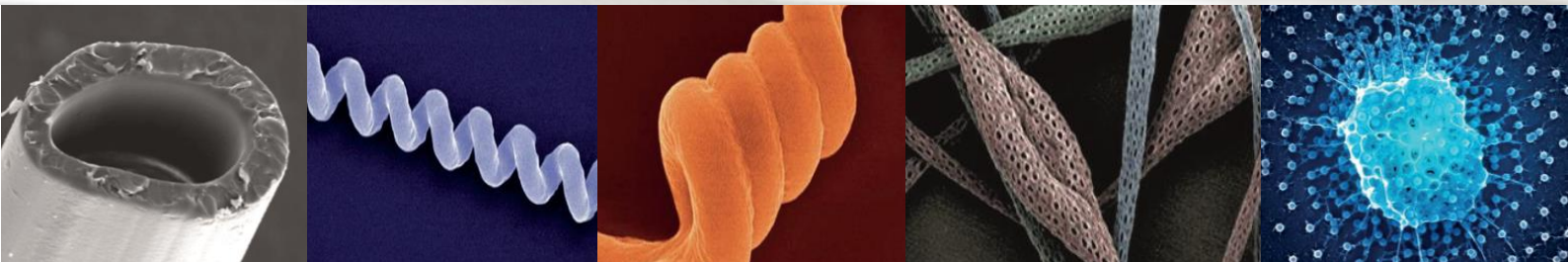


# ***BPS '21***

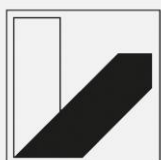


## **Bayreuth Polymer Symposium 2021**

**Online**

**Monday, September 20, 2021**

## **Program and Abstracts**



**UNIVERSITÄT  
BAYREUTH**

**BPS '21** is the 17<sup>th</sup> biennial international Bayreuth Polymer Symposium. Current topics of interest from research areas will be presented including functional polymers, polymer materials, supramolecular polymers, polymer colloids, polymer nanostructures, polymer nanotechnology, micro-plastics, and biomaterials.

A primary objective of this meeting is to bring people together from different areas of polymer, colloid, and material science to discuss different aspects of fundamental and applied research.

**The symposium will be held this year in an online format.**

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## SCIENTIFIC PROGRAM

The scientific program consists of 12 invited lectures (25 minutes) and a poster session with 22 posters introduced by a two-minute oral presentation. The conference language is English.

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## POSTER PRIZES

Two poster prizes will be awarded. These poster awards are sponsored by



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## SYMPOSIUM ORGANIZERS

**BPS '21** is organized by members of Macromolecular Chemistry (Seema Agarwal, Andreas Greiner, Hans-Werner Schmidt, Peter Strohmriegl, Mukundan Thelakkat), Physical Chemistry (Georg Papastavrou, Markus Retsch), Polymer Engineering (Holger Ruckdäschel) and Biomaterials (Thomas Scheibel) of the University of Bayreuth.

The symposium is supported by the Bavarian Polymer Institute, the Collaborative Research Centers SFB 840 „From particulate nanosystems to mesotechnology“, SFB/TRR 225 „Biofabrication“, and SFB 1357 „Microplastics“ funded by the German Science Foundation.



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## BPS WEBPAGE

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## Monday, September 20, 2021

08:00 – 09:00	Login and technical check
09:00 – 09:15	<b>Opening and general information</b> <i>Hans-Werner Schmidt</i>
	<b>Chairs:</b> Hans-Werner Schmidt, Peter Strohrriegl
09:15 – 09:45	<b>1 Eyal Zussman</b> , Technion - Israel Institute of Technology, Haifa, Israel <i>"Electrospinning short polymer nanofibers"</i>
09:45 – 10:15	<b>2 Xing-Hong Zhang</b> , Zhejiang University, Hangzhou, China <i>"Organocatalytic Copolymerization of One-carbon(CO<sub>2</sub>, COS, CS<sub>2</sub>) and Epoxides"</i>
10:15 – 10:45	<b>3 Wilhelm T. S. Huck</b> , Radboud University Nijmegen, Netherlands <i>"The importance of macromolecular crowding in synthetic cells"</i>
10:45 – 11:00	<b>Coffee Break</b>
	<b>Chairs:</b> Georg Papastavrou, Mukundan Thelakkat
11:00 – 11:30	<b>4 George Malliaras</b> , University of Cambridge, UK <i>"Technology for Bioelectronic Medicine"</i>
11:30 – 12:00	<b>5 Guillaume Fleury</b> , University of Bordeaux, Pessac, France <i>"Nano-manufacturing from block copolymer self-assembly - from 2D patterns with exquisite symmetries to 3D structures via iterative self-assembly processes"</i>
12:00 – 12:30	<b>6 Charlotte K. Williams</b> , University of Oxford, UK <i>"Exploiting Precision Polymerization Catalysis to Prepare Fully Bio-based Plastics and Adhesives"</i>
12:30 – 13:30	<b>Lunch Break</b>
13:30 – 14:30	<b>Poster Session – Introduction of Posters</b> <i>Chair: Markus Retsch</i>
14:30 – 15:30	<b>Discussion of Posters</b>
	<b>Chairs:</b> Seema Agarwal, Thomas Scheibel
15:30 – 16:00	<b>7 Richard Hoogenboom</b> , Ghent University, Belgium <i>"Poly(2-oxazoline)s as basis for polymer therapeutics and gene delivery"</i>
16:00 – 16:30	<b>8 Alfred Crosby</b> , University of Massachusetts Amherst, USA <i>"Actuating Mesoscale Polymers for Speed and Assembly"</i>
16:30 – 17:00	<b>9 Christian Pester</b> , The Pennsylvania State University, State College, PA, USA <i>"Patterned and functional coatings via oxygen tolerant photopolymerization"</i>
17:00 – 17:15	<b>Break</b>
	<b>Chairs:</b> Andreas Greiner, Hans-Werner Schmidt
17:15 – 17:45	<b>10 Timothy M. Swager</b> , Massachusetts Institute of Technology, Cambridge MA, USA <i>"Polymers with Intrinsic Free Volume – Design, Synthesis, Applications"</i>
17:45 – 18:15	<b>11 Ulrich Wiesner</b> , Cornell University Ithaca, USA <i>"Block Copolymer Self-Assembly derived Quantum Metamaterials"</i>
18:15 – 18:45	<b>12 Christine Luscombe</b> , University of Washington, Seattle, USA <i>"Semiconducting polymers: New horizons and unmet future challenges"</i>
18:45 – 19:30	<b>Poster Awards and Concluding Remarks</b> <i>Andreas Greiner, Hans-Werner Schmidt</i>

# Speakers

09:15 | L 01

## Electrospinning short polymer nanofibers

Eyal Zussman

Technion- Israel Institute of Technology, Mechanical Engineering, Haifa, Israel

### Abstract:



Sponges composed of short polymer nanofibers are useful for absorption materials, thermal insulation, and tissue engineering scaffolding. The nanofibers serve as building blocks to form a chemically crosslinked and/or physically entangled 3D network. A common nanofibers fabrication method is electrospinning of continuous fibers followed by cutting or homogenization in suspension to obtain a dispersion of short fibers. Alternatively, a high strain rate extensional flow of polymer solution can result in fragmentation caused by disentanglement of polymer chains, evidenced by the appearance of short nanofibers during electrospinning. This work examines the

conditions leading to the creation of short nanofibers, governed by the degree of entanglement and strain rate of the electrospun polymer solution. Short nanofibers' length, diameter, and mechanical properties were modulated by varying molar masses, concentrations, solvents, and electric field strength.

09:45 | L 02

## Organocatalytic Copolymerization of One-carbon(CO<sub>2</sub>, COS, CS<sub>2</sub>) and Epoxides

Xing-Hong Zhang

Zhejiang University, MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Hangzhou, China

### Abstract:



The organocatalytic copolymerization of one-carbon monomers (carbon dioxide(CO<sub>2</sub>), carbonyl sulfide(COS) and carbond disulfide(CS<sub>2</sub>)) with epoxides will be reported. A zwitterionic approach is developed for selective copolymerization of CO<sub>2</sub> and propylene oxide, producing poly(propylene carbonate) with fully alternating structure, using triethylamine and trialkyl boranes as the catalysts. We will also present metal-free routes for COS(CS<sub>2</sub>) with epoxides. One is the synthesis of poly(monothiocarbonate)s with perfectly alternating and regioregular structures, using Lewis bases (amidine, guanidine etc.) plus triethyl borane or thioureas as the catalysts. Colorless and highly transparent poly(monothiocarbonate)s were successfully obtained. The other is synthesis of

poly(thioether)s with low *T<sub>g</sub>*s from COS(CS<sub>2</sub>) with epoxides, only catalyzed by organic bases at high temperatures. These C1-derived polymers have unique mechanical, thermal, optical and even electronic properties.

10:15 | L 03

## The importance of macromolecular crowding in synthetic cells

Wilhelm T. S. Huck

Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, the Netherlands

### Abstract:



A cell is the common unit structure shared by all living organisms, but even 'simple' prokaryotic cells are extremely complex chemical reactors. Despite enormous progress in our understanding of the complex relationships between all the individual components in the cell, we do not understand the basic underlying physical chemistry of the cell. We developed a method based on picoliter water-in-oil droplets that allows us to induce coacervation in *E. coli* cell lysate and follow in vitro transcription and translation under crowded and non-crowded conditions. Crowding creates an artificial cell-like environment in which the rate of mRNA production is increased significantly.

The effect of crowding on the kinetics of the fundamental machinery of gene expression has a direct impact on our understanding of biochemical networks in vivo. Moreover, our results show the intrinsic potential of cellular components to drive phase separation and to facilitate macromolecular organization into membrane-free compartments.

11:00 | L 04

## Technology for Bioelectronic Medicine

George Malliaras

University of Cambridge, UK

### Abstract:



Bioelectronic medicine provides a new means of addressing disease via the electrical stimulation of tissues: Deep brain stimulation, for example, has shown exceptional promise in the treatment of neurological and neuropsychiatric disorders, while stimulation of peripheral nerves is being explored to treat autoimmune disorders. To bring these technologies to patients at scale, however, significant challenges remain to be addressed. Key among these is our ability to establish stable and efficient interfaces between electronics and the human body. I will show examples of how this can be achieved using new electronic materials and devices engineered to communicate with the body and evolve with it. I will highlight the role of polymers play in this field and outline key materials challenges that lie ahead.

11:30 | L 05

## Nano-manufacturing from block copolymer self-assembly - from 2D patterns with exquisite symmetries to 3D structures via iterative self-assembly processes

Guillaume Fleury

University of Bordeaux, Laboratoire de Chimie des Polymères Organiques (LCPO), Pessac, France

### Abstract:



Nanostructured block copolymer (BCP) thin films constitute an elegant tool to generate periodic patterns with periodicities ranging from a few nanometers to hundreds of nanometers. Such well-organized nanostructures are foreseen to enable next-generation nanofabrication research with potent applications in the design of functional materials in biology, optics or microelectronics. This valuable platform is, however, limited by the geometric features attainable from diblock copolymer architectures. Therefore, strategies to control and enrich the variety of structures obtained by BCP self-assembly processes are gaining momentum. In particular, we have demonstrated that macromolecular engineering of complex BCP architectures and interface manipulations can lead to morphological variety and advanced functional properties. Furthermore, additional opportunities inherent to iterative BCP self-assembly will be considered for the generation of "non-native" morphologies and 3D structures.

12:00 | L 06

## Exploiting Precision Polymerization Catalysis to Prepare Fully Bio-based Plastics and Adhesives

Charlotte K. Williams

Oxford Chemistry, University of Oxford, UK

### Abstract:



This lecture will outline recent research developing switchable polymerization catalyses using monomer mixtures to prepare precision copolymers. The switchable catalysts are applied to mixtures of bio-derived epoxides (limonene oxide), anhydrides (terpene derivatives and maleic anhydride), carbon dioxide and lactone/lactide to make polyester/carbonate block polymers. The catalysis and the preparation of these polymers will be discussed, together with the copolymers properties. Focus will be on all polyester pressure sensitive adhesives and, in separate work, upon copolymer additives to toughen polylactide. Sustainability considerations will be discussed, including the broader outlook for some of these materials.



15:30 | L 07

## Poly(2-oxazoline)s as basis for polymer therapeutics and gene delivery

Richard Hoogenboom

Ghent University, Supramolecular Chemistry Group, Department of Organic and Macromolecular Chemistry, Ghent, Belgium

### Abstract:



Poly(2-oxazoline)s are a synthetic class of polyamides that have been studied in great detail since their discovery in 1966. In the new millennium, poly(2-oxazoline)s flourish as biomaterials and polymer therapeutics benefiting from their excellent 'stealth' and antifouling properties, which is especially relevant with the increasing awareness of allergic reaction to PEG-based therapeutics and vaccines. In this lecture, I will present our work on poly(2-oxazoline) biomaterials focusing on polymer therapeutics and non-viral polymer vectors for gene therapy. For polymer therapeutics, we developed a general modification platform based on side chain methyl ester groups for conjugation of APIs through cleavable linkers, as well as the spontaneous formation of amphiphilic

gradient copolymers that serve as micellar drug carriers. New cationic polymers for gene therapy are generated through hydrolysis of the amide side chains leading to the linear polyethyleneimine (L-PEI) as well as more effective analogues.

16:00 | L 08

## Actuating Mesoscale Polymers for Speed and Assembly

Alfred J. Crosby

University of Massachusetts Amherst, Polymer Science & Engineering Department, Amherst, MA, USA

### Abstract:



Nature is masterful at using limited components and basic driving forces to achieve complex tasks, such as multi-structure assembly. This capability is especially true at the mesoscopic size scale, from 100's of nanometers to sub-millimeter, where nature's processes and structures far exceed current engineering capabilities. Across these size scales, controlling the spatio-temporal evolution of a structure's geometry and how structures interact and assemble is critical for linking molecular structure to emergent macroscale performance. Here, we describe our use of building blocks that we call mesoscale polymers to create new paths for assemblies that can have emergent properties. In particular, we provide

experimental results and theory to describe the use of structural asymmetry to mediate swelling processes to control local curvature change and the use of spatially-controlled interfacial interactions to affect their collective assembly.

16:30 | L 09

## Patterned and functional coatings via oxygen tolerant photopolymerization

Christian Pester

The Pennsylvania State University, Department of Chemical Engineering, State College, PA, USA

### Abstract:



The covalent attachment of polymers has emerged as a powerful strategy for the preparation of multi-functional surfaces. Patterned, surface-grafted polymer brushes provide spatial control over a variety of physical properties and allow for fabrication of 'intelligent' substrates which selectively adapt to their environment. This presentation describes recent advances in our group in using photolithography to produce topographically and chemically patterned polymer brush surfaces via surface-initiated (SI) photoinduced electron/energy transfer (PET) reversible addition-fragmentation chain transfer (RAFT) polymerization. Using this oxygen tolerant approach, organic light emitting diodes (OLEDs), anti-microbial

surfaces, and anti-fogging coatings are engineered to highlight user-friendly pathways towards advanced functional surfaces.

17:15 | L 10

## Polymers with Intrinsic Free Volume – Design, Synthesis, Applications

Timothy M. Swager

Massachusetts Institute of Technology, Department of Chemistry, Cambridge MA, USA

### Abstract:



We have had a long-term interest in producing polymers with free volume by including rigid 3D molecular scaffolds. The general designs for creating free volume will be demonstrated. A bottom up, designer monomer, approach produces smaller and more controlled spaces than traditional polymer processing schemes that are used to produce conventional membrane materials. At the core of our efforts is the use of bicyclic fused ring structures, of which triptycene is the most versatile example. I will detail select examples of these materials and highlight their ability to produce superior performance in sensors, ion exchange membranes, gas separation, and catalysis.

17:45 | L 11

## Block Copolymer Self-Assembly derived Quantum Metamaterials

Ulrich Wiesner

Cornell University, Materials Science and Engineering, Ithaca, NY 14850, USA

### Abstract:



Block copolymer (BCP) self-assembly (SA), a hallmark of soft condensed matter physics, continues to attract substantial academic and industrial interest. The dependence of SA structures and length scales on macromolecular characteristics like block fractions and molar mass allows for exquisite control over mesoscale lattice symmetry and parameters uncommon to the atomic lattice scale. This talk will provide an overview of recently emerging BCP solution-based approaches to mesostructured superconductors. This is a particularly fertile area for the exploration of the impact of mesoscale order and porosity on the properties of correlated electron systems leading

to quantum metamaterials. First examples will be discussed suggesting a fruitful convergence of soft matter self-assembly with condensed matter physics.

18:15 | L 12

## Semiconducting polymers: New horizons and unmet future challenges

Christine Luscombe

University of Washington, Materials Science and Department, Seattle, USA

### Abstract:



$\pi$ -Conjugated polymers are being used in the fabrication of a wide variety of organic electronic devices such as organic field-effect transistors (OFETs), organic photovoltaic (OPV) devices, and organic light-emitting diodes (OLEDs). Since the seminal work on the conductivity of polyacetylene by Heeger, MacDiarmid, and Shirakawa was published in 1970s, the field of organic electronics has grown exponentially. Our group has been studying and developing techniques to grow semiconducting polymers using a living polymerization method. This has allowed us to synthesize polymer architectures that we haven't been able to access till now including polythiophene brushes, star-shaped P3HT, as well as hyperbranched P3HT. Our unique synthetic capabilities allows us to specifically control defects in these polymers. Our work in controlling polymer defects and their effect on microstructure and thus optoelectronic properties will be presented.



# Poster Session

## P 01

**Materials mimicking associative learning inspired by Pavlovian conditioning***Hang Zhang* (1), *Hao Zeng* (2), *Arri Priimagi* (2), *Olli Ikkala* (1)

(1) Aalto University, Department of Applied Physics, Espoo, Finland

(2) Tampere University, Faculty of Engineering and Natural Sciences, Tampere, Finland

**Abstract:** In the classical stimuli-responsive and shape memory materials, the responses remain unchanged under repetitive stimuli exposures. Beyond them, one could ask whether an artificial material could “learn” a new responsive or adaptive behavior. Classical conditioning is an associative learning process, common in biological organisms. It was first studied by I. Pavlov by associating food and ringing bell to trigger the salivation of dogs, later refined by E. Kandel using snails. We show agarose gels that originally melt by heating (unconditioned), not by light (neutral), but upon association of heat and light, they learn to melt by light (conditioned). This is accomplished by employing photoacids and Au-nanoparticles in the agarose gel for triggerable plasmonic memory (Nat. Commun. 10, 3267, 2019). This learning process was further achieved in liquid crystalline actuators (Matter 2, 194, 2020; Adv. Mater. 32, 1906619, 2020). We claim that “reductionist’s learnings” inspire algorithmic processes towards materials “intelligence” and adaptations.

**Acknowledgement:** The authors acknowledge financial support from European Research Council and Academy of Finland.

## P 02

**Organogels from diketopyrrolopyrrole ionene/ polythiophene blends show ground state doping in the solid state**

*Dominik Stegerer*<sup>†,‡</sup>, *Martin Pracht*<sup>†</sup>, *Kevin Preis*<sup>§</sup>, *Florian Günther*<sup>Δ</sup>, *Mario Zerson*<sup>§</sup>, *Wafa Maftukhin*<sup>||</sup>, *Wen Liang Tan*<sup>#</sup>, *Renee Kroon*<sup>†,‡</sup>, *Christopher R. McNeill*<sup>#</sup>, *Michael Walter*<sup>||</sup>, *Till Biskup*<sup>‡</sup>, *Sibylle Gemming*<sup>§,○</sup>, *Robert Magerle*<sup>§</sup>, *Christian Müller*<sup>†</sup>, *Michael Sommer*<sup>\*,†,○</sup>

† Chemnitz University of Technology, Institute of Chemistry, Chemnitz, Germany

‡ Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Göteborg, Sweden

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Δ Universidade de São Paulo, Instituto de Física de São Carlos, São Paulo, Brazil

|| University of Freiburg, Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), Freiburg, Germany

# Monash University, Department of Materials Science and Engineering, Clayton, Victoria, Australia

▽ Saarland University, Physical Chemistry and Didactics of Chemistry, Saarbrücken, Germany

○ Chemnitz University of Technology, Center for Materials, Architectures and Integration of Nanomembranes (MAIN), Chemnitz, Germany

‡ Present address: Linköping University, Laboratory of Organic Electronics (LOE), Department of Science and Technology (ITN), Norrköping, Sweden.

**Abstract:** The need for further development in the field of high performance organic n-type materials persists. Especially polymers with deep LUMO are required for efficient doping processes and stable operation of organic devices. Here we use the concept of N-heterocycle quarternisation in a diketopyrrolopyrrole (DPP) based monomer (MePyDPPP<sub>y</sub>) to lower its LUMO by 0.7 eV compared to the neutral analog, dipyrrolyl-DPP (PyDPPP<sub>y</sub>). The drastically changed electronic properties allow for efficient mono-methylation and thus give access to asymmetric functionalization of the symmetric precursor PyDPPP<sub>y</sub>. The resulting polymeric ionene PMePyDPPP<sub>y</sub>T<sub>2</sub> with bithiophene (T<sub>2</sub>) as comonomer forms an organogel with the p-type polymer P(g<sub>4</sub>2T-TT) after solution co-processing. Films made from organogels exhibit ground state electron transfer, which is enabled by the high- and low lying HOMO and LUMO energy levels of P(g<sub>4</sub>2T-TT) (-4.07 eV) and PMePyDPPP<sub>y</sub>T<sub>2</sub> (-4.25 eV), respectively.

The authors gratefully acknowledge financial support from Chemnitz University of Technology

P 03

**Beyond PEO: Highly Efficient and Stable Polymer Electrolytes with Diester Sidechains for Lithium Metal Batteries**Dominic Rosenbach<sup>a,b,\*</sup>, Alexander Krimalowksi<sup>a,\*</sup>, Harimohan Erabhoina<sup>a</sup>, Prof. Mukundan Thelakkat<sup>a,b,c</sup><sup>a</sup> University of Bayreuth, Applied Functional Polymers, 95447 Bayreuth, Germany<sup>b</sup> University of Bayreuth, Bavarian Center for Battery Technology (BayBatt), 95447 Bayreuth, Germany<sup>c</sup> University of Bayreuth, Bavarian Polymer Institute (BPI), 95447 Bayreuth, Germany

**Abstract:** A series of poly(meth)acrylates carrying diester sidechains with varying alkyl spacers are synthesized and evaluated as solid polymer electrolytes (SPEs) in lithium metal batteries. These amorphous polymers having  $T_g$ s in the range of -58-32 °C, are converted into SPEs by adding different amounts of LiTFSI or LiFSI resulting in ionic conductivities up to  $10^{-4}$  S cm<sup>-1</sup> at 70 °C. These SPEs reveal high lithium transport numbers ( $t_{Li^+} = 0.5-0.7$ ) and excellent electrochemical stability (5.4 V vs. Li/Li<sup>+</sup>). Dendrite-free plating/stripping in Li-symmetrical cells is achieved in combination with an ultra-thin membrane and 10 wt% TiO<sub>2</sub>. Extended Distribution of Relaxation Times analysis of impedance data is employed for understanding the cell processes. In batteries using PA4.4-LiFSI-TiO<sub>2</sub> SPE and an optimized LiFePO<sub>4</sub> cathode, excellent capacity retention (> 94 %) and high initial discharge capacities of 152 and 123 mAh g<sup>-1</sup> at 70 and 40 °C, respectively, are demonstrated during long-term cycling.

This work is supported by the Bavarian Center for Battery Technology (BayBATT), Deutsche Bundesstiftung Umwelt (DBU) and the Bavarian State Ministry for Research and Arts under the SolTech project.

P 04

**Photodynamic Control of the Chain Length in Supramolecular Polymers: Switching an Intercalator into a Chain Capper**Elisabeth Weyandt, G. Vantomme, E.W. Meijer

Institute for Complex Molecular Systems, Department of Chemistry and Chemical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands

**Abstract:** The self-assembly of supramolecular polymers is driven by reversible, non-covalent interactions, which makes them intrinsically more dynamic than their covalent counterparts. Due to the unique features and properties of self-assembled systems, strategies to control the polymer length, composition, (co)monomer sequence and morphology still have to be developed for sufficient control of supramolecular polymerization. We designed a family of photo-responsive acyl hydrazone benzene-1,3,5-tricarboxamides (BTAs), that can be disassembled upon UV irradiation. In a co-assembly with achiral, alkyl BTA the acyl hydrazone monomers can modulate the chain length of the supramolecular stacks through mono-directional interactions with the chain ends. By employing a stimuli-responsive co-monomer in a multi-component, self-assembled system, we are able to cooperatively amplify the responsiveness and obtain control of polymer length upon light stimulus.

P 05

**Deformation Signaling in Polymeric Materials via Supramolecular Interactions**Derek Kiebal, Stephen Schrettl, Christoph Weder

Adolphe Merkle Institute (University of Fribourg), Fribourg, Switzerland

**Abstract:** Supramolecular linkages can endow polymer materials with a range of useful functionalities due to the dynamic nature of non-covalent interactions. One example is the ureido-4-pyrimidinone (UPy) hydrogen-bonding motif, which has been employed to make reversible adhesives, self-healing materials, and even tough supramolecular glasses. However, direct monitoring of the formation and cleavage of UPy linkages during processing, under load, or during supramolecular polymerization is difficult. In order to enable such monitoring and gain insights into the response of the supramolecular linkages to different stimuli, we have synthesized a new UPy-bispyrene (UPB) derivative which combines a central UPy motif with two excimer-forming pyrene fluorophores that are connected to the core via short alkyl linkers. The formation of UPB pyrene excimers in solution occurs exclusively via intermolecular association, thus facilitating a direct correlation between UPB fluorescence and UPy dimerization. Incorporation of UPB into (thermoplastic) elastomers by either blending or covalent attachment moreover furnishes materials that change their fluorescence in response to mechanical stresses.

The authors gratefully acknowledge financial support through the National Center of Competence in Research (NCCR) Bio-Inspired Materials, a research instrument of the Swiss National Science Foundation (SNF).

P 06

**Self-assembly of 1,3,5-benzenetricarboxamides with tertiary amino substituents and the preparation of hierarchical superstructures**Andreas Frank, Christian Hils, Melina Weber, Klaus Kreger, Holger Schmalz, Hans-Werner Schmidt

University of Bayreuth, Macromolecular Chemistry and Bavarian Polymer Institute (BPI), Bayreuth, Germany

**Abstract:** Hierarchical self-assembly is an intriguing approach to realize complex superstructures on the nano- and mesoscale. Here, we report on a unique class of 1,3,5-benzenetricarboxamides (BTAs) with tertiary amino substituents and the self-assembly behavior from aqueous solution. We found that the BTA with *N,N*-diethylaminoethyl groups shows a unique two-step self-assembly behavior. Upon heating, a phase separation followed by self-assembly leads to well-defined supramolecular microtubes. The BTA with *N,N*-dimethylaminoethyl groups was used to prepare hierarchical superstructures. For this, we combine two self-assembly concepts, namely the crystallization-driven self-assembly of triblock terpolymers into worm-like patchy micelles immobilized on a supporting polymer fiber with the molecular self-assembly of BTAs. Patch-mediated molecular self-assembly occurs due to the chemical match of the peripheral groups of the BTA and the patches.

This work is supported by the German Science Foundation, Collaborative Research Center SFB 840 „From particulate nanosystems to mesotechnology“, Project A2 and B8.

P 07

**Intermolecular Graft Exchange Between Bottlebrush Polymers Using RAFT Polymerisation**Satu Häkkinen, Billy Dyer, Andrew Kerr, Sébastien Perrier

University of Warwick, Department of Chemistry, Coventry, UK

**Abstract:** RAFT polymerisation may be used to polymerise grafts from a substrate by using the Z-group *grafting from* approach in which initiating sites (i.e., RAFT agents) are bound to the substrate via their Z-groups. In polymerisations conducted in this way, graft radicals fragment off the substrate to propagate and may diffuse freely in the reaction medium. We harnessed this reaction mechanism to conduct intermolecular graft exchange reactions between distinct bottlebrush polymers. A new synthetic strategy is presented which may be used to prepare heterograft copolymers by reinitiating a mixture of their respective homopolymers. Using the same principle, grafts may also be exchanged for linear polymers. The approach provides a convenient means to prepare extensive graft copolymer libraries by simply adjusting the stoichiometry of each exchange reaction.

P 08

**Various methods of polyolefin functionalization using chain-walking catalysts and utilization of products for copolymer synthesis**Oldřich Kotyza, Anatolij Sokolohorskyj, Jan Merna

University of Chemistry and Technology, Prague, Department of Polymers, Prague, Czech Republic

**Abstract:** Nickel (II)  $\alpha$ -diimine chain-walking complexes provide living polymerizations of olefins and enable synthesis of polyolefins with defined structure. Aim of this work is to use the character of olefin polymerizations by these complexes to synthesise functionalized olefins. End-functionalization was performed due to living character of polymerization: (1) by termination of living chain by addition of vinyl "comonomer" containing a functional group (e. g.  $-\text{OH}$ ,  $-\text{COOH}$ ) after polymerization of olefin (2) by transfer of living polyolefin chains from Ni growth centres to an organometallic transfer agent (e. g.  $\text{R}_2\text{Zn}$ ,  $\text{R}_2\text{Mg}$ ) followed by modification of the carbon-metal bond. In-chain functionalization was performed by copolymerization of olefins with polar functional comonomers. Prepared functionalized polyolefins containing hydroxyl groups were used as macroinitiators for ring-opening polymerization of  $\epsilon$  caprolactone (CLO) which provided block and grafted copolymers.

P 09

**Effect of environmental humidity on the ionic transport of poly(ethylene oxide) thin films by local dielectric spectroscopy**Paul Markus<sup>1</sup>, Daniel E. Martínez-Tong<sup>2,3</sup>, Georg Papastavrou<sup>1,4,5</sup>, Angel Alegria<sup>2,3</sup><sup>1</sup>Physical Chemistry II, University of Bayreuth. Universitätsstraße 30, 95440 Bayreuth – Germany.<sup>2</sup>Departamento de Física de Materiales, Basque Country University (UPV/EHU). San Sebastián – Spain.<sup>3</sup>Centro de Física de Materiales (CSIC – UPV/EHU). San Sebastián – Spain.<sup>4</sup>Bavarian Battery Research Center at the University of Bayreuth (BayBatt) – Germany<sup>5</sup>Bavarian Polymer Institute at the University of Bayreuth (BPI) – Germany

**Abstract:** The study of physical properties at the nanometer scale is becoming a key aspect for the identification of structure-property relationships and, understanding the molecular organization in nanostructured polymers. Therefore, we present a novel characterization methodology based on nanoDielectric Imaging and, Spectroscopy (nDI & nDS)<sup>1</sup>. This AFM-based technique allows simultaneous imaging of the sample topography and its dielectric contrast (nDI) by application of an alternating electric field. In addition, it is possible to perform dielectric spectroscopy at fixed locations on the sample's surface (nDS). Within this study, the effect of humidity on the ionic transport in the amorphous phase of poly(ethylene oxide) (PEO) thin films has been studied. PEO is a solid-state electrolyte that is classified as an emerging material for application in energy storage devices. We explored a controlled humidity range between 15 %RH and 50 %RH. By modeling our nDS results, we quantified the conductivity of the amorphous phase within the semicrystalline PEO films. The crystalline fraction of the PEO thin films was extracted and found to be about 36%, independent of humidity. However, the average conductivity increased drastically from  $2 \times 10^{-10}$  to  $5 \times 10^{-9}$  S/cm, by changing the environmental humidity in the explored %RH range.<sup>2</sup>

1. Miccio, et al. *Journal of Applied Physics* **115**, 184305 (2014).2. Markus et al. *Soft Matter* **16**, 3203-3208 (2020).

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P 10

**Role of Interfaces in Controlling the Crystal Orientation in Thin Films of Polythiophenes**Oleksandr Dolynchuk<sup>1</sup>, Philip Schmode<sup>2</sup>, Matthias Fischer<sup>1</sup>, Mukundan Thelakkat<sup>2</sup>, Thomas Thurn-Albrecht<sup>1</sup><sup>1</sup>Martin Luther University Halle-Wittenberg, Experimental Polymer Physics, Halle(Saale), Germany<sup>2</sup>University of Bayreuth, Applied Functional Polymers, Bayreuth, Germany

**Abstract:** Crystal orientation in semicrystalline conjugated polymers plays a significant role in determining the anisotropic material properties. However, it is still not fully understood what governs the crystal orientation in thin films of conjugated polymers. Here we address this fundamental question and show that thin films of poly(3-hexylthiophene) crystallized on graphene exhibit a double-layered face-on and edge-on crystal orientation formed at the interface to graphene and vacuum, respectively. We assume that it is a result of two competing interfacial interactions initiated at the respective interfaces. By increasing the side-chain polarity in poly[3-(6-bromohexyl)]thiophene (P3BrHT), the influence of the interface to vacuum can be reduced, resulting in full face-on orientation in P3BrHT films with a thickness of up to 26 nm. Our findings evidence that crystal orientation in thin films of conjugated polymers can be controlled if interactions with both interfaces are taken into account.

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## P 11

**Effect of crystallinity on the properties of polycaprolactone nanoparticles containing the dual FLAP/mPEGS-1 inhibitor BRP-187**

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**Abstract:** A library of seven polycaprolactones (PCL) based on  $\epsilon$ -caprolactone ( $\epsilon$ CL) and  $\delta$ -caprolactone ( $\delta$ CL) isomers with a constant hydrophobic-hydrophilic balance but a varying degree of crystallinity were used as matrices for particle formulation with the hydrophobic anti-inflammatory drug BRP-187 to investigate the effects of polymer crystallinity on final carrier performance. The resulting drug-loaded particles were evaluated for size distribution, surface potential, drug load, apparent enzymatic degradation as well as their efficacy in inhibiting the 5-lipoxygenase-activating protein (FLAP) *in vitro* in leukocytes. A direct comparison of the particles showed accelerated apparent particle degradation, increased amount of residual surfactant in the formulation, but a decrease in the final yield with increasing  $\delta$ CL fraction. In addition, the *in vitro* studies revealed that the polymer with the ratio of  $\epsilon$ 75- $\delta$ 25 was the most promising carrier material in this polymer library.

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## P 12

**Toolbox of Biodegradable Dendritic (Poly glycerol sulfate)-SS-poly(ester) Micelles for Cancer Treatment: Stability, Drug Release, and Tumor Targeting**

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**Abstract:** For 2021, the American Cancer Society expects that 608,570 American citizens die associated with cancer; thus, it is of high priority to improve the efficacy of chemotherapy to secure our Global Health. In general, micellar drug delivery systems exert the solubility of hydrophobic drugs, enhance their half-time *in vivo*, and control their biodistribution. However, the majority of developed block copolymer micelles do not meet their expectations. Herein, we present well-defined dPGS-SS-poly(ester) micelles with superior stabilities with CMCs of 1.13–3.58 mg/L (134–527 nM), selective tumor accumulation, and good cell compatibility. *In vitro*, the system revealed a low leaching profile but precise drug release in presence of, e.g., GSH and diseases-associated enzymes (Novozyme 435). In HeLa tumor-bearing mice models, dPGS<sub>7.8</sub>-SS-PCL<sub>7.8</sub> micelles exerted an improved tumor growth inhibition at an even 10-fold lower dosage compared to the free drug with no adverse side effects.

## P 13

### Gradient colloidal crystals as temperature integrating optical sensors

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**Abstract:** We demonstrate how the fabrication of colloidal gradient crystals brings totally new functionality to the established class of latex-based photonic crystals. We combine the photonic properties with the irreversible film formation process to access a time-temperature recorder. Key components of this new material are: 1) Particle mixtures show film-formation kinetics with a logarithmic time-dependency. 2) A dual syringe pump method is developed to fabricate binary colloidal crystals with a linear composition gradient along the coating axis. The presented structures consist of two equally sized polymer colloids exhibiting different glass transition temperatures assembled with a gradual change of the particle ratio. Translation of composition-dependency into a localized material property permits a uniquely simple optical readout of different time and temperature combinations. We expect both the thermal recorder and the gradient coating method to be of interest in future research.

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## P 14

### Ultrathin Protein Nanopore Membranes

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**Abstract:** We present a simple procedure to prepare ultrathin membranes based on protein nanopores, which could pave the way to energy-efficient nanofiltration. The transmembrane protein ferric hydroxamate uptake protein component A (FhuA) or its open-pore variant were assembled at the air-water interface of a Langmuir trough, compressed to a dense film, crosslinked by glutaraldehyde, and transferred to various support materials. This approach allows to prepare monolayer or multilayer membranes with a very high density of uniform protein nanopores. The membranes exhibit excellent water permeance, two orders of magnitude superior to comparable, industrially applied membranes. Furthermore, incorporation of either closed or open protein nanopores allows tailoring the membrane's ion permeability. The characterization of freestanding membranes covering holes up to 5  $\mu\text{m}$  in diameter will be presented utilizing, among others, atomic force microscopy (AFM), and helium ion microscopy (HIM).

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## P 15

### Programmable Shape Morphing of Mechanical Metamaterials

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**Abstract:** Mechanical metamaterials are architected materials that obtain unprecedented responses to mechanical forces from their unit cell structures. Auxetic materials with negative Poisson's ratio, usually not found in nature, can be obtained through careful structural design. However, the response of mechanical metamaterials to external forces is generally pre-defined through the manufactured architecture. Here we show that the incorporation of thermoresponsive transducers into metamaterials allows the mechanical response to be programmed after manufacturing. By incorporating actuating struts into re-entrant auxetic unit cell structures, the unit cell angle can be defined through temperature. At the same time, through definition of the unit cell angle, the Poisson's ratio under applied strains can be tuned from negative to positive values. The incorporation of actuators into architectures gives rise to shape morphing metamaterials with tunable mechanical properties.

**Funding:** 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.

P 16

## Biomimetic Fibers with Mechanics like that of Natural Spider Silk

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**Abstract:** Natural spider silk fibers exhibit mechanical and biological properties unmatched by most other known natural or man-made fibrous materials. In comparison to Kevlar, the strongest synthetic polymer fiber material to date, spider silk can absorb three times more energy before it breaks. Combined with their good biocompatibility and biodegradability, silk materials offer versatile applications in high-tech fields. To better understand the natural process, we recombinantly co-produced two different spider silk proteins in *E. coli*, yielding a mixture of homo- and heterodimers. Intermolecular interactions of these proteins in aqueous spinning dopes enabled their self-assembly into higher-order structures. Upon biomimetic spinning, nature-like performing fibers could be obtained concerning all important mechanical features such as tensile strength, elasticity, Young's modulus as well as toughness. Our findings emphasize the importance of protein interplay for functional complexity, ultimately providing a road map to design green high-performance fibers.

This work is supported by the Deutsche Forschungsgemeinschaft SFB 840 TP A08.

P 17

## Peptide-based hybrid hydrogel with tuneable mechanical properties as novel scaffold towards cell niche mimic

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**Abstract:** Peptide-based hydrogels are emerging as promising biomaterials due to their biocompatible and biodegradable properties as well as their intrinsic ability to facilitate cell-material communication. To address weak mechanical properties of supramolecular systems, our group has introduced hybrids by combining classical, covalent dextran polymers that are functionalised with reactive groups and grafted with self-assembling peptides (SAP) via thiol-click chemistry. The peptidic cross-linkers were chosen from so-called depsi peptides, isopeptides with an ester bond in the main chain, which undergo a pH-induced O-N-acyl shift enabling assembly and thereby gelation through  $\beta$ -sheet formation. In this study, the influence of these peptide cross-linker was systematically evaluated, by investigating the effect of varying the charge of the peptides individually and conjoint, as well as analysing the impact of the peptide grafting density.

P 18

## Probing the Co-Nonsolvency-Induced Transitions of Dense Poly(N-isopropylacrylamide) Polymer Brushes

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**Abstract:** Polymer brushes, consisting of densely end-grafted polymer chains to a surface, can exhibit rapid switching transitions between the extremes of extended to fully collapsed. These transitions hold great potential for use in next generation smart materials. In our work, we study mechanisms and dynamics of co-nonsolvency (aqueous mixtures of good solvents that cause polymer collapse)-induced transitions of Poly(N-isopropylacrylamide) (PNIPAM) brushes. We theoretically model preferential solvent adsorption within polymer chains, study how the surfaces adapt and hold memory to the solvent above it (i.e., exposed surface groups), and we develop new optical methods (based on FRET) to laterally resolve PNIPAM chain conformation in high resolution around complex interfaces. Together, our work provides comprehensive understanding of the mechanisms of co-nonsolvency of PNIPAM, how the chains organise themselves during the collapse-re-entry transitions, and how these transitions can be leveraged towards new sensing technologies.

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P 19

**Sonopharmacology: using the principles of polymer mechanochemistry for the activation of drugs***Robert Göstl, Zhiyuan Shi, Pengkun Zhao, Shuaidong Huo, Miancheng Zou, Andreas Herrmann*

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**Abstract:** The ultrasound-mediated activation of drugs from macromolecular architectures using the principles of polymer mechanochemistry (sonopharmacology) is a promising strategy to gain spatiotemporal control over drug activity. Shear force activates a mechanochemically latent site (the mechanophore containing an active pharmaceutical ingredient) incorporated into polymer chains at a higher rate compared to the remaining bonds in the macromolecular framework. We have developed the first examples of polymer systems that are capable of such a task and present multiple strategies: i) disulfide-based polymers for covalently attached drugs, ii) supramolecularly deactivated latent antibiotics in nanoparticle and polymer assemblies, iii) non-covalently loaded ultra-long polyaptamers, and iv) drugs that are encapsulated in metal-organic cages. We moreover solve critical aspects currently restricting potential clinical application of sonopharmacology, such as drug-loading content and potency, mechanochemical efficiency, and frequency and energy of the employed ultrasound.

P 20

**HySS – a new wetting regime for on-demand trapping and release of drops***Anil Kumar Rajak, Jürgen Rühle*

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**Abstract:** On hydrophobic rough surfaces, wetting can be described either by Cassie-Baxter model where a drop sits suspended on the structures or by Wenzel model where the drop is penetrated by the structures. The drop in Wenzel regime sticks to the surface which is very difficult to release and in case of Cassie-Baxter regime, the drop is very difficult to trap. We present a third wetting regime, the so-called High Hysteresis Suspended State (HySS) that can be observed on regular patterned micro-trenches. In this regime, the drop suspends like in Cassie-Baxter regime while exhibiting high hysteresis (up to values  $>70^\circ$ ), as in Wenzel state. We present a full model based on our theoretical calculations and experimental results for highly controlled wetting transition between these states (induced by aspect ratio, mass of the drop and applied pressure), trapping of drops and releasing them by an addition of small energy (induced by tilt or mass). With the introduction with HySS, we are also able to demonstrate a dynamic surface for the on-demand tapping and release of drops.

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## P 21

**Pathways to Microplastics: Results from Accelerated Weathering Studies**

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**Abstract:** The main source of microplastics (MP) found in the environment is fragmentation of macroplastics as a consequence of weathering. To gain further insights into degradation mechanisms, changes in chemical composition, and morphology, we performed long-term accelerated weathering studies on particles and tensile bars. The degradation was monitored by a variety of analytical methods (GPC, SEM, EDX, <sup>13</sup>C MAS NMR spectroscopy, tensile testing, Monte Carlo Simulations). We identified two stages of weathering: stage I is dominated by photooxidation in a near-surface layer; in stage II fragmentation is enhanced via microcrack formation and particle rupturing. <sup>[1]</sup> High proportions of carboxyl, peroxide and keto groups develop, resulting in polar surfaces. Degradation thus leads to the constant release of highly weathered and chemically modified MP particles into the environment.

<sup>[1]</sup> N. Meides, T. Menzel, B. Poetzschner et al., Environ. Sci. Technol. 2021, 55, 7930-7938.

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## P 22

**Polystyrene dispersions as model for polystyrene microplastic particles**

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**Abstract:** Polystyrene (PS) is an important model polymer for the investigation of cytolytic effects of microplastic particles (MP) and nanoplastic particles (NP). Primary MP/NP of PS are available as aqueous dispersions, which could be contaminated by styrene. To fully understand the effects of PS MP/NP, precise knowledge of possible contamination by residual styrene is crucial. Thus, we designed a method for rapid and sensitive analysis of styrene content in PS dispersion, common for MP/NP assessment. We used this protocol to establish an efficient method of purifying PS MP/NP dispersion. Next, we determined the cellular viability of fibroblast cell upon its contact with PS dispersions. We correlated the viability results of our self-synthesized PS with commercial PS. Control experiments clearly showed a very high toxicity of styrene at relevant concentrations. In contrast, purified dispersions showed less toxicity and will enable the study of the effects of size and shape of PS MP and NP. Excessive residual styrene in test samples, could trigger secondary mechanisms and generate an exaggerated picture of the induced effects, in enumeration assays.

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