (water content) of the polymer - surfactants mixtures. The topography of the layers obtained by Atomic Force Microscopy (AFM) allows us to obtain further insights on the conditioning performance of the formulation.

In all cases the adsorption onto the solid surface of the aggregates formed in the bulk is enhanced with the surfactant concentration increase. This behavior can be ascribed to the bigger size of the aggregates formed in the bulk and their high surface charge which favors their deposition onto negatively solid surfaces. Furthermore, first SCF calculations agree qualitatively with experimental results, even the applied model presents some differences with the real experimental scenario. The performance of PDADMAC ? sugar based surfactant complexes has been found to be governed by the charge of the surfactant, the number of sugar rings present in their structure and the length of the hydrocarbon length. Results show that the structure of different sugar-based surfactants, especially rhamnolipids, conditions the adsorption potential of polyelectrolytes in model washing systems. To conclude, the future is extremely bright. There is a significant opportunity to transform biopolymers, such as CHI and cellulose, by changing the molecular weights, molecular distributions, functional groups (including counter-ions), and so on. Such diversity means the powerful tools and methodologies presented above are extremely important in guiding chemists in designing and developing new, better-performing and more sustainable polymers.

Keywords: eco-conception, adsorption…

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Tomato pomace as additive for polypropylene-based 3D printing filaments

C. Martins[1*], M. Durão[1], S. Petronilho[2,3], M. A. Coimbra[3], A. Barros-Timmons[1], I. Gonçalves[4]

[1]*CICECO – Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*
[2]*Chemistry Research Centre-Vila Real, Department of Chemistry, University of Trás-os-Montes and Alto Douro, 5001-801 Vila Real, Portugal*
[3]*LAQV-REQUIMTE – Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*
[4]*CICECO – Department of Materials and Ceramic Engineering, University of Aveiro, 3810-193 Aveiro, Portugal*
[*]*carolinasousamartins@ua.pt*

Tomato industry generates large amounts of organic byproducts which are rich in valuable molecules but represent an economic and environmental concern. Based on a circular economy approach, tomato pomace (i.e., skin and seeds) has been used to tune the mechanical strength of thermoplastic materials [1]. On the other hand, fused deposition modeling (FDM) has been on the spotlight of processing technologies for its ability to minimize plastic waste while processing thermoplastic materials [2]. Some semi-crystalline polymers like polypropylene (PP) are hardly used in FDM due to shrinkage and warpage [3]. To surpass these drawbacks, the development of reinforced PP-based materials has been studied. In this work, the feasibility of using tomato pomace to adjust the physicochemical and mechanical performance of PP-based 3D printing filaments to be used in FDM was evaluated. Figure 1 depicts the strategy followed. Extensive chemical and structural characterization results of the starting materials and of the ensuing composites will be presented and discussed as well as some preliminary results regarding the filament extrusion conditions.

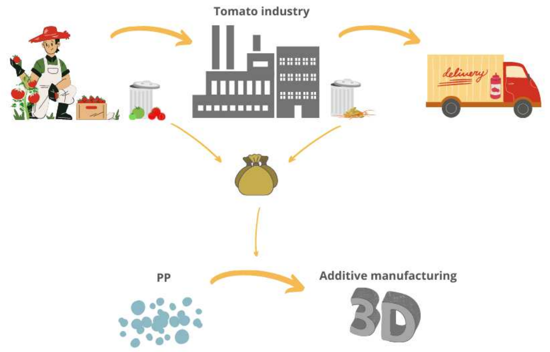

Figure 1 – Tuning the performance of PP-based 3D printing filaments using tomato pomace

Keywords: filament extrusion, additive manufacturing, agri-food byproducts

Acknowledgments

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Novel polymeric antioxidants for polyolefins using eugenol as biogenic building block

Jannik Mayer[1], Elke Metzsch-Zilligen[1], Rudolf Pfaendner[1]*

[1]*Fraunhofer Institute for Structural Durability and System Reliability LBF, Division Plastics,*
Schlossgartenstr. 6, D-64289 Darmstadt, Germany
rudolf.pfaendner@lbf.fraunhofer.de

Polyolefins like polypropylene degrade during processing and lifetime through oxidation and photooxidation. The consequence of this process called autooxidation is the loss of visual and physical properties. [1] To prevent thermal degradation and ensure the maintenance of properties stabilization with suitable antioxidants is mandatory. Most standard antioxidants used today are based on petrochemistry. Due to the low molecular weight these substances show high migration tendency which may cause a contamination of the environment. [2]

In the course of sustainability and to avoid the leaching of stabilizers from plastics Fraunhofer LBF develops novel polymeric antioxidants with biogenic building blocks as useful alternative sources for plastic stabilizers. Thus, novel macromolecular multifunctional antioxidants have been synthesized from eugenol (Figure 1).

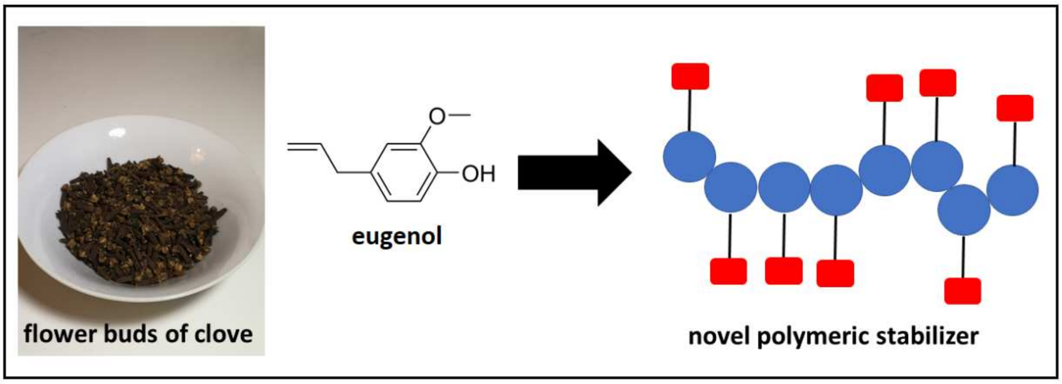

Figure 1 Synthesis of new phenolic macromolecular antioxidants based on eugenol which can be extracted from clove oil. [3]

The antioxidant activity and stabilizing effect in polypropylene was proven by the 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) method, extended extrusion time, oxidation induction time measurements and long term heat stabilization test via accelerated oven ageing.

Keywords: polymeric antioxidants, biogenic building blocks, bifunctional antioxidants, stabilization

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Balancing strength and ductility – Tough and transparent nanopapers through mercerisation

Florian Mayer[1*], Andreas Mautner[1], Alexander Bismarck[1]

[1]*Polymer and Composite Engineering Group, Institute of Materials Chemistry and Research, University of Vienna, Währingerstraße 42, A-1090*
[*]*f.mayer@univie.ac.at*

Recent research has shown the wide variety of possible applications for cellulose nanopapers such as reinforcements in composites,[1] as substrates for printable electronics, and for use in water filtration and treatment.[2] One major shortcoming of these materials currently is their brittle nature and low ductility.[1] To overcome this, an alkaline treatment process, commonly known as mercerisation was investigated. Mercerisation of cellulose fibres is a traditional process to alter mechanical and optical properties by changing the crystal structure from the strong and brittle cellulose I allomorph to the more ductile cellulose II allomorph. While this process has been extensively studied for macroscopic cellulose fibers in the textile industry, as well as for certain nanocellulose fibers in suspension, its effect on already hornified nanopapers has never before been investigated. Therefore, this project investigated mercerisation as an option to prepare dense, ductile and strong cellulose nanopapers.

Cellulose nanopapers were treated with NaOH to (partially) transform the native cellulose I allomorph into the cellulose II allomorph. This transformation was investigated via XRD and it was accompanied by swelling and interdigitation of the individual fibrils, which in turn increased the optical transparency of the nanopapers, another desirable quality for products such as electronics, surface coatings or flexible displays. Furthermore, this partial conversion into cellulose II significantly increased the strain to break (up to 340% compared to an untreated reference sample) while still reaching tensile strengths of over 100 MPa. The relation between maximum stress and maximum strain followed an inverse linear trend depending on the treatment conditions, which allows the easy control and tailoring of the properties of nanopapers for a multitude of applications in which flexibility and ductility as well as high tensile strength are required. Simultaneously, the work of fracture (a value directly corresponding to the toughness of a material) of all samples, could be greatly increased (up to 220% of the reference value) as a result of balancing the ductility of cellulose II with the strength of cellulose I nanofibers.

Keywords: nanocellulose, ductile, mercerisation, alkaline treatment

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High-performance protective polyurea coatings based on aspartate esters and bio-based isocyanate

S. Natour*, V. Gajdošová, Z. Morávková, M. Dušková-Smrčková*

Institute of Macromolecular Chemistry, Prague, Czech Republic.
**natourova@imc.cas.cz / m.duskova@imc.cas.cz*

Polymeric high-performance protective coatings are indispensable for maintaining the integrity and extending the service life of surfaces, by protecting them against undesirable and irreversible damages caused by UV light, water, chemicals, fluctuating weather conditions, scratches, and more. Additionally, coatings minimize the economic losses as they prolong and enhance the quality and appearance of the materials. Among the existing coating materials, polyurea systems often overcome epoxy and polyurethane performance. However, conventional polyurea coating systems exert too fast cure, thus requiring special spray equipment that requires high temperature and pressure. Recently introduced polyaspartic coatings can diminish this limit and are preferred for their high hardness, short curing time, excellent chemical, moisture and wear resistance, relatively long pot life. The polyaspartic coating is a type of polyurea, synthesized through a condensation reaction of secondary amine binders based on aspartate esters and polyisocyanates. The coating-forming properties and the long-term performance largely depend on the chemical structure of the resulting macromolecular network.
We have synthesized the aspartate esters of varied chemical structures to establish the relations between formation–structure–properties of the final coating networks, and to develop versatile high solid solvent borne polyaspartate coatings. These systems are based on *in-situ* crosslinking two-component and low-solvent (≥ 60 wt.-% solids) reactive mixture composed of synthesized aspartate esters and bio-based triisocyanate.

We will present the synthesis of aliphatic and cyclo-aliphatic aspartate ester *via* aza-Michael addition. Then, we will discuss the preparation of polyaspartic-polyurea crosslinked coating formed under ambient conditions. The coatings were characterized by DSC, FT-IR, micro- and nano-indentation. We link the effect of the aspartate unit chain on the film drying rate and hardness build-up. Additionally, the effect of the reaction by-products formed during amine-isocyanate curing will be elucidated. It is worth noting, that the coatings are formed by simultaneous and interdependent physical drying and chemical crosslinking accompanied by the passage of the system through its glass transition region thus leading to a gradient of properties. The structural and chemical changes occurring within the forming layer were studied by Raman confocal microscopy.

Keywords: polyurea, coating, aspartate ester binder, polyaspartic coating, high-solid coating

Supercritical CO2-Induced Exfoliation of Carbon Nanofiller Composites in Salicylic Methyl Glicolide and Chemically-Recycled Polyethylene Terephthalate

Seungchan Noh [1*], Dohyung Kim [1], Hyeri Kim [1], Jaseung Koo [1]

[1] *Department of Organic Materials Engineering, Chungnam National University, Daejeon, 34134, Republic of Korea*

We investigated the mechanical properties and thermal conductivity of biodegradable salicylic methyl glicolide (SMG) and chemically-recycled, Bis(2-hydroxyethyl) terephthalate (BHET)-based Recycled PET (rPET) after embedding with carbon-based fillers. We used eco-friendly and non-toxic supercritical CO_2 to induce two-dimensional exfoliation of graphite using the Rapid Expansion of Supercritical Solutions (RESS) process. This facilitates to formation of a Mixed Morphology Composite Network (MMC network) between exfoliated graphite and multi-wall carbon nanotube (MWNT). The mixed carbon-nanomaterial was compounded with the rPET- SMG matrix after rheological data-based Ludovic simulation for the optimized process conditions and screw profile to improve the dispersibility of the rPET-SMG matrix and nanofillers. The rPET-SMG/MMC nanofiller composites exhibit excellent thermal conductivity due to a high-efficiency heat transfer path of MMC networks and mechanical properties due to enhanced crystallinity of the rPET-SMG matrixes.

Keywords: Biodegradable, Supercritical fluid, Thermal conductivity, Expanded graphite, Carbon nanotube

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Impact of opaque rPET in fiber properties produced via bottle-to-fiber mechanical recycling process

F.Odet[1*], P.Cassagnau[1], N. Ylla [1]

[1]*Univ Lyon, UCBL, CNRS, IMP UMR 5223, F-69622, Villeurbanne, France*
[*]*Felix.odet@univ-lyon1.fr*

Considering the global environmental context, improving the recycling rate of plastics from packaging is a key challenge, currently at 42% in Europe in 2019, 58% for PET more specifically [1]. Among the multiple ways of recycling polymers, mechanical recycling via fiber production is the most important application for PET packaging products, representing 40% of the market volume in 2016 [2]. Recently, Opaque PET appears in the European market, mainly for milk bottles. Formerly in HPDE, the new technology using PET filled with 1 to 10%wt submicron TiO_2 decrease the energy and water consumption from 30% and 20% respectively. However, the presence of filler may disturb the recycling activity especially in high-speed melt spinning. In this process, a high strain rate is applied to thin filaments generating high molecular orientation and stress induced crystallization responsible for the filament mechanical properties, mainly tenacity and dimensional stability [3][4]. The influence of inorganic particles in PET melt spun fiber properties can be negative with a reduction of mechanical properties due to poor orientation and crystallization, or beneficial, as some observe better properties at low content of nano-filler. Opaque PET bottles' influence on high-speed spinning has not been reported yet, it is consequently the aim of this work.

The impact of Opaque PET on melt spun fiber structure and properties has been assessed and compared to the impact of TiO_2 particles incorporated via a commercial masterbatch, to discriminate the particles from the matrix influences. More precisely, high-speed spinning pilot tests have been used to produce two sets of filaments, i) The first set is a blend between standard transparent post-consumer bottles (REF) and opaque PET (0%-30%-50%-100%); ii) The second set is a blend between standard transparent post-consumer bottles and a masterbatch PET/ TiO_2 at different amounts of filler (1%-3%-6%wt). The structure-properties relationship of rPET melts spun fibers has been investigated with crystallinity, amorphous and crystalline phase orientation, and tenacity measurement. It has been observed that the degree of crystallinity decreases with Opaque PET addition and in a lower extent TiO_2 from masterbatch addition, as well as the orientation of both the amorphous and crystalline phases. Tenacity also shows a decrease of properties with TiO_2 and more importantly with Opaque PET addition. Opaque PET and TiO_2 are unfavorable for molecular orientation during melt spinning resulting in decreased mechanical properties. It has been suggested that TiO_2 particles are not fully responsible for the reduced properties of opaque PET since their proprieties are lower than rPET /TiO_2 blends. Other parameters could have negative effects in Opaque PET formulation, such as lower elongation viscosity, particles surface treatment or lower molar mass.

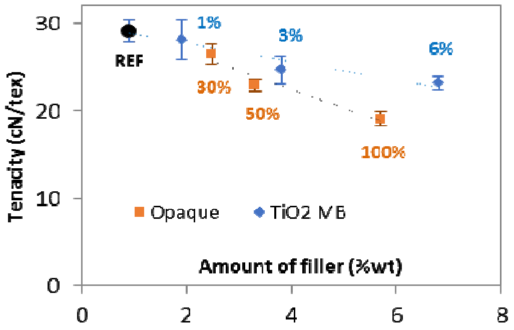

Fig 1 : Tenacity versus the amount of filler for the two sets of formulations (Opaque and TiO2 from

Keywords: Mechanical recycling, rPET, melt spinning, Opaque PET, molecular orientation, tenacity

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The new life of “non recyclable” heterogeneous plastic wastes

S. Gazzotti[1, 2, 3], M.A. Ortenzi[1, 2]*, B. De Felice[3], M. Parolini[3]

[1] *Deparment of Chemistry, University of Milan, Via Golgi 19, 20133 Milan, Italy.*
[2] *Polymeric Materials Research Center “LaMPo”, Department of Chemistry, University of Milan, Via Golgi 19, 20133 Milan, Italy.*
[3] *Department of Enrivornmental Science and Policy, University ofi Milan, Via Golgi 19, 20133 Milan, Italy.*

*marco.ortenzi@unimi.it

The worldwide concern around the environmental accumulation of plastic wastes has become one of the most discussed topics in the scientific community. The development of new strategies to face this problem is of crucial importance and different approaches are being investigated to effectively reduce the pollution generated by an improper or non efficient disposal of plastic waste. Besides the strong efforts spent on the development of biodegradable plastics that could, in principle, avoid the accumulation in the environment, the research is focused on innovative recycling approaches. Although most plastic materials are potentially recyclable, only about 20% of the worldwide plastic wastes are currently recycled, while the remaining 80% are either incinerated to recover thermal energy (25%) or landfilled (55%)[1]. On one hand, the hurdles to an efficient recycling come from an improper management of the end-of-life plastic goods. On the other hand, the highly heterogeneous nature of plastic materials often results in marked challenges when targeting a reprocessing of the wastes to yield high value products. The high versatility of polymeric materials has led to the development of multilayered materials, composites, blends and many other different species. However, although these materials are extremely valuable from an industrial point of view, they add an extremely high degree of complexity to the recycling match because each one is different from the other and cannot be separated efficiently from the other materials.

The aim of the present work is to develop an innovative approach to limit these drawbacks and to give new value to complex mixtures of plastic wastes that would be otherwise incinerated. The work is focused on the recycling of the so-called “Plasmix”, a complex and heterogeneous mixture of plastic wastes that is generated at the end of the sorting procedures in Italian plastic recycling plants. Due to its complex composition, currently plasmix is hardly recovered in view of future uses[2] and is preferably icinerated[3]. First, an analysis of the average composition of the mixture was performed, pointing out it is mainly constituted by polyolefins [polyethylene (PE), polypropylene (PP), polystyrene (PS)] and polyethylene terephtalate (PET). The weight ratio between the components are however not constant and other materials are often present in traces, making the recycling process highly challenging. Then, different extrusion tests were carried out on the mixtures, in order to determine whether the components could mix efficiently or not. In order to improve the miscibility of the polymers different additives were tested, resulting in an homogeneous material, that was succesfully employed for the preparation of specimens through injection molding. All recycled materials were characterized in their thermal, mechanical and rheological properties showing overall good properties, hinting at a possible future industrial applicability.

Keywords: post-consumer plastic waste, circular economy, recycling

Acknowledgments

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Introducing Furan-Based Poly(Ester Amide)s: A New Class Of Bio-Based Materials With Exceptional Properties

L. Papadopoulos[1*], T. Robert[2] and D.N. Bikiaris[1]

[1]*Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece*
[2]*Fraunhofer Institute for Wood Research – Wilhelm-Klauditz-Institut WKI,*
38108 Braunschweig, Germany
[*]*lazaros.geo.papadopoulos@gmail.com*

In recent years, 2,5-furandicarboxylic acid (FDCA) has received considerable attention as it is considered a bio-based substitute for nonrenewable terephthalic acid. It has been mainly incorporated into polyesters, which offer similar thermal and mechanical properties compared to their petrochemical counterparts or even surpass those. However, these materials are not suitable for applications, which require high thermal and mechanical properties. Here, polyamides or poly(ester amide)s (PEAs) are frequently used.

The synthesis of polyamides and poly(ester amide)s derived from 2,5-furandicarboxylic acid frequently leads to amorphous polymeric materials. Formation of intramolecular hydrogen bonds between the oxygen heteroatom in the furan ring and hydrogens of the amide bonds reduces the intermolecular hydrogen bonds that are usually responsible for the high thermal and mechanical performance of these materials. To circumvent this problem, aliphatic–aromatic poly(ester amide)s were synthesized in this study from dimethyl 2,5-furandicarboxylate, 1,10-decanediol, and a preformed aliphatic diol containing two internal amide bonds (amido diol).

The method presented herein allows for the successful synthesis of semicrystalline poly(ester amide)s from 2,5-furandicarboxylic acid without undesired intramolecular hydrogen bonds. A variety of physicochemical characterizations were employed to assess the properties of the synthesized polymers. This finding could set the stage for further bio-based poly(ester amide)s from 2,5-furandicarboxylic acid suitable for high-performance applications.

Keywords: poly(ester amide), 2,5-furandicarboxylic acid, 1,10-decanediol, amido diol, bio-based polymer

Acknowledgments

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An Eco-Friendlier Approach to Additive Manufacturing: Utilization of High Biobased Content, Itaconic Acid Based Polyesters in Digital Light Processing 3D Printing

L. Papadopoulos[1]*, T. Robert[2] and D.N. Bikiaris[1]*

[1]*Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece*
[2]*Fraunhhofer Institute for Wood Research—Wilhelm-Klauditz-Institut WKI, Bienroder Weg 54E, 38108 Braunschweig, Germany*
lazaros.geo.papadopoulos@gmail.com, dbic@chem.auth.gr

Additive manufacturing (AM), also known as three-dimensional (3D) printing, is a production technique for products of high customization regarding their size, shape, and design. Guided by Computer Aided Design (CAD) software, objects are printed layer by layer, achieving accuracy and significantly less waste material compared to traditional processing techniques.

AM can employ different types of polymers, depending on the specifications of the 3D printer. One of the most used polymers are UV curable resins, mainly comprised from acrylic acid based polyesters and polyurethanes. However, acrylic acid based materials can possess allergenic and irritation potential, can be volatile and toxic, especially at low molecular weights, while also not being produced from renewable resources. Therefore, alternative biobased monomers and resins are of high interest.

In this work, we developed unsaturated polyester resins, of high biobased content, and studied their properties and printability with a DLP 3D printer. To this end, monomers from renewable resources were utilized for the synthesis of the polyesters, like itaconic acid, succinic acid and 1.3 propane diol. The produced resins were evaluated regarding their physicochemical properties and the materials produced via 3D printing were characterized as to their thermomechanical properties.

Keywords: DLP 3D printing, biobased polymers, itaconic acid

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Development and study of food packaging composites based on cellulose and PVA/Chitosan

K. Papapetros[1,2*], K.S. Andrikopoulos[1,3], G. Mathioudakis[1], A. Soto Beobide[1], G.A. Voyiatzis[1]

[1] Foundation for Research & Technology-Hellas (FORTH), Institute of Chemical Engineering Sciences (ICE-HT), Stadiou Str., Rio-Patras, GR-265 04, Greece ,
[2] Department of Chemical Engineering, University of Patras, Patras, GR-265 04, Greece
[3] Department of Physics, University of Patras, Patras, GR-265 04, Greece
**kpapapetros@iceht.forth.gr*

The global demand on utilizing sustainable and ecologically friendly products based on renewable raw materials has as result intense research on potential application of cellulose materials, such as micro fibrillated cellulose (MFC), cellulose nano-fibrils (CNF) and nanocrystalline cellulose (NCC), for the development and application of high performance nanoscale industrial materials.

These celluloses are being incorporated into polymer/biodegradable matrices, aiming to enhance the blocking efficiency of the nanocomposites, modify their overall properties towards the generation of new products with minimum environmental impact.

The present work focuses on the development and study of food packaging composites by using the water soluble Polyvinyl Alcohol (PVA) and/or the biodegradable Chitosan as polymeric matrices[1,2]. Both PVA and Chitosan films are produced at lab scale by film casting while the different type of cellulose is dispersed in triple distilled water before being mixed with the polymeric solutions.

The structure of the cellulose samples as well as the polymeric matrices used is extensively studied at molecular and macroscopic scales. The molecular characterization is carried out by using Raman and FTIR spectroscopy, while the morphological and crystallographic study is assumed by SEM and XRD. Molecular characterization of every sample (from pristine to final composites) is able to highlight the molecular and crystallographic changes that take place on the samples, after chemical modification or varying the cellulose loading. In addition, crystallographic changes of the polymer/cellulose blends are extensively studied by XRD and the relevant thermal properties by DSC. Taking into account the EU regulations for food packaging materials, the prepared composites have been tested by using accredited migration cells. Aqueous ethanol solutions are used as food simulants and the migration of molecular species and/or nanoparticles from the composites has been tested for a period of 1-30 days using UV-Vis and / or Surface Enhanced Raman Spectroscopy (SERS).

In conclusion, polymeric films of PVA and/or Chitosan and their composite with micro/nano cellulose have been prepared, thoroughly characterized by several techniques and tested under EU regulations as food packaging materials.

Keywords: Nanocellulose, food packaging, biodegradable

Acknowledgments

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An outlook on Poly(γ-Glutamic acid): a Tunable Biopolymer for next Generation Sustainable Solutions

Mattia Parati[1,*]; Ibrahim Khalil[1]; Fideline Tchuenbou-Magaia[2]; Iza Radecka[1,*]

[1] *School of Sciences, Faculty of Science and Engineering, University of Wolverhampton, Wolverhampton WV1 1 LY, UK.*

[2] *School of Engineering, Computing and Mathematical Sciences, Faculty of Science and Engineering, University of Wolverhampton, Wolverhampton WV1 1LY, UK.*

Polymers are the macromolecular building blocks of most materials. The current issue faced by this industry involves the monomeric moieties used to synthesise these polymers, as they are often derived from crude oil [1]. The main advantage of chemical polymerisation methods is their ability to provide consistent, and reproducible, materials; factors which the biotechnological field still struggles to achieve [2].

Poly-γ-glutamic acid (γ-PGA) is a bio-derived water soluble, edible, non-immunogenic nylon-like polymer that resembles the biochemical characteristics of a polypeptide [2], [3]. This pseudo-polypeptide varies significantly in physico-chemical properties, compared to other bio-derived compounds. The main reason involves it's synthetic route, modulated by the expression of intermembrane enzymes, which regulate it's synthesis, molecular weight (*pgsBCA* cassette) and enantiomeric composition (racemase – *racE*) [4], [5]. As such, the microorganism's genetic make-up, environment, substrate and precursors all play a fundamental role in γ-PGA's synthesis and physico-chemical properties (Figure 1 – C2) [6]. Currently, numerous *Bacillus* strains are known to produce this polymer and secrete it extracellularly. Further, the parameters affecting the chemical composition of γ-PGA have been studied for many of these *Bacillus* strains. For example, it is now well-established that *Bacillus licheniformis* 9945a can synthesise γ-PGA with molecular weights between $1x10^4$ and $1x10^7$ Da and D to L-glutamic acid ratios ranging from 10:90 D:L to 95:5 D:L [6].

Depending upon the pH of the surrounding environment, γ-PGA can exist either in it is acid or anionic form. Further, depending upon the degree of ionisation, γ-PGA can self-arrange into either an α-helix, a β-sheet or a random coil [2]. Given the abundancy of carboxylic groups, the polymer displays high interaction with water and is very easily coupled to other active molecules [2]. Herein we discuss the parameters that allow control of crystallinity (through enantiomeric D/L split), molecular weight and polymeric state (free acid or salt form) of the material. These characteristics make the material suitable for: drug delivery, cosmetics, cryoprotectant, biodegradable plastics, heavy metal sequestration and in agriculture [6].

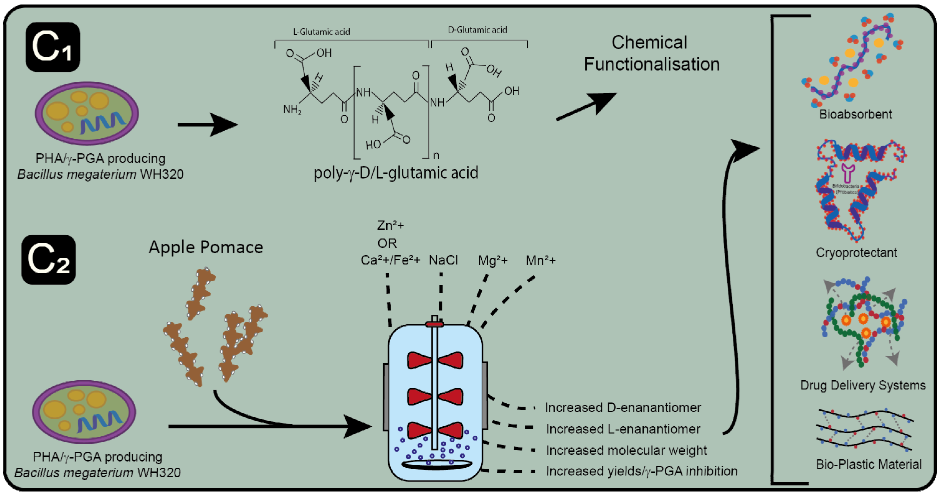

Figure 1: Development in chemical and biological synthesis of polymers. [C1] polymers with specific properties will be synthesised by cell factories, and chemical processes will be employed to modify them for specific applications [6], [1]. [C2] Within an integrated biorefinery concept, substrate and fermentation parameters will be modulated to have cell factories synthesise polymers with specific characteristics, to replace plastics [1]. *represents a probiotic strain, such as *Bifidobacteria*.

Keywords: Polymer chemistry, polymer engineering, biotechnology, biomaterials, circular economy

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Dynamic Vulcanization of Polymer Blends from Poly(Lactic Acid) (PLA) and Bio-Based Ethylene-Propylene-Diene-Rubber (EPDM)

A. Piontek[1*]

[1] *Fraunhofer UMSICHT, Institute for Environmental, Safety and Energy Technology, Oberhausen, Germany*
[*] *alexander.piontek@umsicht.fraunhofer.de*

Poly(lactic acid) (PLA) is a bio-based and biodegradable polymer which exhibits good mechanical properties such as high tensile modulus and strength. Additionally PLA is commercially available in industrial scale and in terms of price comparable to conventional engineering plastics. On the other side PLA is very brittle and shows low flexibility and ductility. These restrictions prevent the utilization of PLA especially in technical applications. Thus, much effort has been made in the past years to overcome these disadvantages to open up new applications for PLA. [1]

One possible way to improve the mechanical properties of PLA is to blend it with other more flexible (bio-)polymers to enhance its ductility. Due to immiscibility of most polymer blend systems it is necessary to use appropiate compatibilizers for the corresponding blend systems. Additionally to physical blending it is possible to use chemical reactions during the compounding step to enhance either the compatibility between the polymeric phases or the physico-chemical properties of the phases themselves. This approach is called reactive extrusion and depends on the type of used polymers and additves to initiate the corresponding chemical reactions.

In the presented work a partly bio-based ethylene-propylene-diene-rubber (EPDM) is used as the soft phase to enhance the ductility of PLA. During the compounding in a co-rotating twin-screw extruder the EPDM is vulcanized using a peroxide to induce radical crosslinking reactions. This procedure is called dynamic vulcanization. With an ethylene-methyl acrylate-glycidyl methacrylate-copolymer a suitable compatibilizer was identified to enhance the compatibility between the polymeric phases and thus the morphology of the blend [2]. Because EPDM exhibits a much higher viscosity than PLA, two bio-based plasticizers, soybean oil and soybean wax, were used to lower the viscosity of the used EPDM. Due to the unsaturated fatty acid side chains of the sobean oil it can participate in the radical reactions, whereas this does not account for the saturated side cahins of the soybean wax. It was shown that the use of soybean oil reduces the crosslinking density of EPDM in contrast to the use of the saturated soybean wax. Rheological investigations were carried out to analyze the influence of the different additives, i.e. the compatibilizer, the peroxide and the plasticzers, on the dynamic vulcanization process. It was shown that only the combination of all additives leads to a higher crosslinking density of EPDM inside the PLA matrix. Especially the use of soybean wax instead of soybean oil increases the elastic component within the rheological properties. This is particularly interesting because the effect of plasticization alone, i.e. without crosslinking, leads to an increase in the viscous component, and thus a decrease in the elastic component.

In total the ductility of the PLA based blends could be increased by the incorporation and dynamic vulcanization of the bio-based EPDM. Compared to neat PLA the notched charpy impact strength and the elongation at break were increased by a factor of around 3 and 26, respectively, whereas the tensile modulus and tensile srength were only decreased by around 40 and 60 %, respectively.

Keywords: PLA, EPDM, bio-based polymers, compatibilization, reactive extrusion, dynamic vulcanization

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Toward vitrimers from poly(amidoamine)s made of Tulipalin A

F. Pippig[1*], M. Danko[1], A. Eckstein[1], K. Mosnácková[2], J. Mosnáček[1]

[1]*Polymer Institute of the Slovak Academy of Sciences v.v.i., Department of Synthesis and Characterization of Polymers, Dúbravská cesta 9, 84541 Bratislava, Slovak Republic*
[2]*Polymer Institute of the Slovak Academy of Sciences v.v.i., Department of Composite Materials, Dúbravská cesta 9, 84541 Bratislava, Slovak Republic*
[*]*falko.pippig@savba.sk*

Tulipalin A is considered as renewable monomer. It is a content of Tulip flowers or it can be produced via chemical synthesis based on itaconic acid. Tulipalin A can be polymerized via radical and ring opening co-polymerizations,[1] Furthermore, it can undergo Michael addition and amide formation.[2] The reaction is leading to polymers with a broad dispersity and adhesive properties. It was found that the polymers made with this strategy have linear or branched structure. One opportunity to extend the scope of application of the material is crosslinking. If the crosslinking is made with bonds which can be cleaved and reformed depending on temperature, p*H* or via irradtion with light than it is possible to create materials which show properties that depend on external conditions. Poly(amidoamine)s made from Tulipalin A were reacted for example with Furandialdhyde (FDA) and with Bis(maleimides) (BM). FDA itself is produced from the renewable raw material 5-Hydroxymethylfurfural (HMF). The reaction with FDA is leading to imine bonds[3] and the reaction with BMs is forming diels-alder adducts[4]. Both of the bonds are known to have a temperature dependend dynamic behavoir. The formation of the networks were analyzed with rheology. The composition was determined with FTIR and NIR measurements. The thermal properties were studied with help of DSC and TG investigations. Finally, the mechanical properties were determined with the help of tensile tests of small samples. The presented polymer networks are aimed to be used as self healing materials or materials which show shape memory properties. The chemistry is selected with a focused on an enviromental friendly strategy.

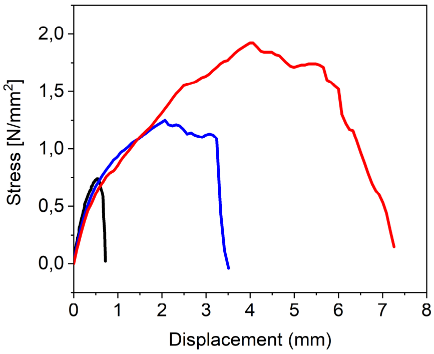

Figure 1: Tensile tests of poly(amidoamine)s made of Tuliplain A with 64 mg (red), 128 mg (blue) and 144 mg (black) of FDA pro 1 g of polymer.

Keywords: Tulipalin A, poly(amidoamine)s, Vitrimers, renewable polymers

Acknowledgments

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Recycling of multilayer films containing PE, PA6 and EVOH and their new application

Kateřina Plevová[1*], Michael Feuchter[1], Nadine Wild[1], Heidi Pichorner[2]

[1] Institute of Materials Science and Testing of Plastics, Montanuniversität Leoben, Otto Glöckel-Str. 2, 8700 Leoben, Austria
[2] *PrimAs Tiefkühlprodukte GmbH, Mösl 1, 6406 Oberhofen, Austria*
[*]*plevova.katerina@unileoben.ac.at*

Multilayer plastic films combine properties of two or more different polymers, such as polyethylene (PE) with good tensile strength and polyamide (PA) with oxygen barrier properties. The layering of various materials enables to design films with a broader range of (good) properties. Such multilayer films are widely used in the food packaging industry. At the end of their service life arises a problem how to recycle or re-use them. [1]

A multilayer film, consisting of incompatible materials, can reach excellent properties. However, a blend of the same incompatible materials has usually unsatisfactroy properties, which is the main issue with the mechanical recycling of multilayer film. To improve the properties of a blend, two approaches are available: (i) adding a compatibilizer or (ii) finding a certain ratio of different materials, which leads to suitable material properties. Adequate compatibilizer should improve miscibility between two or more incompatible polymers and thus improve the mechanical properties of the blend. The former approach (i) appears very challenging with more than two materials, whereas the latter approach (ii) seems more promising. [2]

This work compares both aforementioned approaches for recycling different kinds of packaging films: two multilayer films consisting of low-density polyethylene, polyamide 6 and ethylene vinyl alcohol and two polyethylene films. Blends with different compatibilizers or different material ratios were prepared in a kneader. Afterwards, films were prepared using a vacuum press and their mechanical properties were tested. Films, which exhibited suitable properties for shrink film application, were chosen for industrial-scale testing which is going to be discussed.

Keywords: Mechanical recycling, multilayer films, polyamide 6, polyethylene, ethylen vinyl alcohol

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Tall oil fatty acids based michael donor monomer synthesis for thermoset polymers

Ralfs Pomilovskis[1,2,*], A. Fridrihsone[1], M. Kirpluks[1]

[1]*Polymer Laboratory, Latvian State Institute of Wood Chemistry, Riga, Latvia*
[2] *Institute of Technology of Organic Chemistry, Faculty of Materials Science and Applied Chemistry, Riga Technical University, Riga, Latvia*
[*] *Corresponding author e-mail: ralfs.pomilovskis@kki.lv*

The European Commission established the "European Green Deal" to address climatic and environmental concerns. It's a growth plan to transform the European Union into an affluent society with a modern, resource-efficient, and competitive economy by 2050 while also achieving climate neutrality and a carbon balance [1]. The development of bio-based polymers is critical for this shift to a circular bioeconomy.

Tall oil is obtained as a side stream in pulp production, and distilled tall oil mainly contains oleic and linoleic acid [2]. Its potential for producing high-value bio-based chemicals and materials has gotten little attention thus far.

In this study, the tall oil fatty acids (TOFA) have been successfully used to synthesize Michael donor monomers and further polymeric materials with commercially available acrylates by carbon-Michael nucleophilic addition reaction.

The initial step in the bio-based thermoset synthesis method was to introduce oxirane groups into TOFA's chemical structure. TOFA was epoxidized utilizing *in-situ* produced peroxyacetic acid from acetic acid and hydrogen peroxide in the presence of acidic ion exchange resin Amberlite IR-120 H. The precursors for Michael donor monomers were created via oxirane ring-opening reactions with two different alcohols from epoxidized TOFA. The functional groups essential for the carbon-Michael addition process were obtained by transesterifying polyol -OH groups with t-butyl acetoacetate ester.

The chemicals obtained were part of a two-component room-temperature curing thermoset polymer system. The OH value, acid value, moisture content, and viscosity of the produced polyols and their acetoacetates were investigated. GPC/SEC, FTIR, and MALDI-TOF spectra were used to establish the chemical structure.

A carbon-Michael nucleophilic addition reaction in the presence of catalyst was employed to create thermoset polymers from developed acetoacetates of two tall oil-based and two commercial polyols. Three acrylates with various functionality were utilized in the polymerization operations. The development of polymer formulations with varying crosslink density was enabled by the different chemical structures and functionality of obtained bio-based monomers. The developed polymers were cured at room temperature, resulting in a stiff, transparent materials. DMA, DSC, TGA and universal strength testing equipment were used to investigate the physical and thermal characteristics of the obtained polymers.

Keywords: Bio-based thermoset polymers, Michael donor monomer

Acknowledgments

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Ionic liquid-catalyzed step-growth reaction between difunctional epoxy and dicarboxylic compounds

M. Rebei[1,2*], A.Mahun[1,2], R.K.Donato[3], H. Beneš[1]

[1]*Institute of macromelcular chemistry, Prague, Czech Republic*
[2]*Charles university, Faculty of science, Prague, Czech Republic*
[3]*National University of Singapore, Singapore*
[*]*rebei@imc.cas.cz*

Herein we report the step-growth polymerization reaction between diepoxy resins and diacid compounds in a VOC-free imidazolium ionic liquid (IL) medium. The established fossil-based epoxy resin based on diglycidyl ether of bisphenol A (DGEBA), as well as the synthesized natural-based epoxy 2,2'-[(2-methoxy-1,4-phenylene)bis(oxymethylene)]bis(oxirane) (DGEMHQ), were used for reaction with different dicarboxylic acids (such as adipic, succinic, and malonic acid) under mild conditions (T = 80-120 °C). Moreover, no solvents or catalysts were used (besides the IL), and no direct residue was produced, complying with the most of 12 principles of green chemistry. The oxirane ring-opening of DGEBA and DGEMHQ was followed by FTIR analysis and confirmed with NMR, showing that the oxirane ring was fully consumed within 3 h of reaction. MALDI-TOF was performed to detect the intermediates formed in different reaction steps to define the initiation mechanism. Thermal analysis, such as TGA and DSC, were carried out to study the thermal properties of the obtained products, while the mechanical properties and possible network crosslinking were studied via rheology.

Keywords: Ionic liquid, VOC-free, epoxides, ring-opening, dicarboxylic acid.

Acknowledgments
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Increased weathering degradation of PLA/PBAT blends with incorporation of chloroacetic acids and esters.

Rafael C. Rebelo*[1], Luís P. C. Gonçalves[1], Ana C. Fonseca[1], Josefa Fonseca[2], Manuel Rola[2], Jorge F. J. Coelho[1], Filipe Rola[2], Arménio C. Serra[1]

[1] *CEMMPRE, Department of Chemical Engineering, University of Coimbra, Rua Sílvio Lima-Pólo II, 3030-790 Coimbra, Portugal*
[2]*SICOR-Sociedade Industrial de Cordoaria, S.A., Rua 13 de Maio 1533, Ap.10, 3889-852 Cortegaça, Portugal*
**rafael.rebelo@student.uc.pt*

Keywords: PLA/PBAT blends; Chloroacetic acids/esters; Degradation tests; Outdoor performance.

Introduction: Blends of PLA/PBAT are already on the market (e.g.: Bio-Flex® - FKuR & Ecovio®- BASF) and have the compostability seal (EN 13432 standard). However, composting only occurs under very specific conditions and is only possible on an industrial scale. The degradation of PLA/PBAT in natural environment has already been studied. Under soil conditions, the results showed that PLA and PBAT alone degrade faster than in the mixture.[1] The degradability of the mixture was also evaluated in the open air. Decomposition occurs, but several microplastics are produced.[2] These tests also have the disadvantage of requiring several years to be representative. In this work, the degradability of a commercial PLA/PBAT blend (Bio-Flex®) was studied with the addition of chloroacetic acids (tri-TCA and di-DCA) and the corresponding esters. TCA is used in agriculture. DCA is used in pharmaceuticals, and its esters serve as cellulose plasticizers.[3] PLA/PBAT samples mixed with the additives (acids and esters) were subjected to accelerated degradation tests for outdoor performance (OP) simulation.

Materials and methods: Additives were blended with Bio-Flex in a two rotors laboratorial mixer. Rectangular samples were prepared and tested into Q-LAB QUV/se, for outside performance mimicry using Cycle-C, according to ASTM-G154, during 200h.

Results and Discussion: **I**n this work, we investigate whether chloroacetic acids (DCA and TCA) can accelerate the degradation of PLA/PBAT blends. The presence of strong acids can enhance the hydrolysis of the ester bonds, accelerating the degradation of the polyesters. Apart from the fact that TCA and DCA were efficient, both have lower thermal stability than required. They could also damage metallic parts of processing machines. A new strategy was considered. Three esters were synthesized. They have the thermal stability required for hot processing. The samples of Bio-Flex® blended with esters were characterized before and after the degradation tests, basically by thermal, mechanical, and microscopic properties. SEM, thermal (DSC and TGA) and mechanical properties show that the additives do not significantly change the properties of Bio-Flex® during hot blending. After the degradation tests, SEM shows holes and cracks in the samples, a loss of Tg and a decrease in PLA crystallinity by DSC, and a decline of the mechanical properties.

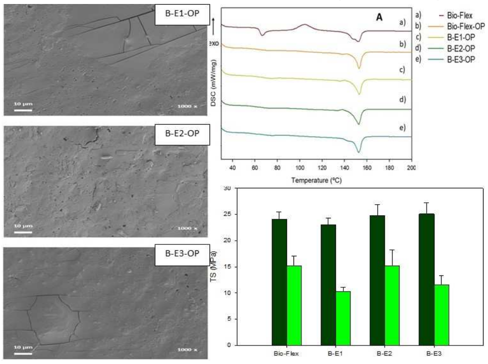

Fig.1 SEM images, DSC profiles and tensile tests after degradation test.

Conclusion: Chloroacetic acids and esters were used for the first time to improve the degradation of PLA/PBAT blends. Moreover, the thermal stability of esters was sufficient for the proposal and their mixing process did not affect the original properties of Bio-Flex. Their suitability for increasing the degradation ratio of PLA/PBAT blends was successfully demonstrated by microscopy and loss of thermal and mechanical properties as well as chromatography.

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Sustainable Modifications of Carboxymethyl Cellulose by Passerini and Ugi multicomponent reactions

L. Remy[1*], A.Charlot[1], E. Fleury[1]
[1] *Université de Lyon, INSA Lyon, IMP-UMR CNRS F-69621 Villeurbanne, France*
** laurent.remy@insa-lyon.fr*

Chemical modification of natural polymers, such as polysaccharides, has been an ever-growing interest of chemists to adjust the properties of valorizable biomass. Multicomponent reactions represent valuable tools to sustainably (multi)fonctionnalize polymers because of their good atom economy and their achievement in mild and one-pot conditions. In particular, for the Passerini three component reaction (P-3CR), an aldehyde (and less reported, a ketone), an isocyanide and a carboxylic acid simultaneously bond to form a dually functionnalized derivative. In our laboratory, we demonstrated the feasability to apply the P-3CR to carboxymethyl cellulose (CMC) [1] in homogeneous medium as well as to periodate oxidized cellulose microfibrills [2] in heterogeneous condition, which are both appealing bio-based materials extensively utilized in a variety of applicative fields (cosmetic, food, paper, composite…). These multicomponent reactions are promising strategies to sustainably yield multifunctionnal polysaccharides. The present study follows on from this work, and will describe new results dealing with the Passerini modification of CMC by using a series of ketone reagents, carried out upon various experimental conditions (type of solvent, temperature, time, amount of reactants…). The objective is to generate a novel panel of fonctionalized CMC derivatives, which can be reactive, for example, in radical polymerization [3]. Thus, we will describe the effect of these parameters on the efficiency of the Passerini reaction, and we will show some examples of reactive CMC coumpound able to lead to chemically cross-linked hydrogels with tunable properties (Figure 1). Additionnaly, we will show illustrations of Ugi modification of CMC, which combines four precursors (amine, aldehyde, carboxylic acid and isocyanide), thus allowing to concurrently bring three different functionnalities to CMC, in aqueous medium. These multicomponent reactions are very attractive means to design tailor-made multifonctionnal polysaccharides in a sustainable manner.

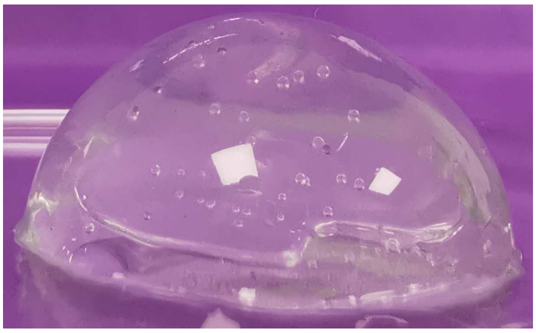

Figure 1 : Chemically cross-linked CMC hydrogels

Keywords: Multicomponent reactions, polysaccharides, sustainable, Passerini reaction, Ugi reaction

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Processing and chemical modification of polyolefin vitrimers by reactive extrusion

B. Rigatelli[1,2], D. Montarnal[2*], E. Drockenmuller[1*]

[1] *Univ Lyon, Université Lyon 1, CNRS, Ingénierie des Matériaux Polymères, UMR 5223,*
F-69003, Lyon, France
[2] *Univ Lyon, CPE Lyon, CNRS, Catalyse, Polymérisation, Procédés et Matériaux, UMR 5128,*
F-69003, Lyon, France
[*] *damien.montarnal@univ-lyon1.fr*
[*] *eric.drockenmuller@univ-lyon1.fr*

Cross-linked polyolefins are characterized by remarkable performances such as dimensional stability at high temperatures, excellent solvent and creep resistance; such materials are employed in a variety of applications in which lifespan is critical (pipes, cables). Nevertheless, due to the abovementioned stability, the recyclability of those compounds remains nowadays an unsolved issue. The necessity of moving towards a more sustainable circular economy by re-designing the chemistry of cross-linked materials appears to be one of the main challenges of the coming decades [1]. Within this context, the outstanding potentiality of covalent adaptable networks (CANs) in the field of recyclable thermoset was recognized for the first time in 2010 [2]. CANs can retain their cross-linked structure displaying high performances at service temperatures, while the activation of dynamic exchange reactions at processing temperatures allows these materials to flow, be re-shaped or be recycled. Among all the different dynamic chemistries available, only a few have been implemented in cross-linked polyolefins. The typical strategy implies the use of a polyolefin (either neat or functionalized) as a starting material and a bifunctional cross-linker carrying the exchangeable bonds [3, 4]. While reactive extrusion is the ideal processing technology to achieve proper cross-linking and envision upscalability to high throughputs, the control of the exchange dynamics and the viscosity increase is crucial [5, 6]. We will present and compare three dynamically cross-linked PEs obtained by reactive extrusion from a commercially available maleic anhydride-grafted PE and a variety of diamines comprising highly exchangeable dynamic bonds. We will address in particular the curing reactions – or eventual side-reactions – at stake in these systems by combining a mechanistic analysis on model compounds and a thorough mechanical and viscoelastic characterization of the PE networks. The (re)processability of such materials will be discussed based on capillary rheometry experiments.

Keywords: covalent adaptable network, reactive extrusion, crosslinked polyolefins

Acknowledgments

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Development of recycling treatments for polymeric waste: Solutions for a circular economy

Daniele Rigotti[1,2], Andrea Dorigato[1,2], Alessandro Pegoretti [1,2]

[1] *Department of Industrial Engineering, University of Trento, Via Sommarive 9, 38123, Trento, Italy*
[2] *National Interuniversity Consortium of Materials Science and Technology, Via Giusti 9, 50121, Firenze, Italy*
daniele.rigotti-1@unitn.it

The recycling of polymers is crucial to save the world from the increasing degradation of the environment and to reduce plastic products' production costs. Moreover, recycling is an important method for polymer waste management, which allows for the recovery of secondary raw materials in the form of granulates or chemical raw materials, which, according to the circular economy principle, can be re-incorporated in a closed material cycle [1]. Our efforts are currently focused on finding solutions for the recycling of end-of-life tires (ELTs) and polyvinyl chloride (PVC) waste.

It was estimated that the consumption of natural rubber in the year 2020 was 27 million tons of which more than 70% was used for the production of tires. About 800 million tires worldwide reach their end of life each year and much of the rubber that they are made, which represents about 50% of their weight, is lost [2]. To effectively close the cycle in a circular economy view, such material at the end of its life must be used for the production of new tires. To achieve this, devulcanization technology is one, if not the only opportunity to achieve this goal. This technology uses the different binding energy between C-C and S-S bonds to selectively break these last bonds involved in vulcanization by applying high shear stress and heat.

The optimization of a mechanical de-vulcanization process was performed using a laboratory roll milling machine, capable of simulating an industrial process. Rubber from ELT was treated varying the processing parameters, to obtain devulcanized rubber (DR) samples with different devulcanization degrees. Ethylene-Propylene Diene Monomer Rubber (EPDM)/DR blends were produced through an internal mixer and subsequently vulcanized through a hot-pressing process, by adding different vulcanizing agents. In this way, a considerable amount of virgin material could be saved and replaced by treated tire scraps. EPDM compounded with elevated amounts of DR could represent an interesting solution to reduce the costs and improve the environmental sustainability of rubber-based products. For instance, these materials could find applications as impact-absorbing devices.

PVC-coated electric cables account for 46% of the European market for electric conductors and this application represents one of the main application sectors for PVC in Europe, absorbing 7% of the production of PVC [3]. However, with increasing volumes being used, recycling is not yet carried out to such an extent as to prevent the landfill of most of the PVC produced. A significant fraction of PVC waste is generated by the recovery process of copper used in electrical cables for separation from insulating casings. Compression molding in the presence of the right adhesive could transform the granulate and the rubber powder, which have become raw materials, into a series of products that in turn are further recyclable. The main applications range from sports surfaces to playgrounds flooring, from acoustic insulation sheaths to urban furniture objects, up to synthetic bark, infill for synthetic grass sports fields, and components for rail transport.

Acknowledgments

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Potential Bio-Based Bonding Material (BBM) for improved recyclability of multi-layered materials and composites. Research within the VIBES project.

G. Romero-Sabat[1*], O. Angurell[1], S. Medel[1]

[1]*LEITAT technological Center, Terrassa, Barcelona*
[*]*gromero@leitat.org*

Plastic (polymer) waste is considered as one of the main issues to be resolved for humankind in the next 10 years. One of the main strategies followed towards that goal is the creation of an effective after-use plastic economy, having an explicit focus into improving the material's recyclability. Within plastic materials, even though thermoplastic polymers possess intrinsic recycling capabilities, the re-processability of thermosets is limited by their molecular structure, thus preventing its inclusion towards a circular economy. Moreover, the use of thermoset fibre reinforced plastics, also know as composite materials, are becoming a pillar for the development in many fields due to their unique properties such as high mechanical strenght, long durability and reduced weight compared to the traditionally used materials. Due to the impossibility of generally separating the embedded fibre and the thermoset plastic matrix, when the end-life of those materials is reached they are either mainly incinerated (42.6%) or diverted into landfills (24.9%)[1]. Together the increase in use and the current lack of a proper recycling pathway of those materials, has lead towards an immediate need for ensuring a proper re-valorisation and recycling systems for fibre reinforced composites.

Thioctic Acid (TA) is a small, feedstock obtained molecule containing a disulfide ring and a carboxilic group in its structure. By Ring Opening Polymerization (ROP) reactions, is possible to generate a fully recyclable[2] poly(Thioctic Acid) (pTA) polymer comprised of a main disulfide backbone and hydrogen-rich side groups capable of generating supramolecular interactions[3]. By coating the composite fibers with pTA enriched with metal ions to increase the polymer stability prior to the composite generation, it was possible to create a supramolecular dynamic binding interphase between the different components of the material.

The material's thermal and mechanical behaviour altogheter with it's specific debonding capabilities and recyclability were assessed alone and as part of the composite structure. Interestingly, it was found that while it's introduction did not affect the material's structural integrity, the application of some external stimulus such as heat, light or chemical baths were able to induce the adhesive's decomposition, easing the separation process.

The broad inclusion of the presented adhesive and their in-development derivatives, can be a potential innovative solution towards the achievement of an improved recyclable composite materials for a wide variety of relevant sectors.

Keywords: Fiber reinforced plastics, recyclability, bio-based, supramolecular adhesive

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Novel electrospun Poly(lactic acid)/Poly(butylene furanoate) biobased blends

Sofia Santi[1], Giulia Fredi[1], Daniele Rigotti[1], Mattia Zanini[1], Dimitrios N. Bikiaris[2], Andrea Dorigato [1]

[1]*University of Trento, Department of Industrial Engineering and INSTM Research Unit, Via Sommarive 9, 38123, Trento, Italy*
[2]*Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece*

Poly(butylene furanoate) (PBF) is the biobased counterpart of poly(butylene terephthalate) and can be synthesized by melt-condensation polymerization of 2,5-furandicarboxylic acid (FDCA) with diols containing four carbon atoms. PBF shows very good thermal stability as well as impressive strength and ductility, overcoming thus the performances of PBT. However, PBF presents high hydrophilicity and therefore an increased tendency to be attacked by microorganisms. One of the more employed strategies for mitigating these drawbacks is blending with other biobased polyesters, like polylactic acid (PLA) [1]. High molecular weight PLA is generally characterized by high mechanical strength (50-70 MPa), which is comparable to non-biodegradable conventional plastics. Despite the above positive features, PLA has some drawbacks, like poor toughness and slow degradation rate. Therefore, the aim of this work is to develop electrospun nanofiber blends constituted by PLA and PBF at different relative ratios. After a detailed analysis of the optimal electrospinning parameters, an in depth thermo-mechanical characterization of the resulting materials has been carried out. The morphological features of the obtained electrospun films were correlated with their most important physical and functional properties.

Acknowledgement

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Influence of solid product of biomass pyrolysis on the biodegradation of PHB

Dagmar Šašinková[1], Markéta Julinová[1], Alena Kalendová[2], Ahmad Fayyazbakhsh[1], Vendula Krátká[1], Marek Koutný[1]

[1]Department of Environmental Protection Engineering, Faculty of Technology, Tomas Bata University in Zlín, T. G. Masaryka Square 5555, 760 01 Zlín, Czech Republic

[2]Department of Polymer Engineering, Faculty of Technology, Tomas Bata University in Zlín, T. G. Masaryka Square 5555, 760 01 Zlín, Czech Republic

Worldwide problem with the plastic pollution of our planet lead to new challenges in science. Nowadays, it is a trend to replace the fossil-based polymers; much better solution is to use biopolymers, such as PHB (poly-3-hydroxy butyrate). It is a material which is bio-based, biodegradable and with the comparable properties with polypropylene. Therefore, using this material instead of fossil-based polymers is much better solution for the environment and future.

However, its high biodegradability brings new possibilities in controling the biodegradation with additives. In this experimental study, PHB was mixed with the solid product of biomass pyrolysis (SPB). SPB was used as delivered, but there were also some modifications, which should improve the properties of PHB. SPB and PHB were blended and then the characterization of the foils was made by XRD and FT-IR. The biodegradation test in the soil took more than 200 days. The most degrade additive was SPB modificated by maleic anhydride (92 % after 130 days) and the best result came from SPB modified by HCl. CO_2 was measured by a mass spectrometer HPR-40 DSA (HIDEN Analytical, 2020, UK). Scanning electron microscopy (Phenom Pro Desktop SEM, Thermo Fisher Scientific, Waltham, MA, USA) and fluorescence microscopy (Olympus BX53 Fluorescence Microscope) were used to observe the biodegradation of the samples.

Keyword:

Biodegradation, biomass pyrolysis, biopolymer, polymer

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Sulfur-based Dynamic Materials

V. Scholiers[1*], S. Maes[1], F. Du Prez[1]

[1]*Polymer Chemistry Research Group, Center of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Faculty of Science, Ghent University, Krijgslaan 281 S4-bis, Ghent B-9000, Belgium*
[*]*Vincent.Scholiers@UGent.be*

Sulfur and more particular sulfur-based chemistries are still today, one of the most trending subjects in polymer and material science, both in academia and industry. Especially in the area of smart dynamic materials, they provide unique opportunities. Indeed, incorporating sulfur-based dynamic covalent crosslinks in the polymer architecture will introduce improved thermomechanical properties and reprocessability. This strategy opens up prospects to tackle the current global waste problem.[1, 2]

In the last 20 years, a multitude of systems have emerged in this popular subfield of dynamic crosslinked crosslinked materials in which the dynamic bond exchange can be triggered by either heat, light, mechanical stress, redox conditions, ultrasound or alkylating agents.[3, 4] Moreover, given the scarceness of the petroleum feedstock, considerable attention has been devoted to biobased monomers (*e.g.* lipoic acid). [5, 6]

In this work, our aim is to introduce sulfur-based dynamic covalent bonds in a material, which can be employed as a next generation coating or sealing. Through incorporation of reversible bonds, these materials will have the ability to be recycled and therefore, establish a real circular economy.

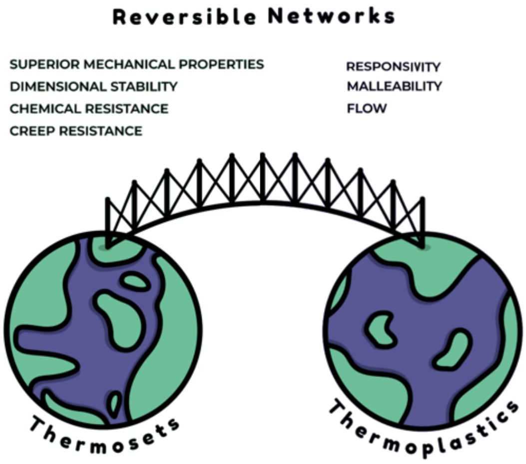

Fig 1: Reversible Polymer Networks as an intermediate bridge between thermosets and thermoplastics.

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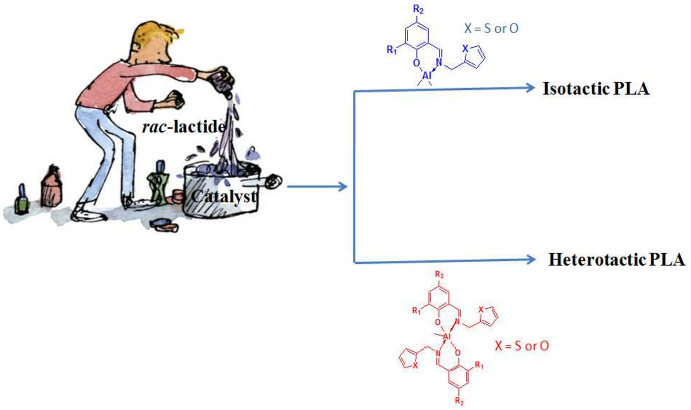
Al(III) complexes containing unsymmetrical phenoxy-imine ligands with thiophene-2-ylmethanimine and furan-2-ylmethanimine side arms: synthesis, characterization and polymerization studies

Sourav Singha Roy[1], Debashis Chakraborty[1*]

[1]Department of Chemistry, Indian Institute of Technology Madras, Chennai, India
[*]dchakraborty@iitm.ac.in

The aliphatic polyesters and polycarbonates are suitable alternatives to the synthetic petroleum-based polymers, especially for biomedical applications, as they are biodegradable and biocompatible.[1] The aliphatic polyester PLA synthesized by the ring-opening polymerization (ROP) of lactide (dilactone of lactic acid) has attracted considerable interest among the researchers since it is derived from annually biorenewable sources such as corn, starch etc. The presence of stereogenic centers in the monomer lactide results in different tacticity in the polymeric chain (isotactic, syndiotactic, heterotactic, and atactic). The stereocontrolled ROP of lactide is crucial as the properties of the polymer are governed by the tacticity of the polymeric chain. Considerable research has progressed over the years in determining appropriate catalysts that result in the control of tacticity in a unique manner, in addition to imparting living characteristics to the ROP. During the ROP, the enantiomeric site control mechanism (ESM) is prevalent when the ligand is chiral and results in the formation of isotactic PLA from racemic lactide (*rac*-LA) and syndiotactic PLA from meso lactide (*meso*-LA). However, the chain end control mechanism (CEM) during the ROP of (*rac*-LA) resulted in the formation of heterotactic PLA. Spassky and coworkers first reported the stereocontrolled ROP of *rac*-LA via ESM to give isotactic PLA using chiral Schiff-base aluminium alkoxide complexes.[2] Nomura and coworkers[3], for the first time, reported achiral aluminium catalyst that produced isotactic stereoblock PLA via CEM. Based on the understanding from our previous work, we devised a high yield synthetic protocol for the synthesis of an unsymmetrical bidentate iminophenolate ligand system with furan-2-ylmethanimine and thiophen-2-ylmethanimine side arms. This novel ligand system was utilized towards the synthesis of Al(III), compounds. The correlation of tacticity of PLA derived from *rac*-LA with the symmetry of the catalyst was explicitly realized from this study. Our continued interest in the chemistry of CO_2 sequestration prompted us to explore the utility of these compounds as catalysts towards the ring-opening copolymerization (ROCOP) of CO_2 with epoxides. Our compounds were found to be very active towards the ROCOP producing isotactic polycarbonates in high yield and turn over frequency (TOF). These compounds produced polycarbonates with high molecular weight and relatively narrow polydispersities.



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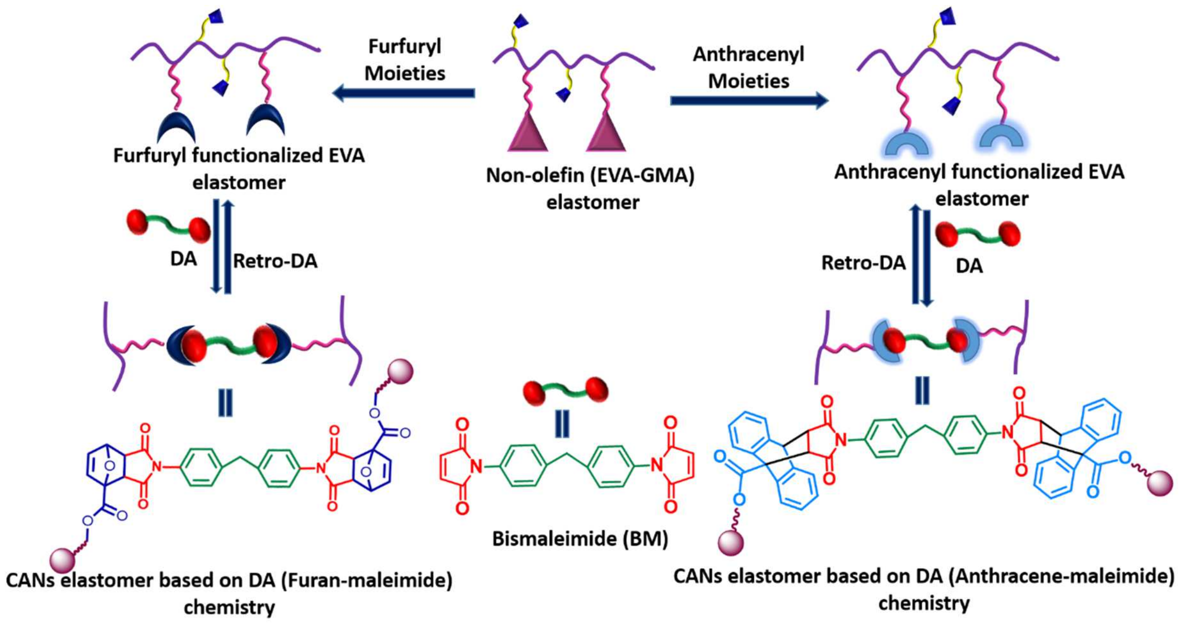
Reversible Cross-linking in Non-Olefin Elastomer based on Covalent Adaptive Networks (CANs) Using Diels-Alder “Click” Chemistry

Sagar Kumar Raut, Shrabana Sarkar, Prantik Mondal, Nikhil K. Singha*
Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India

Introducing the covalent adaptive networks (CANs) into the polymer chains has been an interesting topic for the development of advanced polymers with improved properties. In the CANs polymer, the covalent bonds undergo dissociation or exchange mechanisms to endow the self-healing, shape memory and re-moulding features under various stimuli. Additionally, polymers with CANs is cost-effective, enhance their service life, reduce wastage by recycling. In contrast to non-olefin elastomers, there are no such reports of fluorescence active elastomeric CANs with multifunctional properties by using dynamic Diels-Alder (DA) **“Click”** chemistry. Herein, a commercially available non-olefin elastomer poly (ethylene-*co*-vinyl acetate-*co*-glycidyl methacrylate) (EVA-GMA) was individually functionalized with diene moieties (anthracenyl, furfuryl, *etc*.). These appended diene elastomers were cross-linked with dienophile moiety, e.g. bismaleimide (BM) to develop the CANs within the elastomer network via DA reaction (**Scheme-1**). Unlike the furan-maleimide-derived DA-type elastomeric CANs, anthracene-maleimide-derived DA-type CANs were accomplished at longer time (≈96 h) at 70 °C. Thermal analysis revealed that both DA-type CANs elastomer were thermoreversible and recyclable at 130 °C. Also, these elastomeric CANs in non-olefinic rubbers showed an excellent self-healing and recycling efficiency of over 90 %. Noticeably, anthracene functionalized elastomer showed bright fluorescence properties under UV light and was tuned by varying the molar ratio of BM of CANs. These functionalized EVA-GMA CANs will be potential materials for specialty rubber products, adhesives, functional paints and coatings.



Scheme 1: Schematic diagram of CANs in non-olefin elastomer via DA chemistry

Keywords: Non-olefin, EVA-GMA, CANs, Diels-Alder, Self- healing, and Recycling

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Multilayers packaging recycling: the Terminus strategy

A. Romano, G. Totaro, A. Celli, N. Raddadi, C. Gioia, G. Zanaroli, L. Sisti

Dept. of Civil, Chemical, Environmental and Material Engineering, University of Bologna, Bologna, Italy
Corresponding Author's mail: laura.sisti@unibo.it

Multilayer packaging films are highly versatile and largely exploited materials in the food industry, because they extend the lifetime of goods, helping to reduce food waste. Multilayer films are a combination of two or more thermoplastics co-extruded or laminated to form one homogenous film with distinct individual layers, in this way the ultimate material provides a range of properties which cannot be obtained from monolayer films [1,2]. With the increase of the number of their everyday-life applications, the volume of these laminated products in municipal solid waste has continuously increased and their recyclability has become an environmental and socio-economical issue, since they are unrecyclable and currently 100% of multi-layer packaging is incinerated or landfilled, only for beverage cartons recyclability is demonstrated in practice and at scale [3].

The H2020 TERMINUS project addresses the challenge of unlocking the recycling and reuse of flexible multi-layer and multi-compound packaging through the design of new formulations with smart enzyme-containing adhesive or tie layer polymers. After a specific trigger, the enzyme will start degrading the polyurethane-based adhesive (PUR) or tie layer (TL), thus enabling the delamination of the different layers of packaging, which can then be recycled.

Keywords: Multilayer packaging, Recycling, Enzymatic degradation

Acknowledgments

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Development of degradable polymer networks

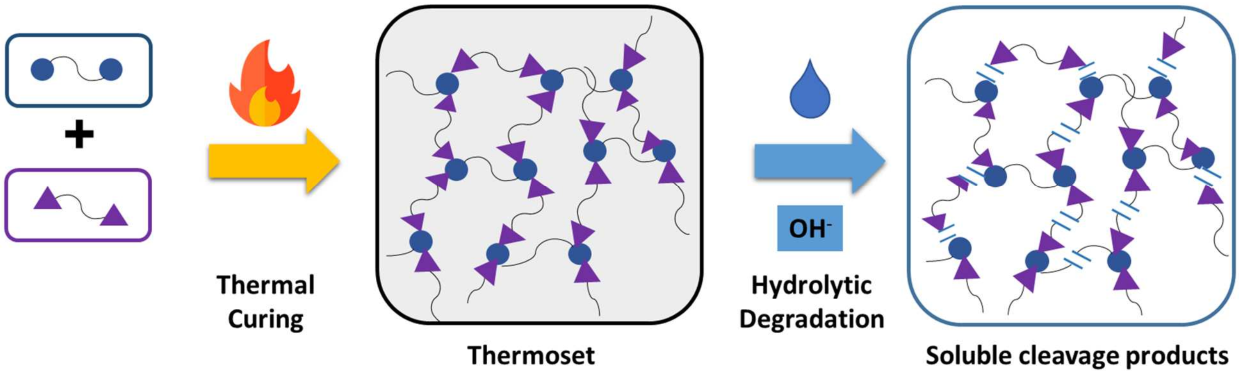
B. Sölle[1,2], E. Rossegger[1], G. Trimmel[2] & S. Schlögl[1]

[1]*Polymer Competence Center Leoben GmbH, Leoben, Austria*
[2]*Technical University of Graz, Institute for Chemistry and Technology of Materials, Graz, Austria*
**bernhard.sölle@pccl.at*

Plastic pollution is one of the greatest challenges in our world. Therefore, it is important, that newly developed polymers are not only sustainable but can be also recycled and/or easily degraded in a controlled manner. Although there has been intense research in the field of degradable thermoplastics, the efficient degradation of technically relevant thermosets is still in its infancy. Since thermosets are three dimensional, infusible networks, they cannot be remolten and reshaped. Thus, their recycling/degradation is more difficult compared to thermoplastics. To recycle highly crosslinked thermosets, numerous covalent bonds have to be cleaved and in the best way, the network is converted into its monomer units. Degradable thermosets typically rely on weak covalent bonds such as esters, acetals, hemiacetals or carbonates, which easily break under the application of an appropriate external trigger.[1]

In the current study, we introduced hydrolytically sensitive ester moieties in various highly crosslinked polymer networks. The curing reaction was monitored by IR-spectroscopy and the mechanical properties were investigated. The thermal properties were determined by DSC. The degradation process was carried out with either pure water or with NaOH solutions at different concentrations. The susceptibility of the ester groups towards hydrolytic cleavage facilitates an efficient and rapid network degradation, which was monitored by gravimetric measurements. The results revealed that the degradation time can be easily controlled by the base concentration over different time scales.

Along with improved recycling properties, degradable thermoset materials are promising candidates when it comes to the design of temporary coatings and adhesives. Temporary coatings and adhesives have a wide range of applications in industry and are employed as protective coatings in manufacturing processes, as corrosion protection for metals and in microelectronic industry.



Preparation and degradation of hydrolytically sensitive thermosets.

Acknowledgments

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Novel biopolymer-based composites as soil conditioners to promote plant growth and forest protection

Alessandro Sorze[1,2*], Andrea Dorigato[1,2], Giulia Fredi[1,2], Alessandro Pegoretti[1,2]

[1]*Department of Industrial Engineering, University of Trento, 38123 Trento, Italy*
[2] *National Interuniversity Consortium of Materials Science and Technology (INSTM), 50121 Firenze, Italy*
[*]Corresponding author: *alessandro.sorze@unitn.it*

This work is part of an European project called ONEforest, which supports the deployment of regional forest management concepts that strengthen forest resilience and sustainable wood supply levering wood-based products. Novel biopolymer-based composites, to be used as soil conditioners for forest protection and preservation, were developed and characterized. The composites were prepared taking advantage from the water absorption properties of xanthan gum[1] and water resistance of casein[2] to match the specific requirements of water regulation and mechanical stability of the soil. Milled beech wood fibres were selected as reinforcing phase. First, xanthan gum and casein were mixed with water and wood fibres at different relative concentrations, and the resulting materials showed a gel-like structure. Water absorption analyses performed in a climatic chamber showed that xanthan gum-based composites were able to absorb water efficienctly also after multiple dehydratation/rehydratation cycles. Rheological analysis showed that increasing the amount of biopolymer and wood fibres in the composite the viscosity and the shear stress could be increased up to one order of magnitude (from 100 to 1000 Pa·s and from 1 to 10 Pa, respectively). Then, the different formulations of the two composites were mixed with soil. A morphological analysis of the prepared composites was conducted by Scanning Electron Microscopy (SEM), which showed that the presence of the biopolymer contributed to agglomerate the soil particles, creating an interconected structure. Thermal analyses of the treated soils in the climatic chamber allowed to simulate the real temperature and humidity conditions to which the soil is usually subjected. These tests highlighted a strong capability of the composites to retain/release water, that is an essential requirement for sustain plants growth in case of heavy rainfalls or arid environments. Rheological and mechanical characterization of the treated soils demostrated that the biopolymers mixed with wood fibres helped to maintain the mechanical stability of the soil. A real case-study was developed to evaluate how the plant growth was affected by the introduction of these biopolymers in the soil, demonstrating the applicability of the developed composites for the support of plant growth.

Keywords: biopolymers, wood-based composites, soil conditioner, forest protection

Acknowledgments

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Sustainable Nanofiltration Membranes for Harsh Environments

Gyorgy Szekely[*]

King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia
[*]*gyorgy.szekely@kaust.edu.sa*

To address increasing environmental concerns, green and sustainable materials that promise to replace fossil-based separation materials, and reduce waste generation are attracting considerable research attention. The challenge is multifaceted and lies in finding sufficiently reactive natural monomers that are soluble in green solvents with opposing polarities. On one hand, the monomers need to be reactive to form a highly crosslinked thin film. On the other hand, one of the monomers need to be soluble in polar solvents, while the other monomer need to be soluble in a non-polar solvent, which is immiscible with the selected polar solvent.

Our group has been exploring various green sources to fabricate solvent-resistant nanofiltration membranes. Sustainable thin-film composite (TFC) membranes were designed and fabricated via interfacial polymerization of green building blocks [1,2].

Chitosan from shrimp-farming waste was derived and turned into a TFC membrane with the plant-based 2,5-furandicarboxaldehyde crosslinker. Moreover, a novel hydrophobic TFC membrane was prepared via interfacial polymerization of plant-based tannic acid and priamine monomers. The cyclohexane, benzene and aliphatic moieties of priamine are suitable to increase the hydrophobicity of the membrane surface, which in turn can result in high permeance of non-polar solvents. In addition, tannic acid is a representative polyphenol compound, which can be extracted from a diverse range of natural materials such as trees, plants, nuts and fruits.

We solubilized date seed biomass (abundantly available from the multimillion-metric-ton date industry) using ionic liquids and dimethyl sulfoxide to fabricate biodegradable nanofiltration membranes [3]. The resultant membranes were coated with mussel-inspired polydopamine via a layer-by-layer deposition method. The obtained membranes demonstrated excellent performance for solvent and oil-in-water separations.

The reaction mechanisms were demonstrated by solid-state NMR, XPS and ATR-FTIR analysis. The optimization of the membrane performance was conducted at different reaction time, and building block concentrations. We found that the separation performance of the membranes obtained from solely green sources was competitive to the fossil-based tailored and commercial membranes.

Keywords: biomass, green solvents, recycling, interfacial polymerization, phase inversion

Acknowledgments

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Investigations on Fully Biobased Epoxy Vitrimer Systems

R. Tannert[1*], J. Weber[1*]

[1]*Hochschule Zittau/Görlitz (University of Applied Science), ZIRKON, Theodor-Körner-Allee 16,*
D-02763 Zittau, GERMANY
Robin.tannert@hszg.de; j.weber@hszg.de

Thermosets have superior mechanical properties compared to thermoplastics. The cross-linked structure leads to good dimensional stability and resistance against high-temperature strain and solvents but cannot be repeared or reprocessed after damage. Vitrimers are a rather new class of polymers which combine advantageous properties of both, thermosets and thermoplastics [1]. Heat or UV-light can stimulate the cross-linked structure to undergo reversible bond rearrangements, which allow remolding of the polymeric materials [2].
The most commonly used chemistry for vitrimer preparation is the esterification of carboxylic acids or acid anhydrides and epoxy derivates in presence of a transesterification catalyst [3]. However, many of vitrimer systems studied so far are still based on a petrochemical feedstock. Additionally, decomposition products might cause environmental issues after their disposal, especially upon littering, which is a problem for single-use products. Therefore, vitrimers that are prepared from biodegradable and renewable resources are needed to fulfill sustainability requirements [4].

In this work, we present approaches toward fully biobased "green" vitrimers using building blocks from natural feedstocks only, e.g. adipic acid, eugenol or carboxymethyl cellulose. We transformed those to epoxy-functionalized derivates, which we used to prepare vitrimers via esterification.
FTIR-spectroscopy proved the successful reaction. The materials showed healing and reforming ability at high temperatures. The thermal and mechanical properties of the materials were determined and compared to each other. Furthermore, selected vitrimer systems can be combined with natural fibres, yielding reinforced materials.

Acknowledgments
Financial Support from the German Federal Ministry of Education and Research (BMBF, FKZ: 13FH2I06IA) is highly acknowledged.

Keywords: vitrimers, biopolymers

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Study of thermal degradation of olive stone residue

Th. Asimakidou, E. Tarani*, K. Chrissafis

Laboratory of Advanced Materials & Devices, Department of Physics, Aristotle University of Thessaloniki, GR541 24 Thessaloniki, Greece
**etarani@physics.auth.gr*

In the last decades, the shortage of timber due to deforestation, inadequate management, and increasing demands to produce biorefinery chemicals has attracted research interest to alternative solutions for sustainable development. As awareness of environmental issues increases and consumption habits change, consumer interest has led to the development of green solutions. Replacing wood with lignocellulosic materials which derive from various agricultural wastes is a viable solution in manufacturing products used for interior construction, as the agricultural and agro-industrial sectors are central pillars of the Greek economy. Agricultural byproducts produced by these activities are accompanied by a large amount of waste that remains practically unused. So, one of the most common difficulties that Southern European countries face is the management of wastes and by-products from olive oil production. Thermochemical treatment of these olive residual wastes can result in a wide range of valuable products. The aim of this study is to exploit hemp stem and olive branch residues as an alternative source for particleboard production binding with conventional Urea-Formaldehyde resin. The thermal properties of these particleboards were examined by Thermogravimetric Analysis (TGA) and compared with wood based (conventional) particleboard. Additionally, the thermal decomposition process of the olive stone sample was performed under an inert atmosphere at 5, 10, 15, and 20 °C/min heating rates using TGA, while the kinetic analysis was performed via model-free and model-based methods. X-Ray Diffraction Analysis (XRD) was used to study the crystal structure of the samples, while the morphological and adhesive properties were investigated by Scanning Electron Microscopy (SEM). Finally, the curing temperature of the Urea Formaldehyde resin was determined by Differential Scanning Calorimetry (DSC). The thermal behavior of the olive stone sample was found to be a typical lignocellulosic material, with the first mass loss and the following stages to be attributed to moisture removal and lignocellulosic degradation substances, respectively. In model-free methods, Ozawa-Flynn-Wall (OFW) and Vyazovkin (VYA) isoconversional methods were used for Effective Activation Energy (Ea) and Pre-exponential factor. In the model based method, the best fitting results were obtained by a three independent parallel reactions model, obeying the n-th order with Fn code and described by the f(α)=(1-α)n equation..

Keywords: olive stone, resin, Urea formaldehude, particleboards, thermal analysis, thermal degradation

Acknowledgments
This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call Special Actions AQUACULTURE-INDUSTRIAL MATERIALS-OPEN INNOVATION IN CULTURE (project code: T6YBΠ- 00161.

Synthesis of Semi-Aromatic Poly(Ether Carbonate)s from Lignin

Ghezae Tekleab[1] and Harm-Anton Klok[1]*

[1]*École Polytechnique Fédérale de Lausanne (EPFL), Institut des Matériaux and Institut des Sciences et Ingénierie Chimiques, Laboratoire des Polymères, Bâtiment MXD, Station 12, CH-1015 Lausanne, Switzerland*
**harm-anton.klok@epfl.ch*

Due to limited deposits of the petrochemical resources, sustainable and bio-based resources are urgently needed to replace them[1]. Lignin, one of the major constituents of lignocellulosic biomass, and the second most abundant biopolymer on earth[2], is still underutilized[3]. Recent studies have shown that depolymerization of lignin can result into various aromatic building blocks[4,5]. In this work, we employed lignin-derived diols to synthesize new poly(ether carbonate)s that, to our knowledge, have never been produced from any bio-based source. To avoid usage of toxic reagents and purification steps, we utilized a green carbonate source in one-pot two-step melt polymerization. Semi-crystalline polymers with high molecular weights, and possessing high thermal stability were obtained.

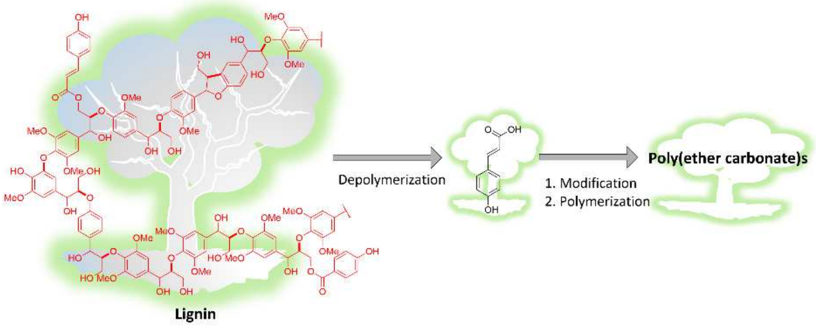

Figure 1: Synthesis of poly(ether carbonate)s from lignin's depolymerization feedstocks

Keywords: bio-based, lignin, lignin-derived, poly(ether carbonate)s, diols, synthesis.

Acknowledgements

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Advances in Polymer Synthesis

Simple strategies to harness heterometallic cooperativity in cyclic ester ring-opening polymerisation

J. A. Garden*, W. Gruszka

School of Chemistry, University of Edinburgh, Edinburgh, United Kingdom
**j.garden@ed.ac.uk*

The ring-opening polymerisation (ROP) of cyclic esters is an efficient route to prepare aliphatic polyesters including biodegradable poly(lactic acid), poly(ε-caprolactone) and poly(δ-valerolactone).[1] These processes usually require a catalyst, and some of the most efficient are homometallic metal complexes featuring one type of metal. The concept of heterometallic (mixed-metal) cooperativity has recently emerged as a method of improving catalyst performance, where two different metals can work together to give activities and selectivites that are "greater than the sum of their parts". However, the origins of these activity enhancements often remain unclear.

This lecture describes a series of heterometallic complexes supported by a ProPhenol ligand as highly active catalysts for cyclic ester ROP. The heterometallic complexes generally outperform the homometallic counterparts, combining high activities with good polymerisation control. Here, we show the direct influence of systematically replacing one Zn centre in a bis-Zn ProPhenol complex with other divalent heterometals such as Mg or Ca (Figure 1).[2] The isolated Ca/Zn complex is significantly more active than the Mg/Zn or bis-Zn analogues; this is attributed to large and Lewis acidic Ca enhancing monomer coordination as well as altering the catalyst electronics by increasing the polarity of the Zn-Et initiating group.

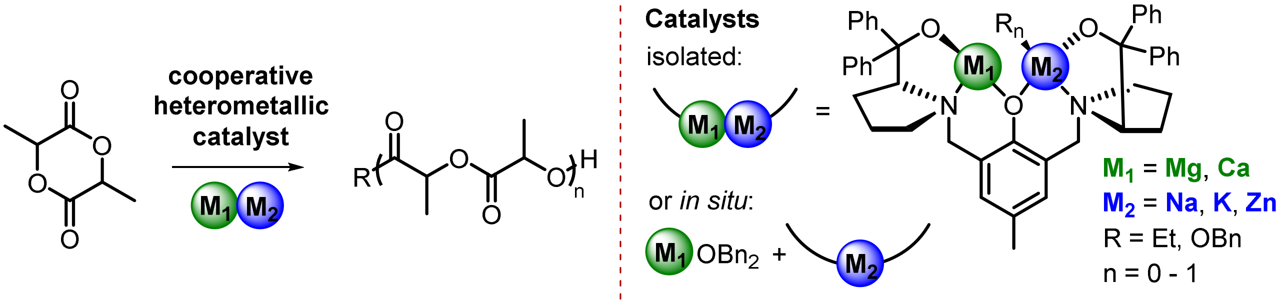

Figure 1. Isolated and *in situ* generated heterometallic ProPhenol catalysts for cyclic ester ROP.

In spite of heterometallic cooperativity delivering improved catalyst performance, heterometallic catalyst development currently lags behind homometallic analogues, which is largely due to the synthetic challenge of preparing heterometallic complexes. This lecture will describe a simple strategy using inorganic salt additives to generate heterometallic Trost ProPhenol catalysts *in situ* (Figure 1). Salt additives can boost the activity of homometallic initiators, giving similar activity enhancements to isolated heterometallic complexes.[3] Notably, these catalysts show extremely high activities, with K/Mg and K/Ca combinations converting > 85 equivalents of *rac*-lactide in just 5 seconds at room temperature. These systems exhibit the highest heterometallic catalyst activities to date in *rac*-lactide ROP.

Keywords: Ring-opening polymerisation, lactones, catalysis, heterometallic cooperativity.

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Radical polymerization of ionized monomers

Igor Lacík

Polymer Institution of the Slovak Academy of Sciences, Dubravska cesta 9, 845 41 Bratislava, Slovakia
igor.lacik@savba.sk

Radical polymerization of ionized monomers has been always associated with the question on the role of counterions present in the polymerization system. Counterions originate either from monomer or from both monomer and added salt. The early studies on polymerization of acrylic and methacrylic acid salts suggested that screening of the repulsive interactions between growing radical chain-end and charged monomer can be effectively screened by counterions, resulting in an increase in propagation rate, rate of polymerization, and molar mass [1]. While this suggestion follows the intuition and experimental observation, detailed understanding of polymerization mechanism of ionized monomers was missing.

The availability of accurate rate coefficients for all kinetic steps is the key factor for true desciption of the polymerization process. Currently, the IUPAC-recommended method pulsed-laser initiated polymerization combined with size-exclusion chromatography (PLP−SEC) is well established for obtaining the propagation rate coefficient, k_p. Consequently, termination and transfer rate coefficients can be estimated, which enable to formulate the mechanistic model and predict by modeling the polymerization kinetics and polymer molar mass [2]. This methodology has been successfully applied for a number of oil- and water-soluble monomers. However, in case of ionized monomers, PLP-SEC may experience difficulties due to low termination rate and characterization of ionized polymers by SEC.

This contribution discusses the strategy for obtainig k_p values for fully ionized monomers by PLP−SEC. The work previously done for polymerization of anionic sodium methacrylate (MAANa) [3] was extended for cationic monomers [2-(methacryloyloxyethyl)]trimethylammonium chloride (TMAEMC) and [3-(methacryloylaminopropyl)]trimethylammonium chloride (MAPTAC) [4]. We established PLP-SEC conditions for determination of k_p values in a broad range of polymerization conditions. At very low counterion content, these interactions dominate and k_p is similar for both monomers. Upon screening of these interactions at higher counterion concentration, k_p values follow the family behavior known for non-ionized monomers. Remarkably, a linear correlation between k_p values and the molar concentration of counterions is observed for high counterion concentrations.

The follow-up questions will be discussed whether this behavior seen for cationic monomers can be generally adopted for other ionized monomers, i.e., MAANa [3] or dimethylaminoethylmethacrylate used as an ionizable analogue of TMAEMC.

Acknowledgments

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Short vs long chains competition during “*grafting to*” process from melt

M. Laus

Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Universitá del Piemonte Orientale “A. Avogadro”, Viale T. Michel 11, 15121 Alessandria, Italy.

The distinguishing feature of polymer brush technology lies in the ability to create new interfaces and surfaces[1]. In addition to the remarkable structural flexibility that allows to obtain surfaces with extremely diversified nature, the use of polymeric brushes has many advantages over other surface modification approaches. The thickness of the polymeric brush and the grafting density can be finely controlled. Moreover, the polymeric brushes are quite stable due to the covalent nature of the bond between the individual polymer chains and the substrate thus allowing functional groups to be introduced. Consequently, brush technology was adopted in several micro and nano-technological applications such as optoelectronics, organic electronics, photolithography, lubricants but also for biopolymer surface modification and engineering of live cell surfaces.

In the “*grafting to”* approach, the brush thickness, and so does the grafting density, is quite low as the “*grafting to”* process involves the (difficult) diffusion of the polymer chains to the substrate surface through the brush that is forming. As a result, diffusion is increasingly hampered and at a certain critical grafting density, the diffusion becomes extremely slow. The growth of the polymeric brush almost entirely ceases when thickness equals to approximately twice of the radius of gyration of the polymer, thus imparting the “*grafting to*” reaction a self-limiting nature.

From a technological point of view, this feature reveals extremely useful to prepare uniform over large scale brush surfaces with high thickness control and reproducibility. The combination of the self-limiting nature and the possibility to prepare and characterize the polymers to be grafted before using them implies that the *“grafting to”* reaction allows to obtain polymeric brushes with a higher level of precision and control. Accordingly, understanding the actual *“grafting to”* mechanism is important for several cutting-edge applications such as deterministic doping of semiconductors using polymers terminated with dopant containing moieties[2].

In this context, it was recently reported the occurrence of mechanochemical effects[3] and preferential grafting of low molecular weight species[4] even using polymers characterized by a narrow molecular weight distribution. As the mechanism guiding the preferential grafting is far from being fully understood, the present contribution focuses on the partition by molecular weight during the *“grafting to”* process. The time evolution of the grafting density reveals fine details of the “*grafting to”* mechanism at the polymer-substrate interface.

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The bright future of 3D printing: Cationic photopolymerization in Hot Lithography

Yazgan Mete,[1] Daniel Bomze,[1] Nicolas Klikovits,[1] Danijela Kojic,[1] Stephan Schandl,[1] Raffael Wolff,[1] Thomas Koch,[2] Jürgen Stampfl,[2] Robert Liska[1]

[1]Institute of Applied Synthetic Chemistry, TU Wien, Austria
[2]Institute of Materials Science and Technology, TU Wien, Austria
[*]*robert.liska@tuwien.ac.at*

UV curing of photopolymerizable formulations has been used for more than a half century for protective and decorative coatings of paper, wood, metals or plastics. Advantages can for sure been found in the high curing speed that allows the conversion of typically (meth)acrylate-based monomers within the fraction of a second. Furthermore, a large variety of monomers is commercially available so that the mechanical properties and other polymer characteristics can be easily tuned.

In the last decade, there has been a strong demand for the curing of thicker layers or even to print arbitrarily shaped 3D cellular structures out of these materials. For the latter one, additive manufacturing technology (AMT), also called 3D printing or Rapid Prototyping, is the method of choice [1]. Different setups are commercially available that allow the printing of photopolymerizable formulations from a simple CAD model. Laser or DLP (Digital light processing) based systems fabricate polymer parts with a feature resolution of about 10 µm. One of the major issues is that only tightly cross-linked networks are formed [2]. These materials suffer also from an inhomogeneous polymer architecture and therefore brittle behavior. To circumvent those problems, the Hot Lithography process has been developed by Cubicure that allows processing of high molecular weight resins, leading to much tougher materials.

In contrast to radical polymerization, the kinetics of the cationic type mechanism is strongly temperature dependent. Therefore, the Hot Lithography process opens the window for entirely new classes of monomers in the field of photopolymerization. Up to now, there were no processes available for cationic photopolymerization that are used at up to 120°C. With this process, we were able to show that polyoxazolines [3], polyesters [4], polyetheresters, polycarbonates or phenolic resins [5] can be directly printed with this technique.

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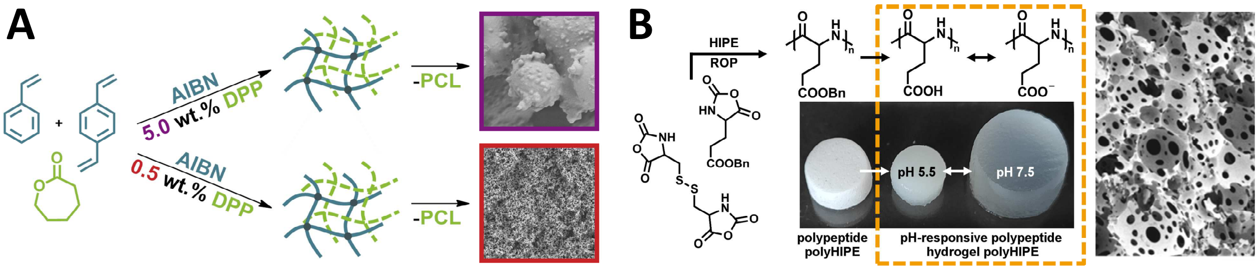
Preparation of Porous Polymers by Ring-Opening Polymerization

D. Pahovnik*, P. Utroša, O. C. Onder, S. Kovačič, E. Žagar

Department of Polymer Chemistry and Technology, National Institute of Chemistry, Ljubljana, Slovenia
**david.pahovnik@ki.si*

Porous polymers are useful materials for a wide range of applications. Porous materials used for separation and catalytic purposes need to be non-degradable, while materials for biomedical applications often require degradable materials that can be prepared by ring-opening polymerization (ROP) of heterocyclic monomers, such as lactones for polyesters and *N*-carboxyanhydrides (NCA) of α-amino acids for polypeptides. Various methods employing ROP to prepare different types of porous materials will be presented. For example, semi-interpenetrating networks (semi-IPN) have been prepared by in situ simultaneous orthogonal polymerizations, where poly(ε-caprolactone) (PCL) was synthesized by ROP of ε-caprolactone (CL), while polystyrene (PS) network was formed by free-radical polymerization of styrene and DVB [1]. Taking advantage of the hydrolytic degradability of PCL domains, the non-degradable porous PS monoliths were prepared by selective removal of PCL domains from IPNs. By varying the relative polymerization rate, the time order of gelation versus phase separation can be modulated, which fundamentally affects the final morphology of the obtained PS porous networks.

On the other hand, fully degradable porous polyesters or polypeptides were synthesized by ROP of suitable monomers directly in the continuous phase of the anhydrous high internal phase emulsions (HIPEs), which served as a soft template. In this way, polyHIPEs based on cross-linked PCL were prepared by organocatalytic ROP of CL and are distinguished by shape memory behavior with excellent shape fixity and shape recovery [2]. ROP in HIPE was further extended to various types of NCA monomers to prepare synthetic polypeptide polyHIPEs [3]. The polymerization rate was found to be an extremely important parameter for the successful preparation of polypeptides with typical polyHIPE morphology because it determines the rate of carbon dioxide release from HIPE during polymerization. By deprotection of the corresponding polypeptide organogels, the stimuli-responsive polypeptide hydrogels with fully preserved polyHIPE morphology were prepared [4]. The hydrogels exhibit pH-dependent behavior, which can be modulated together with their mechanical properties by changing the chemical composition of the polypeptides.



ROP was utilized to prepare various porous polymers ranging from (A) PS monoliths via semi-IPNs to (B) fully degradable stimuli-responsive polypeptide polyHIPE scafolds.

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Supramolecular polymeric systems featuring memory function(s)

Belal Khaled[1], De Smet Lieselot[2], Vebr Aurelien[3], Lyskawa Joel[3], Stoffelbach François[1], Hoogenboom Richard[2], Woisel Patrice[3]*

[1]Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, UMR 8232, Paris, France.
[2] Supramolecular Chemistry Group, Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium.
[3]Univ. Lille, CNRS, INRAE, Ecole Centrale, UMR 8207 - UMET - Unité Matériaux Et Transformations, Lille, France.
**patrice.woisel@centralelille.fr*

Memory refers to any information processing system that can encode, store, retain, and restitute information.[1] Over the past decade, the demand for polymeric materials that have the ability to store their physical and/or physicochemistry state at a given time and provide access to this information at a later time has increased enormously.[2] In essence, such polymeric systems require hysteresis in a certain property when subjected to stimuli-dependent perturbations, thereby allowing to store information in a metastable state. Temperature is undoubtedly the most fundamental thermodynamic parameter that is not only important in our everyday life.[3] Herein, we propose a supramolecular approach that enables polymeric systems to remember the heat treatment at which they were exposed. To the end, different supramolecular and thermoresponsive polymeric memory devices were designed based on poly(N-isopropylacrylamide) (PNIPAm) functionalized with electron rich dialkoxynaphthalene guest units. These polymeric systems can be complexed through host-guest interactions with the tetracationic cyclobis(paraquat-p-phenylene) ($CBPQT^{4+,}4Cl^{-}$) host leading to an important increase of their hydrophilicity and the appearance a characteristic purple color. Linear Naphthalene functionalized side chain PNIPAms behave like thermometers exhibiting a memory function for the thermal history of the solution, which arises from the large hysteresis of the thermoresponsive LCST phase transition.[4-5] This hysteresis is based on the formation of a metastable soluble state that consists of the PNIPAM–$CBPQT^{4+}$ host–guest complex. When heated above the transition temperature, the polymer collapses, and the host–guest interactions are disrupted, leading to the disappearace of the color and making the polymer more hydrophobic,and less soluble in water. Interestingly, these thermometers were also found to be (re)programmable. For polymeric networks,[6-7] we found that they were enable to remember both the temperature and the duration of the heat treatment at which they were exposed. In such materials, the temperature can be easily monitored through heating induced decomplexation of host-guest complexes while the time is monitored through diffusion-controlled release of the free host into the surrounding medium.

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Lactide-Lactone Chain Shuttling Copolymerization Mediated by Aluminum-based complexes : access to new multiblock copolymers

J. Meimoun,[1] C. Sutapin, G. Stoclet,[2] A. Favrelle-Huret,[1] P. Roussel,[1] M. Bria,[2] S. Chirachanchai,[3] F. Bonnet,[2]* P. Zinck [1]*

[1]*Unité de Catalyse et Chimie du Solide (UCCS), UMR 8181, Univ. Lille, CNRS, Centrale Lille, Univ. Artois, F-59650, Villeneuve d'Ascq, France*
[2]*Unité Matériaux et Transformations (UMET), UMR 8207, Univ. Lille, CNRS, INRAE, Centrale Lille F-59650, Villeneuve d'Ascq, France*
[3]*Bioresources Advanced Materials Research Unit (B2A) The Petroleum and Petrochemical College, Chulalongkorn University Pathumwan, Bangkok, 10330, Thailand*
[4]*Plateforme RMN, Univ. Lille, CNRS, Centrale Lille, Univ. Artois, F-59650, Villeneuve d'Ascq, France author's*

Chain shuttling copolymerization (CSP) is a powerful tool allowing the access to multiblock / segmented copolymers with original microstructures in a one-pot one-step route.[1] In this process initially developed for ethylene / 1-alkene systems, the growing macromolecular chain is allowed to "shuttle" by transmetallation via an organometallic chain transfer agent (CTA) between two catalysts presenting a difference in comonomers reactivity ratios, and thus leading to statistical copolymeric blocks of different composition (figure 1). Since this seminal work, the synthesis of original multiblock microstructures by chain shuttling copolymerization was extended to only one other comonomers combination, i.e styrene / conjugated diene, by rare earth based catalysts.[2] This is probably to be ascribed to the complexity of the catalytic system required and the high level of constraints as soon as two different monomers are involved.

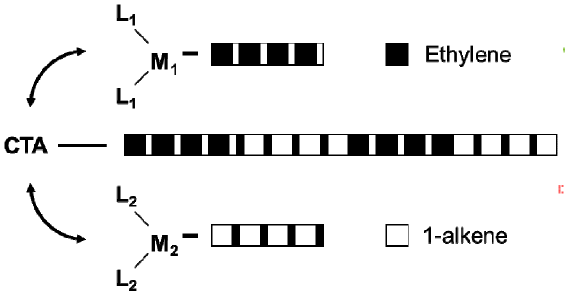

Figure. 1 Ethylene α-olefin chain shuttling copolymerization[1]

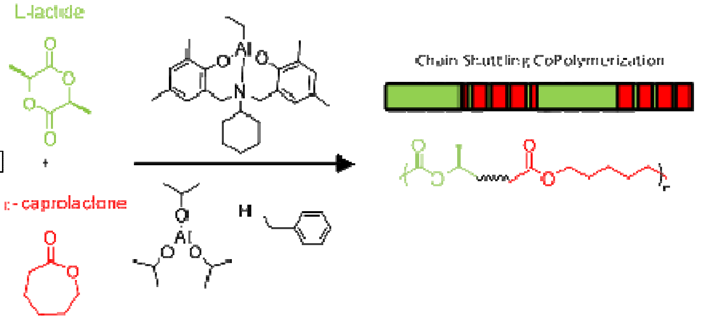

Figure 2. Lactide-lactone chain shuttling copolymerization - this work [3]

We present herein the extension of the concept to the ring opening polymerization of cyclic esters, affording the access to new polylactide based multiblock copolymers.[3] The chain shuttling ring-opening copolymerization of L-lactide and ε-caprolactone is achieved using two aluminum catalysts presenting different selectivities and benzyl alcohol as the chain transfer agent (figure 2). An aminobisphenolate-supported aluminum complex affords the formation of lactone rich poly(L-lactide-co-ε-caprolactone) statistical copolymeric blocks, while Al(OiPr)3 produces semi-crystalline poly(L-lactide) rich blocks. The shuttling between the two catalysts occurs via transalkoxylation, in a similar way to the so-called immortal polymerizations.[4] The structure and properties of the resulting multiblock copolymers are further presented.

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Tailoring Molar Mass Distributions by ATRP and RAFT

Athina Anastasaki[1]

[1] *Laboratory of Polymeric Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland.*

Dispersity is a key parameter in material design, with both low and high dispersity (*Đ*) polymers displaying unique properties and functions. However, most papers in controlled radical polymerization optimize conditions to obtain low *Đ* polymers, following a common misconception that high Đ materials are less desirable and are often accompanied with lower end-group fidelity.[1] In this talk, ATRP and RAFT strategies to regulate polymer dispersity in a wide range of polymers and without affecting their livingness will be presented and discussed. In particular, in ATRP dispersity can be efficiently controlled by simply regulating the deactivator concentration, thus allowing for a range of monomodal molar mass distributions to be obtained (*Đ*=1.05–1.75).[2] Notably, in all cases, high end-group fidelity was confirmed by MALDI-ToF-MS and exemplified by efficient block copolymer formation. Instead, in RAFT polymerization controlling polymer dispersity is more challenging and not possible by simply adjusting the ratio of the typically employed polymerization components. To overcome this, we developed a straightforward and versatile batch method in which control over dispersity is achieved by mixing two RAFT agents with sufficiently different chain-transfer activities in various ratios, affording polymers with monomodal molecular weight distributions over a broad dispersity range.[3] High livingness was demonstrated through the preparation of well-defined block copolymers consisting of a wide range of monomer families and regardless of the initial homopolymer dispersity.

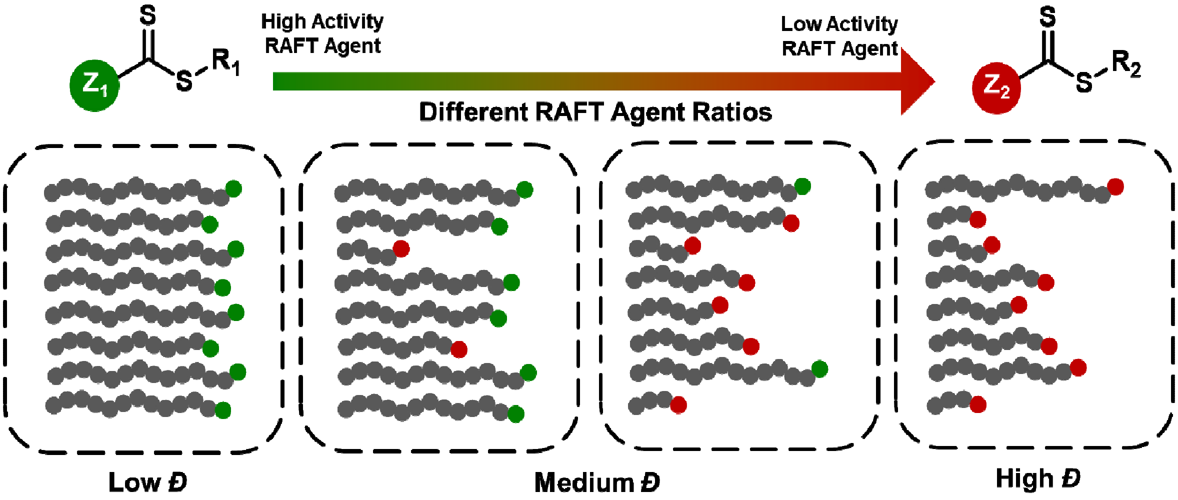

Figure 1: Schematic representation of our proposed approach discussed in reference [3].

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Stereoregular Functional Precision Polymers Prepared From Tailored Chiral Group 6 Metal Alkylidene *N*-Heterocyclic Carbene Catalysts

M. R. Buchmeiser[1*]

[1]*Chair of Macromolecular Compounds and Fiber Chemistry, Institute of Polymer Chemistry, University of Stuttgart, Pfaffenwaldring 55, D-70659 Stuttgart, Germany*
[*]*michael.buchmeiser@ipoc.uni-stuttgart.de*

The synthesis of precise polymer architectures that result from the regio- and stereoselective polymerization of monomers is a prerequisite for the synthesis of precision polymers. In order to be of significant use, e.g. for data storage, peptide mimicking or artificial DNA, the use of functional monomers is a must. This in turn requires polymerization systems and initiators, which allow for the precise polymerization of such monomers and which tolerate functional groups. Here, we report on the regio- and stereospecific ring opening metathesis polymerization (ROMP) of functional, strained olefins by novel, well-defined olefin metathesis catalysts predominantly based on molybdenum/tungsten imido and tungsten oxo alkylidene *N*-heterocyclic carbene (NHC) complexes. Via this approach, functional, (selectively hydrogenated) all-*cis* or all-*trans* isotactic or syndiotactic (st) polymers and copolymers are accessible. Both the prerequisites for and the influence of catalyst structure on either *E*- or *Z*-selectivity of polymerization, syndio- or isotacticity and functional group tolerance will be outlined. Also, selected examples of application will be presented.

Keywords: precision polymers, tacticity, ring-opening metathesis polymerization

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Light-activated antimicrobial surfaces using polymers with controlled structure

M. R. E. Santos[1], P. V. Mendonça[1], R. Branco[2], R. Sousa[3], C. Dias[2], A. C. Serra[1], J. R. Fernandes[4], F. D. Magalhães[3], P. V. Morais[2], and J. F. J. Coelho[1]*

[1]*Department of Chemical Engineering, University of Coimbra, Coimbra, Portugal*
[2] *Department of Life Sciences, University of Coimbra, Coimbra, Portugal*
[3] *Department of Chemical Engineering, University of Porto, Porto, Portugal*
[4] *Physics Department, University of Trás-dos-Montes e Alto Douro, 5000-801 Vila Real, Portugal*
**jcoelho@eq.uc.pt*

Hospital surfaces have been shown to be one of the major vehicles of nosocomial infections caused by drug-resistant pathogens [1]. Smart surface coatings that exhibit multiple mechanisms of antimicrobial action have emerged as an advanced approach to safely prevent these types of infections. This presentation will cover the preparation of innovative antimicrobial surfaces using cationic polymers with controlled structure [2] synthesized via reversible deactivation radical polymerization methods and natural photosensitizers. These additives were incorporated in industrial varnishes that exhibited very high antibacterial activity. These formulations displayed photokilling effect even when irradiated with white light (42 mW/cm2) within only 15 minutes [3]. The use of aqueous industrial varnish allows the formation of homogeneous films that can potentially be applied to various surface substrates to reduce bacterial infections in healthcare settings.

Keywords: Antimicrobial; Polymers; ATRP; light-activated

Acknowledgments
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Substituent effects on the photoinitiation ability of coumarin-based oxime-ester photoinitiators for free radical photopolymerization

N. Giacoletto[1*], F. Hammoud[2,3,4], G. Noirbent[1], M. Nechab[1], D. Gigmes[1], F. Dumur[1], J. Lalevée[2,3]

[1] *Aix Marseille Univ, CNRS, ICR UMR 7273, F-13397 Marseille, France*
[2] *Université de Haute-Alsace, CNRS, IS2M UMR7361, F-68100 Mulhouse, France*
[3] *Université de Strasbourg, France.*
[4] *EDST, Université Libanaise, Campus Hariri, Hadath, Beyrouth, Liban*
[*] nicolas.giacoletto@etu.univ-amu.fr

Light-induced polymerization is a green chemistry technology, exhibiting numerous advantages such as low energy consumption, low or no volatile organic emission, high efficiency, and a spatiotemporal control of the polymerization process. Since most of the benchmark photoinitiation systems require high-intensity UV light sources, the search for new visible light photoinitiators is a significant challenge and this topic has received an increasing attention in recent years. In this field, oxime-esters (OXEs) have long been known as efficient Type I photoinitiators due to their high reactivities in photopolymerization reactions. Generally, their high efficiency is attributed to the direct photocleavage of the N–O bond, producing iminyl and acyloxy (R'C(=O)O●) radicals, which in turn can undergo further decarboxylation reactions.

Recently, a series of coumarin-based oxime-esters was designed and synthesized as visible light photoinitiators (PIs). Interestingly, coumarin-based OXEs could exhibit a dual initiating ability since heat or light could be indifferently used to initiate the decomposition of oxime-esters and efficiently induce free radical polymerizations (FRP). Markedly, coumarins could also act as Type II photoinitiators when combined with an iodonium salt.[1] Chemical mechanism supporting the high polymerization efficiency was fully investigated. In order to evidence the interest of these new structures, direct laser write experiments were carried out (See Figure 1).

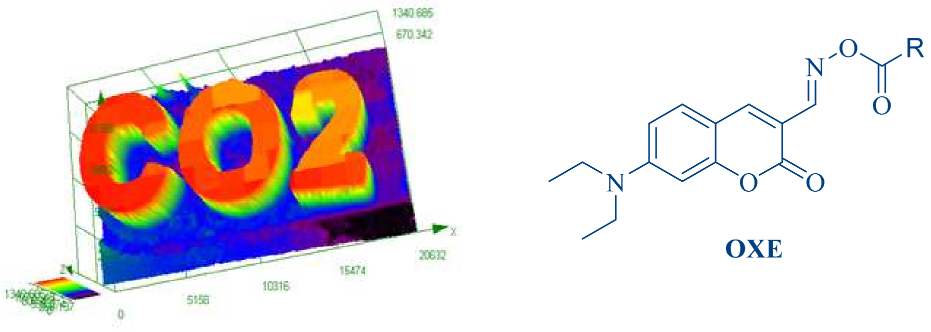

Figure 1: Example of 3D-patterns obtained by direct laser write and chemical structures of investigated OXEs.

Keywords: photoinitiators, coumarin, photopolymerization, oxime-esters.

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Exploring Aromatic *S*-Thioformates as Photoinitiators

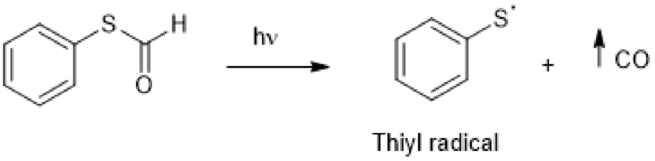
Paul Rieger, Thomas Griesser, Gema Guedes de la Cruz[*]

Montanuniveristät Leoben, Institute of Chemistry of Polymeric Materials, Leoben, Austria
[*]*gema-del-carmen.guedes-de-la-cruz@unileoben.ac.at*

The photochemistry of aromatic *O*- and *N*-acyl derivatives has been intensively studied in polymeric materials over the last two decades.[1,2] The conversion of arylesters to *ortho*- and *para*-hydroxyketones by the photo-Fries rearrangement was first observed by Anderson and Reese in 1960. [3] Interestingly, there are only few reports that deal with the photoreactivity of aromatic *S*-acyl derivatives.[4]

In this work, the photochemistry of *S*-thioformates (see figure 1, left) has been studied with the aim to utilize photogenerated thiyl radicals for the curing of acrylates as well as thiol-acrylate systems. Following this idea, phenyl thioformate was added in a concentration of 1 mM to hexylacrylate as model monomer. For comparison, the initial behaviour of thiophenol as well as diphenyldisulfide was additionally studied in hexylacrylate. Both of those reference molecules are known to form thiyl radicals either by S-H and S-S fission upon UV irradiation and have already been used for the initiation of acrylate polymerization. [5] The S-C, S-S and S-H photocleavage reactions were initiated using multichromatic UV-light. While phenyl thioformate and diphenyldisulfide show a rather similar initiation performance and lead to an acrylate conversion of 98 and 95%, only 89% were reached with thiophenol.

With the aim to initiate photopolymerization under visible light, the bifunctional photoinitiator *S,S´*-(thio*bis*(4,1-phenylene))dimethanethioate was synthesized and evaluated in an acrylate based resin that has been processed by DLP-based stereolithography using visible light of 405 nm. In these experiments, the investigated formulation could be printed successfully in high resolution (as shown in Figure 1, right) highlighting the great potential of *S*-thioformates as visible light photoinitiators.



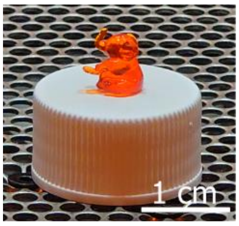


Figure 1. Left: Photoreaction of phenyl thioformate. Right': 3D printed test patterns.

Keywords: Photoinitiators, *S*-Thioformates, Photopolymerization

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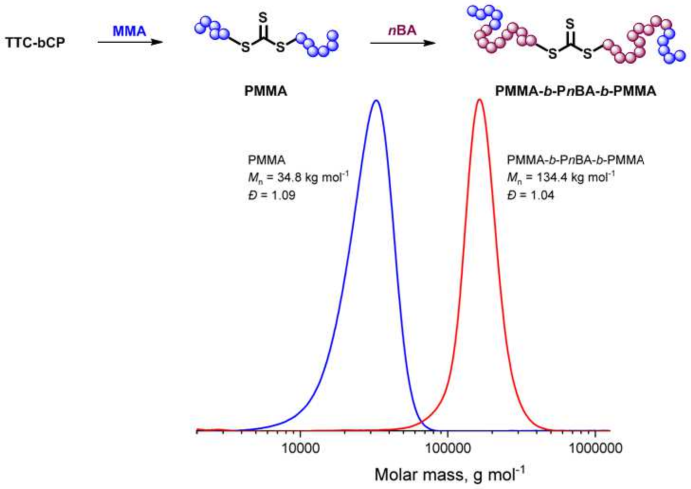
New symmetrical trithiocarbonate: from unprecedented RAFT control to thermoplastic elastomer properties

Maksym Odnoroh[1], Oleksandr Ivanchenko[1], Sonia Mallet-Ladeira[2], Stéphane Mazières[1], Marc Guerre[1*], Mathias Destarac[1]*

[1] *Laboratoire des IMRCP, CNRS UMR 5623, Université Toulouse 3 Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France*
[2] *Institut de Chimie de Toulouse, UAR 2599, Université Toulouse 3 Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France*
**marc.guerre@cnrs.fr, mathias.destarac@univ-tlse3.fr*

We report a new symmetrical trithiocarbonate (TTC-bCP) [1] with the best leaving group ever reported for reversible addition-fragmentation chain transfer (RAFT) polymerization.[2] This trithiocarbonate RAFT agent is particularly suited for the synthesis of narrowly dispersed poly(meth)acrylates of controlled molar mass. As an example, it allowed the preparation of a high molar mass (Mn ~135 kg mol-1) methyl methacrylate-n-butyl acrylate-methyl methacrylate triblock copolymer with unprecedented control (Đ = 1.04) in reversible-deactivation radical polymerization. Furthermore, these well-defined triblock copolymers with thermodynamically immiscible soft and hard outer blocks exhibit thermoplastic elastomer (TPE) properties. Molar masses of the respective hard and soft blocks can be easily varied thanks to RAFT polymerization enabling the synthesis of TPEs with tailored properties.



Keywords: RAFT, triblock copolymers, thermoplastic elastomers

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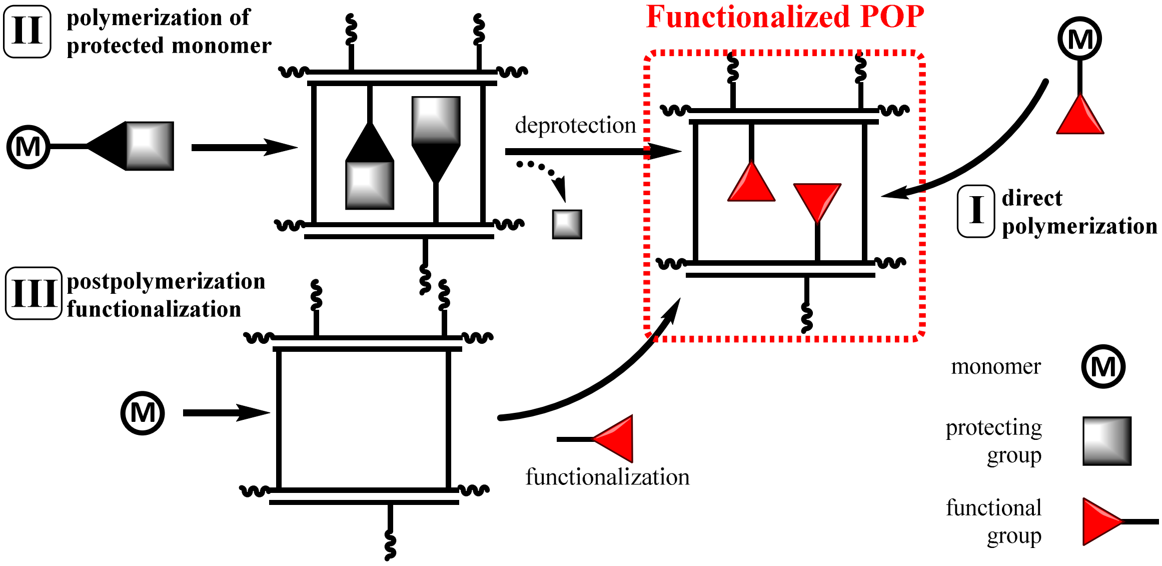
Highly functionalized porous organic polymers of polyacetylene type and their sorption and catalytic applications

L. Havelková[1*], B. Bashta[1], E. Vyskočilová[2], J. Sedláček[1]

[1]*Faculty of Science, Charles University, Prague, Czech Republic*
[2] *University of Chemistry and Technology, Prague, Czech Republic*
[*]*lucie.havelkova@natur.cuni.cz*

The hyper-cross-linked polyacetylene networks with tuneable covalent composition and texture in which the conjugated polyene main chains are cross-linked with arylene linkers will be reported as a new type of Porous Organic Polymers (POPs), with permanent porosity and high specific surface area which are highly promising for gas and solutes sorption, separation and storage and heterogeneous catalysis. To achieve extensive functionalization of polyacetylene-type POPs with heteroatom-containing groups (which is crucial from the application point of view) several synthetic paths were developed, namely: i) the direct homo/copolymerization of monomers with unprotected functional groups [1]; ii) the direct homo/copolymerization of monomers with protected functional groups followed by hydrolytic deprotection of the networks [2] and iii) the postpolymerization covalent functionalization of the surface of hydrocarbon networks with proper agents [3].



Keywords: hyper-cross-linked, polyacetylenes, porous polymers, heterogeneous catalysis, gas sorption, chemisorption

Acknowledgments
Financial support from the Czech Science Foundation (Project 21-02183S) and "Grant Schemes at CU" (reg. no. CZ.02.2.69/0.0/0.0/19_073/0016935) (START/SCI/081) is kindly acknowledged.

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Stimuli-responsive polymer contrast agents for ^{19}F magnetic resonance imaging: Quo vadis?

M. Hrubý[1*]

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, Prague 6, 162 06, Czech Republic*
[1*]*Corresponding Author, E-mail address: hruby@imc.cas.cz, mhruby@centrum.cz*

The dawn of fluorinated contrast agents in magnetic resonance imaging (MRI) greatly improved image quality due to the high sensitivity of ^{19}F MRI negligible amount of endogenous fluorine atoms in the body. We have recently developed a conceptually new stimuli-responsive fluorine-containing polymer platform tailored for the use as contrast agents in ^{19}F MRI. The applicability was demonstarted both in vitro and in vivo on animal models. The doubly pH- and thermo- responsive *N*-(2,2-difluoroethyl)acrylamide (DFEA)-based polymers were used to prepare ^{19}F MRI – visible injectable depots with tuneable dissolution rate [1].The block copolymers hydrophilic biocompabible block – thermoresponsive polyDFEA form core-corona nanogel particles from molecular aqueous solution upon heating from room to body temperature. These nanoparticles are clearly visible in ^{19}F MRI. Should a ferrocene moieties be introduced into such copolymers, these copolymers exhibit responsivity to reactive oxygen species – ROS (**Figure 1**) [2]. Hydrophobic ferrocene is oxidized in the presence of ROS to cationic hydrophilic ferrocinium leading to ROS-triggered nanoparticle disassembly and drug release from such theranostic system. With slight change in fluorinated moiety structure, the oxidation is also visible on ^{19}F MRI making the whole system also ROS-sensing. [3].

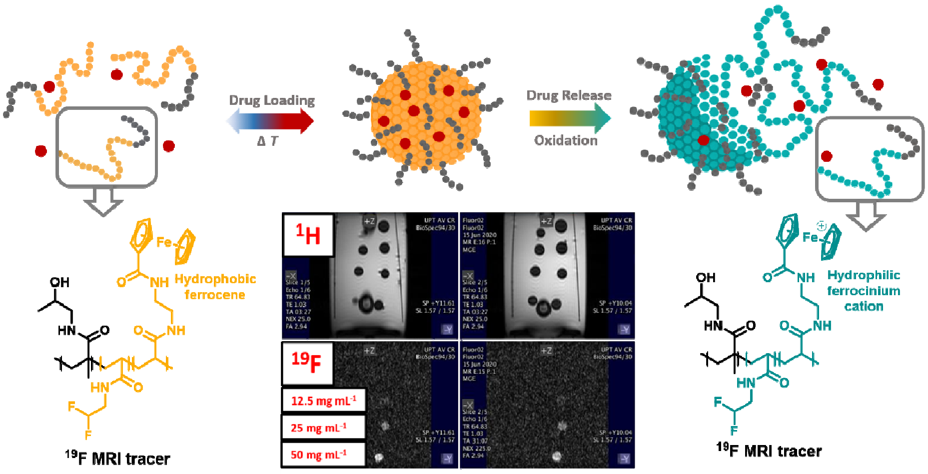

Figure 1. The doubly ROS- and thermoresponsive polymer contrast agent [2].

Acknowledgments: *This work was supported by the Ministry of Education, Youth, and Sports of the Czech Republic (grants #LTC19032 and #LM2018133).*

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Epoxy resin, based on phenolic resin with high content of dimethylene ether bridges

M. Huskić[1*], L. Slemenik Perše[2], E. Jasiukaitytė-Grojzdek[3] T. Kovše[1], I. Pulko[1]

[1]*Faculty of Polymer Technology, Slovenj Gradec, Slovenia*
[2]*Laboratory for Experimental Mechanics, Faculty of Mechanical Engineering, University of Ljubljana, Ljubljana, Slovenia*
[3] *Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Ljubljana, Slovenia*
miroslav.huskic@ftpo.eu

Epoxy resins based on novolac phenol-formaldehyde resins are used in adhesives, structural and electrical laminates, coatings, and casting applications. They offer excellent thermal stability along with high heat and chemical resistance. However, they tend to be much more viscous than the resins based on bisphenol A or other types. Phenolic resins synthesized using mineral montmorillonite (MMT) as a catalyst are liquid at room temperature, due at least in part to the high content of dimethylene ether bridges in their structure. [1] Therefore, they were used for the synthesis of low viscosity epoxy resins.

The phenolic resins were synthesized in the molar ratio phenol:formaldehyde = 1:0.95; 1:0.9; and 1:0.8 using 15% MMT as catalyst. They were all red-coloured viscous liquids. Then they reacted with epichlorohydrin to form epoxy resins. Besides, an epoxy resin was prepared from commercial low molecular weight resin. The chemical structure of all resins was determined by NMR and thermal properties by DSC and TGA. The viscosity of resins, measured at 25 °C, was 1.6-6.1 Pas, which is much lower than the viscosity of most commercial novolac resins.

The resins were cured by commercial hardener Aradur 917 (methyl tetrahydrophthalic anhydride) and accelerator 960-1 (Huntsman) at 120 °C for 1.5 h. The curing process was studied by DSC. The thermal and mechanical properties of the cured epoxy resin were determined by DSC, TGA and DMA.

Keywords: Epoxy resin, phenolic resin, NMR, TGA, DMA, DSC

Acknowledgments

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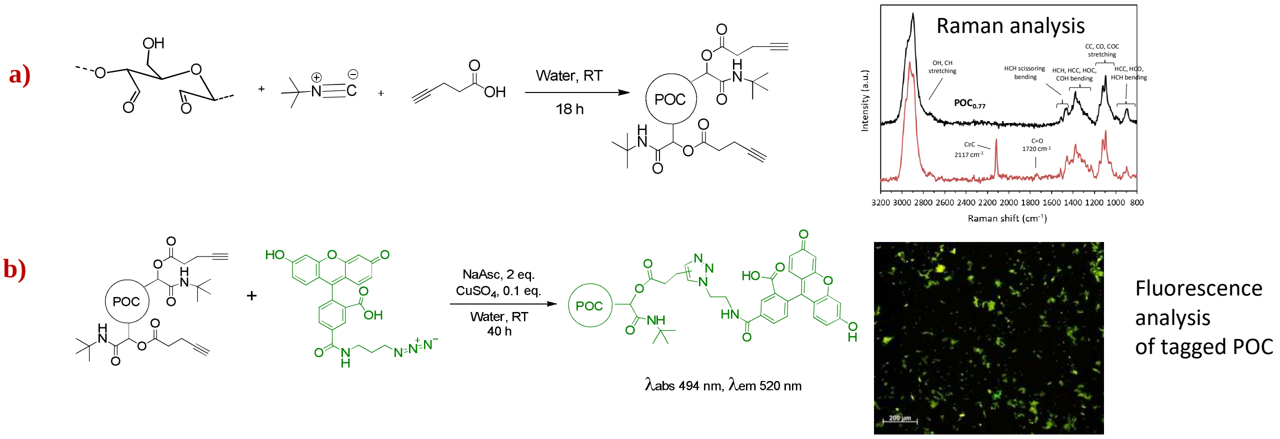
Functionalization of cellulose derivatives by green Passerini three-component reaction

A.Charlot[1*], A. Pettignano,[1] C. Moreau,[2] B. Cathala,[2] J. Leguy[3], L. Heux[3], B. Jean[3], E. Fleury[1]

[1]Université de Lyon, INSA Lyon, IMP-UMR CNRS F-69621 Villeurbanne, France
[2]UR 1268 Biopolymères, Interactions et Assemblages, INRA, F-44316, Nantes, France
[3]Université Grenoble Alpes, CERMAV, F-38000, Grenoble, France
** aurelia.charlot@insa-lyon.fr*

In the context of sustainable development, the use of eco-friendly chemical routes to modify polysaccharides is a powerful tool for biomass valorization. In this frame, the Passerini three-component reaction (P-3CR) is particularly relevant, since this multicomponent reaction allows for coupling 3 reactants (a carboxylic acid, an aldehyde and an isocyanide) in one-pot conditions to obtain a single product through an acyloxycarboxamide ligation. The atom-economy of P-3CR and its compatibility with mild conditions justify its use. Herein, we present the exploitation of P-3CR in homogeneous and heterogeneous aqueous medium in order to respectively modify carboxymethyl cellulose (CMC) [1] and (oxidized) cellulose microfibrills (MFC) [2], both being widely used in a variety of applicative fields. Such a modification allowed for designing new dually functionalized cellulose derivatives. Concerning the modification of CMC, P-3CR was successfully achieved by using a series of model aldehydes and isocyanides, and a specific focus was devoted to the impact of experimental parameters, in order to gain insight on this derivatization chemistry. Also, the adsorption ability of these CMC derivatives onto model amorphous cellulose substrates was studied by quartz crystal microbalance with dissipation monitoring. Concerning MFC, P-3CR was applied to cellulose microfibrils previously subjected to a periodate oxidation step, which allowed for grafting at the surface of periodate oxidized cellulose (POC) reactive alkyne or methacrylate functions, able to post-react through copper catalyzed Huisgen cycloaddition, and aza-Michael reaction in water medium, as shown in Figure 1. This P-3CR emerging synthetic tool opens the way to the design of promising (multi)functional polysaccharide derivatives, in a simple aqueous process.



Fluorescence analysis of tagged POC

Figure 1: a) P-3CR-modification of MFC, and b) post-coupling with a tag by click chemistry b).

Keywords: green chemistry, polysaccharides, passerini reaction, cellulose derivatives

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Novel synthetic approach leading to functional polyolefins

R. Januszewski[1,2*], B. Orwat[2,3], M. Dutkiewicz[4], I. Kownacki[1,2]

[1]*Faculty of Chemistry, Adam Mickiewicz University in Poznan, Uniwersytetu Poznanskiego 8, 61-614 Poznan, Poland*
[2]*Centre for Advanced Technologies, Adam Mickiewicz University in Poznan, Uniwersytetu Poznanskiego 10, 61-614 Poznan, Poland*
[3]*Department of Molecular Physics, Lodz University of Technology, 90-924 Lodz, Zeromskiego 116, Poland*
[4]*Poznan Science and Technology Park, Adam Mickiewicz University Foundation, Rubiez 46, 61-612, Poznan, Poland*
**r.janusz@amu.edu.pl*

Nowadays, over 150 million tons of polyolefins are produced annually worldwide, mainly in catalytic reactions. High chemical resistance, biological inertness and attractive mechanical properties are the factors that have made organic polymers permanent and indispensable elements of everyday life[1]. The common organic polyolefins (polyethylene, polypropylene), as a consequence of their low polarity and lack of functional groups, exhibit poor compatibility to nitrogen- or oxygen-containing compounds, polar pigments and low adhesion to inorganic surfaces. Thus, the introduction of polar functionalities into nonpolar polymers is highly desirable since it would increase the number of potential applications and render these materials even more versatile. The several strategies leading to functional polymers have been developed and the chemical transformation of existing polymers (post-polymerization) has recently emerged as a topic of increasing importance in macromolecular chemistry [2-4]. Among the large group of known organic polymers, polybutadiene is a versatile and convenient starting material for further functionalization, due to the high content of readily accessible double bonds revealing reactivity in a wide range of stoichiometric and catalytic transformations and also thanks to the possibility of controlling the microstructure and molecular weight during anionic polymerization. Therefore, butadiene-based polymers seem to be excellent precursors for the synthesis of organofunctional polymers[5].

In this contribution, an efficient methodology for the synthesis of new organofunctional polyolefins is proposed. It includes the transformation of polybutadiene through catalytic reactions, which in a simple way leads to the unique functional polyolefins. The developed synthetic strategy enables incorporation of a wide variety of organic and organometallic groups into the polymer chains, which cannot be or are technically difficult to be carried out with conventional polymerization protocols.

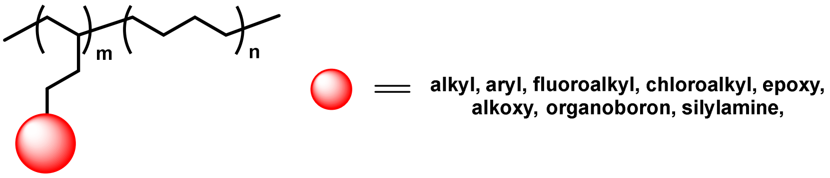

Figure 1. Novel organofunctional polyolefins

Keywords: functional polymers, hydrosilylation, homogeneous catalysis, post-polymerization

Acknowledgments

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Novel Light-Responsive Poly(2-oxazoline)s: Synthesis and Self-Assembly studies

Leonid I. Kaberov[1,2*], Shu Wang[1,2], Purushottam Poudel[1,2], Felix H. Schacher[1,2]

[1]*Institute of Organic Chemistry and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Jena, Germany*
[2]*Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Jena, Germany*
[*]*leonid.kaberov@uni-jena.de*

Amphiphilic polymer materials find a wide range of applications in medicine and diagnostics. Often such polymers are required to be able to adapt their properties depending on surrounding conditions (pH, ionic strength) or external stimuli (temperature, irradiation) for a targeted application in the body. Compared to others, the application of light as a trigger is not that common. Such a trend arises from a need to use UV light for most chromophores. However, the presence of light-sensitive fragments enables the implementation of material state changes (conformation, polarity, etc.) under spatial and temporal control, which is not always possible for other stimuli.

Here we present novel poly(2-oxazoline)s bearing light-responsive fragments based on azobenzene (UV) and 1-hydroxypyrene (visible light). The plethora of available 2-oxazolines provides a great platform for the synthesis of multi stimuli-responsive polymers, while the living nature of cationic ring-opening polymerization of 2-substituted-2-oxazolines enables good control under polymer composition and dispersity. Using both subsequent polymerization and postpolymerization modification, we have formed a library of amphiphilic stimuli-responsive polymers of different structures. The obtained polymers form nanoparticles in water and other solvents, which was proven by dynamic light scattering and transmission electron microscopy. Also, conducted studies prove the light responsiveness of obtained nanoparticles.

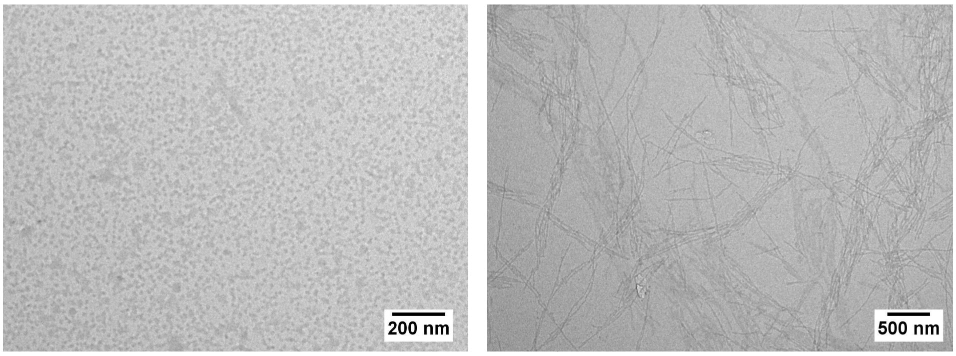

Fig. 1. TEM microphotograph of nanoparticles formed by PEtOx(0.71)-block-PAzBenOx(0.29) in aqueous solution (left) and in methanol (right).

Keywords: poly(2-oxazoline), azo-benzene, photoacid, light-response, self-assembly.

Acknowledgments
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Radical Induced Cationic Frontal Polymerization

P. Knaack[1*], R. Taschner[1], R. Liska[1]

[1]*Institute of Applied Synthetic Chemistry, TU Wien, 1060 Vienna, Austria*
[*]*patrick.knaack@tuwien.ac.at*

With the development of Radical Induced Cationic Frontal Polymerization (RICFP)[1] the hurdle of curing depth could be cleared in cationic photopolymerization (Figure 1). Therein the fact that some Photo Acid Generators (e.g. iodonium and sulphonium salts) do not cleave exclusively under UV irradiation, but also via redox reactions with radicals. In the first step of a RICFP the PAG liberates acid upon irradiation, which initiates an exothermic polymerization. The generated polymerization heat cleaves a thermal initiator into radicals which generate via a redox reaction with the PAG again the active acid. So bubble free and in mechanical aspects perfectly comparable with classically cured epoxy resins can be prepared within minutes without oven or spacial limitations.

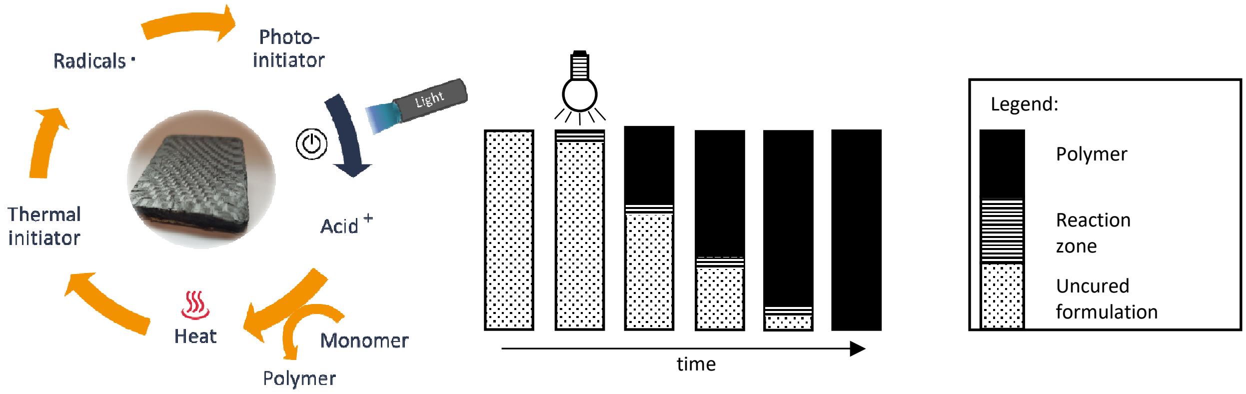

Figure 1: Scheme of the RCIFP process

Since for epoxy monomers the usage in fiber and/or particel filled composites is very common, the implementation of composite preperation techniques into the filed of frontal poymerizaton was investigated.

Results of partice filled composites and preperation procedures of fiber reinforced polymer composites2 shall be presented. Also the preperation of frontaly polymerizable carbon fiber prepregs3 and their possible applicaations will be introduced.

Keywords: frontal polymerization, epoxy, composite

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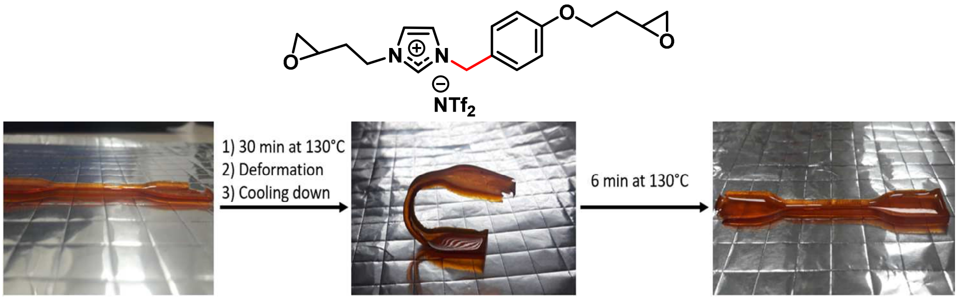
Ionic Liquids: A New Versatile Platform For The Design of a New Multifunctional Epoxy Networks 2.0 Generation

S. Livi[1*], G. Perli[1], J. Baudoux[2], J-F. Gerard[1], J. Duchet-Rumeau[1]

[1] *Université de Lyon - INSA Lyon, UMR CNRS 5223, IMP Ingénierie des Matériaux Polymères, F-69621, Villeurbanne, France*
[2] *Laboratoire de Chimie Moléculaire et Thio-organique, ENSICAEN, Université de Normandie, CNRS, 6 boulevard du Maréchal Juin, 14050 Caen, France*
[*] *sebastien.livi@insa-lyon.fr*

In the field of thermosetting polymers, ionic liquid monomers represent a real opportunity to design new smart and (multi)functional-dedicated polymer materials with enhanced properties such as thermal stabilities, mechanical performances, gas or water barrier properties, anti-bacterial, shape memory and self-healing properties. Very recently, our laboratory have designed more environmentally friendly new polyfunctional di-, tri- and tetra- epoxydized imidazolium ionic liquids in order to prepare a new generation of epoxy-amine networks with functional properties (**Figure 1**). Thus, several architectures have been considered in order to highlight the impact of the architecture on the final properties of the networks by adding one or two aromatic groups, by incorporating ether or ester groups, and by inserting the spacer arms between the imidazolium core and the epoxide functions [1-4].



Thus, epoxy networks with glass transition temperatures including between 60 °C to 140 °C combining with good thermomechanical and mechanical properties, hydrophobic behavior and corrosion protection have been developed. Finally, the main objective of this work is to summarize this pathway highlighting the strengths and weaknesses of these new promising ionic compounds.

Acknowledgments

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Combining Electrochemical and (Photo)Chemical Control for Well-Defined Polymer Synthesis

F. Lorandi[1,2*], F. De Bon,[3] H. Jafari,[2] M. Fantin,[4] J.F.J Coelho,[3] A.A. Isse,[4] K. Matyjaszewski[2]

[1]*Department of Industrial Engineering, University of Padova, Padova, Italy*
[2]*Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, USA*
[3]*Centre for Mechanical Engineering Materials and Processes (CEMMPRE), Department of Chemical Engineering, University of Coimbra, Coimbra, Portugal*
[4]*Department of Chemical Sciences, University of Padova, Padova, Italy*
[*]*francesca.lorandi@unipd.it*

The external regulation of controlled radical polymerizations has provided polymer chemists with the ability of switching reactions on/off *on demand* and precisely controling the polymerization location.[1] Moreover, external stimuli of various kind, including chemical, electro- and photo-chemical, allow for mild reaction conditions, improving the energy efficiency and atom economy of polymerizations.[2]

Electrochemically mediated atom transfer radical polymerization (*e*ATRP) is a versatile and clean process to design well-defined polymers by harnessing electricity.[3] The growth of polymer chains in ATRP is typically governed by a Cu catalyst: a Cu^{I} species activates alkyl halide dormant species generating radicals, while a Cu^{II} species deactivates the propagating radicals. Therefore, the relative amount of activator and deactivator can be established by applying a current/potential, thus finely tuning the polymerization rate and outcome. In this talk, I will discuss mechanistic aspects and advantages of coupling the electrocatalytic cycle of *e*ATRP to other means of polymerization regulation.

The first dual-system concerns the use of copper as electrode material in *e*ATRP. Cu^{0} undergoes a comproportionation reaction with Cu^{II} species in the polymerization mixture, (re)generating the Cu^{I} activator. Depending on the reaction conditions and the applied current/potential, the comproportionation and electrochemical processes can act synergistically to boost the polymerization control, or the electrochemical setup can halt the chemically-regulated polymerization.

In the second dual-system, electrochemical and photochemical reaction setups are combined. The application of an oxidation current/potential allows for stopping the polymerization when switching light on/off cannot offer efficient temporal control (Figure 1). On the other hand, a photoelectrochemical regulation can accelerate the reaction, potentially providing access to unprecedented systems. Furthermore, the electrochemical setup gives the possibility of monitoring *in situ* the generation and distribution of Cu species during the photocatalytic cycle.

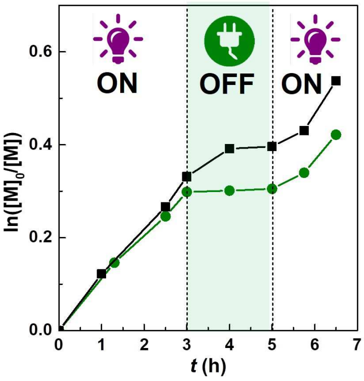

Figure 1. PhotoATRP of 50 vol% butyl acrylate (BA) in DMF. Comparison of reaction kinetics with simple on/off light switching (black dots+line) and electrochemical oxidation step during the light off period (green dots+line).

Keywords: controlled polymerizations, ATRP, electrocatalysis, photocatalysis

Acknowledgments

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Functionalization of dendritic polyolefins prepared by chain-walking polymerization

O. Kotyza, K. Nunvařová, Vojtěch Musil, Jan Janoušek, R. Mundil, A. Sokolohorskyj, Soňa Hermanová, J. Merna*

University of Chemistry and Technology Prague, Prague, Czech Republic
**merna@vscht.cz*

Branching and functionality are key molecular parameters of macromolecules, which determines basic properties of polymeric material. Chain walking (CW) polymerization catalysts allow straight synthesis of branched polyolefin just by ethene homopolymerization. The structure of CW polymers resembles rather the structure of dendrimers then the structure of hyperbranched polymers prepared by condensation polymerization [1]. However, the introduction of polar functional groups remains one of the challenges to catalytic polymerizations, even for those catalyzed by relatively tolerant nickel and palladium alpha-diimine complexes, which belong to the best-studied CW catalysts. These complexes also allow living olefin polymerization, which makes them suitable for end-functionalization and preparation of block copolymers.

The contribution will summarize various strategies for the preparation end-chain and in-chain functionalized branched polyolefins. Functionalization can be achieved utilizing the capability of catalyst to copolymerize olefin with polar monomers, by transformation of living catalytic sites or using chain transfer to organometallic transfer. Obtained polymers can be used as macroinitiators for the preparation of amphiphilic block and grafted copolymers that can self-assemble to nanoparticles highly stable in water dispersions and capable to load hydrophobic cargo [2].

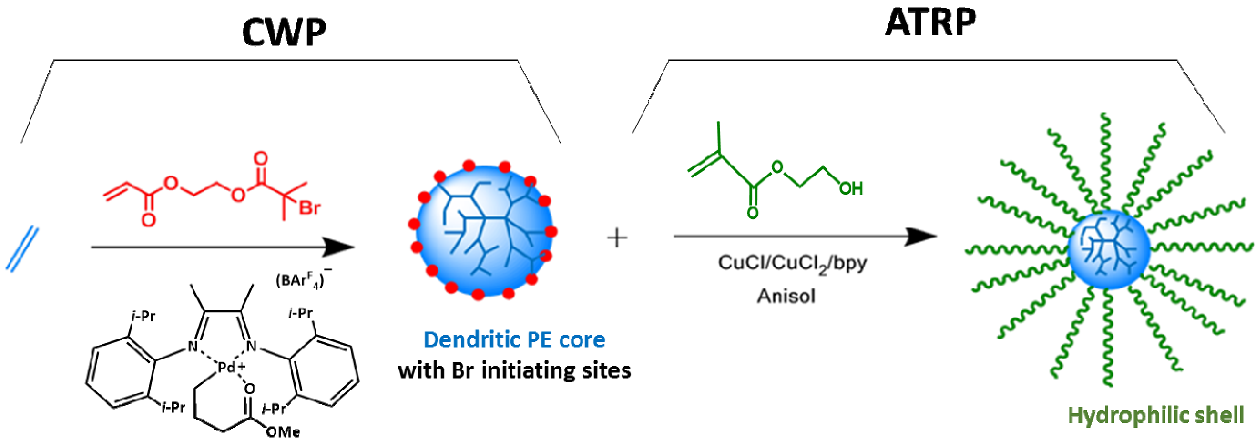

Fig. 1 Synthesis of amphiphilic copolymer dendritic PE-graft-poly(HEMA)

Keywords: chain walking, amphiphilic copolymers, living polymerization, branched polyolefins

Acknowledgments

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Amphiphilic homo and hetero graft copolymers based on poly(dehydroalanine)

Frieda Nagler[1], Johannes B. Max[1], Christian Kropf[3], F. H. Schacher[1,2*]

[1]*Institute of Organic Chemistry and Macromolecular Chemistry (IOMC), Friedrich-Schiller-University Jena, Lessingstraße 8, D-07743 Jena, Germany*
[2]*Jena Center for Soft Matter (JCSM), Friedrich-Schiller-University Jena, Philosophenweg 7, D-07743 Jena, Germany*
[3]*Henkel AG & Co. KGaA, Henkelstraße 67, D-40589 Düsseldorf, Germany*
[*]*felix.schacher@uni-jena.de*

Poly(dehydroalanine) (PDha) is a polyampholyte carrying a carboxylic acid moeiety as well as an amine within each repeating unit.[1] Therefore, depending on the solution pH a polyanion, polyzwitterion or polycation is formed which allows varying interaction with charged small molecules and proteins, or the coating of magnetic iron nanoparticles.[1,2]

Graft copolymers allow the optimization of polymer properties for different applications by alterating the molecular weight of the backbone, or the type and number of side chains.[3] By grafting PDha with hydrophobic side chains, an amphiphilic graft copolymer is obtained that can dissolve depending on the molecular weight and grafting density in aqueous solution as well as different organic solvents. In addition, it can be applied as dispersant for different hydrophobic compounds such as carbon nano tubes, dyes, or drugs.[4] By adding hydrophilic side chains, the water solubility of PDha can be improved and the pH-resposiveness is altered which allows the use as, *e.g.*, template for nanoalloys.[5]

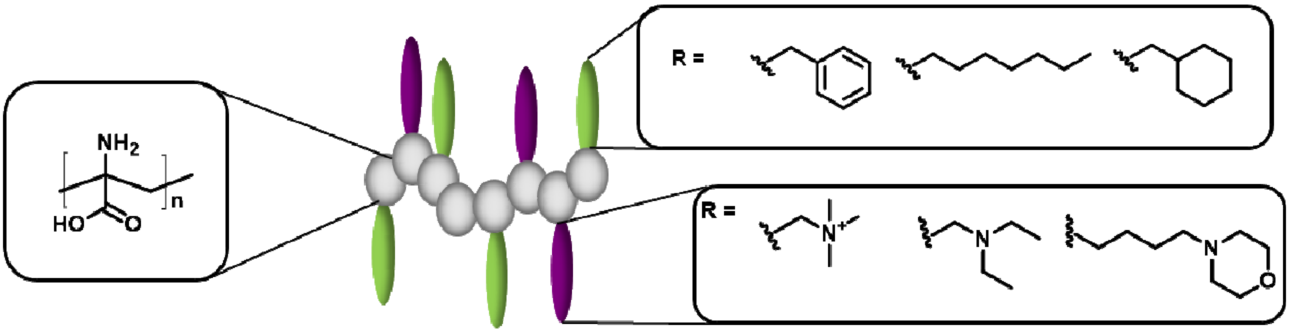

Figure 1: Selected possibilities for hetero graft copolymers based on a poly(dehydroalanine) backbone.

When different side chains are combined, multi-responsive amphiphilic graft copolymers are obtained. *E.g.* graft copolymers possessing temperature-responsiveness or pH-responsiveness as well as the ability to interact with hydrophobic molecules are interessting for various delivery purposes or as switchable emulsifiers.[6]

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From self-healing coatings to vitrimer materials based on hemiacetal ester chemistry

D. Boucher[1,2], J. Madsen[3], V. Ladmiral[1], N. Caussé[2], N. Pébère[2] and C. Negrell[1]*

[1] *ICGM, Univ. Montpellier, ENSCM, CNRS, 34000 Montpellier, France.*

[2] *CIRIMAT UMR 5085-CNRS, UT, INPT, UPS, ENSIACET, 4 allée Emile Monso, 31030 Toulouse, France.*

[3] *Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark.*

**claire.negrell@enscm.fr*

Hemiacetal ester is a very interesting functional group that can besynthesized by different methods, such as the addition of a carboxylic acid onto a vinyl ether[1], the Bayer-Villiger oxidation of a cyclic ketone bearing a vicinal methoxy group[2] or by reaction of a ketone or acetaldehyde with β-hydroxy acids[3]. This function has mostly been used for its ability to dissociate under specific conditions. Thermal dissociation of the hemiacetal ester functional group that leads to the recovery of the carboxylic acid function[1] has been used for the preparation of recyclable[4] and de-crosslinkable[5] polymers. Moreover, kinetics studies revealed that the exchange reaction between acid and vinyl ether proceed through an associative mechanism[6]. These properties are used to react carboxylic acids “on demand”. We chose to exploite this “on demand” reactivity by introducing hemiacetal esters into a bio-based epoxidized polymer matrix or into a vitrimer polystyrene material. On one side, a polymer matrix was established from epoxidized acrylate linseed oil. This oil mixed with an hemiacetal ester repairing agent, an adhesion promotor and a reactive diluent was deposited as a coating and cross-linked under UV. Electrochemical impedance measurements were demonstrated interesting barrier properties in order to highlight the impact of the repairing agent under thermal treatment[7]. On the other side, the development of a polystyrene-based vitrimer harnessing the recently discovered hemiacetal ester exchange reaction of carboxylic acid is presented[8]. Divinyl ether monomer was reacted with 4-vinylbenzoic acid to form a divinyl species containing two hemiacetal ester functions. This dimer was then copolymerized with styrene, butyl acrylate and 4-vinylbenzoic acid to form a cross-linked material presenting pendent acid groups. Vitrimer behavior was demonstrated by rheological creep experiments.

Keywords: Hemiacetal ester, coating, repairing properties, vitrimer behavior.

Acknowledgments

This project was supported by Chimie Balard Cirimat Carnot through the ANR program N°16 CARN 0008-01.

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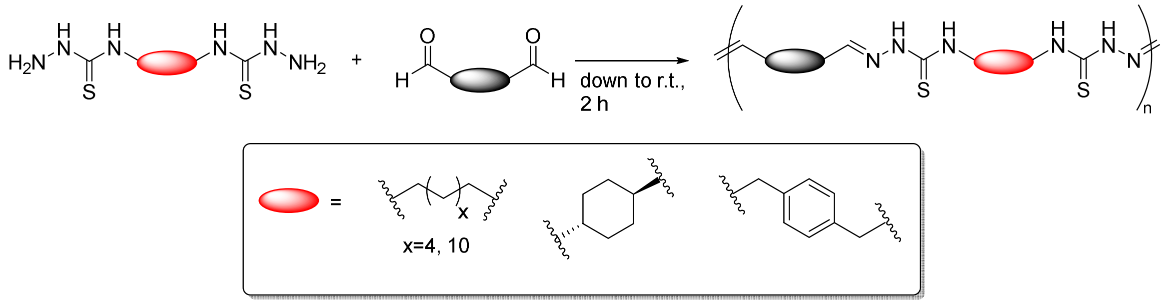
Polythiosemicarbazones by Condensation of Dithiosemicarbazides and Dialdehydes

R. Nickisch[1], P. Conen[1], M. A. R. Meier[1*]

[1]*Karlsruher Insitute of Technology (KIT), Karlsruhe, Germany*
*m.a.r.meier@kit.edu

Thiosemicarbazones (TSC) are a widely used functional group formed by condensation of a thiosemicarbazide with an carbonyl function. They are used as precursor for the synthesis of many sulfur and nitrogen containing heterocycles.[1] Additionally, they exhibit often biological activities of various kind.[2] Their ability to act as a ligand for many metals by various coordination modes is used frequently.[3] More recently, TSCs were applied as organocatalysts for tetrahydropyranylation.[4]

While the research field of TSCs is extensivly studied, polyTSC are rather scacre. Thus, we have established a feasible synthesis procedure for thermoplasts incorporating TSC group in the backbone by polycondensation of dithiosemicarbazides and aromatic dialdehydes. The reaction takes already place at room temperature for several substrates being completed after two to three hours. The obtained polymers exhibit high molecular weights and the selectivity of the reaction was underlined by low dispersities. Aliphatic, cyclic and benzylic moieties are permitted for dithiosemicarbazides and rigid and conjugated aryl ones for dialdehydes. Versatility of the reaction was underpinned by *co*-polymerisation of two different dithiosemicarbazides with terephthaldehyde. Adjusting different ratios allowed precise incorporation of both moieties. Full characterization of all obtained (*co*-)polymers was performed by ^{1}H and ^{13}C-NMR spectroscopy, IR-spectroscopy and size exclusion chromatography. Degradation of the polymers started at ca. 200 °C by decomposition of TSC functions. Glass transition states were observed only for rigid polymers (162 °C-198 °C). We hope that more research can be fascilitated in the intersection of polymer and TSC chemistry by this approach and the comprehensive characteriztaion of its polymers.



- ✓high molecular weight (up to M_n of 38 kDa)
- ✓dual backbone control
- ✓excellent control (*Đ from 1.40-2.41)*
- ✓feasible synthesis protocol

Figure 1: Overview of established synthesis of polyTSCs. Moieties of dithiosemicabazides (red ellipsoid) and features of the reaction are depicted.

Keywords: Thiosemicarbazone, Polycondensation

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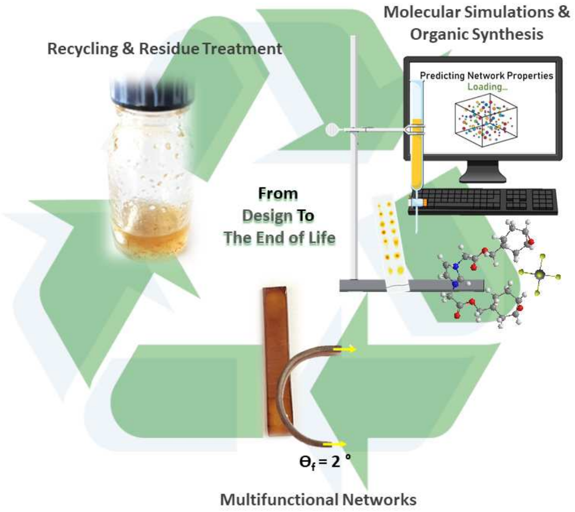
Development of Multifunctional Degradable Epoxy Thermosets: from Design to the End-of-Life

Gabriel Perli,[1] Demir Baris,[2] Sébastien Pruvost,[1] Jean-François Gérard,[1] Jannick Duchet-Rumeau,[1] and Sébastien Livi[1*]

[1]*Univ Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, F-69621 Villeurbanne, France*
[2]*Centre for Theoretical and Computational Molecular Science, The Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, QLD 4072, Australia*
[*]*sebastien.livi@insa-lyon.fr*

The design of new epoxy thermosets is actively investigated in order to develop high-performance materials. Cycloaliphatic epoxy resins present several advantages compared to conventional epoxy resins, including UV resistance, higher hydrophobicity, and electrical resistivity.[1] Owing to these characteristics, cycloaliphatic epoxies (CEs) are promising substitutes to Diglycidyl Ether Bisphenol A (DGEBA) composed of BPA representing a risk for humans and the environment. However, the development of new epoxy-based materials with tailored properties remains a challenge.[2] In this work, we have designed and engineered for the first time degradable multifunctional CEs with a ionic liquid backbone. Initially, a cycloaliphatic epoxidized imidazolium IL (CEIL) was successfully synthesized with high yields. Then, three different networks were produced by curing CEIL and 3,4-Epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate, in the presence or absence of a diaryliodonium hexafluoroantimonate initiator. The networks based on CEIL demonstrated an increased thermal stability, shape memory behavior, and mechanical properties comparable to DGEBA resins, which make them promising candidates to replace Bisphenol A derived polymers. Furthermore, dielectric spectroscopy revealed that by increasing the percentage of CEIL in the networks, it was possible to increase the relative permittivity from 6.6 to 37.3. Most importantly, the CEIL-based materials were fully degraded by a sustainable and economically viable methodology. These promising results go beyond expectations since by combining computational chemistry, organic synthesis, and material science, we are able to develop high-performance environmentally friendly CEs for the continuous progress of a circular economy.



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Organocatalyzed Ring-Opening Copolymerisation of Morpholine-2.5-diones and Lactide: an insight into the ROP mechanisms

Julien Pinaud[1*], T. Burton[1], O. Giani[1]

[1] *ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France*
**julien.pinaud@umontpellier.fr*

Aliphatic polyesters such as polylactic acid (PLA), polyglycolic acid (PGA), and polycaprolactone (PCL) are attractive and widely employed materials for biomedical applications.[1] However, the hydrophobicity and crystallinity of both PLA and PCL, as well as the rapid degradation of PGA, severely limits their use in a homopolymer form. On the other hand, by containing both amide and ester bonds, polydepsipeptides (PDPs) combine the mechanical properties of polyamides and the degradation capacities of polyesters, which make them very attractive for tissue engineering and drug delivery.[2] In essence, PDPs are the simple alternation of α-amino acids (AAs) and α-hydroxyacid monomer units. Depending on the initial AA employed to prepare the cyclic monomer they originate from, *i.e* morpholine-2,5-diones (MDOs), their mechanical and biodegradable properties can thus be tuned to fit the requirements of the desired application. It should be noted however, that MDOs are not commercialy available and are obtained via a two-step synthetic pathway that requires large volumes of solvents and results in low yields.[3] Introducing PDP units in PLA chains thus represent a very interesting solution to impart specific properties to PLA while limiting the quantity of morpholine-2,5-diones employed. With the aim of producing copolymers for highly tunable in-vivo biomedical devices, the ring-opening copolymerization of MDOs and LA has thus been studied (Figure 1).[4]

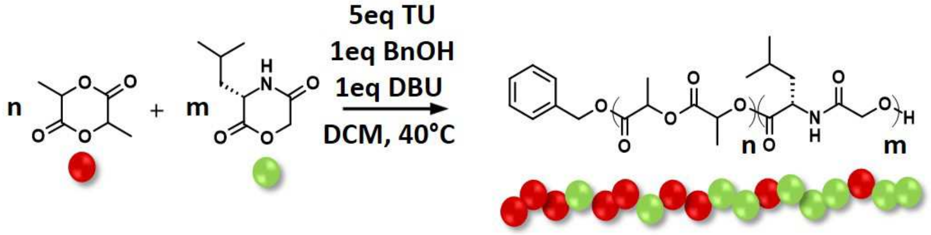

Figure 1: Organocatalyzed ring-opening copolymerization of lactide (red) and 3S-(Isobutyl)morpholine-2,5-dione.

In a first instance, the DBU-catalysed homopolymerisation of the 3S-(Isobutyl)morpholine-2,5-dione was studied. Different alcohols were tested as well as various amounts of a thiourea co-catalyst, which proved to be the key for achieving precise molecular control. A range of polymers with molecular weights between 8.1 and 25.2 kg mol^{-1} were thus produced with narrow chain distributions (Đ = 1.13−1.18) in short periods of time (5 to 10 min). The same was then done with LA. When comparing these kinetics, interesting trends were observed which permits insight into the differences in ROP mechanisms with regards to the capacity to ring-open, to propagate, and to back-bite. When the MDO/LA copolymerisation was carried out, these small differences provoked trends in the polymerisation kinetics which confirmed our initial observations. In this manner, statistical copolymers with varying compositions (MOD:LA = 25:75;50:50; 75:25) were prepared (11.2 to 12.7 kg mol^{-1}; Đ = 1.09−1.26) as determined by DOSY-NMR, SEC, MALDI-TOF and by DSC.

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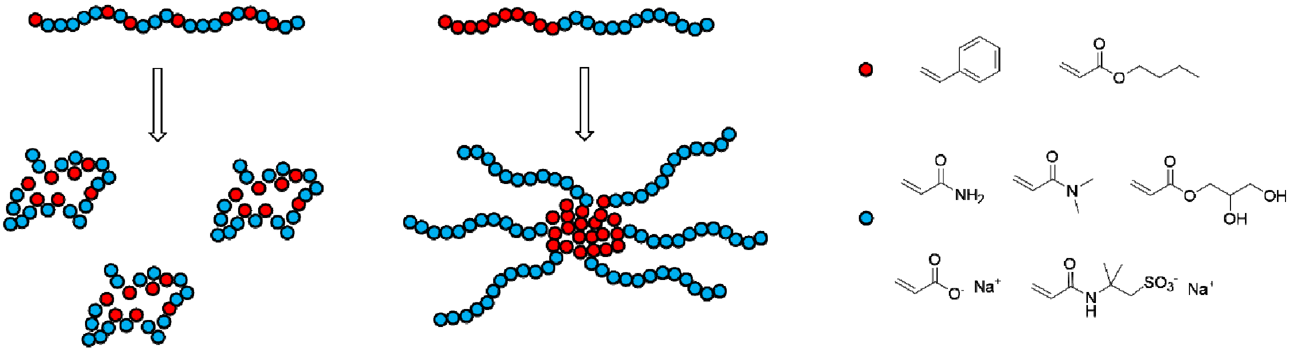
Structure-Dependent Solution Properties of Amphiphilic Copolymers Synthesized by ATRP or RAFT

P.Raffa* , A. Guzik , N. Migliore

[1]*Department of Chemical Product Technology, Faculty of Science and Engineering, Engineering and Technology Groningen (ENTEG) Institute, University of Groningen*
**p.raffa@rug.nl*

Amphiphilic copolymers (or polymeric surfactants) have received increasing attention in the past decades, due to their interesting properties and self-assembly in water. [1] They find application as rheology modifiers, encapsulating agents and/or emulsifiers, in many diverse fields including drug delivery, smart materials, and enhanced oil recovery. Depending on the distribution of hydrophobic and hydrophilic monomers in the structure, amphiphilic polymers can self-assemble in water into a variety of different morphologies, resulting in different solution properties and potential applications. [2] The development of controlled radical polymerization methods, such as ATRP and RAFT, has enabled systematic studies of structure-properties realationships for this class of polymers. For example, amphiphilic polymers with statistic [3] or block [4] structures can be prepared, resulting in different aggregation behavior (Scheme1).
In this contribution, I will illustrate recent work developed in our research group, concerning the synthesis of well-defined amphiphilic polymers via ATRP or RAFT, and their structure-dependent solution properties, with particular emphasis on rheology and surface activity. The particular choice of monomers (Scheme1) allows to also obtain amphiphilic polymers with stimuli-dependent properties, in particular with solution viscosity varying with pH, temperature, and salinity.



Scheme 1. Statistic vs block structures in amphiphilic copolymers and different

Keywords: amphiphilic polymers, self-assembly, rheology, surface activity, stimuli-responsiveness, controlled radical polymerization

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The role of OH-bearing molecules in platinum-catalyzed dehydrocondensation reaction with poly(methylhydrosiloxane)

Ingrid Rebane[1*], Uno Mäeorg[2], Urmas Johanson[1], Tarmo Tamm[1]

[1]*Institute of Technology, University of Tartu, ESTONIA*
[2]*Institute of Chemistry, University of Tartu, ESTONIA*
[*]*ingrid.rebane@ut.ee*

Polysiloxane-based foams have an important role in the industry as gaskets, insulating and cushioning materials, and their use in medicine has increased over the past decade.[1] As there is still a need to overcome the low and inhomogeneous porosity of cellular elastomeric materials, fine-tuning the structure is essential for enhancing the mechanical properties of materials related.[2]

We are addressing the need for a better understanding of the effect of alcohols and water in the platinum-catalyzed dehydrocondensation reaction with the hydride-functionalized polysiloxane (PMHS), which is one of the 'building block' molecules in silicone crosslinking. Analyzing the kinetics of this reaction provides us with a better understanding of how selected molecules that take part in hydrogen formation may affect its rate and the conversion of hydride groups in polysiloxane. A set of alcohols was chosen to cover diverse structural features, from the simplest (MeOH) towards more complex (tAmOH, iOctOH), varying in length and branching of the hydrocarbon chain. All of the considered alcohols are widely used in industry and readily available. The effectiveness in releasing gaseous H_2 from the Si-H groups of poly(methylhydrosiloxane) at different stages is compared.

The results of our analysis show that the most common logic rules of alcohol reactivity do not apply in such reactions and that a set of aspects need to be considered together to understand or predict the outcome and the possible applications. We show that the reactivity of alcohols is not the only dependent on the molecular structure but is strongly influenced by the combination of hydrophobicity, polarity, pK_a and the steric hindrance of the reactive molecules. We have found that despite the simplest structure and favourably low steric hindrance, the reactivity of MeOH (a highly polar molecule) is subdued by the hydrophobicity of the PMHS. The reactivity of iOctOH appears to be supported by its high miscibility with PMHS and its OH-accessibility. For all of the selected alcohols, the structure bulkiness hinders the reaction the most, even in the case of suitably low polarity and relatively high miscibility with the PMHS. The COSMO-RS calculated pK_a in water data correlated well with the alcohol reactivity in the first stage of conversion, but only in combination with hydrophobicity and steric hindrance, it is capable of describing the reactivity of alcohols and the overall conversion.

The results signify the importance of the kinetics analysis, especially for the alcohols MeOH and iOctOH, and their mixtures, and are worth further investigation, for example varying the reactant and catalyst concentrations to get a more complete picture of steric and catalyst support properties. The results can also be directly applicable in the synthesis of foamed silicone materials and provide a better understanding of the role of Lamoreaux' catalyst in the alkoxylation reaction. In this context, the use of Lamoreaux' catalyst is considered to be a cost-effective alternative, a novel approach in characterizing catalyzed dehydrocondensation kinetics under mild conditions.

So far, there has been very little research on this matter, focusing on the macromolecular grafting and end-product analysis, but rarely any discussion on the effects of the molecular properties that may influence the reaction and conversion depth. This is also the first work that describes the use of platinum-based Lamoreaux' catalyst in a dehydrocondensation of PMHS with alcohols. We believe this research will offer great interest to industrial chemistry and the polysiloxane chemistry field in general also will contribute to the research of hydrogen production and its related applications.

Keywords: poly(methylhydrosiloxane), PMHS, Lamoreaux' catalyst, kinetics, alkoxylation, alcoholysis, dehydrocondensation, hydrogen

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POLYSORB®- a versatile monomer for improving thermoplastics and thermosetting properties

H. Amédro[1], N. Jacquel[2], R. Saint-Loup[1*]

[1]*Roquette Freres, Lestrem, France*
[2]*Nestlé System Technology Center, Orbe, Switzerland*
[*]*rene.saint-loup@roquette.com*

Isosorbide or 1,4-3,6 dianhydrohexitol, derivated from starch and more precisely from sorbitol, is one of the chemical intermediates of interest in the field of thermoplastic materials and for curable resins application. It can be used directly as a monomer or after chemical modification.
Hence, isosorbide found its place as a monomer suitable for polycondensates synthesis[1] like polyesters, polycarbonates and thermoplastic polyurethanes. Concerning aliphatic[2] or semi-aromatic polyesters[3], the addition of isosorbide increases glass transition temperature, opening to this new polymer several usual applications of amorphous polymers. The preparation of poly (ethylene-co-isosorbide) terephthalate with different ratios of isosorbide will be particularly detailed.
The study of very high temperature resistant polyester based on Isosorbide, CHDM and PTA will be described and examples of applications will be emphasized.
The structure – properties relationship will permit a focus on the obtention of polyesters with semi-crystalline or amorphous structures. The influence of isosorbide on the polymerization, on the processing of the resulting polyester as well as the modification of the final properties will be enlightened.

Keywords: dianhydrohexitol, isosorbide, polycondensation, polyesters, engineering polymers.

Acknowledgments
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From Classical Coating Resins to Water-Dispersible Polyester Systems using Dimethylol Propionic Acid

K. M. Saller*, G. Hubner, C. Schwarzinger

Institute for Chemical Technology of Organic Materials, Johannes Kepler University, Linz, Austria
**klara.saller@jku.at*

Polyesters are implemented in many different applications, the most important being bottles and fibers (mostly polyethylene terephthalate, PET) but also coatings. In the field of coatings the regulation of volatile organic compound (VOC) emissions have become a serious issue since conventional products contain significant amounts of organic solvents. To overcome this problem new products like high-solids or powder coatings have been developed. Another approach is to substitute the organic solvent with water which makes significant modifications of the polyesters necessary. The carboxylic acid functionality for example may be used for enhancing water-dispersibility after neutralization with base.

In conventional polyesters carboxylic acid groups can simply be introduced as terminating groups if the acid components are used in excess. However, the number of terminating groups in a polyester bulk is low except for very short polymer chains which usually negatively influence material properties such as decreased glass transition temperature, adhesion and cohesion, etc. For this reason additional carboxylic acid groups have to be introduced which is only possible by using multifunctional monomers such as trimellitic anhydride. In a new approach the monomer dimethylol propionic acid (DMPA) with 2 hydroxyl and 1 carboxyl group was tested as a diol component which should leave intact carboxylic acid groups distributed along the polymer chain.

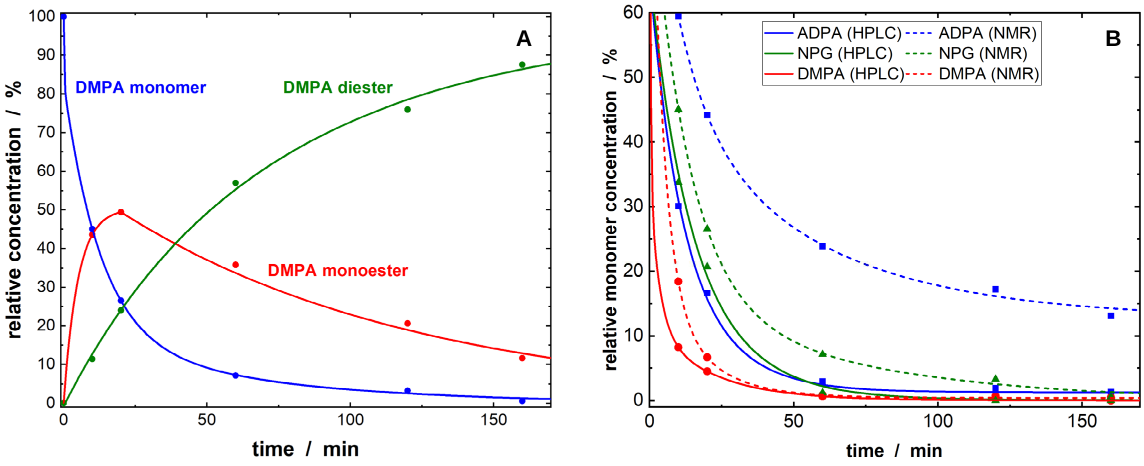


Figure: a) Investigation of dimethylol propionic acid (DMPA) reactivity regarding monomer, monoester and di-/polyester species in ^{1}H NMR spectra. b) Comparison of varying monomer reactivities from both ^{1}H NMR and HPLC-MS, the latter providing more accurate information on residual monomer while NMR peaks of different species frequently overlap in multiple component polyesters (blue dashed line).

Simply adding DMPA to a common isophthalic acid based polyester synthesis led to gelation of the resin due to crosslinking. Thus, reaction of DMPA with several comonomers was tested with the focus on varying monomer reactivities which fundamentally influenced polyester structure. For these investigations several analytical methods were implemented such as HPLC-MS and ^{1}H NMR which allows for example distinction of monomer, monoester and polyester species of DMPA. Additional elucidation of the complex polymer structures is carried out using MALDI-TOF MS. In the end, investigations of monomer reactivities led to the successful optimization of process conditions including multiple step syntheses with up to four different monomers. The final products readily dispersed in water and additionally showed satisfactory glass transition temperatures for storage stability.

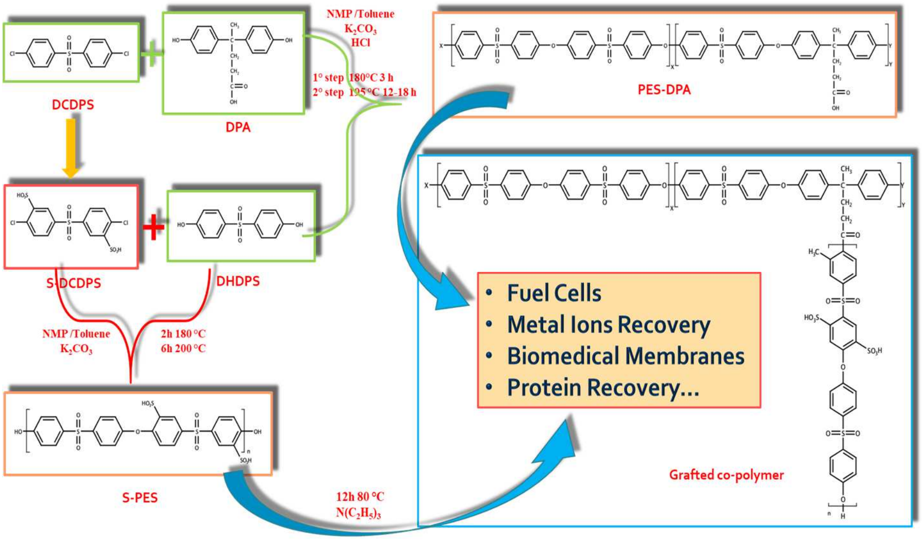
Keywords: dimethylol propionic acid, water-dispersible polyester, polyester characterization

Synthesis and characterization of novel poly(ether sulfone)s copolymers bearing pendant carboxyl groups

A. A. Scamporrino [1*]

[1] *Institute for Polymers Composites and Biomaterials, IPCB CNR Catania, Italy*
* *andreaantonio.scamporrino@cnr.it*

Aromatic poly(ether sulfone)s (PESs) are engineering thermoplastic materials with excellent chemical and thermal stability. Despite this, PESs have some limitations. Lack of hydrophilic groups and the closing arrangement of macromolecular chains lead to the high hydrophobicity of PES, causing the accumulation phenomena on the surface of membranes (biofouling). With the aim to obtain materials well balanced in terms of hydrophobic and hydrophilic character, the insertion of carboxyl and sulfonic groups and their effects on the behaviors of the polymers was verified and applied to the engineering of different kind of membranes for several applications.
New functionalized Poly(ether sulfone)s having different molar ratio of 4,4-bis phenoxy pentanoic acid (diphenolic acid; DPA) units were synthesized and structurally characterized by (^{1}H and ^{13}C)-NMR, MALDI-TOF MS, FT-IR, DSC, and Contact Angle analyses. Thermal degradation processes were also studied by direct-pyrolysis/MS (DPMS), stepwise pyrolysis-gas chromatography/MS and thermogravimetric techniques. The presence of different amount of DPA units along the polymer chains affects the chemical and physical properties of the copolymers. The Tg and the contact angle values decrease as the molar fraction of DPA units increases, whereas the hydrophilicity increases. NMR and MALDI-TOF MS analyses show that all polymer chains are, as expected, randomic and almost terminated with hydroxyl and chlorine as end groups. The thermal stabilities, the pyrolysis products and the thermal degradation mechanisms of the copolymer samples have been identified through the combination of DPMS, Py-GC/MS and TGA data. Their thermal behavior was compared with that of a well-known commercial PES (referred to as PESES) sample.



Synthesis Scheme

Keywords: Poly(ether sulfone)s, Synthesis, Structural Characterization, Thermal Characterization.

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Using aza Michael additions for the design of reactive prepolymers as intermediates for thermoset materials

J.-F. Stumbé[1*], B. Clément[1,2], P. Pichon[2], R. Perrin[2]

[1]*University of Haute Alsace, Laboratory of Photochemistry and Macromolecular Engineering, Mulhouse, France*
[2]*SOPREMA, Strasbourg, France*
[*]*jean-francois.stumbe@uha.fr*

In this work, we introduce the interest of implementing Aza-Michael additions for the design of soft crosslinked materials. In this respect, two strategies have been developped, taking advantage of differences of reactivities between primary and secondary amines towards the nucleophilic addition onto multifunctional acrylates. This versatile chemistry allows indeed in a first strategy to prepare crosslinked materials by reacting together diamines or triamines with di- or triacrylates. Interestingly, it was possible to obtain crosslinked materials with selected degrees of crosslinking by controlling the molecular architecture of the implemented building blocks (molecular weight, structure, functionality) and their respective molar ratios (stoichiometry of the mixtures).

In a second approach, we first designed reactive difunctional and trifunctional prepolymers with controlled macromolecular architectures using either secondary diamines displaying differences of reactivities between both secondary amines, or secondary diamines with no selectivity. It was therefore possible to prepare reactive prepolymers with controlled polydispersities, controlled functionalities (typically secondary amine end groups) that could be reacted further with multiacrylate crosslinking agents to prepare soft coatings materials.

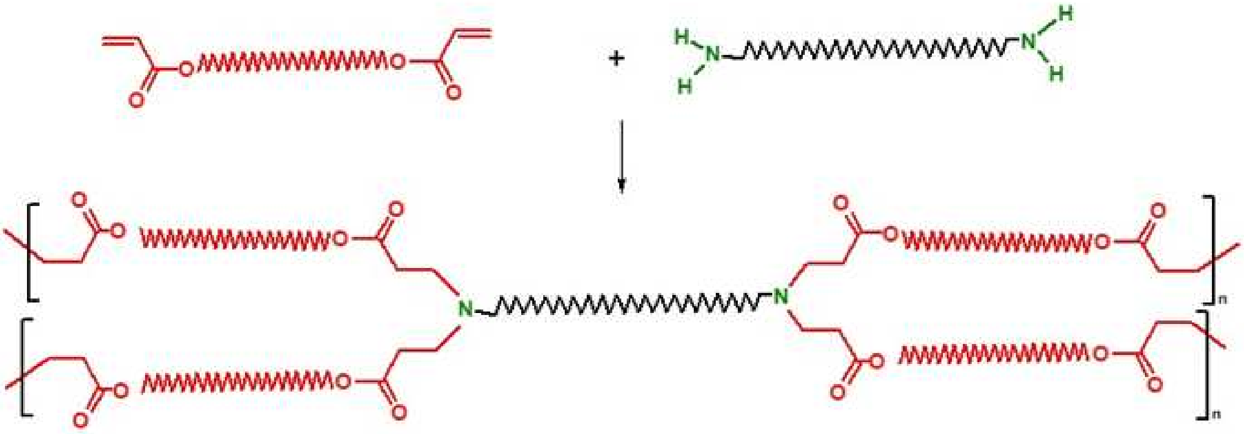

Figure: curing of functional prepolymers according to aza Michael addition

Keywords: aza Michael addition, prepolymer, thermoset, coatings

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New Onium Salts as Initiators for Cationic Polymerization, especially Radical Induced Cationic Frontal Polymerization

Roland Taschner,[1,*] Patrick Knaack,[1] Robert Liska[1]

[1]*Institute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria*
[*]*Correspondence: Roland Taschner (E-mail: roland.taschner@tuwien.ac.at)*

Cationic polymerization is a powerful tool when it comes to adhesive, coating, composite and bulk material production. Suitable monomers for cationic polymerization range from unsaturated molecules like vinyl ethers, to heterolytic compounds such as epoxides. Epoxy-based systems are used in many applications, due to their high reactivity, versatility and mechanical propterites. However, most epoxy resins are still cured by the addition of anhydride- or amine-based hardeners, which takes a lot of time and energy to fully cure. With the introduction of radical induced cationic frontal polymerization (RICFP), a much more energy efficient and fast pathway to cure epoxides and with it, a variety of new applications were obtained.[1] The prevailing initiator class for RICFP applications are iodonium salts, which can be cleaved by light as well as suitable radicals.[2] A lot of research and fine-tuning of the formulations and a lot of research lead to a highly effective and versatile initiator system.

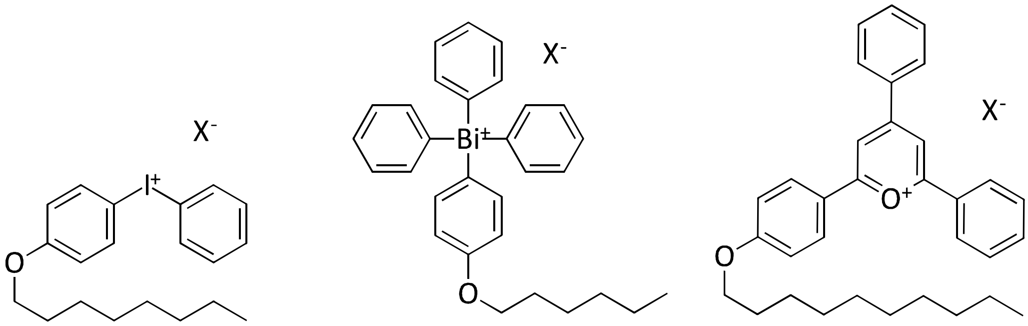

Figure 1: General structures of alkoxylated iodonium-, bismuthonium- and pyrylium-salts

With the introduction of bismuthonium- and pyylium-based salts for frontal polymerization, the well-known iodonium salt is challenged (**Figure 1**). Bismuthonium hexafluoro-antimonates show fast frontal velocities of 6.2 cm min^{-1}, a high polymerization rate and conversions of 84% in an epoxy system.[3] Bismuthonium-based systems show excellent pot life of the epoxy-formulations, which can be cured at the press of a button. Bismuthonium initiator-based formulations lasts over one month with no significant drop in reactivity or frontal velocity. Additionally, the influence of the counterion X$^-$ ist presented as well.

Keywords: Epoxides, Cationic Polymerization, Onium Salts, Iodonium Salts, Photoacid Generators

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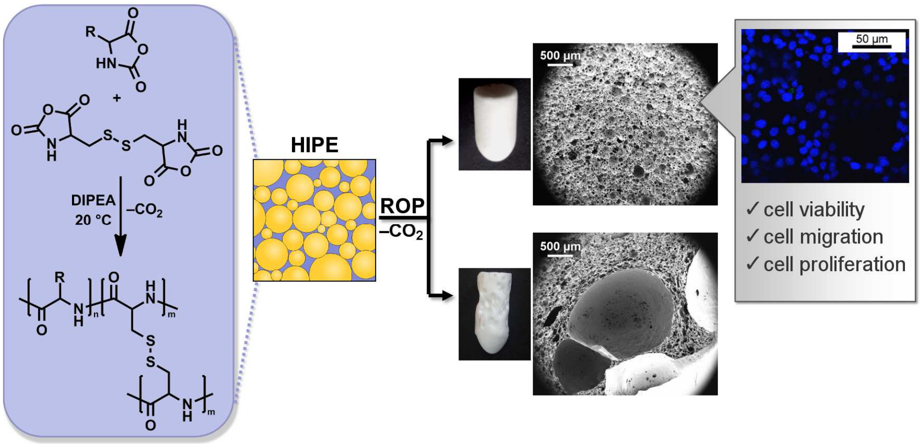
Synthetic polypeptide polyHIPEs prepared by ring-opening polymerization of *N*-carboxyanhydrides

P. Utroša[1*], O. Can Onder[1], S. Caserman[2], M. Podobnik[2], M. Tušek Žnidarič[3], J. Grdadolnik[4], S. Kovačič[1], E. Žagar[1], D. Pahovnik[1]

[1]*Department of Polymer Chemistry and Technology, National Institute of Chemistry, Ljubljana, Slovenia*
[2]*Department of Molecular Biology and Nanobiotechnology, National Institute of Chemistry, Slovenia*
[3]*Department of Biotechnology and Systems Biology, National Institute of Biology, Slovenia*
[4]*Theory Department, National Institute of Chemistry, Ljubljana, Slovenia*
[*]*petra.utrosa@ki.si*

High internal phase emulsion (HIPE) templating is an attractive approach for the preparation of scaffolds with suitable morphology for tissue engineering. So far, polymerized HIPEs (polyHIPEs) were mainly prepared as non-degradable polymers or as degradable polyesters without pendant functionality. Here, we present a method for the preparation of biocompatible, biodegradable and functional polyHIPE scaffolds based on synthetic polypeptides by performing ring-opening polymerization (ROP) of α-amino acid *N*-carboxyanhydrides (NCAs) directly in the continuous phase of oil-in-oil HIPEs [1]. Such a combination of HIPE-templating and ROP of NCA monomers requires strictly controlled experimental conditions, i.e., the polymerization rate must be fast enough to ensure the gelation of the system before the phase separation of the HIPE, but at the same time should allow the controlled release of CO_2 generated during the ROP to prevent foaming of the polyHIPEs. In this way, we prepared γ-benzyl-L-glutamate (BLG) and N^{ε}-carbobenzyloxy-L-lysine polyHIPEs cross-linked with L-cystine. Cell culture studies showed good viability, migration and proliferation of cells on PBLG-polyHIPE scaffolds. The disclosed method allows the preparation of synthetic polypeptide-polyHIPEs with tunable chemical composition and physicochemical properties.



Synthetic polypeptide-polyHIPE scaffolds with controlled morphology and physicochemical properties that provide a suitable microenvironment for cell growth are prepared by ROP of NCAs in the continuous phase of HIPEs.

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Combining post-phthalate ZN catalysts with novel radical initiators for producing PP melt blown webs with optimized barrier properties

Jingbo Wang, Georg Grestenberger, Joachim Fiebig, Lisa-Maria Steiner,
Gerhard Hubner & Markus Gahleitner
Borealis Polyolefine GmbH, Innovation Headquarters, Linz, Austria

Polypropylene-based nonwoven constructions including a meltblown fibre web combining excellent air permeability with high water barrier and filtration efficiency are in use for a wide range of applications from air conditioning over hygiene to medical segment. The wish to avoid phthalate residues in this application was instrumental in kicking off polymer industry's transition to post-phthalate Ziegler-Natta type catalysts, which are increasingly used for many types of polypropylene. Parallel to the scale-up from bench scale to commercial production, the possibilities of alternative visbreaking concepts were explored, replacing conventional peroxides by C-radical generators. Specifically, sterically hindered hydroxylamine esters and 2,3-dimethyl-2,3-diphenylbutane were tested both in pure form and in combination with peroxide. The target was to optimize the balance between processability, barrier and permeability, also by varying the base polymer and visbreaking length. Materials from this development not only are being commercialized, but also formed the base of an ad-hoc support to face mask producers in Austria during the early phase of the COVID-19 pandemic.

Polymerization of methacrylic acid in an uncoventional (bulk like) reaction medium

Samuel Wierzbicki[1*], Kacper Mielczarek[1], Monika Topa-Skwarczyńska[1], Joanna Ortyl[1], Szczepan Bednarz[1]

[1]*Department of Biotechnology and Physical Chemistry, Cracov University of Technnology, Cracow, Poland*
[*]*samuel.wierzbicki@doktorant.pk.edu.pl*

The polymerization of methacrylic acid (MAA) without a classical solvent (organic or water) is an unexplored topic mainly due to the low solubility of poly(MAA) in bulk medium. One of the most promising method for polymerization of MAA in solvent-free conditions is polymerization of MAA in a complex form. Similar molecular complexes to are formed in Deep Eutectic Solvents (DES). DESs are a family of ionic-like fluids with characteristic features of abnormally deep melting point depression for the eutectic composition of certain hydrogen bond donors (HBDs) and acceptors (HBAs) [1]. From a polymer chemistry perspective, also monomers could be components of DESs and serve both as HBD (e.g methacrylic acid) or as HBA (quaternary ammonium vinyl derivatives) [2]. This subtype of DES is known as a Deep Eutectic Monomers (DEMs). DEMs are new systems, not studied previously, and therefore the polymerization processes in such systems are poorly understood [3]. It is known that the anion structure of HBA in DEM determines the strength of hydrogen bonding in molecular complexes formed between HBA and HBD [4], [5]. However, the influence of the anion structure of the quaternary ammonium salt (HBA) on the intermolecular interactions in DEM systems, and therefore the impact of this factor on the polymerization process of DEMs has not been investigated yet.

In our research we examined the impact of anion in quaternary ammonium salts on photopolymerization of MAA. Four ammonium salts with different anions and the same cation (tetrabutylammonium chloride (Cl^-), tetrabutylammonium bisulfate (HSO_4^-), tetrabutylammonium nitrite (NO_3^-) and tetrabutylammonium tetrafluoroborate(BF_4^-)) forming DEM with MAA were investigated. As a part of the study we examined physicochemical properties of DEM such as NMR, FTIR spectroscopy, changes in density and viscosity for compositions with different acid to salt molar ratio. In addition, we determined the conversion curves by RT-FTIR experiment in order to investigate the changes in the initial rate of polymerization.

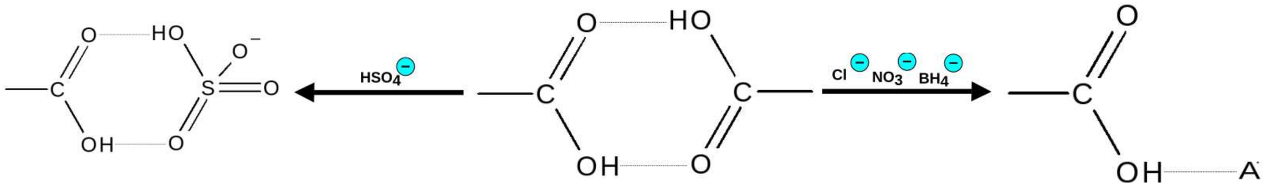

Figure 1. Schematic representation of the hydrogen bond formation between methacrylic acid and different types of anion in tetrabutylammonium salt

Keywords: Radical polymerization, Methacrylic acid, Deep Eutectic Monomers

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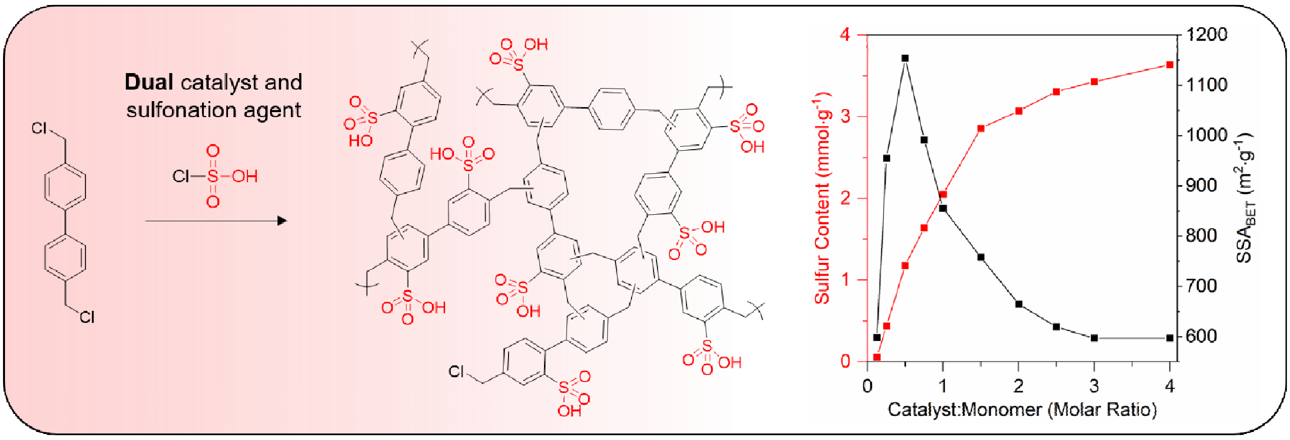
A One-Pot Route to Fine-Tuned Hypercrosslinked Polymer Solid Acid Catalysts

A. Blocher,[1] F. Mayer,[1] P. Schweng,[1] T. Tikovits,[1] R. T. Woodward[1*]

[1]*Institute of Materials Chemistry and Research, Faculty of Chemistry, University of Vienna, Währinger Straße 42, 1090 Vienna, Austria.*
[*]*Corresponding Author's E-mail address: robert.woodward@univie.ac.at*

Hypercrosslinked polymer-based solid acid catalysts are promising alternatives to homogeneous equivalents due to their low-costs and ease of separation from reaction products.[1] Currently, however, their production is time consuming and lacking control. Here, we present the use of a dual polymerisation catalyst and sulfonation agent in the bottom-up synthesis of hypercrosslinked solid acid catalysts. This approach produces highly sulfonated networks in <1 day, as compared to 5-6 days using conventional approaches, while significantly reducing reagent quantities required for their synthesis. By varying the feedstock ratio of aromatic monomers with the multifunctional chlorosulfonic acid catalyst/sulfonation agent, excellent control over the resulting polymers porous properties and sulfonation density are exhibited, demonstrating broad and judicious catalyst design.[2] The ability of these polymers to act as solid acid catalysts is demonstrated on model reactions as well as biomass conversions, such as the selective transformation of fructose into 5-(hydroxymethyl)furfural. We will show that the ability to fine-tune polymer properties has a dramatic effect on their catalytic performance and allows for the identification of key catalyst properties for optimisation.



Keywords: Hypercrosslinked polymers, heterogeneous catalysis, porous polymers

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Sequence-defined Mikto-arm Star-shaped Macromolecules

Resat Aksakal*, Melissa Reith, Irene De Franceschi, Matthieu Soete, Nezha Badi and Filip Du Prez*

Polymer Chemistry Research Group, Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281 S4 bis, B-9000 Ghent, Belgium.
Resat.Aksakal@ugent.be
Filip.DuPrez@ugent.be

In a polymer, the control over the sequence or the polymer length is not necessarily absolute and the properties of the obtained polymer can be affected by the inherent molecular weight distribution. Inspired by synthetic techniques found in nature, notably by the functioning of biomacromolecules such as DNA or proteins, polymer chemists are currently looking for more precision chemistry tools in order to prepare synthetic uniform macromolecules with unprecedented properties.[1] This strong search for ultraprecise, discrete macromolecules (i.e. strictly monodisperse) led to the development of new synthetic approaches or to the reuse/adaptation of already established chemistry tools for their preparation.[2] While some elegant approaches result in the synthesis of discrete macromolecules that are linear, the precision synthesis of sequence-defined star-shaped macromolecules is still a major challenge. In fact, the full potential of discrete macromolecules will only be unleashed when it will become possible to build on the 1D chemical control to reach 3D spatial precision.

In this talk, a robust strategy is presented that not only allows the preparation of sequence-defined mikto arm star-shaped macro-molecules (disperity of 1.00), but also the synthesis of a series of unprecedented discrete, multifunctional complex architectures with molar masses up to 20kDa. The iterative approach reported makes use of readily available building blocks such as acrylates and amino alcohols. It results in asymmetrically branched macromolecules that can consist of monodisperse three-, four- or five-arm macromolecules, with high purity and yields. This effective strategy drastically improves upon synthetic abilities of polymer chemists by enabling simultaneously sequence definition, precision insertion of branching points, as well as the orthogonal end-group functionalization of complex polymeric architectures. This is particularly interesting in biomedical applications for which multiple and different functional moieties on a single discrete macromolecule are needed.

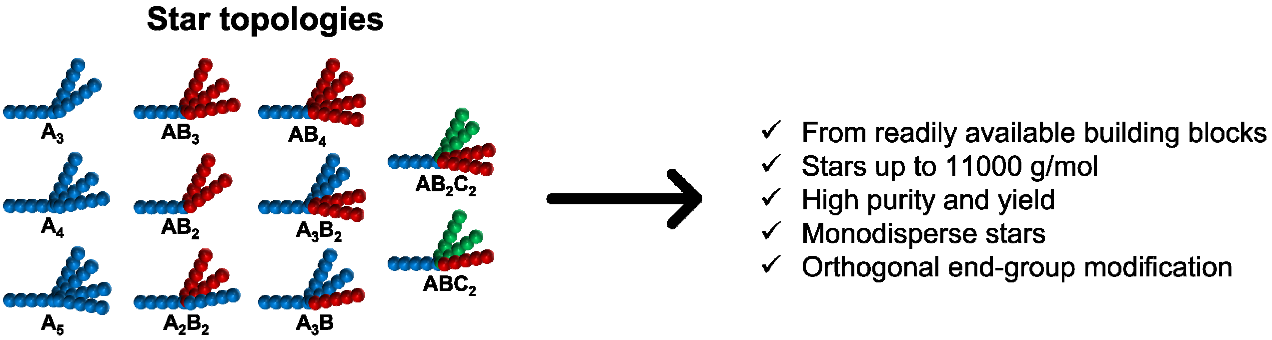

Figure 1: An overview of possible star topologies that can be targeted using the newly described approach.

Keywords: Star polymers, sequence-control, end-group modification

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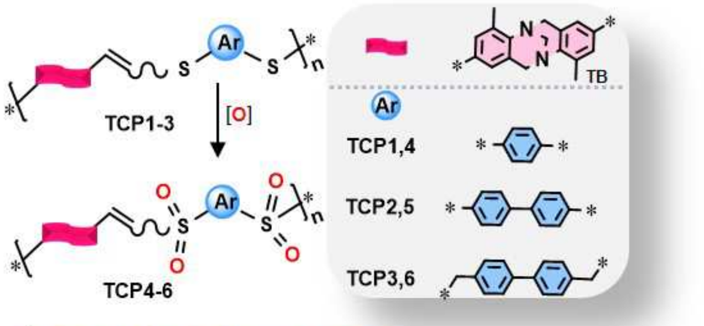
Selective removal of toxic organic dyes using tröger base-containing sulfone copolymers made from a metal-free thiol-yne click reaction followed by oxidation

Alameddine, Bassam*; Baig, Noorullah;Shetty, Suchetha
Department of Mathematics and Natural Sciences, Gulf University for Science and Technology, Kuwait
(alameddine.b@gust.edu.kw, www.gust.edu.kw)

Three copolymers TCP1–3 bearing Tröger's base (TB) units intercalated with various thioether groups were synthesized using a catalyst-free thiol-yne click reaction. TCP1–3 display excellent solubility in common organic solvents allowing for their structural, and photophysical characterization. The thioether groups in TCP1–3 were selectively oxidized into their respective sulfone derivatives under mild oxidation reaction conditions affording the postmodified copolymers TCP4–6. Investigation of organic dye uptake from water by TCP1–6 proved their efficiency as selective adsorbents removing up to 100% of the cationic dye methylene blue (MEB) when compared to anionic dyes, such as Congo red (CR), methyl orange (MO) and methyl blue (MB). The sulfone-containing copolymers TCP4–6 display superior and faster MEB removal efficiencies with respect to their corresponding synthons TCP1–3.



- ✓ Catalyst-free click polymerization
- ✓ Selective oxidation and Selective cationic dye adsorption
- ✓ Oxidized polymers TCP4-6 enhances the dye adsorption

Keywords: Tröger’s base; Click-chemistry; Catalyst-free polymerization; Poly(thioethers); Polysulfones; Dye adsorption

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From linear sequence-defined macromolecules to advanced multifunctional architectures

Nezha Badi,* Resat Aksakal, Irene De Franceschi, Chiel Mertens, Melissa Reith, Matthieu Soete and Filip Du Prez

[1]*Polymer Chemistry Research Group, Center of Macromolecular Chemistry, Department of Organic and Macromolecular Chemistry, Faculty of Science, Ghent University, Krijgslaan 281, Ghent B-9000, Belgium*
**Nezha.Badi@UGent.be*

The last two decades witnessed an evolution in polymer science with the growing interest in precision macromolecular chemistry.[1] Historically, controlling molecular weight, polymer architecture or lowering the dispersity were among the principal targets, however, these parameters are not sufficient if one aims at reaching more advanced properties or creating a material with numerous versatile functionalities. Controlling the primary structure of a polymer, i.e. the way monomers are connected to each other, the place where a certain functional group is introduced, the monomer order, dispersity etc. will lead to the formation of synthetic macromolecules having innovative properties.

In this presentation, synthetic methodologies for the preparation of sequence-defined linear and branched macromolecules will be presented.[2,3] The possibility of post-synthesis functionalisation will be demonstrated and some applications for the formed structures will be highlighted.[4]

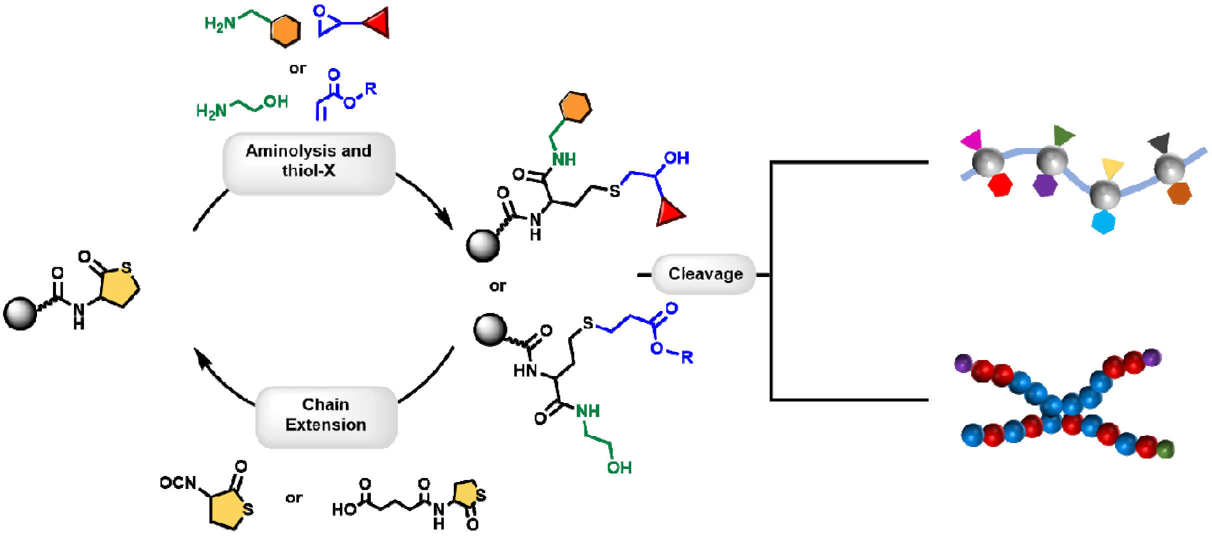

Figure 1. Simplified overview of two possible methodologies for the formation of linear and star-shaped multifunctional sequence defined macromolecules

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Polymers from biobased itaconic acid: synthesis and structure

Szczepan Bednarz[1*], Kacper Mielczarek[1]

[1]*Cracow Univeristy of Technology Faculty of Chemical Engineering and Technology, Kraków, Poland*
[*]*sbednarz@pk.edu.pl*

Itaconic acid (IA) is a natural unsaturated carboxylic acid produced on an industry scale by biotechnological processes. Recently, this monomer has attracted business interest as it is renewable and shares some chemical similarities with the petrochemical monomers acrylic and methacrylic acids. In addition, IA is a monomer that can be polymerized in several ways (Fig. 1), providing a wide range of polymers with interesting properties. For this reason, in the last few years several large R&D projects have been carried out in the European Union, which focused on the technological development of IA in polymers and plastics production: Bio-Qued (budget €11 million), Biocore (€20 million), BioCon-SepT (€13 million). These projects have involved leading European universities as well as chemical industry giants such as Evonik, Arkema, Itaconix or Cargill. Unexpectedly, an obstacle to a greater industrial use of this acid is, among others, limited understanding of IA polymerization processes, including radical polymerization. Here we report our results on the radical polymerization of IA in both water and in deep eutectic mixtures [1-7] leading to low, medium and high molecular weight polymers with linear, branched or crosslinked architecture.

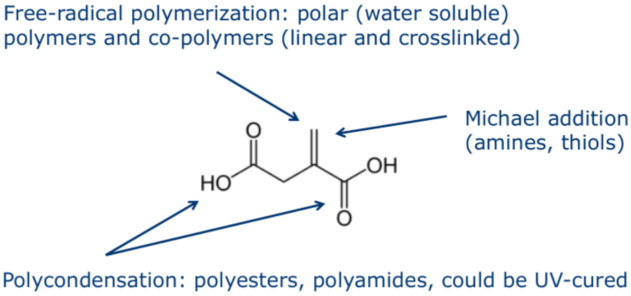

Fig. 1 Itaconic acid structure showing vinyl and carboxylic groups that allows polymerization of this monomer via polyaddition or polycondensation.

Keywords: renewable monomers, radical polymerization, Deep Eutectic Solvents

Acknowledgments

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Non-covalent Supramolecular AB Diblock and Asymmetric A_1BA_2 Triblock Copolymers: Synthesis and Microphase Separation

Saibal Bhaumik,[1] Konstantinos Ntetsikas,[1] Wenpeng Shan,[2] Edwin Thomas[2] and Nikos Hadjichristidis*,[1]
[1]*Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia.*
[2]*Materials Science and Engineering Department, Texas A & M University, College Station, TX 77843. USA.*
**E-mail: nikolaos.hadjichristidis@kaust.edu.sa*

Block copolymers have undergone extraordinary evolution from simple surfactant materials to an expansive class of macromolecules. Self-assembly of block copolymers is considered an attractive means of generating varieties of nanostructures and patterning over a large area. One way towards complex supramolecular structures is to synthesize the suitable functional homopolymer or block copolymer precursors.[1] Many intermolecular interactions like hydrogen bonding, π-π stacking, ionic interactions, and metal-ligand interactions can assist in building complex supramolecular architectures.[2] Reversibility, directionality and self-organization nature makes hydrogen bonding one of the most common motifs to design and construct supramolecular polymers with complex macromolecular architecture. 2,6-Diaminotriazine (DAT) and thymine (Thy) are two common triple hydrogen bonded systems for the construction of supramolecular structures.[3-4] In this work, supramolecular diblock (A-*sb*-B)[5] and asymmetric triblock (A_1-*b*-B-*sb*-A_2)[6] copolymers were synthesized *via* non-covalent hydrogen bonding among well-defined thymine end-functionalized polyisoprene (PI-Thy) or polystyrene-*b*-polyisoprene (PS-*b*-PI-Thy) and diaminotriazine end-functionalized polystyrene (PS-DAT). The complementary DAT/Thy interaction resulted in the microphase separation of the supramolecular diblock (A-*sb*-B) and asymmetric triblock (A_1-*b*-B-*sb*-A_2) copolymer system. Detailed characterization of all functionalized homopolymers and covalently linked block copolymers was carried out *via* proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy, gel permeation chromatography (GPC), matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry and differential scanning calorimetry (DSC). The self-assembly process of supramolecular diblock (A-*sb*-B) and asymmetric triblock (A_1-*b*-B-*sb*-A_2) copolymers was evidenced by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) measurements.

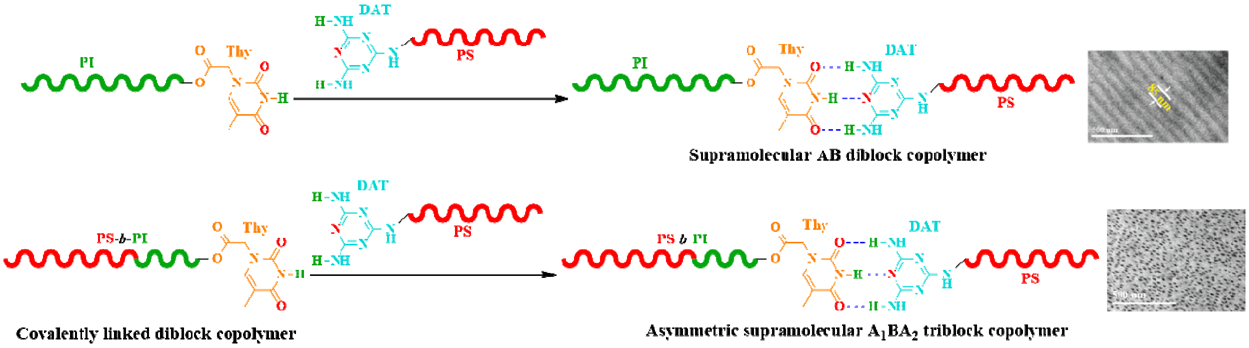

Figure 1: General scheme for the synthesis of hydrogen-bonded diblock (A-*sb*-B) and asymmetric triblock (A_1-*b*-B-*sb*-A_2) copolymers and their corresponding TEM images.

Keywords: Hydrogen bonding, anionic polymerization, supramolecular chemistry, microphase separetion

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Preparation of micro- and nanoparticles by photo-atrp-induced self-assembly in flow reactors in the presence of oxygen

Dmitrij Bondarev[1*], Christyowati Primi Sagita[1,2], Jaroslav Mosnáček[1,3]

[1]*Polymer Institute of Slovak Academy of Sciences, 841 45 Bratislava, Slovakia*
[2]*Faculty of Natural Sciences, Comenius University in Bratislava, 842 15 Bratislava, Slovakia*
[3]*CEMEA, Slovak Academy of Sciences, 845 11 Bratislava, Slovakia*
[*]*dmitrij.bondarev@savba.sk*

Preparation of copolymer amphiphilic micro- and nanoparticles in one pot system combining several approaches: (i) robust and versatile photo-controlled ATRP allows polymerization even in the presence of oxygen [1], (ii) Polymerization-Induced Self Assembly (PISA) can provide a way of achieving supramolecular assemblies in high yields under mild and/or even reproducible conditions and (iii) flow reactors enable fast and controlled polymerizations with even possibility of online analysis and flexible variation of reaction conditions. In addition, these set-up can be used for any suitable monomers including renewable [2]. In this contribution we aimed at block copolymers consisting of hydrophilic blocks from either linear PEG or containing PEG side groups.

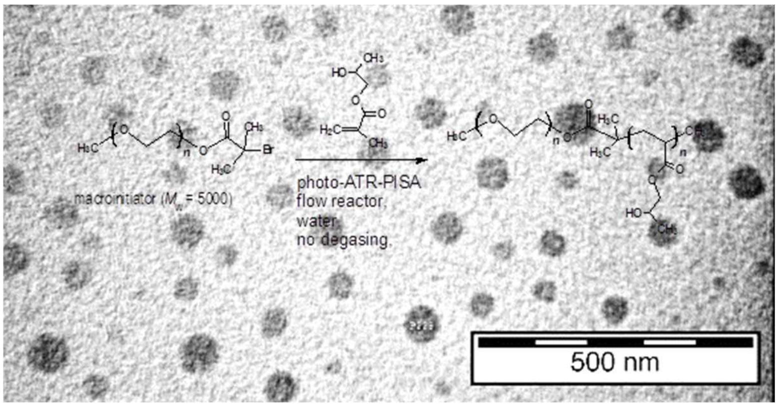

Figure 1: TEM micrograph of particles of PEG-HPMA copolymer prepared by photo-flow ATR-PISA without degassing in water.

These hydrophilic blocks are combined with hydrophobic block based on water soluble monomers like 2-hydroxypropyl methacrylate or glycydyl methacrylate. Resulting copolymers form various supramolecular particles from spherical to worm-like particles and aslo mixed architectures.

Keywords: ATRP, PISA, flow reactor, self-assembly, oxygen-tolerant polymerizations

Acknowledgments
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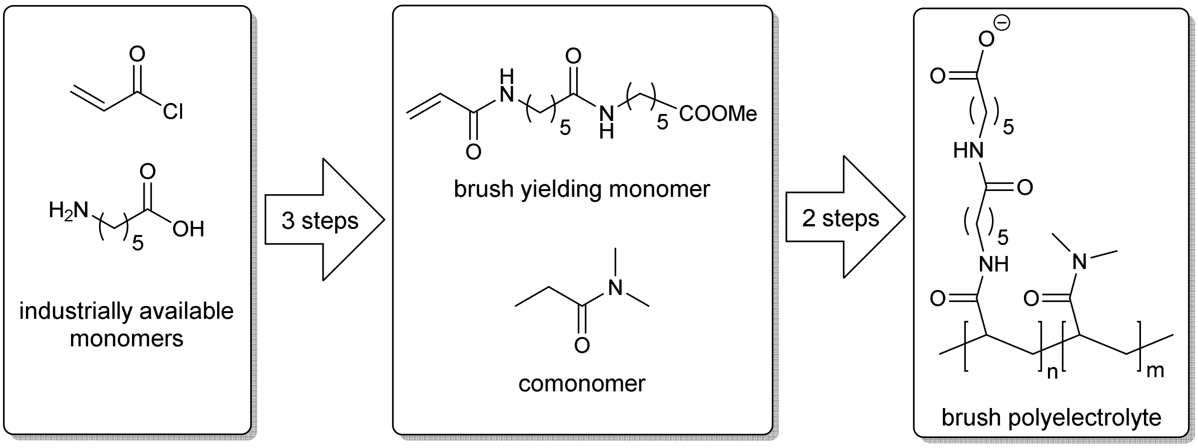
Synthesis and characterization of charged brush polymers

Kristina Durstberger[1], Klaus Bretterbauer[1*]

[1] *Institute for Chemical Technology of Organic Materials, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria*
**Klaus.Bretterbauer@jku.at*

Brush polymers are nanomaterials with adjustable molecular architecture that enables a wide range of applications e.g., antiadhesive materials for antibiofilm coatings [1], intrinsic lubricants [2], and drug delivery systems [3]. Charged polymers, also called polyelectrolytes, are macromolecules that contain charges of the same sign (oppositely polyampholytes include charges of both signs) obtained through functionalization with various anionic or cationic moieties. Variation of the charge density allows the control of properties e.g., (water) solubility, swelling, and rheological features such as viscosity. Herein we describe the synthesis and characterization of polyacrylamide based charged brush polymers with tailored molecular structure. Brushes are designed as polyamide-dimers that allow a structured alignment through hydrogen bonds terminated with carboxylic acid functionalities. The brushes are linked via the acrylamide bond to the backbone. Charge density is controlled by copolymerization and partial deprotection of the carboxylic acid methyl ester. Radical polymerization can be carried out in aqueous and organic solvents allowing the utilization of numerous polar to non-polar comonomers that can affect alignment and/or adhesion of the backbone to surfaces. The described brush polyelectrolyte shows swelling in polar and non-polar organic solvents e.g, *N*,*N*-dimethylformamide, dimethylsulfoxide, dichloromethane, and the free carboxylic acid can readily be exchanged with bulky counterions like tetrabutylammonium. The solvent-conditioned material appears with an easily deformable, rubberlike tough behavior. In contrast, using hard counterions such as lithium the polymer shows no swelling and a hard, brittle structure.



Keywords: brush polymer, polyelectrolyte, tailored polymer, synthesis, characterization

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Synthesis of Polyurethanes through Reactive Extrusion Assisted by Alternative Energy Sources

A. M. Buczko[1*], S. Kemmerling[1], C. Backhaus[1], S. Deshmukh[2], R. Brüll[2], C. Hübner[1], P. Elsner[1]

[1]*Fraunhofer Institute for Chemical Technology ICT, Joseph-von-Fraunhofer-Straße 7, 76327 Pfinztal, Germany*
[2]*Fraunhofer Institute for Structural Durability and System Reliability LBF, Bartningstraße 47, 64289 Darmstadt, Germany*
[*]*aleksandra.buczko@ict.fraunhofer.de*

Hydrophobically modified ethoxylated urethanes (HEURs) are associative polymers widely applied as thickening additives in waterborne systems, such as paints and coatings.[1] The thickening behaviour is ascribed to the telechelic architecture of the HEUR molecules, which contain a hydrophilic backbone end-capped with hydrophobic tails. The hydrophilic core is typically formed through the reaction of poly(ethylene glycol) with diisocyanate which is then modified with short aliphatic alcohol. Traditionally, HEURs are obtained in ton-scale batches, suffering from limited reproducibility and long production times. The industrially accessible option to improve efficiency, reproducibility and flexibility of production is a drop-in transfer from batch to a reactive extrusion (REX) process. As a continuous approach, REX allows easy adjustment of processing parameters and material grades. The ability of the extruder to mix viscous polymer melts ensures good homogenization and uniform quality of the product.[2] However, the residence time in the extruder restricts the reaction time to only a few minutes, in contrast to hour-long batch operations. To assure sufficient conversion in REX the conditions must be tailored to the reaction system.

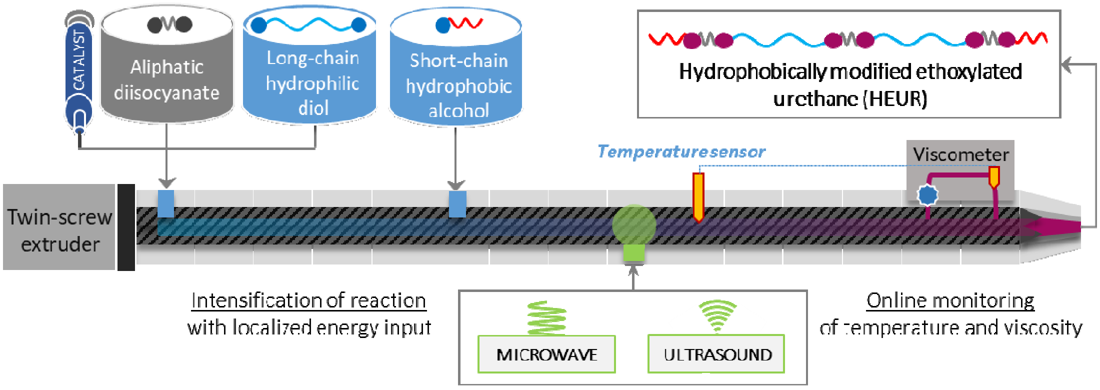

Figure 1. Use of extruder as a continuous reactor for intensified synthesis of polyurethane thickeners

Our work is therefore focused on the development of a REX process for HEUR production, in which ultrasound or microwave locally intensifies the reaction (Figure 1). Our results demonstrate the impact on the conversion, depending on the processing conditions and the input of alternative energy. Online monitoring tools combined with analytical characterization by spectroscopy, size exclusion chromatography and rheometry provide an insight into the structural build-up of the obtained HEURs.

Acknowledgments

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Novel bio based foams using the Aza-Michael reaction

Guilhem Coste[1], Claire Negrell[1], Sylvain Caillol[1]*
[1] *ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France*
[*sylvain.caillol@enscm.fr](mailto:sylvain.caillol@enscm.fr)

Polyurethane is one of the most common material in the world, which are mainly used as foam from our bed mattresses to the insulation of our houses.[1] These polymers are made from petroleum based polyisocyanate and polyols. To go to environmentally friendly solution, it is urgent to manufacture foams with equivalent properties and if it is possible with biobased ressources. Currently, some routes have been tried as bio-based non-isocyanate polyurethane or PHU. However, despite their interesting final properties, their lack of reactivity limit their interest.[2,3] Another attractive route is the Aza-Michael (AM) reaction, e.g. the reaction between a Michael donor (e.g. amine) and a Michael acceptor (e.g. acrylate). In term of green chemistry the Aza-Michael reaction had a 100% atom economy, can be conduct at room temperature and avoid the use of toxic isocyanate.[4] Moreover, the AM reaction showed other similarities with isocyanate/polyols reaction such as the exothermy. Thus, the AM reaction seems highly interesting since biobased multi functional Michael acceptor e.g. acrylates can be obtain from the ring opening of epoxidized vegetable oil.5 In the same way, the Michael donor can also be biobased, the cadaverin can be obtain from lysine and priamine from cardanol. For now, few articles were published about the synthesis of thermosets using this reaction with bio based acrylate and bio based amine.[5] These different publications showed the interest of the reaction in order to obtain materials. Nevertheless, no foams synthesis were described using AM reaction to our knowledge. The only paper describing the foam synthesis is using the Michael addition with acetoacetate monomers. In this work, we present novel foams using commercial acrylated soybean oil and bio based amines. The synthesis condition were optimized in order to obtained a foam under mild conditions. Different formulations were carried out in order to explore the properties of biobased Aza-Michael foams. Thermals and mechanical analysis were carried out in order to measure the difference due to the formulation.

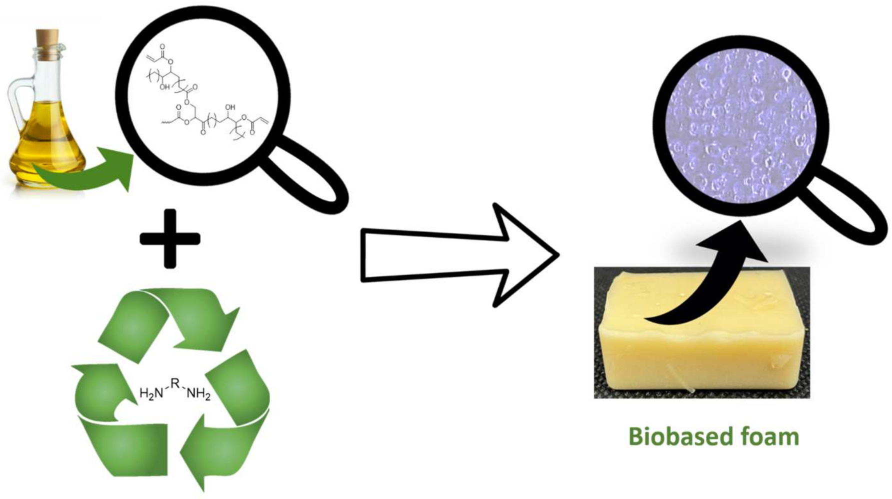

Figure 1: Aza-Michael foam from acrylated soybean oil and amines.

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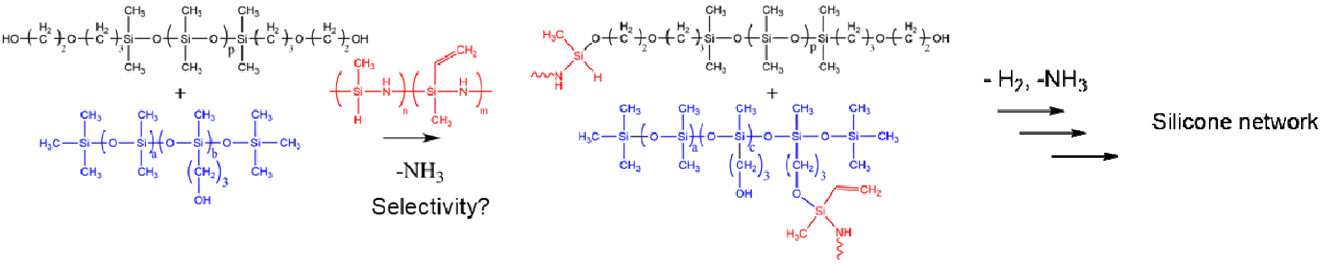
Curing of silicones by use of polysilazane as a coupling agent

René Sønderbæk-Jørgensen[1,2], Kim Dam-Johansen[2], Anne L. Skov[1], Anders E. Daugaard[1*]

[1]Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 227, 2800 Kgs. Lyngby, Denmark
[2]The Hempel Foundation Coating and Science Technology Centre (CoaST), Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Building 229, 2800 Kgs. Lyngby, Denmark
[*]adt@kt.dtu.dk

Commercial room temperature vulcanised (RTV) silicones are popular for their unique properties and broad application span. Standard silicone curing methods such as condensation and hydrosilylation require the use of toxic and expensive metal catalysts, such as tin and platinum. While catalyst free methodologies for curing silicone networks, such as autooxidative curing and 1,3-dipolar cycloaddition, do exist,[1,2] there is a need for additional silicone curing methodologies that allow for effective curing in ambient conditions without residual metal catalysts being trapped within the product.

We have investigated a number of silicone systems exploiting the reactivity of polysilazanes for activation of silicone curing reactions for thin films as well as free standing elastomers. The curing reaction itself was mapped by NMR on model compounds, effectively confirming the selectivity and operational span of the system (Scheme 1). Based on the NMR study, we have designed a range of systems that can be cured without a catalyst at ambient temperature. The method was tested for thin film silicones as well as elastomers. Thin films showed properties comparable to classical condensation silicones, with good adhesive properties and acceptable hydrolytic stability when tested as antifouling coatings. Similarly, soft elastomer systems containing silica as a reinforcing agent were prepared, resulting in elastomers with Young's moduli between 0.2 - 2.38 MPa and elongations between 100-180 %.



Scheme 1: Activated condensation reaction between polysilazane and various alcohol species permits RT curing of silicones

This new versatile methodology for curing silicones offers the possibility of replacing currently used curing systems and preventing the use of metal catalysts.

Keywords: Silicones, Metal Catalyst free, RT condensation

Acknowledgments
The authors would like to thank the Hempel Foundation for financial support to CoaST, The Hempel Foundation Coating Science and Technology Centre, and Siltech (Canada) and Merck KGaA (Germany) for donating materials.

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Monodisperse and reusable soluble supports for upscaling the synthesis of sequence-defined polymers

I. De Franceschi[1], C. Mertens[1], N. Badi[1], F. Du Prez[1*]

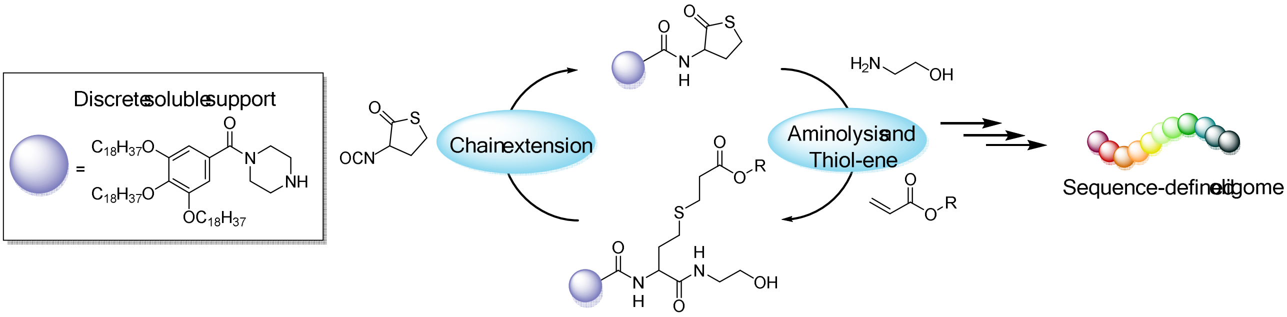
[1] Polymer Chemistry Research Group, Center of Macromolecular Chemistry, Department of Organic and Macromolecular Chemistry, Faculty of Science, Ghent University, Krijgslaan 281, Ghent B-9000, Belgium
[*]filip.duprez@ugent.be

In contrast to biomacromolecules, synthetic polymers generally lack a perfectly defined monomer sequence and one of the challenges of polymer chemists these days is to gain more control over the primary structure of synthetic polymers.[1] For the design of these sequence-defined oligomers, chemists mainly rely on iterative synthetic protocols.

Different strategies could be used to perform their synthesis and until now the use of solid supports proposed for the first time by Merrifield for peptides[2], is the main one. Solid-phase synthesis reactions are carried on using high excess of reagents and producing by-products that can be removed with easy washing and filtrations steps, since they are not covalently attached to the resin. Nevertheless, solid-phase synthesis suffers from some limitations (*e.g.* high equivalents of reactants, non homogeneous reactions, high cost etc.) that only allows the synthesis on milligram scale in the laboratory, making it difficult to upscale the product and limiting the applications[3]. Chemists are now focusing on solution reactions that do not show constraints regarding the reaction scale, trying also to circumvent the disadvantages that could decrease the overall yield, such as column chromatography purification. The use of soluble supports is an alternative that combines the best aspects of solution- and solid-phase synthesis.[4, 5] These supports are soluble in the reaction medium, yet provide properties that can be exploited to isolate the support-attached product from the crude medium.

This work presents a strategy to upscale the synthesis of sequence-defined oligomers prepared with a thiolactone-based protocol using a monodisperse support that can be designed to be reused (Scheme 1). This support composed of three C_{18} alkyl chains[6] has several advantages: it is affordable and easy to prepare, iterative synthesis can be performed in solution, characterisation is facilitated by monodispersity and the purification step is reduced to a simple precipitation in a polar solvent.

As a proof of concept, an octamer with different acrylates has been synthesised and fully characterised by NMR, SEC and MALDI-ToF. Additionally, discrete supports with cleavable linkers have been synthesised and used to build oligomers on a 10 g scale.



Scheme 1: Iterative protocol for the synthesis of sequence-defined oligomer based on thiolactone chemistry using the discrete soluble support.

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The Effect of Solvents on the Propagation Rate Coefficient of Acrylic Acid and Other Self-Associating Monomers

E. Dušička[1*], A. Urbanová[1], A. Kleinová[1], V. Raus[2], I. Lacík[1,3*]

[1] *Polymer Institute of the Slovak Academy of Sciences, Bratislava, Slovakia*
[2] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic*
[3] *Centre for Advanced Materials Application of the Slovak Academy of Sciences, Bratislava, Slovakia*
[*] *edusicka@gmail.com, igor.lacik@savba.sk*

The propagation rate coefficient (k_p) of acrylic acid (AA) in bulk was found to decrease upon the addition of propionic acid (PA), the saturated analogue of AA [1]. Such a change in k_p was unexpected since both acids are of a similar chemical structure and theoretically should show the same intermolecular hydrogen bonding interactions between the carboxylic acid groups.

In order to understand this peculiar decrease in k_p, we employed the pulsed-laser polymerization method in combination with size exclusion chromatography to determine k_p of AA in different media, including H-bonding solvents (DMSO, DMF [2], ethanol [2], methanol, acetic acid, formic acid) and inert solvents (toluene, benzene) in a wide concentration range. Additionally, AA was also polymerized in the presence of up to 20 wt.% of unsaturated carboxylic acids (benzoic acid, BeA, and its 2-methoxy and 3-methoxy derivatives). Arrhenius parameters for k_p of AA in different solvents were determined. FTIR spectroscopy was employed to follow the extent of formation of H-bonded structures, particularly carboxylic acid dimers, and the data were evaluated in the context of the observed k_p changes. The behavior of AA was also compared to that of methacrylic acid polymerized in both bulk and in its saturated analogue, isobutyric acid.

For 20 wt% AA at 25 °C, k_p values of AA were found to decrease to about 30–60 % of the bulk value for all the studied H-bonding solvents except for FA that led to a slight, about 15–20 %, increase in k_p; the dilution of AA with inert solvents afforded k_p values similar to bulk. The addition of BeA and its derivatives either did not vary the k_p value (BeA) or showed up to 20 % increase in k_p (2-methoxy and 3-methoxy derivatives) when compared to bulk AA.

The obtained data indicate that the k_p of AA is lower in environments that provide H-bonding interactions with AA and higher in environments that support the AA-AA H-bond dimerization (inert solvents) or provide dimers of AA with carboxylic acids with conjugated double bonds (BeA and derivatives; cf. unsaturated carboxylic acids). Additionally, a good correlation between the magnitude of k_p of AA and the pK_a of carboxylic acid used as the solvent was observed, with stronger acids (particularly FA) providing higher k_p.

Summarizing both the to-date published k_p values and the results obtained in this study, it is proposed that the effects of different types of solvents on k_p can be predicted in advance based on the presence or absence of H-bond-mediated self-association in the monomer bulk system. Therefore, division into self-associating and non-self-associating monomer families can be implemented.

Acknowledgments

The authors would like to acknowledge BASF SE (Ludwigshafen, Germany) for the financial support and laboratory technician Eva Hipká for helping with some experiments.

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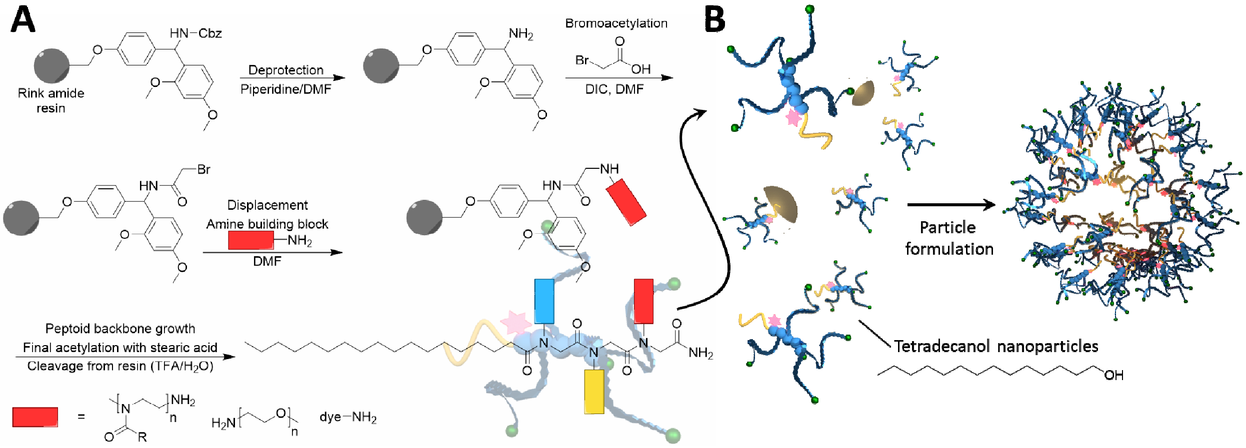
Solid-phase synthesis as strategy for the generation of multifunctional, branched polymers

J. K. Elter[1]*, M. Hrubý[1]*

[1] *Institute of Macromolecular Chemistry CAS, Prague 162 00, Czech Republic*
**elter@imc.cas.cz, mhruby@centrum.cz*

The development of modern drug formulations leads beyond identifyig and optimizing drug molecules. Active substances have to be protected from premature decomposition, and it has to be ensured that they arrive at their target destination in the body to increase their efficiency and prevent negative side effects. For this purpose, different types of polymer-based or polymer-stabilized nanoparticles are developed [1].
The polymeric stabilizers applied in these nanoparticles often have to fulfil numerous functions: They have to be biocompatible, enable sufficient structural stabilization of the nanoparticle, allow for the attachment of functionalities that help the particle to reach its target site and fluorescent markers for *in vitro* and *in vivo* studies, and, last but not least, they have to prevent the escape of the drug molecule from the nanoparticle, which may also be achieved *via* covalent attachment of the latter to the polymer. Combining suitable functionalities for all these purposes in one polymer can be challenging.
This work focuses on the application of solid phase peptoid synthesis to connect different building blocks fulfilling the purposes listed above [2]. The advantage of this novel approach is the possibility to connect an exact number of different functionalities in a preferred to generate tailor-made, highly defined functionalized oligomeric or polymeric systems.



(A) Synthetic stragtegy for the generation of multifunctional, branched polymers by solid-phase peptoid synthesis. (B) Generation of solid lipid-core nanoparticles from the polymeric structures [3].

The presented oligomers and polymers are synthesized from building blocks with terminal primary amine groups which are connected by bromoacetic acid as a linker, thereby forming a peptoid-like backbone with pendant polymeric "arms". Further displacement steps can be carried out to introduce additional functions or reactive groups into the peptoid backbone. A lipophilic anchor introduced at the chain end enables application these polymers to stabilize lipid nanoparticles in solution or in biological membranes [3].

Acknowledgments

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Iron-Catalyzed Atom Transfer Radical Polymerization

M. Fantin[1*], G. Gazzola[1], F. Lorandi[1], E. M. Benetti[1], K. Matyjaszewski[2], S. Dadashi-Silab,[2,3] A. A. Isse[1]

[1]*University of Padova, Via Marzolo 1, Padova, Italy*
[2]*Center for Macromolecular Engineering, Carnegie Mellon University, 4400 Fifth Ave, Pittsburgh, PA, USA*
[3]*Cornell University, Ithaca, NY 14850, United States*

[*]*marco.fantin@unipd.it*

Atom transfer radical polymerization (ATRP) is a technologically and commercially important process of controlled radical polymerization.[1] Typically, ATRP is mediated by copper complexes with amine ligands, which enable an excellent control over the polymerization process. Cu catalysts, however, are expensive, toxic, and poorly soluble in apolar environments. On the other hand, iron is a cheap and abundant catalyst with low toxicity. In this presentation, the well-controlled ATRP with simple Fe catalysts is presented, both in organic and aqueous media.

In apolar environments (e.g. aromatic solvents, bulk hydrophobic monomers, etc.), $FeBr_3$ is a simple and well-soluble catalyst that offers excellent control over polymer growth. In aqueous environments, Fe(III)/EDTA is an inexpensive and cytocompatible catalyst that can control polymer growth both in solution and on surfaces.

Additionally, one of the benefits of ATRP and other controlled radical polymerizations is the ability to control polymer growth in time and space (temporal/spatial control) by using an external stimulus to trigger the polymerization. In this talk, a simple electrochemical system will be discussed using inexpensive Fe and Al electrodes. A Fe electrode can be used to provide the Fe ions to the polymerization solution, start/stop the polymerization on demand, and purify the obtained product by depositing the dissolved Fe ions onto the electrode surface at the end of the polymerization process.

Keywords: ATRP, CRP, controlled radical polymerization, catalysis, electrochemical polymerization

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A photolatent organophosphate for the local activation of dynamic exchange reactions in 3D printed photopolymers

C. Dertnig[1], G. Guedes de la Cruz[1], D. Neshchadin[2], S. Schlögl[3], T. Griesser[1*]

[1]*Institute of Chemistry of Polymeric Materials, Montanuniversität Leoben, Otto-Glöckel-Straße 2, 8700 Leoben, Austria*
[2]*Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9/I, 8010 Graz, Austria*
[3]*Polymer Competence Center Leoben GmbH, Roseggerstraße 12, 8700 Leoben, Austria*
[*]*Corresponding Author, e-mail: thomas.griesser@unileoben.ac.at*

Organophosphates are excellent transesterification catalysts in thiol-acrylate vitrimers because they are highly soluble in common acrylate monomers, effectively accelerate stress relaxation, and do not significantly affect cure performance and shelf life [1,2].

In this contribution, diethyl (2-nitrobenzyl) phosphate has been evaluated for the locally resolved activation of dynamic exchange reactions in photopolymers. The catalytic species diethyl hydrogen phosphate is generated upon UV exposure. The photocatalyst was added to a thiol-acrylate monomer system, which was processed by stereolithography using light of 460 nm. In the 3D printed polymer, stress relaxation experiments on untreated and UV-irradiated samples revealed the successful generation of the catalytic species and its efficiency as a transesterification catalyst. In these experiments, the orthogonality between the photopolymerization reaction and the activation process (i.e. photoreaction of the photolatent catalyst) could be demonstrated. The combination of the advantages of organophosphates as transesterification catalysts with the ability to locally control the activation of dynamic exchange reactions allows interesting applications with spatially resolved healing and shape memory properties.

Keywords: vitrimer, 3D printing, photocatalyst, organic phosphate, shape memory, self-healing

Acknowledgments

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Synthesis and characterization of borinic vitrimers

I. Göde,[1] M. Bonnard,[2] L. Chabaud,[2] A. Guerinot,[1]* M. Pucheault,[2] R. Nicolaÿ.[1]*

[1] Molecular, Macromolecular Chemistry and Materials, ESPCI Paris, CNRS, PSL University, Paris, France
[2] Institut des Sciences Moléculaires, Université de Bordeaux, Bordeaux, France
** amandine.guerinot@espci.psl.eu and renaud.nicolay@espci.psl.eu*

Vitrimers are cross-linked networks containing dynamic covalent bonds [1]. Within these networks, exchange reactions take place through an associative mechanism [2], which provides unique characteristics to these materials [1,2].

Borinic acid chemistry offers unique opportunities to design vitrimers with new properties. Borinic acid derivatives combine the strength of boron-oxygen dynamic bonds, already illustrated with dioxaborolane vitrimers [3], whith specific attributes, such as their hydrolytic stability, their charged or neutral character, and the labile N-B coordination bond in the case of borinato derivatives.

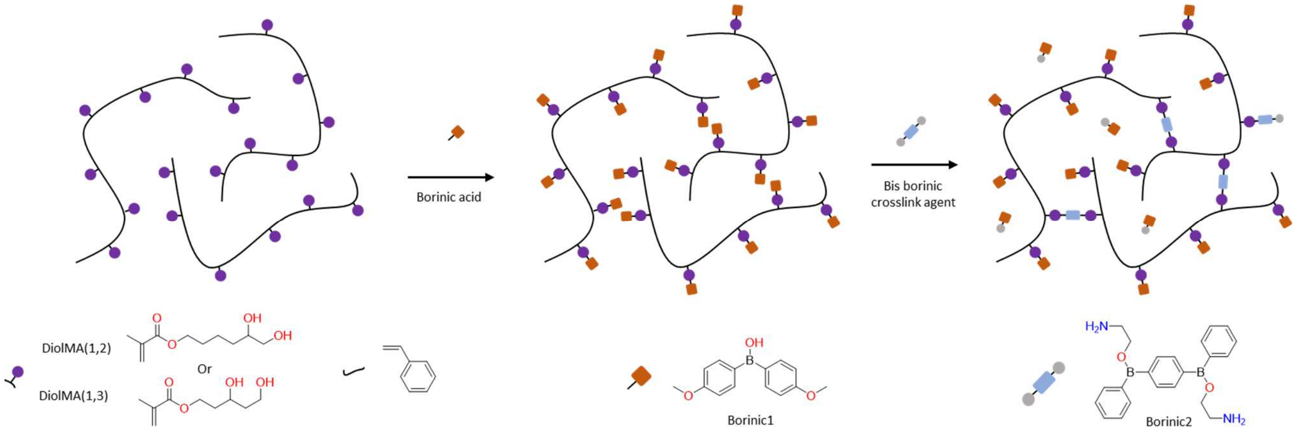

Figure 1. General synthetic scheme for the synthesis of borinic vitrimers.

To obtain these new materials, several free radical copolymerizations were carried out using two different monomers of interest, namely 5,6-dihydroxyhexyl methacrylate, DiolMA(1.2), or 3,5-dihydroxypentyl methacrylate, DiolMA(1.3) (Figure 1). The resulting copolymers were characterized by NMR, DSC, TGA, GPC, indicating that thermally stable (330°C) statistical copolymers with glass transition temperatures around 90 °C had been prepared. In order to obtain a vitrimer (Figure 1), a condensation reaction with dimethoxyphenylborinic acid (Borinic1) was performed followed by a cross-linking reaction with a bis-borinic compound (Borinic2). The first characterizations of these new polymers networks are under process including swelling and thermal stability tests. This approach constitutes an innovative route to obtain new materials from a chemistry still underused in the field of polymer materials

Keywords: Vitrimers, dynamic covalent chemistry, borinic esters, borinato derivatives

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Tailoring Entangled State for Ultimate Mechanical Properties in Linear Polyethylene Using Heterogeneous Catalytic System

Ravindra P. Gote[1,2], Dario Romano[1,2], Joris van der Eem[1], Sanjay Rastogi[1,2*]

[1] Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal, Kingdom of Saudi Arabia
[2]Aachen-Maastricht Institute for Biobased Materials (AMIBM), Faculty of Science and Engineering, Maastricht, Limburg, The Netherlands
e-mail: ravindra.gote@kaust.edu.sa; dario.romano@kaust.edu.sa; Sanjay.rastogi@kaust.edu.sa

Homogeneous catalysis route to ultrahigh molecular weight polyethylene (UHMWPE) with a reduced number of entanglements (disentangled for short) has led us to the remarkable engineering material which can be solid state processed to achieve ultimate mechanical properties.[1] However, for industrial production, there are few major challenges in using a homogeneous catalyst system such as uncontrolled polymer morphology leading to reactor fouling and wall sheeting. Heterogenization of the single-site catalyst is a viable route to overcome this challenge. However, the attempts made in this direction fall short in terms of mechanical properties and overall performance. Herein we report, for first time, a catalytic system that can produce disentangled UHMWPE with fine morphology without reactor fouling and wall sheeting. The characteristics of disentangled state of the nascent samples were characterized by a combination of differential scanning calorimetry and rheology. Solvent free solid-state processing of these polymers resulted in tensile strength and tensile modulus of 3.6 GPa and 150 GPa, respectively along the chain direction. The disentangled state and mechanical properties results were at par with the literature reports on disentangled UHMWPE obtained in the homogenoeus polymerization conditions.[1,2] These observations altogether strengthens the fact that the heterogeneous catalytic system, equivalent to homogeneous, holds potential in providing desired disentangled state, which is a requisite to achieve the ultimate mechanical properties. The work will address morphological variations in catalyst support and nascent polymer and its characterization.

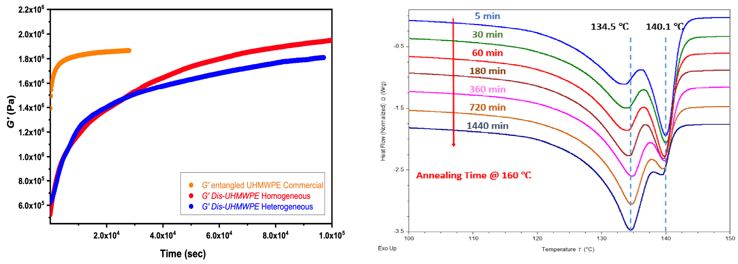

Figure 1: Comparison of storage modulus build-up between commercial, homogeneous and heterogeneous synthesized UHMWPE (left); DSC plots of UHMWPE synthesized using heterogeneous catalytic system to show entanglement density (right)

Keywords: heterogeneous catalysis, disentangled UHMWPE, solid-state processing

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Trichloroacetyl Isocyanate Adducts as a New Class of Initiators for Cu-RDRP

S. Gupta, M. Janata, E. Čadová, V. Raus*

Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2
162 06, Prague 6, Czech Republic
E-mail: raus@imc.cas.cz

In this study, we introduce adducts of trichloroacetyl isocyanate (TAI) as a new class of multifunctional initiators for copper-mediated reversible-deactivation radical polymerization (Cu-RDRP). TAI is known to react extremely rapidly and cleanly (no side products) with a range of functionalities, including hydroxy and amino groups [1], introducing thus Cu-RDRP initiation sites (the trichloroacetyl moiety) into a variety of substrates with unprecedented ease.

Using the TAI/methanol adduct (Figure 1) as a model initiator, we identified conditions for well-controlled Cu(0)- and/or Cu(I)-catalyzed Cu-RDRP of model monomers [styrene, methyl acrylate, and methyl methacrylate (MMA)], performed both in polar and non-polar solvents, affording defined polymers in a wide range of molecular weights. The developed conditions were then successfully applied to other acrylates and methacrylates, including polar ones. Importantly, via kinetic experiments and NMR and viscometry analyses, we established that the TAI-based initiating group can initiate up to three polymeric chains, which may be of a great importance in applications such as surface-initiated grafting. Additionally, using the "bifunctional" ethylene glycol/TAI adduct, model poly(2-hydroxyethyl acrylate) was prepared and subsequently exposed for 24 h to buffers of various pH. The SEC analysis confirmed the hydrolytic stability of the carbamate group within the initiator fragment in the pH range of 5 to 9.

Finally, we demonstrated the utility of the TAI-modification strategy in the chain topology control by performing a (de novo) one-pot synthesis of a graft copolymer, exploiting the *in situ* modification of a pre-formed polymeric backbone with TAI. Additionally, we also exemplified the applicability of the TAI adduct-initiated Cu-RDRP in the modification of natural materials. For instance, unprecedented instantaneous modification and dissolution of cellulose in DMSO upon the addition of a slight stoichiometric excess of TAI was achieved, and the prepared cellulose-TAI adduct was then successfully used for the initiation of Cu-RDRP of MMA. Similarly, the surface of filter paper was modified with TAI with spatial control, allowing for the growth of a macroscopic polymeric brush pattern in a subsequent step. In summary, the multifunctional TAI-based initiators hold a great promise for the facile preparation of complex polymeric architectures.

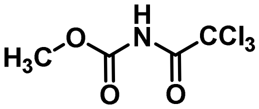

Figure 1. Methanol-TAI adduct

Keywords: Cu-RDRP, Trichloroacetyl Isocyanate, Cellulose, Initiators

Acknowledgments
Financial support from the Institute of Macromolecular Chemistry, CAS, is gratefully acknowledged.

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Synthesis of photoactive compounds and their application as initiators for photoATRP

Mária Gurská[1*], Anita Andicsová-Eckstein[1], Jaroslav Mosnáček[1,2]

[1]*Polymer Institute SAS, Dúbravská cesta 9, 845 41, Bratislava, Slovakia*
[2]*CEMEA SAS, Dúbravská cesta 9, 845 11, Bratislava, Slovakia*
[*]*maria.gurska@savba.sk*

PhotoATRP belongs to the group of reversible deactivation radical polymerization, which is able to prepare well-defined co-/polymers, for use in a variety of material applications. A key feature of this polymerisation is a requirement of a low radical concentration to form a well-defined polymer. Its advantage is tolerant to many functional groups and it is also tolerant to oxygen. Polymerization is mediated by light with a wavelength in the UV region or visible light region [1-3]. The photoactive compounds that absorb different wavelenght of light were designed and prepared. They supposed to have no or positive effect on the photoATRP process and provide a more sensitive system for studying the initiation efficiency and viability of photoATRP through combination of GPC and fluorescence spectroscopy. In the case of light absorption used in photoATRP, the photoactive initiator increases the initiation efficiency due to the absorption of light and its conversion to energy in the initiation stage of polymerization. Photoacive naphthalene-1,8-dicarboxylic acid derivatives (NI) were designed and used in the form of alkyl bromide initiators. The synthesis of NI initiators consists of two steps. The first step was to prepare naphthaleneimide with free OH groups from a commercially available anhydride. The second step consisted of Steglich esterification to form an ester bond with the corresponding carboxylic acids or their derivatives. The prepared initiators were characterized and for the first time applied in photoATRP in the polymerization of methyl acrylate and butyl acrylate in various solvents (DMF, DMSO) in the presence of air. The living end of the polymer was also confirmed by preparation of short oligomers as macroinitiators.

Keywords: photaATRP, photoacive compound, methyl acrylate

Acknowledgments
The authors thank grant agencies for financial support through projects APVV-19-0338, VEGA 2/0129/19. This work was performed during the implementation of the project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 313021T081 supported by the Integrated Infrastructure Operational Programme funded by the ERDF.

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Silane-Functionalized Liquid Butadiene Rubbers as Processing Aids for Silica-Filled Rubber Compounds

Haeun Choi[1], Donghyuk Kim[2], Gyeongdong Yeom[1], Hongil Joo[3], Hyunjong Paik[1*], Heungbae Jeon[3] and Wonho Kim[2]

[1]Department of Polymer Science and Engineering, Pusan National University, Busan, Korea
[2]School of Chemical Engineering, Pusan National University, Busan, Korea
[3]Department of Chemistry, Kwangwoon University, Seoul, Korea
**hpaik@pusan.ac.kr*

Recently, a lot of research are conducted on tire tread compounds, particularly using liquid butadiene rubber (LqBR) as processing aids to produce high-performance tires[1]. However, Non-functionalized LqBR has limitation such as low fuel efficiency due to free chain ends. In order to overcome this disadvantage, we designed a silane-functionalized LqBR that can form covalent bonds with silica (reinforcing fillers) and crosslink with base rubber to enhance the filler-rubber interaction[2]. The silane-functionalized LqBR was synthesized using a di-silane functionalized Azo initiator to form di-functionalized structure. The molecular weight of the synthesized polymer were measured by gel permeation chromatography (GPC). Nuclear magnetic resonance (NMR) spectroscopy was used to calculate the vinyl content and the silane group functionality (ie, f≈2). Compounds with the LqBR showed not only higher fuel efficiency but also lower rolling resistance and better abrasion resistance than commercial processing aids. We conformed applicability of the LqBR on high performance tire tread compounds by eliminating free chain ends.

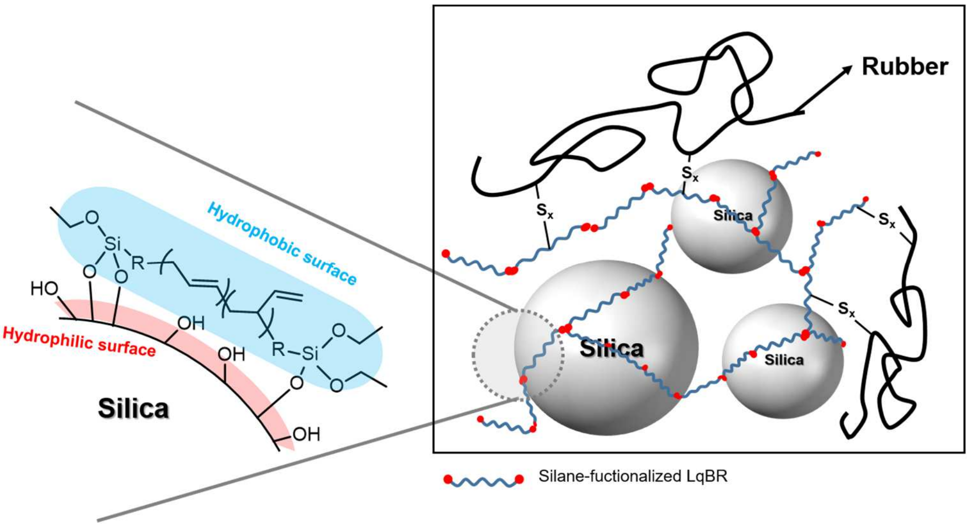

Figure 1. Structure of silica, base rubber and silane-functionalized liquid butadiene rubber in tire tread compounds

Acknowledgments

This work was supported by the Materials and Components Technology Development Program (20015701) grant funded by the Ministry of Trade, Industry, and Energy of Korea (MOTIE)

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Ionic Hyper-Cross-Linked Polyacetylenes with Chiral and Achiral Segments

Alena Hašková[1*], Lucie Havelková[1], Bogdana Bashta[1], Jan Sedláček[1], Eva Vrbková[2], Kateřina Zítová[2], Eliška Vyskočilová[2]

[1]*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Prague, Czech Republic*
[2]*Department of Organic Technology, University of Chemistry and Technology in Prague, Prague, Czech Republic*
[*]*alena.haskova@natur.cuni.cz*

Ionic hyper-cross-linked polyacetylenes were prepared by chain-growth homopolymerization 3,5-diethynylpyridine and postpolymerization heterogenous modification by achiral and chiral quaternizing agent (ethylbromide, (*S*)-(+)-1-Bromo-2-methylbutane). Polyacetylene networks with chiral and achiral segments were also prepared via polymerization of ethylated pyridinium salts. Polyacetylenes with achiral and chiral segments could be prepared by two-step preparation from 4-bromobut-1-yn and 1,3,5-triethynylbenzene a subsequently postpolymerization quaternization by achiral or chiral agent (pyridine, (*S*)-4-(1-Hydroxyethyl)pyridine). Prepared networks reported micro/mesoporous texture and specific surface area S_{BET} up to 519 m^2/g and a high amount of pyridinium segments. The networks were tested as heterogeneous catalyst for the transformation of styrene oxide and carbon dioxide to styrene carbonate (conversation of styrene oxide up to 84 %).

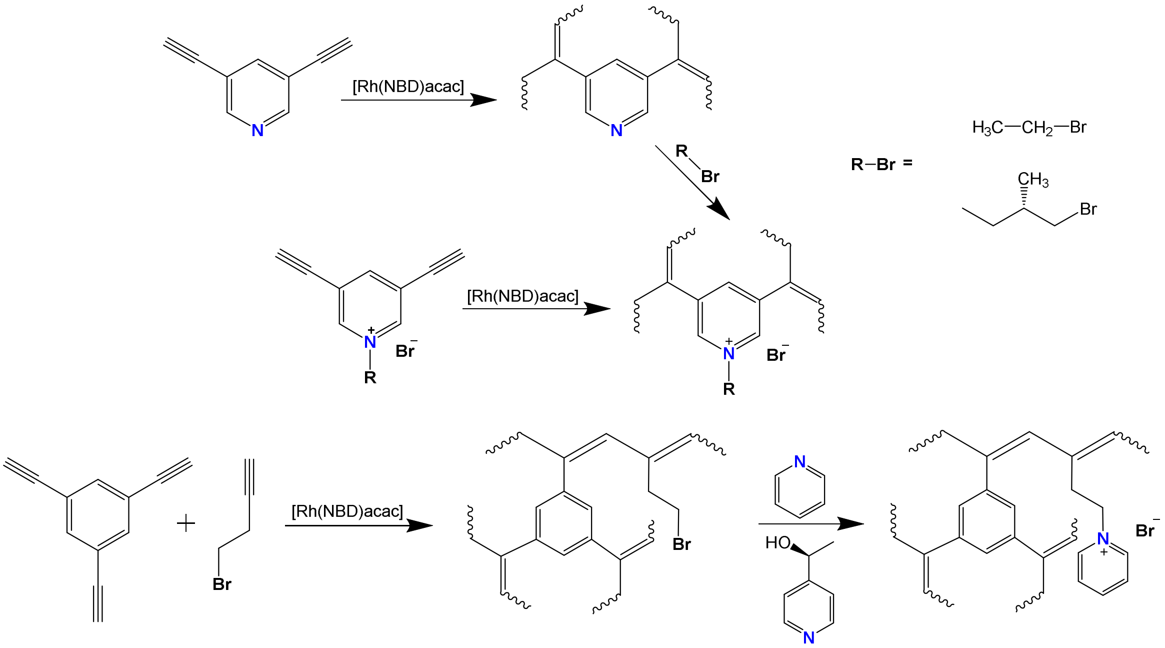

Figure 1. Example of preparation of ionic polymer networks by chain-growth homo- and copolymerization.

Keywords: polyacetylenes, microporous polymers, hyper-cross-linked, ionic polymers

Acknowledgments
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Polybutadiene – a versatile precursor for the synthesis of unique organofunctional polymers

R. Januszewski[1,2*], B. Orwat[2,3], M. Dutkiewicz[4], I. Kownacki[1,2]

[1]*Faculty of Chemistry, Adam Mickiewicz University in Poznan, Uniwersytetu Poznanskiego 8, 61-614 Poznan, Poland*
[2]*Centre for Advanced Technologies, Adam Mickiewicz University in Poznan, Uniwersytetu Poznanskiego 10, 61-614 Poznan, Poland*
[3]*Department of Molecular Physics, Lodz University of Technology, 90-924 Lodz, Zeromskiego 116, Poland*
[4]*Poznan Science and Technology Park, Adam Mickiewicz University Foundation, Rubiez 46, 61-612, Poznan, Poland*
[*]*r.janusz@amu.edu.pl*

Polyolefins have become prominent in the everyday life. Organic polymers excel in chemical and mechanical properties, energy efficiency, are economically and ecologically attractive materials, and continue to experience an ever-growing demand in a wide range of applications [1,2]. Nonetheless, polyolefins are hydrophobic and their application in blending, adhesion, and dyeing remains difficult due to a lack of polar organic groups. Therefore, the synthesis of tailored polyolefins with reactive units and functionality is a key target [3-4]. Among the large group of known organic polymers, polybutadiene is a versatile and convenient starting material for further functionalization thanks to the high content of readily accessible double bonds revealing reactivity in a wide spectrum of stoichiometric and catalytic transformations. Therefore, butadiene-based polymers seem to be excellent precursors for the synthesis of organofunctional polymers [5].

In this contribution, efficient methodologies for the synthesis of novel organofunctional polymers are proposed. It includes the synthesis of two novel polymeric precursors, bearing hydrosilyl or alkyne moieties and their subsequent transformation through catalytic reactions. The developed synthetic strategy enables incorporation of a wide variety of functional units into the polymer chains, which cannot be introduced through conventional polymerization protocols [6-7].

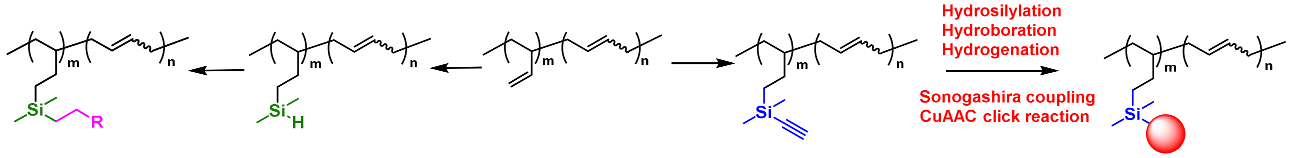

Figure 1. Novel organofunctional polymers

Keywords: functional polymers, homogeneous catalysis, post-polymerization

Acknowledgments

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Poly(vinyl chloride) graft copolymers via SARA ATRP

Seokhyeon Jeong, Dongwoo Kim, Hong Y. Cho, and Hyun-jong Paik*

Department of Polymer Science and Engineering, Pusan National University, Busan, Korea
**paik@pusan.ac.kr;*

Poly(vinyl chloride) (PVC) is one of the widely produced synthetic polymers due to its versatile physical properties. However, its excessive production has recently caused many environmental concerns. Here, we report a new approach to the synthesis of PVC-grafted-(co)polymer (PVC-g-polymer). Supplemental activator and reducing agent atom transfer radical polymerization (SARA ATRP) was used to prepare the grafted PVC. Various monomers such as styrene, methyl methacrylate, and butyl methacrylate were employed to obtain varied physical properties of the PVC-g-polymer. The graft polymerization was confirmed by using ^{1}H NMR and SEC. The glass transition temperature of resulting polymers analyzed using DSC showed a single value. Results suggested that the grafted polymer exhibited an enhanced compatibility without microphase separation compared to the blended polymer. The synthetic method for preparing PVC-g-polymer is expected to be a highly useful in upcycling PVC.

Keywords: Poly(vinyl chloride), Graft copolymer, Supplemental activator and reducing agent atom transfer radical polymerization, Glass transition temperature

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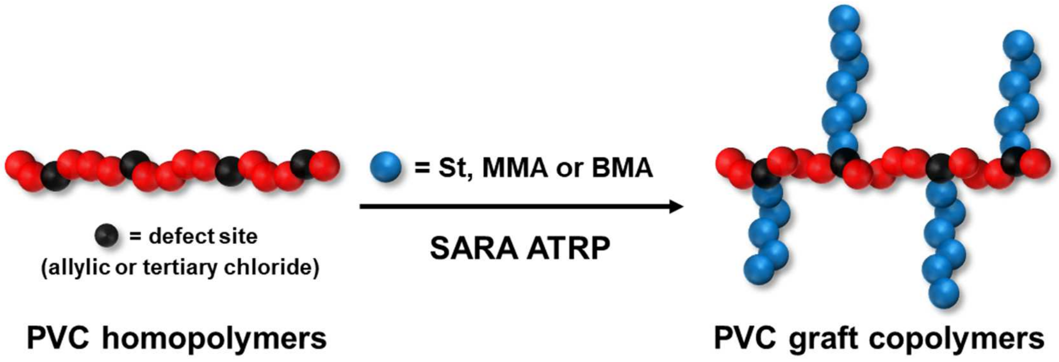

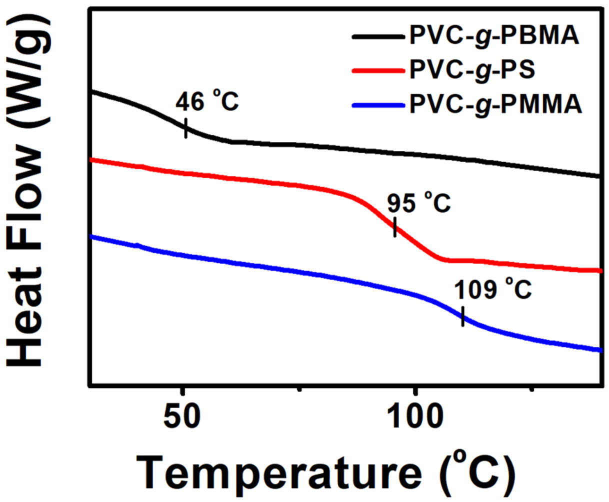

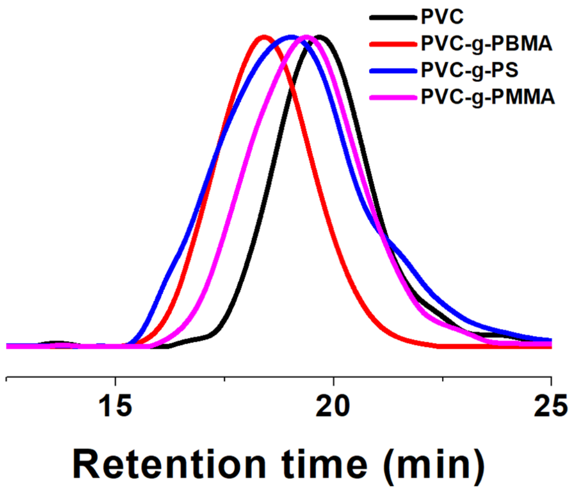

Controlling Graphene Wrinkles through a Phase Transition using Low Critical Solution Temperature Polymer Dispersant

Hyeyoung Joo[1], Minho Kwon[1], Jiyeon Yang[1], Hanyoung Kim[1], Sang-woo Joo[2], Young Sil Lee[3], Hye Jung Lee[4], Seung Yol Jeong[4], Jong Hun Han[5], and Hyun-jong Paik[1*]

[1]*Department of Polymer Science and Engineering Pusan National University, Busan, Korea*
[2]*Department of Chemistry Soongsil University, Seoul, Korea*
[3]*Industry-Academic Cooperation, Gumi, Korea*
[4]*Nano Hybrid Technology Research Center Korea Electrotechnology Research Institute (KERI), Changwon, Korea*
[5]*School of Applied Chemical Engineering Chonnam National University, Gwangju, Korea*
[3]*Industry-Academic Cooperation, Gumi, Republic of Korea*
[*]*hpaik@pusan.ac.kr*

Many techniques for controlling reduced graphene oxide (rGO) deformation have been studied. Some of the techniques involve varying the solvent fraction in the rGO solution and rapid evaporation of aerosol droplets. In this study, a novel method for controlling rGO wrinkles using a low critical solution temperature (LCST) polymer dispersant though a phase transition in a solution has been developed[1]. Reversible addition-fragmentation chain-transfer (RAFT) polyemerization was used to design the structure and composition of the polymer dispersant. Synthesized poly(2-(dimethylaminoethyl)methacrylate-block-styrene) (PDbS) was successfully functionalized on the rGO surface via noncovalent functionalization. In its aqueous phase, the PDbS-functionalized rGO (PDbS-rGO) exhibited good disperisbility. With the phase transion at the LCST behavior, wrinkles were formed on the PDbS-rGO surface[2]. Also, depending on temperature, the aggregation number of the polymer dispersant on the PDbS-rGO surface was varied and subsequently controlled the formation of PDbS-rGO wrinkles. The mechanism of the wrinkle control were confirmed by gold nanoparticles that were grown in polymer dispersant on the PDbS–rGO surface.

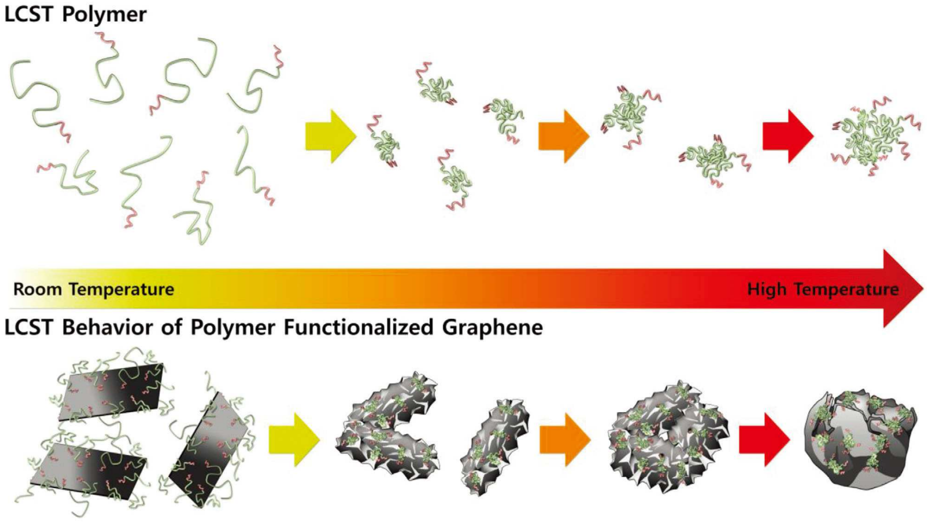

Figure 1. Schematic diagram illustrating the control over wrinkle formation on the graphene surface by varying the temperature of the polymer dispersant.

Acknowledgments

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Synthesis of Diblock Copolymers of Poly(2-oxazoline)s with Poly(lactic acid), Poly(glycolic acid) and Poly(lactic-*co*-glycolic acid) via Macroinitiators

F. Kaps[1*], L. Röther[1], E. Wegener[1], R. Jordan[1]

[1]*Technische Universität Dresden, Dresden, Germany*
**florian_tobias.kaps@mailbox.tu-dresden.de*

Combinations of polymers for high-performance materials are known for decades. One well-known example are amphiphilic block copolymers which consist of hydrophilic and hydrophobic blocks. In block-selective solvents, they self-assemble into polymeric micelles which can be used as carriers for hydrophobic drugs.[1] The biodegradable polyesters poly(lactic acid) (PLA), poly(glycolic acid) (PGA) and especially their corresponding copolymer poly(lactic-*co*-glycolic acid) (PLGA) have been extensively investigated regarding biomedical applications such as drug delivery due to their high biocompatibility.[2] Another promising group of biocompatible polymers are poly(2-oxazoline)s (POx). Block copolymers of POx show high potential as low toxicity drug carriers for various drugs.[3] A major advantage of POx regarding the block copolymer synthesis with other monomer families is the facile introduction of functional groups via the termination reaction of the living cationic ring-opening polymerization (LCROP) of POx.[4] Herein, we expand the field of known copolymers of both groups. Synthesis and characterization of various combinations of hydrophilic and hydrophobic blocks are carried out via LCROP of 2-oxazolines and subsequent coordination-insertion ring-opening polymerization of lactide and glycolide.

Keywords: block copolymer, poly(2-oxazoline)s, poly(lactic acid), poly(glycolic acid), poly(lactic-*co*-glycolic acid)

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Microstructure Characterization of Sulfonated Polystyrene from Different Sulfonation Methods

Hanyoung Kim[1], Minho Kwon[1], Aruna Kumar Mohanty[1], Hyun-jong Paik[1*]

[1]*Department of Polymer Science and Engineering, Pusan National University, Busan 46241, Korea*
[*] *hpaik8877@gmail.com*

Sulfonated polystyrene (SPS) has been a topic of interest in the field of membrane and ion exchange resin for a long time.[1] SPS is synthesized by the sulfonation of polystyrene using various sulfonating agents such as acetyl sulfate and sulfuric acid.[2] Depending on the synthesis method, SPSs vary in their properties due to their different microstructures. However, there are not many studies on the microstructure of SPS. Therefore, analysis of the microstructure of SPS is necessary through well-defined model ionomers. In this study, we compared the microstructures of two different SPSs sulfonated from acetyl sulfate and sulfuric acid. For this comparison, we synthesized well-defined poly((sodium 4-styrenesulfonate)-*random*-styrene) (P(SS-*r*-St)) and poly((sodium 4-styrenesulfonate)-*block*-polystyrene) (PSS-*b*-PSt) ionomers using RAFT polymerization as the model compounds of the SPSs. In the proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, different chemical shifts in the signal appeared depending on the type of microstructures. The peaks in SPS from acetyl sulfate appeared similar to those of the random ionomer, while the peaks in SPS from sulfuric acid resembled those of the block ionomers. This shows that sulfonating agents influence the microstructure of the SPS to become either random or pseudo-block. This was further confirmed by the microstructural evolution by the extension of the SS block on the macro RAFT random ionomer. The effect of the microstructure on the synthesized ionomers was also analyzed using nuclear Overhauser effect spectroscopy (2D NOESY), Fourier transform infrared spectroscopy (FT-IR), and differential scanning calorimetry (DSC).

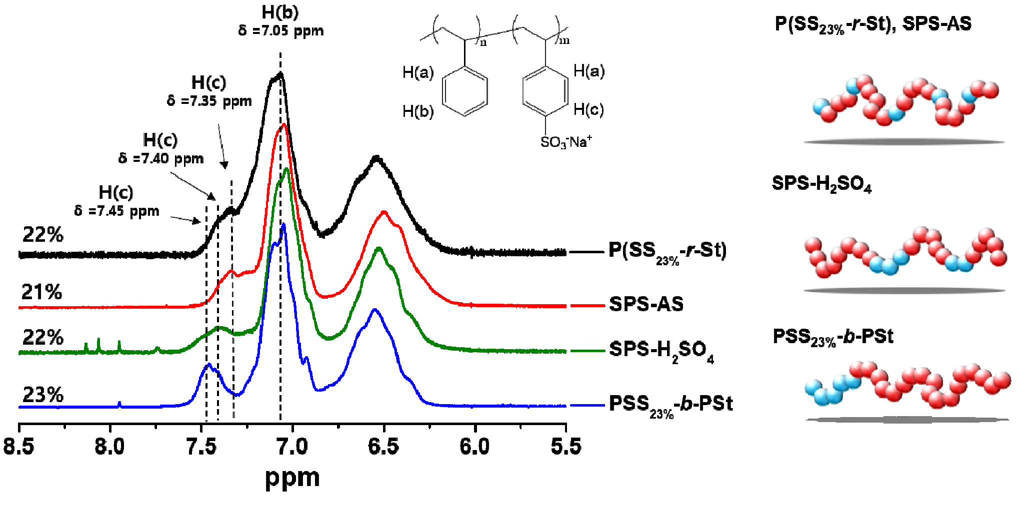

Figure 1. ^{1}H NMR spectrum of SPS-AS, SPS-H_2SO_4, P(SS$_{23\%}$-*r*-St) and PSS$_{23\%}$-*b*-PSt in DMSO-d_6 (5.5 ppm – 8.5 ppm)

Keywords: Sulfonated polystyrene, Microstructure, Random copolymer, Block copolymer, Sulfonation, RAFT polymerization, Styrene, Sodium 4-Styrenesulfonate

Acknowledgments

This work was supported by the Materials and Components Technology Development Program (20010566) grant funded by the Ministry of Trade, Industry, and Energy of Korea (MOTIE)

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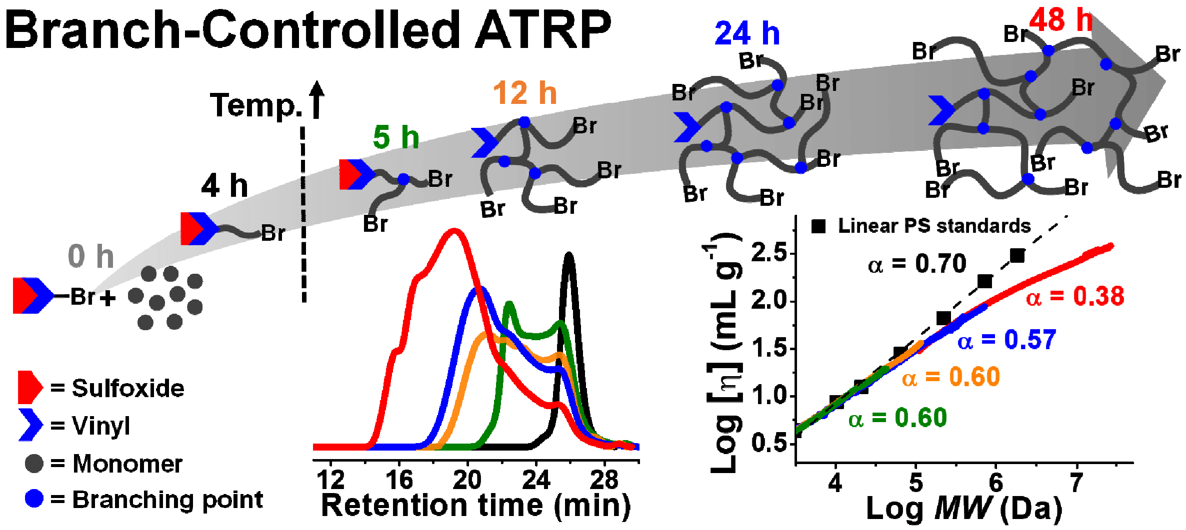
Branch-controlled ATRP via Sulfoxide-Based Vinyl Protection

Dongwoo Kim[1], Sukhyun Jung[1], Hong Y. Cho[1], Heung Bae Jeon[2], Hyun-jong Paik[1]*

[1]*Department of Polymer Science and Engineering, Pusan National University, Busan, Korea*
[2]*Department of Chemistry, Kwangwoon University, Seoul, Korea*
**hpaik@pusan.ac.kr*

A vinyl-containing macroinimer was prepared in situ by utilizing sulfoxide chemistry and was allowed for one-pot synthesis of hyperbranched polymers (HPs). Haloalkanes with sulfoxide-protected vinyl moieties were prepared, after which these moieties were deprotected by heat treatment and transformed into vinyl functional groups.[1] The protected haloalkanes were employed as an initiator for supplemental activator and reducing agent atom transfer radical polymerization to prepare well-defined linear polymers. Subsequent thermal treatment yielded the macroinimers while preserving the high chain-end functionalities. When the temperature was elevated during the linear polymerization, HPs were afforded in a one-pot process via the in situ generations of the macroinimers. A detailed investigation revealed that the sulfoxide-modified ATRP initiator for protecting the vinyl functionality on the polymer chain was successfully utilized for the synthesis of the hyperbranched polymer. This strategy is expected to aid the synthesis of HPs with a tunable distance between the branch points.

Keywords: ATRP, Branch controll, vinyl protection, sulfoxide chemistry



Acknowledgments
This work was supported by the Materials and Components Technology Development Program (20010566) grant funded by the Ministry of Trade, Industry, and Energy of Korea (MOTIE).

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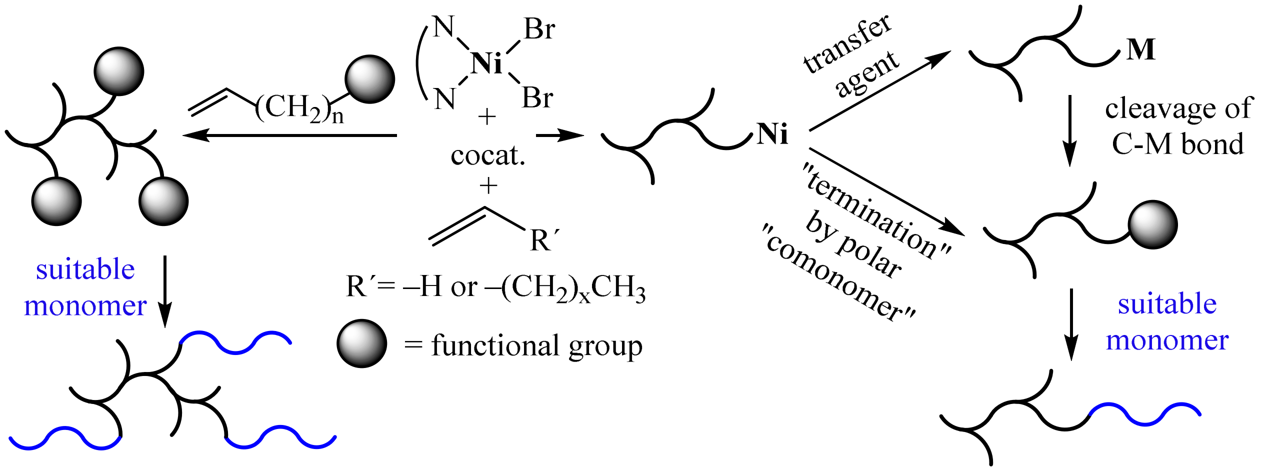
Functionalized branched polyolefins as a tool for block and grafted copolymer synthesis

O. Kotyza*, A. Sokolohorskyj, V. Šofrová, V. Musil, J. Merna

University of Chemistry and Technology, Prague, Department of Polymers, Technická 5, 166 28 Prague, Czech Republic
**kotyzao@vscht.cz*

Incorporation of polar functional groups into nonpolar polyolefin structure solve problems with polyolefin dyability and compatibility with other materials. Functional groups also bring possibilities to use polyolefins in non-traditional applications such as macroinitiators or substrates for copolymer synthesis. This moves polyolefins from basic polymer material to the field of polymer specialities.

Olefin copolymerization with polar monomers is classical domain of tolerant but highly energy demanding free radical polymerization process. In this work, we present several methods how to use coordination copolymerization at mild conditions to introduce functional groups into polyolefin chain utilizing α-diimine complexes of nickel as catalysts. These complexes provide living polymerization of α-olefins and due to chain-walking isomerization allow control over structure of final polymer.[1] Living character of polymerization enables end-chain functionalization by (a) addition of polar vinyl comonomer into polymerization system after polymerization of olefin or (b) by transfer of chain from living growth centre to an organometallic transfer agent followed by cleavage of carbon-metal bond.[2] Lower oxophillicity of Ni α-diimine complexes allow olefin copolymerization with polar comonomers and thus to obtain in-chain functionalized polyolefins.[3] Polyolefins with functional groups at the end of a chain can be used for block copolymer synthesis whereas polyolefins with functional groups along a chain can be used for graft copolymer synthesis.



Scheme of graft and block copolymer synthesis through polyolefin functionalization

Keywords: α-diimine nickel complexes, olefin functionalization, block copolymers, graft copolymers

Acknowledgments
This work was supported by Czech Science Foundation (No. 18-22059S) and from specific university research.

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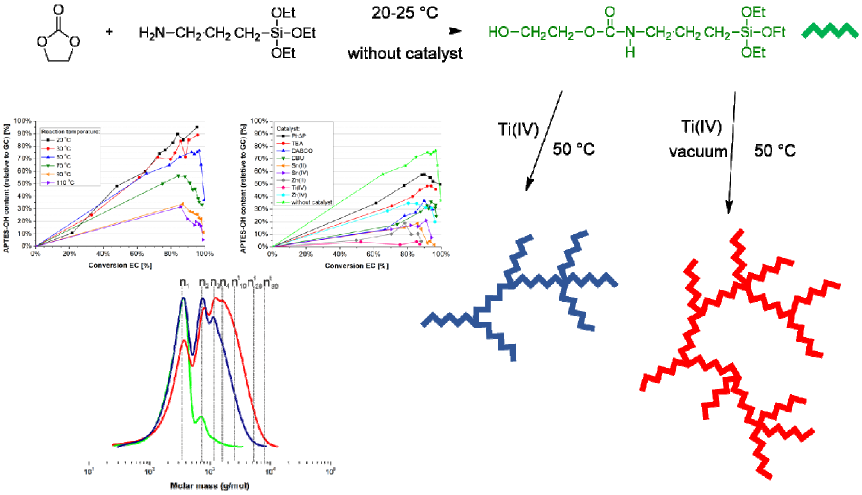
Synthesis of hyperbranched monohydroxyl alkoxysilane oligomers towards silanized urethane prepolymers

S. Kowalczyk[1*], M. Dębowski[1], A. Iuliano[1], S. Brzeski[1], A. Plichta[1]

[1]*Chair of Chemistry and Technology of Polymers, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland*
[*]*skowalczyk@ch.pw.edu.pl*

The aim of this work was the synthesis of hyperbranched oligomers based on trialkoxysilane in various conditions and further application of them in order to modify the urethane prepolymers.
Hydroxyl terminated trialkoxysilane was used as monomer for homo-condensation. It was obtained by reaction of 3-aminopropyl trialkoxysilane (APTES) with ethylene carbonate (EC). The reaction based on the attack of amine at the carbonyl carbon atom followed by ring-opening of the carbonate to give a urethane (carbamate) product. The next step was the condensation via substitution of ethoxy groups on silicon atom with the terminal hydroxyalkyl groups present in the primary product with evolution of ethanol. Accordingly, the impact of temperature and type of catalyst on process efficiency was investigated. Towards quantitative analysis of reaction progress and products the conversion of EC together with ethanol evolution were measured by means of gas chromatography which allowed to determine the formation of monomeric product and indirectly of oligomeric products. It was found out that at room temperature after 24 hours the monomeric product was isolated in majority, whereas at elevated temperature in the presence of Ti based catalyst further condensation of monomer into branched oligomers was preferred, and moreover application of vacuum intensified that process. The obtained products were structurally characterized by ^{1}H and ^{29}Si NMR, MALDI-ToF, Gel Permeation Chromatography. Finally, two different alkoxysilane products: monomeric and oligomeric, were applied for modification of urethane prepolymer forming silanized one (SPUR). The influence of the silanizing agent on the mechanical and thermal properties of the moisture cured products was shown before and after additional conditioning in water.



Keywords: hyperbranched oligomers, 3-aminopropyl trialkoxysilane, ethylene carbonate, silanized urethane prepolymers, silane

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This work was co-financed by the Faculty of Chemistry of the Warsaw University of Technology as part of the dean's mini-grant.

Synthesis of thermally latent bases for applications in polymeric self-healing materials

M. Kriehuber[1], D. Reisinger[1], S. Schlögl[1*]

[1]*Polymer Competence Center Leoben GmbH, Leoben, Austria*
[*]*sandra.schloegl@pccl.at*

The research on chemically induced self-healing materials has gained increased attention over the past years, due to the environmentally friendly possibilities of waste reduction and enhanced longevity of future polymer-based products. Vitrimers are prominent intrinsically healable polymers, which are capable of undergoing thermo-activated dynamic associative exchange reactions. Above the topology freezing transition temperature (T_v), the exchange reactions become significantly rapid, and the polymeric material has the ability to flow comparable to a viscoelastic liquid, although it is still in a crosslinked state.[1] Vitrimers relying on dynamic hydroxyl ester links, require the addition of a transesterification catalyst to facilitate fast bond exchange reactions above T_v. Herein, a library of thermally latent bases for catalyzing the transesterification in vitrimers has been studied (Figure 1). Selected thermo-base generators (TBGs) were synthesized and the thermal decomposition as well as the thermally triggered release (T_{TBG}) of the base were studied in detail employing thermal gravimetric analysis (TGA) and evolved gas analysis (EGA).

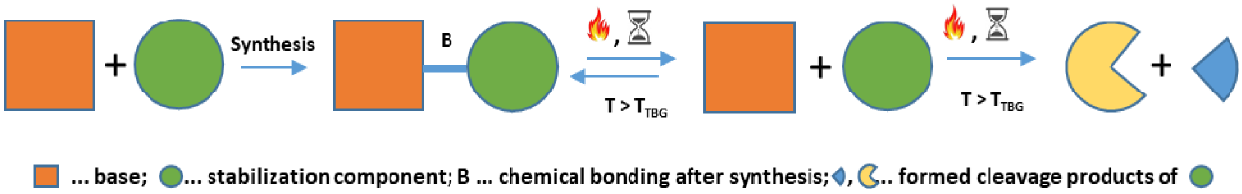

Figure 1: Schematic representation of synthesis, base release and stabilization compound in the decomposition mechanism.

Owing to the structure of the thermolatent base, the decomposition temperature and the inducing period varies over a broad period of temperature range.

Acknowledgments

The research work was performed within the COMET-Module project "Chemitecture" (project-no.: 21647048) at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology and the Federal Ministry for Digital Economic Affairs with contributions by Montanuniversitaet Leoben (Department Polymer Engineering and Science). The PCCL is funded by the Austrian Government and the State Governments of Styria, Upper and Lower Austria.

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RAFT Copolymerization of N-Vinyl Pyrrolidone and Vinyl Acetate

J. Cho, Y.-J. Kwark*

Soongsil University, Seoul, Republic of Korea
**ykwark@ssu.ac.kr*

Copolymerization of *N*-vinylpyrrolidone (NVP) with vinyl acetate (VAc) is successfully performed using *O*-ethyl-S-(1-methoxycarbonyl)ethyldithiocarbonate as a chain transfer agent in RAFT process to give a series of well-defined copolymers. Regardless the initial monomer feed ratio, the synthesis of statistical copolymers fulfills the features of a controlled polymerization with a linear 1st order kinetic plots of monomer conversion, a linear increase of the molar masses, and low dispersity values (Đ < 1.3). We applied conventional linearization methods to estimate reliable values of reactivity ratios for NVP and VAc. As a result, values of copolymerization reactivity ratio for NVP and VAc were obtained with the Fineman-Ross method (2,41 and 0.21), with the inverted Fineman-Ross method (2.30 and 0.27), and with the Kelen-Tudos method (5.69 and 0.38). These results provide information on the copolymer microstructure, indicating a limited monomer compositional drift in the synthesized P(NVP-co-VAc) copolymers.

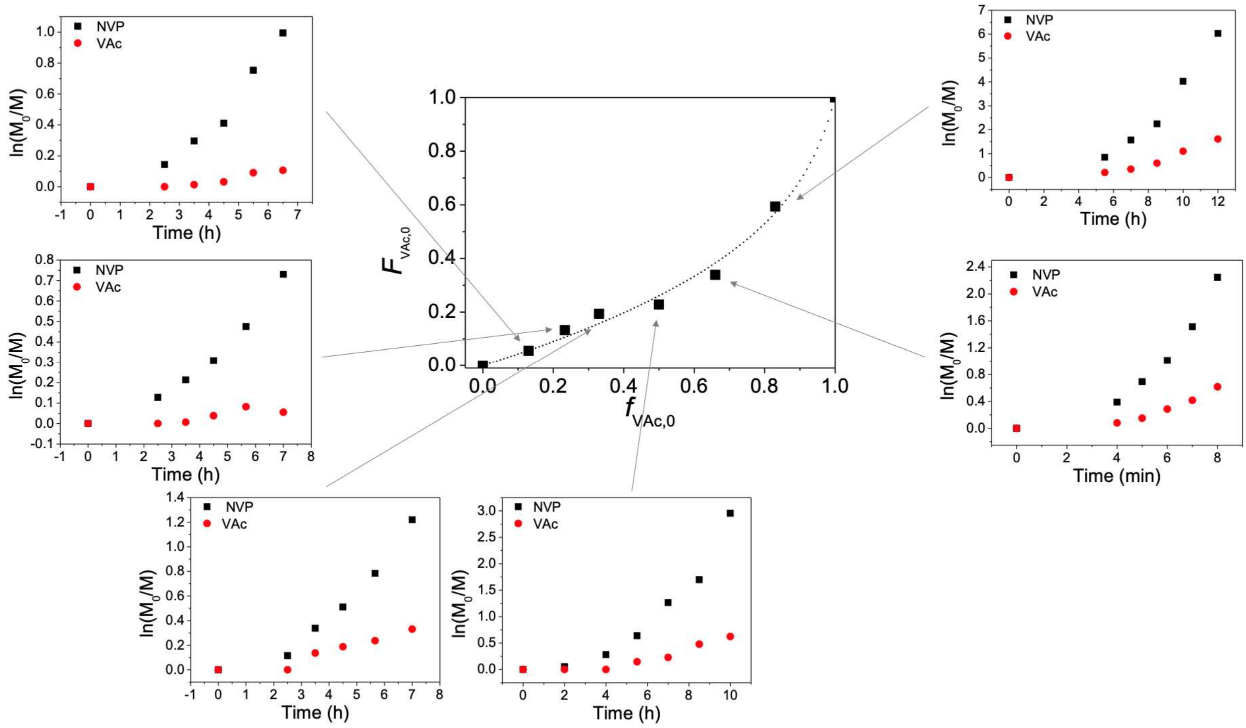

Figure. 1st order kinetic plots for the RAFT copolymerizations of NVP and VAc with a series of initial monomer feed ratio.

Synthesis of modular, tailorable acrylamide-based polyelectrolytes for the use as functional lithium-ion battery electrode binders

F. Leibetseder*, K. Bretterbauer

Institute for Chemical Technology of Organic Materials, Johannes Kepler University Linz, Austria;
**felix.leibetseder@jku.at*

In times of the threat of climate change the electrification of the transportation sector and utilization of solar and wind energy urgently requires innovation of energy storage systems. Lately a specific aspect of the existing lithium-ion batteries has received increasing attention – the polymer cathode binder. Recently, multi-functional binders with carboxylate functionalities were developed for high-capacity lithium sulfur and high voltage lithium spinel batteries. These functional binders offer various benefits to the currently used PVDF in terms of water solubility, absence of swelling in battery electrolytes, a lithium-ion reservoir, and proton scavenging ability [1-5].

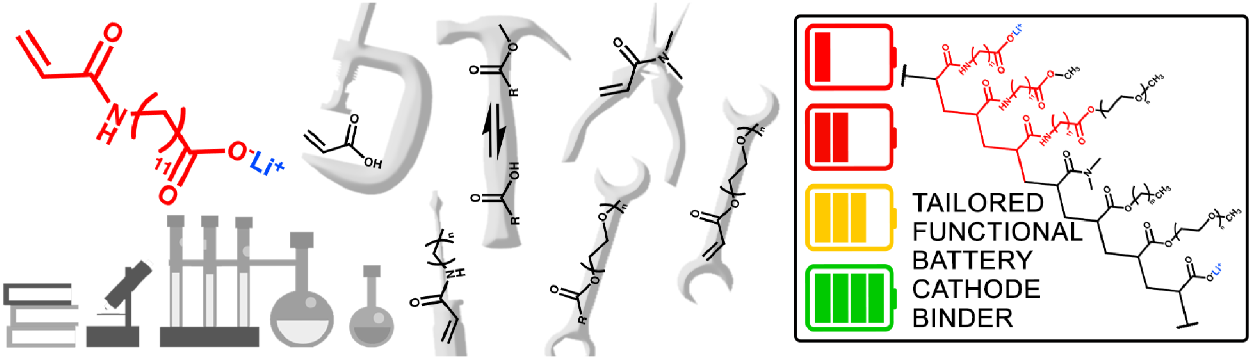

Figure 1: Graphical abstract of functinalities and monomers used in our "synthetic toolbox".

We hereby show new, improved, and straight forward synthesis strategies of functional monomers and subsequent (co)polymerization and post-polymerization modifications. 11-Aminoundecanoic acid was used as the main starting material, because of the important carboxylic acid functionality and the long flexible aliphatic chain. It is converted into its acrylamide and can be polymerized directly with polar comonomers in water. A mayor innovation is the introduction of a methyl ester protecting group, which also enables the polymerization in organic solvents with apolar comonomers. We also demonstrate a direct modification of the polyacid and copolymerization with polyethylene oxide as a lithium ion stabilizing functionality. These routes can also be applied to the analog 6-aminohexanoic acid as starting material. A short impression of the possibilities of our modular approach is shown in Figure 1. This synthetic "toolbox" should enable customizable and adaptable materials compared to previously reported promising electrode materials.

Keywords: Polyelectrolytes, Energy Materials, Lithium-Ion Battery Cathodes, Polymer Binders.

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Reversible Transformations of Polymer Topologies through Visible Light and Darkness

E. Liarou, H. A. Houck, F. Du Prez*

[1]*Ghent University , Ghent, Belgium*
* *Filip.DuPrez@UGent.be*

A fundamentally important characteristic of a macromolecule is shape. Herein, visible light and darkness are used as the only stimuli to reversibly alter the topology of well-defined polymers in a one-pot procedure. For this, linear naphtha-lene-containing polyacrylates are used as scaffolds for the visible light-induced cycloaddition with various substituted triazolinediones (i.e., butyl-, stearyl-, perfluoro- and polymeric), resulting in differently shaped graft polymers, including brushes and combs. The thus formed cycloadduct linkages dissociate in the dark, resulting in the regeneration of the parent linear polymer at ambient temperature, establishing a dual-topology transformation by only switching green light on-and-off. By applying different temperatures during the cycloreversion process, the dissociation rate of the cycload-ducts can be tuned in a facile manner, thus allowing for time control over the regeneration of the parent polymer. By engineering a polymer that consists of differently substituted naphthalenes at the chain ends and on the side chains, the inherently different cycloreversion rates of the formed cycloadducts are leveraged to achieve in situ multi-topology transformations, without external stimuli. The shape transformations have been repeated up to four times sequentially in one pot, without the need of any purification. The topological alterations are microscopically depicted through reversible self-assembly, with the polymers adopting different morphologies upon visible light or darkness. The versatile yet prac-tical nature of this polymer "reshaping" strategy provides facile access to multifaceted polymer systems, and consequent-ly to a plethora of potential applications thereof.

Keywords: polymer topology, reversible polymer shape, visible light-induced polymer transformations, reversible polymer grafting

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Catenated and Linear Polyrings from Tricyclic Polymer Containing Disulfide Linkage

Minji Kim[1], Hongchan Lee[1], and Hyun-jong Paik[1]*

[1]*Department of Polymer Science and Engineering, Pusan National University, Busan, Korea*
**hpaik@pusan.ac.kr*

(Multi)Cyclic polymers consist a class of polymers with characteristic physical properties.[1] This topologically distinct polymer could be obtained using tricyclic polystyrene with disulfide linkage as the building block. [2] The dynamic exchange of disulfide bonds was utilized to prepare diverse architectures such as linear or catenated polyrings. The former was obtained via a redox-based solution polymerization while the latter could be prepared via a thermal heat treatment in bulk state. The catenated polyring, partiaily soluble in organic solvents, was alnayzed using nuclear overhauser effect spectroscopy (2D NOESY), Fourier transform infrared spectroscopy (FT-IR), size exclusion chromatography (SEC) coupled with triple detection, and differential scanning calorimetry (DSC). The Catenated polyring showed lower hydrodynamic volume, lower intrinsic viscosity, and higher glass transition temperature compared to the linear polyring. Such distinctive features suggest that a topologically catenated polyring was formed.

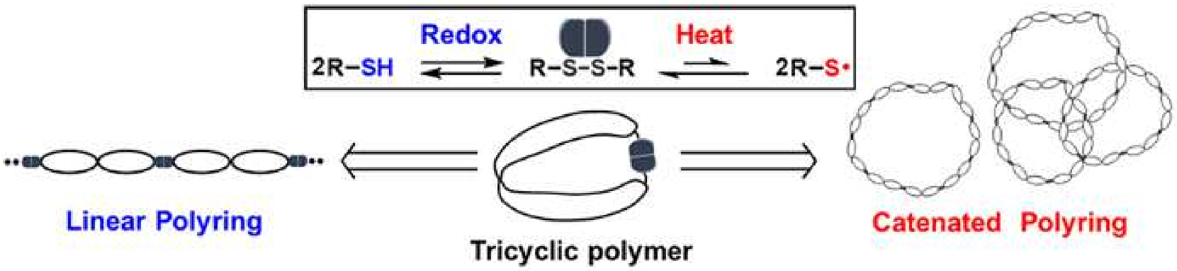

Figure 1. Schematic diagram illustrating the control two architectures in different system.

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Chalcone [2+2] cycloaddition for λ-orthogonal dual-cure photopolymers

S. M. Müller[1], B. Nelson[1], S. Schlögl[2], T. Griesser[1*]

[1]*Montanuniversitaet Leoben, Leoben, Austria*
[2]*Polymer Competence Center Leoben, Leoben, Austria*
[*]*thomas.griesser@unileoben.ac.at*

Photopolymerization driven additive manufacturing is a well-established technique to generate polymer structures with high resolution and complex geometry [1]. The possibilities can even be expanded by using two wavelengths in digital light processing or two photon absorption printing to exert spatial and temporal control over chemical reactions [2]. Herein, a dual-cure system was developed, based on radical polymerization of a thiol-ene system containing acrylate monomers with dimerizable chalcone groups as additional crosslinkers. The λ-orthogonality of the [2+2] cycloaddition reaction of the chalcone moieties enables selective tuning of the material properties. Crosslinking density and material stiffness can be controlled via a second illumination step. Reaction kinetics were tracked with infrared and ultraviolet spectroscopy during the irradiation with various wavelengths, while material properties were investigated by dynamic mechanical testing. Further material testing, including shape memory behavior, as well as 3D-printing experiments with a multi-wavelength setup on macro- and microscale are ongoing.

Keywords: photopolymerization, photochemistry, λ-orthogonality

Acknowledgments

The research work was performed within the COMET-Module project "Chemitecture" (project-no.: 21647048) at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology and the Federal Ministry for Digital Economic Affairs with contributions by Montanuniversitaet Leoben (Department for Polymer Engineering and Science). The PCCL is funded by the Austrian Government and the State Governments of Styria, Upper and Lower Austria. The authors gratefully acknowledge the Montanuniversitaet Leoben for the financial support.

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CARBON DOTS INCORPORATION INTO CATIONIC PHOTOPOLYMERIZATION IN A NANO-PHOTOINITIATING SYSTEM

P. Niezgoda[1,2*], T. Świergosz[1], W. Kasprzyk[1], M. Pilch[1], W. Tomal[1], J. Ortyl[1,2,3]

[1]*Cracow University of Technology, Faculty of Chemical Engineering and Technology, Laboratory of Photochemistry and Optical Spectroscopy, Warszawska 24, 31-155 Cracow,*
[2]*Photo4Chem, Lea 114, 30-133 Cracow, Poland*
[3]*Photo HiTech Ltd., Bobrzynskiego 14, 30-348 Cracow, Poland*
**pawelniezgodaa@gmail.com*

Light-initiated polymerization processes are currently one of the most rapidly growing fields in the chemical market. They are widely used in coatings, paints, or varnishes, but above all in 3D printing technologies. These processes have numerous advantages, from their high kinetics, no need for high temperature processing, low energy consumption and no need for solvents. The latter, thanks to the possibility of using human-safe light sources of Vis-LED type, significantly broadens the horizon of potential applications in such fields as medicine, dentistry, or tissue engineering.

The problem with commercially available initiators for photopolymerization processes is their low absorption maxima, oscillating in the ultraviolet range, which in turn translates into the inability to use them together with highly safe Vis-LEDs. To shift the absorption maxima, so-called photosensitizers are used. In the present work, citric acid-based carbon dots were used as efficient sensitizers of iodonium salts. The dots such as those obtained from citric acid alone (CA-CDs) and with amine doping (N-doped-CA-CDs) and sulfur (N, S-doped-CA-CDs), were used to study the kinetics of cationic photopolymerization of vinyl and epoxy monomers and for the free radical photopolymerization of acrylates as well as hydrogels.

The entire research involved the synthesis of suitable carbon dots, the purification process, then the development of suitable formulations, as well as meticulous studies ranging from spectrophotometry to the aforementioned kinetics of photopolymerization processes. Finally, experiments in 3D printing were also carried out, for an initiator system to print hydrogel materials.

Keywords: Photopolymerization, Photosensitizers, 3D printing, Carbon Dots

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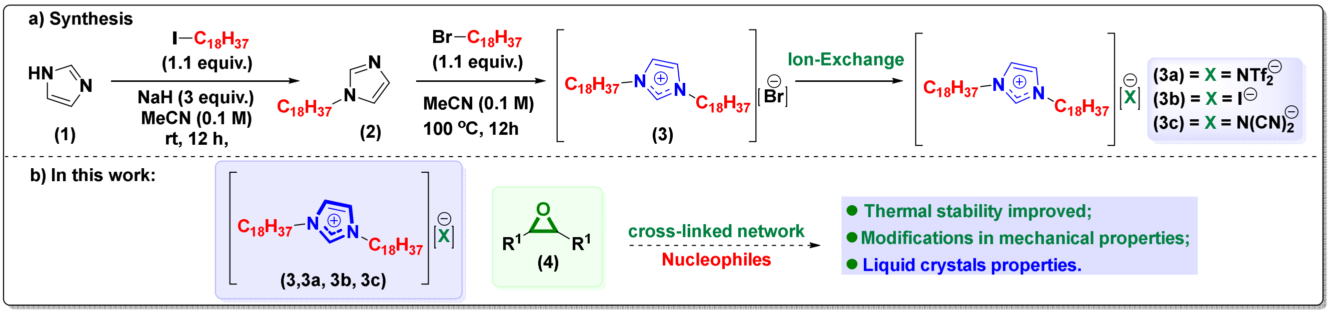
Design of New Liquid Crystalline Epoxy Networks

Celso Yassuo OKADA-JÚNIOR[1]*, Sébastien LIVI[1], and Jannick DUCHET-RUMEAU[1]
[1]*Université de Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, INSA Lyon, F-69621 Villeurbanne, France*
**celso-yassuo.okada-junior@insa-lyon.fr*

Due to their unique properties such as macroscopic orientation under electrical field, reversible phase transition, micro- or nano-structuration, liquid crystalline molecules represent a good alternative to produce multifunctional epoxy networks with enhanced properties.[1] By combining epoxy group (**4, Scheme 1b**) and liquid crystalline molecules (**3-3c, Scheme 1b**), thermally responsive networks whith shape memory behavior can be developed. In this work, epoxy networks with lower *Tg* (< 25°C) have been prepared by using various amine hardeners.[2] The reaction between epoxides and active hydrogens in amines promotes the generation of a cross-linked network, which results in improved thermal stability and modifications of the mechanical properties.[3],[4] Very recently, Ionic liquids (ILs), which are organic salts with an intermediate state between crystalline solid and liquid (anisotropic compound), are a promising generation of liquid crystalline molecules.[5]

Scheme 1. Synthesis of Ionic liquid crystal (*ILC*) and work proposal.



For these reasons, we have decided to design *ILs* based on imidazole, which is a heterocycle containing two nitrogen atoms; in addition, we have obtained after quaternization reactions *ILs* based on Imidazolium **3**.[6] The alkyl chain length plays an essential role in the liquid crystalline phase; for example, when the carbon chain has twelve carbon or more, *VdW* interactions generate a lamellar mesophase (via self-assembly).[7] In this context, our work combines various imidazolium ionic liquids with epoxy-amine to promote networks with novel physical and chemical properties (**Scheme 1b**).

Keywords: liquid crystals, Ionic liquids, Imidazolium, quaternization, epoxy networks, and polymerization.

Acknowledgments

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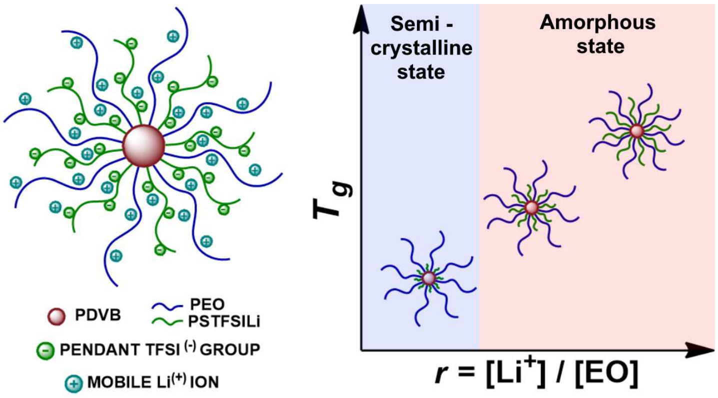
Synthesis and Molecular Characterization of Well-Defined Single-Ion Miktoarm Star Copolymers

C. Pantazidis[1*], G. Nikolakakou[2,3], E. Glynos[2,4], G.Sakellariou[1]

[1]*Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece*
[2]*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1385, 71110 Heraklion, Crete GR, Greece*
[3]*Departement of Chemistry, University of Crete, Heraklion, 700 13 Heraklion, Crete, Greece*
[4]*Departement of Materials Science and Technology, University of Crete, 71003 Heraklion, Crete, Greece*
[*]*chpantaz.chem.uoa.gr*

Over the last year, the synthesis of polyanion copolymers has attracted considerable attention for their utilization in single-ion electrolytes in lithium battery applications.[1] Morphology has a significant impact on the properties of such materials thus, reliable synthetic protocols are needed for different macromolecular architectures.[2] In this work, we report the synthesis and molecular characterization of a number of novel miktoarm star copolymers consisting of poly(ethylene oxide), PEO, and poly(lithium 4-styrenesulfonyl trifluoromethylsulfonyl imide), PSTFSILi, arms and a poly(divinylbenzene), PDVB, core. Initially, a PEO-NMP macroinitiator was synthesized. The “arm-first” method, was employed to produce a PEO star with 22 arms, $(PEO)_{22}$, with a spacious PDVB core, bearing active NMP initiation sites. Subsequent polymerization of the STFSIK monomer (“in-out” method), followed by ion exchange using LiCl, produced well-defined $(PEO)_{22}(PSTFSILi)_{22}$ miktoarm stars. A kinetic study on the polymerization of STFSIK on the PEO star core, was completed, to reveal well-controlled and “living” features. In conclusion, the macromolecular architecture, as well as, the ratio $r = [Li^+]/[EO]$ have a huge impact on the crystallization, and the segmental dynamics of the miktoarm star copolymers.



Keywords: Synthesis, Miktoarm, Star, Polyelectrolytes

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Ring opening (co)polymerization of α-hydroxy-γ-butyrolactone: towards the synthesis of functional polyesters

Chloé Pascouau*, Stéphane Carlotti, Henri Cramail, Frédéric Peruch

Université de Bordeaux, CNRS, Bordeaux INP, LCPO, Pessac, France
cpascouau@enscbp.fr

Over the last decades, the growing awareness of environmental concerns and the fossil resources consumption have raised the need to develop sustainable and degradable polymers. In this way, aliphatic (co)polyesters have emerged as serious candidates, and are already used in various applications thanks to their biodegradable and biocompatible properties. To achieve the synthesis of these polymers, the ring-opening (co)polymerization (ROP/ROCP) of cyclic esters (lactones and lactides), which is a powerful tool to design the structure and architecture of polymers, has been promoted. α-Hydroxy-γ-butyrolactone (HBL) is a bioderived monomer from glucose[1] and analogue to the well-known five-membered γ-butyrolactone used for the synthesis of poly(γ-butyrolactone), a polymer that can be totally recycled back to the initial monomer. However, ROP of γ-lactones faces thermodynamic challenges. Because of their low strain energy, this class of monomers was considered as "non-polymerizable"[2]. Recent advances in the ROP of γ-lactones led to the production of high molar mass PγBL under specific reaction conditions: work at low temperature (below the ceiling temperature (T_c)), high monomer concentration and use of efficient catalyst/initiator systems[3]. Another strategy to overcome the thermodynamic difficulties is to perform the random copolymerization of γ-lactones with higher ring-strain energy monomers, such as the ε-caprolactone (ε-CL). The copolymerization is also a good method to tune the properties of the polymers as their degradability by playing on the chemical nature of the comonomers and their composition[4].
The synthesis of these new functional bio-based copolyesters through the ROCP of HBL and ε-CL monomers (Figure 1) will be discussed in this presentation.

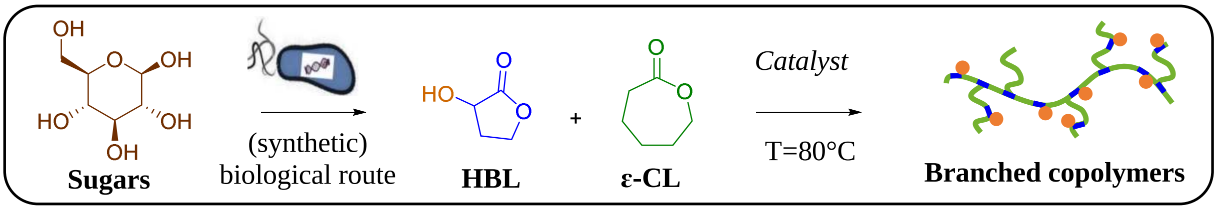

Figure 3: ROCP of HBL with Ɛ-CL

Keywords: γ-lactones, copolyester, ring-opening copolymerization, sustainable polymer.

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ANR and Adisseo for financial support.

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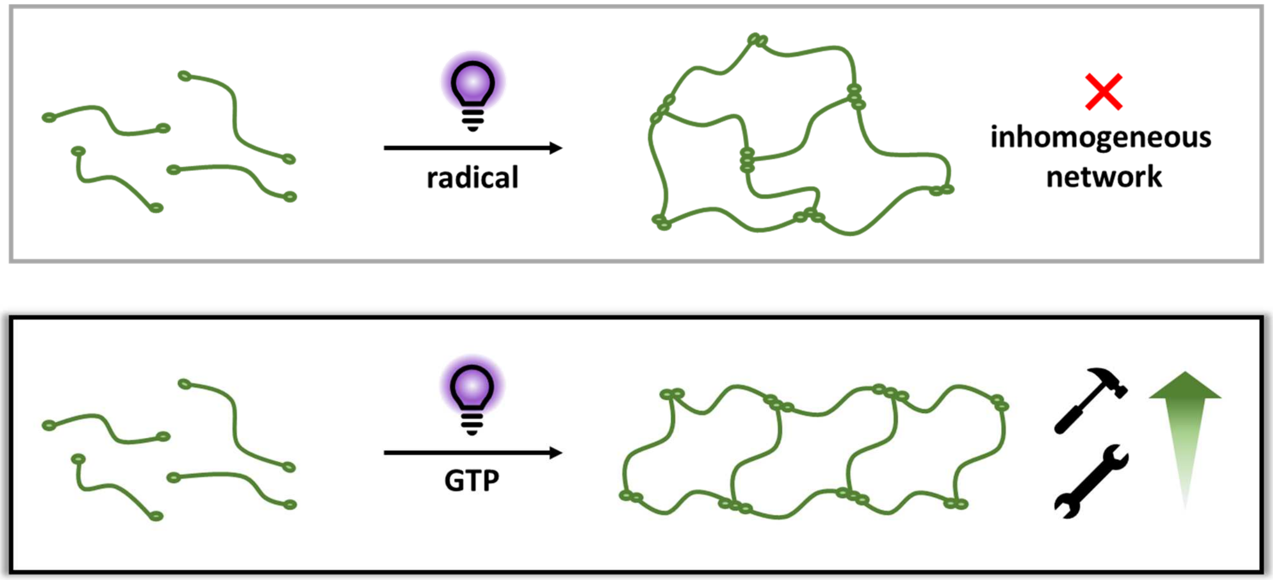
Group transfer polymerization for use in dental applications

F. Pieringer[1], Y. Catel[2], R. Liska[1], N. Moszner[2], P. Knaack[1*]

[1]*Institute of Applied Synthetic Chemistry, TU-Wien, Vienna, Austria*
[2]*Ivoclar AG, Schaan, Liechtenstein*
[*]*patrick.knaack@tuwien.ac.at*

Group Transfer Polymerization (GTP) was first discovered in the 1980s and used to synthesize (meth)acrylic block copolymers in solution at moderate temperatures as an alternative to anionic polymerization. GTP is a living polymerization, as it develops living chain ends, using mainly silylketeneacetal species as the initiator in combination with different catalysts like Brønsted acids [1]. When used with difunctional monomers in a bulk formulation, the controlled polymerization mechanism leads to very homogeneous networks with improved mechanical properties. These properties are of high interest for various possible applications in the industry, such as dental fillings utilizing photopolymerizable systems.



Scheme of the networks homogeneity improvement by use of UV initiated GTP and the resulting good mechanical properties

This work aimed to implement the usually solvent-based GTP into common methacrylic bulk systems used in dental materials. In order to get an overview of the properties of different catalysts, a selection of literature known catalysts was used in experiments with various monomer systems. An iodonium aluminate species, which is commonly used for cationic photopolymerization, and trityl tetrakis(pentafluorophenyl)borate showed remarkably high reactivity upon irradiation with UV-light when utilized as a GTP catalyst.

In various experiments, the influence of moisture and protic groups were investigated. Furthermore, specimens of non-protic monomers were prepared, to compare the mechanical properties of UV-GTP polymerized materials with radically photopolymerized samples.

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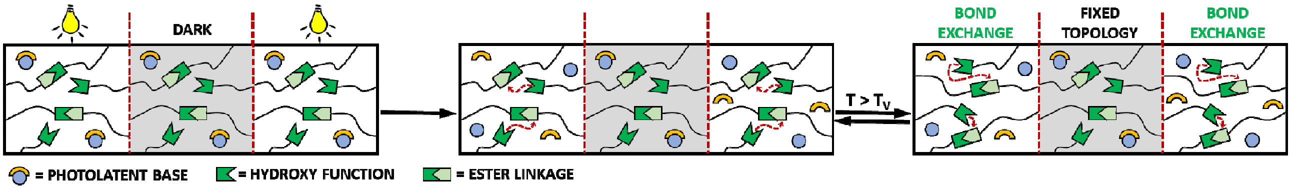
Controlled UV-mediated activation of dynamic exchange reactions in vitrimeric polymers by exploiting thermally stable photolatent bases

D. Reisinger[1], S. Kaiser[1], E. Rossegger[1], W. Alabiso[1], K. Dietliker[2], M. Sangermano[3], S. Schlögl[1*]

[1]*Polymer Competence Center Leoben GmbH, Leoben, Austria*
[2]*SCD Dr. Sommerlade Chemistry Design GmbH, Neuenburg am Rhein, Germany*
[3]*Politecnico di Torino, Torino, Italy*
[*]*sandra.schloegl@pccl.at*

Vitrimers represent an advanced class of polymeric materials capable of rearranging their covalently crosslinked network structure by dynamic associative exchange reactions. Characterized by basic properties as typical for conventional thermosets, vitrimeric polymers are additionally able to flow like viscoelastic liquids when the topology freezing transition temperature (T_v), defined as the onset temperature of the dynamic bond exchange, is exceeded.[1] However, in order to exploit their full potential, the challenge of realizing a controlled and, moreover, spatially resolved onset of the viscoelastic flow at elevated temperatures, i.e. well above T_v, has to be overcome. We developed a streamlined concept in which we take advantage of UV-mediated cleavage of thermally stable photolatent bases for a spatially resolved catalysis of dynamic transesterification, as illustrated in the figure below.[2]



Schematic representation of spatially resolved catalysis of dynamic transesterification activated by UV-mediated cleavage of a photolatent base.

The local photoactivation of vitrimeric properties by the controlled release of an efficient transesterification catalyst, i.e. a strong guanidine or amidine base, within a covalently crosslinked thiol-epoxy-cured matrix system was demonstrated by stress relaxation measurements. Even at temperatures considerably above T_v, only the UV-mediated catalyst release enabled the immediate onset of dynamic covalent bond exchange reactions, i.e. base catalyzed dynamic transesterification. We were able to optimize our system in such a way that the addition of supplementary curing catalysts or solvents is not required and an undesired thermally induced base release can be entirely excluded. In conclusion, our work provides an efficient strategy for the manufacturing of thermally stable, spatially resolved photoactivatable vitrimers, which enable a locally controlled malleability, weldability and repairability of highly crosslinked polymer networks.

Acknowledgments

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Utilization of Simple Continuous Flow Tubular Reactor in the Photoinduced-ATRP of Meth(Acrylates) with the Presence of Oxygen

Christyowati Primi Sagita[1,2*], Dmitrij Bondarev[1] , Jaroslav Mosnáček[1]

[1] *Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41, Bratislava, Slovakia*
[2] *Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, Ilkovičova 6, 842 15, Bratislava, Slovakia*
[*] *christyowati.sagita@savba.sk*

Flow reactors represents an attractive technology in polymerization since it can provide well-defined polymers in an efficient way [1]. Also, for photoinduced-atom transfer radical polymerization (ATRP), the flow system can provide polymerization conditions leading to controlled molecular weight distribution [2]. Concerning the photo-ATRP in the presence of air, previous work already reported was using batch reaction [3]. Hence in this work, we prepared homopolymers from methyl acrylate (MA), methyl methacrylate (MMA), and glycidyl methacrylate (GMA) by photoinduced-ATRP, in the presence of air, using a simple continuous flow tubular reactor. The complex system of this photo-ATRP uses copper(II)bromide-catalyst in ppm amounts and ligand amounts in excess to achieve controlled polymerization. The flow system shows ability to produce homopolymer (**Figure 1**) and copolymers based on PMMA and PMA with controlled molecular weight and dispersity, and also, the effect of various initiators and ligands on the kinetic of each flow homo-polymerization is investigated in comparison with batch polymerization. To prove the livingness of the flow photo-ATRP system in the presence of air, chain-extension experiments are performed.

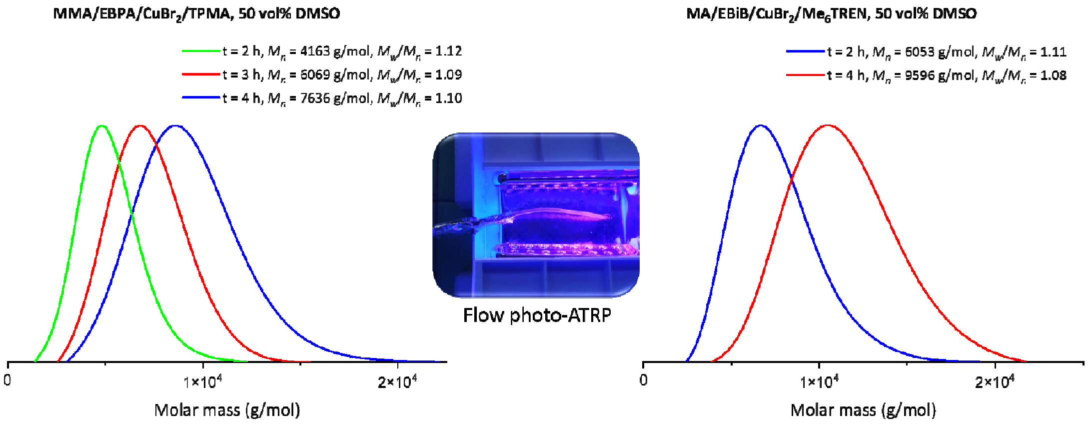

Figure 1. Molecular weight distributions of PMMA (*left*) and PMA (*right*) with an increased residence time of flow photo-ATRP. Photo-polymerization set-up in the insert.

Acknowledgments

The authors thank the Slovak Research and Development Agency for the financial support provided through grant APVV-19-0338 and the Slovak Grant Agency VEGA 2/0161/20.

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A Metal-Free Catalyst for the Ring-Opening Polymerization of Poly(trimethylene carbonate-co-trimethylene ether)

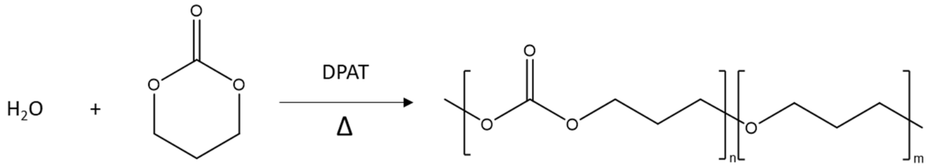
A. Saldívar-Martínez[1*], T. Melander Bowden[1]

[1]*Department of Chemistry, the Ångström Laboratory, Division of Macromolecular Chemistry, Box 538*
Uppsala University, Uppsala, Sweden
[*]*adriana.saldivar@kemi.uu.se*

Aliphatic polyesters and their copolymers have generated much attention due to their use in biomedical and electronic applications. Typically, polyesters are produced by the ring-opening polymerization (ROP) of cyclic esters with metallic catalysts where undesired metal residues are produced. Thus, it is of interest to develop new alternatives based on metal-free catalysts[1].

Diphenylammonium triflate (DPAT) was evaluated as a new metal-free catalyst for the synthesis of a poly(trimethylene carbonate-co-trimethylene ether) (PTMC-co-TME) copolymer via ROP in bulk. The reaction takes place through a monomer activation mechanism[2], where the carbonyl carbon undergoes a nucleophilic attack by an alcohol (initiator or end group). When DPAT is used as the catalyst, a side reaction is observed where the nucleophile attacks the α-carbon instead of the carbonyl carbon, generating an ether bond which leads to a random copolymer including carbonates and ethers.

The catalytic behavior of DPAT in the polymerization of trimethylene carbonate (TMC) was studied using the water present in the system as the initiator with a catalyst-to-monomer ratio of 0.01 ([cat]/[M] = 0.01). The reaction temperature was varied (from 60 to 150 °C) to study its effect on the composition of the obtained copolymers. Scheme 1 shows the general ROP reaction of PTMC-co-TME.



Scheme 1. ROP of PTMC-co-TME with DPAT as the catalyst

The obtainment of PTMC-co-TME copolymers was confirmed by ^{1}H NMR analysis and was further characterized by DSC and TGA techniques. The resulting materials were flexible and transparent with molecular weights ranging from 8,000 to 26,000 g/mol corresponding to a degree of polymerization of 78 to 255. According to ^{1}H NMR, the copolymers showed varying compositions, with a general tendency of the PTME content to increase with a rise in reaction temperature, going from 3 mol % to 9 mol %.

Regarding the thermal properties of the copolymers, DSC measurements revealed amorphous materials with a low T_g of around -22 °C. The TGA analysis showed the copolymers were stable up to ~220 °C.

The synthesis route reported in this study describes a single monomer dependent copolymerization and further facets will be discussed.

Acknowledgments

We are grateful for the funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 860403.

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Design and Synthesis of Sequence-Defined Oligourethanes for Information Transfer

S. Samokhvalova[1], T. Mondal[1], L. Charles[2], J-F. Lutz[1]*

[1]Institut Charles Sadron, CNRS. - UPR22, 23 Rue du Loess, BP 84047, 67034 Strasbourg Cedex 2, France
[2]Institute of Radical Chemistry, Aix Marseille Université, Case 511 Campus scientifique de St Jérôme, Avenue Escadrille Normandie Niémen 13397 Marseille Cedex 20, France
*E-mail: * jflutz@unistra.fr*

Sequence-defined polymers is a growing field of polymer chemistry that focuses on a precise control over primary structure and, therefore, properties.[1] Not only does it help to optimize polymer performance for material applications, but also creates a possibility to study the mechanisms of Life, such as transfer of information in macromolecules.[2] In Nature, information transfer, facilitated by nucleic acids, is an efficient process that has been optimized for billions of years. Even though the idea to apply the same concept to artificial polymers is relatively recent,[3] the possibility to achieve molecular recognition, template-directed synthesis and even self-replication of sequence-defined oligomers has been shown.[4] [5] However, synthesis of longer macromolecular chains that are structurally unrelated to nucleic acids and yet capable of information transfer remains challenging. Here, we discuss the design, synthesis and post-polymerization modification of sequence-encoded oligourethanes in order to transfer sequence-encrypted information to a complementary daughter strand of different chemical nature using a covalent ester strategy (**Fig. 1**). Building blocks containing protected COOH- and OH- side chains were used to construct parent strands via iterative solid-state strategy previously optimized by our group.[6] The parent information sequence can then be potentially translated by first (*i*) selectively deprotecting the pendant groups, (*ii*) functionalizing the deprotected sites by esterification with polymerizable building blocks, (*iii*) polymerizing the daughter strand and (*iv*) releasing the daughter strand by hydrolysis.

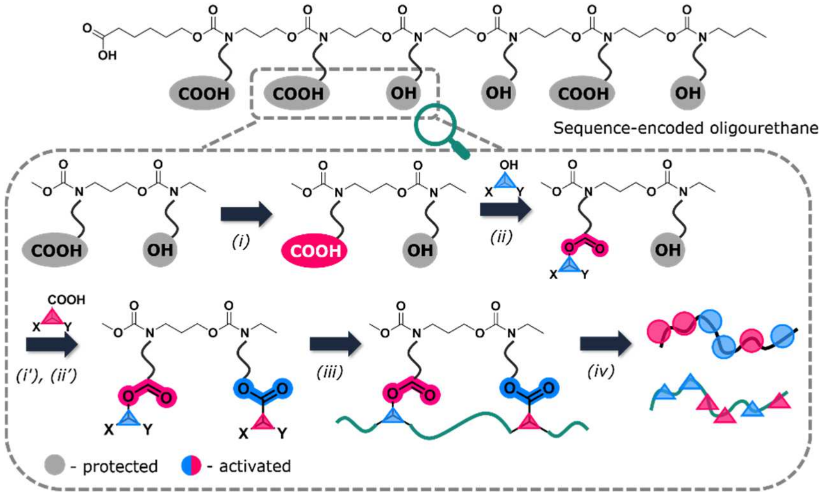

Fig. 1 Information transfer in a sequence-encoded oligourethane. (*i*) Deprotection of the pendant groups, (*ii*) esterification with polymerizable building blocks, (*iii*) polymerization and (*iv*) release of the daughter strand.

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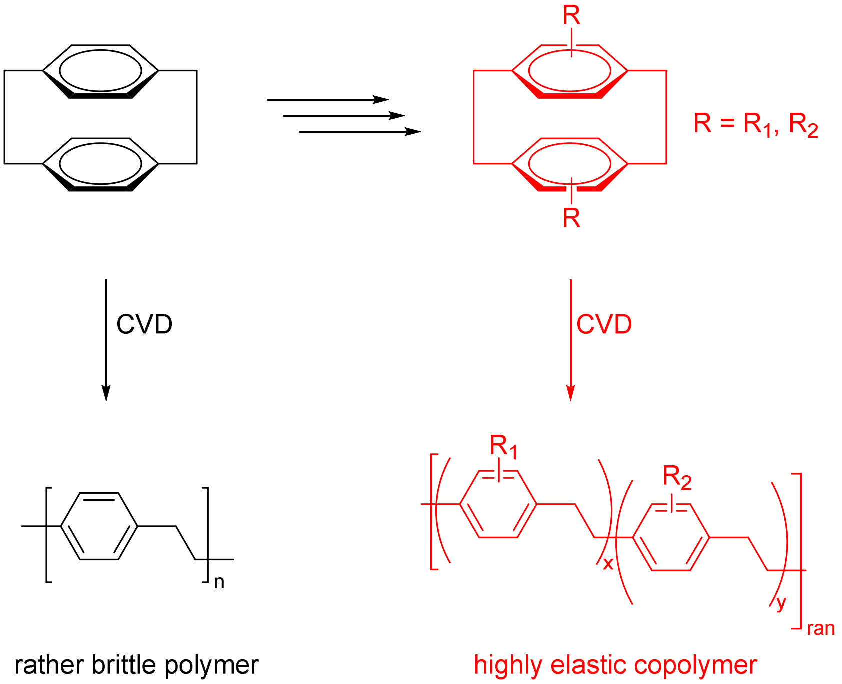
Highly elastic copolymers of poly(p-xylylene) by Chemical Vapor Deposition polymerization

T. Schmitt, A. Greiner*

University of Bayreuth, Macromolecular Chemistry and Bavarian Polymer Institute, Bayreuth, Germany
**greiner@uni-bayreuth.de*

The recent changes to smaller, more wearable and flexible electronic devices bears a challenge of not only constructing but also protecting those electronics. Appliable coatings to resist fluids, moisture, high temperatures or chemicals furthermore need to be flexible to accomodate the devices. The state-of-the-art protection material for high-value electronics is poly(*p*-xylylene) (PPX) applied according to the Gorham chemical vapor deposition (CVD) process (trade name: parylene) [1]. However, the application of PPX to flexible electronics is limited to to its small elongation at break. Therefore, we modified PPX by laterial substituents to an highly elastic PPX-copolymer with lateral substituents (see scheme 1), which showed elongation at break > 450 %.



Scheme 1: Synthesis of PPX (left) and highly elastic PPX-copolymer (right) from [2.2]paracyclophane.

We will present on the poster the synthesis and charaterization of the starting materials as well as of the new PPX-copolymers including the mechanical and thermal characterization.

Keywords: poly-*p*-xylylene, PPX, elastomers, CVD, crosslinking

Acknowledgments

The authors are indepted to Specialty Coating Systems for the donation of DPX-N ([2.2]paracyclophane).

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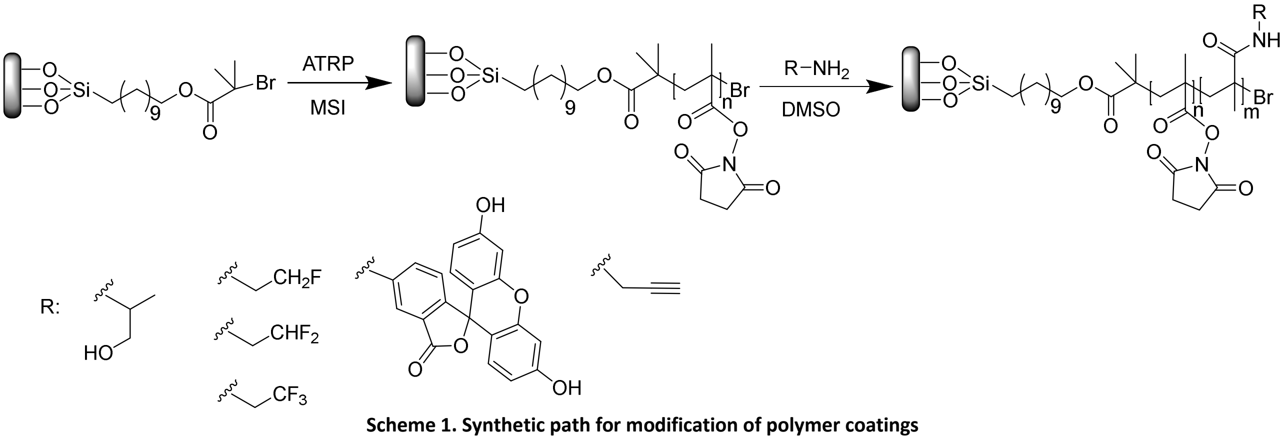
Polymer brush surface coatings based on active esters as platform for post-polymerization modification

Radoslava Sivkova,[1,*] Jan Svoboda,[1] Dietmar Appelhans[2], Ognen Pop-Georgievski[1]

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic*
[2]*Leibniz Institute of Polymer Research Dresden, Dresden, Germany*
[*]*sivkova@imc.cas.cz*

Polymer brush-based surface coatings have attracted attention not only in polymer science, but also in fields like biosensing and biomedicine, bioadhesion, etc.[1] These dense layers, covalently tehtered to the substrate surface, offer unique possibility of achieving control over the interaction between material and environment. Over the years, various strategies for modifiying surfaces and interfaces were developed with the aim of incorporating target functionalities to the polymer coating. Amongst them the post-polymerization modification of reactive polymer brushes is a particularly versatile tool for overcoming the difficulties with direct surface polymerization of monomers containing functional groups incompatible with the polymerization system.

In this contribution we present a simple method for the post-polymerization modification of polymer brush coatings based on N-methacryloxysuccinimide (MSI). Our process originates from a two-step reaction: *(i)* the surface-initiated atom transfer radical polymerization (SI-ATRP) of the active ester monomer, which was optimised in mild conditions; *(ii)* post-polymerization amidation reaction performed in the presence of organic base. The polymerization were performed on flat Si and glass surfaces, possessing a self-assembled monolayer of the ATRP initiator. The polymerization conditions were optimised in order to achieve layer thickness of 10 to 15 nm. Varying the conditions of the amidation allowed control over the reaction conversion with various primary amines, including fluorine containing amines, propargylamine and 5-amino-fluorescein. The introduction of fluorescent moiety to the polymer brush allowed us to demonstrate the homogeneity of the modified film. Furthermore, we demonstrated that hierarchical block-copolymer brushes with second block containing MSI monomeric units also undergo quantitative conversion with primary amines. The effectiveness of the amidation reaction was detailly studied utilizing spectroscopic ellipsometry (SE), fluorescent microscopy, infrared reflection-absorption (IRRAS) and X-ray photoelectron (XPS) spectroscopies.



Scheme 1. Synthetic path for modification of polymer coatings

Acknowledgments

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Preparation of functionalized branched polyethylene and its use as a macroinitiator for ring-opening polymerization

V. Šofrová, O. Kotyza, A. Sokolohorskyj*, J. Merna

[1]*Department of Polymers, University of Chemistry and Technology, Prague,*
Technická 5, 166 28 Prague 6, Czech Republic
**Anatolij.Sokolohorskyj@vscht.cz*

Polyolefins became dominant synthetic polymers. Their application was limited by their nonpolar nature. The insufficiency could be fixed by the incorporation of polar functionalities into the polyolefin structure. Full understanding of the polymer properties lies in the combination of precise synthesis and advanced physical characterization.

This work focuses on the use of chain walking catalysts, such as diimine complexes [1–3] or salicylaldiminato complexes, known for their living polymerization of ethylene, in the preparation of model branched polyethylene with various content of polar groups (e.g. –OH, –COOH, –COOR) (**FIG.**). Model polyethylenes with controlled molar mass and narrow molar mass distribution were prepared on a larger scale enabling further physical and analytical study.

Prepared copolymers bearing polar groups were used as macroinitiators for ring-opening polymerization of caprolactone. The resulting copolymers consist of the nonpolar polyethylene core and polar hydrophilic polycaprolactone shell.

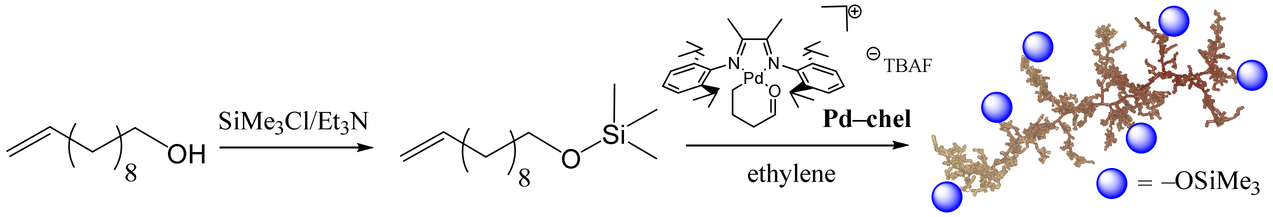

FIGURE: Scheme of preparation of functionalized branched polyethylene with Pd-chel.

Keywords: branched polyethylene, functionalization, ring-opening polymerization, chain-walking, diimine, salicylaldiminato, shell-core

Acknowledgments

This work was supported by the Czech Science Foundation (No. 18-22089S) and from specific university research (MSMT No 20-SVV/2022).

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Hyper-Cross-Linked Porous Polyacetylenes with Achiral and Chiral Organometallic Segments

David Šorm[1*], Bogdana Bashta[1], Jan Sedláček[1], Lada Sekerová[2], Eva Vrbková[2], Eliška Vyskočilová[2]

[1] *Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Prague, Czech Republic*
[2] *Department of Organic Technology, University of Chemistry and Technology in Prague, Prague, Czech Republic*
[*] *sormda@natur.cuni.cz*

Chain-growth polymerization of ethynyl groups of ethynylated salicylideneamine monomers and pre- or postpolymerization metalation with Mt^{2+} ions were used to prepare several types of organometallic hyper-cross-linked porous polyacetylenes promising in the field of heterogeneous catalysis. The networks consisted of polyene main chains cross-linked with achiral or chiral organometallic segments in which Mt^{2+} ions were coordinated by N and O donating atoms. The networks exhibited permanent micro/mesoporosity with a specific surface area up to 800 m^2/g and total pore volume up to 1.6 cm^3/g.

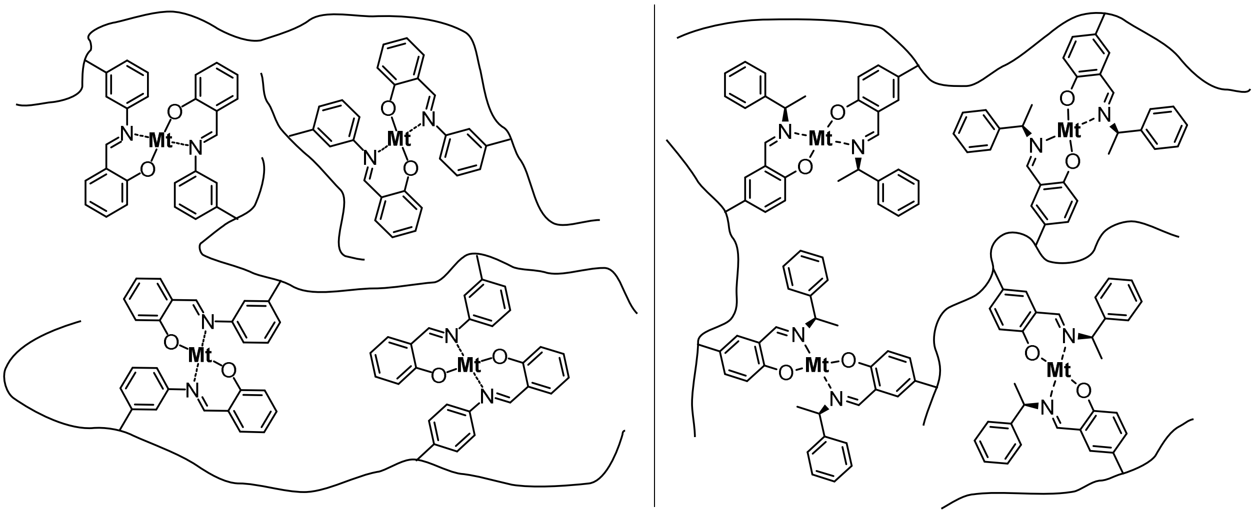

Figure 1: Examples of hyper-cross-linked porous polyacetylenes with achiral organometallic segments (on the left) and chiral organometallic segments (on the right)

Keywords: Hyper-Cross-Linked polymers, Specific Surface Area, Organometallic polymers, Porous polyacetylenes

Acknowledgments

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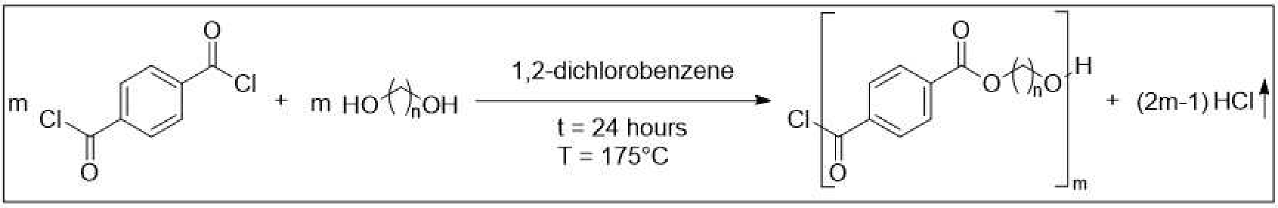
Comonomer ratio variation as a tool to obtain polyesters with high molar masses and control over the molar mass range

L. Van Daele[1*], S. Van Vlierberghe[1], P. Dubruel[1]

[1]*Polymer Chemistry and Biomaterials Research Group (PBM), Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium*
[*]*Lenny.VanDaele@UGent.be*

Poly(ethylene terephthalate) (PET) is an established polymer for various applications, including packaging, textile and biomedical applications. This polyester is part of the polymer family of poly(alkylene terephthalate)s (PATs). The synthesis of this polymer class typically involves a polycondensation reaction during which terephthalic acid or dimethyl terephthalate is reacted with a linear diol (e.g. ethylene glycol in the case of PET) in the presence of a catalyst. Another synthesis approach employs a ring-opening polymerization of cyclic monomers. However, both synthesis methods are associated with certain disadvantages, such as harsh reaction conditions, the requirement of a catalyst and/or limited monomer availability.[1] Furthermore, reports about PATs with high molar masses (>100 kg/mol) are scarce and control over the polymer molar mass range is very challenging. Recently, we reported a new synthesis which allowed for the synthesis of PATs using a single-step solution polymerization under milder reaction conditions in the absence of a catalyst. While this method has certain key advantages, the obtained molar mass was still limited to around 20 kg/mol.[2]



In the present research, we elaborated on our previously described synthesis route in order to obtain polymers with high molar masses and gain control over the molar mass range. To this end, we synthesized a homologous series of PATs with various alkyl chain lengths (n = 5-12) at different comonomer ratios (i.e. n_{diol}/n_{TCL}). At ratios 1.00, 1.01 and 1.10, we obtained an average DP (obtained via gel permeation chromatography) of 153 ± 22, 119 ± 24 and 21 ± 2, respectively, leading to weight-average molar masses (M_w) between 8.1 and 76.7 kg/mol. By using different comonomer ratios, we successfully obtained significantly different molar masses in a reproducible way, enabling straightforward control over the molar mass range. To obtain polymers with even higher molar masses, we further fine-tuned the comonomer ratio for $PAT_{(n = 10)}$. This resulted in polymers with a DP up to 616 and a M_w up to 298 kg/mol, which is among the highest values reported to date in literature.

Thermal characterization of the obtained polymers was performed using thermogravimetric analysis and differential scanning calorimetry (DSC). Degradation temperatures exceeding 300°C were observed as well as glass transition temperatures (T_g) between -5.2°C and 16.0°C and melting temperatures (T_m) from 91.0°C to 148.5°C, depending on the number of methylene groups. In general, both the T_g and the T_m increase with lower number of methylene groups and an increasing molar mass. Finally, using modulated DSC, we were able to provide further evidence for the melt recrystallization phenomenon of PATs.

Keywords: Poly(alkylene terephthalate), polymer synthesis, molar mass, thermal characterization

Acknowledgments

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A two-step synthesis of random amphiphilic *n*-butyl (meth)acrylate-acrylic acid copolymers and their solution properties in water.

P. van den Tempel[1], P. Raffa[2*].

[1]*University of Groningen, Groningen, the Netherlands*
* p.raffa@rug.nl

Over the last 20 years, the field of amphiphilic polymers research was revolutionized by developments of new polymerization techniques, such as Reversible Addition Fragmentation Transfer (RAFT). Interests for organized polymer architectures rose as a direct consequence. Structures such as block, star and grafted polymers have been studied extensively in aqueous solutions. However, the understanding of random amphiphilic polymer behavior, as opposed to block (or macrosurfactant) structures, stayed behind.[1] Structure-property relationships of well-defined random amphiphilic polymers are therefore not extensively investigated up to this day. In this research, amphiphilic poly-acrylic acid-*n*-butyl methacrylate random copolymers (AA-r-nBMA) were prepared via a two-step synthesis (Figure 1), and solution properties were tested as function of molecular weight, monomer ratio and degree of neutralization. In the first step, tert-butyl acrylate-*n*-butyl methacrylate (tBA-r-nBMA) copolymers were prepared in solution using RAFT polymerization. The *tert*-butyl groups were subsequently hydrolyzed selectively, yielding amphiphilic acrylic acid-r-n-butyl methacrylate polymers. The latter step, though being reported in literature for being selective and complete on block co-polymer equivalents, was not complete for random tBA-r-nBMA as the material precipitated over the reaction[2]. The prepared polymers were analyzed by ^{1}H-NMR, FT-IR spectroscopy and thermogravimetric analysis (TGA). After hydrolysis, protonated AA-r-nBMA was partially soluble in water. This allowed us to compare solution properties, such as rheology and surface tension to equivalent block polymers reported in literature.[2] Non-neutralized copolymers showed the existence of an apparent critical micelle concentration.

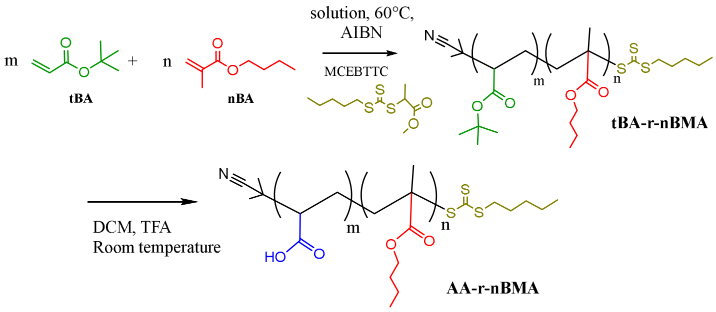

Figure 1 - Scheme of the two-step synthesis of AA-r-nBMA.

Keywords: Surfactants, Random polymers, Amphiphilic, Rheology.

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Polymerization of methacrylic acid in an uncoventional (bulk like) reaction medium

Samuel Wierzbicki[1*], Kacper Mielczarek[1], Monika Topa-Skwarczyńska[1], Joanna Ortyl[1], Szczepan Bednarz[1]

[1]*Department of Biotechnology and Physical Chemistry, Cracov University of Technnology, Cracow, Poland*
[*]*samuel.wierzbicki@doktorant.pk.edu.pl*

The polymerization of methacrylic acid (MAA) without a classical solvent (organic or water) is an unexplored topic mainly due to the low solubility of poly(MAA) in bulk medium. One of the most promising method for polymerization of MAA in solvent-free conditions is polymerization of MAA in a complex form. Similar molecular complexes to are formed in Deep Eutectic Solvents (DES). DESs are a family of ionic-like fluids with characteristic features of abnormally deep melting point depression for the eutectic composition of certain hydrogen bond donors (HBDs) and acceptors (HBAs) [1]. From a polymer chemistry perspective, also monomers could be components of DESs and serve both as HBD (e.g methacrylic acid) or as HBA (quaternary ammonium vinyl derivatives) [2]. This subtype of DES is known as a Deep Eutectic Monomers (DEMs). DEMs are new systems, not studied previously, and therefore the polymerization processes in such systems are poorly understood [3]. It is known that the anion structure of HBA in DEM determines the strength of hydrogen bonding in molecular complexes formed between HBA and HBD [4], [5]. However, the influence of the anion structure of the quaternary ammonium salt (HBA) on the intermolecular interactions in DEM systems, and therefore the impact of this factor on the polymerization process of DEMs has not been investigated yet.

In our research we examined the impact of anion in quaternary ammonium salts on photopolymerization of MAA. Four ammonium salts with different anions and the same cation (tetrabutylammonium chloride (Cl^-), tetrabutylammonium bisulfate (HSO_4^-), tetrabutylammonium nitrite (NO_3^-) and tetrabutylammonium tetrafluoroborate(BF_4^-)) forming DEM with MAA were investigated. As a part of the study we examined physicochemical properties of DEM such as NMR, FTIR spectroscopy, changes in density and viscosity for compositions with different acid to salt molar ratio. In addition, we determined the conversion curves by RT-FTIR experiment in order to investigate the changes in the initial rate of polymerization.

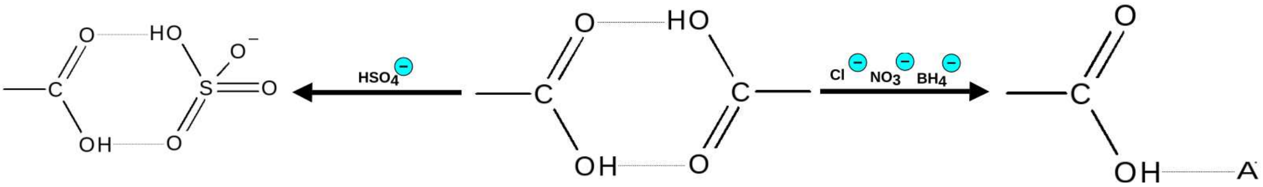

Figure 1. Schematic representation of the hydrogen bond formation between methacrylic acid and different types of anion in tetrabutylammonium salt

Keywords: Radical polymerization, Methacrylic acid, Deep Eutectic Monomers

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Buta-1,3-diene/ethene-based rubber prepared by cobalt and iron bis(arylimino)pyridyl catalysts

Ondřej Železník*, Jan Merna

[1]*Department of Polymers, University of Chemistry and Technology Prague, Praha, Czech republic*
**ondrej.zeleznik@vscht.cz*

One of the most important monomers in tire industry is buta-1,3-diene (BD), as it serves as a basis for various rubber products. That is no surprise, as styrene-butadiene (SBR) copolymer and high-*cis* polybutadiene are the two most important synthetic rubbers in the world. The synthesis of a novel type of elastomeric homopolymer seems like an impossible task as the choice of a new suitable monomers is generally limited. Therefore, copolymerization with common monomers (e.g, ethene) is the only satisfactory alternative to develop an improved elastomer.

Although BD has been copolymerized with many comonomers, the main interest remains in a different approach towards industrially used copolymers (e.g., SBR) or towards the preparation of BD copolymers with ethene (or 1-alkenes in general). The copolymerization of BD with ethene is of great importance as ethene is a cheap monomer and provides highly elastic segments in the polymer chain. However, different polymerization mechanisms of both monomers result in only limited number of catalytic systems capable of their mutual copolymerization. Moreover, most of these catalysts insert BD as 1,4-*trans* isomer, resulting in plastic material instead of an elastomer.[1]

Here, we present the group of bis(arylimino)pyridyl cobalt and iron complexes as active systems for BD/ethene copolymerization, generating copolymers with high 1,4-*cis*-insertion of BD.[2] Effect of various ligand moieties (mainly in *ortho*-aryl: R_1 and backbone positions: R_2, in Figure 1) were studied with focus on catalyst activity and copolymer composition. The most promising catalytic system was further successfully optimized and improved. Successful up-scaling of the copolymerization allowed us to perform basic mechanical testing in a common tire recipe.

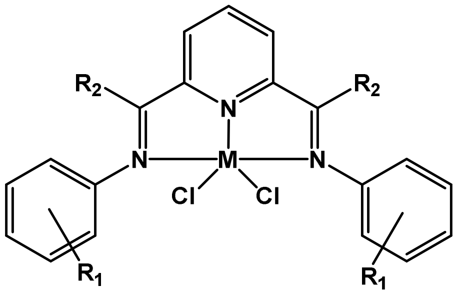

Figure 1: General structure of cobalt and iron complexes used for butadiene-ethene copolymerization

Keywords: butadiene, ethene, copolymerization, catalysis, cobalt

Acknowledgments
This work was generously supported by Synthos S.A. company.

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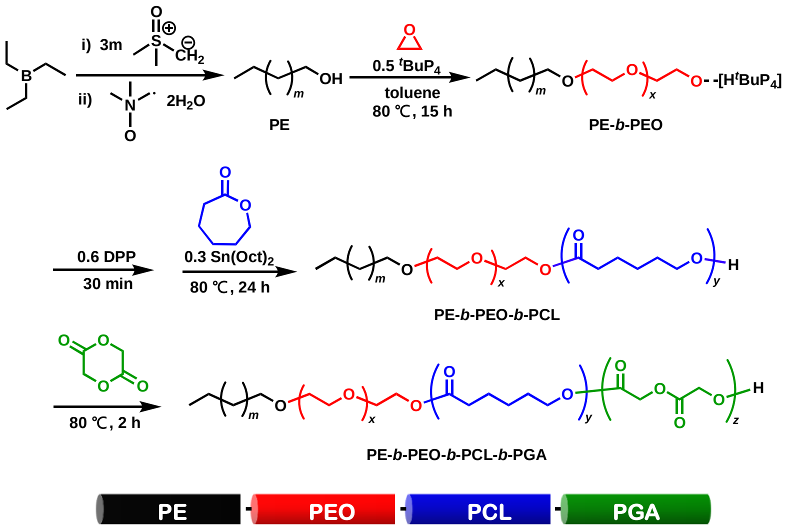
Tetracrystalline Tetrablock Quarterpolymers of Polyethylene, Poly(ethylene oxide), Poly(ε-caprolacone) and Polyglycolide

Pengfei Zhang[1], Viko Ladelta[1], Nikos Hadjichristidis[1*]

[1]King Abdullah University of Science and Technology (KAUST), Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, Thuwal, Saudi Arabia
[*]E-mail address: nikolaos.hadjichristidis@kaust.edu.sa

Multiblock polymers that exhibit more than one crystalline phase have attracted considerable attention due to their special morphology, biocompatibility, biodegradability, and optoelectronic properties. Though, the synthesis of multiblock multicrystalline polymers is always challenging due to the low solubility of the highly crystalline phases and the incompatibility of the catalytic system requirements for each block. In 2014, our group reported the first "base-to-acid" catalyst "switch" strategy, allowing us to combine ring-opening polymerization (ROP) of epoxides and lactones in one pot and to afford well-defined block copolymers[1]. Recently, by combining polyhomologation with ROP, we were able to obtain, for the first time, polyethylene-*b*-poly(ethylene oxide)-*b*-poly(ε-caprolactone)-*b*-poly(*L*-lactide) (PE-*b*-PEO-*b*-PCL-*b*-PLLA) tetracrystalline tetrablock quarterpolymer[2,3]. Still, the last PLLA block suffers epimerization under high temperature which is necessary for dissolving PE. Therefore, a metal catalyst tin(II) 2-ethylhexanoate [$Sn(Oct)_2$], has to be used to maintain its stereoregularity and crystallinity. In this work, we incorporated polyglycolide (PGA), a biobased biodegradable and highly crystallized polymer as the last block, to afford the synthesis of PE-*b*-PEO-*b*-PCL-*b*-PGA tetracrystalline tetrablock quarterpolymer. The phosphazene super base ^{t}BuP$_4$ was used to catalyze the ROP of ethylene oxide (EO) in toluene at 80 °C using a perfectly linear ω-hydroxyl PE (PE-OH) as macroinitiator, obtained by polyhomologation (C1 polymerization). After neutralization of the super base with diphenyl phosphate (DPP), $Sn(Oct)_2$ was introduced as a catalyst for the ROP of caprolactone (CL) and glycolide (GA) at the same temperature in one pot (Scheme 1). The resulting quarterpolymer was characterized by 1D, 2D NMR spectroscopy and size-exclusion chromatography. Differential scanning calorimetry and X-ray diffraction revealed the existence of four crystalline phases. Using a similar methodology, a novel PEO-*b*-PCL-*b*-PGA-*b*-PLLA tetracrystalline tetrablock quarterpolymer was also synthesized.



Tetracrystalline Tetrablock Quarterpolymer

Scheme 1 Synthetic route of PE-*b*-PEO-*b*-PCL-*b*-PGA tetracrystalline tetrablock quarterpolymer by catalyst "switch" strategy

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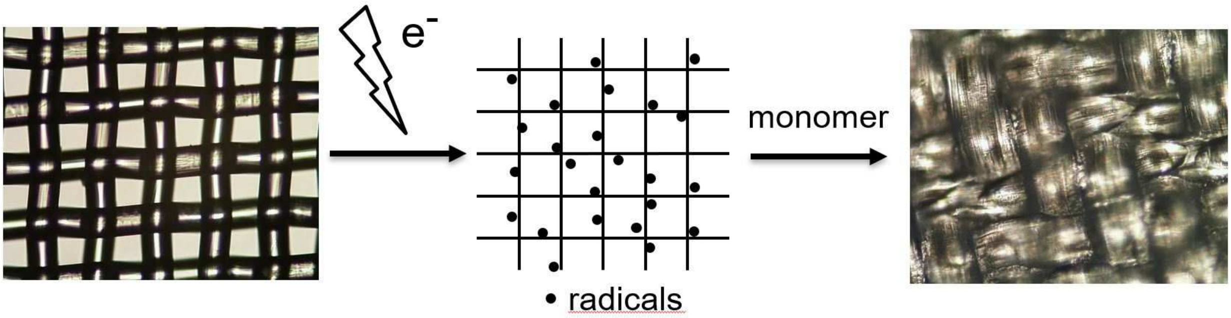
Electron beam-induced graft polymerization of PVDF mesh for heavy metal removal

C. Adolfs[1*], U. Gohs[2], S. Beuermann[1]

[1]*Institute of Technical Chemistry, Clausthal University of Technology, 38678 Clausthal-Zellerfeld, Germany*
[2]*Institute of Lightweight Engineering and Polymer Technology, 01307 Dresden, Germany*
[*]*claudia.adolfs@tu-clausthal.de*

Decontamination of soil and water containing heavy metals may be achieved via reagents that form chelate complexes or insoluble salts.[1,2] In this contribution an approach is presented that involves modification of a PVDF mesh to introduce chelating functional groups. For this purpose, the PVDF mesh is treated with high-energy electrons at room temperature in air. Different types of radicals are formed on the fabric surface and inside the filaments at a dose of 125 kGy.[3] Subsequently, radical polymerization is initiated at the radical sites. The pre-treated PVDF is placed in a solution containing the appropriate monomers at a concentration of 2.0 mol·L^{-1} and polymerization proceeds according to the 'grafting from' method. Water and propylene carbonate are used as solvents. Propylene carbonate causes swelling of PVDF, which leads to both better accessibility of trapped radicals and a more uniform outer surface of the material.



Important functional groups for complex formation contain both nitrogen atoms and carboxylic acids. The monomers used for graft polymerization are either commercially available, such as acrylic acid and (2-dimethylaminoethyl)methacrylate, or are synthesized. An important functional group of the monomer is formed by ketoximes, which are easily synthesized from ketones with hydroxylamine hydrochloride in a planetary ball mill without any solvent. To test for the performance of the materials adsorption experiments are performed using aqueous solutions of Hg(II), Cu(II), and Ni(II) ions.

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LogP_{oct}/SA predicts thermoresponsive behavior of P(DMA-*co*-RA) statistical copolymers

Irem Akar,[1] Jeffrey C. Foster,[1] Xiyue Leng,[1] Amanda K. Pearce,[1] Robert T. Mathers,[2,*] Rachel K. O'Reilly[1,*]

[1] *School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom*
[2] *Department of Chemistry, Pennsylvania State University, New Kensington, Pennsylvania 15068, United States*
* *R.OReilly@bham.ac.uk*
* *rtm11@psu.edu*

Thermoresponsive copolymers that display a lower critical solution temperature (LCST) have been exploited to prepare stimuli-responsive materials for a broad range of applications.[1] LCST behavior can be tuned by controlling polymer composition upon copolymerization of monomers with different hydrophobicity, because the phase transition that happens due to the LCST behavior is greatly affected by the hydrophilic/hydrophobic balance of the copolymers.[2, 3] However, no general methodology has been established to relate polymer properties to their temperature response in solution. Herein, we sought to develop a predictive relationship between polymer hydrophobicity and cloud point temperature (T_{CP}, a proxy for the LCST). A series of statistical copolymers were synthesized based on hydrophilic *N,N*-dimethyl acrylamide (DMA) and hydrophobic alkyl acrylate monomers and their hydrophobicity was compared using surface area-normalized octanol/water partition coefficients (LogP_{oct}/SA). Interestingly, LogP_{oct}/SA of the copolymers and their T_{CP}s showed a good correlation for P(DMA-*co*-RA) copolymers which allowed T_{CP} prediction of a new copolymer P(DMA-*co*-MMA). Of particular importance, this study shows and validates a method to predict the T_{CP} of thermoresponsive copolymers derived from monomers which produce nonresponsive homopolymers (DMA and alkyl acrylates). In such cases, conventional methods like the Flory-Fox equation cannot be used for predicting their thermal behavior. Thus, this prediction tool can be used as a guidance to design new copolymers with desired temperature response prior to synthesis.

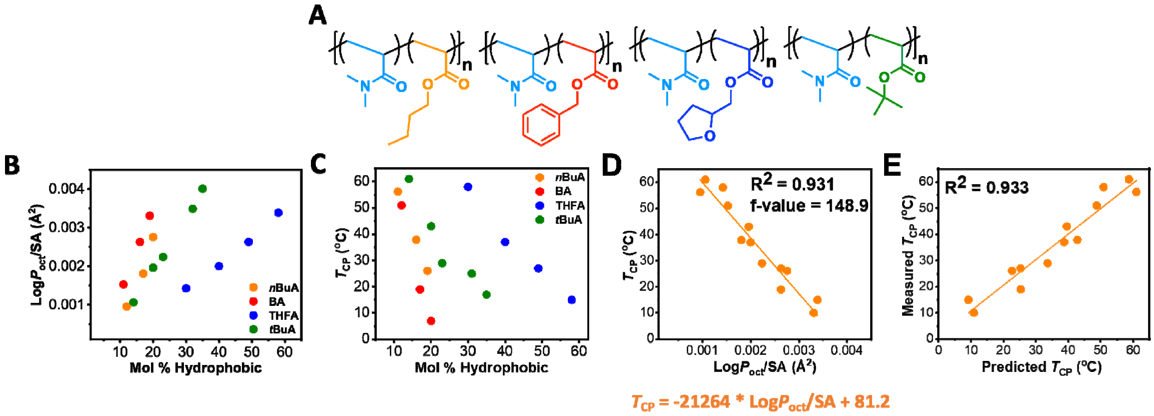

Figure. (A) Chemical structures of the repeating units for the P(DMA-*co*-*n*BuA), P(DMA-*co*-BA), P(DMA-*co*-THFA), and P(DMA-*co*-*t*BuA) copolymers, respectively. (B) Calculated Log P_{oct}/SA values for P(DMA-*co*-RA) copolymer oligomers as a function of the mol % of the hydrophobic comonomer. (C) Plot of T_{CP} as measured by UV–vis spectroscopy vs the mol % of hydrophobic comonomer. (D) Plot of T_{CP} as measured by UV–vis spectroscopy *vs* the calculated Log P_{oct}/SA values for P(DMA-*co*-RA) copolymer oligomers. The solid line represents a linear fit of these data. (E) Comparison between measured T_{CP} values of P(DMA-*co*-RA) copolymers and those predicted from their Log P_{oct}/SA. The solid line represents a linear fit of these data. The equation was generated using the linear fit of the data in the plot of Figure 3D.

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Grafting density governs the thermoresponsive behavior of P(OEGMA-*co*-RMA) statistical copolymers

Irem Akar,[1] Robert Keogh,[1,2] Lewis D. Blackman,[2] Jeffrey C. Foster,[1] Robert T. Mathers,[3,*] Rachel K. O'Reilly[1,*]

[1]School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom
[2]Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry, CV4 7AL, United Kingdom
[3]Department of Chemistry, Pennsylvania State University, New Kensington, Pennsylvania 15068, United States
[*] *R.OReilly@bham.ac.uk*
[*] *rtm11@psu.edu*

Copolymers that exhibit a lower-critical solution temperature (LCST) have been a great interest for various applications from biosensors to drug delivery.[1] It is well understood that the LCST of such copolymers can be controlled by tuning molecular weight or through copolymerization of two known thermoresponsive monomers.[2, 3] However, the lack of a general method that relate copolymer hydrophobicity to their temperature response leads to exhaustive experiments to obtain polymers with desired properties. In this study, our aim was to develop a predictive relationship between polymer hydrophobicity and cloud point temperature (T_{CP}, a proxy for the LCST). A series of statistical copolymers were synthesized based on hydrophilic oligoethylene glycol monomethyl ether methacrylate (OEGMA) and hydrophobic alkyl methacrylate monomers and their hydrophobicity was compared using surface area-normalized partition coefficients (Log P_{oct}/SA).[4] However, while some insight was gained by comparing the T_{CP} and hydrophobicity values, further statistical analysis on both experimental and literature data showed that the molar percentage of comonomer (i.e., grafting density) was the strongest influencer of the T_{CP}, regardless of the comonomer used. The lack of dependence of the T_{CP} on comonomer chemistry implies that a broad range of functional, thermoresponsive materials can be prepared based on OEGMA by simply tuning grafting density.

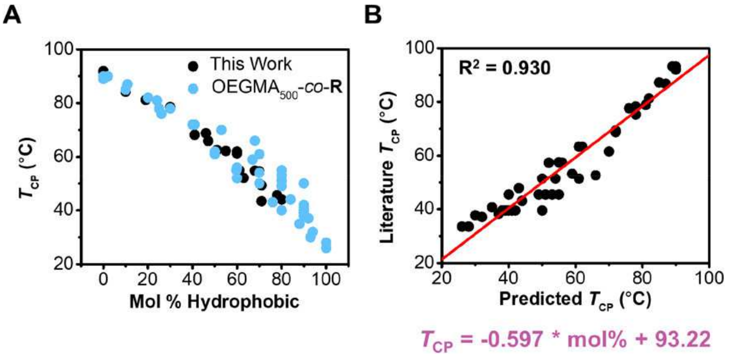

Figure. (A) Plot of T_{CP} *vs* the molar quantity of comonomer. Data from P($OEGMA_{500}$-*co*-R) copolymers obtained from literature sources is overlaid with experimental data from this report. (B) Comparison between literature T_{CP} values and those predicted from molar compositions. The solid red line represents a linear fit of these data.

Keywords: thermoresponsive polymers, hydrophobicity, copolymerization

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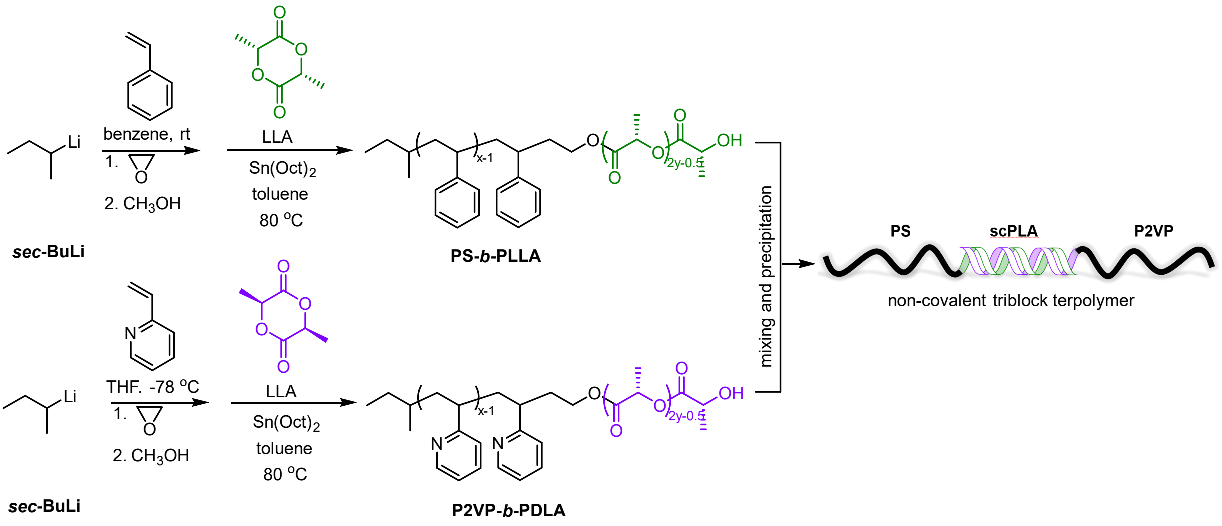
Synthesis and Thermal Properties of Non-Covalent PS-scPLA-P2VP Triblock Terpolymer *via* Polylactide Stereocomplexation

Ameen Arkanji, Viko Ladelta, Konstantinos Ntetsikas, Nikos Hadjichristidis*

King Abdullah University of Science and Technology (KAUST),
Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, Thuwal 23955, Saudi Arabia.

Non-covalent polylactide stereocomplex (scPLA)-based block copolymers have shown enormous potential applications.[1] Most scPLA triblock copolymers that have been reported were prepared from diblock copolymers *via* solution stereocomplexation (PA-*b*-PLLA/PDLA-*b*-PA) of terminal poly(L-lactide), PLLA, and poly(D-lactide), PDLA. Recently, we reported the synthesis and properties of a series of polystyrene-scPLA-polyisoprene (PS-*b*-scPLA-*b*-PI) non-covalent triblock terpolymers (ABC type)[2]. These materials were prepared by mixing PS-*b*-PDLA with PI-*b*-PLLA dichloromethane solutions and precipitation into methanol. The diblock copolymers were synthesized by combining anionic polymerization under high vacuum and ring-opening polymerization (ROP) techniques. Following the same strategy, we report the synthesis, molecular characterization and thermal properties of polystyrene-scPLA-poly(2-vinylpyridine) (PS-*b*-scPLA-*b*-P2VP) terpolymers. First, well-defined *ω*-hydroxyl polystyrene (PS-OH) and poly(2-vinylpyridine) (P2VP-OH) were synthesized by anionic polymerization using *sec*-BuLi as an initiator, followed by termination with ethylene oxide and methanol. PS-OH and P2VP-OH were then used as macroinitiators for the ROP of DLA and LLA, catalyzed by tin(II) 2-ethyl hexanoate, to afford PS-*b*-PDLA and P2VP-*b*-PLLA. PS-*b*-scPLA-*b*-P2VPs were prepared by mixing PS-*b*-PDLA and P2VP-*b*-PLLA dichloromethane solutions, followed by precipitation into methanol. The molecular characteristics of the precursor, as well as of the final block co/terpolymers were determined by ^{1}H NMR spectroscopy and size exclusion chromatography. The formation of the stereocomplex-based materials was verified by differential scanning calorimetry, X-ray diffraction, Fourier-transform infrared, and circular dichroism spectroscopies.



Scheme. General reactions for the synthesis of non-covalent PS-*b*-scPLA-*b*-P2VP triblock terpolymer via anionic polymerization, ring-opening polymerization, and stereocomplexation.

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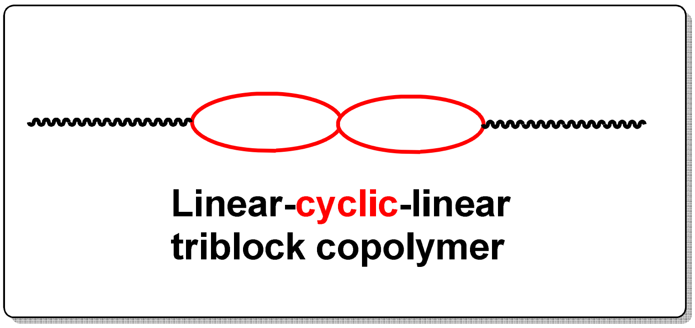
Synthesis and Characterization of Linear-Cyclic-Linear Triblock Copolymer

Suraj Aswale[1], Minji Kim[1], Aruna Kumar Mohanty[1], Hong Y. Cho[1], Heung Bae Jeon[2], Hyun-jong Paik[1*]

[1]*Pusan National University, Busan, South Korea*
[2]Kwangwoon University, Seoul, South Korea
[*]*hpaik@pusan.ac.kr*

Recently, cyclic polymers have attracted much attention due to their unique properties such as lower intrinsic viscosity, lower hydrodynamic volume, and higher glass transition temperture compared to linear polymers.[1] In this work, the synthesis of a new class of triblock copolymer consisting of a spiro-cyclic polymer and linear polymer blocks via ATRP technique is introduced. A cyclic polymer block of polystyrene was first synthesized by ATRP using a tetra-functional initiator, followed by end-group azidationand Cu-AAC click reaction with a hydroxy functionalized di-yne coupling agent. This enabled the construction of a dihydroxy functionalized 8-shaped cyclic polystyrene (cPS). After purification by preparative size exclusion chromatography and high-pressure liquid chromatography (HPLC), esterfication of the hydroxy groups of cPS using α-bromoisobutyryl bromide and subsequent chain extension reaction with methyl methacrylate in an ATRP reaction were carried out. As a result, a triblock copolymer of PMMA-*b*-cPS-*b*-PMMA was successfully synthesized and characterized by using size exclusion chromatogrphy, liquid chromatography[2], proton nuclear magnectic resonance, and fourier-transform infrared spectroscopy.



Keywords: Cyclic polymer, ATRP, Click reaction, Block copolymer

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Microporous Polyacetylene Polymer Networks with Chiral Segments

B. Bashta[1], L. Havelková[1], J. Sedláček[1], J. Brus[2], E. Vyskočilová[3]

[1]*Faculty of Science, Charles University, Prague, Czech Republic*
[2]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic*
[3]*University of Chemistry and Technology in Prague, Prague, Czech Republic*
**(bashtab@natur.cuni.cz, www.natur.cuni.cz)*

Microporous organic polymers, i.e. polymers with permanent porosity and high specific surface are the materials of fast-growing interest due to their multifunctionality and wide area of applications. The structure, composition and properties of such polymers can be widely tuned via polymerization approach and (or) by post-synthetic chemical modification.

Here we present new concept of polyacetylene type microporous polymer networks with chiral segments which were prepared by: (i) chain-growth copolymerization of chiral monoethynylated monomers with ethynylated cross-linkers catalyzed with [Rh(nbd)acac] and (ii) chemical modification of polyacetylene microporous polymer networks containing reactive functional groups with chiral agents.

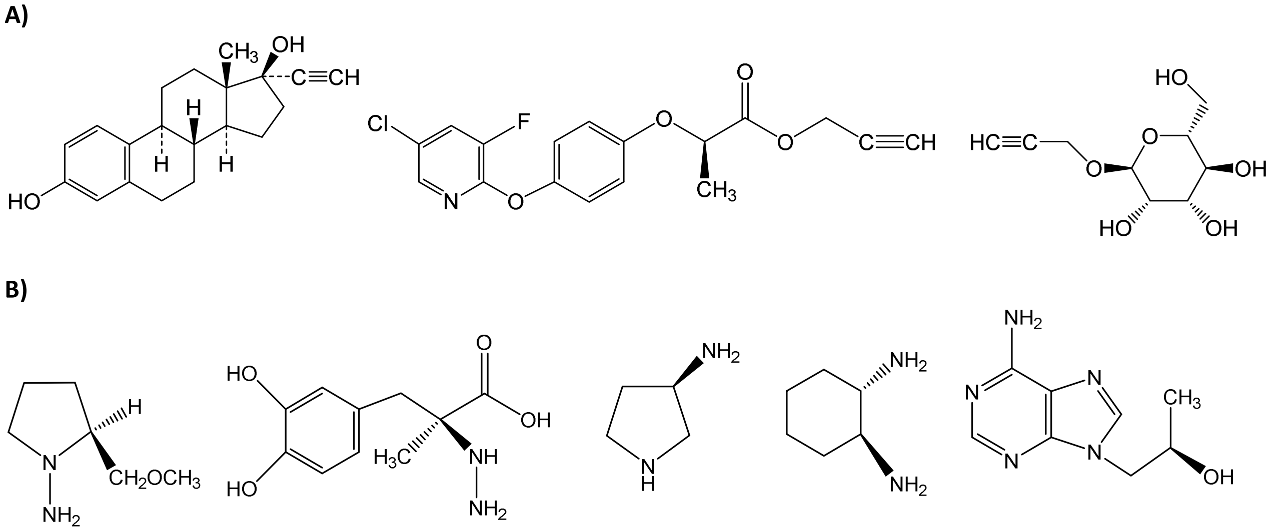

Figure 1: Examples of chiral monomers (A) and chiral modifying agent (B) used to prepare microporous polyacetylene polymer network with chiral segments.

Keywords: Microporous polymers, hyper-cross-linked networks, polyacethylenes, chirality.

Acknowledgments

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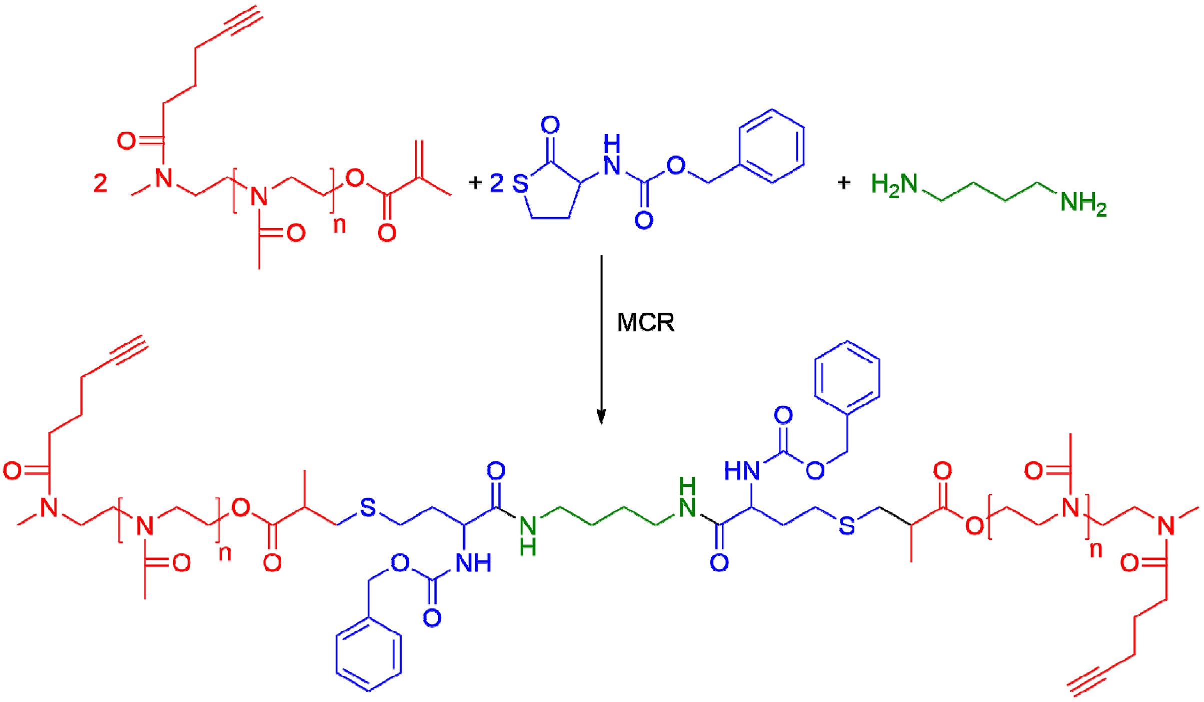
Amine-Thiol-Ene Multicomponent Reaction on Poly(2-oxazoline)s

Tim Bauer[1*], Rainer Jordan[1]

[1] *Chair of Macromolecular Chemistry, Dresden, Germany*
**tim.bauer@tu-dresden.de*

Poly(2-oxazoline)s (POx) are an interesting group of polymers, that have potential applications for example in the field of biomedical usage. [1] The knowledge about the chemistry of POx is already broad, but until now doesn´t include the well-known amine-thiol-ene multicomponent reaction (MCR). [2] To further expand the field of MCRs in the chemistry of POx this special type of MCR was investigated using functionalized oligomers of 2-methyl-2-oxazolin. (Scheme 1)



Scheme 1: Amine-thiol-ene MCR of POx-oligomers, *N*-(carbobenzyloxy)homocysteine thiolactone and butane-1,4-diamine.

Through analysis via SEC and NMR the successful synthesis of the MCR-product was proven. Therefore, the positive aspects of MCRs like atom efficiency and mild reaction conditions can be implemented into the chemistry of POx. [3] Moreover it allows the formation of sequence-controlled block copolymers with a high number of different building blocks.

This sequence-control of POx allows to tailor the properties of the polymer further, aiming to gain agency over the polymer structure similar to polypeptide synthesis in living organisms. [4]

Keywords: functional polymers, poly(2-oxazoline), multicomponent reaction, sequence control

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Applications of carboxylic acid – quaternary ammonium salts mixtures: effect of structure of the salts on photopolymerisation of itaconic acid

S. Bednarz[1*], K. Mielczarek[1], S. Bujok[2], M. Topa-Skwarczyńska[1], S. Wierzbicki[1], R. Konefał[1],
M. Nevoralová[1], H. Beneš[2], J. Ortyl[1]

[1] *Cracow University of Technology, Cracow, Poland*
[2] *Institute of Macromolecular Chemistry, Prague, Czech Republic*
[*] *sbednarz@pk.edu.pl*

Itaconic acid (IA) is a vinyl monomer of renewable origin, industrially produced by biotechnological methods. This makes IA an interesting substitute for petrochemically derived monomers such as acrylic and methacrylic acid.[1] The radical polymerization of itaconic acid gives the polyelectrolyte - poly(itaconic acid) - PIA. However, so far typical methods of polymerization of IA in both aqueous and organic solutions do not allow to obtain polymers with a average molecular weight Mw > 100 000 g/mol.[2]
The only known way (Fig.1) to obtain PIA with high molecular weight (Mw ≈ 900 000 g/mol) is to use an unusual reaction system, which is an equimolar mixture of IA and choline chloride (CC) (quaternary ammonium salt) forming hydrogen-bonding stabilised liquid melt at r.t (so-called Deep Eutectic Monomer - DEM). [3] The high viscosity of the reaction system strongly affects the kinetics of radical polymerization, accelerating the process and increasing the average degree of polymerization.[4]
In this work we present how the chemical structure of the quaternary ammonium salts forming DEM with itaconic acid influences the photopolymerization process, including the effect on the polymerization rate and molecular weight of PIA prepared. Previous studies have been focused on the polymerization process in IA-CC DEM, whereas in this systematic work we take into consideration range of quaternary ammonium salts with different alkyl chain length and additional polar functional groups.

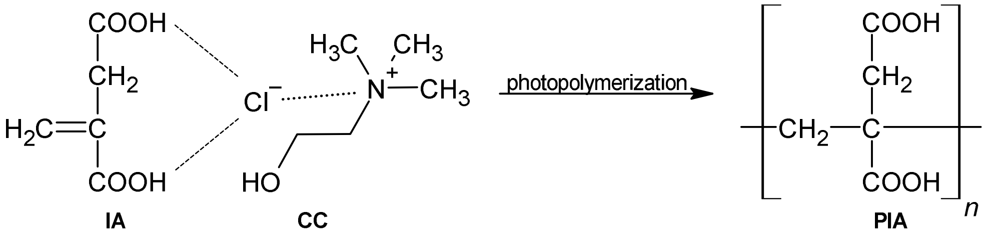

Fig.1 Scheme for obtaining PIA in Deep Eutectic Monomer composed of an equimolar amount of IA and CC

Keywords: free-radical polymerization, bio-based monomers, ionic liquids, quaternary ammonium salts

Acknowledgments

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ATRP synthesis of stretchable and self-healable (poly(EDOT-co-ThBr)-g-PEGMA

M.Božičević [1*], L. Fiket[1], Z. Katančić[1]

[1] *University of Zagreb, Faculty of chemical engineering and technology, Zagreb, Croatia*
mbozicevi@fkit.hr

Given their excellent properties, such as high thermal and environmental stability, good conductivity, ease of synthesis, and ability to modify many other properties, conductive polymers are increasingly being studied in both industrial applications and academic research [1]. Poly(3,4-ethylenedioxythiophene) is one of the most studied conductive polymers due to its remarkable stability, tunable conductivity, easy synthesis by oxidative polymerization or electrochemical synthesis, and wide range of applications [2]. In exploring new materials for use as wearable electronics and electronic skin, PEDOT is a great research option. The lack of mechanical properties such as stretchability and self-healing properties are limiting factors for this purpose, but fortunately polymers can be optimized in many ways. One of the best controlled tools for this is atom transfer radical polymerization (ATRP), which is used in this research to control the molecular weight, chain length, and thus properties of the final products [3]. PEDOT itself is not suitable for such polymerization, so the first thing required is the synthesis of modified PEDOT. This can be easily done by oxidative copolymerization of 3,4-ethylenedioxythiophene (EDOT) monomer and 2-(thiophen-3-yl)ethyl 2-bromo-2-methylpropanoate (ThBr) monomer.ThBr has the same thiophene group as EDOT but is functionalized with α-bromoisobutyryl bromide (BiBB) to be suitable for ATRP synthesis, which takes place at the alkyl halide group [4]. Finally, poly(ethylene glycol) methacrylate (PEGMA) is used as ATRP monomer to improve the desired mechanical properties. Branches of PEGMA are grafted onto the ThBr part of the polymers (Figure 1) to increase the stretchability and achieve self-healing properties through hydrogen bonding. In this research, the conditions of ATRP synthesis are investigated, such as different reaction times and different temperatures. All synthesized products are characterized by different techniques such as NMR, FTIR, GPC, TGA and DSC. Mechanical properties, conductivity and self-healing are also investigated.

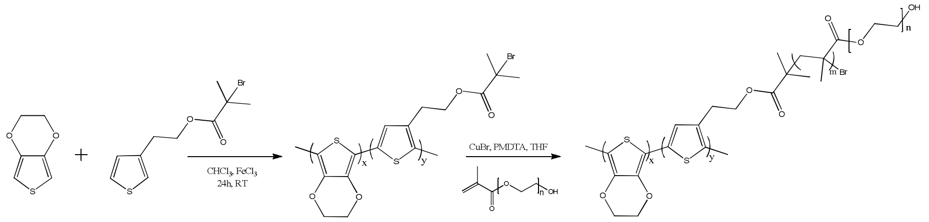

Figure 1. Reaction scheme of ATRP (poly(EDOT-co-ThBr))-g-poly(ethylene glycol) methacrylate synthesis

Keywords: ATRP, wearable electronics, PEDOT, grafting, molecular tailoring

Acknowledgments
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Reactive Extrusion Synthesis of Isocyanate-Free Hydropbically Modified Ethoxylated Urethanes

D. Wołosz[1], A. M. Buczko[2*], P. G. Parzuchowski[1], A. Świderska[1], R. Brüll[3] and P. Elsner[2]

[1]*Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland*
[2]*Fraunhofer Institute for Chemical Technology ICT, Joseph-von-Fraunhofer-Straße 7, 76327 Pfinztal, Germany*
[3]*Fraunhofer Institute for Structural Durability and System Reliability LBF, Bartningstraße 47, 64289 Darmstadt, Germany*
[*]*aleksandra.buczko@ict.fraunhofer.de*

The safety concerns related to one of the basic components used in conventional polyurethane (PU) chemistry – diisocyanates – raise the demand for alternative PU products. [1] One of the promising class of materials are poly(hydroxy-urethane)s (PHUs), which are obtained through polyaddition of cyclic carbonates with amines. Their synthesis route not only omits isocyanates, but also uses CO_2 as a building block incorporated during the formation of the cyclic carbonate monomers. Thus, the resulting architecture of PHUs imparts unique properties, not present in the standard PU materials. The intrinsic hydrophilicity, gained with the free OH group present at each urethane bond, makes PHUs particularly suitable for application as rheological thickeners for waterborne systems. Such PU-based additives – hydrophobically modified ethoxylated urethanes (HEURs) – are telechelic polymers containing a water-soluble core end-capped with hydrophobic groups, which increase the viscosity of aqueous solutions by forming micelle-based networks.[2] Despite the broad applicability in paints, inks or coating products, the sustainability of this class of materials remains an open issue.

Effective development of PHUs is often hindered already at the production step. Use of suitable solvents compromises the green approach due to their inherent toxicity, while the bulk polymerization suffer from moderate product homogeneity and low reaction yields[1]. Therefore, use of reactive extrusion (REX) as solvent-free synthesis method has the potential to overcome the kinetic limitations of the PHU system. As REX is well suited for highly viscous melts, it not only improves monomer diffusion compared to typical batch polymerizations, but also allows to substantially reduce the reaction time.

Therefore, we applied the REX approach to prepare isocyanate-free HEUR (IFHEUR), obtained through hydrophobic functionalization of PHU chains. The insight into the structural characteristics of the synthesized IFHEUR was gained through spectroscopic investigation, while the rheological study demonstrated their thickening performance in aqueous solutions. Thus, we report a sustainable alternative for the preparation of PU-based rheological thickeners.

Keywords: poly(hydroxy-urethane), hydrophobically modified ethoxylated urethane, reactive extrusion

Acknowledgments

This research was possible thanks to the bilateral exchange of scientists between Poland and Germany funded by NAWA (contract no. PPN/BDE/2019/1/00012) and DAAD (PPP Programme Project-ID: 57514636). The collaboration with the EU project SIMPLIFY (grant agreement No 820716), providing support in financing the analytical characterization, is gratefully acknowledged.

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Dark sulfur: Quantifying unpolymerized sulfur in inverse vulcanized polymers

Joseph J. Dale[1*], Tom Hasell[2]

[1]*University of Liverpool, Liverpool, United Kingdom*
[2]*University of Liverpool, Liverpool, United Kingdom*
[*]*Joseph.dale@liverpool.ac.uk*

The global increase in the quantity of elemental sulfur waste from the desulfurization of crude oil has led to the expansion of investigations into new sulfur based materials. Since 2013, the discovery by Chung *et al.* has promoted ever growing research into the field of inverse vulcanization. [1] A one-pot, solvent free synthesis wherein ring-opening of elemental sulfur at elevated temperatures, before reaction with a vinylic comonomer, yields a high sulfur content polymer product with variable and tunable properties for a wide variety of uses, such as in heavy metal capture[2], antimicrobial[3], or Li-S battery[4] applications. Interest is growing with regards to the commercialisation and scale-up of this procedure. As such, questions arise in respect of polymer stability, degradation, and lifetime. Inverse vulcanized polymers are subject to aging with time, particularly in polymers synthesised using renewable crosslinkers such as limonene, pinene, or myrcene, often to the detriment of their characteristics. Herein the lifetime of inverse vulcanized polymers is investigated, with it shown that the glass transition temperature (T_g) may change over the aging period. This study subsequently prompted the discovery of unreacted sulfur, stable in an amorphous form, within the polymer matrix and not reacted into the polymer structure. It has commonly been considered that if crystalline sulfur was unobserved in these polymers by methods of powder X-ray crystallography (PXRD) or differential scanning calorimetry (DSC), then all sulfur was reacted into the polymer structure. A detailed study is presented on the quantification of free amorphous sulfur within inverse vulcanized polymers, in which free sulfur is shown to increase over a period of aging. Owing to the dynamic nature of the sulfur-sulfur bond, it is shown also that through the application of heat this aging may be reversed, with sulfur re-incorporated back into the polymer chains, by means of homolytic S-S cleavage. It goes without saying that this potential for polymer regeneration would be a key characteristic for the application of these materials in a commercial setting.

Keywords: Inverse Vulcanization, Sulfur polymers, Dark sulfur, lifetime, regeneration

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Hybrid alkyds, the glowing route to reach cutting-edge properties

Maxinne Denis[1,2*], Damien Le Borgne[2], Sylvain Caillol[1] , Claire Negrell[1]

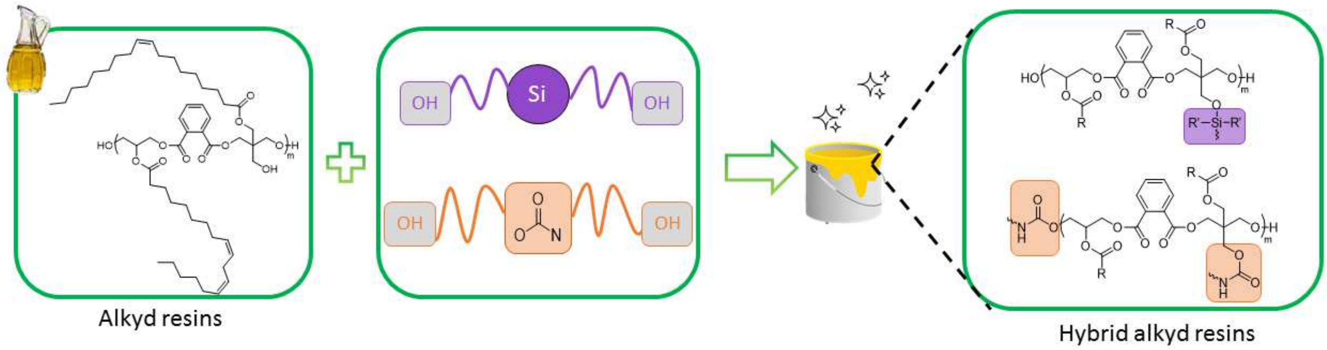
[1]*ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France*
[2]*Lixol, groupe Berkem, 20 Rue Jean Duvert, 33290 Blanquefort, France*
[*]*Corresponding author: maxinne.denis@enscm.fr*

Alkyd resins were polymerized for the first time in the mid-1920s and they quickly found a prominent place among coatings and paint binders in industrial field [1]. Indeed, they provide numerous advantages such as good thermal resistance, excellent gloss, fast drying time [2]. In the 1950's, the emergence of synthetic polymers with more specific properties for advanced applications weakened the position of the alkyd resins for the coating industry [3]. However, since the past decade, due to growing up environmental concerns a new researches on alkyd resins were carried out. Indeed, alkyd resins are mostly composed of biobased raw materials which makes them more "environmentally friendly" than other polymers based on fossil ressources. in order to enhance alkyd properties, bridge the gap with new materials, and remain competitive in terms of applicative properties, other polymers such as epoxy, acrylates, polyurethanes or siloxanes have been used to form alkyd hybrids. Recently, our team highlighted the various stategies to enhance alkyd properties and develop alkyd hybrid polymers in a review article [4].

Recent researches have been focused on the modification of alkyd resins with an oligomer containing silicon for coating applications on wood sample. Silicon-modified polymers are well know to exhibit excellent thermal properties and provide outdoor properties. The results of the study have showed that silicon modified alkyd resins exhibited better coating properties such as faster drying time, higher gloss and hardness and allowed to determine the optimal content of oligomer. Moreover, other heteroatomes can be associated to silicon modified alkyd in order to provide a synergistic effect and bring new properties such as fire resistance.

Currently, due to low chemical and corrosion resistance, a novel hybrid alkyd-polyhydroxyurethane (PHU) has been investigated for metal coating applications. The coatings properties have been studied throught salt spray test and accelerated weathering tester, and exhibited better performance with the introduction of urethane functions. Moreover, the hybridization of alkyd resins with PHU have enhanced the adhesion properties of the coatings.

Keywords: Alkyd, coating, hybrid, siloxanes, polyhydroxyurethanes



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Theory and Modelling of Polymers and Their Properties

Polymer Nanocomposites via Simulations Across Scales: from Atoms to Macroscopic Properties

H. Reda[1], A.F. Behababani[2], A. CHazirakis[2], A. Paower[2], V. Harmandaris[1,2*]

[1]*Computation-based Science and Technology Research Center, The Cyprus Institute, Nicosia 2121, Cyprus.*
[2]*Department of Mathematics and Applied Mathematics, University of Crete, GR-71409, Heraklion & Institute of Applied and Computational Mathematics, Foundation for Research and Technology Hellas, IACM/FORTH, GR-71110 Heraklion, Greece.*
[*]*harman@uoc.gr*

Nowadays, computαtional approaches can be used in order to provide a direct insight at the properties of complex polymer-based materials across multiple spatiotemporal scales. Molecular simulations in particular have the advantage of accurately describing the chemistry of the systems under study, and of predicting their behavior at the molecular level. However, the study of polymers via molecular simulations is a very challenging field, due to the broad spectrum of the underlying length and time scales. Here, we present a hierarchical multi-scale methodology for predicting the macroscopic properties of polymer-based nanostructured systems, that involves atomistic and coarse-grained simulations. The coarse-grained (CG) models are derived through a “bottom-up” data-driven strategy, using information from the detailed atomistic scale, for the given chemistry. The systematic linking between the atomistic and the chemistry-specific CG scale, allows the study of a broad range of molecular weights, for specific polymers, without any adjustable parameter [1-3]. At the same time, machine learning (ML) algorithms have been developed to re-introduce atomic detail in the CG scale, and thus obtaining atomistic configurations of high molecular weight polymers [3].

We apply the entire methodology to (a) cisPB polymer melts [4], and (b) cisPB/silica nanocomposites [5]. For both systems we provide a detailed study of their dynamical and rheological macroscopic properties. For the polymer melts, we report predictions about the self-diffusion coefficient of polymer chains, the relaxation modulus and the zero shear-rate viscosity, as a function of molecular length probing the transition from oligomers, to Rouse-like, up to the well-entangled systems.

Concerning the polymer nanocomposites, we examine the structure and the dynamics of polymer chains at the polymer/nanoparticle interphase, by probing directly the density and the conformations of polymer chains, as well as and the segmental and terminal dynamics of the adsorbed, “bound” layer. In all cases the results are compared against experimental data and theoretical predictions.

Keywords: Molecular simulations, polymer nanocomposites, machine learning methods, …

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Adsorption and Shear Flow of Flexible chains on bioinspired substrates. A tool for eco-sustaineable polymer design.

Irene Adroher-Benítez[1], Tatiana I. Morozova[2], Nicolás A. García[3], Jean-Louis Barrat[1,2], Gustavo S. Luengo[4*] and Fabien Léonforte[4]

[1] *Laboratoire Interdisciplinaire de Physique, Université Grenoble Alpes-CNRS, Grenoble, France.*[2] *Institut Laue-Langevin, Grenoble, France.* [3]*Instituto de Física del Sur, UNS-CONICET, Bahía Blanca, Argentina.*
[4]*L'Oréal Research and Innovation, Aulnay-Sous Bois, France*
[*]*gluengo@rd.loreal.com*

Polymers play a main role in most cosmetic products. In the case of hair care, their cosmetic performance is determined by the way polymers adsorb in the hair surface, which is highly conditioned by the physico-chemical properties of its external structure. For some years now, cosmetic industry has been making a great effort to develop new sustainable products that have better performance and at the same time are truly respectful with the environment. However, despite the large amount of experimental work already done in this direction, it remains to be known which physical quantities play a determining role in polymer adsorption onto hair-like substrates, as well as in the stability of these polymeric coatings.

With this aim, we have analyzed the behavior of polymers of cosmetic interest in realistic surfaces, modeled from actual experimental images of human hair. In particular, in the work presented here we have prepared coarse-grained models for two different families of polymers. First, we have modeled semi-flexible linear chains in which each bead correspond to a monomer. With this model we aim to study the performance of simple molecules of natural origin. Second, we have created a branched stiff polymer model with 17 beads per monomer. This more complex system is intended to mimic some of the macromolecules currently used in the cosmetic industry.

For these two models we have performed implicit-solvent Molecular Dynamics simulations to study the quantities involved in the polymer adsorption onto a heterogeneous surface. We have analyzed the structure of the resulting coating and compared the results for the two types of polymers. Then, we have used Brownian dynamics simulations to apply a linear shear flow on the adsorbed polymer layer. This way we have tested the stability of the coating and we have analyzed the dynamics of the polymer desorption.

Keywords: natural polymers, cosmetics, structured surfaces…

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Coarse-grained polymer models with correct dynamics

Florian Müller-Plathe[*1], Jurek Schneider[1], Zhenghao Wu[1,2], Tianhang Zhou[1]

[1] *Department of Chemistry, Technical University of Darmstadt, Germany*
[2]*Present address: Department of Civil and Environmental Engineering, Northwestern University, Evanston, United States*
[*]*f.mueller-plathe@theo.chemie.tu-darmstadt.de*

Simplified coarse-grained models for the simulation of polymers generally suffer from the problem of artificially accelerated molecular mobility, which precludes their use for the prediction dynamical and rheological polymer properties. Coarser models, i.e. with more real atoms collected into a single interaction site or superatom, generally show a stronger spurious acceleration. When a level of coarse-graining is reached where one superatom represents a substantial fragment of a polymer chain, the interactions between different chains necessarily become soft-core: Different chains may occasionally cross one another. At this point, the polymer dynamics becomes not only quantitatively wrong (too fast), but also qualitatively (no reptation).

This is the case for common soft-core polymer models, for example dissipative-particle dynamics and also hybrid particle-field molecular dynamics. The situation can be remedied by introducing slip-springs, which are temporary bonds between atoms normally not bonded. They have their own rules of motion: they can slide up and down chains and also teleport from one chain end to any other. It is shown that, while they do not strictly suppress chain crossing, they do enforce reptation-like dynamics on polymer melts [1, 2], including elastomers [3], and solutions [4], opening to the way to use very coarse (and very cheap) polymer models for the calculation of dynamical and rheological polymer properties.

Keywords: Dissipative-particle dynamics, hybrid particle field, slip-springs, polymer dynamics

Acknowledgments
This work has been in parts supported by the Collaborative Research Centre Transregio 146 Multiscale Simulation Methods for Soft Matter Systems *of Deutsche Forschungsgemeinschaft.*

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On the structure of α and β forms of poly(3-hydroxybutyrate)

J. Czernek[1*], J. Brus[1]

[1]*Institute of Macromolecular Chemistry CAS, Prague, The Czech Republic*
[*]*czernek@imc.cas.cz*

The recently solved [1] crystal structure of the β form of poly(3-hydroxybutyrate) and the previously known α form [2] were investigated by means of high-level quantum chemical calculations, which were performed for dimeric models comprising 58 atoms (see Figure 1). In particular, the breakdown into electrostatic, induction, and dispersion contributions to a total stabilization of these two crystalline forms was reliably described. This will be discussed in the context of interchain interactions in crystals of polyesters with a general aim of understanding the structure – mechanical properties relationship.

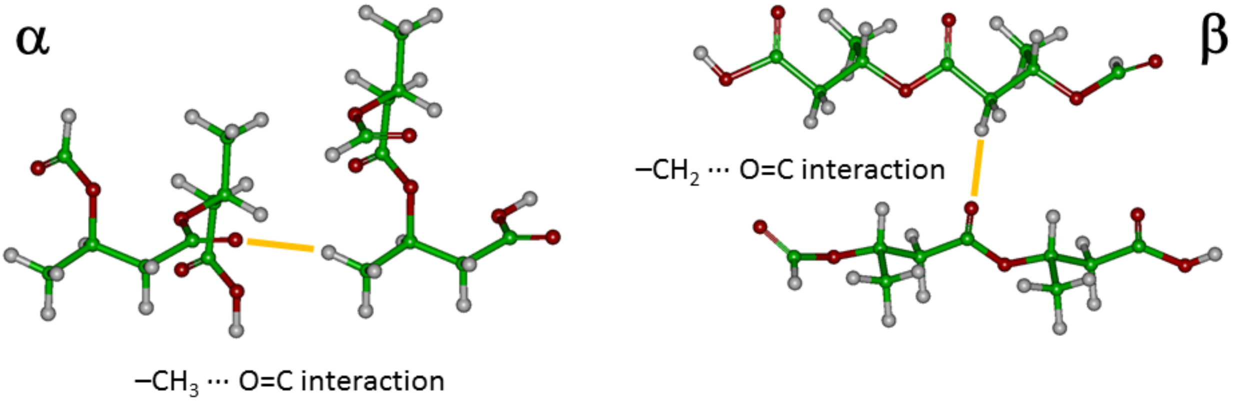

Figure 1. Dimeric models of α and β polymorphs of poly(3-hydroxybutyrate). Dominant intermolecular contacts are highlighted.

Keywords: poly(3-hydroxybutyrate), polymorphism, DFT

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Hidden Volume Phase Transitions in Polymer Gels

M. Dušková-Smrčková[1,*], J. Šomvársky[2], M. Steinhart[1], and Karel Dušek[1,†]

[1] *Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Prague, Czech Republic*
[2] *Dept. of Macromol. Physics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Rep.*
[*] *m.duskova@imc.cas.cz*

Fifty-four years have elapsed from the prediction of the existence of volume phase transition (VPT) in swollen polymer gels by Dušek[1] and forty-four years from its experimental discovery by Tanaka[2]. The gels exerting this phenomenon are commonly called nowadays as stimuli-responsive gels or smart gels. The number of published papers dealing with this phenomenon reached the order of 10^4. In cross-linked gels–solvent systems, the transition is a result of a balance between attractive and repulsive forces contributing positively and negatively to the chemical potential of the solvent. Such balance can be tuned by adjusting the coiling state of network chains (supercoiling, pre-stretching), introduction of charges, and specific polymer-solvent interactions (hydrogen bonding, hydrophobic association). The specific interactions are effective already in uncross-linked systems and the poly(N-isopropyl acrylamide), (PNIPAm)-water system is a striking example.

Despite a large number of publications on volume phase transition in gels, there are not so many chemical systems known to show up the temperature-induced transition. For most of the systems, the dependence of equilibrium swelling degree on temperature is more or less steep and smooth and corresponds to a two-phase equilibrium between swollen gel and pure solvent. The volume phase transition corresponds to a three-phase equilibrium between pure solvent and two polymer phases of different degrees of swelling. For such systems, the dependence of $\Delta\mu_1$ vs. polymer concentration is characterized by the so-called van der Waals (vdW) loop, and the equilibrium is determined either by solving equations showing equalities of chemical potentials or by Maxwell construction. For conventional gels, the vdW loop is absent. This contribution aims to show that for some gels the vdW loop is located inconveniently in the positive (more frequent) or negative parts of the dependence.If one can shift the loop to the region of $\Delta\mu_1 = 0$, the "hidden" transition becomes observable.[3] Alternatively, one can ask whether a swelling-temperature dependence showing an inflection point can be transformed into one having the vdW loop. It is the purpose of this contribution to show that such conditions for VPT can be found; these are mechanical strains generated externally or internally. Already in prediction paper[1], it was found that uniaxial extension can facilitate the volume phase transition. Later, the effect of mechanical strain was extensively studied in various laboratories. We will examine if at all and which types of mechanical strains can make the transition visible under normal conditions. For a demonstration of the strain effect, we have used the model of χ-transition determined by the concentration dependence of the interaction function $g(\varphi_2)$of interaction parameter $\chi(\varphi_2)$.

Keywords: swelling, volume phase transition, stimuli-responsive gel, smart gel, gel collapse

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Establishing the rules for the self-organisation of conducting polymers on the graphene surface

T. Hacıefendioğlu[1*], E. Yıldırım[1,2,]

[1]*Chemistry Department, Middle East Technical University, Ankara 06800, Turkey*
[2]Department of Polymer Science and Technology, Middle East Technical University, Ankara 06800, Turkey
[*]*tugba.haciefendioglu@metu.edu.tr*

As one important member of graphene (Gr)-based composites, conducting polymers (CPs)-graphene nanocomposites have drawn large amount of attention in recent research areas due to their superior enhanced electrical electrochemical and dielectric properties which make them ideal candidate for organic electronics.[1–3] However, lack of knowledge about the configuration preferences of CPs on graphene, may prevent the engineering of these nanocomposites with enhanced morphology at interface for any application. To get more insight to rules for the self-organization of the CPs on graphene surface, DFT studies were conducted and general approaches for alignment preferences were determined.

To establish the rules for the alignment of CPs, one member of the common CP families in the literature were chosen and structural optimizations were performed using accurate and precise DFT method (M06-2X-D3) which reflects the effect of dispersion on the electron polarization density on Gr surface. Interaction energies and charge transfer between the components, configurational and directional preferences of CPs on Gr were determined. Results showed that the origin of this difference is explained by the affinity to position graphene carbons in the center of electron rich aromatic centers of CPs. Also, the distance between the intramolecular aromatic ring centers has a significant effect of the placement of CPs on Gr surface. These established rules will help both academia and industry to reach an architecture which resulting in high conductivity crystalline domains at the interface.

Keywords: DFT calculation, acceptor units, graphene surface, intramolecular aromatic ring center, allignment preference

Acknowledgments

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Optimizing Chain Topology of Bottle Brush Copolymer for Promoting the Order-Disorder Transition

June Huh[1*], Jihoon Park[1], Joona Bang[1], Dae Ryook Yang[1]

[1]*Department of Chemical and Biological Engineering, Korea University, Seoul, 02841, Republic of Korea*
[*]*junehuh@korea.ac.kr*

Bottle brush copolymers (BBCs), where either copolymer side chain as a macromer or two or more kinds of side chains as comacromers are grafted densely to a linear polymer backbone, have attracted much interest owing to their intriguing phase behaviors which are similar but distinctively different from those of their linear counterpart. In analogy with block copolymers with a linear chain topology, some BBCs in molten state can form spatially periodic mesophases of which periodicities and phase transitions such as order-disorder transitions (ODT) are strongly dependent upon the comonomer /comacromer sequence in the side/main chain of BBC. As an example, BBC with diblock side chains, often referred to as core-shell bottle brush copolymer (CS-BBC), has been reported to exhibit the promoted ODT behavior when compared to that of diblock chain.[1] Here we computationally investigate the ODT behavior of some topological isomers of CS-BBC, where the topological variants are considered by varying the linking point between diblock chains along their chain paths. We consider a general description for polymer architecture comprised of M symmetric diblocks connected somehow to each other where each symmetric diblock chain consists of N monomers. A CS-BBC chain and its topological isomers can be constructed by linking diblocks at the points characterized by a fractional index λ which runs from 0 (the end of A-block) to 1 (the end of B-block), as depicted in Figure 1. For simulating molten states of these polymers each having a given set of architectural parameters of {M, N, λ }, a dissipative particle dynamics (DPD) is employed with velocity-Verlet algoithm to time-integrate the equation of motions for A and B particles (monomers) that constitutes polymers with a given architecture. The ODTs of simulated copolymers were then determined using scattering function and compared to theoretical results determined by the random phase approximation (RPA) equation.

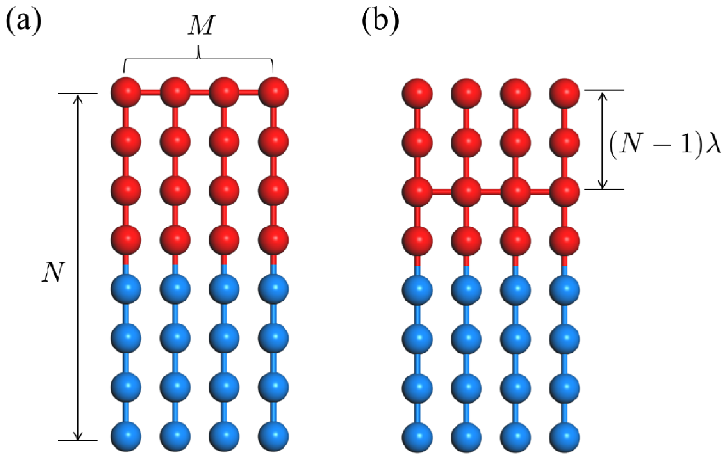

Figure 1. Illustration of polymer architectures consisting of M symmetric diblocks with N monomers: (a) CS-BBC (λ = 0) and (b) its topological isomers (λ > 0)

Keywords: bottlebrush polymers, self-assembly, order-disorder transition

Acknowledgments

This study was supported by the National Research Foundation of Korea (2020R1A4A2002903)

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Acid-base equilibria in complex macromolecular systems - simulations and experiments

Raju Lunkad[1], Pablo Blanco[1], Roman Staňo[1], David Beyer[2], Christian Holm[2], and Peter Košovan[1*]

[1]*Department of Physical and Macromolecular Chemistry, Faculty of Science Charles University, Prague, Czechia*
[2]*Institute for Computational Physics, University of Stuttgart, Germany*
[*]*peter.kosovan@natur.cuni.cz*

In this lecture we use specific examples from our recent research to demonstrate how molecular simulations can be used to predict how the charge on model peptides, polyelectrolytes and synthetic polyampholytes depends on the pH. In all these systems, the ionization response is highly non-ideal. Therefore, it often considerably deviates from the ideal behavior, predicted by the Henderson-Hasselbalch equation. However, the simultaneous presence of anionic acid groups and cationic base groups in some of these systems sometimes leads to an unexpected cancellation of effects, resulting in adsorption on the wrong side of the isoelectric point [1] or a seemingly ideal dependence of the ionization states on pH [2]. By comparing the simulation predictions with carefully performed experiments, we demonstrate that, despite using very simple models, such simulations can quantitatively predict the charge on model ampholytes at various conditions.[3]

Keywords: (optional, Calibri, 11 pt.) keyword 1, keyword 2, keyword 3…

Acknowledgments
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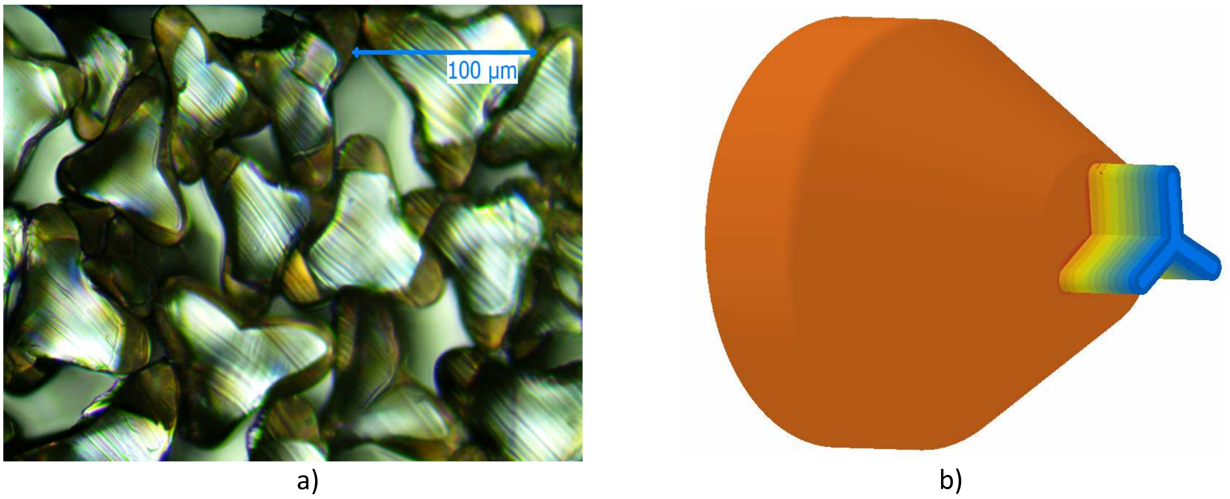
Simulation of melt spinning bicomponent trilobal filaments to predict morphology

H. M. Kaleem Ullah [1,2], J. Lejeune[1*], J. Vera Sorroche[2], A. Cayla[1], C. Campagne[1], E. Devaux[1]
ENSAIT-GEMTEX

[1]*Univ. Lille, ENSAIT, ULR 2461 GEMTEX - Génie et Matériaux Textiles, Lille, France*
[2]*CETI, Tourcoing, France*
[*] *joseph.lejeune@ensait.fr*

The main objective of wearing clothes is to maintain a thermal confort. In particular a human body can cool itself by four main methods radiation (60%), convection (15%), evaporation (20%) and conduction (5%)[1]. The PHOTONITEX project aims to develop a new smart textile, which goals is to improve the thermal wellness of the wearer by regulating the microclimate of the space between the wearer and the textile by reflecting the human body infrared. A new kind of bicomponent filaments to improve the thermal and hydric confort is develop. Theses filaments are composed of polyethelene terephtalate at the tip and polyamide at the core (Figure 1.). The studied trilobal section is harder to fabricate than a circular section but present the advantage of being more reflexive of light. Therefore it was chosen but then depending on the processing parameter it is impossible to spin. The processing difficulties emerges from the difference in surface tension and rheology [2] of the two materials. In order to avoid a time, energy and money consuming trial and error experimental process, a numerical model is developped and presented to predict the morphology and filaments feasability depending on the experimental processing parameters, with the Compuplast virtual extrusion laboratory software.



a) b)

Figure 1 trilobal cross sections of the co melt spinning of PET (tips) and PA6 (center) a) experimental b) numerical

Keywords: simulation, polymer flow, multicomponent melt spinning, textile, compuplast Virtual Extrusion Laboratory, polymers, co extrusion

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The authors wishes acknowledge support from EU Interreg France-Wallonie-Vlaanderen through the Photonitex project.

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Model-based kinetic design of poly(methyl methacrylate) chemical recycling

Eli K. C. Moens,[1] Yoshi W. Marien,[1] Kyann De Smit,[1] Kevin M. Van Geem,[1] Paul H. M. Van Steenberge,[1] Dagmar R. D’hooge[1,2*]

[1]Laboratory for Chemical Technology (LCT), Department of Materials, Textiles and Chemical Engineering, Ghent University, Technologiepark 125, 9052 Zwijnaarde, Belgium.
[2]Centre for Textile Science and Engineering (CTSE), Department of Materials, Textiles and Chemical Engineering, Ghent University, Technologiepark 70A, 9052 Zwijnaarde, Belgium.
[*]dagmar.dhooge@ugent.be

An outstanding societal challenge is to avoid the further accumulation of solid plastic waste.[1] One approach to tackle this challange is chemical or feedstock recycling via thermal degradation. In this work, a unified matrix-based kinetic Monte Carlo (*k*MC) modeling framework is applied at lab-scale to study the kinetics of both polymerization of methyl methacrylate (MMA) and degradation/depolymerization of poly(methyl methacrylate (PMMA). The novelty lies in the *in silico* design at the level of individual molecules.[2, 3] In the framework, the exact position at which structural defects and functionalities (*e.g.* head-to-head defects and unsaturated chain-ends) are incorporated in the polymer chains as well as how these chains unzip during degradation are tracked. Crucial is the consideration of diffusional limitations during both polymerization and degradation/depolymerization.

Specific PMMA feedstocks have been synthesized based on the information of prior *k*MC simulations, which allowed further validation of the *k*MC model. In addition to different molar mass distributions (MMDs), different relative amounts of structural defects and functionalities present in the feedstocks are targeted, as the degradation behaviour of PMMA depends on it.[4] A combination of thermogrametric analysis (TGA) and lab-scale degradation experiments targeting isothermicity with measurement of the evolution of the MMD makes it possible to obtain mechanistic and intrinsic kinetic information at the level of elementary reactions. The obtained results demonstrate that by combining the presented framework with dedicated experimental techniques a powerful tool is obtained that can be used to kinetically design polymerization processes that yield polymers with a desired degradation/depolymerization behaviour.

Keywords: poly(methyl methacrylate), thermochemical recycling, kinetics

Acknowledgments

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Comparison of Thermo-mechanical Properties of Epoxy-Amines and Polyurethanes Resins: Experiments Versus Molecular Simulations

Mathilde Orselly[1,2,*], Julien Devémy[2], Agathe Bouvet-Marchand[1], Alain Dequidt[2], Patrice Malfreyt[2], Cédric Loubat[1]

[1]*Université Clermont Auvergne, Aubière, France*
[2]*SPECIFIC POLYMERS, Castries, France*
[*]*mathilde.orselly@specific.polymers.fr*

Epoxies and polyurethanes are some of the most prominent thermosetting polymers valued nowadays due to their wide range of applications. These classes of polymers are of interest for instance for structural components in aerospace applications as well as electronics packaging or various types of coatings, thanks to their high versatility. Indeed, the final material can be easily modulated by the chemical structure, leading to diverse thermal and mechanical properties.

Therefore, it is of great importance to be able to characterize these materials and comprehend the influence of the structural network on their properties. Aside from the usual experimental testing, computational chemistry has shown to be a great asset to this task, in particular by using molecular simulations. [1]

In the scope of this project, all-atom molecular dynamics performed on Lammps with the CHARMM force field were used to characterise various epoxy resins and polyurethanes, such as aliphatic or bisphenol-based ones. A multi-step crosslinking algorithm as well as several methodologies to obtain key properties, such as density, glass transition temperature (Tg), and elastic modulus, were designed. A quantitative comparison was made and was proven to be in good agreement with experimental data for a large range of systems (cf Figure 1).

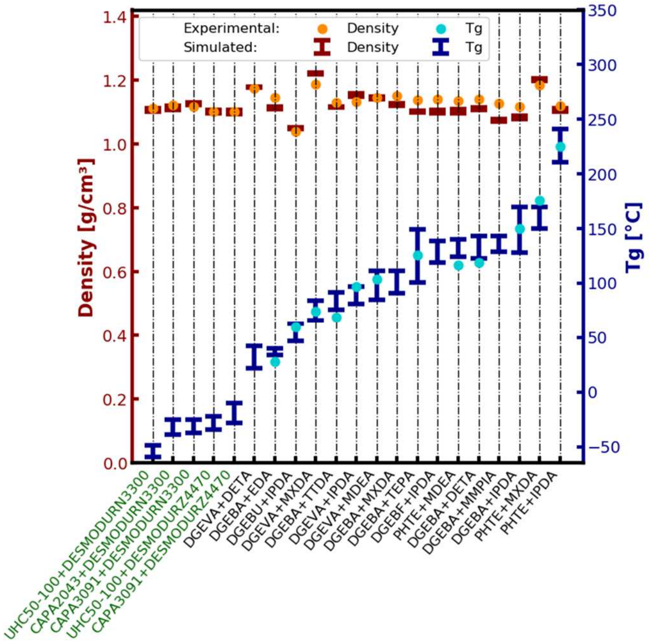

Figure 1 : Comparison of experimental vs simulated properties such as density and glass transition temperature for both epoxy (in black) and polyurethane (in green) resins

Keywords: Molecular simulations, Cross-linking, Thermosets, Epoxy, Polyurethane, Glass Transition, Young's Modulus, Atomistic Descriptions

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InnoMat.Life: Establishment of a grouping framework to assess safe use of polydisperse polymer particles

Patrizia Pfohl[1*], Amelie Vogel[2], Emeka Emecheta[2], Alexander Roloff[2], Burkhard Stahlmecke[3], Carmen Wolf[3], Mike Wenzel[3], Kerstin Hund-Rinke[4], Dana Kühnel[5], Tim Steska[5], Martin Wiemann[6], Andrea Haase[2], Wendel Wohlleben[1]

[1]BASF SE, Ludwigshafen, Germany; [2]German Federal Institute for Risk Assessment (BfR), Berlin, Germany; [3]Institut für Energie- und Umwelttechnik e.V. (IUTA), Duisburg, Germany; [4]Fraunhofer IME, Schmallenberg, Germany; [5]Helmholtz-Zentrum für Umweltforschung (UFZ), Leipzig, Germany, [6]IBE R&D gGmbH Institute for Lung Health, Münster, Germany
[*]patrizia-marie.pfohl@basf.com

Because of the ubiquity of microplastics in the environment, safety concerns have come up for polydisperse polymer powders, which are not covered by regulations. Microplastic concerns matter not only for degradation of mismanaged waste, but also for intentionally micronized particles, as used in 3D printing by laser sintering. It is still unclear which descriptors are most relevant to describe the potential toxicity of microplastic particles: e.g. the molecular structure, as used by the OECD concept of polymers of low concern (PLC), particle morphology, size and/or surface-induced interactions including uptake/release of noxious compounds (Figure 1). The huge variety of polymer materials, as well as the fast innovation in new materials, makes the analysis of every single material regarding regulatory demands nearly impossible.[1] For this reason, the BMBF InnoMat.Life project has established a grouping scheme and a tiered testing approach for solid polymer particles, while learning from and adapting nanomaterial grouping frameworks that had been validated against in-vivo assessments, e.g. NanoGRAVUR.[2]

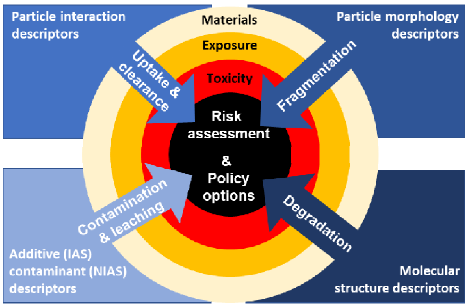

Figure 1: Descriptors for the grouping of polydisperse polymer powders: two categories of descriptors of chemical composition (IAS & NIAS, molecular structure), two categories of physical structure (particle interaction and particle morphology).

Here we compared micro- and nanoscaled polymer particles (MNP) differing in polymer type (polyamide PA, polyurethane PU, polyethylene PE), size distribution (7-200 µm), and, in the case of PU, polymer backbone (ester/ether, aliphatic/aromatic, crosslinking). We quantified many of the physical-chemical properties that are thought to be relevant, including abiotic and in-vitro reactivities. We assessed aerosol generation and the fragmentation into nanoplastics < 100 nm. We identified the most robust hypotheses and suitable test methods to justify that two (or more) polymer powder materials are sufficiently similar to each other, in order to conduct the risk assessment jointly for a group of materials. Fragmentation of polymer microparticles to MNPs and water-soluble degradation products differed significantly between polymer backbones. Polymer backbone modulated the biological interaction, contaminant adsorption and lifecycle more than other properties. The final grouping scheme relies on the most relevant properties with respect to human and environmental exposure and hazard.

Keywords: microplastics, grouping, risk assessment, read-across

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Molecular Dynamics Simulations of Hybrid Polymer Nanocomposites

Albert John Power[1,2,*] and Vagelis Harmandaris[1,2,3]

[1]*Depratment of Mathematics and Applied Mathematics, University of Crete, Heraklion, Crete, Greece.*
[2]*Institute of Applied and Computational Mathematics, Foundation for Research and Technology Hellas, Heraklion, Greece.*
[3]*Computation-based Science and Technology Research Center, The Cyprus Institute, Nicosia 2121, Cyprus.*
**ajpower@math.uoc.gr*

The study of Polymeric Complex Materials is an intense research area due to the broad spectrum of systems, applications, length and time scales that involved [1-4]. In this work, the properties of polymer chains (PE and PEO) around of inorganic nanoparticles (pure Gold, grafted Gold and Silica) are investigated using classical atomistic molecular dynamics simulations. The structural, conformational, and dynamical properties of the chains were analyzed and compared to the behavior of the bulk polymer system. All properties are examined as a function of distance from the nanoparticles. A typical snapshot of the model systems is shown in (Fig. 1).

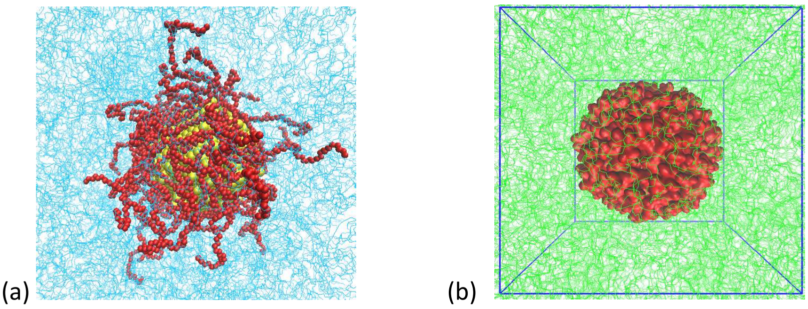

Figure 1: (a) Hybrid PE/Grafted Gold Nanoparticle System; (b) Hybrid PEO/Silica Nanoparticle System.

Keywords: Nanocomposite, Polymer, Molecular Dynamics Simulations.

Acknowledgments

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From Bond Tension to Chain Tension and Back

Liel Sapir[1], James Brock[2], Danyang Chen[1], Qi Liao[3], Sergey Panyukov[4], and Michael Rubinstein*[,1,5,6]

[1]*NSF Center for the Chemistry of Molecularly Optimized Networks and Thomas Lord Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708, United States*
[2]*Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599, United States*
[3]*Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*
[4]*P. N. Lebedev Physics Institute, Russian Academy of Sciences, Moscow, Russia 117924*
[5]*Departments of Chemistry, Biomedical Engineering, and Physics, Duke University, Durham, North Carolina 27708, United States*
[5]*Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, N21W10 Kita-ku, Sapporo 001-0021, Japan*
**mr351@duke.edu*

Polymer chains are under positive tension due to restriction of their conformational space that increases as the chains are being extended. However, on the level of single bonds within the chain the tension can be positive or negative. The bond tension, which has both entropic and enthalpic contributions, depends on chain tension and pressure. We show that in certain polymeric systems this dependence is counterintuitive; bond tension decreases (i.e. bonds are being compressed), while the chain tension increases (i.e. the chain is being extended). For example, increasing the grafting density of a polymer brush results in chains being extended along the direction normal to the surface. However, the elastic stress is balanced by increased internal pressure within the brush, which acts to compress bonds. The balance between these two effects results in overall bond tension reduction (bond compression) over a wide range of grafting densities. We also observe a similar effect in biaxial compression of polymer networks. We present a theory for the dependence of bond tension on both pressure and chain tension, and show that bond tension can be used as a gauge for chain tension in various polymer systems.

Keywords: Chain Tension, Bond Tension, Polymer Elasticity

Properties of Polybutadiene and Styrene-Butadiene Copolymers via Atomistic and Systematic Coarse Grained Models

Anastassia Rissanou,[1,2,3]* Antonis Chazirakis,[1,2] Vagelis Harmandaris[1,2,3]

[1] *Institute of Applied and Computational Mathematics (IACM), Foundation for Research and Technology Hellas, (FORTH), IACM/FORTH, GR-71110 Heraklion, Greece.*
[2]*Department of Mathematics and Applied Mathematics, University of Crete, GR-71409, Heraklion, Greece.*
[3]*Computation-based Science and Technology Research Center, The Cyprus Institute, Nicosia 2121, Cyprus.*

The systematic coarse graining of polymeric systems is a usual route in order to extend the range of spatiotemporal scales and systems accessible to molecular simulations. Here we present a hierarchical bottom-up methodology in order to obtain coarse-grained (CG) models for copolymers[1], derived from more than one species of monomers, via detailed atomistic simulations. In the proposed scheme each monomer type is represented as a different CG particle (Figure 1 Left). The effective CG interactions are obtained via a dual stage multi-component iterative Boltzmann inversion (IBI) optimization scheme, in which the same component terms of the CG model are obtained from homopolymer simulations, whereas the interactions between different CG type particle (mixed terms of the CG model) from the simulation of a single copolymer, of symmetric composition of the different microstructures. As an example, the proposed optimization scheme is initially applied on polybutadiene (PB) copolymers consist of cis-1,4, trans-1,4 and vinyl-1,2 isomers The derived CG copolymer model is examined with respect its transferability across molecular weight and the copolymer composition. Structural properties such as the chain dimensions and the local packing, as it is demonstrated though the pair radial distribution functions (Figure 1 Right) are presented via the detailed atomistic and the systematic CG simulations, as a function of monomeric concentrations. Moreover, dynamic properties (i.e., segmental and terminal dynamics) of PB copolymers are calculalated, for various compositions. The effect of the vinyl-1,2 component in conformational properties of PB copolymer melts is particularly emphasized, due to the different local packing imposed by side groups. The predicted results are compared against theoretical predictions and composition mixing rules are used to predict the properties of the PB copolymers. In the following the same methodology is applied on styrene-butadiene (SBR) copolymers, examining the transferability of the CG model through its ability to explore the conformational phase space of such systems

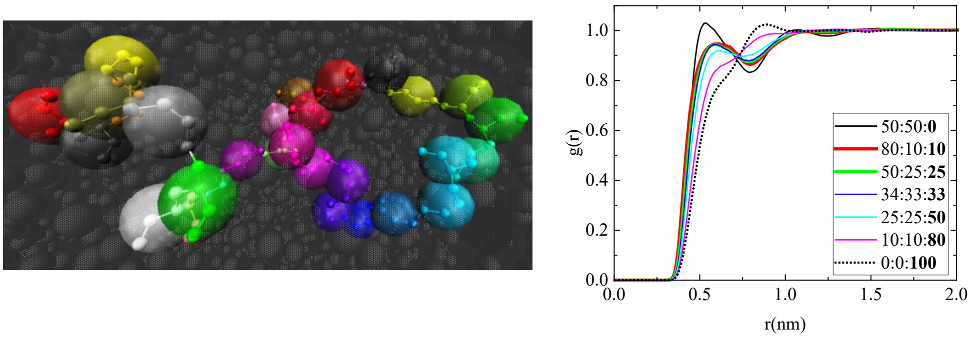

Figure 1: (Left) Mapping of PB copolymer from the atomistic to the CG representation; (Right) Radial distribution function of 30mer PB copolymers with various TCV proportions at 433K with increasing percentage of vinyl stereochemistry.

Keywords: Systematic Coarse Graining, copolymers, model tranferability

Acknowledgments
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Keywords: auxetic behavior, structural damage, process simulation, machine learning

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Increasing the *k*MC potential from linear to branched polymers: the case of surface-initiated polymerization and its 3D representation

A. D. Trigilio[1], F. J. Arraez[1], M. Edeleva[1], Y.W. Marien[1], P.H.M. Van Steenberge[1], D. R. D'hooge[1,2*]

[1]*Laboratory for Chemical Technology, Ghent University, Technologiepark 125, 9052 Gent, Belgium*
[2]*Centre for Textile Science and Engineering, Ghent University, Technologiepark 70a, 9052 Gent, Belgium*
[*]*dagmar.dhooge@ugent.be*

Kinetic Monte Carlo (*k*MC) modeling has been proved to be a reliable tool to describe the time evolution of processes in many research fields, including (bio) chemical engineering and biology. Through the Gillespie[1] stochastic simulation algorithm (SSA), *k*MC modeling is applied by defining the so-called reaction channels in which chemical reactions are sampled from probability distributions. In the polymer reaction engineering field, SSA has allowed a detailed macromolecular interpretation, provided that advanced data structures are used to store the results and capture the required characteristics. Such dedicated adaption ultimately leads to the accurate modeling of microscopic and macroscopic properties[2, 3], including also the specific case of 3D effects.

Another aspect is the improvement of the computational time required to perform the simulations, specifically in the search operations to identify which macrospecies will react in a sampled reaction. In this regard, several *options* have been studied by Trigilio, et al. [4], from the once deprecated linear search to more complex tree-like structures and numerical-methods derived strategies. As a result, the linear search emerged as a viable option if the search space is small, while high order trees or section methods are suitable for larger systems.

The previous analysis was done for linear polymer synthesis, but one should realize that *k*MC optimization is even more relevant for branched polymer synthesis or synthesis involving substrates. One interesting case is surface-initiated polymerization (SIP), in which polymer interfaces are created through the deposition of polymeric layers to flat surfaces. The resulting polymers have applications as adhesive materials, chemical lubricants, anti-corrosion coating, and bio-compatibility enhancers, making them suitable for a wide range of applications in areas such as sample purification, biosensing, antifouling coatings, drug and gene delivery, catalysis and control of enzyme activity, as well as the fabrication of capacitors, batteries, and fuel cells.

The advanced computational modelling of SIP allows following the temporal evolution of the molecular properties of individual free and surface-tethered polymer chains in a 3D space (e.g., the radio of gyration and the system conformational distribution[5]). It enables the optimization of the synthesis conditions and control strategies for producing well-defined polymer interface surfaces with precise control over the layer properties such as polymer architecture, composition, molar mass, and thickness. So far, we have successfully applied improvements to the SSA for the solution phase reactions of the SIP, while ongoing work deals with algorithmic enhancements to the surface-tethered polymer in the 3D structure.

Keywords: **Stochastic modelling, Monte Carlo, 3D configurations, computational efficiency**

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Molecular Simulation of the Structural Behavior of Imidazolium Ionenes Within Ionic Liquid Solvents

G. D. Barbosa[1], M. Maurya[1], P. Sappidi[1], X. Liu[1], K. E. O'Harra[1], J. E. Bara[1], C. H. Turner[1*]

[1]*Department of Chemical and Biological Engineering, The University of Alabama, Tuscaloosa, AL, USA*
[*]*hturner@eng.ua.edu*

Ion-containing polymers have been used as novel gas sorbents and as electrolytes in many advanced devices, such as electrochemical membranes for capacitors, lithium-ion batteries, and fuel cells. Most of these ion-containing polymers are polyelectrolytes, wherein the cation is pendant from the polymer backbone. On the other hand, in ionene-based polymers, the charge lies within the polymer backbone, which imparts a high charge density and unique electrostatic interactions.

It has been found that by grafting different functional groups to these polymers, their separation performance can be significantly enhanced in gas separation membrane applications. Since ionenes are condensation polymers, they offer a much more tailorable platform to accommodate very sophisticated functionalities associated with high-performance polymers, such as polyamides, polyesters, and polyimides. In many studies, it has been shown that the performance of the ionenes can be tuned by incorporating alkyl spacers and counterions. However, there is not much known at the molecular level about changes in the structural behavior of ionenes upon inclusion of various functionalities and counterions. This information is crucial for synthesizing new ionenes for a specific application.

Here, we have used molecular dynamics (MD) simulations to study the structural and conformational properties of alkyl and ether substituted imidazolium-based ionenes solvated in different imidazolium ionic liquids.[1-3] We have considered four imidazolium-based ionenes: poly(decylimidazolium) (PD10), poly(tetraethyleneglycolimidazolium) (PE10), alternating copolymer (P(ED)5), and a block copolymer (PE5D5). The results show that the type of polymer linkage and the polymer architecture significantly affect the inter- and intramolecular interactions. The ether-based linkages show more intramolecular interactions, resulting in a coiled structure (low radius of gyration), whereas a pure alkyl-containing polymer has a more open structure. In addition, a strong interaction between the anion and imidazolium groups of the polymer chain is observed, which plays an important role in changing the structure and conformation of the polymer chain. Our results help explain the molecular-level behavior of different ionenes when immersed in different solvents, and this provides critical information for tuning the structures and resultant properties of ionene-based polymers

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Design and Structural Characterization of Sequence-Reversed Proteins via Atomistic Simulations

M. Arnittali[1,2,3*], A.N. Rissanou[1,2,3], V. Harmandaris[1,2,3]

[1]*Computation-based Science and Technology Research Center, The Cyprus Institute, Nicosia 2121, Cyprus;*
[2]*Institute of Applied and Computational Mathematics (IACM), Foundation for Research and Technology Hellas, (FORTH), IACM/FORTH, GR-71110 Heraklion, Greece;*
[3]*Department of Mathematics and Applied Mathematics, University of Crete, GR-71409, Heraklion, Greece.*
**Corresponding Author's E-mail: m.arnittali@cyi.ac.cy*

Nature provides peptides and proteins as a major source of inspiration for the engineering of responsive, protein-based nanomaterials for medical and biotechnology applications. The function of a protein depends strongly on its structure. Despite the scientific progress in this field, remains an unsolved puzzle how proteins dictate their unique three-dimensional structures and their physicochemical properties. A detailed understanding of sequence-structure relations of proteins would provide us with the key insights to develop novel bio-inspired materials with desired functionalities.

In nature, the most abundant structural motif that is found is the α-helical coiled coil motif and it represents a convenient and widely used system, since it combines structural simplicity, remarkable functional versatility, and structural plasticity in a large variety of topologies and folding states. Nowadays, several mathematical and computational techniques are used to study proteins in aqueous solutions. Recently, we examined the thermal stability of two well-characterized, highly regular four-α-helical bundle proteins, which are the repressor of primer (Rop) protein and its loopless mutation RM6 at three different temperatures (300 K, 350 K, 368 K) through Molecular Dynamics (MD) simulations [1,2].

Moreover, a fundamental aspect, with strong implications on the design of proteins, concerns the reverse sequence problem, i.e., *how does the reversing of a protein's sequence affects its structure and consequently its functionality*. To address this challenge, we perform all-atom MD simulations of a reversed amino acid sequence model protein. As an example, we use the retro-protein Rop (rRop) and we examine the state of the molecule (i.e., if its native state corresponds to a monomer or a dimer), the folding, as well as its structural and conformational properties. To investigate different evolution paths, we also performed a series of atomistic simulations starting from different initial configurations either as a monomer or as a dimer in aqueous solution. The results reveal a clear *modified (corrupted) α-helical part*, compared to the parent protein (Rop). Furthermore, in the case of an initial configuration with two remoted monomers a tendency of the monomers to approach each other is observed providing a rough indication for a dimeric native state of rRop.

Finally, we used Metadynamics simulations, as an alternative approach and calculated the free energy profiles of Rop and rRop proteins, using different collective variables (e.g., the distance between the center of mass of the monomers). Metadynamics enable us to explore the conformational phase space of proteins. The method was evaluated for Rop protein where the calculated energy landscape includes its native state as a global minimum.

Keywords: proteins, α-helix, Metadynamics, Molecular Dynamics Simulations

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Soft character of star-shaped polymers: estimation of penetrability by atomistic simulations

Petra Bacova [1,2,3*], Eirini Gkolfi[2,3,4] , Vagelis Harmandaris[2,3,4]

[1] *Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, IMEYMAT, Campus Universitario Río San Pedro s/n., Universidad de Cádiz,*
Puerto Real, Cádiz 11510, Spain
[2] *Institute of Applied and Computational Mathematics (IACM), Foundation for Research and Technology Hellas (FORTH), GR-70013 Heraklion, Crete, Greece*
[3] *Computation-based Science and Technology Research Center, The Cyprus Institute, 20 Constantinou Kavafi Str., Nicosia 2121, Cyprus*
[4] *Department of Mathematics and Applied Mathematics, University of Crete, GR-71409 Heraklion, Crete, Greece*
[*] *petra.bacova@uca.es*

The importance of the microscopic details related to the local packing on the final performance of the materials has been recently discussed in relation to the neat melts of polymer-grafted nanoparticles.

In this study we focus on the homopolymer star-like polymers, which belong to the family of soft nano-objects, whose dynamical behaviour ranges from the linear-like to the colloidal-like.

We used atomistic molecular dynamics simulations to preserve the chemical details of the polymer in melt and we chose two representative dissimilar polymer types, polystyrene and poly(ethylene oxide), to address the possible polymer-specific dependence. We varied the number of arms in the stars to tune the effect of the geometric constrains stemming from the multi-arm architecture [1]. The "effective softness" of the model systems was quantified by measuring various properties related to the their penetrability, with the goal of providing a detailed picture about the intercorrelation of the microstructure and the overall structural [2] and dynamical properties [3]. The shape of the molecules and internal density profiles are discussed in relation to the spatial arrangement of the stars in melt and in relation to the distribution of the free volume in the systems. In addition, we investigate the intramolecular dynamical gradient, which is responsible for the deviations from the established theoretical models [2]. Our results provide a chemistry-specific insight into the microstructure, going beyond the generic models, and thus contribute to the elucidation of the structure-dynamics relation in materials with branch-like architecture, such as those used e.g., in all-polymer nanocomposites.

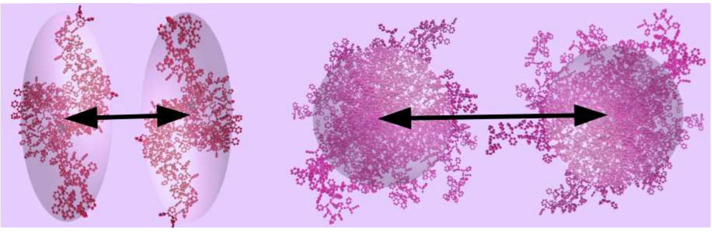

Fig.1: Schematic illustration of the mutual arrangements of the star-like molecules with different shapes and number of arms.

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Understanding and modelling the parameters affecting ice and barnacle adhesion on coatings for material design guidance.

D. Boucher[1], D. C. Webster[1*]

[1]*Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, ND 58108, USA*
[*]*dean.webster@ndsu.edu*

The term bio-foulant usually designates the numerous bio-organisms living in marine environment and able to adhere onto submerged objects. By their accretion onto marine vessels, bio-foulants have been an issue for years, leading to an increase of weight and fuel consumption, as well as speed and maneuverability loss of the vessels over time. Among the most prominent strategies aiming to reduce fouling, can be found the use of apolar low modulus coatings,[1,2] the conception of well-structured surfaces (specific topography, amphiphilicity),[1,2] zwitterionic materials,[1,2] and/or the use of lubricated surfaces that would induce the slippage of the foulants.[2] However, due to the complexity of the different bio-organisms attachment behaviors, and despite extensive studies in this field, a lot still remains to be understood and no eco-friendly universal solution has emerged yet. In addition, due to the opening of new waterways in cold seas, ships are more and more exposed to a new type of foulant: the accretion of ice, which is adding a new challenge to the conception of anti-fouling coatings.

An interesting relationship was recently highlighted by a previous work of our team, in the case of coatings with amphiphilic surfaces, between the adhesion of some macro-foulants (barnacles) and the adhesion of ice.[3,4] The identification of this relationship suggests that optimizing coatings properties against barnacle adhesion may also optimize their properties against ice adhesion and vice versa. However, most of the studies aiming at reducing the accretion of these foulants are mainly based on empirical methods and often lack of theoretical understanding. This work thus aims at reaching a better understanding of the factors, in the coating conception, influencing the adhesion of these specific foulants. Multiple parameters in the coating formulation will be varied in this study, and the experimental ice and barnacle adhesion results will be compared with the variation of physical properties and theoretical modellings (such as affinity prediction of a lubricant for the coating matrix) in order to attribute these results to tendencies. The final objective of this work will be to convert the observed tendencies between experimental results, theoretical predictions and physical observations, into an understanding that could therefore be exploited, during the conception of anti-fouling coatings, in order to anticipate and optimize the anti-fouling efficiency against ice and barnacles.

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Investigation of a dilute solution of ring and star polymers in confined geometries: theory and simulations

Z.Danel[1*], J.Halun[2], P. Karbowniczek[1], P. Kuterba[3]

[1]*Faculty of Materials Engineering and Physics, Cracow University of Technology, 30-084 Cracow, Poland*
[2]*Institute of Nuclear Physics, Polish Academy of Sciences, 31-342 Cracow, Poland*
[3]*Faculty of Physics, Astronomy and Applied Computer Sciences, Jagiellonian University in Cracow, 30-348 Cracow, Poland*
[*]*zusatenko@pk.edu.pl*

The calculations of the dimensionless layer monomer density profiles for a dilute solution of phantom ideal ring polymer chains and star polymers with f = 4 arms in a Θ-solvent confined in a slit geometry of two parallel walls with repulsive surfaces and for the mixed case of one repulsive and the other one inert surface were performed. Taking into account the Derjaguin approximation [1], the dimensionless layer monomer density profiles for phantom ideal ring polymer chains and star polymers immersed in a solution of big colloidal particles with different adsorbing or repelling properties with respect to polymers were calculated. The density-force relation for the above-mentioned cases was analyzed, and the universal amplitude ratio B was obtained. Taking into account the small sphere expansion [2] allowed calculate the monomer density profiles for a dilute solution of phantom ideal ring polymers immersed in a solution of small spherical particles, or nano-particles of finite size, which are much smaller than the polymer size and the other characteristic mesoscopic length of the system. Besides, we performed molecular dynamics simulations of a dilute solution of linear, ring, and star-shaped polymers with N = 300, 300 (360), and 1201 (4 × 300 + 1-star polymer with four arms) beads accordingly. The obtained analytical and numerical results for phantom ring and star polymers [3] are compared with the results for linear polymer chains in confined geometries.

Keywords: critical phenomena, surface effects, renormalization group, polymers.

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Polymer blends compatibilization using block copolymers.

J. Jůza[1*], I. Fortelný[1]

[1]*Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Heyrovského nám. 2, CZ 162 06 Praha 6, Czechia*
[*] *juza@imc.cas.cz*

Polymer blends can be compatibilized among other using block or graft copolymers with blocks that are identical, miscible with or adhere to related components of a polymer blend. Using models by Leibler [1] and Noolandi [2], relatively simple calculation estimating the decrease in the interfacial tension with a content of copolymer in the intarfecial layer as an intermediate result were made previously for special cases called dry brush and wet brush regime.

Recently, the solution without the dry- and wet-brush approximations, but still not too complicated, was published [3].

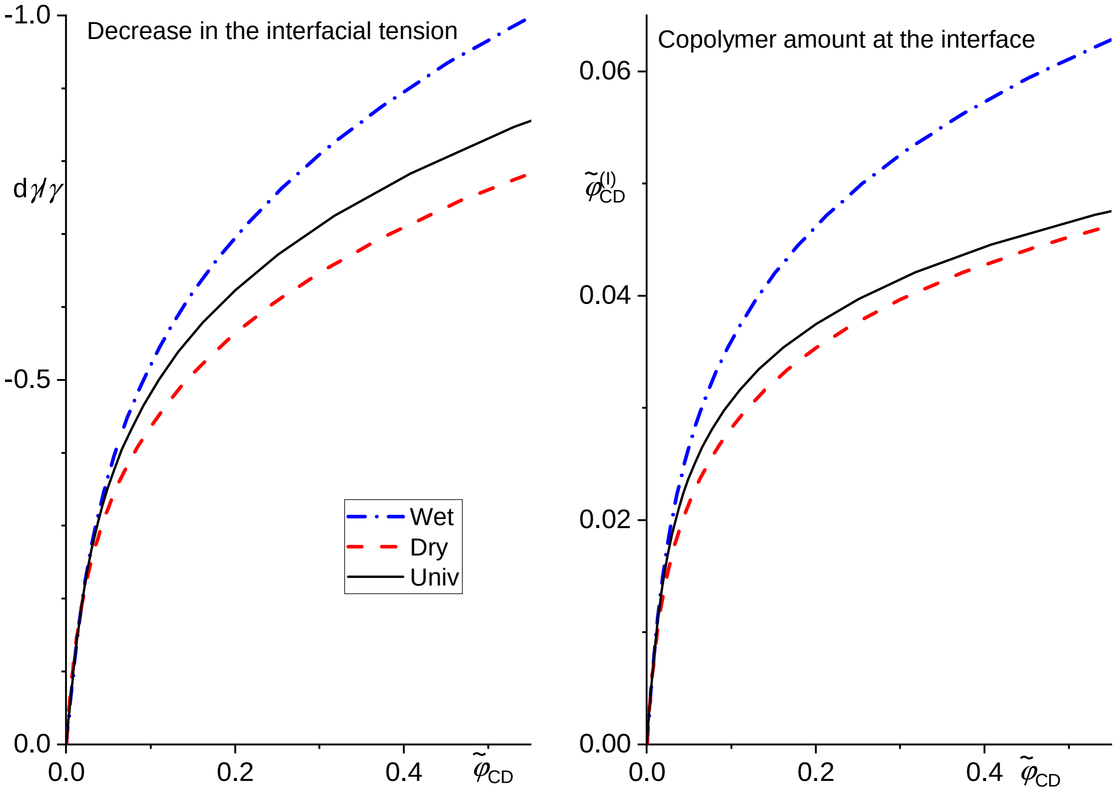

Figure: Comparison of the copolymer amount at the interface and the decrease in the interfacial tension obtained using the new formula for copolymer blocks per 240 segments and homopolymer chains 250 segments long with the dry- and wet-brush models.

This solution is consistent with the above mentioned regimes under the validity condition of those regimes. It enables estimated of compatibilizing effect of copolymer keeping nearly the relative simplicity of simplified models.

Keywords: polymer blends, interfacial tension, compatibilization

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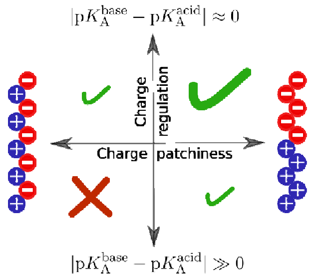
Both Charge-Regulation and Charge-Patch Distribution Can Drive Adsorption on the Wrong Side of the Isoelectric Point

Raju Lunkad[1], Fernando L. Barroso da Silva[2], and Peter Košovan*

[1]Department of Physisal and Macromolecular Chemistry, Charles University, Hlavova 8, 128 43 Prague, Czech Republic
[2]Department of Biomolecular Sciences, School of Pharmaceutical Sciences at Ribeirão Preto, University of São Paulo, Brazil and Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States
E-mail: lunkadraju@natur.cuni.cz and peter.kosovan@natgur.cuni.cz

The mechanism of protein–polyelectrolyte complexation on the wrong side of the isoelectric point has long puzzled researchers. Two alternative explanations have been proposed in the literature: (a) the charge-patch (CP) mechanism, based on the inhomogeneous distribution of charges on the protein, and (b) the charge-regulation (CR) mechanism, based on the variable charge of weak acid and base groups, which may invert the protein charge in the presence of another highly charged object. To discern these two mechanisms, we simulated artificially constructed short peptides, containing acidic and basic residues, arranged in a blocklike or alternating sequence. Our simulations of these peptides, interacting with polyelectrolytes, showed that charge patch and charge regulation alone can both lead to adsorption on the wrong side of the pI value. Their simultaneous presence enhances adsorption, whereas their absence prevents adsorption. Our simulation results were rationalized by following the variation of the charge regulation capacity and dipole moments of these peptides with the pH. Specifically for lysozyme, we found that charge patch prevails at physiological pH, whereas charge regulation prevails near the pI, thereby explaining seemingly contradicting conclusions in the literature. By applying the same approach to other proteins, we developed a general framework for assessing the role of the CP and CR mechanisms in existing case studies and for predicting how various proteins interact with polyelectrolytes at different pH values.[1]



Keywords: Peptides and proteins, Adsorption, Monomers,Polarity, Acid and base chemistry

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The authors thank Pablo M. Blanco and other colleagues in the Soft Matter group for their helpful discussions on the topic and insightful comments. This work was supported by the Czech Science foundation, grant 19-10429S. F.L.B.d.S. is also deeply thankful to the support by “Fundação de Amparo à Pesquisa do Estado de São Paulo” [Fapesp 2020/07158-2], the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) [305393/2020-0] and SNIC [2021/1-43].

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Strain hardening in glassy polymers: theory and simulations

Thomas Merlette[1,2*], Florence Clement[2], Paul Sotta[3], Didier R. Long[4]

[1]*Univ Lyon, ENS de Lyon, Laboratoire de Physique, UMR 5672, Lyon, France*
[2]*Solvay, Saint-Fons, France*
[3]*Univ Lyon, INSA Lyon, IMP, UMR 5223, Villeurbanne, France*
[4]*Univ Lyon, INSA Lyon, MATEIS, UMR 5510, Villeurbanne, France*
[*]*thomas.merlette@ens-lyon.fr*

We have recently proposed a 3D model for the deformation of glassy polymers based on the heterogeneous nature of the dynamics [1-3]. In this model, the evolution of the relaxation times distribution during stretching is described from the linear regime up to yield and up to a few tens of percent of deformation. Here, we extend this model to large amplitude deformations, where strain-hardening may be observed for some polymers [4]. We propose that the local monomer orientation leads to an increase of free energy barriers for α-relaxation at the length scale 3-5 nm during deformation. This effect is described by considering a local nematic order parameter and calculating its evolution during deformation. The order parameter of fast domains relaxes very rapidly and thus does not increase significantly, whereas it increases in slow domains. The local increase of free energy barriers (due to higher orientation) enhances the ageing dynamics, which may counterbalance the rejuvenating effect of the stress, leading to strain hardening. As deformation goes on, the volume fraction of subunits with higher free energy barriers increases and the stress goes on increasing upon deformation.

The model is solved in 3D.

The simulations describe the onset of strain-hardening at strain values of a few 10 % beyond strain softening. The resulting strain-hardening moduli are found to be in the range of 10^7-10^8 Pa. They increase as temperature decreases from Tg-10 K to Tg-30 K, which is consistent with experimental data. The obtained relaxation times distribution show that the dynamics becomes faster and more homogeneous up to strain softening and then slows down and gets more heterogeneous during strain hardening, which is also consistent with experimental data. The model predicts that the nematic order parameter ranges between 0 and 0.2 at a macroscopic strain of the order of 50 %. The evolution of the average nematic order parameter during deformation is semi-quantitatively consistent with experimental data.

The theory also enables to account for some aspects of the so-called Bauschinger effect. In particular, the strain hardening modulus is higher (respectively lower) when a tensile test (respectively a compressive test) is performed on a system which has been prestrained in tension along the same axis.

Keywords: strain hardening, order parameter, free energy barriers, monomer orientation, bauschinger effect.

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Self-assembly of Core-Shell Bottle Brush Copolymers : A Dissipative Particle Dynamics Study

Jihoon Park[1], Jeong Won Kang[1], Joona Bang[1], June Huh[1,2*]

[1] *Department of Chemical and Biological Engineering, Korea University, Seoul, 02841, Republic of Korea*
[2] *Department of Life Sciences, Korea University, Seoul, 02841, Republic of Korea*
[*]*junehuh@korea.ac.kr*

The self-assembly behavior of core-shell bottle brush (CSBB) copolymer, a bottle brush polymer comprised of AB diblock copolymer as side chains, was investigated by using dissipative particle dynamics (DPD) simulations. Order-disorder transition (ODT) behavior was investigated as a function of the backbone length (M) , which was compared to that of linear diblock counterpart. Furthermore, to interpret the architecture effect, the investigation was extended to a general bottle brush architecture expressed in terms of grafting position (P) for side chains along the side chains. Architectural effect on of molecular packing of CSBB into ordered structure was also analyzed and discussed.

Keywords: bottle brush polymer, DPD, self-assembly

Acknowledgments

References

Self-assembly of polydisperse Y-shaped polymer brushes under good solvent conditions

P. Fridrich[1], Z. Posel[1*]

[1] *Jan Evangelista Purkyně University, Faculty of Science, Department of Informatics, Ústí nad Labem, Czech Republic*
*zbysek.posel@ujep.cz

Polymers attached to the surface, e.g. polymer brushes [1], represent a unique way how to functionalize the surface. Its morphology is controlled by brush parameters such as grafting density, composition, chemical nature etc. and determine the response of the surface to external environment. Mixed binary brushes [2] contain two different homopolymer branches attached to single point on the surface and exhibit a wide range of morphologies ranging from aggregates to ripple structure. Compositional fluctuations during the grafting process that hampers formation of morphology can be controlled by using Y-shaped initiators [1] where each deposition point accepts different type of polymer. Phase behavior of Y-shaped brushes is described in theory and by simulation studies mainly for monodisperse cases. Nevertheless, real polymers are always polydisperse and using highly polydisperse polymer brings new options to control the formation of surface morphology.

Here, we employ Dissipative Particle Dynamics (DPD) to study the influence of polydispersity on self-assembly of Y-shaped polymer brushes. We vary brush grafting density, composition of the branches and their incompatibility to describe complex behavior of brushes at good solvent conditions. Moreover, we introduce the polydispersity by varying chain length of one branch and keeping other branch of the brush monodisperse. We consider low and high polydispersity and restrict our investigations to polydispersity indexes (PDI) that are used in experiments. We model the polydispersity by Schultz-Zimm distribution [3].

We show that our results for monodisperse systems agree with previous experimental and theoretical works and that ripple structure and aggregates are observed. Furthermore, the scaling of the brush height in our model agrees with theoretical predictions and with previous modeling results. In polydisperse systems, only disordered structures or aggregates are assembled by brushes with PDI < 1.5 sparsely grafted onto the surface with grafting density lower that 0.1 chains/nm^2. Moreover, increasing the grafting density above 0.5 chains/nm^2 triggers formation of perforated layer (PL) that is not observed in monodisperse systems. PL phase window widens with increasing the PDI up to 2 and the grafting density up to 1.0 chains/nm^2. At high grafting densities and PDIs the PL phase is stable over wide range of phase diagram. Finally, we show that increasing PDI lead to asymmetry of phase diagrams. High content of polydisperse chains prefer formation of aggregates over the ripple structure and increase the order-disorder transition while high content of monodisperse chains favours ripple structure and lowers the order-disorder transition.

Keywords: Self-assembly, polydispersity, Y-shaped brush, modeling

Acknowledgments

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STRUCTURE AND SELF-ASSEMBLY OF DI-PEPTIDES THROUGH ATOMISTIC SIMULATIONS AND EXPERIMENTS

Anastassia Rissanou[1,3,4,*], Giorgos Simatos[2], Anna Mitraki[2], Vagelis Harmandaris[1,3,4]

[1]Department of Mathematics and Applied Mathematics, University of Crete, GR-71409, Heraklion,, Greece.
[2]Department of Materials Science and Technology, University of Crete, GR-70013 Heraklion, Greece.
[3]Institute of Applied and Computational Mathematics (IACM), Foundation for Research and Technology Hellas, (FORTH), IACM/FORTH, GR-71110 Heraklion, Greece.
[4]Computation-based Science and Technology Research Center; The Cyprus Institute, Nicosia 2121, Cyprus.

In the field of bio-inspired materials, the non-covalent self-assembly of relatively simple peptide based molecules has gained increasing attention for the formation of biologically functional materials, all with nanoscale order. Self-assembly is often associated with human medical disorders. Our work concerns the modeling of small biological molecules, such as peptides, where the self-assembly propensity and the conformational properties, are studied through all-atom Molecular Dynamics simulations in explicit solvent and compared with experimental findings. Four dipeptides have been studied: diphenylalanine (FF), Alanine-Isoleucine (Ala-Ile), dialanine (Ala-Ala) and Isoleucine-Isoleucine (Ile-Ile) Of particular interest is FF peptide, the study of which reveals a strong self-assembling propensity in water in contrast to its behavior in methanol. These dipeptides belong to two different classes "Val-Ala" (Ala-Ile and Ile-Ile) and "Phe-Phe" (FF) and a systematic comparison in the self-assembly features among them has been performed.

We propose a consistent combination of complementary simulation and experimental methods, covering a broad range of length and time scales. The examined samples from both simulations and scanning electron microscopy experiments cover a board range of concentrations as well, since these are usually in different concentration windows (i.e., high values in simulations vs low values in experiments). However, in the present study, there is an overlapping concentration regime and a qualitative agreement between simulation and experimental results is observed. The structural and conformational properties of all dipeptides is investigated in details in water and in methanol solvents. The effect of temperature on the formed structures is found to be small, from both simulation and experiments, when temperature varies from 278 to 300 K. Furthermore, the differences of Ala-Ile and Ile-Ile dipeptides from dialanine (Ala-Ala) and diphenylalanine (FF) dipeptides in similar conditions are highlighted. Based on various measures (i.e, the potential of mean force (Figure 1)), the strength of the self-assembly propensity of the four dipeptides in aqueous solutions attains the following order: FF > Ala-Ile > Ala-Ala > Ile-Ile.

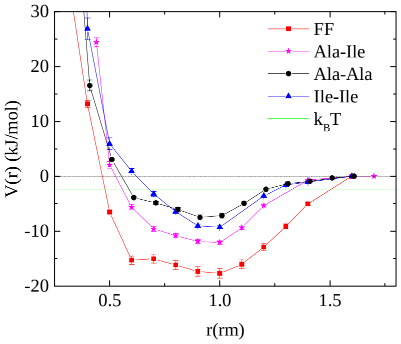

Figure 1. The PMF as a function of distance between the centers of mass of two dipeptides in water at 300K. Solid horizontal line corresponds to the thermal energy, *$k_B T$*.

Keywords: Dipeptides, Molecular Simulations, Self-assembly

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Channels with Helical Modulation Display Stereospecific Sensitivity for Chiral Superstructures

Renáta Rusková[1] and Dušan Račko[1,*]

[1]*Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia*
[*]*dusan.racko@savba.sk*

By means of coarse-grained molecular dynamics simulations, we explore chiral sensitivity of confining spaces modelled as helical channels to chiral superstructures represented by polymer knots. The simulations show that helical channels exhibit stereosensitivity to chiral knots localized on linear chains by effect of external pulling force and also to knots embedded on circular chains. The magnitude of the stereoselective effect is stronger for torus knots, the effect is weaker in the case of twist knots, and amphichiral knots do exhibit no chiral effects. The magnitude of the effect can be tuned by the so-far investigated radius of the helix, the pitch of the helix and the strength of the pulling force. The model is aimed to simulate and address a range of practical situations that may occur in experimental settings such as designing of nanotechnological devices for the detection of topological state of molecules, preparation of new gels with tailor made stereoselective properties, or diffusion of knotted DNA in biological conditions.

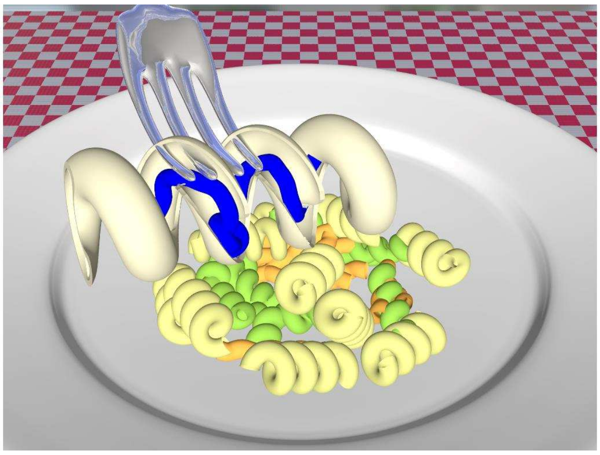

Figure Right-handed trefoil knot in a left handed stereospecific helical channel, as computed by means of coarse-grained molecular dynamics simulations of DNA investigated in nanochannels for detection of topological state of molecules. The picture features authors’artistic view.

Keywords: polymer; knot; topology; chirality; DNA; molecular dynamics; coarse-grained simulations; confinement; nanochannel; nanotechnology

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Machine Learning based and Simulation supported Modelling of Polymerization

P. Sievers[1*], J. Fiosina[2], M. Drache[1], S. Beuermann[1]

[1]*Institute of Technical Chemistry, TU Clausthal, Clausthal-Zellerfeld, Germany*
[2]*Institute of Informatics, TU Clausthal, Clausthal-Zellerfeld, Germany*
[*]*Philipp.Sievers@TU-Clausthal.de*

The properties of polymers depend on their structure, which is in turn determined by the polymerization process. Due to the high complexity of the polymerization reaction, it is difficult to predict the polymer properties from the reaction conditions or vice versa. Machine learning methods (ML) have proven to be a versatile tool for processing of complex data. However, the downside of ML is the large amount of learning data, which is required for the training of ML. Generating that amount of data by lab experiments is expensive and laborious. This gap can be filled by simulations, which can generate large amounts of training data with reasonable computing power once a kinetic model is established. Furthermore, simulations can provide versatile information about the microstructure such as molecular weight distributions (MWDs), branching levels and types, and copolymer composition, which can be difficult to obtain in an experiment.

Therefore, we use our in-house built Monte Carlo simulator mcPolymer[1] to generate training datasets for the machine learning process. As examples the well-established models of a butyl acrylate polymerization in octanone as solvent at low temperatures (60 °C – 80 °C)[2] as well as a vinyl acetate polymerization (at 60 °C) in methanol[3] are used. The simulation results consist of the concentrations for all components and the molecular weight distribution (MWD) for all polymer species at different times.

Training datasets were generated by varying the monomer concentration, the initiator concentration and the temperature and stored in a database. The problems were formulated as multivariate and multi-target regression[7] and several machine learning methods (like linear regression, random forest[4], XGBoost[5], CatBoost[6]) were applied to predict the evolution of the monomer concentration and MWD with time. The experimental results show that the proposed technique allows very good performance for the test dataset ($R^2 > 0.97$) using the coefficient of determination as an criterion. The best prediction was achieved with a CatBoost model. It was also possible to predict initial recipe simulation parameters from a given MWD (reverse engineering).

Keywords: kMC simulation of polymerization, machine learning, butyl acrylate, vinyl acetate

Acknowledgments

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Rich and Diverse Microstructure and Dynamics of Polyethylene Formed by Chain-Walking Polymerization

Jiri Brus[1]*, Martina Urbanova[1], Larisa Janisova[1], and Jan Merna[2]

[1] *Institute of Macromolecular Chemistry, Czech Academy of Sciences, Czech Republic*
[2] *University of Chemistry and Technology Prague, Czech Republic*
**brus@imc.cas.cz*

Polyethylene (PE) is a typical plastic and symbolizes huge dollar transactions every year. PE chains in solid state occupy mainly *trans* and two kinds of *gauche* conformations, between which there is a little energy difference, and therefore the polymer adopts different structures under different conditions. Linear PE in solid state has three crystalline phases: orthorhombic, monoclinic and triclinic. There are also non-crystalline and interfacial phases, and their existence strongly affects the physical properties. Fine tuning of the molar mass and molecular topology then allows control over the processing and mechanical properties. In polymer chemistry, chain-walking (CW) polymerization is a revolutionary concept leading to a dendritic type of branching. This process is characterized by an accurate control of polymer architecture and topology. The extent of CW, displayed in the number of branches formed and positions of branches is controlled by the choice of a catalyst.

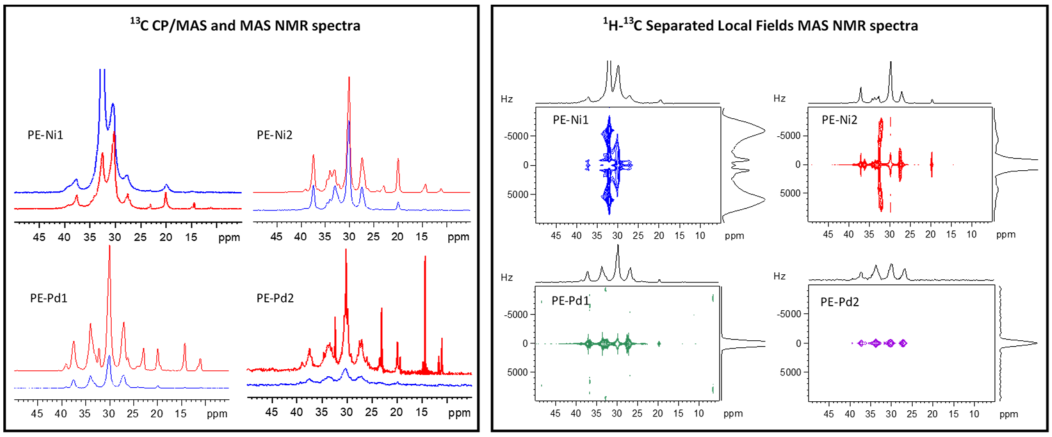

Figure 1. ^{13}C CP/MAS and MAS NMR spectra of various PE systems, and the corresponding ^{1}H-^{13}C dipolar profiles

In the present investigation we demonstrate rich local structure and diverse segmental dynamics of various of PE prepared CW polymerization. The polyethylenes used in this work were synthesized with α-diimine palladium and α-diimine nickel catalysts, when the former one exhibits higher propensity to CW, whereas the Ni one undergoes CW in less extent. For complete structure analysis various techniques of high-resolution and solid-state NMR spectroscopy were used.

A comprehensive analysis of a wide range of high-resolution and solid-state NMR spectra then unveiled presence of various local structural motifs, completely disordered highly branched segments and/or perfectly arranged blocks in the crystalline-like domains. The observed structural differences are then directly associated with significant differences in segmental dynamics and the corresponding physicochemical properties. Depending on the used catalytic systems the resulting polymer exhibited domain-like morphology with crystalline domains surrounded by amorphous phase and weakly branched interface up to a hyper-branched gel-like materials.

Based on an in-depth structural analysis performed, it is clear that even for a simple polymer such as polyethylene, extremely rich structure and architecture of polymer chains can be achieved and controlled using advanced catalytic systems.

Acknowledgments

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