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EPF Inter-Congress Workshop

28 June 2021

PROGRAMME AND ABSTRACTS

European Polymer Federation

INSTITUTE OF
MACROMOLECULAR
CHEMISTRY
CZECH ACADEMY OF SCIENCES

EPF Inter-Congress Workshop

28 June 2021

Dear friends and colleagues, members of the large family of polymer science and technology, we are sending you personal greetings from Prague – the historic city in the heart of Europe and the capital of the Czech Republic.

As a consequence of the worldwide pandemic situation, the Board of the European Polymer Federation decided to postpone the Congress of the European Polymer Federation (EPF) by one year. The next scheduled Congress will thus be held in Prague in the year 2022 instead of 2021. On behalf of the European Polymer Federation, of the Institute of Macromolecular Chemistry of the Czech Academy of Sciences and of the Czech Chemical Society, we cordially invite you to visit Prague to attend this important meeting. It is planned to be held from 26th June to 1st July 2022 at the Prague Congress Centre.

As a way of supporting and stimulating contacts between members of the polymer community we organise this one-day **on-line EPF Inter-Congress Workshop** during the period at the end of June 2021, when the Congress was to take place originally.

Please join us.

Jiří Kotek

EPF 2022 Chairman, President of the European Polymer Federation

Petr Štěpánek

EPF 2022 Co-Chairman

Programme

9:00–9:10		**Jiří Kotek *(Czech Republic)*** Opening remarks
9:10–9:35	**ML1**	**Filip Du Prez** *(Belgium)* Circular Thermoset Materials: Dream or Reality?
9:35–9:55	**SL1**	**Sissi de Beer** *(The Netherlands)* Controlled Surface Properties by Responsive Polymer Coatings
9:55–10:15	**SL2**	**Jennifer Garden** *(United Kingdom)* Cooperative Multimetallic Main Group Complexes as Highly Active Ring-Opening Polymerisation Catalysts
10:15–10:35	**SL3**	**Haritz Sardon** *(Spain)* Chemical Recycling and Upcycling of Polymers in a Circular Economy
10:35–10:50		*Break*
10:50–11:15	**ML2**	**Jean-François Gérard** *(France)* Thermodynamics and Chemistries at the Fiber-Matrix Interface/Interphases as Most Often Forgotten Issues for Polymer-Based Composite Materials Design
11:15–11:35	**SL4**	**Robert Luxenhofer** *(Finland)* Unraveling a New Mechanism for Order-Order Transition in Amphiphilic Block Copolymers
11:35–11:55	**SL5**	**Athina Anastasaki** *(Switzerland)* Tailoring Polymer Dispersity in Controlled Radical Polymerization
11:55–12:15	**SL6**	**Vagelis Harmandaris** *(Greece)* Structure and Dynamics of Polymer Melts and Polymer Nanocomposites via Simulations across Scales: From Atoms to Macroscopic Properties
12:15–13:15		*Lunch*
13:15–13:40	**ML3**	**Brigitte Voit** *(Germany)* Double-Crosslinked Responsive and Dynamic Hydrogels for Microfluidic Application
13:40–14:00	**SL7**	**Alexander Zelikin** *(Denmark)* Green Self-Immolative Polymers for Nature-Inspired Macromolecular Design
14:00–14:20	**SL8**	**Maria Kovacova** *(Slovakia)* From Antibacterial Polymer Nanocomposites to Bioimaging. The Use of Carbon Quantum Dots
14:20–14:40	**SL9**	**Roberto Simonutti** *(Italy)* Exploiting Precision Polymers for the Fabrication of Polymeric Nanoparticles
14:40–14:50		**Jiří Kotek *(Czech Republic)*** Closing remarks

Main Lectures

CIRCULAR THERMOSET MATERIALS: DREAM OR REALITY?

Filip Du Prez

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“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? Why not try to find a universal solution for recycling and scalable (re)processing of crosslinked, so-called thermosetting materials? Indeed, thermosets are indispensable for many (sustainable) applications, but are also one of the most difficult materials to recycle.

Thermoset recycling is indeed 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. Most of them deal with the re-use of thermoplastics (PE, PP, PS,…) but more and more attention is shifting towards the sustainability improvement of thermosets. This class of materials has an annual production of more than 40 million tons but has yet to find its place within a modern circular economy because of the permanently covalent crosslinked nature (e.g. wind blade and tire recycling).

One of the major developments in the thermoset world, 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 reversible 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 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 of this new generation of polymer materials, mainly based on smart chemical design.

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2. Yann Spiesschaert, Christian Taplan, Lucas Stricker, Marc Guerre, Johan M. Winne, Filip E. Du Prez, *Polym. Chem.,* **11**, 5377-5585 (2020).
3. Yann Spiesschaert, Marc Guerre, Ives De Baere, Wim Van Paepegem, Johan M. Winne, Filip E. Du Prez, *Macromolecules*, **53**, 7, 2485–2495 (2020).
4. Marc Guerre, Christian Taplan, Johan M. Winne, Filip E. Du Prez, *Chem. Sci.,* **11**, 4855-4870 (2020).
5. Christian Taplan, Marc Guerre, Johan M. Winne, Filip E. Du Prez, *Mater. Horiz.,* **7**, 104-110 (2020).

THERMODYNAMICS AND CHEMISTRIES AT THE FIBER-MATRIX INTERFACE/INTERPHASES AS MOST OFTEN FORGOTTEN ISSUES FOR POLYMER-BASED COMPOSITE MATERIALS DESIGN

Jean-François Gérard

Co-authors: J. Duchet, F. Lortie … and numerous IMP PhD students

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Polymer matrix composites have been the subject of great interest in recent years. In fact, they can meet certain requirements for the development of materials that can be considered to lead to substantial energy savings. Combining a polymer matrix, most often still thermosetting, having a low density and likely to provide plasticity and damping properties, with high modulus and/or strength fibers such as carbon, glass or even natural fibers, opens the possibility of lightweight materials for aeronautical structures, automobiles, etc. Currently, many works propose new formulations for polymer matrices such as those based on biosourced synthons/monomers to respond to potential oil scarcity, monomer substitutions entering into toxicology regulations such as bisphenol-A based prepolymers, reversible and/or allowing self-healing chemistries, modifications with low mass compounds or considering polymer blends as matrices. Nevertheless, the response of the complete composite material is most often not directly related to the matrix properties and its association with fibers. Indeed, the essential element constituting a composite material is the fiber/matrix interface or rather the transition zone between the fiber surface and the polymer matrix in volume, called ‘interphase’.

This presentation will focus on showing involved interfacial phenomena for different interfaces/interphases formed between a fiber (carbon ex-PAN, glass, etc.) and matrices of various natures (thermoplastics or thermosets). We will focus first on the essential step of wetting the fiber by the polymer matrix in the molten state or before polymerization, i.e. the formation of interatomic and intermolecular bonds (VdW and H-) at the interface. In the case of sized fibers (which is most often the case) during this wetting (or impregnation) step, an interphase can be formed by diffusion of the matrix components (monomers or polymer chains) or even by dissolution of the sizing. This step prior to the formation of the interface/interphase in the final composite material is described according to thermodynamical approaches and description of the possible reactions between the various compounds present in particular in the case of glass fiber sizing (which could concern sol-gel chemistries). After formation (reactive systems leading to a thermoset or thermoplastic) or solidification/crystallization (thermoplastic) of the matrix around the fiber, it will be shown that interphases of different natures can be formed. These ones are evidenced by different techniques (microscopies and spectroscopies). The relationships between the characteristics of these interphases and their ability to transfer mechanical stress from the matrix to the fiber (‘composite’ effect) of these interphases are highlighted from micromechanical studies considering model microcomposites based on a single fiber. In addition, such studies allow to understand the effect of water exposure which is essential for the development of new polymer-based composite materials.

This presentation is dedicated to Prof. Jean-Pierre PASCAULT who passed away on April 4th, 2020, and proposed me to join his laboratory as a senior CNRS researcher to work on fiber/matrix interfaces in composite materials just after my PhD accomplishment.

DOUBLE-CROSSLINKED RESPONSIVE AND DYNAMIC HYDROGELS FOR MICROFLUIDIC APPLICATION

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Responsive polymeric materials are becoming a highly studied field not only with regard to basic synthetic approaches and sophisticated characterization, but especially with regard to their use in technical applications, e.g. as sensors and actuators in microsystems and microfluidic applications.

We have developed multiresponsive hydrogels making use of interpenetrating network approach and the concept of graft copolymer networks, retaining responsivity for up to four different stimuli in one hydrogel.[1,2] The hydrogels have been adapted for integration into microfluidic devices as volume-changing gels, adjusting degree of swelling as well as mechanical stability and allowing their use as effective sensors and actuators as needed for a chemical valve function. First examples of their use as chemical transistors and the development of logical modules for achieving basic logic gate functions through a microfluidic setup are shown.[3]

Further optimization has been achieved by combining in double-crosslinked systems permanent and dynamic and reversible crosslinking.[4,5] For that, on the one hand, redox-responsive hydrogels based on poly(N-isopropylacrylamide) (PNiPAAm) or poly(acrylamide) (PAAm), consisting of a reversible disulfide cross-linking agent N,N'-bis(acryloyl)cystamine (BAC) and a permanent cross-linking agent N,N′-methylenebisacrylamide (BIS) have been realized and intensively studied with regard to reversible swelling, mechanical properties, and the possibility for photostructuring for microfluidic integration. Here, dynamic redox responsive behavior could be translated into micrometer hydrogel dots in microsystems. In addition, first results are presented to use reversible redox bonding for capturing peptides. The second approach is based on host-guest interactions, integrating bismacromonomers based on β-cyclodextrin units (β-CD-PMOXA) and adamantane units (Ada-PMOXA) end-functionalized vinyl-bearing PMOXA macromonomers. The dissociative nature introduced by these polyoxazoline bismacromonomers into polyacrylamide hydrogels influenced their physical properties, including swelling behavior and mechanics. Rheological experiments proved that the E-modulus of the network was significantly increased by the supramolecular host-guest interactions and could be reversible reduced by adding free β-CD. In addition, in the open state, the host moieties can capture specific targets from the fluid.

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Special Lectures

CONTROLLED SURFACE PROPERTIES BY RESPONSIVE POLYMER COATINGS

Sissi de Beer

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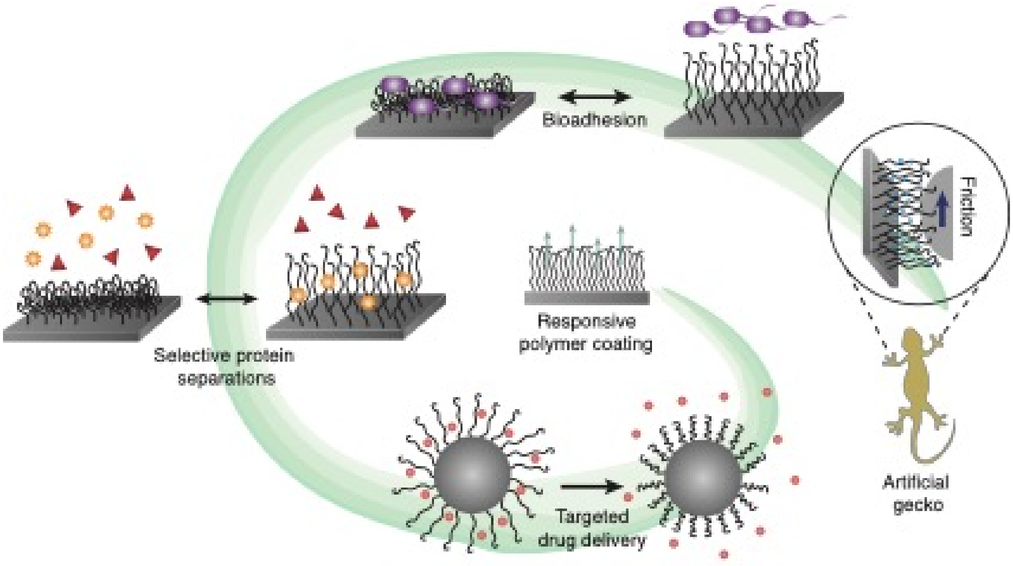
Controlling the wetting, adhesive and friction properties of surfaces is essential in many applications, ranging from the biomedical to the process technology fields.

Such control can be achieved using stimulus responsive polymers. Coatings composed of these polymers are able to adapt their physicochemical properties to changes in the surrounding environment, such as temperature, light or humidity.[1]

In this presentation, I will present a microscopic interpretation and picture of the response of these polymers to changes in their environment. Moreover, based on that, I will provide design rules to optimal control of the wetting, adhesive and friction properties of coatings composed of end-grafted stimuli-responsive polymers.



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COOPERATIVE MULTIMETALLIC MAIN GROUP COMPLEXES AS HIGHLY ACTIVE RING-OPENING POLYMERISATION CATALYSTS

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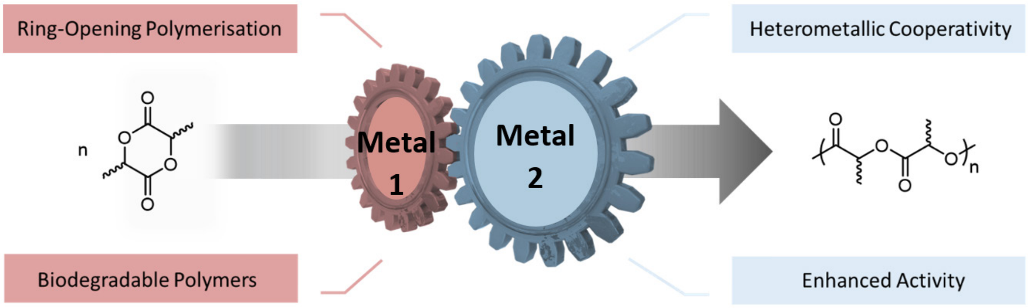
The ring-opening polymerisation (ROP) of cyclic esters is an attractive method of synthesising useful and degradable polymer materials.[1] These processes usually require the presence of a catalyst; some of the most efficient are homogeneous metal complexes. While the vast majority of ROP catalyst development has focussed on tailored ligand design, heterometallic (mixed-metal) activity enhancement is an equally promising yet underexplored method of improving catalyst performance.[2]



This lecture will describe a series of multimetallic main group complexes as highly active catalysts for cyclic ester ROP. Through the incorporation of heterometals, the catalytic efficiency of these complexes can be enhanced by up to 10 times compared to the monometallic analogues. To the best of our knowledge, the heterometallic K/Zn_2 Trost ProPhenol complex developed in our laboratory is the fastest heterometallic catalyst reported to date for *rac*-lactide ROP ($k_{obs} = 1.7 \times 10^{-2}\ s^{-1}$).[3] However, the choice of the heterometal is key; not all heterocombinations lead to enhanced catalyst performance. Our results demonstrate that multiple factors influence the heterometallic cooperativity, including the metal coordination geometry, available monomer coordination sites and the ligand flexibility. This lecture will showcase the potential of heterometallic ROP catalysis and provide underpinning methodologies for future heterometallic catalyst design.

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4. A. J. Gaston, Z. Greindl, C. A. Morrison and J. A. Garden, *Inorg. Chem.*, **2021**, *60*, 2294.

CHEMICAL RECYCLING AND UPCYCLING OF POLYMERS IN A CIRCULAR ECONOMY

Haritz Sardon

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Since the industrial synthesis of the first polymeric materials and their commercialisation in the 30's, breakthroughs and innovations in polymer chemistry have mainly contributed to the improvement of our daily life.[1] Consequently, the annual world consumption of plastics is exponentially and continuously increasing. The resulting accumulation of polymeric materials in the environment makes the development of environment-friendly and cost effective routes for recycling, a main challenge for next generations. Degrade polymers is a difficult task because of their high stability. Nowadays, less than 8% of the polymers produced each year are recycled and most of them are mechanically recycled: grinding and melt-processing, to obtain a low-quality material that will also rapidly ends up as a waste.

Besides mechanical recycling and pyrolysis, the final method and probably the most challenging one to date is the chemical recycling. The polymer is used as a starting reagent to generate high purity monomers using simple and efficient transformations. Specifically, from chemical depolymerisation innovative added-value building blocks could be synthesized to prepare highly added value polymers (smart chemical recycling approach) from commodity polymers.[2] Our work is focused in the implementation of plastic recycling principle in carbonyl containing polymers such as polyesters, polycarbonates and/or polyurethanes which account to the 25-30 % of the total plastic production. To afford this goal, an innovative protic ionic salt, cheap, easy-to-produce and recyclable, has been developed to catalyse the depolymerisation.[3] Resisting up to 400 °C, this organocatalyst is active at the high reaction temperatures required for degrading polymers. It already allowed us to degrade polyethylene terephthalate (PET), and Bisphenol A based polycarbonate (BPA-PC), in a fully sustainable cycle.

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3. Organocatalysed depolymerisation of PET in a fully sustainable cycle using thermally stable protic ionic salt Jehanno C., Flores I., Dove A.P., Müller A.J., Ruipérez F., & Sardon H.* Green Chem. 2018,20, 1205-1212.

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UNRAVELING A NEW MECHANISM FOR ORDER-ORDER TRANSITION IN AMPHIPHILIC BLOCK COPOLYMERS

Lukas Hahn[1], Theresa Zorn[2], Josef Kehrein[3], Tobias Kielholz[4], Benedikt Sochor[5], Ekaterina S. Lisitsyna[6], Nikita A. Durandin[6], Timo Laaksonen,[6,7] Vladimir Aseyev[8], Christoph Sotriffer[3], Maike Windbergs[4], Ann-Christin Pöppler,[2,*] and Robert Luxenhofer[1,8,*]

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Thermoresponsive hydrogel formation upon cooling in aqueous media is rarely described for synthetic polymers in the literature. However, if the sol/gel transition occurs in the physiologically relevant range (0-40 °C), there are many possible applications in areas such as drug delivery and biofabrication. Here, a novel inverse thermoresponsive polymer self-assembly mechanism based on a poly(2-oxazoline)/poly(2-oxazine) amphiphile is investigated in detail. Dynamic light scattering and small-angle X-ray scattering confirmed worm-to-spheres transition upon heating on the nanoscale level while wide-angle X-ray scattering indicated a more uniform ordering of the macromolecular chains on the scale of 4-7 Å. NMR spectroscopy shows reduced mobility of various polymer segments in the hydrogel state, especially in the hydrophobic aromatic region. More importantly, it also reveals close proximity of the phenyl ring of the hydrophobic block with hydrophilic repeat units confirmed by solution and solid-state NMR investigations, suggesting interactions between the two. This unusual interaction is corroborated *in silico* by molecular dynamics modeling. We propose a novel order-order transition based on unexpected and previously not described interactions between the hydrophilic and the hydrophobic repeating units, which opens new avenues to control and design macromolecular self-assembly.

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TAILORING POLYMER DISPERSITY BY CONTROLLED RADICAL POLYMERIZATION

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Dispersity can significantly affect polymer properties and is a key parameter in materials design with both low and high dispersity polymers displaying complementary properties and functions. Tailoring polymer dispersity not only enables the synthesis of a wide range of polymeric materials but also enhances our fundamental understanding on complex polymerization mechanisms. New synthetic strategies to control polymer dispersity in both atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain-transfer (RAFT) polymerization will be presented and critically discussed. By either varying the catalyst concentration (in ATRP) or by mixing RAFT agents of different reactivity, good control over the dispersity of a range of polymer classes can be efficiently achieved in both homopolymers and block copolymers. Ultimately, a synthetic approach to simultaneously control both sequence and dispersity in synthetic macromolecules will be shown enabling the preparation of sequence-controlled multiblocks with gradually ascending (Đ=1.16 →1.60), descending (Đ=1.66 →1.22), alternating low and high dispersity values (Đ=1.17 →1.61 →1.24 →1.70 →1.26) or any combination thereof. We believe that this new concept will open the door for the synthesis of advanced materials with concurrent control over both dispersity and sequence that can be then used in various applications including phase-separation, rheology, macromolecular folding and drug delivery.

STRUCTURE AND DYNAMICS OF POLYMER MELTS AND POLYMER NANOCOMPOSITES VIA SIMULATIONS ACROSS SCALES: FROM ATOMS TO MACROSCOPIC PROPERTIES

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Nowadays, computer simulations 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 describing the chemistry of the systems under study, and of predicting their behavior at the molecular level. However, the study of such systems 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.[4]

We apply the entire methodology to (a) cisPB polymer melts,[5] and (b) cisPB/silica nanocomposites.[6] 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.

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GREEN SELF-IMMOLATIVE POLYMERS FOR NATURE-INSPIRED MACROMOLECULAR DESIGN

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Polymers that undergo triggered end-to-end decomposition, known as “self-immolative polymers” (SIP), present unique opportunities for fundamental and applied sciences. In our work, we focus on polydisulfide polymers, more specifically those based on a natural metabolite, lipoic acid. These polymers can undergo main chain scission or degrade via self-immolation, thus, uniquely, being able to deconstruct via two distinctly different mechanisms. Furthermore, self-immolation can be triggered at any disulfide in the polymer chain (not only at the chain end), providing further opportunities for macromolecular design.

One opportunity we investigate in detail is to use polydisulfides to collect and propagate chemical activation signals. We used SIP to design zymogens: non-active derivatives of enzymes that release the native, catalytically active protein upon polymer degradation. SIP acts as a macromolecular antenna that extends from the enzyme active site into solution, wherein it can interact with activating agents and via self-immolation, degrade to release the active enzyme. Antenna extends into solution and can interact with activators that otherwise have no access to the enzyme active site. In doing so, SIP enable zymogen activation. SIP degradation is fast and using this tool, we achieved zymogen reaction via protein-protein interaction with kinetics measured in minutes, at physiological conditions.

My presentation will detail the synthesis of SIP and their degradation behaviour, as well as design and performance of zymogens and further opportunities in macromolecular design using polydisulfides.

SL8

FROM ANTIBACTERIAL POLYMER NANOCOMPOSITES TO BIOIMAGING. THE USE OF CARBON QUANTUM DOTS

Maria Kovacova[1*], Zdenko Spitalsky[1], Zoran Markovic[2]

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The threat of the spread of multi-drug resistant bacteria and the emergence of nosocomial infections is currently one of the greatest biological threats of the 21st century, which was also highlighted by the World Health Organization report. Therefore, a lot of effort and money are being spent on research and developing new drugs, methods, and materials that would effectively fight against such risks or prevent such risks. The main objective is to reduce the number of infected people and their mortality. For this reason, attention is also drawn to a wide range of materials and nanoparticles that could be used to create antibacterial agents, surfaces, medical devices, and others. At the same time, they would not burden the environment and have no side effects. One example of such nanoparticles is the carbon quantum dots (CQDs), which are known and used photosensitizers. We developed a new type of CQDs, which are hydrophobic. The main advantage of these hydrophobic photosensitizers is, that they are easily incorporable into various polymer matrices, thereby greatly expanding their field of application. This contribution generally points out the importance of antibacterial polymer nanocomposites in biomedical applications. In particular, it draws attention to the physicochemical and antibacterial properties of hydrophobic CQDs and their ability to produce reactive oxygen species under certain conditions using the principle of photodynamic therapy. Photodynamic therapy has been known method for centuries and is now a commonly used method in medicine and cosmetics. If CQDs are used as a nanofiller to the polymer matrix, it can create a stable antibacterial material that does not degrade, and it is suitable for the modification of surfaces. It could be used to produce antibacterial windows, floors, walls, furniture finishes, and other room equipment, where high hygiene standards are required (hospitals, food industry, ultra-clean rooms). Another interesting application is using a polymer nanocomposite in the manufacture of medical devices, particularly urinary and renal catheters, as patches in the treatment of wounds or warts. Alternatively, polymer nanocomposite can be used as an antibacterial polymer membrane for filtering contaminated water.[1,2]

Moreover, another type of CQDs was prepared, this time hydrophilic CQDs, by a low-cost green hydrothermal route. As the main precursor, citric acid was used. At last, pristine CQDs were doped with halogens (fluorine and chlorine). They have favorable properties, as tunable photoluminescence, quantum yield, resistance to photobleaching, and excellent biocompatibility. Nanoparticles are localized in the cell membrane or cytoplasm depending on the encapsulation/functionalization. Given these indisputable advantages, these CQDs could serve as a handy tool for cell bioimaging.[3]

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EXPLOITING PRECISION POLYMERS FOR THE FABRICATION OF POLYMERIC NANOPARTICLES

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Amphiphilic block copolymers (BCP) can spontaneously segregate (self-assembly) in distinct phases, due to opposed interactions with a selective solvent, generating polymeric nanoparticles (NPs) in solution. NPs are considered very promising carriers for intravenous drug delivery, thanks to their stability in physiological conditions and tunability of particle morphology and size. The final particle morphology can be predicted to some extent from structural parameters and by thermodynamic considerations, but the picture is further enriched by kinetic effects rising from the macromolecular nature of the amphiphiles. In fact, it is possible to obtain morphologies ranging from core-corona micelles to vesicles and wormlike micelles. Several methodologies for the synthesis of amphiphilic precision BCP can be exploited, particularly relevant are controlled radical polymerizations, as Reversible Addition-Fragmentation chain-Transfer (RAFT), Photo-induced Electron/energy Transfer (PET)-RAFT[1] polymerization, or living ring opening polymerization (ROP). Polymerization-Induced Self-Assembly (PISA) can be also employed together with RAFT and PET-RAFT. These methods allow the synthesis of block copolymers with effective control over ratio between the two blocks, the molecular weight and molecular weight distribution. RAFT is a robust and reliable technique that can be used with a large variety of vinyl monomers (acrylates, acrylamides, functional styrenes, dienes) meanwhile ROP catalyzed by organic bases with low nucleophilicity is suitable for monomers like lactide, glycolide, ring strained lactones and cyclic carbonates. In both cases preformed polymers, like poly(ethylene oxide), can be used as first block on which polymerize the second one. By means of a careful choice of the common solvent and a controlled process of switching to the selective solvent (water in this case) it is possible to obtain a large variety of morphologies for simple diblock copolymers. More specifical the complex self-assembly behavior of two families of BCP, poly(styrene)-block-poly(dimethylacrylamide) (PS-b-PDMA)[2,3] and poly(ethyleneoxide)-b-poly(lactic acid) (PEO-b-PLA),[4] will be described by means of Dynamic Light Scattering (DLS), Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM) and Cryogenic Electron Microscopy (Cryo-EM.

Finally, the morphology of NPs directly obtained by PISA-PET-RAFT for the system poly(butylacrylate)-block poly(dimethylacrylamide) will be described.

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