MACROMOLECULAR COLLOQUIUM FREIBURG

20 – 22 February 2019

WEDNESDAY, 20 FEBRUARY 2019

Registration desk opens at 11 a.m.

Get access with your access code to the abstracts on
https://www.advancedsciencenews.com/freiburg-2019/

14:00 **Opening Remarks**
PRASAD SHASTRI
Meeting Chair
Director of the Institute for Macromolecular Chemistry, University of Freiburg

SPECIAL SESSION: Polymers and the Digital Age

Chair: Rolf Mülhaupt

14:10 PAOLO SAMORI (University of Strasbourg, France)
Taming Complexity in Polymer Opto-Electronics: Tailoring Multifunctional Devices and Chemical Sensors

14:40 MAGNUS BERGGREN (Linköping University, Sweden)
Organic Bioelectronics – Nature Connected

15:10 JEAN-FRANCOIS LUTZ (University of Strasbourg, France)
Digital Polymers: Emergence of a New Class of Synthetic Macromolecules

15:30 COFFEE BREAK

16:30 BIRGIT ESSER (University of Freiburg, Germany)
Redox Polymers as Electrode-Active Materials for Organic Batteries

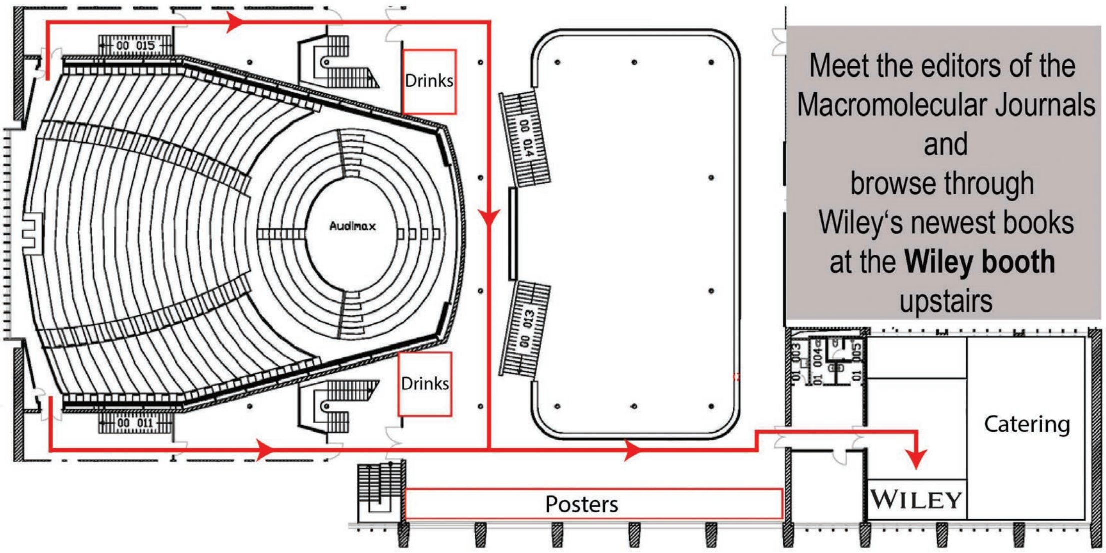
16:50 MICHAEL SOMMER (Chemnitz University of Technology, Germany)
N-type Conjugated Polymers for Organic Transistors, Solar Cells and Thermoelectrics

17:10 KLAUS MEERHOLZ (University of Cologne, Germany)
Solution-Processed Organic Semiconductors and their Applications

17:30 PAUL BLOM (Max Planck Institute for Polymer Research Mainz, Germany)
Charge Transport in Organic Semiconductors

18:50 COVESTRO LECTURE
BERNHARD RIEGER (Technical University of Munich, Germany)
Catalytic Precision Polymerization: Sustainable Materials from Simple Monomers

18:30 GET TOGETHER (Foyer)



Meet the editors of the Macromolecular Journals and browse through Wiley‘s newest books at the **Wiley booth** upstairs

Thursday, 21 February 2019

Chair: Prasad Shastri

9:00 JOHN ROGERS (Northwestern University, USA)
Materials for Flexible, Bio-Integrated Electronics

9:40 ALEXANDER BÖKER (Fraunhofer Institute for Applied Polymer Research Potsdam-Golm, Germany)
Programmable Soft Matter: From Active Membranes to Self-Replication

10:00 DOMINIK WÖLL (RWTH Aachen University, Germany)
Superresolution Fluorescence Microscopy of Polymer Structures

10:20 INTRODUCTION OF POSTERS

Chair: Felix Schacher

1 I. ILIC (MPI of Colloids and Interfaces Potsdam), S. Chaleawlert-Umpon, M. Antonietti, C. Liedel
Batteries from Lobster and Vanilla: Polymers from Chitosan and Vanillin as Active Material in Sustainable Batteries

2 CH. BAUMANN (DWI - Leibniz Institute for Interactive Materials Aachen), R. Göstl
Tailor-Made Force Probes for Wavelength-Orthogonal Stress-Sensing

3 N. HAUCK (Leibniz Institute of Polymer Research Dresden), N. Seixas, S. P. Centeno, R. Schlüßler, G. Cojoc, J. Guck, D. Wöll, L. A. Wessjohann, J. Thiele
Droplet-Assisted Microfluidic Fabrication and Characterization of Multifunctional Polysaccharide Microgels Formed by Ugi Four-Component Reaction

4 D. KLINGER (Freie Universität Berlin)
From Striped Ellipsoids to Janus Nanoparticles: Controlling Colloid Shape, Morphology and Function via Phase Separation of Functional Polymers

5 Y. BOURGAT (TU Braunschweig), P. Klahn, H. Menzel
Hydrogels for Triggered Drug Release

6 A. SCHMID (University of Applied Sciences Dresden), S. Hecht, C. Henning, K. Harre
Influence of Additives on the Properties of Biopolymers

7 ST. WIEDMANN (University of Freiburg), T. Trötschler, M. Luitz, M. Werner, S. Gröer, B. Pásztói, B. Kerscher, A. Szabó, J.-F. Lutz, B. Iván, R. Mülhaupt
Thermoresponsive Micelle-Inspired Polymer Ionic Liquids as Compartmentalized Nanosystems and Molecular Shuttles

8 T. WALTHER (Chemnitz University of Technology), K. Trommler, A. Seifert, H.-J. Hähnle, Ch. Hamers, St. Spange
Inter- and Intramolecular Reactions of Amino Bearing Polymers in Aqueous Solutions

9 R. HOFFMANN (Fraunhofer IFAM, University of Bremen), S. O. Schopf, H. Naatz, V. Baric, L. Mädler, A. Hartwig
Inverse Nanocomposites – High Particle Percolation without Running into Viscosity Problems

10 T. GLEEDE (Max Planck Institute for Polymer Research Mainz), Th. Kuckhoff, E. Rieger, M. Wagner
Living Anionic Polymerization of Aziridines Tolerates Water and Gives Fast Access to Amphiphilic Multi-Block Copolymers

11 M. RAISCH (Chemnitz University of Technology), F. Kempe, O. Brügner, M. Walter, Ch. Gualandi, M. Sommer
Transient Mechanochromic Polymers for Highly Sensitive and Anisotropic Stress Sensors

12 INDUSTRY PRESENTATION: MALVERN PANALYTICAL GmbH: V. SHAHI, M. R. Pothecary, C. Schindler, J. D. Stenson, L. Meeker, B. MacCreath, B. Tartsch, B. Schäfer
The Best of Both Worlds: Combining Multi-Detector GPC and UPLC to Achieve Complex Polymer Characterization at UPLC Speeds and Resolutions

13 INDUSTRY PRESENTATION: TOSOH BIOSCIENCE: S. DAMODARAN
Gel Permeation Chromatography: A Tool to Determine the Effects of Processing and Deterioration of Polymers

14 F. SOBOTTA (Friedrich Schiller University Jena), F. Hausig, J. C. Brendel
Polymerization-Induced Self-Assembly (PISA): Efficient Synthesis of Functional Micelles

15 P. HUMMEL (University of Bayreuth), D. S. Reig, Z. Wang, S. Rosenfeldt, B. Graczykowski, G. Fytas, M. Retsch
One Component Silver-Polystyrene Nanocomposites: The Interplay of Thermoplasmonics and Elastic Mechanical Properties

16 E. STEIERT (Johannes Gutenberg University Mainz), L. Radi, M. Fach, M. Konhäuser, B. Breitenbach, D. Bamberger, P. Wich
Polysaccharides and Proteins as Versatile Biopolymer Material for Nanoparticles

17 S. PEPLAU (Humbildt-Universität zu Berlin), N. ten Brummelhuis
Preparation of Sequence-Controlled Polymers Using Traceless Protecting Groups

18 A. KOLBERG (University of Freiburg), Ch. Wenzel, K. Hackenstrass, R. Schwarzl, Ch. Rüttiger, M. Gallei, R. Netz, Th. Hugel, B. N. Balzer
Stretch Me If You Can! Temperature-Dependent Hydration Effects of Stretched Polymers

19 M. MÜLLER (Leibniz Institute for Polymer Research Dresden), B. Urban, S. Schwarz, D. Vehlow, B. Reis, H. Schmidt
Water Based Concepts to Deposit Polyelectrolyte Coatings at Model and Applied Substrates for Biomedical Applications

20 E. M. SCHOENEBERGER (University of Hamburg), G. A. Luinstra
Innovative Filament for FFF 3D Printing Based on Diblock Copolymers

21 F. BRANDL (Clausthal University of Technology), F. Brandl, F. Lederle, C. Härter, A. F. Thünemann, S. Beuermann
From Gaseous Vinylidene Fluoride to Electroactive Poly(vinylidene fluoride) – Inducing β-Phase Crystallinity by Formation of Block Copolymers and Composite Materials

22 L. FRITZE (RWTH Aachen University), O. Ayhan, A. Lik, Th. Lorenz, M. Crumbach, N. A. Riensch, H. Helten
Silicon/Boron Exchange Routes to Conjugated Organoboron Polymers

11:40 COFFEE AND POSTERS
Chair: N.N.v

12:30 MARIE WEINHART (Freie Universität Berlin, Germany)
Thermoresponsive Polyglycidyl ether Coatings for Tissue Culture Applications

12:45 KATJA LOOS (University of Groningen, The Netherlands)
Poly(vinylidene fluoride) Based Multiferroic Composites

13:00 MARTIN van DUIN (Arlanxeo GmbH, Germany)
Morphology and Micro-Mechanics of Nano-Dispersed Rubber Blends

13:20 LUNCH BREAK
Chair: Günter Reiter

15:00 UWE BUNZ (Heidelberg Univeristy, Germany)
Small Libraries of Poly/paraphenyleneethynylene)s as “Universal” Chemical Tongues

15:20 CHRISTIAN PESTER (The Pennsylvania State University, USA)
Patterned Polymer Brushes for Solution-Processable OLEDs

15:40 PETER KRIMMER (stAPPtronics GmbH, Austria)
Smart Footwear – Innovative Textile Sensors for More and Healthier Movement in your Everyday Life

16:00 THOMAS FRÖIS (Texible GmbH, Austria)
Opportunities of Smart Textiles due to Digitalization

16:20 COFFEE BREAK
Chair: Andreas Walther

17:00 ANDRÉ GRÖSCHEL (University of Duisburg-Essen, Germany)
Block Copolymer Nanostructures Directed by Curvature and Topological Defects

17:20 MANFRED WILHELM (Karlsruhe Institute of Technology, Germany)
On-Line Benchtop Correlation of Molecular Weight Distribution and Chemical Composition via SEC-IR/-NMR and -QCL

17:40 KERSTIN BLANK (Max Planck Institute of Colloids and Interfaces Potsdam, Germany)
Coiled Coils as Mechanoresponsive Material Building Blocks: Towards Molecular Control of Smart Biomimetic Hydrogels

18:00 HANS BÖRNER (Humoldt-Universität zu Berlin, Germany)
From Sequence to Precise Functions: Translating Peptides to Precision Polymers

18:20 End of the Session

19:30 DINNER (Mensa Rempartstrasse) Doors open 19:15

FRIDAY, 22 FEBRUARY 2019

Chair: Michael Sommer

9:00 ROLF MÜLHAUPT (University of Freiburg, Germany)
Tailoring All-Hydrocarbon Composites for Circular Economy

9:30 PETER in't VELD (BASF SE, Germany)
Modeling of Complex Formulations and Polymer Systems

9:50 INTRODUCTION OF POSTERS

Chair: Michael Sommer

1 D. KLEINSCHMIDT (RWTH Aachen University), M. Fernandes, M. Mork, M. Rueping, A. Pich
Switchable Colloidal Catalysts Based on Temperature-Responsive Microgels

2 B. HAEHNLE (University of Ulm), A. Kuehne
New Organic Light-Emitting Capacitors Based on π-Conjugated Polymer Particles

3 J. GAITZSCH (University of Basel), P. C. Welsch, J. Folini, W. Murad, J. C. Anderson, W. Meier
Refitting Radical Ring-Opening Polymerisation for Biodegradable and Responsive Nanoparticles

4 J.-H. KRUSE (Friedrich Schiller University Jena), I. Romanenko, J. Eichhorn, M. Lechner, C. Streb, F. H. Schacher
Towards Catalysis under Flow Conditions in Block Copolymer Membranes

5 J. MARKWART (Johannes Gutenberg University Mainz), A. Battig, B. Schartel, F. Wurm
Structural Variation in Phosphorus-Containing Polymeric Flame Retardants: P-N vs. P-O

6 X. YAO (University of Freiburg), J. Wang, H. Chen, X. Ma, H. Tian, A. Walther
Stimuli-Responsive Luminescent Supramolecules and Polymers

7 J. KIRSCHNER (L'Institut de Science des Matériaux de Mulhouse), M. Bouzrati-Zerelli, Ch. P. Fick, M. Maier, C. Dietlin, F. Morlet-Savary, J. P. Fouassier, J.-M. Becht, J. E. Klee, J. Lalevée
Silyl Glyoxylates and Derivatives as a New Class of High Performance Visible Light Photoinitiators

8 M. FRÖLICH (Karlsruhe Institute of Technology), M. A. R. Meier
Reading the Sequence of Monodisperse Sequence-Defined Oligomers

9 M. HOFFMANN (Heinrich Heine University Düsseldorf),T. Freichel, D. Laaf, R. Wawrzinek, Ch. Rademacher, S. Sarafova, L. Elling, N. L. Snyder, L. Hartmann
Lactose-Functionalized Precision Glycomacromolecules for Understanding the Role of Galectin-3 in Tumor Migration

10 P. KLEIN (University of Wuppertal), U. Scherf
Polycyclic Ladder Polymers Made by Reductive Dehalogenation Polycondensation of AA-, AB- and AA/BB-type Monomer Systems as Novel Class of Polymers of Intrinsic Microporosity (PIMs)

11 R. OTTER (Johannes Gutenberg University Mainz), P. Besenius
Regulated Supramolecular Assembly of Peptide-Functionalized Polymers into Core-Shell Nanorods

12 W. ZHANG (Univerity of Freiburg), M. Samadi, N. Teske, V. P. Shastri
Synthesis and Uptake Behavior of Cyclic-(arginine-glycine-aspartic) Acid (cRGD) Modified Polymeric Nanoparticles

13 INDUSTRY PRESENTATION: LS INSTRUMENTS: M. REUFER
Polymer Rheology with Diffusing Wave Spectroscopy

14 INDUSTRY PRESENTATION: POSTNOVA ANALYTICS: G. HEINZMANN, F. Meier, M. Spallek, S. Spek, K. Langer, T. Klein
Poly(lactic-co-glycolic acid) Nanoparticles in Cell Media Used as Biocompatible Substrates in Pharmaceutical Applications: Comprehensive Characterization with Centrifugal Field-Flow Fractionation (CF3) Coupled with Online Dynamic Light Scattering (DLS)

15 CHR. HENSCHEL (University of Potsdam), Ch.-H. Ko, A. Laschewsky, Ch. M. Papadakis
Self-Assembly and Co-Nonsolvency of Hydrophobic/Thermoresponsive Block Copolymers: Influence of Chemical Structure and Block Lengths

16 T. LEBHERZ (University of Stuttgart/Daimler AG), M. Frey, A. Hintennach, M. R. Buchmeiser
Influence of Morphology on Electrochemical Performance of Monolithic Sulfur-Poly(acrylonitrile) Composites Used as Cathode Materials in Lithium-Sulfur Batteries

17 J. HÖHNER (RWTH Aachen University), J. Köhler, H. Keul, C. Rodriguez-Emmenegger, M. Möller
Arborescent Polymers via Living Radical Polymerization

18 T. JOHANN (Johannes Gutenberg University Mainz), M. Bros, H. Frey
Hydroxamic Acid Functional Polyethers: A Versatile Class of Polymeric Chelators for Surface Coating and Medical Application

19 I. KRAMBERGER (University of Fribourg), I. K. Tennie, P. Liu, A. F. M. Kilbinger
Switchable 19F Magnetic Resonance Imaging Contrast Agents Prepared by Ring-Opening Metathesis Polymerisation

20 PH. JÖCKLE (Karlsruhe Institute of Technology), Ph.W. Kamm, I. Lamparth, N. Moszner, A.-N. Unterreiner, Ch. Barner-Kowollik
Comparing Overall Initiation Efficiencies of (para-substituted) Mono-, Bis- and Tetraacylgermane Radical Initiators
21 T. WINTER (Technische Universität Darmstadt), Chr. Rüttiger, S. Schöttner, X. Su, T.A. Hatton, M. Gallei
Metallopolymer Architectures for the Preparation of Redox-Responsive Materials
22 A. FAHMI (Rhein-Waal University of Applied Sciences), V. Nirwan, N. Herman
Electrospun Hybrid Nanofibers

11:30 COFFEE AND POSTERS
Chair: Matthias Barz

12:15 FELIX SCHACHER (Friedrich Schiller University Jena, Germany)
Polymeric Photoacids – Monomer Design, Photostability, and First Steps Towards Light-Mediated Release
12:30 MALTE WINNACKER (Technical University of Munich, Germany)
Sustainable Biopolymers from Terpenes and Novel Functional Biomaterials
12:45 KAREN LIENKAMP (University of Freiburg, Germany)
Antimicrobially Active Polyzwitterions – A Paradigm Change?

13:00 LUNCH BREAK
Chair: Prasad Shastri

14:15 XINLIANG FENG (Technische Universität Dresden, Germany)
Polymer Synthesis Enabled by Interfaces: Towards a World of Organic 2D Materials
14:35 BERNHARD SCHMIDT (Max Planck Institute of Colloids and Interfaces Potsdam, Germany)
Novel Self-Assemblies via Double Hydrophilic Block Copolymers in Aqueous Solution
14:50 AXEL NEFFE (Universität Hamburg, Germany)
Fe-Catalyzed Ring-Opening Polymerization of Bio-Based Monomers
15:05 STEFAN NAUMANN (University of Stuttgart, Germany)
Polarized Olefins as (Organo-)Catalysts for the Controlled Polymerization of O-Heterocyclic Monomers
15:20 KATHARINA KOSCHEK (Fraunhofer Institute for Manufacturing Technology and Advanced Materials Bremen, Germany)
Chemical Approaches to Fiber Reinforced Polymers with Integrated Functions

15:35 POSTER AWARDS donated by WILEY

15:40 Closing Remarks
PRASAD SHASTRI
Meeting Chair
Director of the Institute for Macromolecular Chemistry, University of Freiburg
15:45 End of the Colloquium

Taming Complexity in Polymer Opto-Electronics: Tailoring Multifunctional Devices and Chemical Sensors

Paolo Samorì

One among the greatest challenges in organic electronics is the fabrication of multifunctional devices, that is, that can respond to multiple and independent stimuli. Such a challenge can be accomplished by developing multicomponent materials in which each component imparts a well-defined function to the ensemble. The controlled combination of such components and their integration in real devices can be achieved by mastering the supramolecular approach.

My lecture will review our recent works on the combination of carbon-based nanomaterials, and in particular organic semiconductors, with photochromic molecules (diarylethenes or azobenzenes) in order to realize smart, high-performing, and light-sensitive (opto)electronic devices as well as flexible non-volatile optical memory thin-film transistor device with over 256 distinct levels.

The developed knowledge is of high relevance also for the fabrication of chemical sensors possessing sensitivities, selectivities, response speeds, and reversibilities beyond the state-of-the-art.

---

[1] For reviews see: a) X. Zhang, L. Hou, P. Samorì, *Nat. Commun.* **2016**, *7*, 11118; b) E. Orgiu, P. Samorì, *Adv. Mater.* **2014**, *26*, 1827.

[2] For modulating charge injection at metal-organic interface with a chemisorbed photochromic SAM see: a) N. Crivillers, E. Orgiu, F. Reinders, M. Mayor, P. Samorì, *Adv. Mater.* **2011**, *23*, 1447; b) T. Mosciatti, M. G. del Rosso, M. Herder, J. Frisch, N. Koch, S. Hecht, E. Orgiu, P. Samorì, *Adv. Mater.* **2016**, *28*, 6606.

[3] For hybrid structure combining organic semiconductors blended with Au nanoparticles coated with a photochromic SAM see: C. Raimondo, N. Crivillers, F. Reinders, F. Sander, M. Mayor, P. Samorì, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 12375.

[4] For blends energy level phototuning in a photochromic–organic semiconductor blend see: a) E. Orgiu, N. Crivillers, M. Herder, L. Grubert, M. Pätzel, J. Frisch, E. Pavlica, G. Bratina, N. Koch, S. Hecht, P. Samorì, *Nat. Chem.* **2012**, *4*, 675; b) M. El Gemayel, K. Börjesson, M. Herder, D. T. Duong, J. A. Hutchison, C. Ruzié, G. Schweicher, A. Salleo, Y. Geerts, S. Hecht, E. Orgiu, P. Samorì, *Nat. Commun.* **2015**, 6, 6330.

[5] For the fabrication of memory devices: T. Leydecker, M. Herder, E. Pavlica, G. Bratina, S. Hecht, E. Orgiu, P. Samorì, *Nat. Nanotech.* **2016**, *11*, 769.

[6] For the novel nanomesh scaffold-based photodetector: L. Zhang, X. Zhong, E. Pavlica, S. Li, A. Klekachev, G. Bratina, T. W. Ebbesen, E. Orgiu, P. Samorì, *Nat. Nanotech.* **2016**, *11*, 900.

[7] For chemical sensors: a) M. A. Squillaci, L. Ferlauto, Y. Zagranyarski, S. Milita, K. Müllen, P. Samorì, *Adv. Mater.* **2015**, 27, 3170; b) M.-A. Stoeckel, M. Gobbi, S. Bonacchi, F. Liscio, L. Ferlauto, E. Orgiu, P. Samorì, *Adv. Mater.* **2017**, *29*, 1702469.

P. Samorì
ISIS, CNRS, Université de Strasbourg
8 allée Gaspard Monge
67000 Strasbourg, France

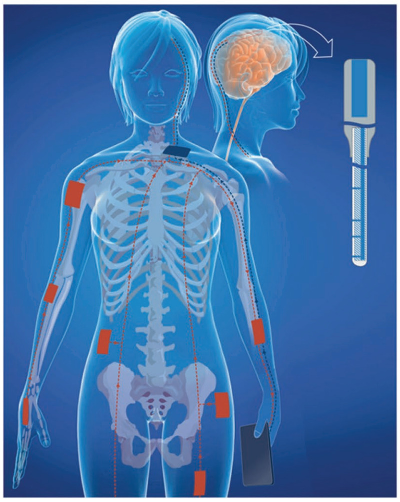
Organic Bioelectronics – Nature Connected

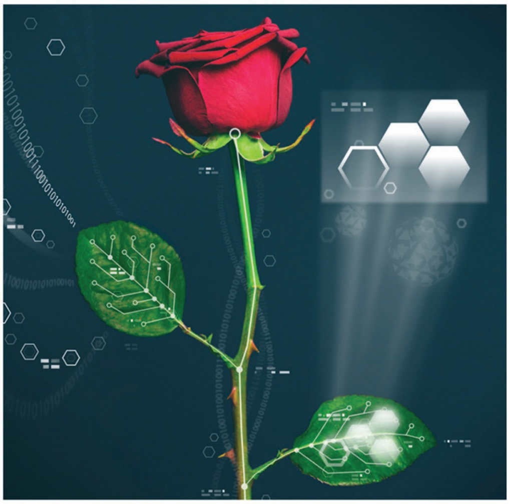
Magnus Berggren

Organic electronic materials exhibit an array of desired characteristics making them excellent as the signal translator across the gap between biology and technology. These biocompatible materials, often complexed with polyelectrolytes and other functional materials, can be included in device structures, which are flexible, stretchable, and even gelled, and can also process electronic, ionic, and charged biomolecules in combination. This makes the organic electronic materials unique in several respects to record and regulate functions and physiology of biological systems.

Here, a short review of some of the recent progresses from the Laboratory of Organic Electronics is given. In the BioComLab effort, a body area network is used to "connect" electronic skin patches with drug delivery components. This system provides a feedback system, also connected to the cloud for future health care. Sensors, converting biochemical signals into electric ones, are typically built up from organic electrochemical transistors and selectivity is typically provided from receptor mediation and oxidase approaches. Conversely, the organic electronic ion pump converts an electronic addressing signal into the delivery of specific biomolecules, such as a neurotransmitter, to actuate and control functions of for instance, the neuronal system. With the BioComLab technology, the wide array of neuronal disorders and diseases are targeted, such as epilepsy, Parkinson's disease, and chronical pain.

In the e-Plant effort, the BioComLab technology is applied to the plant kingdom to record and impact the signaling pathways of phytohormones, thus allowing us to regulate the growth and expression of specific components of flowers and trees. Further, organic electronic materials can also be applied from aqueous solution directly into the biological system, thus enabling a unique approach to manufacture devices and electrodes in vivo. We are currently exploring this in vivo-manufacturing concept in several settings to define devices and circuits in various plants, to generate a seamless interface between organic bioelectronics and biological systems, in general.


BioComLab


Electronic Plants

M. Berggren
Laboratory of Organic Electronics
ITN, Linköping University
601 74 Norrköping, Sweden

Digital Polymers: Emergence of a New Class of Synthetic Macromolecules

Jean-François Lutz

It has been shown in recent years that information can be stored at the molecular level in synthetic polymers.[1,2] To achieve such a property, different comonomers are used as a molecular alphabet and assembled together into a defined information sequence. For instance, an alphabet based on two different monomers allows writing of binary information in a linear polymer chain.[3] But of course such digital polymers cannot be synthesized using a standard chain-growth or step-growth polymerization mechanism because these approaches lead to polydisperse samples containing pronounced sequence defects. Instead, so-called multi-step growth strategies have to be employed.[4] For instance, solid-phase iterative chemistry allows synthesis of a wide variety of uniform sequence-defined digital polymers.[3,4] This approach is not restricted to oligomers and long digital chains containing more than 100 coded residues have been prepared.[5] Moreover, the information stored in these chains can be easily decoded by tandem mass spectrometry. As shown very recently, not only short but also long digital sequences can be deciphered using this analytical technique.[6] Furthermore, a sequencing software allows decryption in some milliseconds.[7]

Since multi-byte digital encryption and decryption of a synthetic polymer chain has now been clearly demonstrated, the next important challenge in this emerging field of research will be the application of such digital polymers in technological areas; for example, for the development of molecular memories. However, such applications are quite demanding and imply to move from simple proofs-of-concept at the single-chain level to complex multi-chain libraries allowing storage and manipulation of larger amounts of information. In this lecture, I will highlight new directions that are currently under investigation in my laboratory for the development of such complex "coded matter." In particular, I will describe simple strategies for the preparation of polymer materials allowing high-density information storage. Specific emphasis will be put on the development of planar digital micro-arrays as well as on the 3D organization of digital polymers.[8]

---

[1] J.-F. Lutz, M. Ouchi, D. R. Liu, M. Sawamoto, *Science* **2013**, *341*, 1238149.

[2] H. Colquhoun, J.-F. Lutz, *Nat. Chem*. **2014**, *6*, 455.

[3] R. K. Roy, A. Meszynska, C. Laure, L. Charles, C. Verchin, J.-F. Lutz, *Nat. Commun*. **2015**, *6*, 7237.

[4] J.-F. Lutz, J.-M. Lehn, E. W. Meijer, K. Matyjaszewski, *Nat. Rev. Mater*. **2016**, *1*, 16024.

[5] A. Al Ouahabi, M. Kotera, L. Charles, J.-F. Lutz, *ACS Macro Lett*. **2015**, *4*, 1077.

[6] A. Al Ouahabi, J.-A. Amalian, L. Charles, J.-F. Lutz, *Nat. Commun*. **2017**, *8*, 967.

[7] A. Burel, C. Carapito, J.-F. Lutz, L. Charles, *Macromolecules* **2017**, *50*, 8290.

[8] R. Szweda, M. Tschopp, O. Felix, G. Decher, J.-F. Lutz, *Angew. Chem., Int. Ed.*, Early View.

J.-F. Lutz
Institut Charles Sadron
CNRS UPR 22, Université de Strasbourg
23 rue du Loess, 67034 Strasbourg
Cedex 2, France
E-mail: jflutz@unistra.fr

Redox Polymers as Electrode-Active Materials for Organic Batteries

Birgit Esser, Fabian Otteny, Pascal Acker, Martin Speer, and Gauthier Desmaizieres*

In face of the climate change, there is a strong and growing demand for the storage of renewable energies. Reliable electricity storage devices such as batteries and electrochemical capacitors are required. Organic electrode materials have attracted great interest, as they can be prepared from renewable, sustainable, or less-limited resources, they are easy to recycle as well as potentially safer and cheaper to produce, leading to a low carbon footprint. A promising class of organic electrode materials is redox polymers—polymers containing groups that can be reversibly reduced or oxidized.

In this talk, organic redox polymers with aliphatic as well as conjugated backbones will be presented containing π-systems as redox-active functionalities. The synthesis and electrochemical properties of these polymers will be discussed as well as their application as electrode-active materials in batteries.

Prof. B. Esser, F. Otteny, P. Acker, M. Speer, G. Desmaizieres
Institut für Organische Chemie, Universität Freiburg
Friedrichstr. 39, 79098 Freiburg, Germany
E-mail: www.esser-lab.uni-freiburg.de; besser@oc.uni-freiburg.de

Solution-Processed Organic Semiconductors and their Applications

K. Meerholz

Organic light emitting diodes (OLEDs) based on electroluminescent conjugated polymers are considered as a promising alternative for display and lighting applications, mainly due to their better compatibility with low-cost production techniques and large substrates. A challenge is multiple-layer deposition to improve the efficiency of the devices and, as a result, their lifetime.

This lecture introduces recent trends in the field of OLED with an emphasis on solution-processed devices. We have in the past developed photochemically cross-linkable semiconductors for the fabrication of complex multilayer OLED[1] with a potential for eventually becoming organic lasers[2] and RGB-pixelation.[3,4] Recently, we also introduced organic memories (OMEM) with multi-bit storage capacity.[5,6]

[1] C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker, K. Meerholz, *Nature* **2003**, *421*, 829.

[2] B. H. Wallikewitz, M. de la Rosa, J. H. W. M. Kremer, D. Hertel, K. Meerholz, *Adv. Mat.* **2010**, 22, 531.

[3] M. C. Gather, A. Köhnen, A. Falcou, H. Becker, K. Meerholz, *Adv. Funct. Mat.* **2007**, *17*, 191.

[4] F. Ventsch, M. C. Gather, K. Meerholz, *Org. Electronics* **2010**, *11*, 57.

[5] P. Zacharias, M. C. Gather, A. Köhnen, N. Rehmann, K. Meerholz, *Angew. Chem. Int. Ed.* **2009**, *48*, 4038.

[6] R. C. Shallcross, P. O. Körner, E. Maibach, A. Köhnen, K. Meerholz, *Adv. Mat.* **2013**, *34*, 4807.

K. Meerholz
University of Cologne, Germany

Charge Transport in Organic Semiconductors

Naresh Kotadiya, Gert-Jan Wetzelaer, Denis Andrienko, and Paul W. M. Blom

Charge transport is an important issue with regard to the understanding and optimization of electronic devices made from organic semiconductors. Conjugated polymers and amorphous small-molecule hole-transporting materials are commonly used in organic light-emitting diodes. Characterization of their main functionality, hole transport and electron transport, has been complicated by the presence of large contact barriers and trapping effects. Using a recently developed technique to establish Ohmic hole contacts, we investigate the bulk hole transport in a series of organic semiconductors with a broad range of ionization energies. The measured charge-carrier mobility dependence on charge concentration, electric field, and temperature is used to extract the energetic disorder and molecular site spacing. Excellent agreement of these parameters as well as ionization energies with simulation results paves the way to predictive charge-transport simulations from the molecular level.

N. Kotadiya, G.-J. Wetzelaer, D. Andrienko, P. W. M. Blom
Max Planck Institute for Polymer Research
Ackermannweg 10, Mainz, Germany

COVESTRO LECTURE

Catalytic Precision Polymerization: Sustainable Materials from Simple Monomers

Bernhard Rieger

Carbon dioxide and its relevance to climate change currently receive worldwide attention. That is why considerations are taken to use CO_2 more intensely as a C1 component for high-value products.[1] With regard to the range of polymeric materials, the lecture focuses on aliphatic polycarbonates (*ali*-PC) and on variable isotactic polyhydroxybutyrates (PHB), which both can be catalytically produced from epoxides and carbonic oxides.

The first part of the lecture deals with the mechanisms of polymerization of different catalyst types, which differ fundamentally from the olefin polymerization reaction: whereas one catalyst center controls olefin polyinsertion processes, bi-functional catalysts are required in the CO_2/epoxide-copolymerization sequence.[2] Here, a novel concept of bi-functional Zn(II)-based catalysis will be introduced, that moves the reactivity determining step away from the epoxide ring opening to the CO_2-insertion reaction.[3] This makes the catalytic synthesis of block-copolymers possible, in which the CO_2-molecule is used as a switch to turn block-formation on and off.

The second part focuses on some fascinating material features of the ali-PC and discusses the potential of this class of materials.[4] As a recent finding, blends of polypropylene carbonate (PPC) and PHB will be presented, which for the first time afford properties that resemble those of purely oil-based plastics, like ABS and even PS.[5]

[1] a) S. Klaus, M. Lehenmeier, C. E. Anderson, B. Rieger, *Coord. Chem. Rev.* **2011**, *255*, 1518; b) B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem.* **2011**, *123*, 8662.

[2] a) S. Kissling, M. Lehenmeier, P. Altenbuchner, A. Kronast, M. Reiter, P. Deglmann, U. Seemann, B. Rieger, *Chem. Commun.* **2015**, *51*, 4579; b) M. Lehenmeier, S. Kissling, P. Altenbuchner, C. Bruckmeier, P. Deglmann, A. Brym, B. Rieger, *Angew. Chem. Int. Ed.* **2013**, *52/37*, 9821; c) B. Rieger, S. Kissling, P. Altenbuchner, M. Lehenmeier, L. Herdtweck, P. Deglmann, U. Seemann, *Chem. Eur. J.* **2015**, *21*, 8148.

[3] a) R. Eberhardt, M. Allmendinger, G. A. Luinstra, B. Rieger, *Organometallics* **2003**, *22*, 211; b) G. A. Luinstra, G. R. Haas, F. Molnar, V. Bernhart, R. Eberhardt, B. Rieger, *Chem. Eur. J.* **2005**, *11*, 6298; c) S. I. Vagin, R. Reichardt, S. Klaus, B. Rieger, *J. Am. Chem. Soc.* **2010**, *132*, 14367; d) S. Klaus, M. W. Lehenmeier, E. Herdtweck, P. Deglmann, A. K. Ott, B. Rieger, *J. Am. Chem. Soc.* **2011**, *133*, 13151; e) M. W. Lehenmeier, C. Bruckmeier, S. Klaus, J. E. Dengler, P. Deglmann, A. K. Ott, B. Rieger, *Chem. Eur. J.* **2011**, *17*, 8858.

[4] G. A. Luinstra, *Polym. Rev.* **2007**, *48*, 192.

[5] a) C. Bruckmeier, B. Rieger, M. Lehenmeier, R. Reithmeier, V. Herranz, S. Kavakli, *Dalton Trans.* **2012**, *14*, 5026; b) O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger, A. Greiner, *Green Chem.* **2016**, *18*, 760; c) M. Reiter, S. Vagin, A. Kronast, C. Jandl, B. Rieger, *Chem. Sci.* **2017**, *8*, 1876; d) S. Kernbichl, M. Reiter, F. Adams, S. Vagin, B. Rieger, *J. Am. Chem. Soc.* **2017**, 6787.

B. Rieger
WACKER-Chair of Macromolecular Chemistry
Technische Universität München
Lichtenbergstr 4, 85747 Garching, Germany
E-mail: rieger@tum.de

Materials for Flexible, Bio-Integrated Electronics

John Rogers

Biological systems are mechanically soft, with complex, 3D curvilinear shapes; modern electronic technologies are rigid, with simple, 2D layouts. Technologies that eliminate this profound mismatch in physical properties create opportunities for devices that can intimately integrate with the body, for diagnostic, therapeutic, or surgical function with important, unique capabilities in biomedical research and clinical healthcare. Over the last decade, a convergence of new concepts in materials science, mechanical and electrical engineering, and advanced manufacturing has led to the emergence of diverse, novel classes of "biocompatible" electronic platforms. This talk describes the key ideas, and presents some of the most recent device examples, including wireless, skin-like electronic "tattoos" for continuous monitoring of vital signs in neonatal intensive care, microfluidic/electronic systems that can capture, store, and perform biomarker analysis on sweat, and 3D open-mesh electronic mesostructures for active cellular scaffolds.

J. Rogers
Northwestern University, USA

Programmable Soft Matter: From Active Membranes to Self-Replication

*M. Mathieu, H. Charan, U. Glebe, S. Zhang, S. Reinicke, D. John, M. Zimmermann, F. Mehr, N. Puretskiy, M. Sperling, M. Reifarth, D. Grigoriev, and A. Böker**

This contribution discusses various approaches to create programmable soft matter either by directly incorporating functional biomolecules into polymeric materials or by transferring concepts conceived by nature to fully artificial materials.

The first approach involves the synthesis of polymer–protein conjugates and their self-assembly to form biofunctional membranes. We introduce a new strategy using engineered natural protein channels decorated with polymer chains followed by self-assembly at a fluid interface to form ultrathin, permeable, and highly selective membranes. A similar strategy can be used to incorporate sensitive enzymes into a fluid-like polymer membrane environment, thus allowing to almost completely retain their initial activity after immobilization and even boosting their temperature stability.

The second example is aiming toward creating artificial materials systems that are able to self-replicate. To achieve this, an indispensable prerequisite is the multi-directional control of interactions between the building blocks of materials. Thus, we aim to create a new class of multi-patch colloidal particles via an advanced micro-contact printing technique yielding patches of different chemical or physical functionalities. The new production process allows precise control over the patch location and chemistry and thus also gives particles that go well beyond known ABA- or ABC-type Janus particles.

---

[1] Z. Sun, U. Glebe, H. Charan, A. Böker, C. Wu, *Angew. Chem.* **2018**, doi: 10.1002/anie.201806049.

[2] D. John, M. Zimmermann, A. Böker, *Soft Matter* **2018**, *14*, 3057.

[3] M. Zimmermann, D. John, D. Grigoriev, N. Puretskiy, A. Böker, *Soft Matter* **2018**, *14*, 2301.

[4] S. Zhang, C. Bisterfeld, J. Bramsk, N. Vanparijs, B. G. De Geest, J. Pietruszka, A. Böker, S. Reinicke, *Bioconjugate Chem.* **2018**, *29*, 104.

[5] H. Charan, U. Glebe, D. Anand, J. Kinzel, L. Zhu, M. Bocola, T. M. Garakani, U. Schwaneberg, A. Böker, *Soft Matter* **2017**, *13*, 2866.

[6] S. Reinicke, H. C. Rees, P. Espeel, N. Vanparijs, C. Bisterfeld, M. Dick, R. R. Rosencrantz, G. Brezesinski, B. G. de Geest, F. E. Du Prez, J. Pietruszka, A. Böker, *ACS Appl. Mater. Interfaces* **2017**, *9*, 8317.

Superresolution Fluorescence Microscopy of Polymer Structures

Dominik Wöll, Oleksii Nevskyi, Eric Siemes, Alex Oppermann, Sarah K. Turnhoff, Dmytro Sysoiev, Walter Richtering, and Thomas Huhn*

Super-resolved fluorescence imaging has been frequently used for biological and biomedical applications.[1] Applying these methods to material science, and in particular to polymer systems, is a challenging task due to the need for appropriate dyes and labeling strategies for often non-aqueous and apolar systems. Many super-resolution imaging techniques are based on the switching of fluorophores between a fluorescent and a non-fluorescent state. The sulfone derivatives of diarylethenes[2] have been found to be suitable photoswitches with a strongly fluorescent closed form.[3] We demonstrated their power for resolving different polymer systems including block copolymer structures[4] with the different super-resolution techniques, photoactivated localization microscopy (PALM), reversible switchable optical fluorescence transition (RESOLFT), and super-resolution optical fluctuation imaging (SOFI).[5] The successful story of diarylethene super-resolution imaging is continued for different scientific questions in polymer science such as the distribution of cross-linkers in various polymer networks.[6]

---

[1] S. W. Hell, *Nat. Methods* **2009**, *6*, 24.

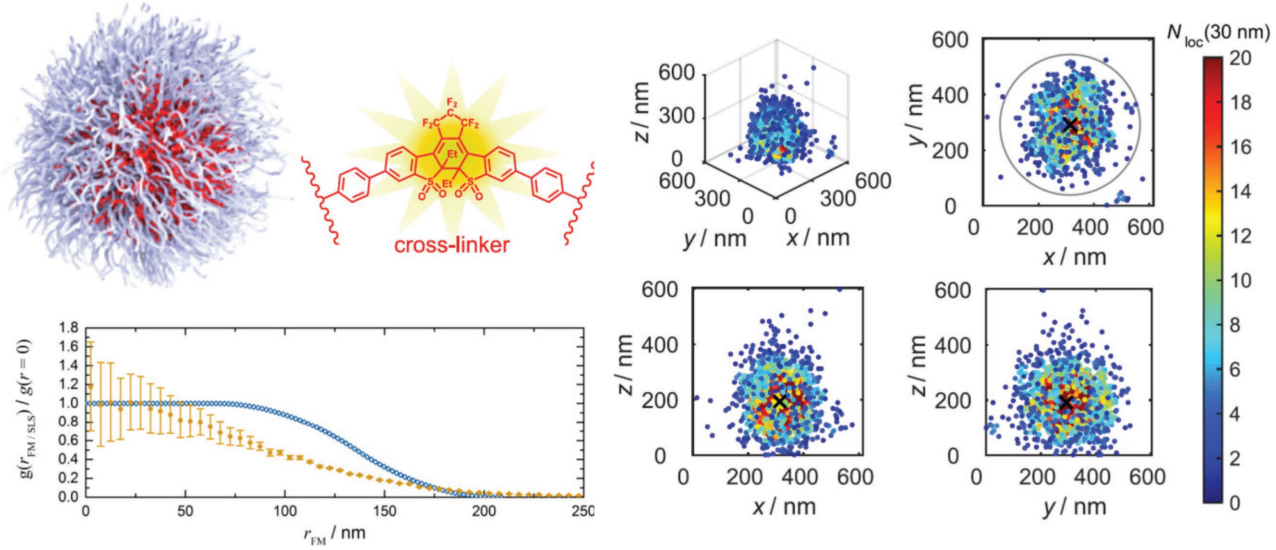
[2] M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, *114*, 12174.

[3] K. Uno, H. Niikura, M. Morimoto, Y. Ishibashi, H. Miyasaka, M. Irie, *J. Am. Chem. Soc.* **2011**, *133*, 13558.

[4] O. Nevskyi, D. Sysoiev, A. Oppermann, T. Huhn, D. Wöll, *Angew. Chem. Int. Ed.* **2016**, *55*, 12698.

[5] O. Nevskyi, D. Sysoiev, J. Dreier, S. C. Stein, A. Oppermann, F. Lemken, T. Janke, J. Enderlein, I. Testa, T. Huhn, D. Wöll, *Small* **2018**, *14*, 1703333.

[6] E. Siemes, O. Nevskyi, D. Sysoiev, S. K. Turnhoff, A. Oppermann, T. Huhn, W. Richtering, D. Wöll, Angew. *Chem. Int. Ed.* **2018**, *57*, 12280.



Scheme 1. Diarylethene photoswitches as cross-linkers in microgels: localizations from super-resolved PALM imaging (right) show the 3D positions of single cross-linkers. Comparison with SLS data on the same microgels exhibits that the radial distribution of cross-linker and of polymer density are significantly different, presumably due to the higher incorporation rate of the diarylethene cross-linker at early stages.

D. Wöll, O. Nevskyi, E. Siemes, A. Oppermann, S. K. Turnhoff,
W. Richtering
Institute of Physical Chemistry, RWTH Aachen University
Landoltweg 2, 52074 Aachen, Germany
E-mail: woell@pc.rwth-aachen.de

D. Sysoiev, T. Huhn
Department of Chemistry, Universität Konstanz
Universitätstr. 10, 78457 Konstanz, Germany

Batteries from Lobster and Vanilla: Polymers from Chitosan and Vanillin as Active Material in Sustainable Batteries

Ivan Ilić, S. Chaleawlert-Umpon, M. Antonietti, and C. Liedel

When talking about lobsters and vanilla, probably only odd minds think about energy storage. Still, main ingredients of both may be combined to form a polymer with high charge storage capability.[1]

Chitosan, made by deacetylating chitin (e.g., from crab shells) reacts with vanillin (not only gained from vanilla but rather from lignin and therefore from low value side products of the wood industry) and forms imines, which can be reduced to secondary amines.[2,3] We studied the resulting polymer as a cathode material for organic batteries, and during cyclic voltammetry tests, it showed narrow redox peaks, as well as higher capacity compared to other sustainably derived polymers. Besides the good energy storage properties, it also acts as binder material, which additionally increases the sustainability of resulting polymeric electrodes.

Of course, also lignin may not only be used as a feedstock for vanillin but may be used as such without modification as active electrode material in more sustainable batteries.[4–6] Often however, the undefined structure and the low capacity, resulting from the low density of electrochemically active groups, impede practical applications. The chitosan-vanillin polymer in contrast has a higher redox potential than lignin, a more clearly defined structure, and a higher density of redox active groups, and may therefore actually find applications in sustainable energy storage.

---

[1] I. Ilić, M. Antonietti, S. Chaleawlert-Umpon, C. Liedel, unpublished.
[2] J. Desbrières, C. Martinez, M. Rinaudo, *Int. J. Biol. Macromol.* **1996**, *19*, 21.
[3] R. S. Jagadish, K. N. Divyashree, P. Viswanath, P. Srinivas, B. Raj, *Carbohydr. Polym.* **2012**, *87*, 110.
[4] G. Milczarek, O. Inganäs, *Science* **2012**, *335*, 1468.
[5] S. Chaleawlert-Umpon, T. Berthold, X. Wang, M. Antonietti, C. Liedel, *Adv. Mater. Interfaces* **2017**, *4*, 1700698.
[6] S. Chaleawlert-Umpon, C. Liedel, *J. Mater. Chem. A* **2017**, *5*, 24344.

Tailor-Made Force Probes for Wavelength-Orthogonal Stress-Sensing

*Christoph Baumann and Robert Göstl**

Molecules reporting on mechanical forces in polymers via the alteration of their optical properties (mechanochromophores) are of great interest in materials science as they allow the direct detection of stress concentrations thus helping to understand failure mechanisms and to improve material performance.[1] For this purpose, we recently developed the most sensitive steady-state mechanochromophore known today, which is based on the Diels–Alder adduct of π-extended anthracene and maleimide.[2] However, functional materials typically are non-uniform, compartmentalized, or hierarchically structured demanding the locally resolved and parallel detection of forces; a technology remaining elusive. To tackle this challenge, we revised the design and synthesis of these mechanochromophores allowing the fine-tuning and orthogonalization of their optical properties, that is, fluorescence emission and absorption wavelengths, while their excellent mechanochemical performance was retained. This will allow us to investigate mechanical failure pathways on complex macromolecular structures in high-performance composites as well as in biomimetic systems.

---

[1] R. Göstl, J. M. Clough, R. P. Sijbesma, in *Mechanochemistry in Materials*, Royal Society of Chemistry **2017**, pp. 53–75.

[2] R. Göstl, R. P. Sijbesma, *Chem. Sci.* **2016**, *7*, 370.

C. Baumann, R. Göstl
DWI - Leibniz Institute for Interactive Materials
Forckenbeckstr. 50, 52056 Aachen, Germany
E-mail: goestl@dwi.rwth-aachen.de

Droplet-Assisted Microfluidic Fabrication and Characterization of Multifunctional Polysaccharide Microgels Formed by Ugi Four-Component Reaction

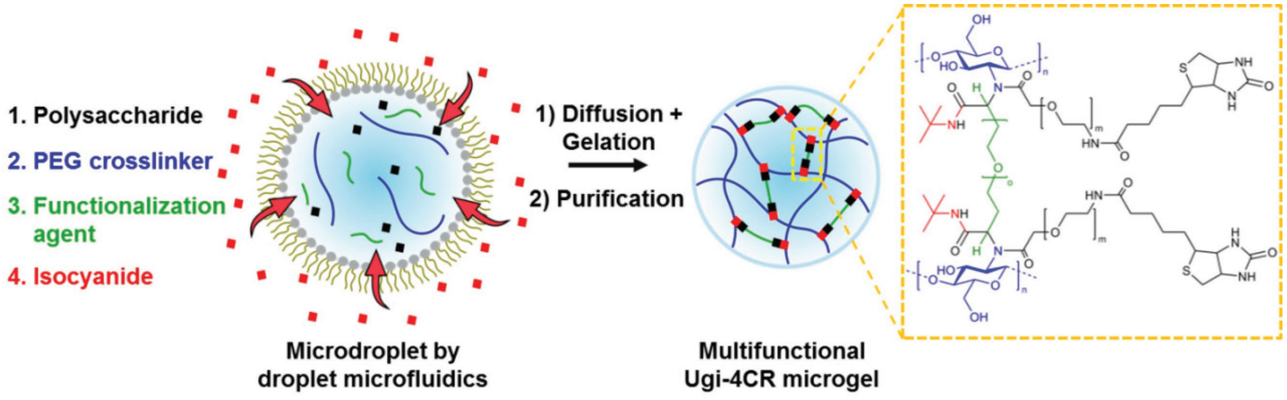
Nicolas Hauck, Nalin Seixas, Silvia P. Centeno, Raimund Schlüßler, Gheorghe Cojoc, Paul Müller, Jochen Guck, Dominik Wöll, Ludger A. Wessjohann, and Julian Thiele**

Polysaccharide-based microgels have broad applications in multi-parametric cell cultures, cell-free biotechnology, and drug delivery, since they are renewable, nontoxic, often biodegradable, and easily available from natural sources. While hydrogel synthesis from polysaccharides often requires prefunctionalization of respective building blocks to introduce certain functionality, in multicomponent reactions, like the Ugi four-component reaction, one building block can be simply exchanged by another to introduce and extend functionality in a library-like fashion.

Droplet-assisted microfluidics is utilized for processing the four building blocks of the Ugi reaction (carboxylic acid, amine, aldehyde, and isocyanide) into non-colloidal, homogeneous microgels with low size distribution. Microfluidics is employed as it allows for efficient mixing of multiple components on the micron-scale. Beyond the synthesis of polysaccharide microgels based on hyaluronic acid, alginate, and chitosan, exemplarily in depth analysis of hyaluronic acid-based Ugi four-component microgels is carried out by colloidal probe atomic force microscopy, confocal Brillouin microscopy, and fluorescence correlation spectroscopy to elucidate the capability of this multicomponent reaction for fabricating tailored polysaccharide microgel networks. By varying the amount and length of the cross-linker, the impact on the Young's modulus and diffusion coefficient is studied. It could be shown that the Ugi four-component reaction is well suited for forming polysaccharide-based microgels with uniform elasticity, porosity, and distribution of functional groups. Moreover, multifunctional building blocks allow for cross-linking of microgels and incorporating of functional groups in parallel as demonstrated for biotin-functionalized, chitosan-based microgels. These microgels are used as scaffolds for the immobilization of streptavidin-labeled enzymes as shown for the model enzyme horseradish peroxidase, which retains its activity inside the microgels.

---

[1] N. Hauck et al., *Polymers*, **2018**, *10*, 1055.



N. Hauck, J. Thiele
Institute of Physical Chemistry and Polymer Physics
Leibniz-Institut für Polymerforschung Dresden
D-01069 Dresden, Germany

N. Seixas, L. A. Wessjohann
Department of Bioorganic Chemistry
Leibniz-Institut für Pflanzenbiochemie
D-06120 Halle (Saale), Germany

S. P. Centeno, D. Wöll
Institute of Physical Chemistry
RWTH Aachen University
D-52074 Aachen, Germany

R. Schlüßler, G. Cojoc, P. Müller, J. Guck
Center for Molecular and Cellular Bioengineering
Biotechnology Center, Technische Universität Dresden
D-01307 Dresden, Germany

From Striped Ellipsoids to Janus Nanoparticles: Controlling Colloid Shape, Morphology and Function via Phase Separation of Functional Polymers

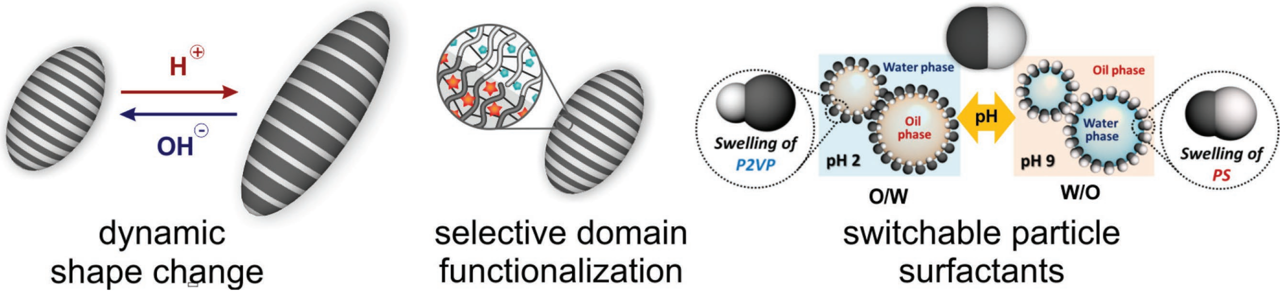
Daniel Klinger

The ability of nature to control shape and functionality of nanoparticles in biological systems is a well of inspiration for chemists and materials scientists. However, the synthetic formation of bio-inspired polymeric nanoparticles remains challenging: it requires combining shape anisotropy, stimuli responsiveness, spatially control over internal chemistry, and nano-structured morphology in a single colloidal system. We have previously addressed this challenge by developing shape-changing nano-ellipsoids with axially stacked lamellae. In this approach, we controlled the phase separation of PS-*b*-P2VP block copolymers (BCPs) in the nanoparticle confinement via functional surfactants. This strategy represents a new platform for the development of a broad range of synthetic nanoparticles with novel properties.[1]

Herein, we extend this preparation method to introduce a variety of functionalities in shape anisotropic particles. On one hand, we use block copolymers with inherent functionalities such as poly(ferrocenylsilane) blocks to introduce redox-sensitive moieties in BCP ellipsoids.[2] On the other hand, we use blends of functionalized homopolymers and BCPs to precisely tune the final ellipsoids' properties. Firstly, the domain spacing can be adjusted via homopolymer addition. Secondly, the addition of functionalized homopolymers allows for the spatially controlled incorporation of chemical functionalities, for example, cross-linkable moieties, in the respective domains.[3] This modular approach can be further extended to PS/P2VP Janus nanoparticles with switchable amphiphilicity and is a key factor to selectively adjust the material's properties to a specific application.[4]

---

[1] D. Klinger, C. X. Wang, L. A. Connal, D. Audrus, S. G. Jang, S. Kraemer, K. L. Killops, G. H. Fredrickson, E. J. Kramer, C. J. Hawker, *Angew. Chem. Int. Ed.* **2014**, *53*, 7018.
[2] B. V. K. J. Schmidt, J. Elbert, D. Scheid, C. J. Hawker, D. Klinger, M. Gallei, *ACS Macro Lett.* **2015**, *4*, 731.
[3] B. V. K. J. Schmidt, C. X. Wang, S. Kraemer, L. A. Connal, D. Klinger, *Polym. Chem.* **2018**, *9*, 1638.
[4] K. H. Ku, Y. J. Lee, G.-R. Yi, S. G. Jang, B. V. K. J. Schmidt, K. Liao, D. Klinger, C. J. Hawker, B. J. Kim, *Macromolecules* **2017**, *50*, 9276.



Prof. D. Klinger
Freie Universität Berlin
Königin-Luise-Str. 2-4, 14195 Berlin, Germany

Hydrogels for Triggered Drug Release

B. Yannick, P. Klahn, and H. Menzel

Hydrogel nanoparticles have gained particular interest in recent years and have become one of the most promising drug delivery systems. They show very good compatibility with therapeutic proteins. Furthermore, they can be functionalized to make them stimuli-responsive. Stimuli such as pH, temperature, redox, ionic strength, electric and magnetic fields can be used. The presence of specific enzymes as trigger for the release of the drug is of particular interest, because this enables on demand availability of the drug. The fight of implant-associated infections is a field of application where this kind of triggered release would be particular beneficial and would help to prevent unspecific and overuse of antibiotics.

To face this challenge, new alginate/peptide nanoparticles, which is biocompatible and have the ability of building covalent link with a drug such as ciprofloxacin, have been prepared. This alginate/peptide system self-assembled into nanoparticles via an ionic gelation between negatively charged alginate and a positively charged peptide as cross-linker. To make these particles enzyme responsive, the drug (ciprofloxacin) was linked to the functional peptide, which is cleavable by an enzyme released as consequence of the inflammation caused by the infection. Cleavage of the peptide then led to the disruption of the hydrogel network and release of the drug. Therefore, the enzyme production of the body upon as consequence of the infection caused release of the drug.

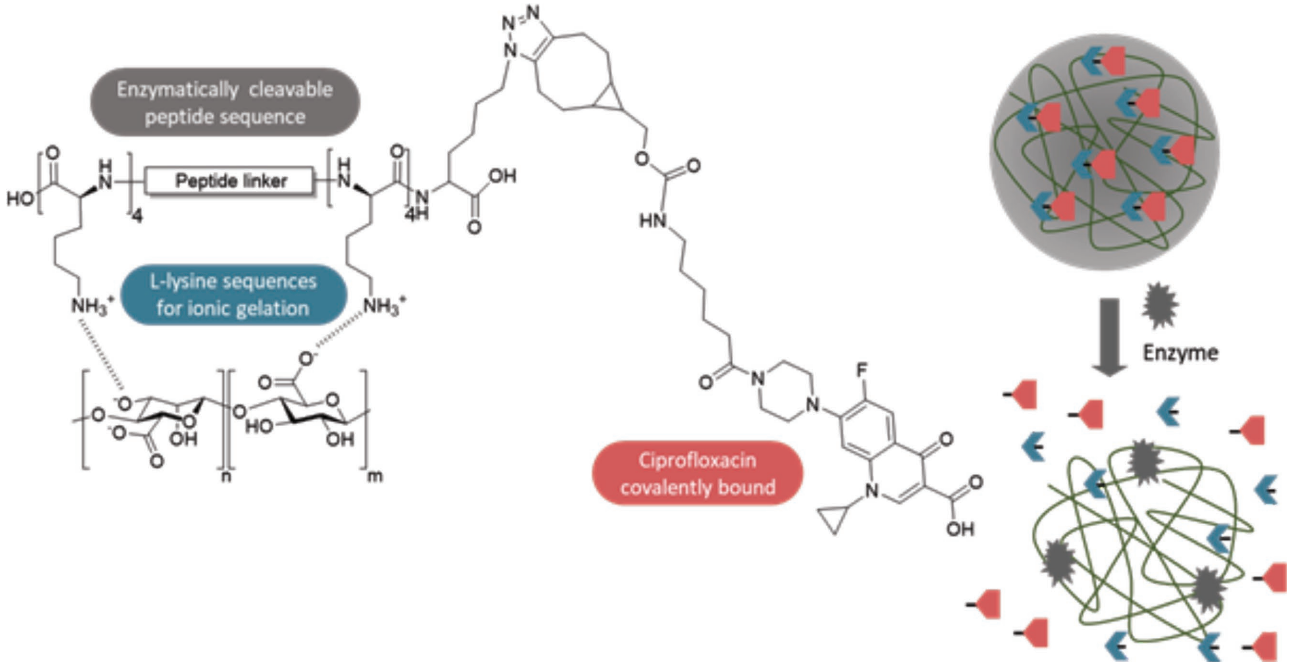


Figure 1. Hydrogels based on poly-l-lysine and alginate ionic gelation.

B. Yannick, P. Klahn, H. Menzel
Insitut für Technische Chemie
Technische Universität Braunschweig
Universitätsplatz 2, 38106 Braunschweig, Germany

Influence of Additives on the Properties of Biopolymers

A. Schmid, S. Hecht, C. Henning, and K. Harre*

For the past years, different applications for biopolymers have been researched. The implementation of biopolymers in electronics requires certain modifications of these biopolymers. Otherwise, the properties of most biopolymers do not meet the requirements of the electronic industry.[1] Polylactic acid (PLA) was used as a biopolymer in these investigations. Because of the brittle character of PLA, cellulose acetate (CA) was used as one additive to improve the mechanical properties of the PLA.[2] Zinc pyrophphosphate (ZnPP) was used as a flame retardant for PLA.[3] Samples with different amounts of CA and ZnPP, respectively, were compounded, as well as samples with both CA and ZnPP. The influence of these additives on the properties of the product was characterised with the aid of different methods. Thermal properties were measured by differential scanning calorimetry (DSC). As the use for screen printing or bonding technologies requires special surface properties, different methods are applied to investigate surface properties of our compound materials. The surface energy and its dispersive and polar interactions were calculated based on contact angle measurements of different test liquids. The majority of the surface energy is caused by dispersive interactions. The surface roughness was investigated using 3D microscopy to judge the quality of the surface. The three point bending test was performed on the samples. Thus, the E-modulus of the samples was calculated. The flammability of the samples was investigated with a fire test. The addition of ZnPP into the polymer matrix caused a low flammability of these samples. Different electrical properties like the dielectric strength and the dielectric constant were investigated as well. The results of our study show, that the use of additives can improve the properties of biopolymers in a manner that they can be used as substrates for wiring boards in several electrical applications.

---

[1] A. Géczy, D. Nagy, I. Hajdu, presented at the 21st Int. Symp. for Design and Technology in Electronic Packaging (SHTME), **2015**, pp. 45–49.

[2] A. Staat, et al., presented at the 38th Int. Spring Seminar on Electrical Technology (ISSE), **2015**, pp. 21–25.

[3] T. Ishikawa, I. Maki, K. Takeda, *J. Appl. Polym. Sci.* **2004**, 92, 2326.

A. Schmid, S. Hecht, K. Harre
Faculty of Agriculture, Environment, Chemistry
University of Applied Sciences, Dresden, Germany
E-mail: anna.schmid@htw-dresden.de

C. Henning
Faculty of Electrical Engineering
University of Applied Sciences, Dresden, Germany

Thermoresponsive Micelle-Inspired Polymer Ionic Liquids as Compartmentalized Nanosystems and Molecular Shuttles

*Steffen Wiedmann, Tobias M. Trötschler, Manuel Luitz, Marcel Werner, Saskia Gröer, Balázs Pásztói, Benjamin Kerscher, Ákos Szabó, Jean-François Lutz, Béla Iván, and Rolf Mülhaupt**

Constructing smart and highly functional polymer systems requires the precise design of stimuli-responsive macromolecules and directed nanostructure formation.

By micelle-inspired tailoring of polymer ionic liquids (PILs), which are obtained by incorporation of ionic liquid (IL) groups into sophisticated macromolecular architectures, new compartmentalized nanosystems have been developed.

Two strategies were employed for the generation of the compartmentalized thermoresponsive PIL nanosystems, both of them making use of lower critical solution temperature (LCST)-type polyoxazoline (POx) segments. In the first strategy, amphiphilic diblock copolymers composed of a hydrophobic polyisobutylene (PIB) block, a poly(2-ethyl-2-oxazoline) (PEtOx) block, and an IL cation connecting both blocks are designed, leading to the formation of micellar self-assemblies (**Figure 1**A). The second strategy is based on the construction of unimolecular PIL micelles, which consist of a hyperbranched polyether core, an inner IL shell, and an outer POx shell (Figure 1B).

By simple variation of the PEtOx block length, diblock copolymers with different cloud points and critical micelle concentrations in aqueous solution are obtained. Moreover, the block length ratio governs self-assembly behavior. Depending on the hydrophilic/hydrophobic balance, spherical, elongated, or worm-like micelles are formed, as visualized by TEM. The spherical and elongated copolymer micelles are highly water-soluble and can be applied for temperature-switchable solubilization of hydrophobic molecules, whereas the nanoworm micelles turned out to form thermoresponsive hydrogels.

For the thermoresponsive unimolecular PIL micelles, both the POx shell size and the oxazoline monomer(s) employed can be readily varied. By this means, cloud points are fine-tuned in a broad temperature range from 21 to 100 °C. Furthermore, the possible use of these materials as thermoresponsive shuttles was successfully tested by reversibly transporting a dye between an organic and an aqueous phase in response to a temperature change.

Hence, the novel nanostructured PILs hold promise for plenty of specialty applications, for example, as temperature-switchable solubilizing agents and smart molecular shuttles.

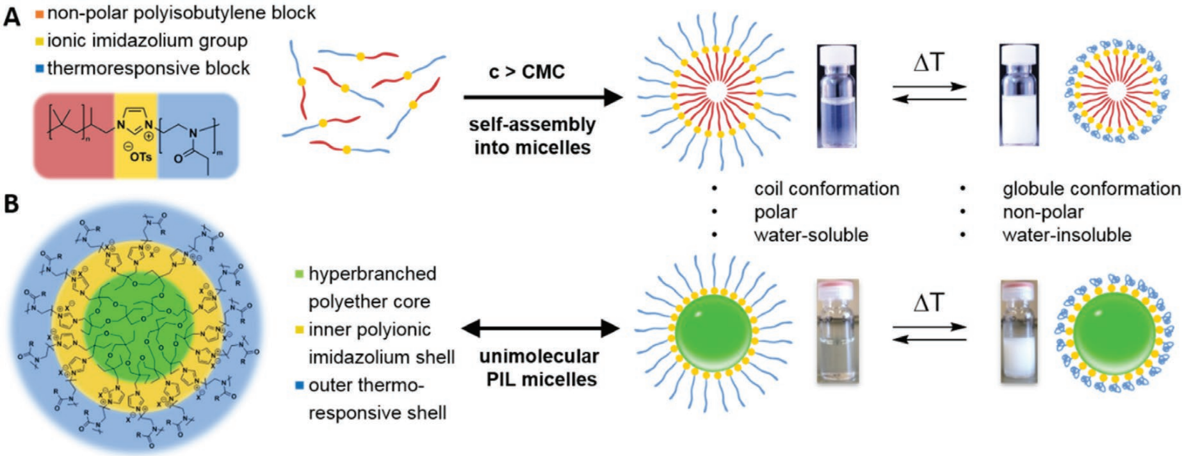


Figure 1. A) Chemical structure and thermoresponsive behavior of ionic diblock copolymers and their micellar self-assemblies and B) unimolecular PIL micelles.

S. Wiedmann, T. M. Trötschler, M. Luitz, M. Werner, S. Gröer,
B. Kerscher, R. Mülhaupt
Institute for Macromolecular Chemistry
University of Freiburg, Freiburg, Germany
E-mail: rolf.muelhaupt@makro.uni-freiburg.de

S. Wiedmann, T. M. Trötschler, B. Kerscher, R. Mülhaupt
FMF – Freiburg Materials Research Center
University of Freiburg, Freiburg, Germany

S. Wiedmann, M. Werner, R. Mülhaupt
FIT – Freiburg Centre for Interactive
Materials and Bioinspired Technologies
University of Freiburg, Freiburg, Germany

B. Pásztói, Á. Szabó, B. Iván
Polymer Chemistry Group
Institute of Materials and Environmental Chemistry
Research Centre for Natural Sciences
Hungarian Academy of Sciences, Budapest, Hungary

J.-F. Lutz
Precision Macromolecular Chemistry
Institute Charles Sadron
CNRS, Strasbourg, France

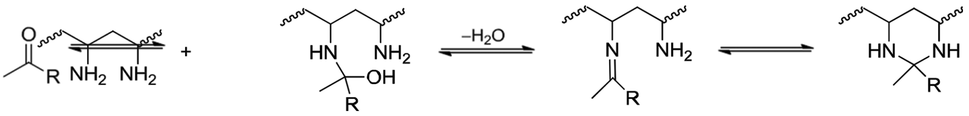
Inter- and Intramolecular Reactions of Amino Bearing Polymers in Aqueous Solutions

Tina Walther, Katja Trommler, Andreas Seifert, Hans-Joachim Hähnle, Christoph Hamers, and Stefan Spange*

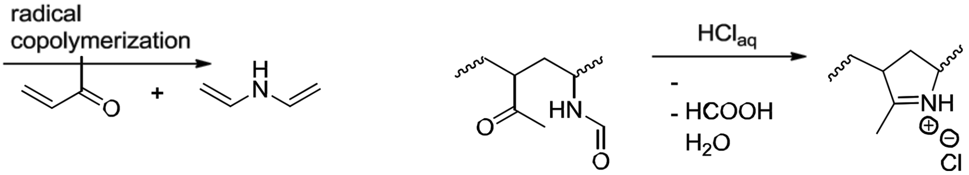
The intermolecular as well as the intramolecular reaction of amino bearing homopolymers and copolymers with reactive keto compounds in water was investigated. For this purpose, polyvinylamine (PVAm) was used for intermolecular reactions and copolymers of *N*-vinylformamide (NVF) which is a precursor for vinylamine moieties were used for intramolecular reactions.

Unexpectedly, PVAm reacts with acetone in aqueous solution,[1] which offers the possibility to generate a reversible cross-linking system with diketones in water. However, both imine and aminal moieties are generated along the PVAm backbone by reaction with ketones. The imine/aminal proportions are determined by the molecular structure of the ketone. The extent of the reversible chemical reaction is very sensitive to the substituent R, pH value and preparation of the PVAm sample (**Scheme 1**).

A series of diketones such as 1,4-cyclohexanedione[2] and substituted acetone derivatives have been synthesized and tested for this purpose. Molecular structure formation of the gels was studied by means of solid state ^{13}C-NMR spectroscopy. Furthermore, the free radical copolymerization of NVF with vinyl ketone monomers produces alternating copolymers.[3] A subsequent acidic hydrolysis generates free amino groups which react immediately with keto groups in vicinity. In consequent, five membered iminium rings along the polymer chains were formed (**Scheme 2**).



Scheme 1. The reversible reaction of PVAm with ketones.



Scheme 2. Free radical copolymerization of NVF and methyl vinyl ketone and the subsequent acidic hydrolysis to iminium five ring polymers.

---

[1]] K. Trommler, S. Seifert, A. Seifert, H.-J. Hähnle, S. Anders, L. Kroll, S. Spange, *Macromol. Chem. Phys.*, unpublished.

[2] H.-J. Hähnle, C. Hamers, A. Esser, H. Meixner, M. Buchan, N. Schall, S. Spange, K. Trommler, H. Würfel, S. Seifert, T. Walther, *US20170362776A1*, **2017**.

[3] T. Walther, A. Seifert, H.-J. Hähnle, C. Hamers, S. Spange, *Macromol. Chem. Phys.*, unpublished.

T. Walther, K. Trommler, A. Seifert, S. Spange
Department of Polymer Chemistry
Chemnitz University of Technology
Straße der Nationen 62
09111 Chemnitz, Germany

Dr. H.-J. Hähnle, Dr. C. Hamers
BASF SE, Carl-Bosch-Straße 38
67056 Ludwigshafen, Germany

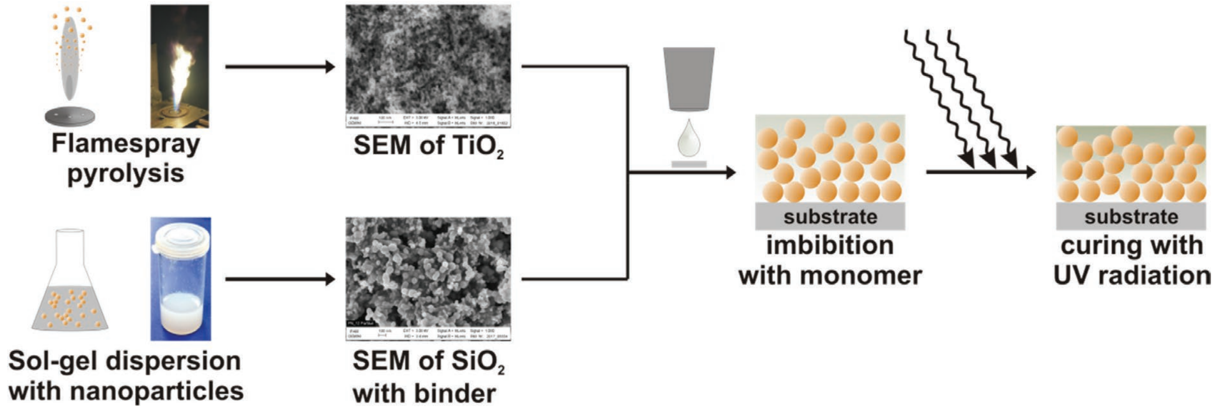
Inverse Nanocomposites – High Particle Percolation without Running into Viscosity Problems

*Ron Hoffmann, Sven O. Schopf, Hendrik Naatz, Valentin Baric, Lutz Mädler, and Andreas Hartwig**

Nanocomposite materials consisting of inorganic scaffolds and polymers have become increasingly interesting due to their high variety of possible applications as functional materials. Nanocomposites are usually prepared by the integration of nanoparticles into monomers or polymers by dispersing the particles into the liquid phase.[1] This approach leads to highly agglomerated compounds with limited percolation. High filler content is restricted by the strongly increasing viscosity which makes processing impossible. Therefore, it is difficult to improve composites' properties which depend on particle–particle contacts, like electrical or thermal conductivity.

This restriction can be circumvented by the new concept of inverse nanocomposites. For this, in the first step, a porous particle scaffold is prepared which ensures a high degree of particle–particle contacts.[2] In this first step, a nanoparticle scaffold is created from either flame spray pyrolysis and subsequent layer-to-layer-transfer or via a sol–gel-process with a polymeric binder. These layers reveal high structural resilience against exposure to liquids.[3] The pores of the scaffold with diameters from molecular level up to some micrometers are then filled with a monomer which is subsequently polymerized.[4] **Scheme 1** denotes the two different processing methods toward mesoporous nanoparticle layers. Inverse nanocomposite is defined by us as a nanocomposite which is formed by preparation of a particle scaffold first, which is afterward infiltrated by the organic matrix material.

Through a four-step process, inverse nanocomposites could be prepared. In the example of ITO particles, it could be shown that the electric conductivity increases if the pores are filled with the monomer (in other words, by the addition of a non-conductive material) and a further strong increase is observed upon monomer polymerization. The conductivity increase is explained in the first step by increasing the number of particle–particle contacts by capillary forces and in the second step by the polymerization shrinkage. In addition, influence of the "nanoscopic" compartments on the polymerization is shown as well as mechanical and thermomechanical properties of the obtained inverse nanocomposites.



Scheme 1. Preparation of inverse nanocomposites by formation of highly mesoporous nanoparticle scaffolds by either flame spray pyrolysis (FSP) or a wet-chemical sol–gel-process followed by monomer imbibition and subsequent polymerization via UV-irradiation.

---

[1] P. W. de Oliveira, C. Becker-Willinger, M. H. Jilavi, *Adv. Eng. Mater.* **2010**, *12*, 349.

[2] H. Zhang, M. Popp, A. Hartwig, L. Mädler, *Nanoscale* **2012**, *4*, 2326.

[3] S. O. Schopf, A. Hartwig, U. Fritsching, L. Mädler, *Transp. Porous Media* **2017**, *119*, 119.

[4] H. Naatz, R. Hoffmann, A. Hartwig, F. La Mantia, S. Pokhrel, L. Mädler, *J. Phys. Chem. C* **2018**, *122*, 2796.

R. Hoffmann, A. Hartwig
Fraunhofer Institute for Manufacturing Technology
and Advanced Materials
Wiener Str. 12, 28359 Bremen, Germany
E-mail: andreas.hartwig@ifam.fraunhofer.de

R. Hoffmann, A. Hartwig
Department 2 (Biology/Chemistry), University of Bremen
Leobener Str. 3, 28359 Bremen, Germany

S. O. Schopf, H. Naatz, V. Baric, L. Mädler
Leibniz Institute for Materials Engineering, IWT
Badgasteiner Str. 3, 28359 Bremen, Germany

S. O. Schopf, H. Naatz, V. Baric, L. Mädler
Department 4, Faculty of Production Engineering
University of Bremen
Badgasteiner Str. 1, 28359 Bremen, Germany

Living Anionic Polymerization of Aziridines Tolerates Water and Gives Fast Access to Amphiphilic Multi-Block Copolymers

*Tassilo Gleede, Thomas Kuckhoff, Elisabeth Rieger, Manfred Wagner, and Frederik R. Wurm**

The synthesis of well-defined polyamines remains a challenge in polymer science. Polyethyleneimine (PEI) and derivatives are normally produced via cationic polymerization of poly(2-oxazoline)s.[1] Gene delivery applications, for instance, require accurate control over polymer architecture and weights. Living anionic polymerization (LAP), the superior method for well-defined polymers, is an ideal platform to prepare PEI architectures from activated aziridines with high structural control.[2,3]

A major paradigm of LAP is the demanding synthesis, as high purity of reagents and solvents are essential to produce well-defined high molar mass polymers. Traces of water will terminate carbanionic or initiate oxyanionic polymerizations. This poster presents the living anionic polymerization of aziridines, which remain living with high control over molar mass and dispersity although in the presence of protic "impurities" such as water and alcohols.[4]

A second paradigm in LAP is that statistical copolymerization produces gradient copolymers or no copolymers (if the monomer reactivities are too different). Again, LAP of activated aziridines breaks this paradigm, as the statistical copolymerization with ethylene oxide leads to perfect diblock copolymers with basically no tapering. Various polymer structures such as multiblock polymers with linear or branched architecture are accessible, which can act as non-ionic surfactants.[5]

We believe that the anionic ROP of aziridines in combination with other anionically polymerizable monomers and its efficient desulfonation process will provide straightforward access to novel polyamides and amines with interesting properties for a great number of applications.

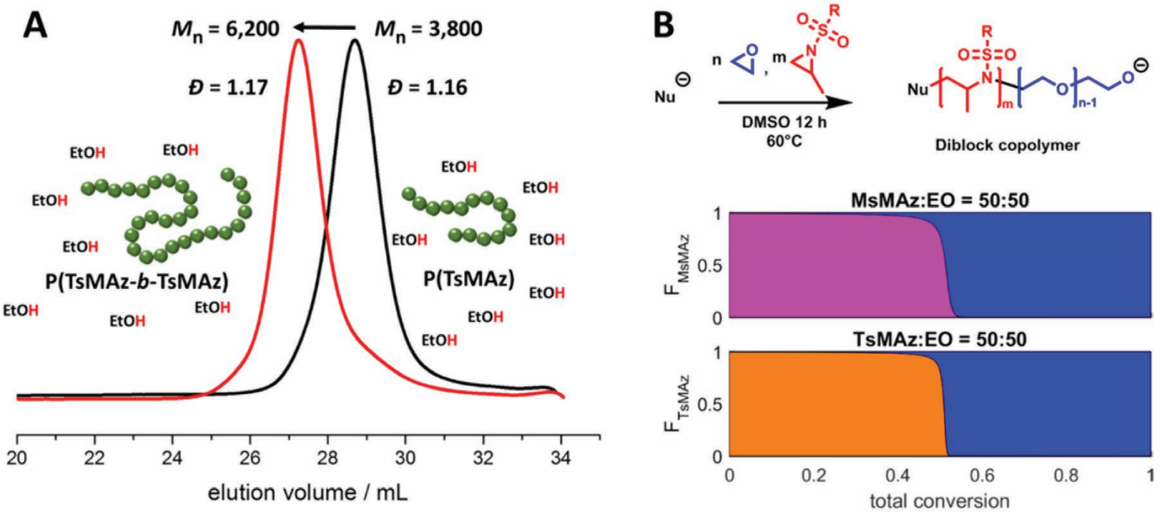


Figure 1. A) SEC traces (RI signal) of chain extension of P(TsMAz) and P(TsMAz-b-TsMAz), polymerization was performed with 90 equivalent excess of ethanol (compared to 1 equivalent initiator). B) Mean composition (F) of the polymer chains versus total conversion determined by the Meyer-Lowry fit. Top: Simulated monomer distribution of a 50:50 block copolymer based on the reactivity ratios of MsMAz (pink) and EO (blue); bottom: TsMAz (orange) and EO (blue).

---

[1] B. D. Monnery, R. Hoogenboom, in Cationic Polymers in Regenerative Medicine, Royal Society of Chemistry, London **2015**, pp. 39–61.

[2] I. C. Stewart, C. C. Lee, R. G. Bergman, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 17616.

[3] E. Rieger, J. Blankenburg, E. Grune, M. Wagner, K. Landfester, F. R. Wurm, *Angew. Chem. Int. Ed.* **2018**, *57*, 2483.

[4] T. Gleede, E. Rieger, L. Liu, C. Bakkali-Hassani, M. Wagner, S. Carlotti, D. Taton, D. Andrienko, F. R. Wurm, *Macromolecules* **2018**, *51*, 5713.

[5] T. Gleede, E. Rieger, J. Blankenburg, K. Klein, F. R. Wurm, *J. Am. Chem. Soc.* **2018**, *140*, 13407.

T. Gleede, T. Kuckhoff, E. Rieger, M. Wagner, F. R. Wurm
Max-Planck-Institut für Polymerforschung
Ackermannweg 10, 55128 Mainz, Germany

Transient Mechanochromic Polymers for Highly Sensitive and Anisotropic Stress Sensors

*Maximilian Raisch, Fabian Kempe, Oliver Brügner, Michael Walter, Chiara Gualandi, and Michael Sommer**

Stress-related phenomena are ubiquitous in polymer science and are present during processing, aging, and usage of biological tissue and polymeric materials. The ability to sense, image, and quantify forces, stress or strain allows to understand fundamental processes as well as to design advanced materials. Due to the force-induced spiropyran (SP)→merocyanine (MC) transition, SP are mechanically addressable, molecular force sensors.[1] However, reversing the SP→MC transition (i.e., the MC→SP back reaction) usually requires light as additional trigger rendering real-time imaging of dynamic processes a challenge. Here, we design a new SP monomer that lacks the commonly used nitro group and thus causes the corresponding MC form to be unstable.[2] Suzuki copolymerization of this monomer[3–6] yields high molar mass main chain mechanochromic materials that only show color during maintained stress. Upon stress release, these polymers immediately undergo the MC→SP back reaction and subsequently discolor.[7] The fast discoloration allows for repeated switching and real-time imaging of stress in a high T_g, amorphous, and tough polyarylene.[7] The strain at which such polymers respond with mechanochromism is usually >50%. We also show that electrospinning produces nanofibers with pre-oriented SP copolymer chains that are mechanochromic at strains as low as 6%. Nanofiber/PDMS composite films show isotropic and anisotropic response depending on fiber alignment.[8]

---

[1] M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White, J. S. Moore, *Chem. Rev.* **2009**, 109, 5755.

[2] O. Brügner, T. Reichenbach, M. Sommer, M. Walter, *J. Phys. Chem. B.* **2017**, *121*, 2683.

[3] M. Sommer, H. Komber, *Macromol. Rapid Commun.* **2013**, *34*, 57.

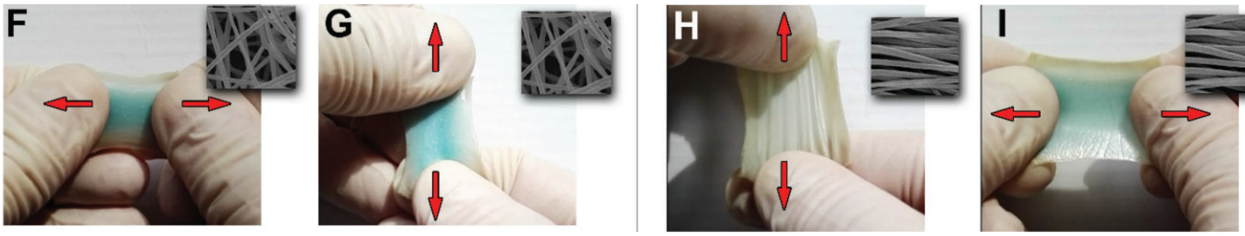
[4] H. Komber, S. Müllers, F. Lombeck, A. Held, M. Walter, M. Sommer, *Polym. Chem.* **2014**, *5*, 443.

[5] L. Metzler, T. Reichenbach, O. Brügner, H. Komber, F. Lombeck, S. Müllers, R. Hanselmann, H. Hillebrecht, M. Walterbef, M. Sommer, *Polym. Chem.* **2015**, *6*, 3694.

[6] S. B. Schmidt, F. Kempe, O. Brügner, M. Walter, M. Sommer, *Polym. Chem.* **2017**, *8*, 5407.

[7] F. Kempe, O. Brügner, H. Buchheit, S. N. Momm, F. Riehle, S. Hameury, M. Walter, M. Sommer, *Angew. Chem. Int. Ed.* **2018**, *57*, 997.

[8] Raisch, et al., *Adv. Mater.*, accepted.



M. Raisch, F. Kempe, O. Brügner, M. Walter, C. Gualandi,
Prof. M. Sommer
Polymerchemie, Institut für Chemie
Technische Universität Chemnitz
Straße der Nationen 62, 09111 Chemnitz, Germany
E-mail: michael.sommer@chemie.tu-chemnitz.de

The Best of Both Worlds: Combining Multi-Detector GPC and UPLC to Achieve Complex Polymer Characterization at UPLC Speeds and Resolutions

V. Shahi, M. R. Pothecary, C. Schindler, J. D. Stenson, L. Meeker, B. MacCreath, B. Tartsch, and B. Schäfer

Gel-permeation chromatography (GPC) is the most widely used tool for the measurement of molecular weight and molecular weight distribution of natural and synthetic polymers. Advanced detectors such as light scattering are increasingly used to overcome the limitations of conventional GPC measurements and offer *absolute* molecular weight. A viscometer measures intrinsic viscosity, a key structure factor that can be used to calculate branching levels and can be combined with molecular weight data to calculate hydrodynamic radius. In combination, these data allow detailed structural information of a polymer to be generated in a single GPC measurement which can be compared with other samples in Mark–Houwink plots. This can be used to study substitution or branching levels.

Typical analytical SEC measurements can take approximately 25–45 min and consume 25–45 mL of solvent. This is time-consuming and can be expensive in terms of solvent. Ultra-high-pressure liquid chromatography (UPLC) systems use novel SEC column gel technologies with robust, small particles (<3 μm) to achieve similar or better sample resolution using smaller columns. This increases productivity, while significantly reducing run-time and cost. An additional benefit of the reduced solvent use is to effectively make UPLC a “greener” technology than traditional analytical SEC.

Until recently, issues with band-broadening, or dispersion, limited the ability to connect multi-detector and UPLC system, as the loss in resolution and data quality was too great. In this presentation, we will show how Malvern’s OMNISEC REVEAL and the Waters ACQUITY APC systems can now be combined to bring complete multi-detector measurements at UPLC resolutions and efficiencies. This talk will include a discussion of the pitfalls of combining these two techniques and a range of measurements to show how a large number of applications can now be addressed in this manner.

V. Shahi, M. R. Pothecary, C. Schindler, J. D. Stenson
Malvern Panalytical
Houston, TX, USA

L. Meeker, B. MacCreath
Waters Corporation
Milford, MA, USA

B. Tartsch, B. Schäfer
Malvern Panalytical
Kassel, Germany

Gel Permeation Chromatography: A Tool to Determine the Effects of Processing and Deterioration of Polymers

Subin Damodaran

Polymers are characterized by their physical and chemical properties. These properties can be tailored by molecular weight, presence of branching, molecular structure, and shape of the polymers. For polymeric materials, the molar mass and molar mass distribution play a vital role in the determination of mechanical, bulk, and solution properties. These properties govern polymer processing and end-use performance of a given material. The shape and breadth of molar mass distribution will depend on the mechanism, kinetics, and condition of the polymerization and will dictate the end-use properties of the polymer. Polymer properties such as, hardness, tear strength, impact resistances, wear, brittleness, toughness, and tackiness are important in determining the success or failure of a given material.

Gel permeation chromatography (GPC) can be successfully applied to most of the polymers at ambient or high temperature conditions to determine their process–property relations. In addition, the shelf life of a polymer or the changes in molar mass characteristics of a polymer while in use can be analyzed and calculated with ease by using GPC.

S. Damodaran
Tosoh Bioscience GmbH
64347 Griesheim, Germany
E-mail: subin.damodaran@tosoh.com

Polymerization-Induced Self-Assembly (PISA): Efficient Synthesis of Functional Micelles

*Fabian H. Sobotta, Franziska Hausig, and Johannes C. Brendel**

Here, we present a novel platform for the straightforward preparation of functional diblock copolymer micelles. The system combines a one-pot sequential RAFT polymerization with the polymerization-induced self-assembly for the in situ formation of micelles with full conversion of monomers. Micellar morphology can be tuned by modifying the key parameters of the polymerization, for example, molar mass, temperature, concentration, polymer and solvent composition. The core-forming thioether-based polymer can easily be oxidized to a highly water-soluble sulfoxide, which leads to rapid degradation of these micelles (**Figure 1**).[1]

For example, the increased concentration of reactive oxygen species, present in inflamed or cancerous tissue, represents a promising trigger for the degradation of these micelles. In addition, the usage of *N*-substituted piperazine-derived polymers as first block results in pH-responsive micelles. In contrast to the majority of cationic nanocarriers, the micelles showed no cytotoxicity, while maintaining good uptake efficiency in several cell lines.

The straightforward preparation, morphological variability, and inclusion of redox- and pH-sensitive groups render our approach as an attractive new pathway to functional materials for biomedical applications.

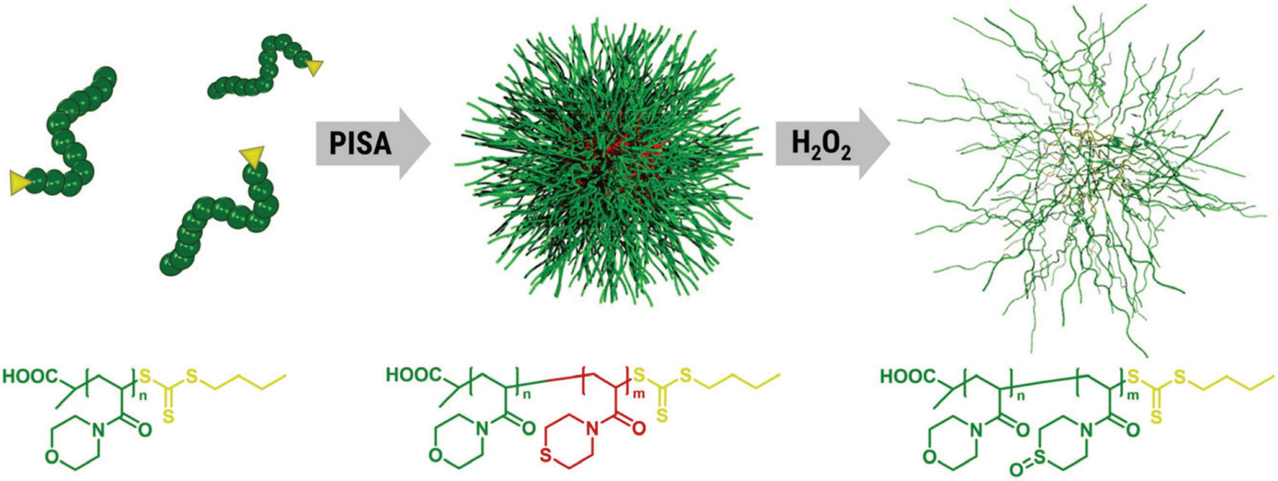


Figure 1. Schematic representation of the PISA and degradation of oxidation-responsive diblock copolymer micelles.[1]

---

[1] F. H. Sobotta, F. Hausig, D. O. Harz, S. Hoeppener, U. S. Schubert, J. C. Brendel, *Polym. Chem.* **2018**, *9*, 1593.

F. H. Sobotta, F. Hausig, J. C. Brendel
Laboratory of Organic and Macromolecular Chemistry
Friedrich Schiller University Jena
Humboldtstrasse 10, 07743 Jena, Germany
E-mail: johannes.brendel@uni-jena.de

F. H. Sobotta, F. Hausig, J. C. Brendel
Jena Center for Soft Matter
Friedrich Schiller University Jena
Philosophenweg 7, 07743 Jena, Germany

One-Component Silver-Polystyrene Nanocomposites: The Interplay of Thermoplasmonics and Elastic Mechanical Properties

Patrick Hummel and Markus Retsch

Metal–polymer nanocomposites are an interesting material class, which allows combining the superior plasmonic, electrical, and thermal properties of metal nanoparticles with the good processability of polymers.

To achieve stable nanoparticles in a polymer matrix, the nanoparticle surface has to be modified with a polymer brush. A versatile way to do this is grafting polymer chains to presynthesized nanoparticles, by a ligand exchange approach.

For this purpose, we used RAFT polymerization to synthesize polystyrene ligands with various, defined molecular weights and a terminal thiol moiety. Subsequently, we exchanged the short alkane ligand attached to silver nanoparticles with about 5 nm diameter with our polymer ligands. The purification of large quantities of these hybrid particles has been a tedious and time-consuming issue up to now. We introduced centrifugation at the Θ conditions of the polymer ligand as an easy and fast purification process, which ultimately yields gram-scale amounts.[1]

The particle–particle distance in such one-component hybrid materials is adjustable and depends on the molecular weight of the ligand. The resulting nanostructure was fully characterized by transmission electron microscopy and small-angle X-ray scattering. By using Brillouin light scattering, we elucidated the nanomechanical properties of this hybrid material and combined these measurements with finite element modeling and thermography. We found a counterintuitive decrease of the speed of sound with increasing Ag content and a strong influence of the hybrid material composition. The mesoscopic order of this material can be varied drastically by thermal annealing going from a dispersed phase to a clustered state and back. Finally, the strong light absorption and thermalization of the Ag nanoparticles results in a pronounced local heating effect. Consequently, this thermoplasmonic heating can be used to change the acoustic and, therefore, mechanical properties locally.[2]

---

[1] P. Hummel, A. Lerch, S. M. Goller, M. Karg, M. Retsch, *Polymers* **2017**, *9*, 659.

[2] D. Saleta Reig, P. Hummel, Z. Wang, S. Rosenfeldt, B. Graczykowski, M. Retsch, G. Fytas, unpublished.

Polysaccharides and Proteins as Versatile Biopolymer Material for Nanoparticles

*Elena Steiert, Lydia Radi, Matthias Fach, Matthias Konhäuser, Benjamin Breitenbach, Denise Bamberger, and Peter R. Wich**

Nature's polymers, such as polysaccharides and proteins, show remarkable versatility as multifunctional materials. They can be easily modified with the toolkit of bioorganic chemistry and are particularly attractive because of their degradability and biocompatibility.

We present our latest results on different particle systems that contain modified polysaccharides (acetalated dextran). They can be formulated into nano- and microparticles and are able to transport proteins, DNA, and RNA, as well as small hydrophobic drugs. Ac-DEX-based particles can release their encapsulated payload under mild acidic conditions, including those found in sites of inflammation, tumor tissue, or endocytic vesicles. The low toxicity and payload versatility make Ac-DEX particles ideal platforms for a wide range of biotherapeutic delivery applications, including gene delivery and immunotherapy.[1,2]

We also present a universal approach for the preparation of a new class of protein-based nanoparticles for the delivery of therapeutic payloads. A high-density lipophilic surface modification renders the proteins soluble in organic solutions and allows the use of solvent evaporation techniques for the formation of nanoparticles. Unlike previous approaches, we preserve the native structure of the proteins and the particles are stable without denaturation or crosslinking. This new type of biopolymer material shows low toxicity at high concentrations and successfully delivers a range of different drugs like chemotherapeutics or antibacterial proteins.[3,4]

---

[1] D. Bamberger, D. Hobernik, Matthias Konhäuser, M. Bros, P. R. Wich, *Mol. Pharmaceutics* **2017**, *14*, 4403.

[2] B. Breitenbach, I. Schmid, P. R. Wich, *Biomacromolecules* **2017**, *18*, 2839.

[3] M. Fach, L. Radi, P. R. Wich, *J. Am. Chem. Soc.* **2016**, *138*, 14820.

[4] E. Steiert, L. Radi, M. Fach, P. R. Wich, *Macromol. Rapid Commun.* **2018**, *39*, 1800186.

E. Steiert, L. Radi, M. Konhäuser, B. Breitenbach, D. Bamberger,
P. R. Wich
Institut für Pharmazie und Biochemie
Johannes Gutenberg-Universität Mainz, Germany
E-mail: p.wich@unsw.edu.au – www.wichlab.com

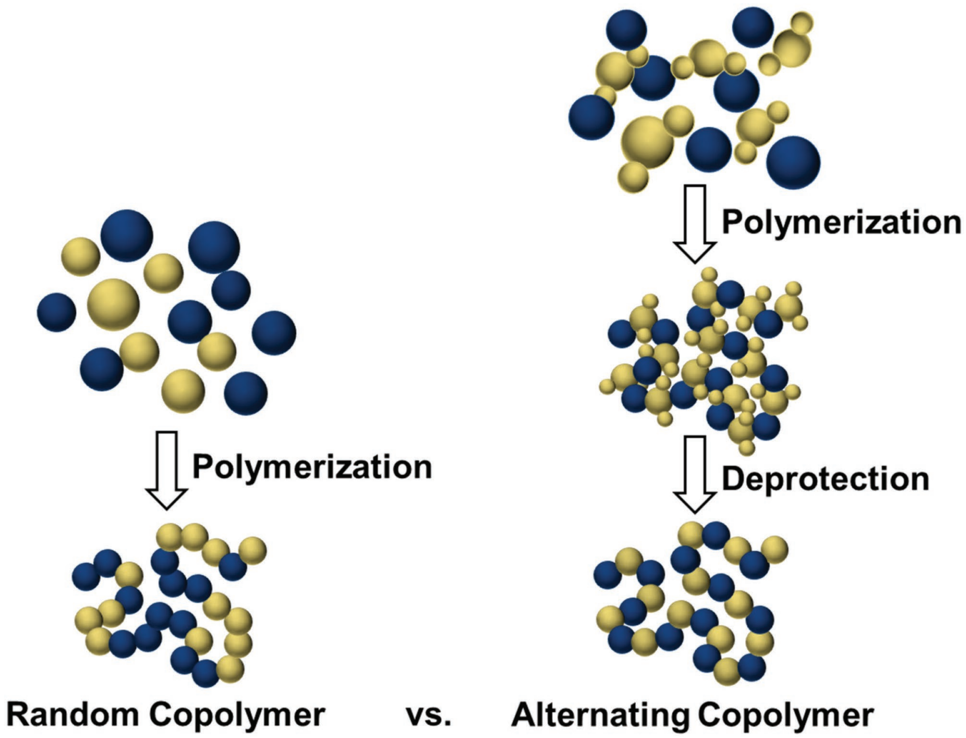
M. Fach
Department of Micro- and Nanotechnology
Technical University of Denmark
Produktionstorvet Building 423, 2800 Lyngby, Denmark

P. R. Wich
School of Chemical Engineering
University of New South Wales, Sydney, Australia

Preparation of Sequence-Controlled Polymers Using Traceless Protecting Groups

Stefan Peplau and Niels ten Brummelhuis*

By increasing the control over the monomer sequence in a polymer backbone, we aim to gain access to highly functional materials. Here, we present a new polymerization strategy for the synthesis of highly alternating copolymers by using commercially available monomers and sterically hindered, non-homopolymerizable derivatives of common monomers. Three promising modified monomers (α-trimethylsilylstyrene, α-pinacolboranestyrene, and ethyl-2-(trimethylsilylmethyl)-acrylate) were prepared and their free-radical polymerization with styrene, methyl methacrylate, and methyl acrylate was investigated using kinetic studies. The resulting copolymers were additionally characterized by GPC, MALDI, and NMR analysis. It could be shown that sterically hindered monomers could be used to create strongly alternating copolymers, and the bulky protecting groups could be removed in a traceless fashion after polymerization to be used in post-polymerization functionalization reactions.



S. Peplau, N. ten Brummelhuis
Institut für Chemie, Humboldt-Universität zu Berlin
Brook-Taylor-Str. 2, 12489 Berlin, Germany
E-mail: Stefan.Peplau@chemie.hu-berlin.de

Stretch Me If You Can! Temperature-Dependent Hydration Effects of Stretched Polymers

Adrianna Kolberg, Christiane Wenzel, Klara Hackenstrass, Richard Schwarzl, Christian Rüttiger, Markus Gallei, Roland Netz, Thorsten Hugel, and Bizan N. Balzer*

Both the Worm Like Chain and Freely Jointed Chain models are used to describe the stretching behavior of polymers but how well do they mimic the complexity of molecules and their environment?

Recently, a combined theory and experimental study, using AFM-based single-molecule force spectroscopy, showed that this is not the case for polyethylene glycol (PEG). Entropic hydration effects almost exactly compensate the chain conformational entropy loss at high stretching. The release of water molecules that form double hydrogen bonds with PEG in its relaxed state is induced by stretching. Thus, the stretching response of PEG is predominantly of enthalpic origin.[1]

Here, we use our experience in covalently attaching a single polymer to an AFM cantilever tip to quantify well-defined single-molecule stretching with a high degree of reproducibility and a high yield. Most interestingly, varying the temperature has contrasting behavior for different polymer systems, such as PEG and poly(*N*-isopropylacrylamide) (PNIPAM).

The combination of these experiments with molecular dynamics simulations in explicit water indicates that hydration for the mechanics of macromolecules is widely underestimated. A polymer chain might often better be described as a temperature-dependent enthalpic spring than as an entropic spring

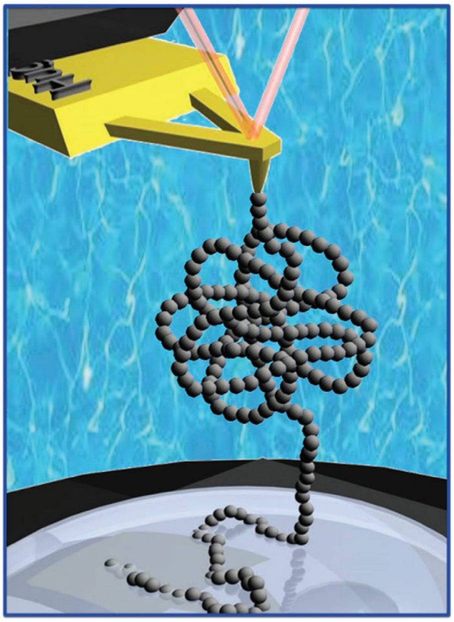


Figure 1. Schematic representation of an AFM-based single-molecule stretching experiment.

---

[1] S. Liese, M. Gensler, S. Krysiak, R. Schwarzl, A. Achazi, B. Paulus, T. Hugel, J. P. Rabe, R. R. Netz, *ASC Nano* **2017**, *11*, 702.

A. Kolberg, C. Wenzel, K. Hackenstrass, T. Hugel, B. N. Balzer
Institute of Physical Chemistry, University of Freiburg
Albertstraße 23A, 79104 Freiburg, Germany
E-mail: adrianna.kolberg@physchem.uni-freiburg.de

R. Schwarzl, R. Netz
Institute of Theoretical Bio- and Soft Matter Physiks
Freie Universität Berlin
Arnimallee 14, 14195 Berlin, Germany

C. Rüttiger, M. Gallei
Ernst-Bertl-Institute for Technical and Macromolecular Chemistry
TU Darmstadt, Alarich-Weiss-Straße 4
64287 Darmstadt, Germany

Water Based Concepts to Deposit Polyelectrolyte Coatings at Model and Applied Substrates for Biomedical Applications

M. Müller, B. Urban, S. Schwarz, D. Vehlow, B. Reis, I. Skorupa, and H. Schmidt

Three basic experimental concepts given in Figure 1 are reviewed to deposit functional polyelectrolyte–based coatings at Ge model and applied substrates, which are wet-adhesive and serve as platforms for biomedical applications.[1]

First, PEL deposition by adsorption from single-component PEL solutions was performed in dependence of charge density. The irreversibly adsorbed amount of cationic starches was shown to increase with decreasing charge density, meaning lowest charge density resulted in highest adsorbed amount according to the relation $\Gamma = -K\,\sigma_0\, I^2/q_\mathrm{m}$ (Γ, adsorbed amount; K, constant; σ_0, surface charge density; I, segment length; q_m, PEL charge density).[2] Also profound rinse stability of PEL films with low charge density was obtained.[1]

Second, consecutive adsorption from cationic poly(L-lysine) (PLL) or cationic cellulose (EDAC) and anionic CS solutions was performed in dependence of adsorption cycles and outermost layer charge according to the known LbL approach.[3] Exponentially increasing adsorbed amounts with adsorption step as well as part pull-out of the last adsorbed outermost layer by the present PEL was found. No significant dependence of the rinse stability of PEM coatings on outermost layer charge was found, since net stoichiometry of the whole PEM assembly is assumed to be independent on outermost layer variation.[1]

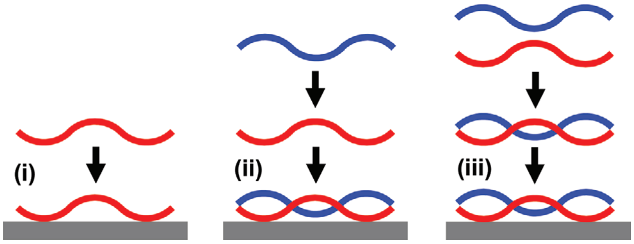


Figure 1. a) Deposition of single PEL component, b) consecutive deposition of oppositely charged PEL components, and c) deposition of preformed complexes of oppositely charged PEL at planar model substrate (reprinted from ref. [1]).

Third, results on adsorbed amount and rinse stability of coated PEL complex (PEC) nanoparticles (NP), which were prepared by mixing EDAC or PLL and CS solutions prior to coating, are reported. Increasing deviation from the stoichiometric molar mixing ratio $n^-/n^+ = 1.0$ related to anionic (n^-) and cationic (n^+) repeating resulted in the rinse out of the respective excess PEL component (EDAC(+) or PLL(+) for $n^-/n^+ < 1$, CS(–) for $n^-/n^+ > 1$). This effect is unique for PEC coatings, where n^-/n^+ variations are rather global, compared to PEM coatings, where n^-/n^+ variations are rather local at the outermost layer.[1]

Conclusively, the three PEL deposition concepts show good wet adhesion if interfacial excess charge is kept low. For single PEL component coatings, this can be achieved by low charge density, while for PEM and PEC coatings films by the lack of excess charge. Moreover, dehydration, shrinking, and chain entangling associated with the drying process as well as volume phase separation close to the solid/liquid interface might contribute. Especially, for single PEL component (i.e., cationic starch) adsorption, the effect of substrate surface charge density (σ_0, numerator of equation above) should be further studied. In this context, a recent technology based on P and B ion implanted silicon wafers with flat surfaces offers surface near-electrostatic gradient fields above the microstructural charge patterns of the silicon wafers.[4]

Finally, the potential of the three coating types for the functionalization of biomaterials or biomedical devices is illustrated. Concerning biopassivation, PEM and PEC coatings terminated or excessed by polycations or polyanions repel basic or acidic proteins, respectively.[5,6] Concerning bioactivation, PEM and PEC coatings provide active loading and releasing of therapeutic antibiotics,[7] bisphosphonates,[8] or growth factors[9] to address implant-based infections or local healing of bone defects via the bone substitute material. Moreover thermoresponsive PEM and PEC coatings enable switchable release of drugs from implants, so that the onset time of medication can be chosen by the clinician.[10]

M. Müller, B. Urban, S. Schwarz, D. Vehlow, B. Reis
1Leibniz-Institut für Polymerforschung Dresden
Hohe Str. 6, 01069 Dresden, Germany

M. Müller
2FR Chemie und Lebensmittelchemie
Technische Universität Dresden, 01062 Dresden, Germany

I. Skorupa
3Helmholtz-Zentrum Dresden-Rossendorf
Bautzner Landstrasse 400, 01328 Dresden, Germany

H. Schmidt
Technische Universität Chemnitz
Reichenhainer Straße 39, 09126 Chemnitz, Germany

H. Schmidt
5Leibniz-Institut für Photonische Technologien Jena
Albert-Einstein-Str. 9, 07745 Jena, Germany

[1] M. Müller, B. Urban, S. Schwarz, *Langmuir*, **2018**, *34*, 8129.

[2] N. G. Hoogeveen, M. A. Cohen-Stuart, G. Fleer, *J. Coll. Interf. Sci.* **1996**, *182*, 133.

[3] G. Decher, J. D. Hong, J. Schmitt, *Thin Solid Films* ***1992***, *210/211*, 831.

[4] H. Schmidt, C. Baumgart, I. Skorupa, M. Helm, O. G. Schmidt, M. Müller, *US 2014/0291143 A1*.

[5] M. Müller, T. Rieser, P. L. Dubin, K. Lunkwitz, *Macromol. Rapid Commun*. **2001**, *22*, 390.

[6] M. Müller, B. Keßler, N. Houbenov, K. Bohata, Z. Pientka, E. Brynda, *Biomacromolecules* **2006**, *7*, 1285.

[7] B. Torger, M. Müller, *Spectrochim. Acta A*, **2013**, *104*, 546.

[8] M. Müller, B. Torger, D. Wehrum, D. Vehlow, B. Urban, B. Woltmann, U. Hempel, *Biointerphases*, **2015**, *10,* 011001.

[9] R. Petzold, D. Vehlow, B. Urban, A. L. Grab, E. A. Cavalcanti-Adam, V. Alt, M. Müller, *Coll. Surf. B* **2017**, *151*, 58.

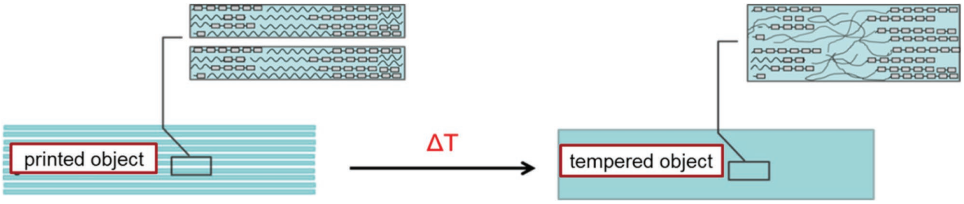
[10] M. Müller, B. Urban, D. Vehlow, M. L. Möller, *Coll. Polym. Sci.* **2017**, *295*, 1187.

Innovative Filament for FFF 3D Printing Based on Diblock Copolymers

*E. Schoeneberger and G. A. Luinstra**

FFF (fused filament fabrication) 3D printing is a simple, competitive, and effective method for producing 3D objects of any favored shape. During the FFF printing procedure, a thermoplastic material (the filament) is melted and extruded through a nozzle to produce 3D parts layer by layer. Challenges are the anisotropic mechanical properties of the printed devices resulting from a limited inter-layer adhesion between the filament layers.[1,2] Innovative filament materials for FFF made of diblock copolymers are a promising opportunity to improve the inter-layer adhesion in printed objects. Thermoplastic diblock copolymers of a low- and a high-melting polymer enable a post-curing process at a temperature below the melting point of the high-melting component. With this process, it might be possible to conglomerate the layers without shrinkage or changes in the shape of the item (**Scheme 1**).

The selected model-compound for the diblock copolymer is PE-block-polyamide-6. The synthesis is based on the preparation of terminally functionalized polyethylene with highly active iron-based bis(imino)pyridine catalysts in a one-pot-synthesis.[3,4] The functionalized polyethylene component represents a precursor for a subsequent anionic polymerization (ROP) of ε-caprolactam. A scale-up of the copolymer synthesis enables the production of filament for FFF by extrusion. The optimum conditions for the synthesis of the functionalized polyethylene block were found after catalyst screening and kinetic investigations. The resulting hydroxyl-functionalized polyethylene could be converted successfully to an *N*-acyl caprolactam macroinitiator for the anionic ROP of ε-caprolactam. Various copolymers were synthesized in bulk and analyzed by NMR, IR, DSC, and SEM allowing a description of the chemical composition, thermal characteristics, and morphology of the diblock copolymers.



Scheme 1. Schematic diagram of the post-curing process of printed devices made of diblock copolymers.

---

[1] J. Y. Wong, A. C. Pfahnl, *Aviat. Space Environ. Med.* **2014**, *85*, 758.

[2] J. W. Stansburya, M. J. Idacavageca, *Dent. Mater.* **2016**, *32*, 54.

[3] B. L. Small, M. Brookhart, A. M. Bennett, *J. Am. Chem. Soc.* **1998**, *120*, 4049.

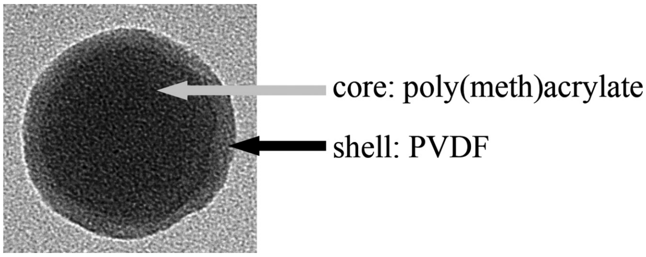
[4] G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. Solan, S. Stroemberg, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1999**, *121*, 8728.

E. Schoeneberger, G. A. Luinstra
Institute for Macromolecular and Technical Chemistry
University of Hamburg, Bundesstraße 45
20146 Hamburg, Germany
E-mail: elsa.schoeneberger@chemie.uni-hamburg.de

From Gaseous Vinylidene Fluoride to Electroactive Poly(vinylidene fluoride) – Inducing β-Phase Crystallinity by Formation of Block Copolymers and Composite Materials

Florian Brandl, Felix Lederle,* Cathrin Härter,* Andreas F. Thünemann, and Sabine Beuermann*

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline polymer that shows five crystalline phases (α-, β-, γ-, δ-, and ε-phase). The β-phase is associated with piezo-, pyro-, and ferroelectric properties. Since synthesis and processing of PVDF generally yields the α-phase, special treatment such as supercooling, pressure, or mechanical treatment is required to obtain β-phase material. In this contribution, several other ways to increase the β-phase content in the crystalline domains of PVDF are presented. Block copolymers are synthesized starting with a PVDF–I macroinitiator obtained from iodine transfer emulsion polymerization followed by a photo-induced radical polymerization with a non-fluorinated monomer, for example, methyl methacrylate.[1,2] Moreover, the impact of precipitation conditions such as precipitant and ion concentration on PVDF phase crystallinity from PVDF blends and co/homopolymers is presented. In addition, a strategy for obtaining composite particles consisting of a poly(meth)acrylate and a PVDF shell directly from the emulsion polymerization of gaseous vinylidene fluoride is presented, which yields β-phase PVDF.[3]



---

[1] F. Brandl, M. Drache, S. Beuermann, *Polymers* **2018**, *10*, 1008.

[2] N. Golzari, J. Adams, S. Beuermann, *Polymers* **2017**, *9*, 306.

[3] F. Brandl, A. F. Thünemann, S. Beuermann, *Polym. Chem.* **2018**, accepted.

F. Brandl, F. Lederle, C. Härter, S. Beuermann
Institute of Technical Chemistry
Clausthal University of Technology
Arnold-Sommerfeld-Str.4, 38678 Clausthal-Zellerfeld, Germany
E-mail: Sabine.Beuermann@tu-clausthal.de

A. F. Thünemann
Federal Institute for Materials Research and Testing (BAM)
Unter den Eichen 87, 12205 Berlin, Germany

Silicon/Boron Exchange Routes to Conjugated Organoboron Polymers

*Lars Fritze, Ozan Ayhan, Artur Lik, Thomas Lorenz, Merian Crumbach, Nicolas A. Riensch, and Holger Helten**

Conjugated organoboron polymers are currently attracting considerable attention, as the incorporation of the vacant p-orbital of trivalent boron into the backbone of conjugated polymers leads to materials with intriguing optical and electronic properties. This has enabled applications in organic electronic and optoelectronic devices (OLEDs, OFETs, OPVs, etc.), for biomedical imaging, and as selective chemosensors for certain anions or biologically relevant amines.[1] We have recently developed a general, highly efficient, and environmentally benign organocatalytic route to various donor–acceptor type organoborane polymers and oligomers.[2] Furthermore, a series of cyclolinear inorganic–organic hybrid polymers with unsaturated B=N units in the main chain will be presented.[3,4] This includes a BN analogue of poly(*p*-phenylene vinylene)[3b] and the first examples of poly(iminoborane)s, which are inorganic main group polymers that have been previously elusive.[4] Novel routes to borazine-based cyclomatrix network polymer microspheres will also be discussed.[5]

---

[1] a) F. Jäkle, *Top. Organomet. Chem.* **2015**, *49*, 297; b) L. Ji, S. Griesbeck, T. B. Marder, *Chem. Sci.* **2017**, *8*, 846.

[2] a) A. Lik, L. Fritze, L. Müller, H. Helten, *J. Am. Chem. Soc.* **2017**, *139*, 5692; b) A. Lik, S. Jenthra, L. Fritze, L. Müller, K.-N. Truong, H. Helten, *Chem. Eur. J.* **2018**, *24*, 11961.

[3] a) T. Lorenz, A. Lik, F. A. Plamper, H. Helten, *Angew. Chem. Int. Ed.* **2016**, *55*, 7236; b) T. Lorenz, M. Crumbach, T. Eckert, A. Lik, H. Helten, *Angew. Chem. Int. Ed.* **2017**, *56*, 2780; c) H. Helten, *Chem. Eur. J.* **2016**, *22*, 12972.

[4] a) O. Ayhan, T. Eckert, F. A. Plamper, H. Helten, *Angew. Chem. Int. Ed.* **2016**, *55*, 13321; b) O. Ayhan, N. A. Riensch, C. Glasmacher, H. Helten, *Chem. Eur. J.* **2018**, *24*, 5883.

[5] N. A. Riensch, A. Deniz, S. Kühl, L. Müller, A. Adams, A. Pich, H. Helten, *Polym. Chem.* **2017**, *8*, 5264.

Thermoresponsive Polyglycidyl ether Coatings for Tissue Culture Applications

Marie Weinhart, Silke Heinen, Daniel Stöbener, and Anke Hoppensack

Cell sheet engineering as a scaffold-free approach towards in vitro engineered tissue represents a milestone in tissue engineering and regenerative medicine. In order to fabricate and harvest confluent cell sheets without the help of enzymes, functional polymer coatings on cell culture substrates are required that allow for cell adhesion, proliferation, and triggered cell sheet detachment.[1] Besides poly(*N*-isopropyl acryl amide), thermoresponsive polymers such as poly(oxazoline)s and poly(glycidyl ether)s[2,3] have recently been demonstrated within proof-of-concept studies as functional coatings for cell sheet fabrication. However, surface design guidelines for such functional thermoresponsive coatings are rare.

From a detailed structure–cell response correlation with defined monolayer coatings of thermoresponsive poly(glycidyl ether)s on gold surfaces, we extracted such design guidelines.[4,5] The gained knowledge has been applied to prepare thermoresponsive coatings on more cell culture–relevant glass and polystyrene surfaces via grafting-to and grafting-from strategies.[6,7] Confluent cell sheets of human endothelial cells, smooth muscle cells, and fibroblasts are accessible with these coated surfaces and allow us to create artificial three-layered blood vessel constructs for subsequent maturation in a tissue bioreactor (**Figure 1**).

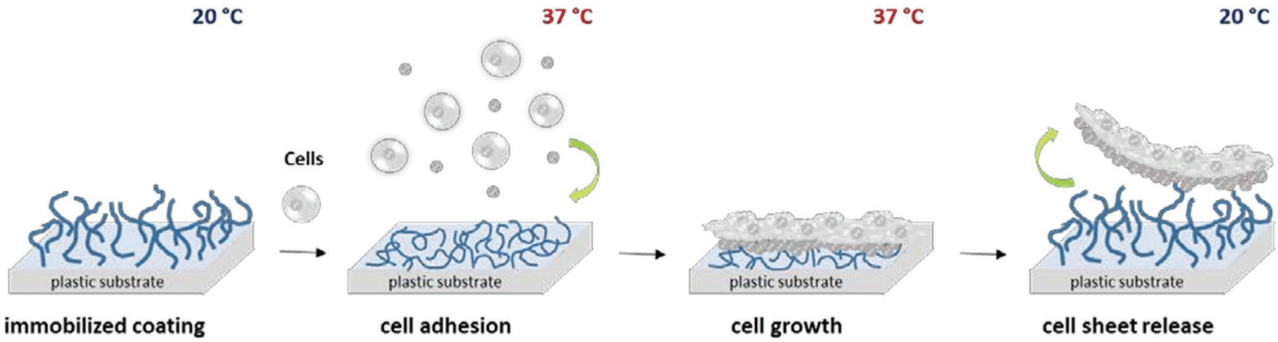


Figure 1. Thermoresponsive coatings on polystyrene substrates for effective cell sheet fabrication.

---

[1] Z. Tang, T. Okano, *Regen. Biomater.* **2014**, *1*, 91.

[2] S. Heinen, S. Rackow, A. Schäfer, M. Weinhart, *Macromolecules* **2017**, *50*, 44.

[3] D. D. Stöbener, D. Donath, M. Weinhart, *J. Polym. Sci. A, Polym. Chem.* **2018**, *56*, 2496.

[4] T. Becherer, S. Heinen, Q. Wei, R. Haag, M. Weinhart, *Acta Biomater.* **2015**, *25*, 43.

[5] S. Heinen, J. L. Cuellar-Camacho, M. Weinhart, *Acta Biomater.* **2017**, *59*, 117.

[6] D. D. Stöbener, M. Uckert, J. L. Cuellar-Camacho, A. Hoppensack, M. Weinhart, *ACS Biomater. Sci. Eng.* **2017**, *3*, 2155.

[7] S. Heinen, S. Rackow, J. L. Cuellar-Camacho, I. S. Donskyi, W. E. S. Unger, M. Weinhart, *J. Mater. Chem. B* **2018**, *6*, 1489.

M. Weinhart, S. Heinen, D. Stöbener, A. Hoppensack
Institute of Chemistry and Biochemistry
Freie Universität Berlin, Berlin, Germany

Poly(vinylidene fluoride) Based Multiferroic Composites

Katja Loos

Multiferroic materials possess at least two ferroic orders, that is, ferroelectricity, ferromagnetism, and ferroelasticity, and are considered as promising candidates for application in multifunctional devices. For instance, combining ferroelectricity and ferromagnetism (or ferrimagnetism), multiferroic thin films can store information in the form of both magnetization (M) and electric polarization (P). This makes them excellent candidates as storage media in four-state memory devices that store four memory states per area, that is, (+M,+P), (+M,–P), (–M,+P), (–M,–P). The memory density in four-state memory is twice as much as in the conventional two-state memory.

Besides commonly used ceramic composites, polymer-based multiferroic materials, which combine piezoelectric polymers and inorganic magnetostrictive phases, have been attracting a growing research interest since they can be readily fabricated by cheap low-temperature processing methods resulting in flexible materials with lower leakage currents and dielectric losses. In particular, semicrystalline polymers such as poly(vinylidene fluoride) (PVDF) have strong piezo-, pyro-, and ferroelectric properties. PVDF has superior piezoelectric properties as compared with other types of polymeric materials due to its polar crystalline structure.

Preparing well-defined nanocomposites based on fluorinated polymers is not straight forward. The dense packing of fluorine atoms causes a low surface energy of PVDF, which results in strong demixing of this polymer with most inorganic fillers. The uneven distribution of the nano-objects inside the polymer matrix, as well as their aggregation, reduces the contact area between them and the polymer resulting in a material with weak multiferroic properties. Additionally, the aggregation of nano-objects is inevitably accompanied by increased conduction losses that lead to electric failure at low fields.

A very elegant way to freely tune all size parameters and aspect ratios of a multiferroic nanocomposite is the use of morphologies that arise from the self-assembly of block copolymers as a template. PVDF-based block copolymers,[1,2] with their ability to self-assemble into well-ordered morphologies, deserve particular interest as precursors for novel functional nanostructured materials with extraordinary properties.[3–6] With this, it becomes possible to tailor well-defined nanocomposites[7,8] (see **Figure 1**) with excellent multiferroic response.

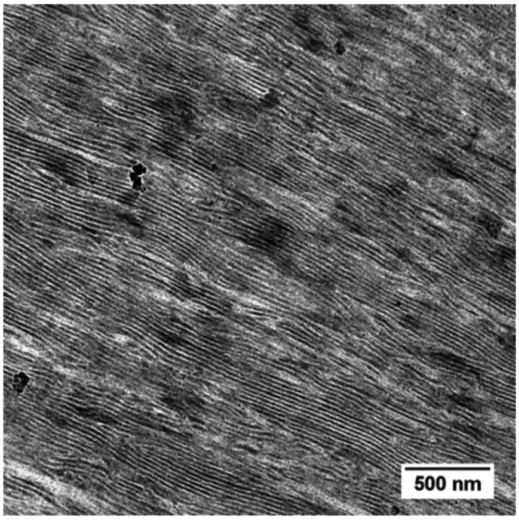


Figure 1. TEM image of a PVDF/Ni nanocomposite with a well-defined lamellar morphology, obtained after nickel plating of a polymer template.[7]

---

[1] T. Soulestin, V. Ladmiral, F. D. Dos Santos, B. Ameduri, *Prog. Polym. Sci.* **2017**, *72*, 16.

[2] V. S. D. Voet, G. ten Brinke, K. Loos, *J. Polym. Sci. Pol. Chem.* **2014**, *52*, 2861.

[3] V. S. D. Voet, D. Hermida-Merino, G. ten Brinke, K. Loos, *RSC Adv.* **2013**, *3*, 7938.

[4] V. S. D. Voet, G. van Ekenstein, N. L. Meereboer, A. H. Hofman, G. ten Brinke, K. Loos, *Polym. Chem.* **2014**, *5*, 2219.

[5] I. Terzic, N. L. Meereboer, K. Loos, *Polym. Chem.* **2018**, *9*, 3714.

[6] N. L. Meereboer, I. Terzic, S. Saidi, D. H. Merino, K. Loos, *ACS Macro Lett.* **2018**, *7*, 863.

[7] V. S. D. Voet, M. Tichelaar, S. Tanase, M. C. Mittelmeijer-Hazeleger, G. ten Brinke, K. Loos, *Nanoscale* **2013**, *5*, 184.

[8] V. S. D. Voet, K. Kumar, G. ten Brinke, K. Loos, *Macromol. Rapid Comm.* **2015**, *36*, 1756.

K. Loos
Macromolecular Chemistry and New Polymeric Materials
Zernike Institute for Advanced Materials
University of Groningen
Nijenborgh 4, 9747 AG Groningen, The Netherlands

Morphology and Micro-Mechanics of Nano-Dispersed Rubber Blends

Martin van Duin, Christoph Gögelein, and John Beelen

The fatigue properties of cross-linked blends of ethylene propylene diene rubber (EPDM) with low natural rubber (NR) content and reinforced with carbon black (CB) have been studied. It is found that such EPDM/NR compounds have superior crack growth resistance and fatigue lifetime. For low NR contents, transmission electron microscopy revealed that the NR phase forms small droplets of 20–50 nm. Remarkably, these droplets are even smaller than the primary CB particles. Atomic force microscopy shows that the NR phase droplets have a higher loss factor and a smaller elastic modulus than the surrounding EPDM matrix. Rheometer measurements are used to study the effect of phase morphology on the rubber mechanical properties. These rheological data are compared with the prediction of the Eshelby model describing the effect of elastic inclusions on solids. A complex interplay between the rubber phase morphology and the solubility of both the sulfur cross-linking system and CB is observed, which cannot be predicted theoretically. It is proposed that the soft NR droplets effectively inhibit the crack propagation in the EPDM matrix.

M. van Duin, C. Gögelein, J. Beelen
Arlanxeo Performance Elastomers
HPE Innovation, PO Box 185, 6160 AD Geleen
The Netherlands

Small Libraries of Poly/(para phenyleneethynylene)s as "Universal" Chemical Tongues

Uwe Bunz

The simple discrimination of complex analytes (beverages, food-stuffs, prescription drugs, etc.) is important for economic and health-related reasons. As one cannot construct specific sensors or assays for complex analytes, alternative methods are needed. Hypothesis-free arrays of charged fluorescent dye–conjugated polymers successfully differentiate nonsteroidal anti-inflammatories, colas, white wines, and whiskies according to their differential fluorescence intensity modulation.

In biology, non-specific interactions are ubiquitous and important, while in chemistry, non-specificity/non-selectivity is suspect. We present simple tongues consisting of fluorescent polyelectrolytes. The mechanism of action of these tongues is differential quenching of the fluorescence of the poly(aryleneethynylene)s by the complex mixture of colorants in the analytes (the interactome). The differential binding and signal generation of the interactomes to the polymers result from hydrophobic and electrostatic interactions only. The collected quenching data, that is, the response patterns, are analyzed by linear discriminant analysis. Our tongues do not need any sample preparation, work in water, are analyzed in a plate reader, and are equal or superior to state-of-the-art mass spectrometric methods with respect to speed, resolution, and efficiency of discrimination.

U. Bunz
Heidelberg Univeristy, Germany

Patterned Polymer Brushes for Solution-Processable OLEDs

Christian W. Pester

We describe a new experimental methodology for sequential photopatterning based on surface-initiated controlled radical polymerization (CRP). By combining the benefits of light-mediated CRP, reduction photolithography, and stopped-flow techniques, this new platform affords facile access to chemically patterned surfaces on the micron scale. We illustrate the utility of our technique by patterning RGB pixel layouts for solution-processable organic light-emitting diodes through light-mediated CRP of newly designed monomers bearing phosphorescent iridium complexes. Within only a few processing steps, this affords large-scale patterning of micron-sized, spatially separated, red-, green-, and blue-emitting iridium-based surface-tethered polymer brushes.

Prof. C. W. Pester
Department of Chemical Engineering
Pennsylvania State University
University Park, PA 16802, USA

Opportunities of Smart Textiles due to Digitalization

Thomas Fröis

In our Spin-Off TEXIBLE, we develop and produce technical textiles, so-called Smart Textiles. Digitization and the associated Internet of Things are essential for us and our cooperation partners. Be it a smart sports shirt from the company QUS, which measures the heart and respiratory rate or the health-tracking insole of Stappone, which helps to maintain the correct posture. Sensor integration in everyday products is on the rise.Demographic change offers a great deal of potential for innovation and new products. The changing needs of this customer group require new business models, such as personalized travel for seniors, delivery services, or portals for shared leisure activities.

The digitization of the so-called Silver Society is already in full swing. We at TEXIBLE support the field of care by our intelligent bed insert which recognizes wetness and occupancy in addition to the normal bed protection. The innovative alerting enables targeted care. The caregivers and those affected will have more rest, especially at night, and thus more energy for the following day. Depending on the care situation, further incontinence products can be dispensed with altogether, whereby the feeling of independence is maintained longer. At any time know how the loved one is!

Block Copolymer Nanostructures Directed by Curvature and Topological Defects

André H. Gröschel

Every shape, no matter how complex, can be described by topology, that is, the curvature of an object is bound to an exact number of defects and classified by universal laws that cannot be broken.[1] Curvature and defects thus play a crucial role for the properties of any geometric object and on all length scales, for example, for transport phenomena in atom lattices, the shape and function of biological particles, and the mechanical stability of materials. In soft matter, the emergence of packing order and defects of rigid particles[2] (or molecules)[3] arranged on 2D curved interfaces is likewise dominated by mathematical rules. Regarding block copolymers, the knowledge of how substrates influence morphology is of particular interest to understand microphase separation on surfaces, in thin films, or in emulsions (confinement conditions).

In this presentation, I introduce concepts that utilize surface curvature and topological rules to construct unusual polymer microphases and nanoparticles thereof, or to grow complex topographic pattern from particle surfaces. Examples include the solution and confinement assembly of block copolymers, hierarchical structure formation, and ionic complexation of surface-tethered polymer brushes.[4–8] Equipping particles with topographic pattern is relevant to control particle packing, the formation of particle lattices, close-range interactions with the cell membrane, and for locomotion (e.g., rotation of nanoscrews). In the near future, we aim to transfer these concepts to microparticles with tetrahedral and toroidal shape, and seek to synthesize polymer nanoparticles mimicking the physicochemical behavior or viruses.

---

[1] M. J. Bowick, L. Giomi, *Adv. Phys.* **2009**, *58*, 449.
[2] G. Meng, J. Paulose, D. R. Nelson, V. N. Manoharan, *Science* **2014**, *343*, 634.
[3] X. Xing, H. Shin, M. J. Bowick, Z. Yao, L. Jia, M.-H. Li, *Proc. Natl. Acad. Sci.* **2012**, *109*, 5202.
[4] T. I. Löbling, O. Borisov, J. S. Haataja, O. Ikkala, A. H. Gröschel, A. H. E. Müller, *Nat. Commun.* **2016**, *7*, 12097.
[5] A. Steinhaus, T. Pelras, R. Chakroun, A. H. Gröschel, M. Müllner, *Macromol. Rapid Commun.* **2018**, 1800177.
[6] A. Steinhaus, R. Chakroun, M. Müllner, T.-L. Nghiem, M. Hildebrandt, A. H. Gröschel, unpublished.
[7] T. I. Löbling, J. S. Haataja, C. V. Synatschke, F. H. Schacher, M. Müller, A. Hanisch, A. H. Gröschel, A. H. E. Müller, *ACS Nano* **2014**, *8*, 11330.
[8] J. M. Malho, M. Morits, T. I. Löbling, Nonappa, J. Majoinen, F. H. Schacher, O. Ikkala, A. H. Gröschel, *ACS Macro Lett.* **2016**, *5*, 1185.

A. H. Gröschel
Physical Chemistry and Center for Nanointegration Duisburg-Essen
(CENIDE), University of Duisburg–Essen
47057 Duisburg, Germany

On-Line Benchtop Correlation of Molecular Weight Distribution and Chemical Composition via SEC-IR/-NMR and -QCL

*Carlo Botha, Jennifer Kübel, Johannes Höpfner, Britta Mayerhöfer, Timo Beskers, Sascha Morlock, and Manfred Wilhelm**

Polymers have three important molecular characteristics: the molecular weight distribution (MWD), chemical composition distribution (CCD), and the topology (see **Figure 1**). The MWD is usually determined using size exclusion chromatography (SEC). SEC detectors commonly in use, such as refractive index detectors, light scattering, or viscometers, do not provide information about the chemistry or topology. More and more advanced analytical techniques are needed to cope with the development of sophisticated synthetic routes for polymeric materials and in addition the more complex formulations used in today's products. As simple 1D experiments do not suffice to provide the necessary information. The development of on-line coupled techniques, especially liquid chromatography (LC) in conjunction with molecular spectroscopy, is one promising approach to correlate this information. In the conventional analysis of complex samples, information is generally obtained in separate but not correlated off-line experiments. With reference to current spectroscopic methods such as IR and NMR, these techniques are very powerful tools in obtaining detailed insights regarding chemical structures. Nevertheless, when it comes to analyzing complex materials like blends, copolymers, or unknown samples, the correlated measurement of MWD and CCD properties is of paramount importance, but a tedious task with dedicated separate off-line analysis (**Figure 1**).

For the simple on-line correlation of MWD and CCD, the hyphenation of IR or NMR spectroscopy with SEC is a promising approach to obtain information.[1,2] The intrinsic problem that arises when hyphenating SEC to spectroscopy is (a) the relatively low sample concentration after chromatographic separation, as well as resulting in (b) low signal-to-noise (S/N) ratios as well as strong solvent signal overlapping in the regions of interest for the analyte under investigation, especially when employing non-deuterated solvents and (c) complex infrastructure for high field NMR.Therefore, the full optimization of hyphenated benchtop SEC-IR/-NMR and -QCL systems with reference to the sensitivity, selectivity and solvent signal suppression is of importance and will be discussed within this framework.

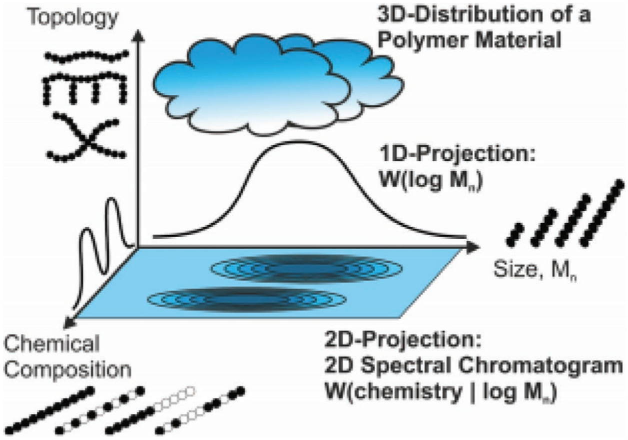


Figure 1. Illustration of a polymer material as a cloud in the 3D space of the three molecular characteristics.

In a first approach, our group previously reported on the hyphenation of SEC to FTIR, with custom built flow cells and numerical solvent signal suppression. Where a limit of detection (LOD, S/N > 3) for a carbonyl group in PMMA as low as 30 µg was established via SEC-IR.[3] As this was a promising approach, the aim to gain improved sensitivity was pursued. Which led to exploring different infrared light sources. We present first results on a SEC hyphenated to a tunable external cavity quantum cascade laser (QCL) in the mid infrared electromagnetic wavelength range (EC-QCL-IR) light source. It has a much higher light intensity (factor 10^4), but limited bandwidth.[4] The SEC-EC-QCL-IR also has the best sensitivity when operated at a single wavenumber. Which makes it an ideal tool for investigating specific features of interest, such as end-groups, organic functional groups, and branching points. The LOD for PMMA could consequently be reduced by a factor 60 to 0.5 µg, which relates to one carbonyl per 400 kg mol^{-1}, was established in single wavenumber mode. Therefore, SEC-EC-QCL-IR is a complementary technique to SEC-FTIR, but not a replacement (see **Figure 2**).

C. Botha, J. Kübel, J. Höpfner, B. Mayerhöfer, T. Beskers, S. Morlock, M. Wilhelm
Polymeric Materials Research Group, Institute for Chemical Technology and Polymer Chemistry, Engessserstr. 18, 76131 Karlsruhe, Germany
E-mail: manfred.wilhelm@kit.edu

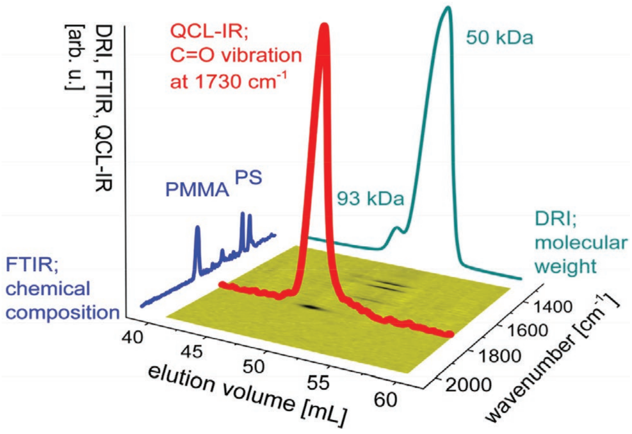


Figure 2. Correlation of SEC-FTIR and SEC-EC-QCL-IR measurements of a PMMA sample.[4]

Following the hyphenation of FTIR and EC-QCL-IR to SEC, the next approach was the hyphenation of a medium resolution (MR), benchtop 1H-NMR spectrometer to an SEC instrument, where the NMR acts as an on-line chemical sensitive detector. The commercial spectrometer consists of a permanent magnet with a magnetic field strength of 1 T (62 MHz for 1H-NMR).The approach is to retain typical SEC selectivity while obtaining 1H-NMR on-line data with the highest possible sensitivity through rigorous optimization of the setup, custom built flow cells, pulse sequences, and numerical data evaluation. The setup is run on non-deuterated solvent and thus the solvent suppression relies on selective pulse sequences and mathematical solvent signal reduction. A typical sensitivity in the order of 100:1 for non-overloaded semi-preparative columns is obtained for PMMA and is sufficient for first applications.[5,6]

A detailed description on the method development will be provided.

Application examples of a PS/PMMA blend and PS-b-PMMA block copolymer are given to illustrate the potential and benefits of the hyphenated techniques and the necessity for optimization.

---

[1] H. Pasch, *Polym. Chem*. **2013**, *4*, 2628.

[2] H. Pasch, B. Trathnigg, *Multidimensional HPLC of Polymers*, Springer **2013**.

[3] T. F. Beskers, T. Hofe, M. Wilhelm, *Polym. Chem.* **2015**, *6*, 128.

[4] S. Morlock, J. M. Kübel, T. F. Beskers, B. Lendl, M. Wilhelm, *Macromol. Rapid Commun.* **2018**, *39*, 1700307.

[5] J. Höpfner, K.-F. Ratzsch, C. Botha, M. Wilhelm, *Macromol. Rapid Commun.* **2018**, *39*, 1700766.

[6] M. Cudaj, G. Guthausen, T. Hofe, M. Wilhelm, *Macromol. Chem. Phys.* **2012**. *213*, 1933.

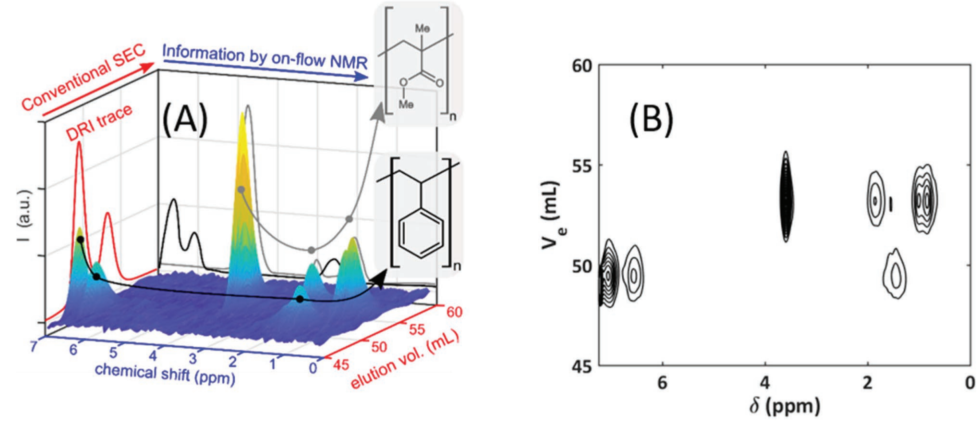


Figure 3. Illustration of SEC-MR-NMR measurements on a PS/PMMA blend.[5] A) Dot-lines indicating the relevant peaks of PS and PMMA, respectively. B) Corresponding contour plot.

Coiled Coils as Mechanoresponsive Material Building Blocks: Towards Molecular Control of Smart Biomimetic Hydrogels

Alberto Sanz de Leon, Constantin Huster, Patricia Lopez Garcia, Melis Goktas, Isabell Tunn, Emilia M. Grad, Klaus Kroy, and Kerstin G. Blank

Coiled coils (CCs) are highly abundant motifs in structural proteins. Consisting of two (or more) α-helices wound around each other in a superhelical fashion, they represent essential structural elements of the cytoskeleton and the extracellular matrix (ECM). Synthetic CCs are further used as dynamomechanical supramolecular cross-links in biomimetic hydrogels. Considering their function as mechanical building blocks, surprisingly little is known about the structural determinants that define the molecular mechanical properties of CCs and how these affect the linear and nonlinear mechanical properties of CC-based self-assembled materials.

Using atomic force microscope (AFM)-based single-molecule force spectroscopy, we have established the sequence-structure-MECHANICS relationship of a series of synthetic CCs. We show that CC mechanical stability depends on coiled coil length, helix propensity, and hydrophobic core packing as well as on the pulling geometry. Based on this knowledge, we have developed a library of CCs with tuneable mechanical properties and synthesized a series of poly(ethylene glycol)-based hydrogels using these CCs as dynamic cross-links. The resulting hydrogels consist entirely of mechanically characterized molecular building blocks and allow for establishing a direct relationship between molecular and bulk mechanics. Using theoretical models, we obtain a direct correlation between the single-molecule parameters and the bulk mechanical response of the hydrogel, as determined with rheology. Equipped with a fluorescence reporter system, the CCs will self-report on their mechanical state and allow for visualizing cross-link rupture in real time. This will not only provide unprecedented insights into material failure mechanisms, but also yield a smart ECM-mimic for investigating the molecular forces involved in cellular mechanosensing.

A. S. de Leon, Patricia Lopez Garcia, Melis Goktas, Isabell Tunn, Emilia M. Grad, Kerstin G. Blank
Max Planck Institute of Colloids and Interfaces
14424 Potsdam, Germany

C. Huster, K. Kroy
Institute for Theoretical Physics
University of Leipzig
04109 Leipzig, Germany

E. M. Grad
Institute for Molecules and Materials
Radboud University
6525 AJ Nijmegen, The Netherlands

From Sequence to Precise Functions: Translating Peptides to Precision Polymers

*Hans G. Börner**

Recently enormous efforts have been spend to advance polymer synthesis methods, enabling monomer sequence control in precision polymers.[1] After principles of advanced synthesis routes have been established, one of the upcoming challenges will be finding applicable sequences to demonstrate the potentials of fully synthetic polymers, which exhibit a defined monomer sequence. Here, we summarize recent advances and present our approach to extract interesting primary structures by combinatorial means and finding minimal sequences by sequence analysis to design precision polymers (**Figure 1**). Those polymers offer the possibility to mimic aspects of functional biomacromolecules with non-biological monomer building blocks and might enlarge the functional space available for polymers useful for drug delivery,[2] adhesives,[3] or nanoengineering of surfaces.[4]

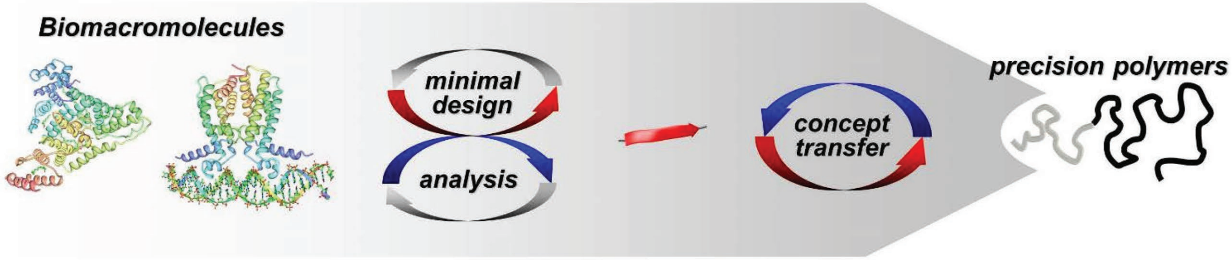


Figure 1. Abstracting principles from peptides to design precision polymers.

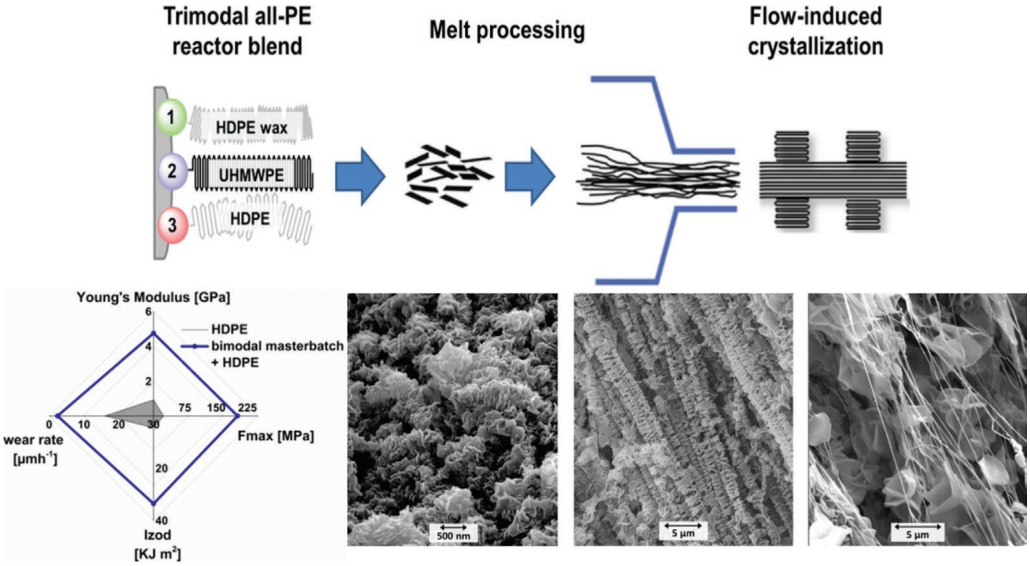
[1] a) J. F. Lutz, M. Ouchi, D. R. Liu, M. Sawamoto, *Science* **2013**, *341*, 628; b) N. ten Brummelhuis, P. Wilke, H. G. Börner, *Macromol. Rapid Commun.* **2017**, *38*, 1700632; c) H. G. Börner, *Macromol. Rapid Commun.* **2011**, *32*, 115.
[2] a) S. Wieczorek, A. Dallmann, Z. Kochovski, H. G. Börner, *J. Am. Chem. Soc.* **2016**, *138*, 9349; b) C. Lawatscheck, M. Pickhardt, S. Wieczorek, A. Grafmüller, E. Mandelkow, H. G. Börner, *Angew. Chem. Int. Edit.* **2016**, *55*, 8752; c) D. Remmler, T. Schwaar, M. Pickhardt, C. Donth, E. Mandelkow, M. G. Weller, H. G. Börner, *J. Controlled Release* **2018**, accepted; d) S. Wieczorek, D. Remmler, T. Masini, Z. Kochovski, A. K. Hirsch, H. G. Börner, *Bioconjugate Chem.* **2017**, *28*, 760.
[3] P. Wilke, N. Helfricht, A. Mark, G. Papastavrou, D. Faivre, G. H. Börner, *J. Am. Chem. Soc.* **2014**, *136*, 12667.
[4] a) F. Hanßke, E. Kemnitz, G. H. Börner, *Small* **2015**, *11*, 4303; b) V. Samsoninkova, B. Seidt, F. Hanßke, W. Wagermaier, H. G. Börner, *Adv. Mater. Interf.* **2016**, *4*, 1600501; c) S. Große, P. Wilke, H. G. Börner, *Angew. Chem. Int. Edit.* **2016**, *55*, 11266.

Prof. H. G. Börner
Laboratory for Organic Synthesis of Functional Systems
Department of Chemistry, Humboldt Universität zu Berlin
Brook-Taylor-Straße 2, D-12489 Berlin, Germany
E-mail: h.boerner@hu-berlin.de

Tailoring All-Hydrocarbon Composites for Circular Economy

*Timo Hees, Fan Zhong, Carl. M. Schirmeister, and Rolf Mülhaupt**

The transition from linear economy with its throw-away culture to circular economy with effective reuse and product-stewardship systems prompts challenges for sustainable polymer development. Among plastics, hydrocarbon materials are the clear leaders in terms of production scale and life cycle assessment. High molar mass hydrocarbons serve as highly versatile, cost-, resource-, eco- and energy-efficient, durable lightweight materials produced by solvent-free environmentally benign catalytic olefin polymerization. Upon thermolysis, they are readily converted back into low molar hydrocarbon oil and gas useful as raw materials and energy source. However, in engineering applications, they require reinforcement with fibers and fillers which impair recycling. In terms of sustainability, it is highly desirable to develop all-hydrocarbon composites (All-HC) in which matrix and reinforcement are made of the same hydrocarbon polymer. In the past, all-hydrocarbon composites have been obtained by specialized processing such as hot compaction of stretched tapes, fiber lamination, or melt extrusion through convergent dies. Recent breakthroughs in ethylene polymerization on multisite catalysts afford All-HC processable by conventional injection molding. During polymerization, nanophase separation of ultrahigh molar mass polyethylene (UHMWPE) prevents massive entanglement and enables injection molding of polyethylene with high UHMWPE content. During injection molding, flow-induced 1D crystallization produces ultrastrong, extended-chain UHMWPE with diameter of 100 nm resembling nanofibers which nucleate HDPE crystallization to form shish-kebab-like reinforcing phases. Self-reinforced polyethylene exhibits an exceptional combination of simultaneously improved stiffness, strength, toughness, and abrasion resistance without impairing sustainability. Bimodal HDPE-wax/UHMWPE reactor blends represent new additives for All-HC melt compounding. Neither alien materials nor nanoparticles are required. For the first time, recycling of all-HC wastes by melt processing is feasible. At temperatures below 260 °C, no stretch-coil relaxation takes place and the same nanostructures are formed again. The orientation of 1D nanostructures is governed by means of 3D printing which enables to design and fabricate unique material systems. Moreover, the UHMWPE 1D nanostructure formation enables the alignment of single-crystal nanoplatelet fillers to yield nacre-like materials by standard injection molding (**Figure 1**).



---

[1] T. Hees, F. Zhong, M. Stürzel, R. Mülhaupt, *Macromol. Rapid Commun.* **2019**.

T. Hees, F. Zhong, C. M. Schirmeister, R. Mülhaupt
Freiburg Materials Research Center
(FMF) and Institute for Macromolecular Chemistry
Albert-Ludwigs-University Freiburg

Switchable Colloidal Catalysts Based on Temperature-Responsive Microgels

Denise Kleinschmidt, Marta S. Fernandes, Matthias Mork, Magnus Rueping, and Andrij Pich*

Exploring and controlling chemical reactions by the use of responsive polymers is a challenge often addressed to modern polymer chemistry.[1,2] In the given work, we present the synthesis of a versatile, colloidal microgel-catalyst based on the temperature-responsive polymer poly(*N*-isopropylacrylamide) (PNIPAM) containing a covalently bound organocatalyst L-proline. Embedding this catalyst into the polymeric matrix enables to control its catalytic performance by adjusting the network structure around it.

The microgel-catalysts were synthesized via a one-step precipitation polymerization enabling a flexible incorporation of up to 10 mol% of the organocatalyst into the microgel network without the loss of colloidal stability. The obtained microgel-catalysts were characterized with various methods and show high catalytic activity and selectivity in model reactions in diverse solvents for multiple reaction cycles, furthermore enabling recycling and re-use of the catalyst. We believe this approach has the potential to generate basic knowledge on a wide range of chemical processes within colloidal polymeric networks.

---

[1] Y. Lu, S. Proch, M. Schrinner, M. Drechsler, R. Kempe, M. Ballauff, *J. Mater. Chem.* **2009**, *19*, 3955.
[2] A. Pich, A. Karak, Y. Lu, A. K. Ghosh, H.-J. P. Adler, *J. Nanosci. Nanotechnol.* **2006**, *6*, 3763.

D. Kleinschmidt, M. S. Fernandes, M. Mork, M. Rueping, A. Pich
RWTH Aachen University Germany
E-mail: kleinschmidt@dwi.rwth-aachen.de

D. Kleinschmidt, A. Pich
Leibniz Institute for Interactive Materials, Germany

M. Rueping
King Abdullah University of Science and Technology, Saudi Arabia

New Organic Light-Emitting Capacitors Based on π-Conjugated Polymer Particles

Bastian Haehnle and Alexander J. C. Kuehne*

AC driven organic light-emitting capacitors (OLECs) are a powerful alternative to widely applied DC driven organic light emitting diodes (OLEDs). OLECs circumvent charge accumulation reducing annihilation effects detrimental to OLED device performance and they can be easily connected to standard AC power lines. However, conventional manufacturing of OLECs is disadvantageous as it requires complicated multistep processing into several layers. Here, we present a new type of OLEC based on monodisperse π-conjugated polymer particles, which self-assemble into a hierarchical device architecture in a single processing step (**Figure 1**a).[1] The monodisperse π-conjugated polymer particles with diameters of several hundred nanometers are produced by Suzuki-type dispersion polymerization. Suzuki coupling always yields Pd-black as a side product, which is often thought to be detrimental to the optical performance of the material. Here, we turn this drawback into an advantage and use the Pd-black nanoparticles as low workfunction nanoelectrodes, which can be addressed by the external AC field (Figure 1b). During processing into OLEC devices, the conjugated polymer particles are dispersed in a matrix consisting of a high-k dielectric and then sandwiched between two electrodes. The dielectric matrix protects the polymer particles from moisture and oxygen and prevents direct charge injection from the sandwich electrodes into the organic semiconductor. The external electric field can be applied to induce charges through the Pd-nanoelectrodes acting as nanometer sized ambipolar charge generators. Recombination of injected charges in the conjugated polymer leads to electroluminescence in the particles. I will discuss the synthesis of conjugated polymer particles with incorporated Pd-nanoelectrodes, their assembly into OLEC devices by printing methods, and the emission characteristics of the resulting light emitting devices.

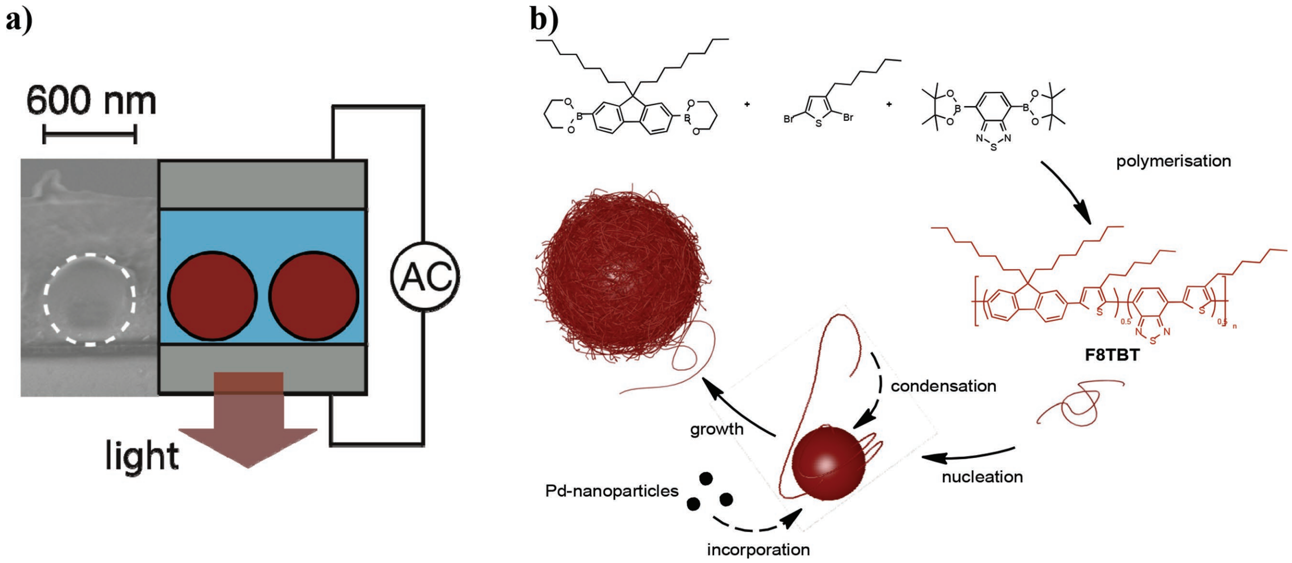


Figure 1. a) SEM image and schematic illustration of the OLEC device cross section. b) Reaction scheme and dispersion polymerisation mechanism for the formation of monodisperse π-conjugated F8TBT particles with incorporated Pd-nanoparticles.

---

[1] A. Mikosch, S. Ciftci, A. J. C. Kuehne, *ACS Nano* **2016**, *10*, 10195.

B. Haehnle, A. J. Kuehne
Institute of Organic Chemistry III/Macromolecular Chemistry
Ulm University, Germany
E-mail: haehnle@dwi.rwth-aachen.de

Refitting Radical Ring-Opening Polymerization for Biodegradable and Responsive Nanoparticles

Jens Gaitzsch, Pascale C. Welsch, Jenny Folini, Wigdan Murad, James C. Anderson, and Wolfgang Meier

Amphiphilic block-copolymers are ideal for self-assembly into nanoparticles and have shown a very high potential for drug delivery as well as for nanoreactors.[1] While the majority of self-assembly studies are done with nondegradable polymers, aliphatic polyesters are also feasible candidates for the formation of polymeric nanoparticles and they are biodegradable. We therefore work on radical ring-opening polymerisation (RROP) to create such nanoparticles.

First, we revisited monomer synthesis and achieved a milder synthetic protocol by introducing a cobalt-based catalyst. The catalyst reduced the reaction temperature from over 100 °C down to room temperature and shortened reaction times. 5 mol-% of the catalyst worked 4 different monomers, showing the verstality of this protocol. We also developed a new route towards DMMDO (4,7-dimethyl-2-methylene-1,3-dioexpane) via a cyclic carbonate facilitating the Petasis chemistry. The new route now unlocked the first pH sensitive CKA, which can form pH sensitive polyesters.

We then used RROP to obtain a dimethylated version of poly(caprolactone) (PdmCL) from DMMDO, a cyclic ketene acetal (CKA). The monomer proved to form PdmCL using free radical polymerisation (FRP). Amphiphilic block-copolymers were then generated by FRP of DMMDO with a PEG-based macroinitiator. The resulting polyester-based block-copolymers self-assembled into nanoparticles that were degradable by esterase and proved to be biocompatible. The nanoparticles proved to be a good drug delivery system as well as an effective protective shell for an entrapped enzyme. The encapsulated horse radish peroxidase (HRP) was released and fully activated upon degradation of the nanoparticles by esterase (**Figure 1**).[2]

Our data shows that polyesters from RROP are already readily available and are especially promising in applications involving biodegradable self-assembled nanoparticles.

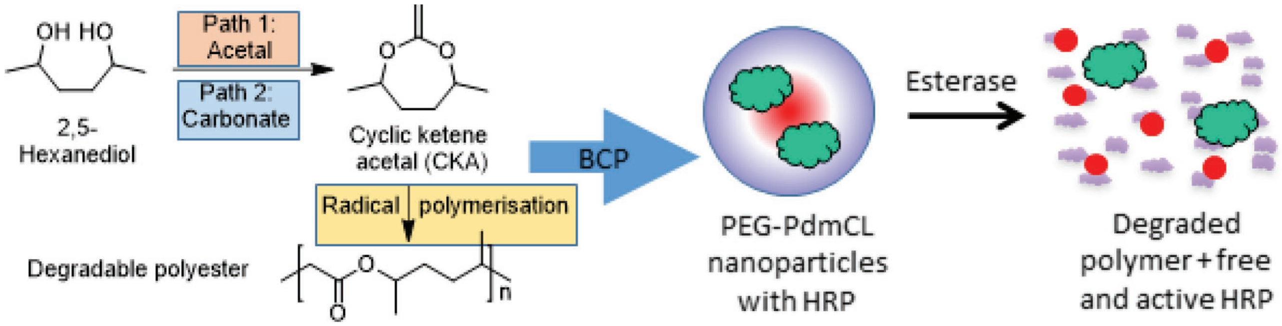


Figure 1. Deploying RROP, the monomer DMMDO is converted into PEG-PdmCL, which self-assembles into nanoparticles. These nanoparticles can host HRP which is released and activated upon the addition of esterase.

---

[1] J. Gaitzsch, X. Huang, B. Voit, *Chem. Rev.* **2016**, 116, 1053.

[2] J. Gaitzsch, P. C. Welsch, J. Folini, C.-A. Schoenenberger, J. C. Anderson, W. P. Meier, *Eur. Polym. J.* **2018**, 99.

J. Gaitzsch, P. C. Welsch, J. Folini, W. Murad, W. Meier
Department of Chemistry University of Basel
Mattenstrasse 24a, BPR1096, 4058 Basel, Switzerland

James C. Anderson
Department of Chemistry
University College London
20 Gordon Street, London WC1H 0AJ, United Kingdom

Towards Catalysis under Flow Conditions in Block Copolymer Membranes

J. H. Kruse,* I. Romanenko, J. Eichhorn, M. Lechner, C. Streb, and F. H. Schacher

The challenge of the transition from fossil fuels to renewable energies requires the establishment of a variety of new energy sources. In this regard, the production of elemental hydrogen and the subsequent transformation of the created chemical energy into other forms of energy like electricity is an important aspect. But for the application of natural energy sources like sunlight to produce hydrogen from water, it is necessary to apply photocatalysts. In that regard, an interesting class of photocatalysts are polyoxometalates (POMs).[1] These were initially used in oxidative organic synthesis, but the interest has shifted to applications as water oxidation catalysts.[2] To unfold these interesting catalytic properties, it is necessary to embed these catalysts into a suitable environment, for example, into nanoporous polymeric membranes to combine the advantageous properties of POMs and block copolymers.[3]

In this work, we will present the preparation of such catalytically active block copolymer membranes starting from the synthesis of amphiphilic block copolymers. Four well-defined polystyrene-*block*-poly(*N,N*-dimethylaminoethyl methacrylate) (PS-*b*-PDMAEMA), poly(styrene-*co*-isoprene)-*block*-poly(*N,N*-dimethylaminoethyl methacrylate) (PS-*co*-I-*b*-PDMAEMA), polystyrene-*block*-polyisoprene-*block*-poly(3-chloro-2-hydroxypropyl methacrylate (PS-*b*-PI-*b*-PClHPMA), and polystyrene–*block*-polyisoprene-*block*-poly(vinylbenzylchloride-*co*-triethyleneglycolemethacrylatemethyl ether) (PS-*b*-PI-*b*-PVBCL-co-PTEGA) block copolymers were synthesized via anionic and controlled radical (NMP) polymerization techniques. The obtained materials were successfully used for the preparation of nanoporous membranes using non-solvent induced phase separation (NIPS) processes afterward.

PS-*b*-PDMAEMA and PS-*co*-I-*b*-PDMAEMA membranes were further used for the electrostatic attachment of negatively charged catalytically active polyoxometalates (POM). The obtained catalytically active membranes were tested in oxidation catalysis both under batch and flow conditions.[4] In case of PS-*b*-PI-*b*-PClHPMA and PS-*b*-PI-*b*-PVBCL-*co*-PTEGA that possess easily modifiable –CH_2Cl groups, the catalyst attachment was performed via covalent binding.

---

[1] S. Herrmann, C. Ritchie, C. Streb, *Dalton Trans.* **2015**, *44*, 7092.
[2] C. Streb, *Dalton Trans.* **2012**, *41*, 1651.
[3] M. Bonchio, M. Carraro, G. Scorrano, E. Fontananova, E. Drioli, *Adv. Synth. Catal.* **2003**, *345*, 1119.
[4] I. Romanenko, M. Lechner, F. Wendler, C. Hörenz, C. Streb, F. H. Schacher, *J. Mater. Chem. A* **2017**, *5*, 15789.

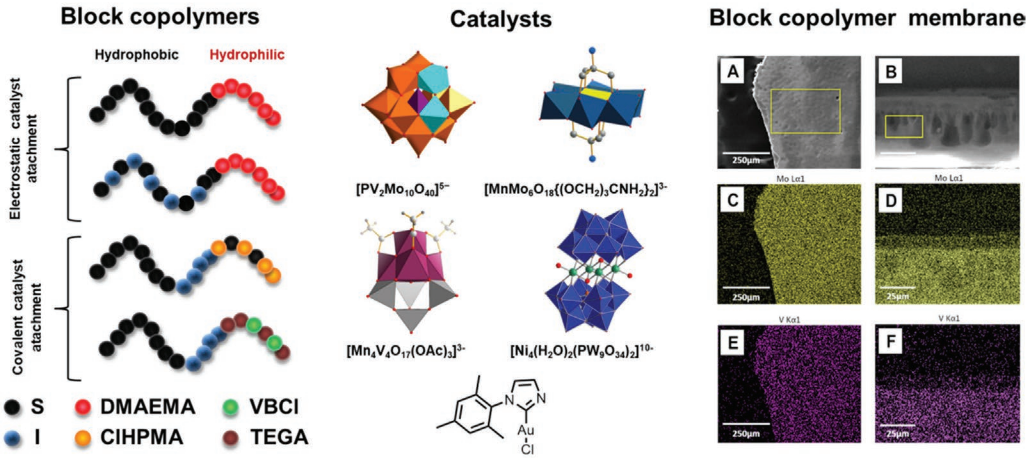


Figure 1. Scope of designed block copolymers and catalysts for electrostatic and covalent attachment. SEM micrographs of membrane top view (A) and cross-section (B) and EDX mapping of Mo and V on membrane surface (C,E) and cross-section (D,F).

J. H. Kruse, I. Romanenko, J. Eichhorn, F. H. Schacher
Institute of Organic Chemistry and Macromolecular Chemistry (IOMC)
Friedrich-Schiller-University Jena
Humboldtstraße 10, D-07743 Jena, Germany
E-mail: jan-hendrik.kruse@uni-jena.de

J. H. Kruse, I. Romanenko, F. H. Schacher
Jena Center for Soft Matter (JCSM), Friedrich-Schiller-Universität Jena
Philosophenweg 7, 07743 Jena, Germany

M. Lechner, C. Streb
Institute of Inorganic Chemistry I
Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany

Structural Variation in Phosphorus-Containing Polymeric Flame Retardants: P-N vs. P-O

*Jens C. Markwart, Alexander Battig, Bernhard Schartel, and Frederik R. Wurm**

With the broad use of polymers, the risk of fires increases and causes annual costs of several billion Euros in Germany alone.[1] The need for flame retardant plastics is obvious and several mainly low molecular weight organic compounds (halogenated aromatics or organophosphates) or inorganic additives (like red phosphorus or metal hydroxides) have been developed.[2–4] Despite their application, these materials have several drawbacks: halogenated compounds are environmentally persistent and release toxic substances during degradation.[5,6] Inorganic additives, on the other hand, need to be deployed in high amounts and therefore deteriorate the mechanical properties of the polymer matrix, due to their low effectiveness.[7] We established a reliable synthesis to prepare a family of monomers (cf. **Figure 1**) with adjustable P-O versus P-N-ratios that can be transformed into branched or cross-linked materials by radical thiol-ene polyaddition or ATMET.[8] Such poly(phosphoester)s, poly(phosphoramidate)s, poly(phosphorodiamidate)s, and poly(phosphoramide)s were studied as model flame retardant additives in commercial epoxy resins.[9] The precise variation of the binding pattern around the central phosphorus atom influences the performance of the additives dramatically and will allow us to understand their flame retardant mechanism based on a precise chemical synthesis.

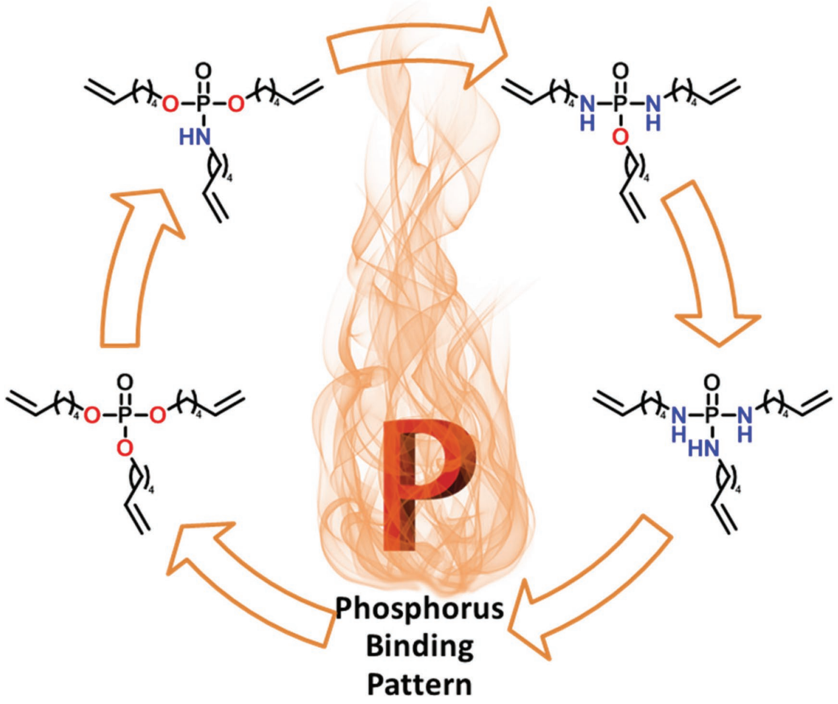


Figure 1. Systematic variation of the binding pattern of P-containing flame retardants.

---

[1] S. Bundesamt, *Gesundheit - Todesursachen in Deutschland* **2016**, p. 51.
[2] I. Belyamani, J. U. Otaigbe, W. R. Fielding, *Polym. Eng. Sci.* **2015**, *55*, 1741.
[3] K. M. Xu, K. F. Li, Y. P. Deng, X. Yan, C. P. Xie, *Adv. Mater. Res.* **2012,** *430–432*, 110.
[4] E. Michels, H. Staendeke, *Phosphorus Sulfur Relat. Elem.* **1987,** *30*, 637.
[5] K. Täuber, F. Marsico, F. R. Wurm, B. Schartel, *Polym. Chem.* **2014**, *5*, 7042.
[6] K. N. Bauer, H. T. Tee, M. M. Velencoso, F. R. Wurm, *Prog. Polym. Sci.* **2017**.
[7] M. Le Bras, S. Bourbigot, S. Duquesne, C. Jama, C. Wilkie, The Royal Society of Chemistry **2005**.
[8] F. Marsico, A. Turshatov, R. Pekoz, Y. Avlasevich, M. Wagner, K. Weber, D. Donadio, K. Landfester, S. Baluschev, F. R. Wurm, *J. Am. Chem. Soc.* **2014,** *136*, 11057.
[9] J. C. Markwart, A. Battig, M. Martinez-Velencoso, B. Schartel, F. R. Wurm, *in preparation*.

J. C. Markwart
Graduate School Materials Science in Mainz
Staudinger Weg 9, 55128 Mainz, Germany

A. Battig, B. Schartel
Bundesanstalt für Materialforschung und -prüfung (BAM)
Unter den Eichen 87, 12205 Berlin, Germany

J. C. Markwart, F. R. Wurm
Max-Planck-Institut für Polymerforschung,
Ackermannweg 10, 55128 Mainz, Germany
E-mail: wurm@mpip-mainz.mpg.de

Stimuli-Responsive Luminescent Supramolecules and Polymers

Xuyang Yao, Jie Wang, Hui Chen, Xiang Ma, He Tian, and Andreas Walther*

Smart luminescent materials have drawn great attention due to their intriguing photo-luminescent behaviors and responsiveness to environmental stimuli, such as light, pH, redox, mechanical force, etc., which makes them potential candidates as luminescent sensors. Utilizing supramolecular assembling systems and polymer matrix to achieve stimuli-responsive luminescent materials have become important methods which help to reduce the demanding design and tedious chemical synthesis of luminescent molecules.[1] Tunable and multicolor photoluminescence were achieved by introducing aggregation-induced emission (AIE) or vibration-induced emission (VIE) molecules into host–guest supramolecular systems.[2,3] Metal-free polymers with efficient room temperature phosphorescence were prepared with different phosphors in a highly facile way and their application as encryption ink was explored based on the humidity-responsiveness of polyacrylamide matrix.[4] These investigations contribute to the development of smart luminescent materials but further effort is still needed to explore the structural effect of polymer matrix on the photo-luminescent properties.

---

[1] X. Yao, T. Li, J. Wang, X. Ma, H. Tian, *Adv. Opt. Mater.* **2016,** *4*, 1322.
[2] J. Wang, X. Yao, Y. Liu, H. Zhou, W. Chen, G. Sun, J. Su, X. Ma, H. Tian, *Adv. Opt. Mater.* **2018,** *6*, 1800074.
[3] X. Yao, X. Ma, H. Tian, *J. Mater. Chem. C* **2014,** *2*, 5155.
[4] H. Chen, X. Yao, X. Ma, H. Tian, *Adv. Opt. Mater.* **2016,** *4*, 1397.

X. Yao, A. Walther
A3BMS Lab-Adaptive, Active and Autonomous Bioinspired Material Systems
Institute for Macromolecular Chemistry
University of Freiburg, Freiburg, Germany
E-mail: dr-yao@hotmail.com

X. Yao, A. Walther
Freiburg Institute for Advanced Studies (FRIAS)
University of Freiburg, Freiburg, Germany

X. Yao, J. Wang, H. Chen, X. Ma, H. Tian
Key Laboratory for Advanced Materials and Institute of Fine Chemicals
East China University of Science & Technology
Shanghai 200237, P. R. China

Silyl Glyoxylates and Derivatives as a New Class of High Performance Visible Light Photoinitiators

Julie Kirschner, Mariem Bouzrati-Zerelli, Christoph P. Fick, Maximilian Maier, Céline Dietlin, Fabrice Morlet-Savary, Jean Pierre Fouassier, Jean-Michel Becht, Joachim E. Klee, and Jacques Lalevée**

Silyl glyoxylates and derivatives are proposed as a new class of high performance photoinitiators for the free radical polymerization of methacrylate resins upon near-UV or blue light emitting diodes (LEDs) upon exposure to violet LEDs (385, 405 nm) or blue LED (477 nm) under air or in laminate. Remarkably, they can be used in combination with an iodonium salt and an amine or added to CQ /iodonium/amine systems. Thin adhesives as well as thick composites can be easily obtained.[1,2] These new derivatives exhibit excellent polymerization performances under violet or blue LED and remarkable bleaching properties compared to CQ-based systems.

Remarkably, silyl glyoxylates can be used in combination with an iodonium salt for the synthesis of interpenetrating networks (IPNs). The silyl glyoxylate/iodonium systems are able to initiate both radical and cationic polymerizations through the simultaneous polymerizations of a radical monomer and a cationic monomer (e.g., bisGMA and 2-vinyloxyethoxyethyl methacrylate blend). The resulting polymers present enhanced mechanical properties and better bleaching properties compared to those obtained with pure methacrylate resin.

---

[1] M. Bouzrati-Zerelli, J. Kirschner, C. P. Fik, M. Maier, C. Dietlin, F. Morlet-Savary, J. P. Fouassier, J.-M. Becht, J. E. Klee, J. Lalevée, *Macromolecules* **2017**, *50*, 6911.

[2] J. E. Klee, F. Szillat, M. Maier, H. Ritter, J. Lalevée, J. P. Fouassier, F. Morlet-Savary, C. Dietlin, C. P. Fik, *EP16778051.9* and *EP3359118*, **2017**.

J. Kirschner, M. Bouzrati-Zerelli, C. Dietlin, F. Morlet-Savary,
J. P. Fouassier, J.-M. Becht, J. Lalevée
Institut de Science des Matériaux de Mulhouse IS2M – UMR CNRS
7361 – UHA, 15 rue Jean Starcky, 68057 Mulhouse Cedex, France

C. P. Fick
ETH Zurich, Rämistr. 101, 8092 Zürich, Switzerland

M. Maier
BASF Polyurethanes GmbH, Elastogranstr. 30, 49448
Lemförde, German

J. E. Klee
Denstply Sirona Restorative, De-Trey-Str. 1, 78467 Konstanz, Germany
E-mail: julie.kirschner@uha.fr; jacques.lalevee@uha.fr;
Joachim.Klee@dentsplysirona.com

Reading the Sequence of Monodisperse Sequence-Defined Oligomers

M. Frölich and M. A. R. Meier

Sequencing of DNA and its full read-out is one of the most important achievements in science over the last years.[1] DNA is the most extensively studied and best-known example of sequence-defined macromolecules from nature, storing essential genetic information via a chemical quaternary code. In recent years, the field of sequence-controlled and sequence-defined synthetic macromolecules has continuously emerged from a niche to an important research topic within the scientific community.[2] Several approaches for the synthesis of sequence-defined macromolecules have been reported.[3] Among these, multicomponent reaction-based methodologies are very promising due to their high variability and efficiency.

In our approach, isocyanide-based multicomponent reactions were used for the synthesis of sequence-defined oligomers. Through iterative Passerini three-component reactions and subsequent deprotection steps, several oligomers were successfully synthesized.[4] Via ESI MS/MS analysis, it was possible to fragment the oligomers and thus read out the sequence of these oligomers, leading to possible application sin cryptography.[5] Here, new strategies for a simplified and in the future automated read-out will be discussed in detail. For instance, the use of mass-markers as starting compounds of the iterative synthesis significantly eases MS/MS data interpretation (see **Figure 1**).

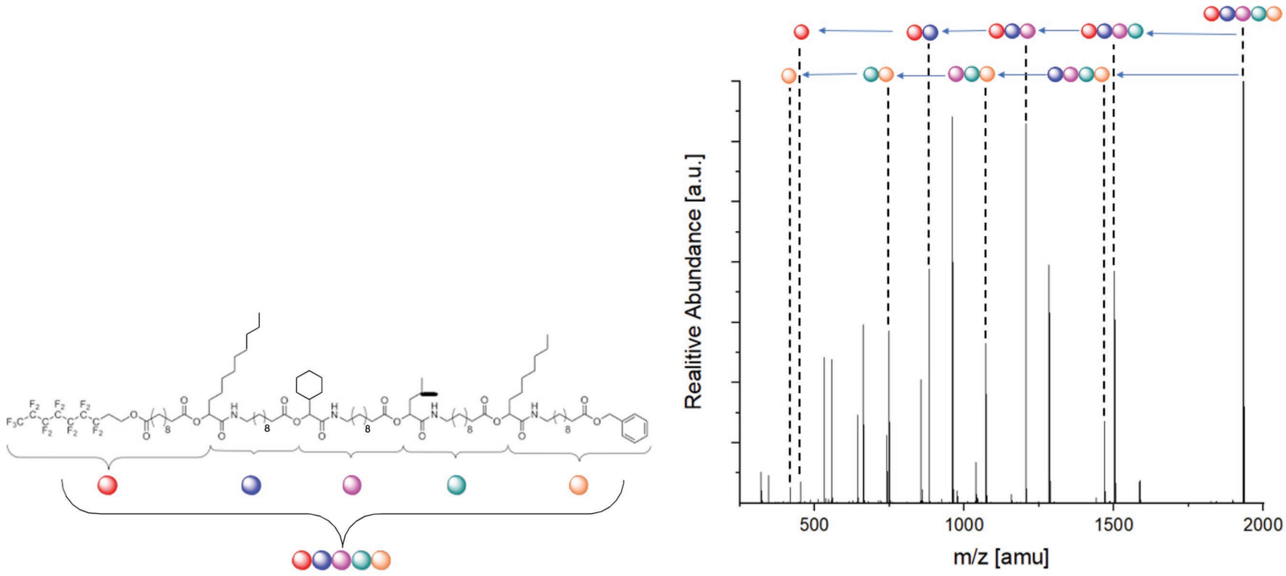


Figure 1. Example of the decoding of a sequence-defined tetramer.

---

[1] J. C. Venter, M. D. Adams, E. W. Myers, P. W. Li, R. J. Mural, G. G. Sutton, H. O. Smith, M. Yandell, C. A. Evans, R. A. Holt, et al. Science **2001**, *291*, 1304.

[2] J. F. Lutz, *ACS Macro Lett.* **2014**, *3*, 1020.

[3] S. C. Solleder, R. V. Schneider, K. S. Wetzel, A. C. Boukis, M. A. R. Meier, *Macromol. Rapid Commun.* **2017**, *38*, 1.

[4] S. C. Solleder, D. Zengel, K. S. Wetzel, M. A. R. Meier, *Angew. Chemie Int. Ed.* **2016**, *55*, 1204.

[5] A. C. Boukis, K. Reiter, M. Frölich, D. Hofheinz, M. A. R. Meier, *Nat. Commun.* **2018**, *9*, 1439.

M. Frölich, Prof. M. A. R. Meier
Karlsruhe Institute of Technology, Straße am Forum 7
76131 Karlsruhe, Germany

Lactose-Functionalized Precision Glycomacromolecules for Understanding the Role of Galectin-3 in Tumor Migration

*Tanja Freichel, Miriam Hoffmann, Dominic Laaf, Robert Wawrzinek, Christoph Rademacher, Sophia Sarafova, Lothar Elling, Nicole L. Snyder, and Laura Hartmann**

Many diseases are caused by the dysregulation of protein or glycan biosynthesis in cells. The investigation of the underlying processes and mechanism is therefore of significant interest regarding the development of new therapeutics or diagnostics. An important class of tumorgenesis-associated proteins are the galectins, which are characterized by their conserved β-galactoside-binding carbohydrate recognition domain. Galectin-3, one of the best studied members of this family of lectins, has been identified as a potential target for the investigation of new multivalent ligands especially due to its ability to self-aggregate into multivalent lattices. Here, we applied a bottom-up strategy based on the previously established solid phase synthesis of precision glycomacromolecules to derive novel glycomimetic ligands and explore their potential for targeting cancer cells overexpressing galectin-3.

Through the step-wise assembly of tailor-made building blocks using Fmoc-peptide coupling protocols, monodisperse, sequence-controlled oligo(amidoamine) scaffolds were synthesized and further functionalized with lactose ligands as well as non-sugar binding motifs. Conjugation of these precision glycomacromolecules onto lipids allowed for the preparation of liposomes carrying selected glycomacromolecular ligands. Enzyme-linked immunosorbent assay (ELISA)-type and surface plasmon resonance (SPR) inhibition studies demonstrated the suitability of those lactose-functionalized macromolecules and liposomes as galectin-3 ligands. First in vitro studies on human cancer cells using selected lactose-based glycomacromolecules demonstrated the ability of these compounds to serve as ligands for galectin-3 which could be modulating tumor cell migration.

T. Freichel, M. Hoffmann, L. Hartmann
Institute of Organic Chemistry and Macromolecular Chemistry
Heinrich-Heine-University Düsseldorf
Universitätsstraße 1, 40225 Düsseldorf, Germany

D. Laaf, L. Elling
Laboratory for Biomaterials, Institute for Biotechnology and
Helmholtz-Institute for Biomedical Engineering, RWTH Aachen
University, Pauwelsstraße 20, 52074 Aachen, Germany

R. Wawrzinek, C. Rademacher
Max Planck-Institute of Colloids and Interfaces Mühlenberg 1
14476 Potsdam, Germany

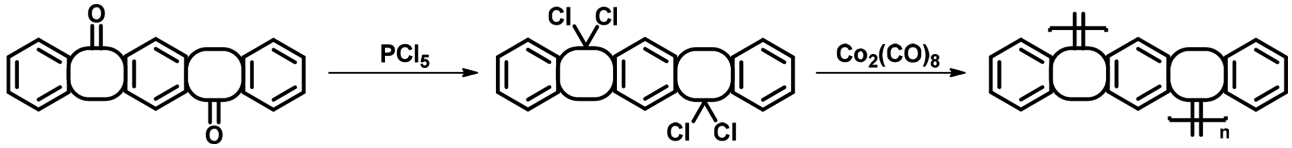
S. Sarafova
Biology Department, Davidson College
North Carolina 28035, United States

N. L. Snyder
Chemistry Department, Davidson College
North Carolina 28035, United States

Polycyclic Ladder Polymers Made by Reductive Dehalogenation Polycondensation of AA-, AB- and AA/BB-type Monomer Systems as Novel Class of Polymers of Intrinsic Microporosity (PIMs)

*P. Klein and U. Scherf**

Poly(indenofluorene) and poly(diindenonaphthalene) are low bandgap polyhydrocarbons with long wavelength absorption features ranging into the near infrared (NIR) region.[1,2] The low bandgap character was assigned to the contribution of quinoidal resonance states to the electronic ground state mainly driven by the twisted exocyclic double bonds as result of the crowded steric situation around these double bonds.[3]



In continuation of this work, we have tested related pentacyclic tetrachloro-monomers that contain seven-membered (cycloheptatriene) instead of the initial five-membered (cyclopentadiene) connector rings by introducing one or two additional vinylene groups into the monomers. All polymers show steric strain around the exocyclic double bond, resulting in different conformations. Deliberate control over the connecting ring's size yields polymers with unique optical and morphological properties. Surprisingly, all linear polymers showed high BET surface areas up to 600 m² g^{-1} and good solubility in organic solvents, expanding the class of linear conjugated polymers of intrinsic microporosity (c-PIMs).[4]

---

[1] H. Reisch, U. Wiesler, U. Scherf, N. Tuytuylkov, *Macromolecules* **1996**, *29*, 8204.

[2] E. Preis, U. Scherf, *Macromol. Rapid Commun.* **2006**, *27*, 1105.

[3] P. U. Biedermann, J. J. Stezowski, I. Agranat, *Chem. Eur. J.* **2006**, *12*, 3345.

[4] G. Cheng, B. Bonillo, R. S. Sprick, D. J. Adams, T. Hasell, A. I. Cooper, *Adv. Funct. Mater.* **2014**, *24*, 5219.

P. Klein, U. Scherf
Bergische Universität Wuppertal
Gaußstr. 20, 42119 Wuppertal, Germany
E-mail: scherf@uni-wuppertal.de

Regulated Supramolecular Assembly of Peptide-Functionalized Polymers into Core-Shell Nanorods

Ronja Otter and Pol Besenius*

Polymer peptide conjugates combine different favorable characteristics like the easy scalability of the synthetic polymer with the high structural definition of the peptide part. Here, we present a pH-switchable supramolecular system in aqueous media using a covalent water soluble polymer as a shielding block to an aggregating peptide block.[1,2]

The peptide block was synthesized via SPPS and standard peptide coupling methods and consisted of an alternating phenylalanine histidine sequence. Homo- and heterotelechelic PEG and polysarcosine polymers were prepared using parallel and antiparallel encoded β-sheet sequences. The assembly of the system is dictated by the hydrophobicity of the phenylalanines, the intra- and intermolecular hydrogen bonding and interaction of the peptide backbone resulting in ß-sheet directed anisotropic growth of core-shell nanorods. The protonation of the imidazoles in the histidine side chains at acidic pH values results in the disassembly of the system due to the repulsive Coulomb interactions.

The polymer peptide conjugates were characterized by NMR, GPC, and MALDI-TOF MS measurements. The pH-dependent aggregation of the peptide-polymer conjugates was monitored using CD spectroscopy. Nanorod formation of the different conjugates with varying chain lengths was observed via transmission electron microscopy (TEM). Parallel β-sheet-driven folding and intermolecular assembly of the conjugates leads to interstrand cross-linking and hydrogelation, which was investigated through rheology.

Recent investigations into coupled redox- and pH-regulated assemblies will be presented. These allow us to tune the time-domain of supramolecular assembly and hydrogelation.

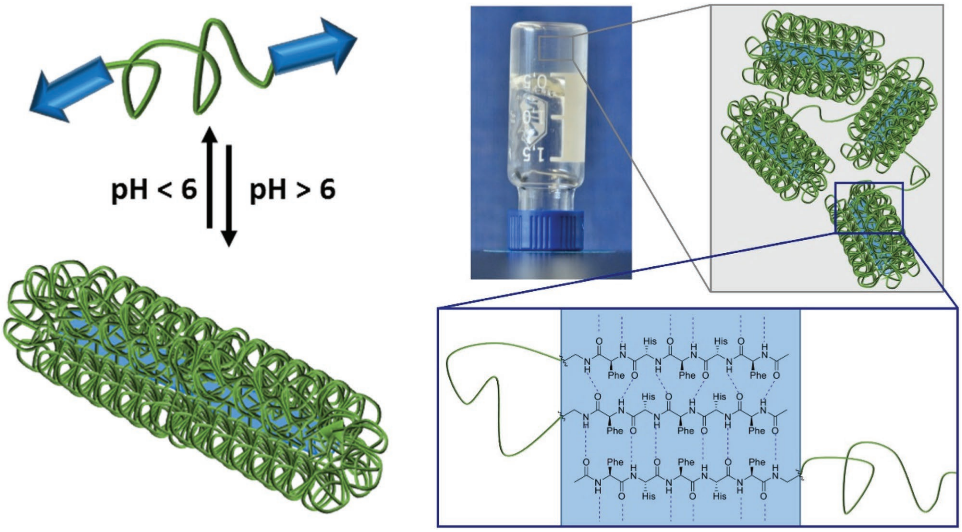


Figure 1. Schematic representation of the pH-dependent ß-sheet directed assembly of folded amphiphilic polymer peptide conjugates into core-shell nanorods (left) and formation of supramolecular hydrogels due to interstrand crosslinking.

---

[1] R. Otter, K. Klinker, D. Spitzer, M. Schinnerer, M. Barz, P. Besenius, *Chem. Commun.* **2018**, *54*, 401.

[2] R. Otter, N. A. Henke, C. Berac, T. Bauer, M. Barz, S. Seiffert, P. Besenius, *Macromol. Rapid Commun.* **2018**, *39*, 1800459.

R. Otter, P. Besenius
Institute of Organic Chemistry
Johannes Gutenberg-University Mainz, Germany
E-mail: Otter@uni-mainz.de

Synthesis and Uptake Behavior of Cyclic-(arginine-glycine-aspartic) Acid (cRGD) Modified Polymeric Nanoparticles

*Weihai Zhang, Mariam Samadi, Nele Teske, and V. Prasad Shastri**

Integrins are directly involved in cell–matrix interactions and play a crucial role in controlling cellular differentiation, proliferation, migration, and morphogenesis. The Arg-Gly-Asp (RGD), a prominent sequence in many cell adhesive proteins, serves as the binding motif (domain) for integrins and the cell plasma membrane and constitutes a major recognition system for cell adhesion. RGD has high affinity to $\alpha_v\beta_3$ integrin which are expressed by endothelial cells and whose expression is associated with angiogenesis. It has been shown that systemic administration of cRGD can arrest tumor progression and tumor-associated neoangiogenesis.[1] Therefore, cRGD-modified nanoparticles (NPs) could be used in vivo for interfering with the angiogenic processes. NPs were prepared using polycaprolactone copolymer bearing alkyne moiety on a hydrophilic spacer and this enabled direct modification of the NP surface with cRGD via click reaction in aqueous environment. Treatment of human pulmonary microvascular endothelial cells (HPMEC) and human umbilical vein endothelial cells (HUVECs) with cRGD-modified NPs revealed differences in their uptake. In this poster, the underlying mechanism regulating the uptake of cRGD-modified NPs in endothelial cells will be presented and discussed.

---

[1] J. Haier, U. Goldmann, B. Hotz, N. Runkel, U. Keilholz, *Clin. Exp. Metastasis* **2002**, 19, 665.

W. Zhang, M. Samadi, N. Teske, V. P. Shastri
Institute for Macromolecular Chemistry, University of Freiburg
D-79104 Freiburg, Germany
E-mail: weihai.zhang@makro.uni-freiburg.de

Polymer Rheology with Diffusing Wave Spectroscopy

Mathias Reufer

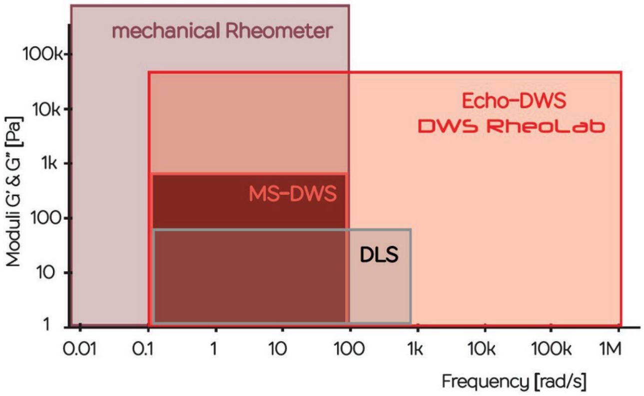
Diffusing wave spectroscopy[1] is a modern light scattering technique for the quantitative measurement of microscopic motion in soft matter systems. An important application of DWS is microrheology at high frequencies up to 10 MHz.[2] This is particularly interesting for polymeric systems as it allows the full characterization of samples without time consuming time-temperature superposition (TTS).

We present several application examples such as polymer solutions and melts. In particular, we demonstrate the ability to measure the elastic modulus G′ and viscous modulus G″ over a huge frequency range at acquisition times of 1–3 min. This fast acquisition time allows monitoring rapid changes in the microstructure such as phase transitions. On the other hand, the method is also very well suited for studies at very long time scales such as aging because the samples are contained in sealed cuvettes and measured contact-free.

---

[1] D. A. Weitz, D. J. Pine, in *Dynamic Light Scattering* (Ed: W. Brown), Oxford University Press, New York **1993**, pp. 652–720.

[2] P. Zakharov, F. Cardinaux, F. Scheffold, *Phys. Rev. E* **2006**, 73.



Dr. M. Reufer
LS Instruments AG, Switzerland

Poly(lactic-co-glycolic acid) Nanoparticles in Cell Media Used as Biocompatible Substrates in Pharmaceutical Applications: Comprehensive Characterization with Centrifugal Field-Flow Fractionation (CF3) Coupled with Online Dynamic Light Scattering (DLS)

Gerhard Heinzmann, Florian Meier, Markus Spallek, Silvia Spek, Klaus Langer, and Thorsten Klein

Centrifugal field-flow fractionation (CF3) is a powerful subtechnique of field-flow fractionation. While in asymmetrical flow field-flow fractionation (AF4) separation is only based on the hydrodynamic size, CF3 additionally exploits density differences of the analytes resulting in an enhanced separation force and thus improved resolution. Moreover, online dynamic light scattering (DLS) enables recording of hydrodynamic sizes in real-time rendering; this setup a powerful hyphenation (CF3-DLS) for the separation and characterization of nano- and microparticles over a wide size range

In this presentation, CF3-DLS is used to characterize PLGA (poly(lactic-co-glycolic acid)) sub-microparticles. In order to investigate their behavior under physiological conditions, the PLGA-particles were dissolved in cell medium and incubated for defined time durations at 37 °C. CF3-DLS analysis was subsequently performed using cell medium as carrier solution thereby closely mimicking the conditions during incubation. By these means, CF3-DLS provides valuable insights in the behavior of a biocompatible particle system, which shows promising properties toward the application in pharmaceutical applications, for example, drug delivery (**Figure 1**, **2**).

This work was part of MINAC: Mechanisms of the Interaction of Nanoparticles with Cells MINAC support code: 0315773D.

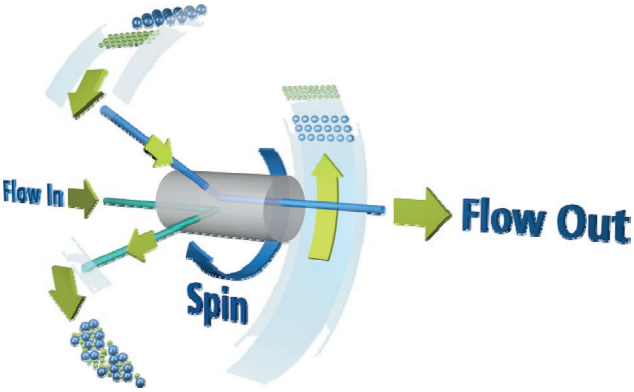


Figure 1. Principle of centrifugal field-flow fractionation.

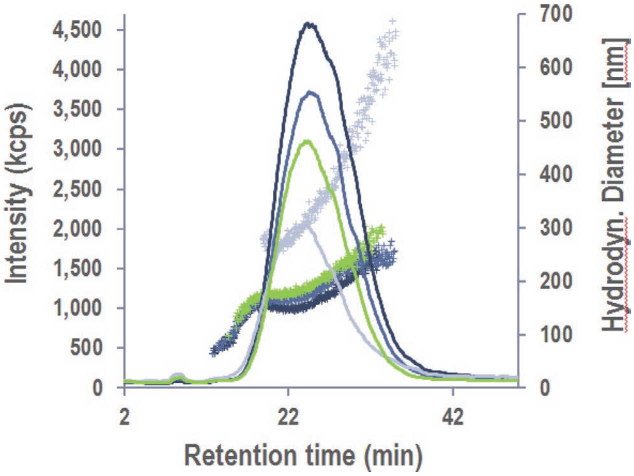


Figure 2. Time-dependent online dynamic light scattering measurement of PLGA-nanoparticles after separation in centrifugal field-flow fractionation.

G. Heinzmann, F. Meier, M. Spallek, T. Klein
Postnova Analytics GmbH
Max-Planck-Str. 14, 86899 Landsberg, Germany

S. Spek, K. Langer
Institute of Pharmaceutical Technology and Biopharmacy
University of Muenster, Schlossplatz 2, 48149 Münster, Germany

Self-Assembly and Co-Nonsolvency of Hydrophobic/Thermoresponsive Block Copolymers: Influence of Chemical Structure and Block Lengths

Cristiane Henschel, Chia-Hsin Ko, André Laschewsky, and Christine M. Papadakis

Amphiphilic and thermoresponsive polymers offer a plethora of potential commercial applications, above all in the fields of cosmetics and detergents. However, certain behaviors of these polymers are still not fully understood and this hinders the full exploitation of their potential. One example is the so-called "co-nonsolvency" of polymers which become insoluble in certain mixtures of solvents, despite being fully soluble in each of them individually. The most classical example of such a system is poly(*N*-isopropylacrylamide) (PNIPAM) in a solvent mixture of water–methanol, although a few others are known. Although a number of studies have investigated the co-nonsolvency of homopolymers, the co-nonsolvency of copolymers has, as of now, not been extensively studied. With that in mind, our work focused on evaluating how the self-assembly behavior of block-copolymers with a thermoresponsive block, which exhibits co-nonsolvency, is affected by the presence of an additional permanently hydrophobic block. In our case, this hydrophobic block consists of polystyrene (PS) or poly(methyl methacrylate) (PMMA), while the thermoresponsive block consists either of PNIPAM or poly(*N*-isopropylmethacrylamide) (PNIPMAM). The block copolymers were synthesized by consecutive reversible addition fragmentation chain transfer (RAFT) reactions and the aggregation of the copolymer in water and co-nonsolvents was evaluated via turbidimetry and scattering methods. The results provide information on the complex associative behavior of these copolymers in solution and how it is influenced by the chemical composition of the copolymer, sizes of the blocks, temperature, and solvent mixture.

C. Henschel, A. Laschewsky
Institut für Chemie, Universität Potsdam
Potsdam-Golm, Germany

C.-H. Ko, C. M. Papadakis
Physik-Department, TU München
Garching, Germany

A. Laschewsky
Fraunhofer Institute for Applied Polymer Research IAP
Potsdam-Golm, Germany

Influence of Morphology on Electrochemical Performance of Monolithic Sulfur-Poly(acrylonitrile) Composites Used as Cathode Materials in Lithium-Sulfur Batteries

*Tim Lebherz, Martin Frey, Andreas Hintennach, and Michael R. Buchmeiser**

Lithium–sulfur (Li–S) batteries are considered a promising post Li-ion technology due to their high theoretical capacity (1672 mAh g^{-1}) and high specific energy density (2600 Wh kg^{-1}). Furthermore, sulfur is a well-available, cheap, and nontoxic cathode material. However, their practical use is still limited by some issues.[1] One way to address both the insulating nature of sulfur and the polysulfide shuttle is the usage of a sulfur-poly(acrylonitrile) composite (SPAN) as active material. The composite was first described by Wang et al. in 2002 and was synthesized by the reaction of poly(acrylonitrile) (PAN) with elemental sulfur at temperatures >300 °C.[2] The sulfur is covalently bound to the condensed, polyaromatic backbone and forms vinylogous and phenylogous thioamide groups while the reaction. These groups function as anchoring groups during the reduction and oxidation of the sulfur species.[3–5]

In our work, we present two different ways to synthesize PAN-based monoliths as precursors for SPAN-based cathode materials with a defined morphology. On the one hand, we synthesized PAN-monoliths via solvent induced phase separation including RAFT-polymerization of acrylonitrile with ethylene glycol dimethacrylate as cross-linker; on the other hand we synthesized PAN-monoliths via thermally induced phase separation.[6–8] Both methods delivered different PAN-based monoliths with a defined pore structure.The PAN-monoliths were converted to SPAN-monoliths at 550 °C in the presence of an excess of elemental sulfur according to literature.[9,10] Both SEM images and determination of pore size distributions (nitrogen sorption) showed a monolithic structure after the conversion but a different porosity of the materials compared to the precursor materials. This means that the monolithic structure fully prevailed while the porosity changed significantly. The SPAN-monoliths were processed to cathodes and were electrochemically characterized with a carbonate-based electrolyte system.[11] Both the specific pore volumes and the monomer contents in the PAN-based precursors correlate with the specific discharge capacities of the cells. In addition, the best monolithic SPAN system showed high discharge capacities of 900 mAh per g_{sulfur} (@2 C), a high cyclic stability over more than 200 cycles and performed even better than a state-of-the-art fibrous SPAN-system.[9]

---

[1] A. Manthiram, Y. Fu, S. H. Chung, C. Zu, Y. S. Su, *Chem. Rev.* **2014**, *114*, 11751.

[2] J. Wang, J. Yang, J. Xie, N. Xu, *Adv. Mater.* **2002**, *14*, 963.

[3] J. Fanous, M. Wegner, J. Grimminger, Ä. Andresen, M. R. Buchmeiser, *Chem. Mater.* **2011**, *23*, 5024.

[4] J. Fanous, M. Wegner, M. B. M. Spera, M. R. Buchmeiser, *J. Electrochem. Soc.* **2013**, *160*, A1169.

[5] J. Fanous, M. Wegner, J. Grimminger, M. Rolff, M. B. M. Spera, M. Tenzer, M. R. Buchmeiser, *J. Mater. Chem.* **2012**, *22*, 23240.

[6] M. R. Buchmeiser, *Polymer* **2007**, *48*, 2187.

[7] J. M. Spörl, A. Ota, R. Beyer, T. Lehr, A. Müller, F. Hermanutz, M. R. Buchmeiser, *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 1322.

[8] K. Okada, M. Nandi, J. Maruyama, T. Oka, T. Tsujimoto, K. Kondoh, H. Uyama, *Chem. Commun.* **2011**, *47*, 7422.

[9] M. Frey, R. K. Zenn, S. Warneke, K. Müller, A. Hintennach, R. E. Dinnebier, M. R. Buchmeiser, *ACS Energy Lett.* **2017**, *2*, 595.

[10] S. Warneke, M. Eusterholz, R. K. Zenn, A. Hintennach, R. E. Dinnebier, M. R. Buchmeiser, *J. Electrochem. Soc.* **2017**, *165*, A6017.

[11] S. Warneke, A. Hintennach, M. R. Buchmeiser, *J. Electrochem. Soc.* **2018**, *165*, A2093.

T. Lebherz, M. R. Buchmeiser
Institute of Polymer Chemistry University of Stuttgart
70569 Stuttgart, Germany

T. Lebherz, A. Hintennach
Daimler AG, RD/EBT, HPC G012-BB 71034 Böblingen, Germany

M. Frey
Daimler AG, RD/EBB, HPC X461 71059 Sindelfingen, Germany

M. R. Buchmeiser
German Institutes of Textile and Fiber Research (DITF) Denkendorf
73770 Denkendorf, Germany
E-mail: michael.buchmeiser@ipoc.uni-stuttgart.de

Arborescent Polymers via Living Radical Polymerization

Julian Robin Höhner, Jens Köhler, Helmut Keul, Cesar Rodriguez-Emmenegger, and Martin Möller

The arborescent, or Comb-Burst polymer architecture belongs to the dendrigraft family which can be described as treelike.[1,2] Living or controlled polymerization techniques enable the formation of linear core polymers. Post functionalization of the core polymer leads to a linear core polymer with either coupling or initiating sites. "Grafting onto" or "grafting from" are applicable to prepare a graft copolymer. This graft copolymer is named the 0. generation of an arborescent polymer. Performing another functionalization and grafting step, an arborescent polymer of 1. generation is built up. Iterating the functionalization and grafting step, arborescent polymers of higher generations are accessible. This reaction cascade is schematically depicted.

Since a precise polymerization control is a prerequisite, the synthesis of arborescent polymers was mainly limited to ionic polymerization techniques. Most commonly anionic polymerization followed by functionalization with coupling sites was performed. Subsequently, branches are introduced by grafting onto the coupling sites.[1–3]

Here, we present the synthesis of arborescent polymers using controlled radical polymerization in a "grafting from" approach. Contrary to ionic polymerization, radical polymerization enables the use of hydrophilic monomers. Furthermore, the reaction conditions are mild and water can be used as solvent.

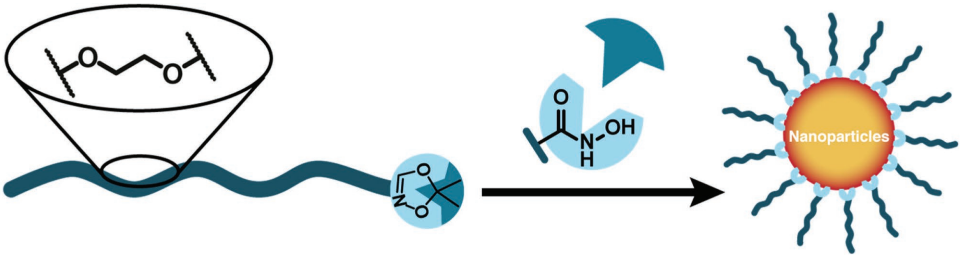
Based on computer simulations, arborescent polymers promise interesting behavior at interfaces.[4] Post cross-linking of arborescent polymers leads to microgel like structures. In this controlled manner, the influence cross-link density and sequence length has on flexibility in the transition from arborescent polymers to microgels can be studied.

J. R. Höhner, J. Köhler, H. Keul, C. Rodriguez-Emmenegger, M. Möller
DWI Leibniz-Institut für Interactive Materialien, RWTH Aachen
Forckenbeckstr. 50, 52074 Aachen, Germany

Hydroxamic Acid Functional Polyethers: A Versatile Class of Polymeric Chelators for Surface Coating and Medical Application

*Tobias Johann, Matthias Bros, and Holger Frey**

In the last two decades, biomimetic materials with chelating moieties, such as catechols have been investigated intensely. Particularly catechol-bearing polymers that mimic mussel-foot proteins containing L-dopamine have drawn huge interest, as their adhesive properties enable interaction with nearly every surface. Applications like self-healing hydrogels, solubilization of nanoparticles, or the formation of supramolecular networks have been demonstrated.[1] In previous works, our group developed the synthesis of catechol functional polyethers to combine the biocompatible properties of polyethers like poly(ethylene glycol) (PEG) with the adhesiveness of catechols.[2] PEG is known as the "gold standard" biocompatible, water-soluble polymer.[3] However, catechols are unstable under aqueous conditions and lead to irreversible cross-links via oxidative coupling. This reaction also forms highly toxic Michael systems, impeding their use for medical applications. As an alternative to catechol moieties, we report the use of hydroxamic acids as an oxidatively stable alternative. For this purpose, we developed an approach starting from hydroxamic acid bearing initiators for the oxyanionic ring opening polymerization of epoxide monomers to synthesize hydroxamic acid functional polyethers. We introduce the 1,4,2-dioxazole group as a suitable protecting group under the strongly basic reaction conditions. To demonstrate the scope of these compounds, several alpha-functional polyethers based on ethylene oxide (EO) were prepared. After cleavage of the protective groups, the hydroxamic acid-functional polymers revealed excellent complexation of numerous metal ions in aqueous solution as well their applicability in coating of nanoparticles and metal surfaces. It was shown that these polymeric chelators show the same complexation properties as low molecular weight hydroxamic acids, albeit with lowered toxicity. Hence, the combination of hydroxamic acids with polymers is a promising alternative to catechols with similar applicability, permitting high oxidative stability. The hydroxamic acid functional polyethers offer promise for iron-depletion therapies, biomedical purposes as well as materials science and surface coating (**Figure 1**).



---

[1] E. Faure, C. Falentin-Daudré, C. Jérôme, J. Lyskawa, D. Fournier, P. Woisel, C. Detrembleur, *Prog. Polym. Sci.* **2013**, *38*, 236.

[2] K. Niederer, C. Schüll, D. Leibig, T. Johann, H. Frey, *Macromolecules* **2016**, *49*, 1655.

[3] J. Herzberger, K. Niederer, H. Pohlit, J. Seiwert, M. Worm, F. R. Wurm, H. Frey, *Chem. Rev.* **2016**, *116*, 2170.

T. Johann, Prof. H. Frey
Institute of Organic Chemistry
Johannes Gutenberg University Mainz
Duesbergweg 10-14, DE-55128 Mainz Germany
E-mail: hfrey@uni-mainz.de

Dr. M. Bros
Department of Dermatology
University Medical Center of the Johannes Gutenberg University Mainz
Langenbeckstrasse 1, DE-55131 Mainz, Germany

Switchable 19F Magnetic Resonance Imaging Contrast Agents Prepared by Ring-Opening Metathesis Polymerization

*I. Kramberger Tennie, P. Liu, and A. F. M. Kilbinger**

There is a growing interest in developing stimuli-responsive magnetic resonance imaging (MRI) contrast agents which are sensitive to physiological variations in tissue microenvironment. Over the past two decades, many such Gd^{3+}-based MRI probes have been reported. However, due to the large water proton background, it is difficult to quantify stimulus-triggered change in MRI contrast.[1] With negligible background signal, wide chemical shift range, and excellent sensitivity second only to ^{1}H nucleus, ^{19}F MRI allows for tracking of a fluorinated contrast agent and measuring its response to a stimulus in a quantitative manner. Local rotational restriction, low spin-spin relaxation time T_2, poor water solubility and signal-to-noise ratio, on the other hand, are the major challenges of ^{19}F MRI.[2,3] Polymers are particularly suitable for such applications as a higher density of fluorinated species per polymer chain can be achieved compared to their single-molecule counterparts and different molecular switches can be incorporated into their side chains.

Here, we present MRI contrast-switchable water-soluble fluorinated polymers prepared by ring-opening metathesis polymerization (ROMP) with the 3rd generation Grubbs catalyst. Each monomer was equipped with a fluorinated and a stimuli-responsive moiety. The responsiveness of ^{19}F NMR relaxation times was obtained by modulation of either rotational correlation time τ_R or the magnetic properties of a proximate metal atom. In the first instance, the presence of pH-responsive subunits resulted in a reduced mobility of polymeric chains, shorter ^{19}F NMR relaxation times and a very broad ^{19}F NMR signal at pH 7.4 (Figure 1a). At a lower pH, the ^{19}F NMR signal was recovered due to improved solubility and flexibility of the submonomer units in water. Redox-responsive fluorinated polymers equipped with ferrocene moieties (**Figure** 1b) also exhibited a sharp ^{19}F NMR signal under non-oxidizing conditions. Upon oxidation, on the other hand, very short ^{19}F NMR relaxation times were observed due to paramagnetic relaxation enhancement (PRE) caused by ferrocenium cation. In both cases, the MRI contrast-switching was fully reversible and could provide an efficient means of probe tracking and (de-)activation by a physiological or pathological stimulus.

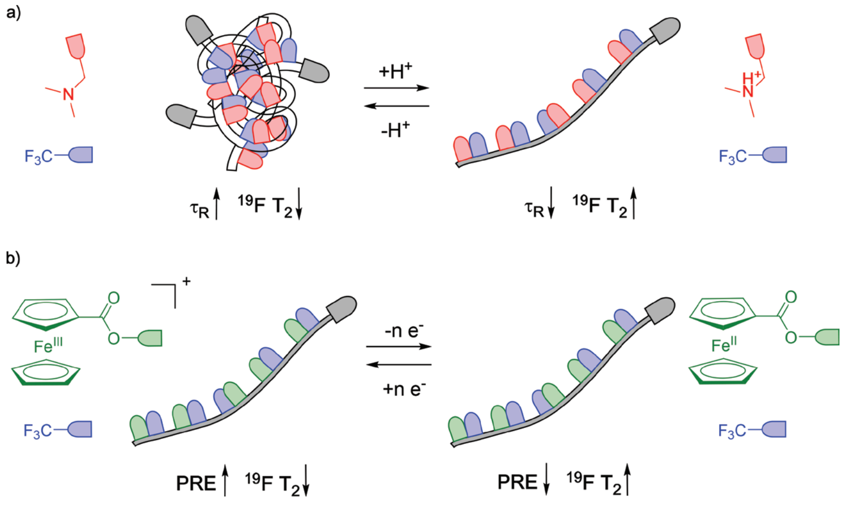


Figure 1. Schematic representation of fluorinated polymers, which exhibit a sharper and increased 19F NMR signal due to either a) increased rotational tumbling rate or b) paramagnetic relaxation enhancement.

---

[1] E. L. Que, C. J. Chang, *Chem. Soc. Rev.* **2010**, *39*, 51.

[2] I. Tirotta, V. Dichiarante, C. Pigliacelli, G. Cavallo, G. Terraneo, F. B. Bombelli, P. Metrangolo, G. Resnati, *Chem. Rev.* **2015**, *115*, 1106.

[3] J. Ruiz-Cabello, B. P. Barnett, P. A. Bottomley, J. W. M. Bulte, *NMR Biomed.* **2011**, *24*, 114.

I. K. Tennie, P. Liu, A. F. M. Kilbinger
Department of Chemistry, University of Fribourg
Chemin du Musée 9, CH-1700 Fribourg, Switzerland
E-mail: andreas.kilbinger@unifr.ch

Comparing Overall Initiation Efficiencies of (para-substituted) Mono-, Bis- and Tetraacylgermane Radical Initiators

Philipp Jöckle, Philipp W. Kamm, Iris Lamparth, Norbert Moszner, Andreas-Neil Unterreiner, and Christopher Barner-Kowollik**

We have quantified the overall initiation efficiency of eight mono-, bis-, and tetraacylgermane visible light photoinitiators with *para*-methoxy- and fluorine substitution patterns via pulsed laser polymerization (PLP) cocktail experiments in methyl methacrylate (MMA, bulk) with subsequent high-resolution electrospray mass spectrometry (ESI-MS) analysis. A PLP-ESI-MS cocktail experiment is a post mortem approach, which takes all critical events from light absorption to final macromolecular growth into account. Provided by the stoichiometric ratio of the number of benzoyl moieties, one would expect for the comparison of bis- versus mono-, resp. tetra- versus bis- an overall initiation efficiency of 2 and for tetra- versus monoacylgermanes a factor of 4. In contrast, a non-stoichiometric increase of 40–90% in the overall initiation efficiency is observed with increasing number of benzoyl moieties per initiator (maximum value of 7.6 1.8 for tetrabenzoylgermane vs benzoyltrimethylgermane). In addition, a strong correlation of the overall initiation efficiencies and the ratio of $n\pi^*$-extinction coefficients for unsubstituted acylgermanes is observed (deviation <7%). Acylgermanes with *para*-methoxy- and -fluorine-substitution patterns reveal only a weak correlation with the ratio of the $n\pi^*$-extinction coefficients (deviation of 20–50%). Substitution patterns have a strong influence on the branching between singlet and triplet hyperpotential energy surfaces of acylgermanes.[1,2] Further, time-dependent density functional theory (TDDFT) calculations suggest increasing channel branching possibilities when enlarging the system size from bis- to tetraacylgermanes. Thus, these investigations can be considered as an important step toward an in-depth mechanism of understanding relaxation pathways within the excited states manifold of these systems.

---

[1] W. Feuerstein, S. Höfener, W. Klopper, I. Lamparth, N. Moszner, C. Barner-Kowollik, A.-N. Unterreiner, *ChemPhysChem* **2016**, *17*, 3460.

[2] P. Jöckle, C. Schweigert, I. Lamparth, N. Moszner, A.-N. Unterreiner, C. Barner-Kowollik, *Macromolecules* **2017**, *20*, 8894.

[3] P. Jöckle, P. W. Kamm, I. Lamparth, N. Moszner, A.-N. Unterreiner, C. Barner-Kowollik, *Macromolecules* **2018**, unpublished.

P. Jöckle, P. W. Kamm, C. Barner-Kowollik
Macromolecular Architectures
Institut für Technische Chemie und Polymerchemie
Karlsruhe Institute of Technology (KIT)
Engesserstrasse 18, 76131 Karlsruhe, Germany
E-mail: philipp.joeckle@kit.edu

P. Jöckle, P. W. Kamm, Andreas-Neil Unterreiner
Molekulare Physikalische Chemie
Institut für Physikalische Chemie
Karlsruhe Institute of Technology (KIT)
Fritz-Haber-Weg 2,76131 Karlsruhe, Germany

P. Jöckle, P. W. Kamm, C. Barner-Kowollik
School of Chemistry, Physics and Mechanical Engineering
Queensland University of Technology (QUT)
2 George Street, QLD 4000, Brisbane, Australia

I. Lamparth, N. Moszner
Ivoclar Vivadent AG
Bendererstrasse 2, 9494 Schaan, Liechtenstein

Metallopolymer Architectures for the Preparation of Redox-Responsive Materials

*Christian Rüttiger, Sebastian Schöttner, Xiao Su, T. Alan Hatton, and Markus Gallei**

Stimuli-responsive polymers are well known to influence the macroscopic material's properties in the bulk state or at surfaces, for instance, by changing the polymer conformation by external stimuli, that is, temperature, light or solvents.[1] Compared to those classical stimuli, electrical field or the addition of chemical oxidation/reducing reagents are much less investigated. Within that field redox-responsive polymers especially metallopolymers are in focus of researchers for different applications in the last decade.[2] As one example, immobilized redox-switchable metallopolymers on cellulose-based substrates obtained after surface-initiated atom transfer radical polymerization (SI-ATRP) lead to switchable porous materials for triggered polarity and flux control.[3] Moreover, metallopolymers are excellent candidates for the preparation of selective electrochemical separation devices[4] or preceramic materials yielding advanced ceramics after thermal treatment.[5]

The preparation of highly ordered, porous functional materials has attracted significant attention due to the tremendous potential for various applications in fields of ion separation technologies, (optical) sensors, catalysis, or photonic materials.[6,7] The self-assembly of block copolymers can be used for the creation of almost perfectly structured materials on a length scale of a few ten nanometers. Using sequential living anionic polymerization strategies, various block copolymer architectures containing metallopolymers with their unique capability of self-organization in solution or in the bulk state can be prepared. Recently, polyisoprene- or polystyrene-based block copolymers with a second ferrocene-containing block segment were used for the preparation of ordered porous materials by different approaches comprising classical self-assembly and combination with the non-solvent induced phase separation process (SNIPS).[8,9] The resulting nanostructured materials are suitable for the preparation of redox-switchable cellulose-based materials, advanced porous ceramics, or smart redox-triggered membranes.

---

[1] K. M. Herbert, S. Schrettl, S. J. Rowan, C. Weder, *Macromolecules* **2017**, *50*, 8845.
[2] M. Gallei, C. Rüttiger, *Chem. Eur. J.* **2018**, *24*, 10006.
[3] C. Rüttiger, S. Mehlhase, S. Vowinkel, G. Cherkashinin, N. Liu, C. Dietz, R. W. Stark, M. Biesalski, M. Gallei, *Polymer* **2016**, *98*, 429.
[4] X. Su, K.-J. Tan, J. Elbert, C. Rüttiger, M. Gallei, T. F. Jamison, T. A. Hatton, *Energ. Environ. Sci.* **2017**, *10*, 1272.
[5] C. Rüttiger, V. Pfeifer, V. Rittscher, D. Stock, D. Scheid, S. Vowinkel, F. Roth, H. Didzoleit, B. Stühn, J. Elbert, E. Ionescu, M. Gallei, *Polym. Chem.* **2016**, *7*, 1129.
[6] F. H. Schacher, P. A. Rupar, I. Manners, *Angew. Chem., Int. Ed.* **2012**, *51*, 7898.
[7] T. Winter, X. Su, T. A. Hatton, M. Gallei, *Macromol. Rapid Commun.* **2018**, 1700648, DOI: 10.1002/marc.201700648.
[8] C. Rüttiger, H. Hübner, S. Schöttner, T. Winter, C. Gennady, B. Kuttich, B. Stühn, M. Gallei, *ACS Appl. Mater. Interfaces* **2018**, *10*, 4018.
[9] S. Schöttner, C. Rüttiger, M. Gallei, *Polymers* **2017**, *9*, 491.

C. Rüttiger, S. Schöttner, M. Gallei
Ernst-Berl-Institute for Technical and Macromolecular Chemistry
Technische Universität Darmstadt
Alarich-Weiss-Str. 4, D-64287 Darmstadt, Germany
E-mail: c.ruettiger@mc.tu-darmstadt.de; m.gallei@mc.tu-darmstadt.de

X. Su, T. Alan Hatton
Department of Chemical Engineering
Massachusetts Institute of Technology
MA 02139, USA

Electrospun Hybrid Nanofibers

*V. Nirwan, N. Herman and A. Fahmi**

Hybrid nanofibers become an important avenue to construct 1D nanostructure essential for the next generation of multifunctional compartments. In this poster, electrospinning tools will be presented as an alternative route to conventional nanofabrication methods for the fabrication of functional 1D-nanostructured hybrid materials. We explore the potential of electrospun hybrid nanofibers based on inorganic moieties developed in situ within self-assembled soft polymeric matrix to fabricate nanostructured hybrid nanofibers.[1] The main advantage of the in situ preparation is that the size and the size-distribution of the inorganic moieties can be controlled within the soft polymeric matrix.[2] Moreover, the ability of the polymeric matrix to self-assemble into ordered nanostructures can be exploited to direct the spatial arrangement of the inorganic moieties within the electrospun hybrid nanofibers.[3] The mechanism of the structures formation will be proposed with respect of the applied process under different conditions and parameters.

---

[1] A. Fahmi, *Adv. Polym. Sci.* **2015**, *267*, 351.

[2] A. Al-Kattan, V. P. Nirwan, E. Munnier, I. Chourpa, A. Fahmi, A. V. Kabashin, *RSC Adv.* **2017**, **7**, 1759.

[3] K. Stefanos, E. Ioannou, O. C. J. Andrén, I. S. Chronakis, A. Fahmi, M. Malkoch, G. Toskas, V. Roussis, J. Appl. Polym. Sci. **2018**, 135, 45949.

V. Nirwan, N. Herman, A. Fahmi
Faculty of Technology and Bionics
Rhein-Waal University of Applied Sciences
Marie-Curie-Straße 1, D-47533 Kleve, Germany
E-mail: Amir.Fahmi@hochschule-rhein-waal.de

Polymeric Photoacids – Monomer Design, Photostability, and First Steps Towards Light-Mediated Release

Felix Helmut Schacher, Felix Wendler, Jessica Tom, Maria Sittig, and Benjamin Dietzek

Light represents an attractive stimulus to release encapsulated cargo from drug delivery vehicles as its application can be controlled quite well both spatially and temporally. One straightforward methodology to impart light-response into polymeric materials is the use of photoacids, functional groups which undergo rather large changes in acidity upon irradiation with light of a suitable wavelength. With that, light stimulation can be translated into (local) changes in pH and—in an aqueous environment—also into changes in net charge and swelling degree.

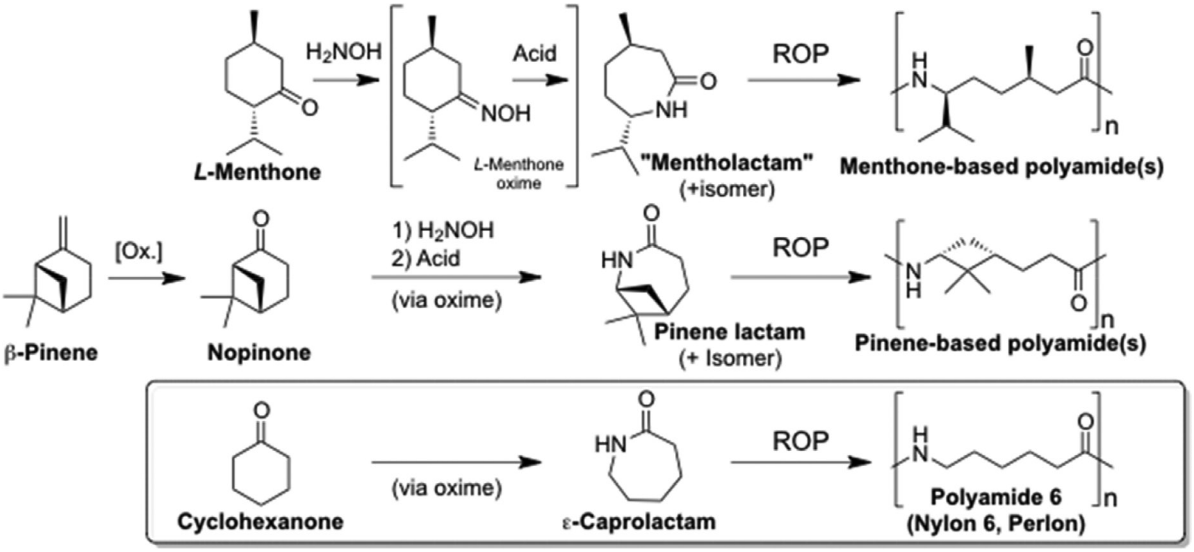
We herein present the synthesis and characterization of amphiphilic terpolymers and block copolymers containing photoacids based on 1-naphthol using reversible addition fragmentation chain transfer radical polymerization (RAFT). The respective photoacid comonomers were synthesized starting from 1-naphthol derivatives and with regard to photostability of the backbone linkage upon prolonged exposure to light irradiation we vary both the type of linkage as well as the distance of the active unit from the polymer backbone. After co- and terpolymerization, the resulting materials were characterized using size exclusion chromatography and UV/Vis absorption spectroscopy, the latter also enabling the determination of pKa in the ground as well as the excited state pK*. The concept was further extended to block copolymer micelles featuring photoacids in the hydrophobic core and upon irradiation reversible dissociation/re-association could be shown using light scattering experiments. As a model hydrophobe, Nile Red was encapsulated and light-triggered release where the release kinetics depended on the actual photoacid content could be demonstrated for different samples.

F. H. Schacher, F. Wendler, Dr. J. Tom, M. Sittig, Prof. B. Dietzek
Institut für Organische Chemie und Makromolekulare Chemie
Friedrich-Schiller-Universität Jena
Lessingstraße 8
07743 Jena, Germany

Sustainable Biopolymers from Terpenes and Novel Functional Biomaterials

Malte Winnacker, Jacob Sag, Andreas Beringer, and Bernhard Rieger*

Nature can provide a variety of building blocks for the synthesis of sustainable and functional polymers from renewable resources, whose exploration and utilization is a key issue in modern polymer chemistry. This natural pool of compounds is interesting and important in terms of alternative feedstock and green chemistry in general, but also and especially with regards to the novel and significant molecules and structures, that can thus be utilized for the preparation of advanced materials and that are not easily accessible via fossil-based pathways.[1,2] In this context, terpenes are very versatile and suitable building blocks for the synthesis of sustainable polymers, due to their abundance, low costs and in particular in terms of their interesting structures comprising, for example, side groups, stereocenters, and/or additional functionalities.[3] Polyamides are very important polymers for applications in many fields (consumables, biomedicine, automotive, ...), and their impact is growing. They are mainly synthesized via polycondensation of dicarboxylic acids and diamines or via ring-opening polymerization (ROP) of lactams (cyclic amides). In this context, we investigate the transformation of cyclic biobased terpenoid ketones (e.g., menthone or nopinone [derived from pinene]) to polyamides via their corresponding lactams.[4] This procedure works thus in analogy to the established fossil-based polyamide 6 (polycaprolactam, nylon 6, Perlon) synthesis via ε-caprolactam and leads to novel sustainable polyamides with side groups and stereocenters, which have an important impact on the properties (thermal, mechanical, ...) of the resulting polymers (**Figure 1**).



We also investigate new strategies for the utilization of these and related polymers, their (hydrophilized) copolymers and blends as biomaterials for the interactions with living cells. Also covalent attachment of biomolecules to these polymers is performed.[5] Thus, the properties of several components are combined, which results in enhanced features of the bioconjugates.[6]

Dr. M. Winnacker, J. Sag, A. Beringer, Prof. B. Rieger
WACKER-Lehrstuhl für Makromolekulare Chemie and Catalysis
Research Center Technische Universität München
Lichtenbergstraße 4, 85747 Garching bei München, Germany

[1] M. Winnacker, B. Rieger, *Macromol. Rapid Commun.* **2016**, *37*, 1391.
[2] R. Mülhaupt, *Macromol. Chem. Phys.* **2013**, *214*, 159.
[3] M. Winnacker, B. Rieger, *ChemSusChem* **2015**, *8*, 2455.
[4] Selected examples: a) M. Winnacker, J. Sag, *Chem. Commun.* **2018**, *54*, 841; b) M. Winnacker, M. Neumeier, X. Zhang, C. M. Papadakis, B. Rieger, *Macromol. Rapid Commun.* **2016**, *37*, 851; c) M. Winnacker, S. Vagin, V. Auer, B. Rieger, *Macromol. Chem. Phys.* **2014**, *215*, 1654.
[5] J.-F. Lutz, H. G. Börner, *Prog. Polym. Sci.* **2008**, *33*, 1.
[6] M. Winnacker, *Polym. Int.* **2017**, *66*, 1747.

Antimicrobially Active Polyzwitterions – A Paradigm Change?

K. Lienkamp, M. Kurowska, and A. Al Ahmad*

Polyzwitterions have been extensively explored as non-fouling coatings in the context of biomaterials and the prevention of biofilm formation on technical products.[1] They are highly cell-compatible and resist the adhesion of proteins, bacteria, and other biological entities.[2] It is believed so far that this is a passive property related to the strong water-binding of polyzwitterions, which otherwise have no intrinsic bioactivity. Indeed, the polyzwitterions that were explicitly tested so far showed no antimicrobial activity.[3]

Surprisingly, we recently found two polyzwitterions from which intrinsically antimicrobial polymer coatings could be obtained.[4] Additionally, they were protein-repellent, cell-compatible and reduced the growth of bacterial biofilms on surfaces.[4] The coatings were made from poly(oxonorbornene)-based carboxybetaines, which were surface-attached and cross-linked in one step by simultaneous UV-activated CH insertion and thiol-ene reaction. Importantly, this process was applicable to both laboratory surfaces like silicon, glass and gold, and real life surfaces like polyurethane foam wound dressings. Thus, the materials are promising candidates for biomedical applications.Is this a change in paradigm in the way we have to think about the bioactivity of polyzwitterions? And what makes some polyzwitterions antimicrobial and others inactive? To explore these questions, the chemical structure and physical properties of the two polyzwitterions and two reference surfaces (an antimicrobial but protein-adhesive cationic polymer coating, and a protein-repellent but not antimicrobial sulfobetaine polyzwitterion coating), were characterized using a number of surface characterization techniques, and correlated to their bioactivity. For this data, we begin to understand the factors that govern antimicrobial activity of polyzwitterions.

---

[1] a) A. Laschewsky, *Polymers* **2014**, *6*, 1544; b) J. B. Schlenoff, *Langmuir* **2014**, *30*, 9625; c) S. Lowe, N. M. O'Brien-Simpson, L. A. Connal, *Polymer Chem.* **2015**, *6*, 198; d) S. Jiang, Z. Cao, *Adv. Mater.* **2010**, *22*, 920; e) Z. Zhang, J. A. Finlay, L. Wang, Y. Gao, J. A. Callow, M. E. Callow, S. Jiang, *Langmuir* **2009**, *25*, 13516.

[2] G. Cheng, G. Li, H. Xue, S. Chen, J. D. Bryers, S. Jiang, *Biomaterials* **2009**, *30*, 5234.

[3] a) P. Sobolciak, M. Spirek, J. Katrlik, P. Gemeiner, I. Lacik, P. Kasak, *Macromol Rapid Commun*. **2013**, *34*, 635; b) Z. Cao, L. Mi, J. Mendiola, J.-R. Ella-Menye, L. Zhang, H. Xue, S. Jiang, Angew. *Chem., Int. Ed*. **2012**, *51*, 2602.

[4] a) M. Kurowska, A. Eickenscheidt, D. L. Guevara-Solarte, V. T. Widyaya, F. Marx, A. Al-Ahmad, K. Lienkamp, *Biomacromolecules* **2017**, *18*, 1373; b) M. Kurowska, A. Eickenscheidt, A. Al-Ahmad, K. Lienkamp, *ACS Applied Bio Materials* **2018**, https://doi.org/10.1002/acsabm.1028b00100.

K. Lienkamp, M. Kurowska
Freiburg Center for Interactive Materials and
Bioinspired Technologies (FIT)
Albert-Ludwigs-Universität Freiburg
E-mail: lienkamp@imtek.uni-freiburg.de

K. Lienkamp, M. Kurowska
Department of Microsystems Engineering
(IMTEK), Albert-Ludwigs-Universität Freiburg

A. Al Ahmad
Department of Operative Dentistry and Periodontology
Center for Dental Medicine
Albert-Ludwigs-Universität Freiburg

Polymer Synthesis Enabled by Interfaces: Towards a World of Organic 2D Materials

Xinliang Feng

Interface has been playing a key role in most “bottom-up” synthesis methods and is advantageous for directing the orientation of the molecules or precursors. By looking back at the history, the interfacial synthesis has been largely developed for the controlled polymer synthesis, which can be dated back to 1930s by Gee et al. who achieved polymer monolayers at an air–water interface. Typically, the reactions at the interfaces between air–water (or gas–liquid), liquid–liquid, liquid–solid, and gas–solid (or vacuum–solid) have been explored to offer paramount control over the morphology and the structure of polymers. While the synthetic linear polymers and cross-linked polymers are the main resultant structures in the historic interfacial polymer synthesis, it turns out only in recent years that a controlled 2D covalent reaction can take place if a finely designed interface is provided. A subsequent consequence of adsorption, nucleation, arrangement, and polymerization of suitably designed precursors or intermediates, guided by a confined 2D geometry of interface, can yield a structurally well-defined, periodic organic 2D material such as 2D polymer.

In this lecture, we will present our recent efforts on the bottom-up synthetic approaches toward novel organic 2D materials with structural control at the atomic/molecular-level or at the meso-scale. First, we will introduce the latest development on the synthetic 2D conjugated polymers including 2D Schiff-base type covalent polymers and 2D metal-dithienene/diamine coordination polymers at the air–water or liquid–liquid interfaces. The resulting 2D conjugated polymers exhibit single- to multi-layer feature, good local structural ordering and with a large size. The functional exploration of such 2D conjugated (coordination) polymers for the electrical, magnetic, and mechanical properties, as well as serving as efficient electrocatalytic water splitting catalysts will be demonstrated. Next, we will introduce the self-assembly of a host–guest enhanced donor–acceptor interaction, consisting of a tris(methoxynaphthyl)-substituted truxene spacer, and a naphthalene diimide substituted with *N*-methyl viologenyl moieties as donor and acceptor monomers, respectively, in combination with cucurbit[8]uril as host monomer toward monolayers of 2D supramolecular polymers at liquid–liquid interface. Third, we will present the supramolecular approaches to synergistically control the multi-component assembly, which results into 2D conducting polymers, such as polypyrrole and polyaniline nanosheets featuring 2D structures and with adjustable mesopores with/without on various functional free-standing surfaces. The unique structure with adjustable pore sizes (5–20 nm) and thickness (35–45 nm), enlarged specific surface area as well as high electrical conductivity make 2D conducting polymers promising for a number of applications. Finally, we will present a controlled synthesis of few-layer 2D polymer crystals on the water surface assisted by soft templates; we achieved micrometer-sized either horizontally or vertically grown 2D polyamide crystals by tailoring templating layers. The future perspective and outlook regarding the goal toward highly crystalline organic 2D materials will be also provided.

X. Feng
Center for Advancing Electronics Dresden and
Department of Chemistry and Food Chemistry
Technische Universitaet Dresden, Germany
E-mail: xinliang.feng@tu-dresden.de

Novel Self-Assemblies via Double Hydrophilic Block Copolymers in Aqueous Solution

Bernhard V. K. J. Schmidt

Self-assembly of block copolymers has a long tradition in polymer science. Especially amphiphilic block copolymers have been utilized frequently in the formation of micellar or vesicular structures in aqueous solution.[1] In the present contribution, a novel approach is shown, utilizing completely water soluble double hydrophilic block copolymers for self-assembly.

The formation of nano- to micro-scale aggregates from completely water-soluble block copolymers in aqueous solution is achievable, yet the choice of blocks is essential. Self-assembled structures are accessible even though completely water-soluble blocks are employed that do not show changes in water solubility in the observed temperature and pH range. The self-assemblies are formed due to significant differences in the hydrophilicity of the blocks and their distinct affinity to water, that is, the hydrophilic effect.[2,3] To facilitate future applications in drug-delivery, mostly block copolymers consisting of biocompatible blocks

will be presented, for example, poly(N-vinylpyrrolidone), poly(ethylene oxide), poly(2-ethyl-2-oxazoline), or poly(saccharides).[4–6] As the formed structures entail a complete hydrophilic nature, significant enhanced membrane permeability compared to traditional amphiphilic systems is expected. Furthermore, increased and controllable stability of the formed assemblies can be obtained via cross-linking moieties that do not alter the hydrophilic nature of the self-assembled structures. Moreover, the utilization of DHBCs in the synthesis of metal-organic mesocrystals will be discussed.[7] In such a way, crystal growth can be modulated to obtain unprecedented metal-organic polymer composites with remarkable morphologies.

In summary, a new concept of block copolymer self-assembly based on completely water-soluble and biocompatible polymers is presented as well as the effect of DHBCs on the formation of metal-organic mesocrystals (**Scheme 1**).

[1] D. E. Discher, A. Eisenberg, *Science* **2002**, *297*, 967.

[2] S. M. Brosnan, H. Schlaad, M. Antonietti, *Angew. Chem, Int. Ed.* **2015**, *54*, 9715.

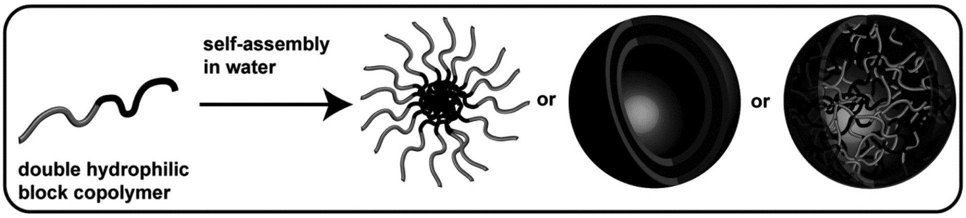
[3] B. V. K. J. Schmidt, *Macromol. Chem. Phys.* **2018**, *219*, 1700494.

[4] J. Willersinn, B. V. K. J. Schmidt, *Polymers* **2017**, *9*, 293.

[5] J. Willersinn, A. Bogomolova, M. B. Cabré, B. V. K. J. Schmidt, *Polym. Chem.* **2017**, *8*, 1244.

[6] N. Al Nakeeb, J. Willersinn, B. V. K. J. Schmidt, *Biomacromolecules* **2017**, *18*, 3695.

[7] J. Hwang, T. Heil, M. Antonietti, B. V. K. J. Schmidt, *J. Am. Chem. Soc.* **2018**, *140*, 2947.



Scheme 1. Double hydrophilic block copolymer self-assembly.

B. V. K. J. Schmidt
Department of Colloid Chemistry Max Planck
Institute of Colloids and Interfaces
14424 Potsdam, Germany
E-mail: bernhard.schmidt@mpikg.mpg.de

Fe-Catalyzed Ring-Opening Polymerization of Bio-Based Monomers

Axel T. Neffe

Ring-opening polymerization (ROP) of lactones by organometallic catalyst via a coordination-insertion mechanism is the standard procedure in order to synthesize hydrolytically degradable polymers with good control of molar mass and low polydispersity. Suitable monomers can be designed to contain amino acids or their derivatives, which allows structural variation while using biobased building blocks. 3-substituted morpholine-2,5-diones that can be advantageously be synthesized by the iodide-catalyzed ring-closure of α-halyoacyl amino acids,[1] are converted to the polydepsipeptides consisting of alternating α-amino and α-hydroxy acids by ROP, though this reaction is considerably less effective than the ROP of lactide or glycolide. We hypothesized that the chain transfer in the catalytic cycle can be supported while suppressing the formation of unreactive coordinated species by using a soft Lewis acid catalyst. A systematic variation of catalyst hardness and steric crowding investigating the efficacy of the classical $Sn(Oct)_2$ as standard in comparison to $Fe(OAc)_2$, $Mg(OEt)_2$, $In(OEt)_3$, $Al(OEt)_3$, and $Fe(OEt)_3$ in the ROP of 3(S)-(s-butyl) morpholin-2,5-dione (BMD) was conducted. The metal ethoxides gave only very limited molar masses coinciding with partial racemization (Mg, In), or did not catalyze the ROP at all (Al, $Fe(OEt)_3$). In contrast, $Fe(OAc)_2$ catalyzed the ROP effectively, resulting in oligoBMD with a $M_n = 5.8$ kDa, a polydispersity of 1.1 and a conversion ratio of 86 mol%, while no racemization was observed. This catalyst likewise performed well in the polymerization of serine- and tyrosine-based morpholinediones, outperforming $Sn(Oct)_2$. The use of Fe-based catalysts may be advantageous because of the lower environmental impact and lower toxicity of iron catalysts compared to tin catalysts. The depsipeptides can, for example, be used in the formation of submicron particles relevant for drug delivery purposes.[2]

---

[1] T. Naolou, A. Lendlein, A. T. Neffe, *Eur. Polym. J.* **2016**, *85*, 139.

[2] N. Brunacci, C. Wischke, T. Naolou, A. T. Neffe, A. Lendlein, *Eur. J. Pharm. Biopharm.* **2017**, *116*, 61.

Axel T. Neffe
Institute for Technical and Macromolecular Chemistry
University of Hamburg, Germany

Axel T. Neffe
Work partially performed at: Institute of Biomaterial Science and
Berlin-Brandenburg Center for Regenerative Therapies
Helmholtz-Zentrum Geesthacht
Teltow, Germany

Polarized Olefins as (Organo-)Catalysts for the Controlled Polymerization of O-Heterocyclic Monomers

*Patrick Walther, Alexander Balint, and Stefan Naumann**

N-heterocyclic olefins (NHOs), a novel class of polymerization catalyst, are characterized by a highly polarized double bond, which renders the molecules strongly basic and nucleophilic. This property can conveniently be tailored by the chemical structure of the catalyst and be employed for diverse polymerization reactions, both in metal-free setups as well as for dual catalytic processes where the NHO operates in conjunction with a Lewis acid. A prime example for these capabilities is the organocatalytic and solvent-free polymerization of propylene oxide (PO).[1] Traditionally challenging

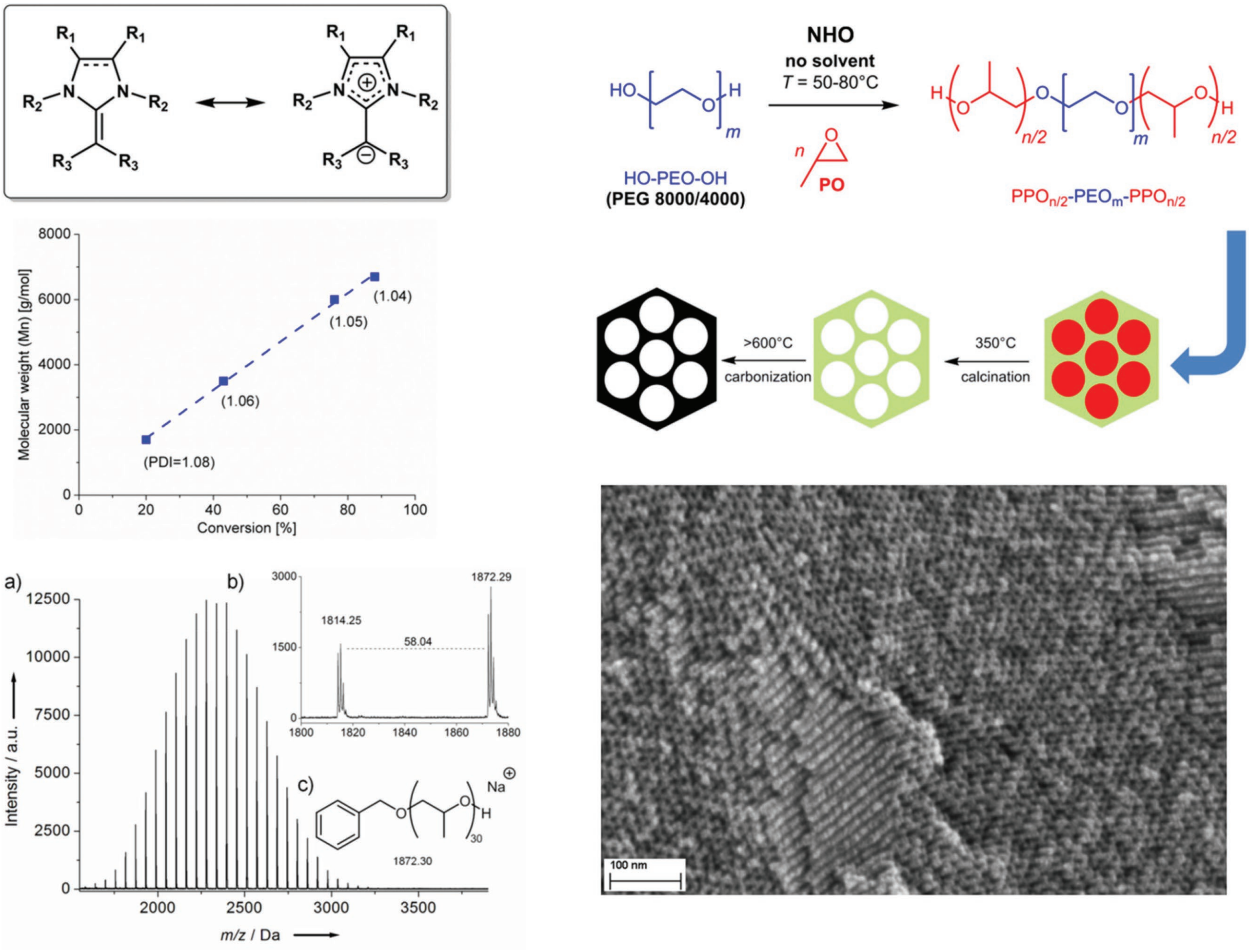


Figure 1. Left: Mesomeric structure rationalizing the strong polarization of NHOs and controlled polymerization of PO. Right: Preparation of amphiphilic triblock copoly(ether)s and conversion into (ordered) mesoporous carbon materials.

P. Walther, A. Balint, S. Naumann
Institute of Polymer Chemistry
University of Stuttgart
Pfaffenwaldring 55, D-70569 Stuttgart, Germany
E-mail: stefan.naumann@ipoc.uni-stuttgart.de

for metal-free ring-opening polymerization, the application of NHOs allows for an efficient conversion of this monomer (TON > 2000) with full control over molecular weights and end groups (M_n up to 12 kDa, $Đ_M \leq 1.09$). The polymerization mechanism is characterized by a base-nucleophile dualism, resulting in two different pathways being accessible: anionic and zwitterionic polymerization. By design of the NHO structure, this dualism can be shifted to exclusively favor a clean, anionic process. Crucially, in this setup transfer-to-monomer, a constant issue for anionic PO polymerization, is suppressed sufficiently to employ NHO-mediated catalysis as a tool to construct more complex poly(ether)s. This way, amphiphilic triblock-copoly(ether) PPO_n-PEO_m-PPO_n ("reverse Pluronics", n up to 200) could be prepared with molar masses exceeding 30 kDa while retaining excellent control over molecular weight distributions ($Đ_M \leq 1.03$).[2] This provides access to "reverse Pluronics" well beyond the limited commercial availability, allowing for higher molecular weights and defined, adaptable block-sizes in an operationally simple process. These polymers were then converted into a series of (ordered) mesoporous carbons via organic self-assembly to showcase the need for tailor-made copolymers as structure-directing agents. The diameter of the columnar pores generated in this manner can be tuned by adjusting the block size of the lipophilic PPO-entities. By applying the NHO in combination with very simple Lewis acids ($MgCl_2$, LiCl) as Lewis pair, the monomer scope can be extended to other O-heterocyclic monomers, including "non-polymerizable" ν-butyrolactone (GBL) and the macrolactone μ-pentadecalactone (PDL).[3–6] The presence of the metal halides is found not only to modulate polymerization rates and copolymerization parameters,[5] but also to influence the polymer topology (linear vs macrocyclic poly(GBL)) (**Figure 1**).[6]

---

[1] a) S. Naumann, A. W. Thomas, A. P. Dove, *Angew. Chem. Int. Ed.* **2015**, *54*, 9550; b) *Angew. Chem.* **2015**, *127*, 9686.

[2] A. Balint, M. Papendick, M. Cluass, C. Müller, F. Giesselmann, S. Naumann, *Chem. Commun.* **2018**, *54*, 2220.

[3] S. Naumann, D. Wang, *Macromolecules* **2016**, *49*, 8869.

[4] P. Walther, S. Naumann, *Macromolecules* **2017**, *50*, 8406.

[5] S. Naumann, P. B. V. Scholten, J. Wilson, A. P. Dove, *J. Am. Chem. Soc.* **2015**, *137*, 14439.

[6] P. Walther, W. Frey, S. Naumann, *Polym. Chem.* **2018**, *9*, 3674.

Chemical Approaches to Fiber Reinforced Polymers with Integrated Functions

Katharina Koschek, Hannes Schäfer, Tobias Urbaniak, and Katharina Haag

Fiber reinforced polymers (FRP) represent a technologically important class of materials used for light weight constructions in, for example, aerospace and automotive industry. FRPs based on conventional thermosetting matrices exhibit excellent mechanical properties due to their irreversibly crosslinked structure. This determines, however, the choice of industrial production processes and much more important complicates repair and recycling issues as well as functional integration. With the aim to overcome these restrictions, we follow a synthetic concept for stimuli-responsive polymers as matrix for FRPs based on reversible non-covalent interaction and covalent bonds, respectively. In case of reversible bonding, crosslinked polyester based polymers allow for repair and recycling of FRPs. In contrast, functionalized polyesters incorporated in thermosets like benzoxazines show thermoresponsive behavior enabling thermoforming approaches for FRP manufacturing and shape memory behavior for self-deployable structures.

K. Koschek, H. Schäfer, T. Urbaniak, K. Haag
Fraunhofer IFAM
Wiener Straße 12, 28359 Bremen, Germany