

POLYDAYS 2016

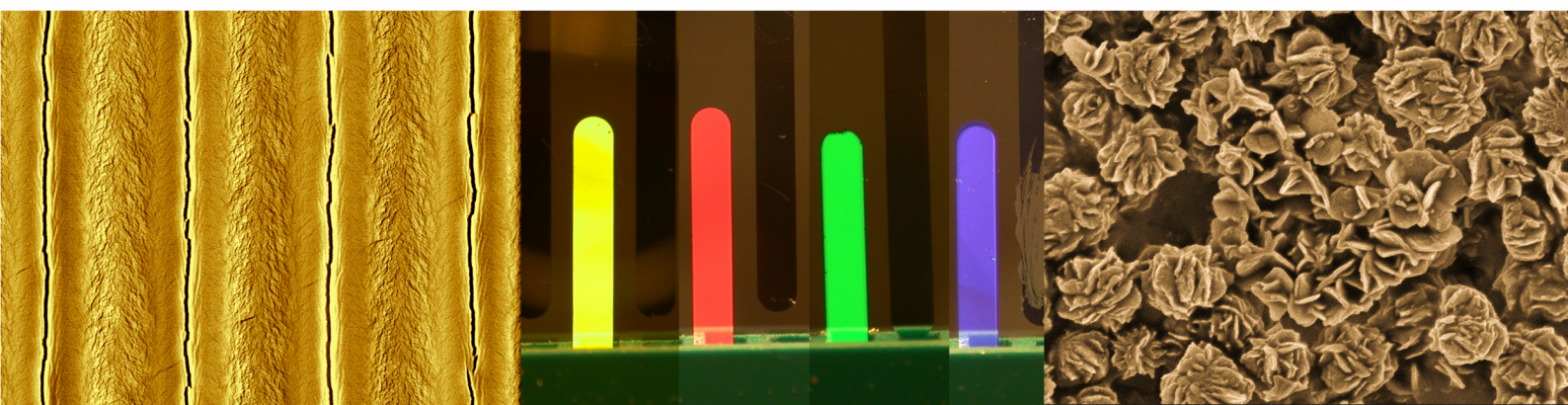
Integrating function into polymers:

- Bio-inspired and bio-based polymers
- Motion and transport in and on polymers

September 28 - 30, 2016

University of Potsdam

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Wednesday September 28		
12:30 – 14:00	Registration	
14:00 – 14:15	Welcome	
14:15 – 15:00	<i>Session Chair: Dieter Neher</i> Henning Sirringhaus «Charge and spin transport physics of high mobility organic semiconductors» Plenary Talk (Room 0.01)	
15:00 – 15:30	Coffee Break	
	Bio-inspired and bio-based polymers (Room 1.01) <i>Session Chair: Rainer Haag</i>	Motion and transport in and on polymers (Room 0.01) <i>Session Chair: Dieter Neher</i>
15:30 – 16:00	Markus Antonietti «Porous Polymers for Energy Conversion and Energy Storage»	Anna Köhler «On the role of delocalization in the photogeneration of charges in organic solar cell»
16:00 – 16:30	Günter Reiter «Non-equilibrium Properties of Crystallizable Polymers in Thin Films»	Emil List-Kratochvil «The Resistive Memory Hybrid Electronic Devices: Fundamental Considerations and Emerging Device Applications»
16:30 – 16:50	Gesine Gunkel-Grabole «Biomimetic polymer architectures at interfaces»	Ingo Salzmann «Molecular Doping of Conjugated Oligo- and Polymers: Fundamental Mechanisms and Dopant Design Rules»
16:50 – 17:10	Nina Kasyanenko «DNA-Polymer Complexes Containing Silver Nanoparticles and Fluorescent Dyes»	Olga Guskova «Charge transport in crystalline phases of small conjugated molecules consisting of electron-acceptor core and electron-donor flanking units»
17:10 – 17:30	Jiayin Yuan «Porous gradient polymer membranes: from fabrication to actuation»	John Love «Dispersive Charge Transport and Recombination in Polymer Solar Cells»
17:30 – 18:00	Coffee Break	
18:00 – 20:00	Poster Session Snacks and drinks	

Thursday September 29		
09:15 – 10:00	<i>Session Chair: Helmut Schlaad</i> Peter Fratzl «Adaptive polymeric materials in biological organisms» Plenary Talk (Room 0.01)	
10:00 – 10:45	Olli Ikkala «Self-Assemblies, Hierarchies and Biomimetics based on Polymers Combining Supramolecular and Supracolloidal Motifs» Plenary Talk (Room 0.01)	
10:45 – 11:15	Coffee Break	
	Bio-inspired and bio-based polymers (Room 1.01) <i>Session Chair: Andreas Lendlein</i>	Motion and transport in and on polymers (Room 0.01) <i>Session Chair: Jürgen P. Rabe</i>
11:15 – 11:45	Rainer Haag «Multivalent 1D, 2D and 3D Polymers as Potent Inhibitors for Pathogens»	Daniela Wilson «Emergent Functions of Polymeric Nanocapsules with Controlled Shapes»
11:45 – 12:05	Marie Weinhart «Thermoresponsive Polyglycidylether Brushes for Cell Sheet Fabrication: A Correlation of Surface Parameters and Cell Response»	Joachim Dzubiella «Rational design of stimuli-responsive nanoreactors»
12:05 – 12:25	Marga Lensen «Micro- and Nano-Patterning of PEG-Hydrogels to control Cell Adhesion, Migration and Growth»	Arri Priimägi «Azobenzene-based surface patterns revisited: New insights with new materials?»
12:25 – 14:00	Lunch	
	Bio-inspired and bio-based polymers (Room 1.01) <i>Session Chair: Helmut Schlaad</i>	Motion and transport in and on polymers (Room 0.01) <i>Session Chair: Svetlana Santer</i>
14:00 – 14:30	Eva Malmström «Surface Modification of Cellulose Substrates – Covalent and Non-Covalent Approaches using Controlled Polymerization»	Marina Saphiannikova «Light-induced deformations in azobenzene functionalized polymers: orientation approach vs. photofluidization concept»
14:30 – 15:00	Michael Meier «Sustainable approaches to monomers and polymers from renewable resources»	Dick Broer «Mechanically active polymer surfaces at liquid crystal network coatings»
15:00 – 15:20	Axel Neffe «Design Strategy for the Elucidation of Protein-Protein-Binding Epitopes, and Application of the Derived Peptides in Biomaterials»	Oswald Prucker «Artificial Cilia»
15:20 – 15:40	Niels ten Brummelhuis «Controlling monomer sequence using supramolecular interactions»	Jarosław Myśliwiec «Photophysical Transformations of Luminescent Derivatives of Pyrazoline»

**Thursday
September 29**

15:40 – 16:15 **Coffee Break**

16:15 – 17:15 *Session Chair: Jürgen P. Rabe*
Alexei Khokhlov
 «Biomimetic organo-catalysis by nanostructured macromolecules»
Gerhard Kanig Lecture (Room 0.01)

18:30 **Dinner**

**Friday
September 30**

Bio-inspired and bio-based polymers

(Room 1.01)

Session Chair: André Laschewsky

Motion and transport in and on polymers

(Room 0.01)

Session Chair: Reimund Gerhard

09:15 – 09:45	Harm-Anton Klok «Engineering Cell Surfaces with Synthetic Polymers»	Katja Loos «From metallic gyroid structures to piezoelectric nanoporous networks»
09:45 – 10:05	Wei Chen «Cyclo(RGD)-Decorated Redox-Responsive Nanogels Mediate Targeted Chemotherapy of Integrin Over-Expressing Human Glioblastoma In Vivo»	Alexander Böker «Two-dimensionally ordered AuNP arrays via microcontact printing on lamellar diblock copolymer films»
10:05 – 10:25	Yan Lu «Thermosensitive Microgels as “active” nanoreactors for tuning the catalytic activity of metal/metal oxide nanoparticles»	Rychkov Dmitry «Improving Charge Trapping on Polymer Surfaces»
10:25 – 10:45	Andreas Thünemann «(Bio)polymers tune the catalytic activity of silver nanoparticles»	Oliver Reich «Combination of fiber optical methods for monitoring dynamic changes during the switching process of PNIPAM particles»

10:45 – 11:15 **Coffee Break**

11:15 – 12:00 *Session Chair: Svetlana Santer*
Metin Sitti
 «Synthetic and Bio-hybrid Untethered Mobile Microrobots»
Plenary Talk (Room 0.01)

12:00 – 12:15 **Farewall Talk**

12:15 **Lunch**

Charge and spin transport physics of high mobility organic semiconductorsH. Sirringhaus

*^aCavendish Laboratory, University of Cambridge, Thomson Avenue,
Cambridge CB3 0HE, UK*

Keywords: Charge transport, Spin, Organic semiconductors

Over recent years there has been tremendous progress in developing low-temperature, solution-processible organic semiconductors that provide high charge carrier mobilities for both n-type and p-type device operation, good operational stability and other functionalities such as efficient electroluminescence, sensing or memory functions for a variety of applications. Here we are interested in understanding the charge transport physics of high mobility conjugated polymers and molecular semiconductors and the relationship between molecular structure, polymer microstructure and charge transport. Many of the recently discovered high mobility polymers, in particular donor-acceptor copolymers, are characterised by a puzzling lack of pronounced crystalline order. In this presentation we will present our current understanding of the transport physics of these materials and of the reasons why these materials exhibit such high carrier mobilities. We will also present new approaches to study the transport of spin currents through these materials.

Porous Polymers for Energy Conversion and Energy Storage

Markus Antonietti^a, Dariya Dontsova^a, Nina Fechner^a, Menny Shalom^a

^a*Max Planck Institute for Colloids and Interfaces, Research Campus Golm,
14424 Potsdam, Germany, antonietti@mpikg.mpg.de*

Keywords: Energy polymers, 2d-polymers, polymer frameworks, photoelectrocatalysis

Some recent observations made polymeric graphitic Carbon Nitride a valuable extension to current semiconducting organic materials. This is due to the ease of synthesis, but also due to its extreme chemical stability. Made from urea under early-Earth conditions, as reported already by Justus Liebig in 1832, it just recently turned out to be a novel catalyst which- among other reactions- can even chemically activate CO₂ or photochemically turn water into hydrogen and oxygen. This opens the door to artificial photosynthesis on the base of a sustainable and most abundant polymer base.

I will also present first schemes on chemical reactions where the electronic properties of C₃N₄ are generalized to other reactions, with C/N-nanostructures successfully mimicking oxidation enzymes with high conversions and selectivity. Copolymerization is here used to adjust electronic properties and coupled reactivity. Such polymers can be “hybridized” with enzymes to generate more complex molecules photochemically via cofactor coupling, as shown by the highly efficient chiral reduction of ketones by light.

Another promising application field of polymers is in electrodes for batteries and supercapacitors. Here polymer technology is (foreseeable) able to replace rare and noble metals for electron storage, but also in common electrocatalysis. I will exemplify some cases of materials with high specific surface area where new polymers are made by monomer prealignment and unconventional two-dimensional condensations reactions. To our surprise, in many cases it is the polymer species showing the highest activity and not a further carbonized product. If time allows, I will also talk about the application of such systems in advanced electrochemistry.

On the role of delocalization in the photogeneration of charges in organic solar cells

Steffen Tscheuschner,^a Stavros Athanasopoulos,^b
Heinz Bässler,^c and Anna Köhler^{a,c*}

^a *Experimental Physics, University of Bayreuth, Bayreuth, 95440, Germany.*

^b *Departamento de Física, Universidad Carlos III de Madrid, 28911 Leganés, Madrid, Spain*

^c *Bayreuth Institute of Macromolecular Research (BIMF), University of Bayreuth, Bayreuth, 95440, Germany.*

While it is meanwhile well established that the delocalisation of excited states and charge carriers plays a key role in the dissociation and recombination of opposite charges at interfaces, it is at present difficult to implement this in current theoretical approaches. Here we present a model,[1,2] based on the work by Arkhipov and coworkers[3] as well as Baranovskii and co-workers[4]. The key idea is that the delocalization of the charge carrier reduces the binding energy of the dissociating “cold” charge-transfer state through an additional “kinetic” energy term, quantified in terms of an “effective mass”. The effects of dipoles present at the interface in the dark are also considered. Spectroscopy of the charge-transfer state at bilayer solar cells as well as measurements of the current-voltage curves over a broad temperature range support the theoretical predictions.

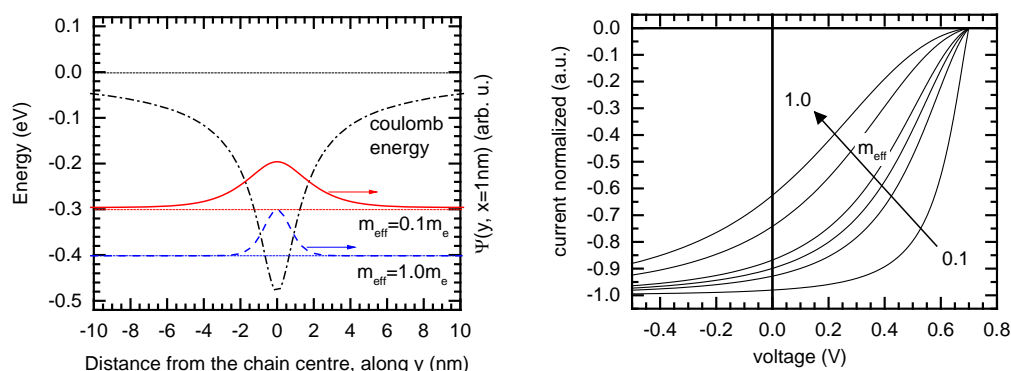


FIGURE 1. (a) The calculated impact of delocalisation on the fill factor. (b) The binding energy of the charge transfer state for the well delocalized case (effective mass = 0.1) and for the localized case (effective mass = 1)

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Non-equilibrium Properties of Crystallizable Polymers in Thin Films

Günter Reiter^a, Bin Zhang^{a,b}, Sivasurender Chandran^a

^a Institute of Physics, Albert Ludwig University of Freiburg, 79104 Freiburg, Germany

^b School of Materials Science & Engineering, Zhengzhou University, Zhengzhou 450002, China

Keywords: Dewetting, Transient Cooperative Processes, Sample History, Metastable States

Despite an extensive number of investigations, it is becoming increasingly obvious that we have not yet reached a clear understanding of properties of polymers in thin film. The origin of (some of) the puzzling behavior of thin polymer films is still not satisfactorily unveiled. We will present various findings, mainly observed in dewetting experiments, which demonstrate the influence of sample preparation and sample history on properties of crystallizable polymers.

We first compare the high velocity dewetting behavior, at elevated temperatures, of atactic polystyrene (aPS) and isotactic polystyrene (iPS) films, with the zero shear bulk viscosity (η_{bulk}) of aPS being approximately ten times larger than that of iPS [1]. As expected, for aPS the apparent viscosity of the films (η_f) derived from high shear dewetting was less than η_{bulk} , displaying a shear thinning behavior. Surprisingly, for iPS films, η_f was always larger than η_{bulk} , even at about 50 °C above the melting point, with $\eta_f / \eta_{\text{bulk}}$ following an Arrhenius behavior. The corresponding activation energy of $\sim 160 \pm 10$ kJ/mol for iPS films suggests a cooperative motion of segments, which were aligned and agglomerated during fast dewetting.

In the second part, we investigated the stability and crystallization behavior of a polygon-network of thin filaments of polyethylene (PE), generated by dewetting during spin-coating of a ultra-thin film [2]. Due to the shear forces occurring in the course of dewetting, the PE-chains in the filaments were stretched, corroborated by their partial decoration with edge-on lamellar crystals resulting in so-called shish-kebab structures. Above 134 °C, the filaments exhibited a liquid-like behavior and were thus prone to decay to droplets according to the Plateau-Rayleigh instability. Intriguingly, even at temperatures up to 100 degrees above the melting temperature of PE filaments as small as 50 nm did not decay into droplets. We tentatively conclude that polymer chains confined in nanoscopic filaments kept a long-living memory of the dewetting induced stretching.

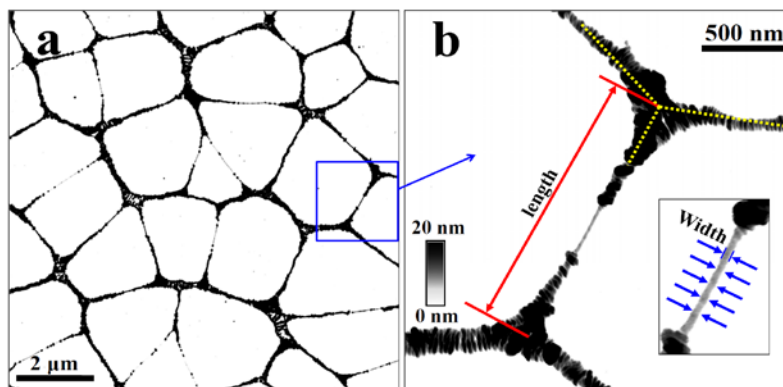


FIGURE 1. Dewetting patterns observed by atomic force microscopy of samples produced by spin-coating a dilute solution of 0.02% of UHMWPE in p-xylene onto a 70 °C hot silicon wafer.

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The Resistive Memory Hybrid Electronic Devices: Fundamental Considerations and Emerging Device Applications

Emil J.W List-Kratochvil

Institut für Physik, Institut für Chemie & IRIS Adlershof, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 6, 12489 Berlin, Germany

Keywords: resistive memory devices, optical switching, inkjet printed electronics

Electrically tunable resistors realized in two terminal structures seem to be one of the most versatile innovations in the semiconductor industry with many possible applications such as logic circuitry or neuromorphic systems. In particular, inorganic resistive switching devices utilized as non-volatile memory are close to commercialization. Also resistive switching effects in organic devices have been presented in a multitude of devices and novel materials. Recently the fabrication of organic resistive switches using environmentally friendly inkjet-printing methods and their integration into fully functional hybrid crossbar array structures has been demonstrated [1].

To further expand the usage of organic resistive switches in integrated devices in this contribution we show a unique imaging device concept and its utilization in an organic, flexible detector array with a simple passive matrix wiring. The application of photo-switchable non-volatile resistive multi-bit 2-terminal devices as pixels is demonstrated. This approach is based on a vertical stack consisting of an organic photo diode (OPD), acting as photosensitive element and an organic non-volatile multi-bit resistive switch (ORS), acting as image information storage element. In addition to a basic on/off operation mechanism, a grey-scaling capability based on the multi-bit capability of the ORS is demonstrated up to 4-bit. Moreover, in the serial connected device stack the OPD not only acts as the light-sensitive element but given its high rectifying behavior also renders a selector element allowing for passive matrix addressing in the array. The proper functionality of this concept is demonstrated in single elements and array structures up to 32 by 32 cells (1024 bit), integrated into an organic and flexible passive-matrix image detector array. [2]

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Biomimetic polymer architectures at interfaces

Gesine Gunkel-Grabole^a, Cornelia Palivan^a, Wolfgang Meier^a

^aUniversity of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

Keywords: biomimetic membrane, block copolymer, polymersome, surface immobilization

Amphiphilic block copolymers can self-assemble into membranes that structurally resemble cell membranes.[1] Yet the polymers can add additional properties to a biomimetic membrane such as increased stability and tunability. The huge variety of monomers available to synthesize block copolymers gives access to a library of functionalities that are explored to specifically modulate interactions.

Planar polymer membranes on solid support form an excellent model system to study membrane-specific properties and interactions, and they can be employed to generate biomimetic surfaces with predetermined activity. Besides the formation of planar membranes, amphiphilic block copolymers can also self-assemble into spherical, nanometer-sized architectures such as micelles and vesicles.[2] Through chemical modification of the polymer chains, the nanoarchitectures can be decorated with reactive moieties to facilitate their immobilization and to yield functional nanostructured surfaces. Overall, this advantageous combination of synthetic polymers and biomimetic membranes opens up a plethora of potential applications as biofunctional surfaces and beyond.

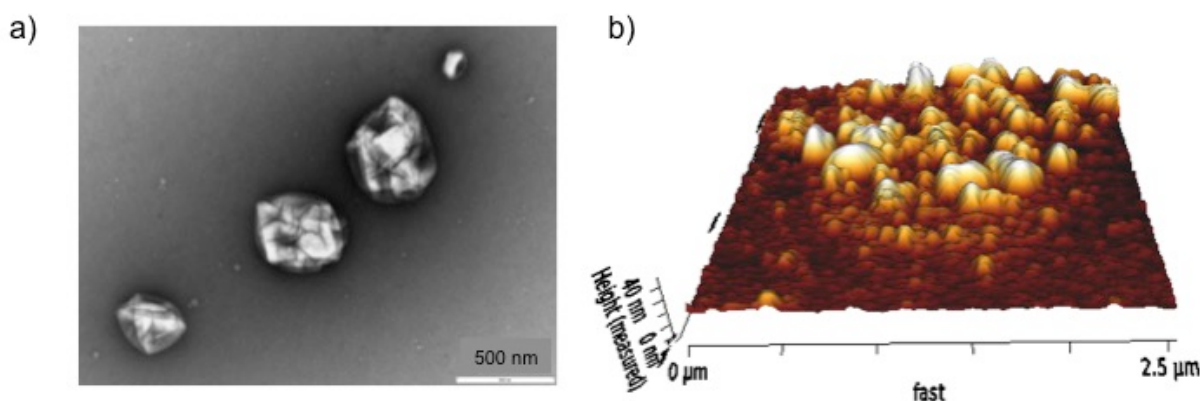


FIGURE 1. Biomimetic polymer vesicles in solution after their preparation, visualized by transmission electron microscopy (a). These nanoarchitectures remain intact after covalent immobilization on solid substrates as evidenced by atomic force microscopy measurements (b).

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Molecular Doping of Conjugated Oligo- and Polymers: Fundamental Mechanisms and Dopant Design Rules

I. Salzmann^a, G. Heimel^a, M. Oehzelt^b, S. Winkler^b, N. Koch,^{a,b}

^aHumboldt Universität zu Berlin, Institut für Physik, Berlin, Germany

^bHelmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

Keywords: molecular electrical doping, electronic structure, conjugated oligo- and polymers

In contrast to inorganic semiconductors, the potential of doping organic semiconductors (OSCs) for enabling new functionality and improving opto-electronic device performance has only recently been established. There, *p*-doping OSCs is done by the admixture of strong molecular acceptors like, e.g. tetrafluoro-tetracyanoquinodimethane (F4TCNQ). Compared to inorganics, however, the doping efficiency remains conspicuously low for OSCs, which highlights the fact that, still, the underlying fundamental mechanisms are less well understood.

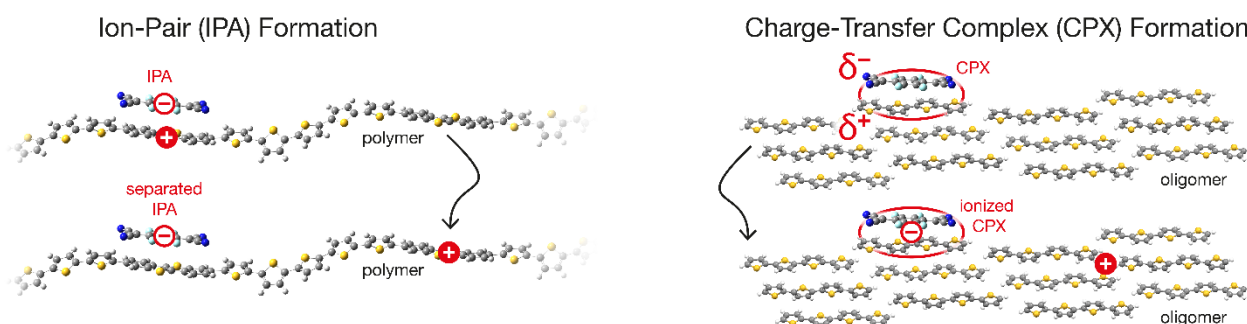


FIGURE 1. The two fundamental processes observed upon molecular doping: IPA (left) and CPX formation (right).

Here, the broad range of phenomena observed upon molecularly doping conjugated polymers (CPs) and molecules (COMs) is discussed, from which, finally, two different competing scenarios emerge [1]: (i) the formation of both OSC and dopant ions through integer-charge transfer, i.e., an ion pair (IPA), and (ii), the emergence of OSC/dopant ground-state charge transfer complexes (CPXs) through supramolecular hybridization (Figure 1). Experimental evidence for the exclusive occurrence of always one scenario is presented for a number of prototypical doped CPs/COMs, with a special focus on the F4TCNQ doping of poly(3-hexylthiophene) (P3HT), which is juxtaposed with that of quaterthiophene (4T), where IPA formation occurs for the polythiophene while CPX formation is found for the 4T oligomer instead [2].

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DNA-Polymer Complexes Containing Silver Nanoparticles and Fluorescent Dyes

Nina Kasyanenko^a, Vladimir Bakulev^a, Igor Perevyazko^a, Tatiana Nekrasova^b, Olga Nazarova^b, Alexandr Slita^c, Yulia Zolotova^b, Euginii Panarin^b

^a*Faculty of Physics, St. Petersburg State University, 198504,
Ul'janovskaja street 1, Petrodvoretz, Saint-Petersburg, Russia*

^b*Institute of Macromolecular Compounds, Russian Academy of Sciences, 199004,
Bolshoy pr. 31, Saint-Petersburg, Russia*

^c*Research Institute of Influenza, Molecular Virology Department, 15/17,
Prof. Popova str., St. Petersburg, Russia, 197376*

Keywords: DNA-PDMAEM complexes, silver nanoparticles, DAPI

Creation of multifunctional nanoplateforms is one of the new approaches to complex treatment and diagnosis with the monitoring of the curative process. The inclusion of various components into the drug wdelivery system may reduce the toxicity and enhance or modify the therapeutic effects of medicines. In particular, unique optical, electrochemical and catalytic properties of metal nanoparticles (NPs) and nanoclusters (NCs) provide the ability to create new systems for treatment and diagnosis of diseases, biocatalysis and imaging of objects. For example, the ability of metal nanoparticles to enhance the quantum yield of luminescence can be used.

The aim of the research was to construct and examine complexes on the basis of DNA-polycation compact structure with the inclusion of silver nanoparticles and luminescent dye as a model system for delivery of genes and drugs with the possibility of modification and enhancement of their action. In the present study we have tested the ability of silver nanoparticles to enhance the luminescence of dyes in such systems. The model system, which is the result of DNA interaction with silver NPs stabilized by PDMAEM has been studied. The luminescent dye 4',6-Diamidino-2-phenylindole, DAPI, was also used. This compound is a well-known drug and specific DNA marker. The complexes were examined with dynamic light scattering, viscometry, sedimentation, electrophoresis, atomic force and scanning electron microscopy. The fluorescence of DAPI in DNA-PDMAEM complexes in compact and in coil-like states with and without silver NPs was investigated. Commercial calf thymus DNA (Sigma) with a molecular mass of 11×10^6 was used; molecular mass was calculated from the value of the intrinsic viscosity of DNA in 0.15 M NaCl. Molecular mass of PDMAEM was 20,000. T-98G cell culture (ATCC® CRL-1690™) was used in the experiments for the study of transfection activity of PDMAEM-Ag complexes with pGFP plasmid. DNA-polymer complexes with luminescent silver NCs were also examined. Silver NPs were indicated in a solution with plasmon resonance peak, and silver NCs were observed with the apearance of the luminescence. The analysis of DNA polyelectrolyte swelling in a solutions with components under study and DNA persistent length was done.

Charge transport in crystalline phases of small conjugated molecules consisting of electron-acceptor core and electron-donor flanking units

Olga Guskova^{a,b}

^a*Institute Theory of Polymers, Leibniz-Institute of Polymer Research Dresden,
Hohe Str. 6, 01069 Dresden, Germany*

^b*Dresden Center for Computational Materials Science (DCMS),
Technische Universität Dresden, 01062 Dresden, Germany*

Keywords: multiscale simulation, diketopyrrolopyrrole, bithiophene, charge transport

In recent years, diketopyrrolopyrrole (DPP)-containing molecules have received growing scientific interest from polymer chemists and physicists for their characteristic properties. In such materials the bicyclic DPP core is usually flanked on both sides with aromatic rings [1]. Especially, mono- or bithiophene-containing motifs (TH) have been widely incorporated into conjugated chains [2], since polymers combining electron-acceptor core and electron-donor thiophene flanking units demonstrate unique structural, spectroscopic and electrochemical characteristics. First of all, these materials are designed to combine the best properties of both components. On the other side, the coupling of building units enables structurally synergistic effects, which facilitate both enhanced molecular packing and long-range order.

In the spotlight of this talk will be the structural, electronic and intrinsic transport properties of a model system consisting of diketopyrrolopyrrole core with bithiophene flanking units described at different time and length scales. On the molecular level, the conformational and electronic properties, *e.g.* ionization potential, electron affinity, band gaps, the barriers to inter-ring rotation are characterized using density functional theory calculations. For self-exchange reaction as a model for intermolecular transport, the total reorganization energies are evaluated. On the supramolecular level, the crystal packing prediction of rigid DPP-TH molecules is applied. This approach predicts the realistic charge transfer pathways for the calculation of charge transfer couplings between adjacent DPP-TH molecules, *i.e.* interacting dimers, and identifies the dominant transport paths for selected crystal arrangements. Finally, charge transfer rates and charge carrier mobilities are evaluated.

The obtained results shed light not only on the material properties of the samples containing low-molecular species, but also serve as a benchmark system for further classical force-field simulations of DPP-TH polymers.

The funding by ESF Young Investigators Group “CoSiMa – Computer Simulations for Materials Design” at DCMS, project AG10 “Boosting functional design of ambipolar organic semiconductors for advanced flexible electronics” is highly appreciated.

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Porous gradient polymer membranes: from fabrication to actuation

Karoline Taeuber, Huijuan Lin, Jiang Gong, Ryan Guterman, Jiayin Yuan*

Max Planck Institute of Colloids and Interfaces, D-14424 Potsdam, Germany

Keywords: poly(ionic liquid), porous membrane

Functional porous membranes with high surface area can be applied in broad fields, including catalysis, separation, filtration and energy applications.[1] There are a number of established methods for the preparation of porous membranes from neutral or weakly charged polymers. However, porous membranes from strong polyelectrolytes are far more difficult to prepare. Here we present our approach to porous polymer membrane materials from poly(ionic liquid)s.[2]

Poly(ionic liquid)s (PILs), a subset of polyelectrolytes, are the polymerization products of ionic liquids (ILs). They combine the advantages of polymeric materials, such as durability and good processability with the unique properties of ILs, such as tunable solubility in organic solvents with different polarity, ion conductivity, and high thermal stability.[3] We have exploited these favorable properties to fabricate porous membranes from imidazolium based PILs and polyacids, triggered by electrostatic complexation between them.[4-6] The pore structure forms as a result of microphase separation and is further stabilized by ionically crosslinked networks between the PIL polycation and the in-situ neutralized multivalent organic acids. The as-obtained membrane features a gradient profile in the cross-linking density along the membrane cross-section, triggered by the penetration of the base molecule from the top to the bottom into the material. The membrane pore sizes can be tuned from nanometer to micrometer scale by varying the degree of electrostatic complexation. Furthermore, the membrane features high actuation speed in response to acetone and humidity on account of its gradient in cross-linking density combined with its porous nature that enhances the mass transport inside the membrane. Such membranes may serve as environmental sensors to detect pH and solvent quality.[7]

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Dispersive Charge Transport and Recombination in Polymer Solar Cells

John A. Love, Dieter Neher

*University of Potsdam, Institut für Physik und Astronomie
Karl-Liebknecht-Straße 24–25, 14476 Potsdam-Golm, Germany*

Keywords: Semiconducting polymers, Solar Cells, Charge transport

Consistent improvements in the performance of organic optoelectronic devices over the last several decades have pushed them ever closer towards commercial relevance and the realization of their great potential as transformative technologies. One of the major challenges facing organic semiconductors, in contrast to their inorganic counterparts, is relatively poor charge transport. Charge transport does not follow classic band transport, but occurs via hopping through a broad distribution of localized electronic states. Yet, despite its fundamental importance, charge transport, and the role of thermalization in semiconducting polymer systems, remains highly debated.

Here we address the question of how thermalization of photogenerated charge determines the dynamics of charge transport and non-geminate recombination in the PCDTBT:PCBM polymer solar cell system. We do this by combining state of the art steady state and dynamic charge extraction methods under application-relevant conditions. We introduce a new device architecture with a perovskite charge generation layer which allows the measurement of transient mobility individually of holes and electrons directly in the bulk heterojunction blend film as a function of temperature, time, density, and field. We compare the results to steady state charge transport and recombination measurements to help explain the solar cell characteristics of bulk a bulk devices.

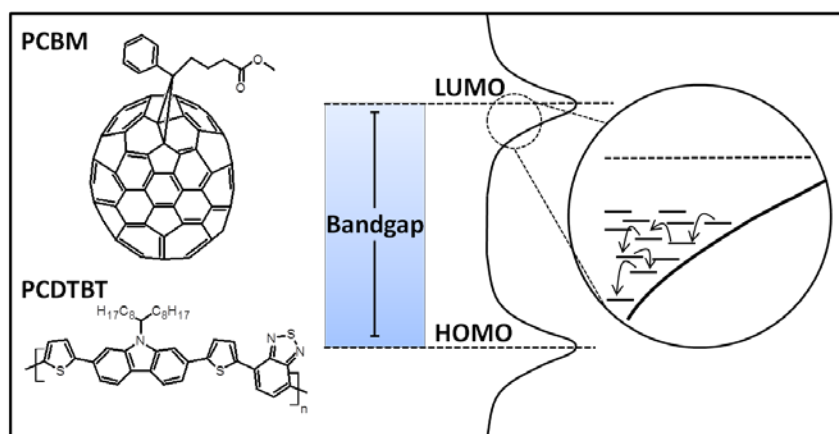


FIGURE 1. Chemical structures of PCDTBT and PCBM and a schematic representation of the distribution of energetic states.

Adaptive polymeric materials in biological organisms

Peter Fratzl

Max Planck Institute of Colloids and Interfaces, Potsdam

Keywords: cellulose, collagen, growth, adaptation

Most natural tissues respond to functional requirements by adapting their structure at all scales. Some of these structural adaptations are genetically coded, but often they are just emerging within an organism in response to environmental challenges. While many of these adaptive changes are the result of coordinated cell activity, there are also examples where organisms secrete a polymeric matrix capable of modifying its properties without the intervention of cells. The lecture will review recent advances in the understanding of such systems with particular emphasis on the role of water in generating internal stresses and/or organ movements in cellulose [1], collagen [2], bone [3] or dentin [4]. We will also address the importance surface stress on shape generation of extracellular tissue components during the growth of organic [5] and inorganic tissues [6], as well as during healing [7]. Many interesting material behaviours derive from heterogeneity, such as the combination of dissimilar components [8], structural gradients [9] or chemical bonds with different strengths [10].

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Self-Assemblies, Hierarchies and Biomimetics based on Polymers Combining Supramolecular and Supracolloidal Motifs

Olli Ikkala

*Aalto University, Department of Applied Physics, Molecular materials,
P.O. Box 15100, FIN-00076 Aalto, Espoo, Finland*

Keywords: Self-assembly, hierarchy, supramolecular, supracolloidal

Materials in Nature involve hierarchical self-assemblies ranging from molecular scale to macroscale in order to allow synergistic properties by combining different functional units. Inspired by them, in this talk, recent examples are described to achieve self-assembled polymeric structures at different scales by benefitting supramolecular or supracolloidal routes. Cellulose has regained interest due to its sustainability and in particular due to its native nanocellulosic forms involving the mechanically strong cellulose I hydrogen bonded crystal structure. Rod-like cellulose nanocrystals (CNC) show cholesteric liquid crystallinity, leading to chiral optical properties upon templating inorganic components, as amply studied previously. By contrast, we show chiral plasmonics by adsorption of gold nanoparticles on the dispersed CNC's due to the individual rod twisting [1]. Nanocellulose aerogels can be functionalized using carbon nanotubes, which allows mechano-electric function, as the conductivity systematically depends on the compression level [2,3]. Transparent high tensile strength but flexurally resilient nanocellulose / carbon nanotube aerogels and films can be useful in soft electronic templating [4]. As another length scale, tunable hierarchical self-assemblies can be obtained by combining small molecular additives to polymers based on supramolecular interactions, as amply shown previously for diblock copolymers. As recent results, we show use of halogen bonding to allow highly self-aligned polymer-surfactant complexes [5] as well as hydrogen bond modified azobenzene-ABC triblock terpolymers and their Janus objects [6].

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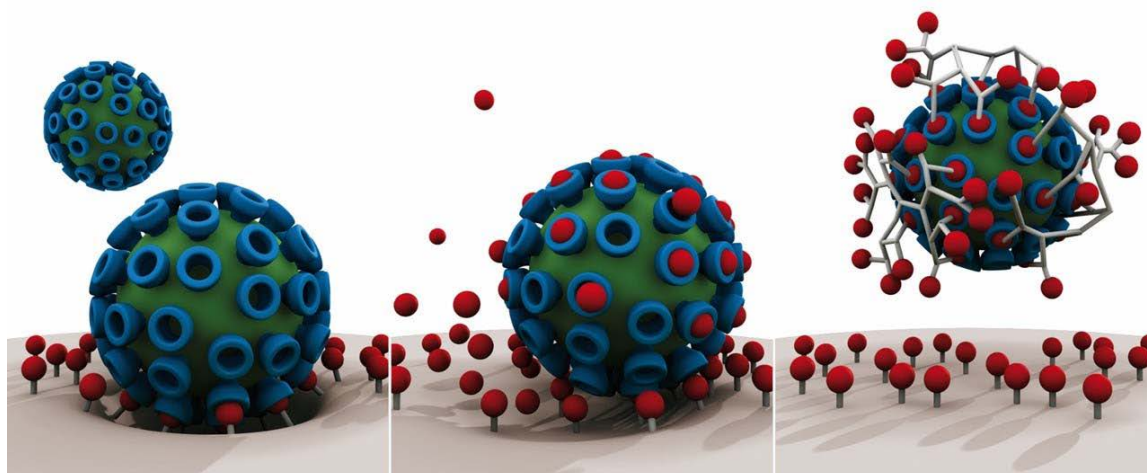
Multivalent 1D, 2D and 3D Polymers as Potent Inhibitors for Pathogens

Rainer Haag^a, Benjamin Ziem^a, Sumati Bhatia^a

Institut für Chemie und Biochemie, Takustrasse 3, Freie Universität Berlin

Keywords: multivalent nanosystems, application, pathogen inhibition

Multivalency is a ubiquitous phenomenon in nature involving complex binding mechanisms for achieving non-covalent strong yet reversible interactions. Interfacial multivalent interactions at pathogen-cell interfaces (left) can be competitively inhibited by multivalent scaffolds (right) that prevent pathogen adhesion to the cells during the initial stages of infection, while monovalent inhibition fails to inhibit the biological pathway (middle). The lack in understanding of complex biological systems makes the design of an efficient multivalent inhibitor a toilsome task and is the reason why as of yet no multivalent anti-infective has emerged on the market until now. This talk will focus on the design and application of multivalent nanosystems as potent inhibitors for pathogens.



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Emergent functions of Polymeric Nanocapsules with Controlled Shapes

D.A. Wilson

*Institute for Molecules and Materials, Radboud University Nijmegen.
Heyendaalseweg 135, Nijmegen*

Making a nanomotor has been a dream of many researchers in the field of nanotechnology and has been often associated with *futuristic visions* of building “tiny cars”, “aircrafts” or “submarines” as small as bacteria or “microscopic surgeons” able to reach infected organs and cure diseases. From molecular machines to micron size self-propelling rods chemists used a combination of bottom-up and top-down approaches often involving intricate synthetic routes and in the end with limited control over the directionality of the movement and restricted applicability. [1]

Herein we report a supramolecular approach to design synthetic swimmers using self-assembly of amphiphilic block copolymers as a primary tool to generate polymeric nanocapsules with controlled shape and catalysis as a driving force for the autonomous movement.[2,3] The movement of the nanomotor is driven by the fast discharge of jet gases obtained during the catalytic reaction with active catalysts (platinum nanoparticles, enzymes or a combination of multiple enzymes) just like a miniature nanorocket. The gases are produced during the catalytic decomposition of the fuel (hydrogen peroxide) inside the nanocavity where the active catalyst (motor) is entrapped. I will discuss new methods for enzymes entrapment and their high efficiency in entrapment and nanomotor assembly resulting in nanomotors able to propel at extreme low concentrations of fuel however still with much efficiency.[4] The method of entrapment is applicable to different enzymes, which provides a broader scope to our nanomotor design. Insight into the mechanism of movement, applications and further manipulation of the nanomotors under external stimuli will be discussed.[5,6] Furthermore recent developments on greater control over the movement of the nanomotors under chemical gradients or temperature will be presented.[7]

Acknowledgement. Financial support from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2012)/ ERC-StG 307679 “StomaMotors” is kindly acknowledged.

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Thermoresponsive Polyglycidylether Brushes for Cell Sheet Fabrication: A Correlation of Surface Parameters and Cell Response

Silke Heinen, Jose Luis Cuellar, Marie Weinhart*

Institute of Chemistry and Biochemistry, Freie Universität Berlin, Berlin, Germany

Keywords: thermoresponsive surface, grafting density, cell adhesion, cell sheet detachment

Thermoresponsive polymer coatings optimized for cell sheet fabrication are the basis of scaffold-free tissue engineering, a milestone in regenerative medicine.[1] A variety of thermoresponsive polymers like PNIPAM,[2] polyoxazoline,[3] polyglycidylethers[4] and others have been applied so far for cell sheet fabrication. However, design guidelines and structure-cell response correlations for such coatings are rare. Herein, we present a detailed surface structure – cell response correlation (Fig. 1) with defined monolayer coatings of thermoresponsive polyglycidylethers. These coatings do not require additional cell promotion biomolecules in order to attract and fabricate confluent cell sheets and thus are particularly well suited for such correlations.

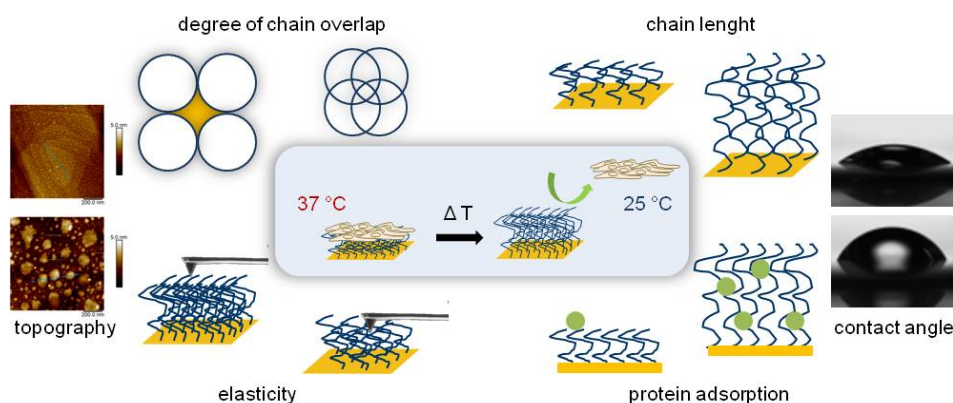


FIGURE 1. Surface design parameters for effective cell sheet fabrication on thermoresponsive surfaces.

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Rational design of stimuli-responsive nanoreactors

Joachim Dzubiella^{a,b*}, Stefano Angioletti-Uberti,^c Rafael Roda^a,
Matej Kanduc^a, Won Kyu Kim^a, Yan Lu^a, Matthias Ballauff^{a,b}

^a Institut für Weiche Materie und Funktionale Materialien,
Helmholtz-Zentrum Berlin, Berlin, Germany

^b Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany

^c International Center for Soft Matter Research, Beijing University of Chemical Technology,
Beijing 100029, China

Keywords: thermosensitive hydrogels, nanoparticle catalysis, hybrid nanoreactors, modeling and theory

The catalysis by metal nanoparticles is one of the fastest growing fields in nanoscience. However, the optimal control of catalytic activity and selectivity in nanoparticle catalysis remains a grand scientific challenge. Here, we describe our ongoing efforts how to theoretically derive design rules for the optimization of nanoparticle catalysis (in the fluid phase) by means of thermosensitive yolk-shell and core-shell carrier systems [1-3]. In the latter, nanoparticles are stabilized in solution by an encapsulating, thermosensitive hydrogel shell. The latter contains and shelters the reaction. The physicochemical properties of this polymeric 'nanogate' react to stimuli in the environment and thus permit the reactant fluxes and with that the catalytic reaction to be switched and tuned, e.g., by the temperature [1-3], salt concentration, or solvent composition. Hence, the novel hybrid character of these emerging 'nanoreactors' opens up unprecedented ways for the control of nanocatalysis due to new designable degrees of freedom, if theoretical understanding and rational design principles are available.

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Micro- and Nano-Patterning of PEG-Hydrogels to control Cell Adhesion, Migration and Growth

Marga C. Lensen

*Nanostrukturierte Biomaterialien, Technische Universität Berlin, Sekr. TC 1,
Straße des 17. Juni 124, 10623 Berlin, Germany*

Keywords: poly(ethylene glycol), hydrogels, patterning, cell migration

Our research focuses on 3 intertwined aspects: i) synthesis of novel biomaterials, ii) development of micro- and nano-patterning methodologies and iii) control of cellular responses to engineered biointerfaces and scaffolds.

It has been recognized that cell adhesion critically depends on the chemical, physical and mechanical properties of the surface. Since the subsequent processes of cell migration and proliferation (growth) follow the initial cell adhesion event, we aim at controlling cellular behaviour to biomaterials' surfaces by employing patterns of chemistry, topography and elasticity; separately and in combination. The basic biomaterials that we have employed are bulk PEG-based hydrogels, which are – in principle - resistant to nonspecific protein adsorption and cell adhesion. This allows us to introduce surface patterns that enable specific biointeraction, e.g. the adhesion of desired cell types in a controlled density at a predetermined location and with spatio-temporal control of cells' responses.

While PEG-based hydrogels are inherently anti-adhesive, we have discovered that on topographically or elastically patterned PEG hydrogels cells do adhere, even in the absence of any specific biofunctionalisation. Nevertheless, as far as the (bio)chemical patterning is concerned, we have constructed hierarchical patterns of gold nanoparticles on (hard) surfaces that can be biofunctionalized and transferred to soft hydrogel interfaces as well. Our research is aimed at the elucidation of the underlying biophysical and biochemical principles that are responsible for the cell adhesion on PEG-based hydrogel surfaces when they are patterned.

We have prepared 3D-micropatterned gels by two strategies; namely by means of a porogen approach and by a uniaxial freezing method. The cell migration through the micrometer-sized channels has been investigated and was found to be strikingly different than on 2D surfaces.

Further current studies involve the investigation of the chemical, mechanical and 3D-patterning of PEG nanocomposite hydrogels with hydroxyapatite, and the kinetics of cell migration on the patterned hydrogels in dependence of pattern sizes, shapes and periodicities.

Photoinduced Surface Patterns Revisited: New Insights with New Materials?

Arri Priimagi

Department of Chemistry and Bioengineering, Tampere University of Technology, Finland

Keywords: Azobenzene, Photoresponsive Polymer, Surface Patterning, Supramolecular

This contribution focuses on a relatively old topic dealing with azobenzene-containing polymers, namely the photoinduced surface patterning (Fig. 1a). The phenomenon was demonstrated already in 1995, yet it has not redeemed its promise as a simple, one-step patterning method that could challenge the more conventional microfabrication techniques. However, inspired by recent advances in fabrication techniques, materials development, and theoretical modelling, the field is going through a revival from both fundamental and applied perspectives.

- How much (or how little) azobenzene needed in order to create the surface patterns?
- What is the maximum size of objects that can be moved with light?
- Is the patterning process light-reversible?

These questions will herein be addressed via three case studies,[1-3] all employing supramolecular materials (Fig. 1b) where non-covalent intermolecular interactions are used to attach the azobenzenes into a passive host matrix. All azobenzene-based material movements are triggered by photoisomerization and are therefore inherently related to one another, and therefore we believe our observations to provide useful insights also for photomobile materials and photoactuation.

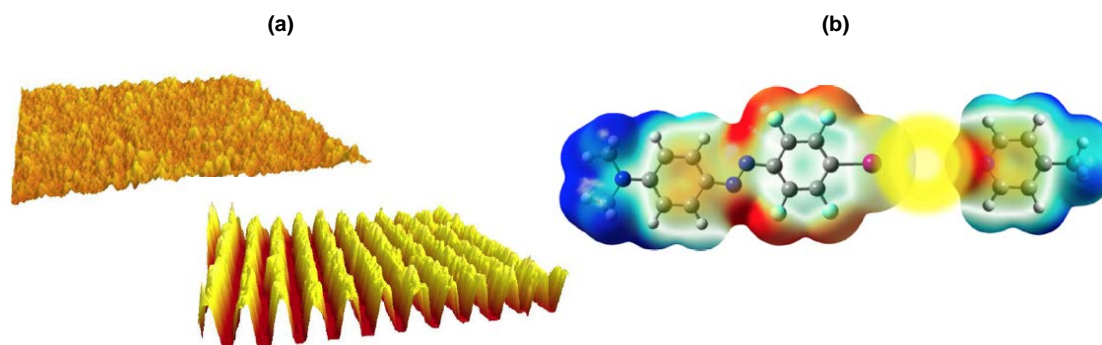


FIGURE 1. (a) The power of the photoinduced surface patterning process: an initially flat film with a thickness of 250 nm forming a surface pattern with a modulation depth of 600 nm upon interference irradiation.[4] (b) Noncovalent interactions between the photoactive molecules and the host material provide a great asset when designing materials with efficient photomechanical response.

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Surface Modification of Cellulose Substrates – Covalent and Non-Covalent Approaches using Controlled Polymerization

Eva Malmström, Anna Carlmark

KTH Royal Institute of Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden

Keywords: cellulose, surface modification, controlled radical polymerization, PISA

Cellulose is the most abundant renewable resource on earth. It is biocompatible, biodegradable, inexpensive and has interesting chemical and physical properties. Cellulose is composed of $\beta(1\rightarrow4)$ linked D-glucose units with a multitude of hydroxyl groups. Various plant species produce cellulose with different morphology and crystallinity, resulting in cellulose substrates with different dimensions [1]. Surface modification is often necessary to render cellulose suitable as reinforcement in biocomposites to allow for appropriate compatibility with a matrix polymer or to bring about properties such as superhydrophobicity or responsivity. Surface modification can be accomplished by ring-opening polymerization (ROP) of cyclic esters directly from the hydroxyl groups available on cellulose [2]. The use of controlled radical polymerization, such as ATRP, has also proven useful [3].

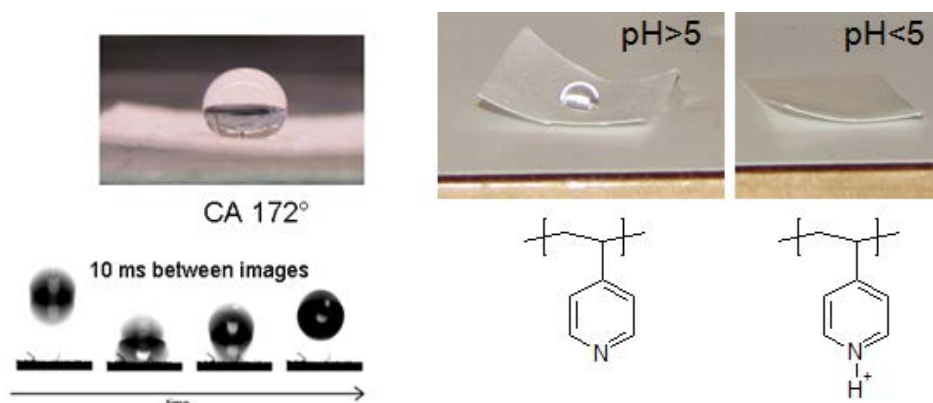


FIGURE 1. Left: A cellulose substrate becomes superhydrophobic after grafting using ATRP and subsequent post-modification. Right: A biofibre substrate becomes pH responsive after grafting with poly(4-vinylpyridine).

The scope of this contribution is to discuss some of our most recent findings regarding surface modification of cellulose and characterization of the corresponding nanocellulose-based materials.

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Light-induced deformations in azobenzene functionalized polymers: orientation approach vs. photofluidization concept

Marina Saphiannikova^{a,b}, Vladimir Toshchevikov^a

^a*Institute Theory of Polymers, IPF Dresden, Hohe Str. 6, 01069 Dresden, Germany*

^b*Dresden Center for Computational Materials Science, TU Dresden, 01062 Dresden, Germany*

Keywords: azobenzene polymers, photofluidization, orientation approach, anisotropic stress

Recently, in literature appeared quite a number of claims that cyclic isomerization of azobenzene (azo) chromophores may cause an athermal transition of the glassy azo-functionalized polymers or, more general, glassy azo-functionalized materials into a fluid state. Here we provide a critical overview of recently published findings and show that observations presented not only fail to support this photofluidization concept but rather show the contrary. The glassy azo-materials remain in the solid state under light illumination [1]. Thus, the sound claims made in the titles of recent studies contradict the experimental observations presented in their texts. Further, we discuss a number of rigorous studies which present strong evidence against the photofluidization concept, including our own theoretical predictions made in the frame of orientation approach [1]. This approach provides values of anisotropic light-induced stress large enough to deform glassy azo-polymers with diverse chemical structures. The values of the stress are in a perfect accord with recent experimental findings, which show deformation of the bonds in metal and graphene multilayers adsorbed on the top of illuminated azo-polymers [2].

The financial support of the DFG grant GR 3725/2-2 is gratefully acknowledged.

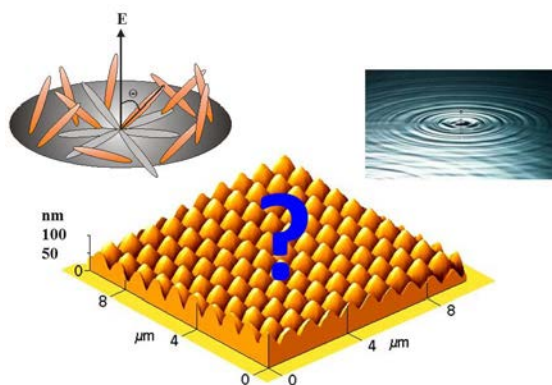


FIGURE 1. Do glassy azobenzene materials display photofluidization?

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Sustainable approaches to monomers and polymers from renewable resources

Michael A. R. Meier

*Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry (IOC),
Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany;
email: m.a.r.meier@kit.edu; web: www.meier-michael.com*

Keywords: renewable resources, polycondensation, catalysis, multicomponent reactions

In ages of depleting fossil reserves and an increasing emission of greenhouse gases, it is obvious that the utilization of renewable feedstocks is one necessary step towards a sustainable development of our future. In order to develop truly 'green' approaches, using renewable resources is insufficient. The available feedstocks rather have to be used in a sustainable fashion by combining as many of the principles of green chemistry as possible and by accessing and comparing the sustainability of chemical transformations. Within this contribution, new approaches for the synthesis of monomers as well as polymers from plant oils, lignin and carbohydrates will be discussed, thereby highlighting developed sustainable (catalytic) modification strategies. For instance, the access to nitrogen containing monomers for the sustainable synthesis of renewable polyamides and polyurethanes from plant oils will be introduced. Moreover, novel catalytic approaches towards the functionalization of cellulose and lignin will be discussed. Finally, the use of multi-component reaction offers manifold opportunities for the design of novel materials from renewable resources.

Mechanically active polymer surfaces at liquid crystal network coatings

Dirk J. Broer

*Eindhoven University of Technology
Department of Chemical Engineering & Chemistry
Institute for Complex Molecular Systems*

Keywords: Surface topography, dynamic surface, liquid crystal polymer network

Polymers that perform a programmed and reversible shape change have a wide application potential varying from micro-robotics to spacecrafts. A possible mechanism is based on a triggered change of the degree of order in liquid crystal polymer systems. We are utilizing similar techniques to change the topography of surfaces. This can be in the form of responsive cilia integrated at the surface which can be utilized for transport of species. But it can also be a triggered change of topography of the surface of interest for haptic applications. Our morphing principle is based on liquid crystal networks. Also here the underlying mechanism is a change of order parameter. In addition, free volume can be created controlling the oscillating dynamics of triggered species. Free volume leads to temporary volume increase precisely spatially controlled by patterns of the liquid crystal director. The triggers are temperature, light, pH or changes in environment. The focus of the lecture is on UV actuation.

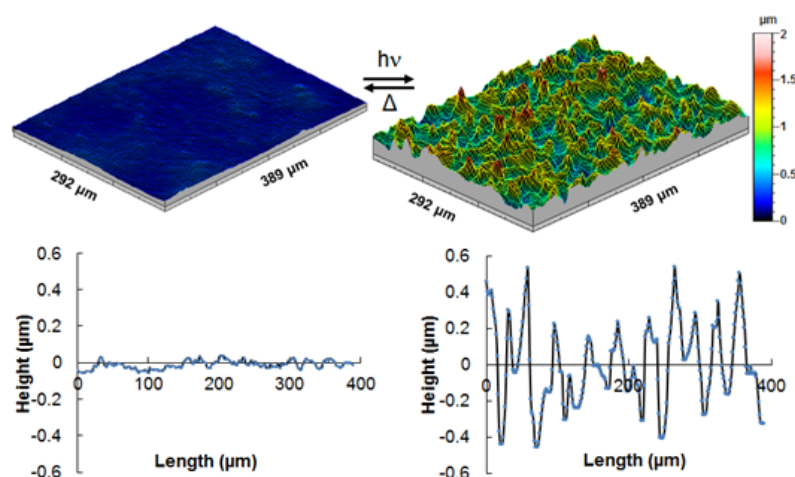


FIGURE 1. Interference microscope images and the corresponding surface profiles of polydomain liquid crystal polymer surfaces measured in the dark (left) and under illumination (right).

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Design Strategy for the Elucidation of Protein-Protein-Binding Epitopes, and Application of the Derived Peptides in Biomaterials

Axel T. Neffe^a, Stefania Federico^a, Susanna Piluso^a, Candy Löwenberg^a, Benjamin F. Pierce^a, Ulrich Nöchel^a, Christian Wischke^a, Andreas Lendlein^a

^a *Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies, Helmholtz-Zentrum Geesthacht, Kantstrasse 55, 14513 Teltow, Germany*

Keywords: Artificial Extracellular Matrix; Peptide Design; Binding Epitope Identification

Specific non-covalent interactions of biological macromolecules determine the mechanical properties and 3D organization of the extracellular matrix (ECM). One of these interactions was postulated between the small soluble ECM protein decorin and collagen. Here, a design strategy is presented that allowed to elucidate the binding epitope of decorin to collagen.[1] For this purpose, the crystal structure of decorin was analyzed separately for the two distinct sites of the horseshoe-shaped protein. Peptides representative for the consensus sequences of the inner and outer site were synthesized by solid-phase synthesis. Analytical HPLC, 2D NOESY and TOCSY NMR spectra, and MALDI ToF MS proved the purity (>95%) and identity of the peptides. In surface plasmon resonance experiments, the binding affinity to collagen only of peptides related to the inner surface of decorin could be shown, with the strongest binding peptide having a dissociation constant of 170 nM. In demonstration experiments, the power of such specifically binding peptides for biomaterial design was shown. First, dimers of the peptide synthesized by copper-catalyzed alkyne-azide cycloaddition were shown to increase the storage modulus G' of a collagen gel in a concentration-dependent manner by up to one order of magnitude. In addition, attaching a collagen binding peptide to a dye reduced the rate of diffusion in a collagen gel, which may be useful for controlled release of bioactives. Furthermore, mixing collagen with hyaluronan covalently functionalized with a decorin-derived peptide enabled the formation of dynamic ECM-like structures,[2] in which an increase of storage modulus by two orders of magnitude was achieved. The control of collagen fibrillogenesis in such gels mimicks the function of decorin in the ECM. In circular dichroism studies, it could be shown that the peptide sequences adopt the secondary structures as their parent structures in the intact decorin. In summary, a strategy for identification of relevant binding motifs in protein-protein-interaction is presented, whose implementation could be successfully shown and which provided novel peptide sequences for biomaterial design and applications.

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Artificial Cilia

Oswald Prucker, Jürgen Rühle

IMTEK – Department of Microsystems Engineering, University of Freiburg, Germany

Keywords: photolithography, C-H insertion crosslinking (CHIC), Cilia, photolithography

Handling of liquids in sub millimeter sized channels is essential for microfluidic systems. We developed microactuators inspired by small oscillating hairs called cilia found in nature. Our microactuators are based on polymers filled with magnetic nanoparticles and motion of the structures in liquids is achieved through exposure to varying magnetic fields. A combination of two different variants of a photochemical process to generate such surface architectures has been used to manufacture surface-attached polymer micro-flaps that resemble a cilia covered surface.

The process uses copolymers that contain a small amount of photoreactive groups. The polymers are deposited onto a surface and a subsequent illumination with UV light triggers a crosslinking reaction and at the same time also an attachment to the surface. Using polymers with different photoreactive groups that respond to UV light of different wavelengths one can use this general approach to generate arrays of small flaps on the surface. Each individual flap is only attached to the surface at one end. The flaps are filled with magnetic nanoparticles and can be actuated by using magnetic fields.

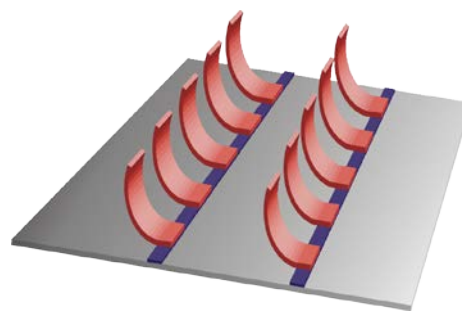


FIGURE. Artificial Cilia.

In our presentation we will discuss the influence of the properties of various materials used for the flap generation on the behavior of the artificial cilia. This includes measures that are important to enable sufficient actuation in moderate magnetic field strengths and design principles and chemical modifications that reduce the risk of a structure collapse to the surface due to a too high tackiness of the cilia. Finally, we will discuss the overall fabrication process with an emphasis on the parameters that allow the generation of large area arrays as these are needed in a microfluidic device and on device integration.

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Controlling monomer sequence using supramolecular interactions

Niels ten Brummelhuis^a, Meral Yalcin, Maria T. Heilmann^a

^a*Humboldt-Universität zu Berlin, Department of Chemistry,
Brook-Taylor-Str. 2, 12489, Berlin, Germany.*

Keywords: sequence control, hydrogen bonding, inclusion complexation

Nature shows that function can be reached by controlling the sequence of functional monomers in biopolymers, which enables their folding into well-defined 3D-structures. Such a control over monomer sequence is currently impossible for chain-growth polymerizations. If monomer sequences are to reach a complexity similar to biopolymers, and thereby also allow for the evolution of novel functions for synthetic polymers, new synthetic strategies are needed.

In this work we use supramolecular interactions to preorganize monomers in such a way that their polymerizable groups are brought into close proximity to each other, thereby strongly enhancing their tendency towards subsequent polymerization. Here we show that both hydrogen bonding interactions, which is used to form well-defined binary complexes, and hetero-inclusion of two different interacting monomers in γ -cyclodextrin can be used to preorganize monomers. This results in a pairwise incorporation of the interacting monomers.

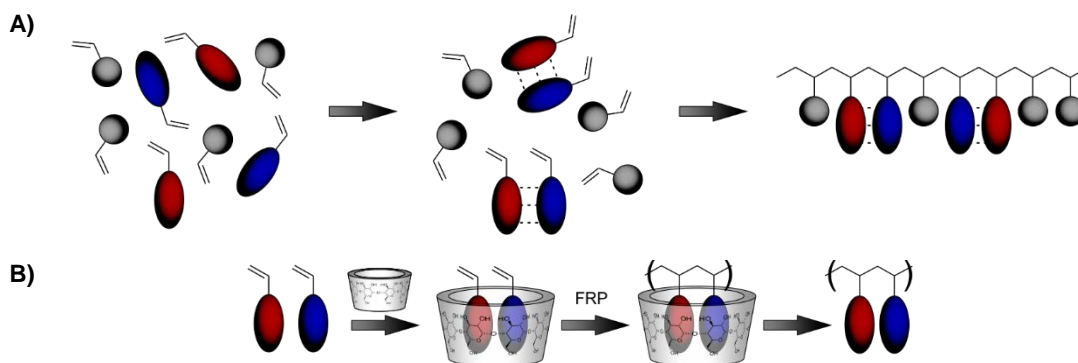


FIGURE 1. Preorganization of monomers through supramolecular interactions such as H-bonding (A) or inclusion complexation (B) and the influence thereof on the copolymerization.

Photophysical Transformations of Luminescent Derivatives of Pyrazoline

Jaroslav Mysliwiec^a, Adam Szukalski^a, Andrzej Miniewicz^a

^aWroclaw University of Science and Technology
Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland

Keywords: photoisomerisation, photoinduced birefringence, all-optical switching, light amplification

Discovery of *E/Z* or *trans-cis* photoisomerization in the azobenzenes and their derivatives had the tremendous impact on the whole domain of photochromic materials including photochromic polymers and liquid crystals. Here we show similar configurational photoinduced transformation in a simple luminescent derivative of pyrazoline (E)-3-(4-nitrostyryl)-1-phenyl-4,5-dihydro-1H-pyrazole (abbreviated as PY-pNO₂) being a part of the whole family of pyrazolines in which phototransformation process was observed [1,2]. The X-ray crystallographic investigations in grown crystals show two different structures comprising of either *cis* or *trans* molecules.

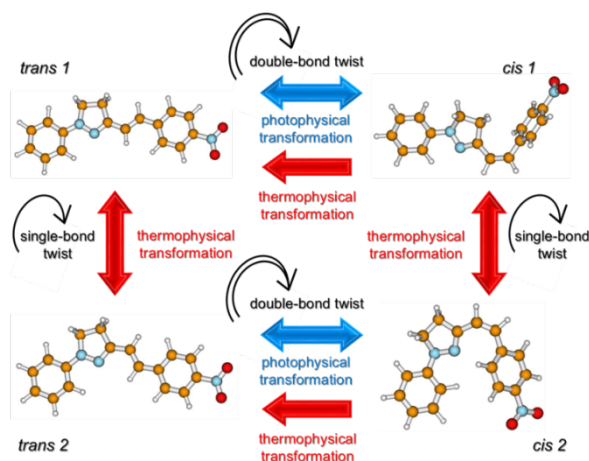


FIGURE 1. Scheme of photophysics of PY-pNO₂. The transitions due to double bond twist are possible only via photophysical transformation after photon absorption while that due to single bond twist may occur thermally.[1]

The performed quantum chemical calculations confirm the existence of both configurations at the room temperature. Photophysical properties derived from quantum chemical calculations predict possibility of *trans* to *cis* switching by light. Indeed, molecules of PY-pNO₂ embedded in PMMA polymeric matrix when illuminated with 532 nm linearly polarized laser light show the induced optical anisotropy, i.e. birefringence characteristic for photoisomerizable molecules similar like in the group of the azobenzene derivatives.

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Biomimetic organo-catalysis by nanostructured macromolecules

Pavel V. Komarov,¹ Vladimir I. Lozinsky,¹ Pavel G. Khalatur^{1,2} and Alexei R. Khokhlov^{1,2,3}

¹*Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia*

²*Department of Advanced Energy Related Nanomaterials, Ulm University, Ulm, D-89069 Germany*

³*Physics Department, Moscow State University, Moscow, 119992 Russia*

khokhlov@poly.phys.msu.ru

Based on the principles of the conformation-dependent design of copolymer sequences and the methods of controlled radical copolymerization, we propose a novel concept for the rational design of bio-inspired polymer-supported organo-catalysts (*synzymes*) from polymerizing synthetic (non-natural) monomers mimicking the amino acid residues responsible for catalysis or/and binding to target molecules in natural enzymes. A key ingredient of our approach is that the target globular conformation of protein-like, core-shell morphology can appear spontaneously in the course of controlled radical polymerization in a selective solvent. By combining four types of monomers with different hydrophobicity/hydrophilicity and polymerizable double bonds, we predict, both experimentally and in *in-silico* design, the formation of stable polymer globules with a dense hydrophobic core rich in the hydrophobic monomer units and a hydrophilic shell containing various blocks with incorporated catalytically active groups. Compared to the enormous combinatorial diversity of four-letter copolymer sequences, the number of specific sequences leading to such a core-shell morphology is relatively small. One may say that our methodology acts as a "sieve" that removes unsuitable copolymer sequences and leaves mainly desirable sequences.

As a case study, the design of a functional analog of α -chymotrypsin with self-assembly ability in a selective solvent is performed. The functional groups present in the designed copolymer, *viz.*, the hydroxyl group in N-acryloyl-2-ethanolamine, the carboxyl group in N-acryloyl- β -alanine and imidazole in N-acryloyl-histamine, also constitute the catalytic center of α -chymotrypsin, *viz.*, serine, aspartic and histidine amino acid residues, respectively. Due to a specific monomer sequence distribution, the hydrophilic segments, bearing functional hydroxyl, carboxyl and imidazole groups, are mainly concentrated close to the globule surface, thus providing an increased probability for catalytic triad formation, whereas the hydrophobic segments, containing a varying number of N-vinylcaprolactam monomer units, are mainly located in a globular core. Although the enzyme-inspired synthetic copolymer is found to be a highly dynamic system, whose structural lability is higher than that of semirigid proteins, and catalytic centers emerge more or less randomly, these drawbacks are compensated by the fact that the number of potentially active catalytic triads can be approximately one or even two orders of magnitude higher than what is typical for natural counterparts. In this regard, each designed polymer globule with multiple catalytic sites behaves as a surface nanoreactor, maintaining its structural integrity in solution. Certainly, the conformational flexibility should reduce a "catalytic quality" of each individual chymotrypsin-like triad, but their quantity is capable of compensating this. The catalytic behavior of the product is tested by monitoring the hydrolysis of 4-nitrophenyl propionate. It is found that when the prepared copolymer exists in a globular state, it catalyzes the reaction with remarkable efficiency, while swollen polymer coils are practically inactive. Importantly, the catalytic activity of these copolymers is observed at much lower concentrations than that for their counterparts with alternating or random hydrophobic-hydrophilic sequences.

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Engineering Cell Surfaces with Synthetic Polymers

Harm-Anton Klok

Ecole Polytechnique Fédérale de Lausanne (EPFL)

Institut des Matériaux, Laboratoire des Polymères

STI - IMX - LP (Bâtiment MXD), Station 12, CH-1015 Lausanne (Switzerland)

Email : harm-anton.klok@epfl.ch

Keywords: cell surface engineering, cell therapy, immune cells, polymer conjugates.

Cells provide attractive opportunities to develop innovative drug delivery systems. Red blood cells e.g. are uniquely designed to circulate in the bloodstream for extended periods of time. Immune cells, in particular lymphocytes from the adaptive immune system, are attractive as they potentially provide possibilities to home in to the disease site in a highly selective manner. Modifying the surfaces of these cells with synthetic polymers or polymer nanoparticles provides manifold opportunities to further enhance their functionality. Successful polymer cell surface engineering, obviously, requires conjugation chemistries that proceed under biological conditions and in high yields and without compromising cell viability and function. This presentation will discuss various polymer cell surface modification strategies and compare these different approaches in terms of the possibilities they offer to modify cell surfaces as well as their impact on cell viability and function. It will be shown that under appropriate conditions live cells can be surface modified with synthetic polymers while retaining their viability and functional properties.

From metallic gyroid structures to piezoelectric nanoporous networks

Katja Loos

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

Keywords: block copolymers, self assembly, porous structures

In this study we present two approaches to obtain nanoporous materials from block copolymer precursors. The first example is schematically depicted in Figure 1. A supramolecular complex of PS-*b*-P4VP diblock copolymer and amphiphilic PDP was used as a precursor for the nanoporous template for subsequent metal plating. PDP molecules interact *via* hydrogen bonds with the pyridine rings to form a PS-*b*-P4VP(PDP)_x complex (Figure 1a). The block lengths of the block copolymer and the amount of

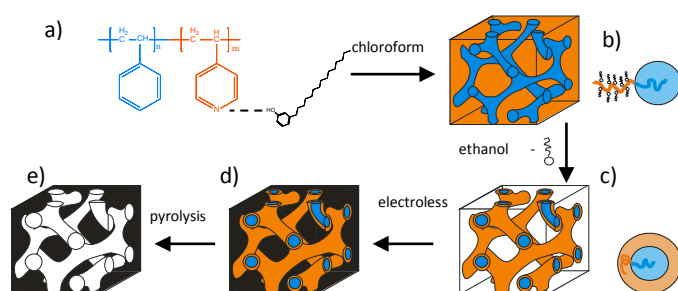


Figure 1. Preparation of the gyroid metallic nanofoams.

PDP were selected in such a way that the self-assembly gave rise to a bicontinuous gyroid morphology with a PS network in a matrix of P4VP(PDP)_x (Figure 1b). The PDP side chains were selectively removed in ethanol (Figure 1c), after which the P4VP chains collapsed onto the PS, thus forming a polar corona around the PS network struts. Subsequently, electroless deposition was performed such that the metal was distributed uniformly throughout the macroscopic thickness of the template (50

– 100 μm, Figure 1d). The metal nanofoam, obtained after the removal of polymer template, preserved the well-defined gyroid structure with long range order (Figure 1e & Figure 2).

Nanoporous metal foams represent a new, very promising class of materials that combine the properties of metals, such as catalytic activity, thermal and electrical conductivity, and the properties of nanoporous materials: low relative density and high specific surface area. These unique properties allow nano-porous metal foams to be used for a large number of possible applications as, for example: high power-density batteries, substitutes for platinum-group catalysts, hydrogen storage materials, actuators etc.

As a second example, we present the use of poly(vinylidene fluoride) containing block copolymers as precursors for nanoporous networks. PVDF is well-known for its excellent piezoelectric behavior, and therefore an interesting material to apply in nanofabrication.

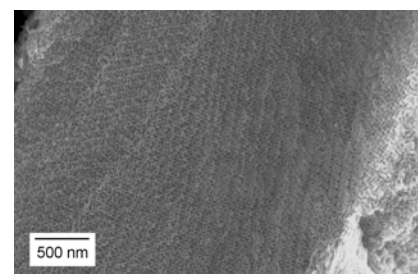


Figure 2. SEM image of an inverse gyroid Ni replica obtained after the polymer template removal by pyrolysis.

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Cyclo(RGD)-Decorated Redox-Responsive Nanogels Mediate Targeted Chemotherapy of Integrin Over-Expressing Human Glioblastoma In Vivo

Wei Chen ^a, Yan Zou ^b, Zhiyuan Zhong ^{*,b}, and Rainer Haag ^{*,a}

^a *Institute of Chemistry and Biochemistry, Freie Universität Berlin, Berlin, Germany*

^b *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, China.*

Keywords: PVA nanogel, cRGD-targeting, stimuli-responsive, glioblastoma treatment

Introduction

Advanced nanosystems for controlled drug delivery have received tremendous attention, since these nanosystems confer prolonged circulation time, efficient tumor-targeted accumulation via the enhanced permeability and retention (EPR) effect, reduced side effects, and improved drug tolerance.[1] Compared to other nanosystems, nanogels with internally crosslinked 3D structures are able to stably encapsulate bioactive compounds such as drugs, peptides/proteins, and DNA/RNA in their polymeric networks, and moreover, nanogels actively participate in the drug delivery process due to their intrinsic properties such as stimuli-responsive behavior, swelling and softness, to achieve a controlled drug release at the target site.[2,3]

Results and Discussion

cRGD-decorated redox-responsive PVA nanogels (cRGD-SS-NGs) with an average diameter of 142 nm were prepared by inverse nanoprecipitation, “click” reaction and cRGD conjugation. DOX release from cRGD-SS-NGs was inhibited under physiological conditions, while accelerated at endosomal pH and in response to cytoplasmic concentration of glutathione (GSH). The in vitro cytotoxicity assays revealed that DOX-loaded cRGD-SS-NGs presented great killing activity towards $\alpha_v\beta_3$ integrin over-expressing human glioblastoma U87-MG cells, which was significantly higher than that for non-targeted nanogels. The in vivo pharmacokinetics studies showed that DOX-loaded cRGD-SS-NGs had a much longer circulation time than free DOX. The in vivo imaging and biodistribution studies revealed that DOX-loaded cRGD-SS-NGs had much better tumor targetability towards human U87-MG glioblastoma xenograft in nude mice compared to nanogels without cRGD decoration or free DOX. The therapeutic studies in human U87-MG glioblastoma xenografts exhibited that tumor growth was effectively inhibited by treatment with DOX-loaded cRGD-SS-NGs, while continuous tumor growth was observed for mice treated with non-decorated nanogels and free DOX. Furthermore, the treatment with DOX-loaded cRGD-SS-NGs had much fewer side effects.

Conclusion

This is the first demonstration that cRGD-decorated, reduction-responsive nanogels (cRGD-SS-NGs), based on the FDA approved PVA material, afford a tumor-targeted and reduction-triggered intracellular release of DOX into human glioblastoma xenografts in mice, which results in efficient inhibition of tumor growth with little adverse effect.

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Two-dimensionally ordered AuNP arrays via microcontact printing on lamellar diblock copolymer films

Alexander Böker^a, Tom Wagner^b, Meirav Oded^b, Roy Shenhar^b

^a *Fraunhofer-Institut für Angewandte Polymerforschung IAP, Lehrstuhl für Polymermaterialien und Polymertechnologien, Universität Potsdam, Geiselbergstraße 69, 14476 Potsdam, Germany*

^b *DWI – Leibniz Institut für Interaktive Materialien, Forckenbeckstraße 50, D-52056 Aachen, Germany*

^c *Institute of Chemistry and the Hebrew University Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem, Israel 919040*

Keywords: block copolymers, electrostatic assembly, microcontact printing, gold nanoparticles

The construction of nano-sized, two-dimensionally ordered nanoparticle superstructures is important for various advanced applications such as photonics, sensing, catalysis, or nano-circuitry. Currently, such structures are fabricated using the templated organization approach, in which the templates are mainly created by photo- or laser-lithography and other invasive top-down etching procedures. In this work, we present an alternative bottom-up preparation method for the controlled deposition of nanoparticles into hierarchical structures. Lamellar polystyrene-block-poly(2-vinylpyridinium) thin films featuring alternating stripes of neutral PS and positively charged P2VP-domains serve as templates, allowing for the selective adsorption of negatively charged gold nanoparticles. Dense nanoparticle assembly is achieved by a simple immersion process, whereas two-dimensionally ordered arrays of nanoparticles are realized by microcontact printing (μ CP), utilizing periodic PDMS wrinkle grooves loaded with gold nanoparticles [1]. This approach enables the facile construction of hierarchical nanoparticle arrays with variable geometries.

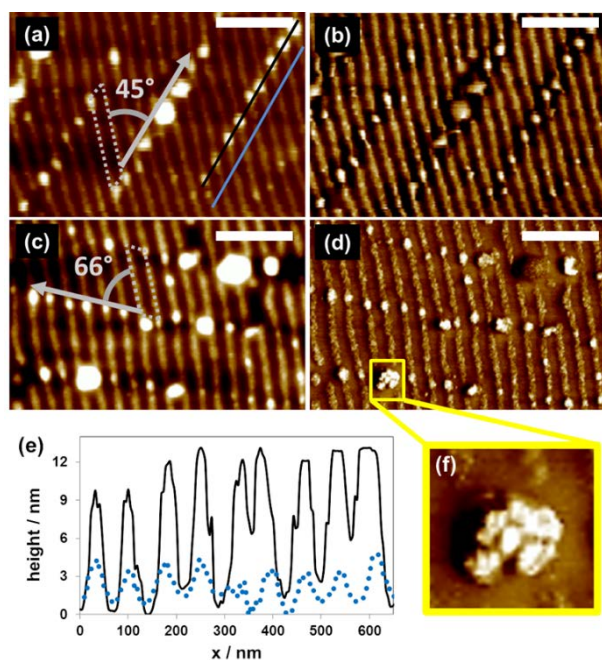


FIGURE 1. (a,c) AFM height images of 2D ordered AuNPs selectively deposited on positively charged qP2VP domains. z-range: ± 8 nm. The dotted parallelograms indicate the rhomboid AuNP arrangements. (b,d) Corresponding AFM phase images. Phase contrast: $\pm 15^\circ$. Scale bars: 250 nm. (e) Superimposed AFM cross-sections along black and blue lines in (a). (f) Magnified AuNP cluster from (d).

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Thermosensitive Microgels as “active” nanoreactors for tuning the catalytic activity of metal/metal oxide nanoparticles

He Jia, Rafael Roa, Joachim Dzubiella, Matthias Ballauff, Yan Lu

*Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin,
yan.lu@Helmholtz-berlin.de*

Environmentally responsive microgels have been subjects of great interest in the last two decades due to their versatile applications in fields like drug delivery, chemical separation and catalysis [1]. Thermosensitive core-shell microgel particles, in which the core consists of polystyrene whereas the shell consists of a poly (N-isopropylacrylamide) (PNIPA) network, have been used as “nanoreactors” for the deposition of metal nanoparticles (such as Ag, Au, Pd, and Pt). We demonstrate that the catalytic activity of the metal nanoparticles can be tuned by the volume transition within the microgel by using the catalytic reduction of 4-nitrophenol as the model reaction [2]. In addition to this, thermosensitive Au-PNIPA yolk-shell microgel systems in which a single Au-nanoparticles is immobilized in a hollow shell of PNIPA have been developed [3]. The catalytic selectivity of this hybrid system can be tuned by temperature as is shown by the competitive reduction of the hydrophilic 4-nitrophenol and the hydrophobic nitrobenzene by borohydride.

In addition, Cu₂O@PNIPA core-shell nanoreactors have been synthesized using Cu₂O nanocubes as the core [4]. The PNIPA shell not only protects the Cu₂O nanocubes from oxidation, but also improves the colloidal stability of the system. The Cu₂O@PNIPA core-shell microgels can work efficiently as photocatalyst for the decomposition of methyl orange under visible light. A significant enhancement in the catalytic activity has been observed for the core-shell microgels compared with the pure Cu₂O nanocubes. Most importantly, the photocatalytic activity of the Cu₂O nanocubes can be further tuned by the thermosensitive PNIPA shell. A theory for the diffusion- and solvation-controlled contribution to the reaction rate of such a “nanoreactor” has been also discussed [5]. Hence, the microgel particles present an “active” carrier system for applications in catalysis.

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Improving Charge Trapping on Polymer Surfaces

Dmitry Rychkov^a, Xunlin Qiu^a

^a University of Potsdam, Potsdam, Germany

Keywords: polymer electrets, charge transport and storage, traps, ferroelectrets, hysteresis, dielectric barrier discharge

Reliable charge storage in polymers has become one of the most important prerequisites for modern polymer-electret applications ranging from electroacoustic transducers to other sensors and actuators and to bio-medical devices. The key phenomenon is called electret effect and refers to quasi-permanent charge (or polarization) in dielectrics. A good electret should be able to retain excess charges and/or orientational polarization over a wide range of times and temperatures. In space-charge electrets, this requirement can usually be fulfilled by use of non-polar materials with good electret properties—for example in fluoropolymers such as polytetrafluoroethylene (PTFE) or fluoroethylene-co-propylene (FEP). For these materials, the stability of the electret charge depends essentially on their respective surface and nearsurface properties. This opens a promising avenue for the improvement of electret properties – surface modification. Here we describe this approach in detail and provide relevant experimental data.

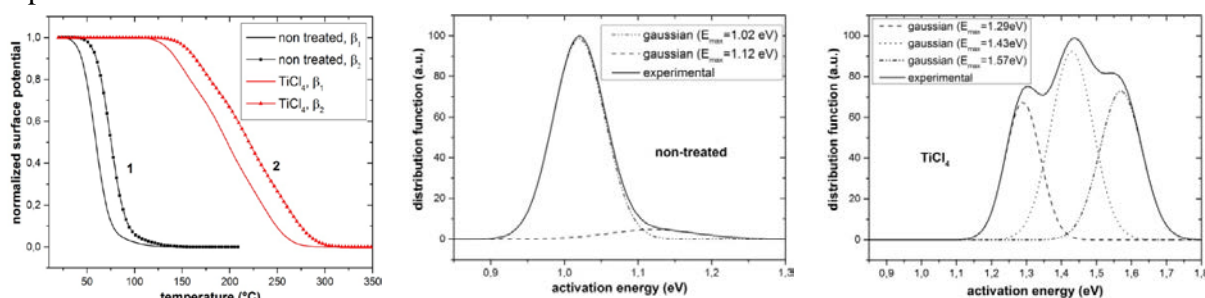


FIGURE 1. Charge decay and trap energy spectra in Teflon electrets.

The above requirements in terms of charge stability also apply to the new electroactive materials that are named ferroelectrets. They are nonpolar polymer films or film systems with cavities. The cavities inside the polymer foams can be internally charged by means of dielectric barrier discharges in sufficiently high electric fields. During charging, charges of opposite polarity are generated and trapped at the top and bottom internal surfaces of the gas-filled cavities, respectively. The charged cavities can be considered as man-made macroscopic dipoles, whose direction can be reversed by switching the polarity of the applied electric field, and the resulting electric-displacement-versus-electric-field curves exhibit hysteresis behaviour (Fig. 2).

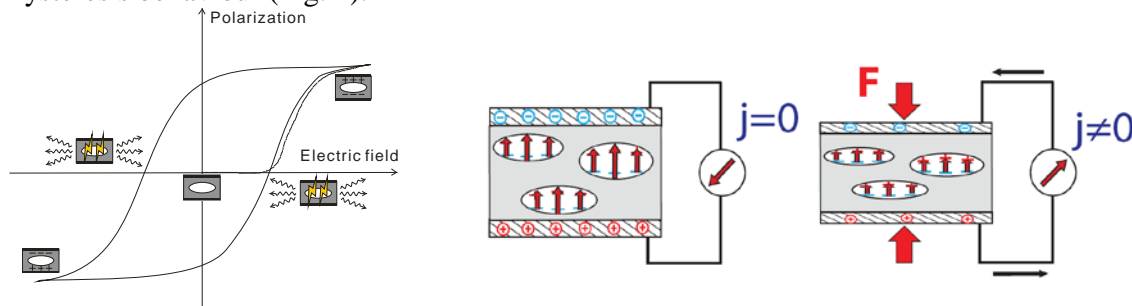


FIGURE 2. Schematic depiction of the hysteresis curve of polymer foams under electric fields, and the piezoelectricity of polymer foams (ferroelectrets).

In this contribution a brief overview of the state of the art of ferroelectrets is provided, and recent results regarding the thermal poling of ferroelectrets are reported and discussed.

(Bio)polymers tune the catalytic activity of silver nanoparticlesAndreas F. Thünemann, and Claudia Kästner*Federal Institute for Materials Research and Testing (BAM)**Unter den Eichen 87, 12205 Berlin, Germany***Keywords:** Small-angle X-ray Scattering, 4-nitrophenol, Alumin, Glutathion

We report on the development of ultra-small core-shell silver nanoparticles synthesized by an up-scaled modification of the polyol process [1]. It is foreseen to use these thoroughly characterized particles as reference material to compare the catalytic and biological properties of functionalized silver nanoparticles. Small-angle X-ray scattering (SAXS) analysis [2,3] reveal a narrow size distribution of the silver cores with a mean radius of $R_C = 3.0$ nm and a distribution width of 0.6 nm. Dynamic light scattering (DLS) provides a hydrodynamic radius of $R_H = 10.0$ nm and a PDI of 0.09. The particles' surface is covered with poly(acrylic acid) (PAA) forming a shell with a thickness of 7.0 nm, which provides colloidal stability lasting for more than six months at ambient conditions. The PAA can be easily exchanged by biomolecules to modify the surface functionality. Replacements of PAA with glutathione (GSH) and bovine serum albumin (BSA) have been performed as examples. We demonstrate that the particles effectively catalyze the reduction of 4-nitrophenol to 4-aminophenol with sodium borohydride. The tunable catalytic activity of $(436 \pm 24) \text{ L g}^{-1} \text{ s}^{-1}$ is the highest reported in literature for silver nanoparticles.

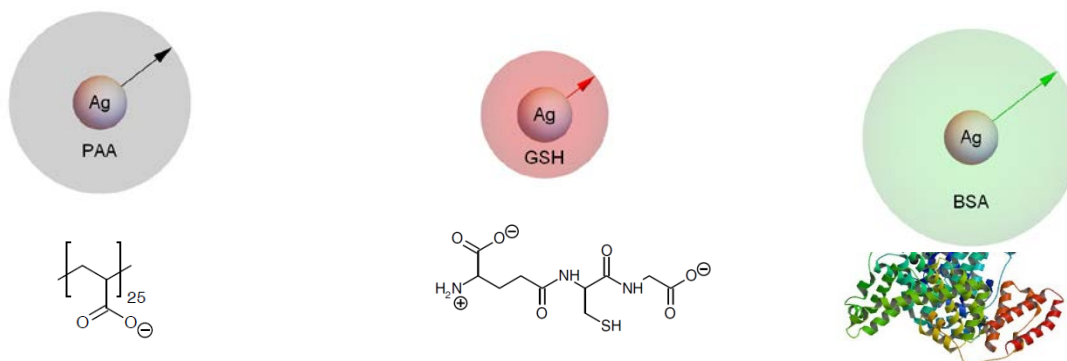


FIGURE 1. Chemical structures of the (macro)molecules that form a shell around the silver cores and provide long-term stability in dispersion. Shell thicknesses are indicated by arrows. Parent particles p_{PAA} are stabilized with poly(acrylic acid) (left). The p_{GSH} are stabilized with glutathione and p_{BSA} with bovine serum albumin (right).

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Combination of fiber optical methods for monitoring dynamic changes during the switching process of PNIPAM particles

Peter Werner, Roland Hass, Oliver Reich

University of Potsdam, Institute of Chemistry, Physical Chemistry-innoFSPEC, Potsdam/Germany

Keywords: PDW, PAT, PNIPAM, LCST

Smart polymers like Poly(*N*-isopropylacrylamide) (PNIPAM) have great potential for diverse applications like drug delivery systems, protein separation, biosensors, or catalyst carriers. According PNIPAM is one of the most investigated polymers within recent decades. PNIPAM exhibits a reversible coil-to-globule and globule-to-coil transition induced by a temperature change around the lower critical solution temperature (LCST). However, the complete mechanism behind these effects is not fully understood so far.

To determine more details about the mechanism and the structural changes of PNIPAM particles around the LCST, new measurement techniques may be helpful. With the implementation of different inline process analytical techniques (PAT), dynamic changes during the transition process of PNIPAM are detectable.

In this contribution a combination of different PAT in an automated lab reactor for the analysis of the coil-to-globule and globule-to-coil transition of a highly concentrated PNIPAM suspension is presented. One of these techniques is Photon Density Wave (PDW) spectroscopy. This is a method to characterize independently the absorption and scattering properties of highly turbid liquid suspensions. Another PAT applied is Focused Beam Reflectance Measurement (FBRM). This technique measures the chord length distribution of the particles and provides size information during the transition process. With the different PAT (PDW spectroscopy, FBRM, turbidity probe and particle vision measurement) the influence of different heating and cooling rates on the coil-to-globule and globule-to-coil transition could be measured. It could be found out that the whole transition process starts and ends far under and above the LCST. Also, with different heating and cooling rates a direct influence on the LCST and a change in the typical hysteresis could be seen. In addition, an inverse hysteresis is observed by PDW spectroscopy and turbidity measurement for the PNIPAM transition process.

Synthetic and Bio-hybrid Untethered Mobile Microrobots

Metin Sitti

*Physical Intelligence, Max Planck Institute for Intelligent Systems,
Vaihingen, Heisenbergstraße 3, 70569 Stuttgart, Germany*

Untethered mobile microrobots have the unique capability of accessing to small spaces and scales directly. Due to their small size and micron-scale physics and dynamics, they could be agile and portable, and could be inexpensive and in large numbers if they are mass-produced. Mobile microrobots would have high impact applications in health-care, bioengineering, mobile sensor networks, desktop micromanufacturing, and inspection. In this presentation, synthetic and bio-hybrid mobile microrobots from few micrometers up to hundreds of micrometer overall sizes and various locomotion capabilities are presented. Going down to micron scale, one of the grand challenges for mobile microrobots is miniaturization limitation on on-board actuation, powering, sensing, processing, and communication components. Two alternative approaches are explored in this talk to solve the actuation and powering challenges. First, biological cells, e.g. bacteria, attached to the surface of a synthetic microrobot are used as on-board microactuators and microsenors using the chemical energy inside or outside the cell in physiological fluids. Bacteria-propelled microswimmers are steered using chemical and pH gradients in the environment and remote magnetic fields towards future targeted drug delivery and environmental remediation applications. As the second approach, external actuation of untethered magnetic microrobots using remote magnetic fields in enclosed spaces is demonstrated. New magnetic microrobot locomotion principles based on rotational stick-slip and rolling dynamics are proposed. Novel magnetic composite materials are used to address and control teams of microrobots. Such untethered microrobot teams are demonstrated to manipulate live cells and microgels with embedded cells for bioengineering applications, and to self-assemble into different patterns with remote magnetic control.

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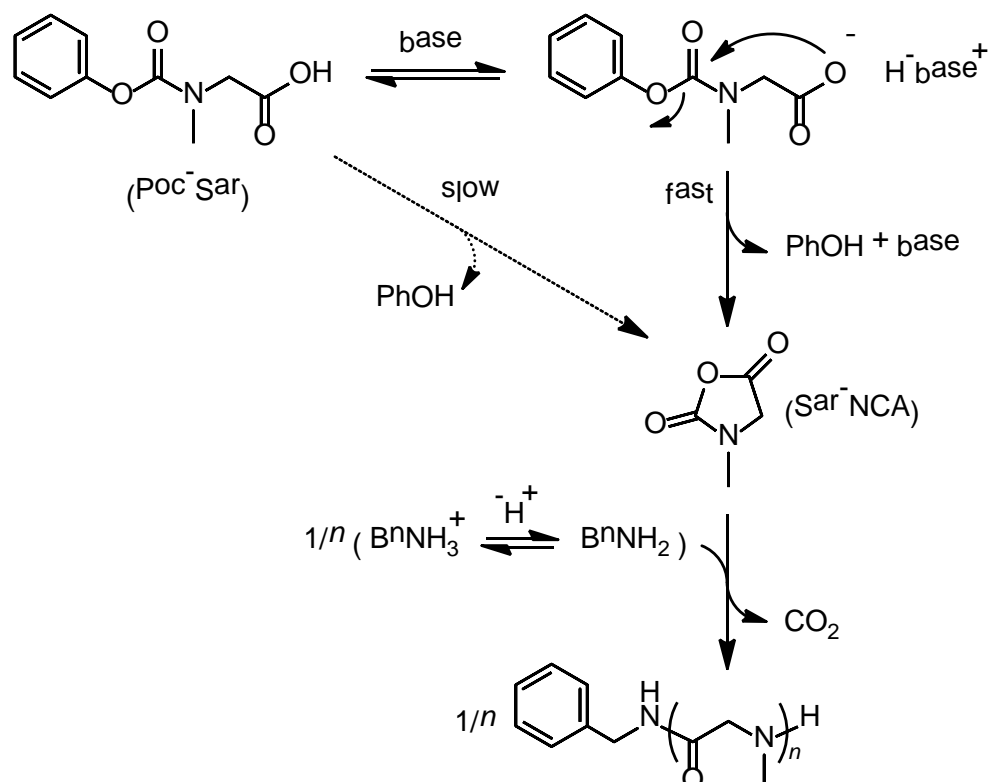
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Simplifying the synthesis of polypeptoids

Afroditi Doriti,^a Sarah M. Brosnan,^a Helmut Schlaad^{b*}^a Max Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, Research Campus Golm, Potsdam 14424, Germany.^b University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Straße 24-25, Potsdam 14476, Germany**Keywords:** polypeptoids, NCA, in situ monomer synthesis

Polypeptoids, *i.e.* poly(*N*-alkylglycine)s, are promising materials for pharmaceutical applications as they are biocompatible and can be degraded by reactive oxygen species under physiologically relevant conditions. Additionally, compared to their isomers, polypeptides, they are soluble in a larger variety of solvents. However, the tedious synthesis and the sensitivity of *N*-alkylglycine *N*-carboxyanhydride (NCA) monomers hinders their more widespread use. Herein, we report a method that simplifies their synthesis, avoiding the direct use of NCA.

Polysarcosine is synthesized using the air and moisture stable *N*-phenoxy-carbonyl-*N*-methylglycine (Poc-Sar), which reacts to form the respective Sar-NCA *in situ*. The formation of the NCA and subsequent polymerization, initiated by a primary amine, is accelerated by a non-nucleophilic tertiary amine base (see Scheme). The method produces polysarcosines with molar masses of 3.6-20 kg/mol and dispersities of ~1.1 within 24 hours.[1]



Scheme 1. Synthesis of polysarcosine through *in situ* synthesis of *N*-methylglycine-NCA from an activated urethane precursor in the presence of tertiary amine base and primary amine initiator.

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Controlling the sequence: cyclocopolymerization as a tool to create periodic monomer sequences

Falk Kubatzki^a, Niels ten Brummelhuis^a

^a Junior Research Group ten Brummelhuis, Humboldt-Universität zu Berlin,
 Brook-Taloyr-Str.2, D-12489 Berlin, Germany
 falk.kubatzki@chemie.hu-berlin.de

Keywords: cyclocopolymerization, sequence control, bifunctional monomer

Nature provides innumerable examples of highly complex and functional structures based on biopolymers such as proteins, nucleic acids and/or carbohydrates. The defined monomer sequences of these polymers are linked to their function through hierarchical folding and self-assembly. Though a similar degree of control over the primary structure is not possible in chain-growth polymerization, the material properties of synthetic polymers are nevertheless strongly linked to their microstructure.

By controlling the sequence in chain-growth polymerization it might be possible to create polymers with novel properties [1] which *e.g.* proof beneficial for applications in the fields of catalysis or materials chemistry [2].

Here we investigated the cyclocopolymerization, *i.e.* the copolymerization with multifunctional monomers that results in the formation of linear polymers cyclic side-chains,[3] for the preparation of periodic copolymers. Bifunctional styrene derivatives were copolymerized with electron-deficient monomers such as maleic anhydride, *N*-phenyl maleimide and pentafluorostyrene in free-radical copolymerizations. The kinetics of the polymerization were studied as well as the formation of charge-transfer complexes between the monomers.

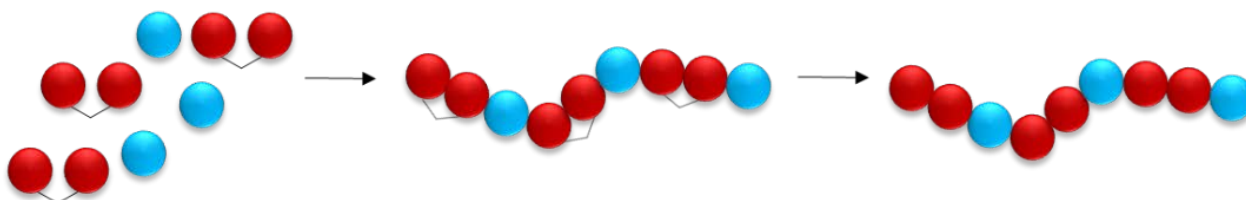


FIGURE 1. Schematic concept to create AAB sequences using cyclocopolymerization.

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Influence of Hydrogen-Bonding on the Copolymerization of Functional Monomers

Meral Yalcin, Niels ten Brummelhuis*

Department of Chemistry, Humboldt-Universität zu Berlin,
 Brook-Taylor-Str. 2, 12489 Berlin, Germany
meral.yalcin@chemie.hu-berlin.de

Keywords: supramolecular interaction, hydrogen bonds, sequence control

As nature shows with biomacromolecules function can be achieved by controlling the monomer sequence in polymers. While it is relatively easy to control the monomer sequence in step-growth polymerization, *e.g.* through solid-phase synthesis, this is difficult to achieve in chain-growth polymerizations such as free-radical polymerizations. In this work we attempt to influence the monomer sequence by using directional supramolecular interactions, *i.e.* hydrogen bonding. We show that hydrogen bonding can be used to form well-defined complexes in which the polymerizable units of the functional monomers are brought in close proximity to each other. Upon polymerization, the monomers in the supramolecular complex are incorporated subsequently in the polymer chain, resulting in a stronger tendency towards the formation of alternating copolymers or the pairwise incorporation of the functional monomers when they are copolymerized with non-functional monomers.

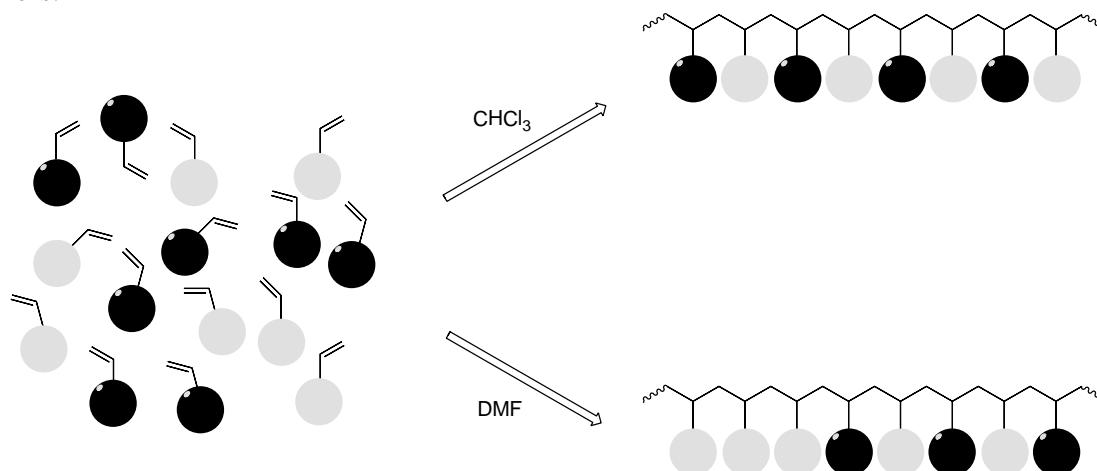


FIGURE 1. The supramolecular interaction between functional monomers leads to the pairwise incorporation of these monomers.

Peptide mimetic precision polymers

Eva Maron^a, Hans G. Börner^{a*}

^a*Department of Chemistry, Synthesis of Functional Systems, Humboldt-University Berlin, Germany*

Keywords: peptide mimicking, precision polymers

Interplay of biology and synthetic polymer chemistry created highly diverse materials. Peptide-poly(ethylene glycol) conjugates have been identified as generic platform to find specific interaction to selected targets (see figure 1).[1] Copying the structural motif of these bioconjugates to fully synthetic polymers can be achieved by using the synthetic tools of precision polymer chemistry, that have reached significant feasibility.[2] Controlled radical polymerization not only enable consistent chain growth, but also gave a method to position functionalities in synthetic polymers precisely to achieve well defined polymeric chains.[3] A successful translation of selected fragments from peptide-PEG conjugates into fully synthetic polymers can be monitored by examination of the transferred behaviors of the polymer like e.g. drug delivery or nanoengineering of surfaces.

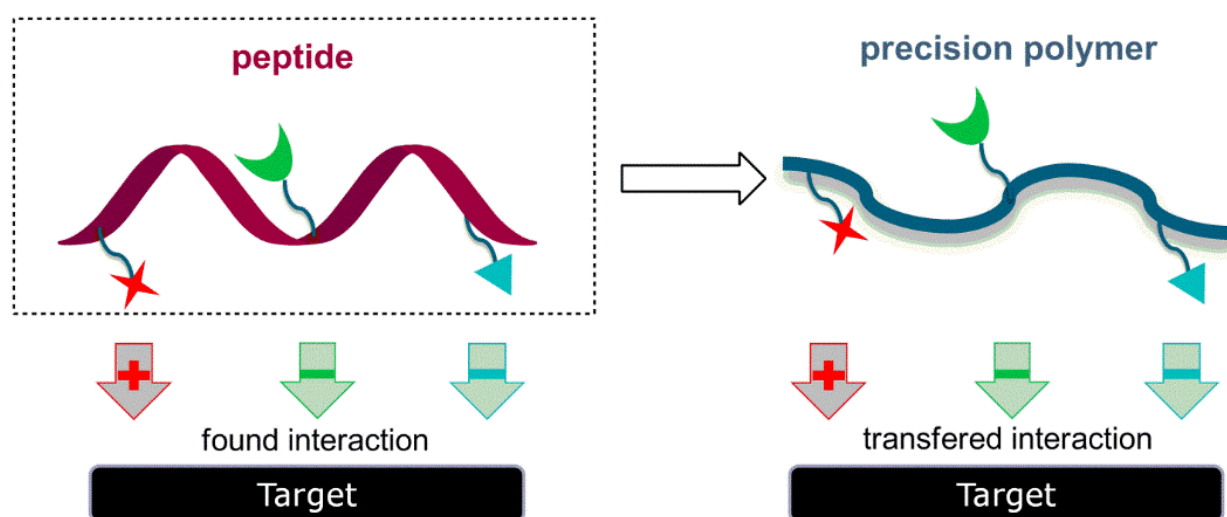


FIGURE 1. Transfer of minimal sequences from peptides to be mimicked by fully synthetic precision polymers.

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New functionalizable and degradable polymers based on cystine

Felix N. Führer and Helmut Schlaad

*University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Str. 24-25, 14476 Potsdam,
Germany*

Keywords: metathesis polymerization, amino acids, disulfide bridge

The disulfide bridge is a covalent bond that can easily be cleaved and re-formed under reductive and oxidative reaction conditions, respectively. Incorporation of this functional group into a polymer backbone would give polymers that are suitable for degradation or self-healing under mild reaction conditions.

The *N-tert*-butoxycarbonyl (BOC) protected derivative of cystine, which is the disulfide-bridged dimer of the naturally occurring amino acid cysteine, can be converted into an unsaturated macrocyclic monomer in two synthetic steps. The resulting monomer can be polymerized via entropy-driven ring opening metathesis polymerization (ROMP), using a Ru-based (Grubbs) catalyst, to yield polymer with molar mass of >20 kDa. The polymer can be degraded by a mild reducing agent, e.g. DTT, or by alcoholysis. Deprotection of the amino group can be achieved under acetic conditions, leading to a water soluble polymer that can be further functionalized for instance with anhydrides.

Linkage of purely artificial building blocks by the enzyme sortase

Xiaolin Dai^{a,b}, Ulrich Glebe^{a,b}, Alexander Böker^{a,b}

^aFraunhofer Institute for Applied Polymer Research IAP, Geiselbergstr. 69, 14476 Potsdam-Golm, Germany.

^bLehrstuhl für Polymermaterialien und Polymertechnologie, Universität Potsdam, 14476 Potsdam-Golm, Germany

Keywords: Sortase, enzyme, silica nanoparticles, polymer blocks

Sortase A (SrtA) is an enzyme that catalyzes the covalent linkage of the peptide recognition sequences -LPXTG and -GGGGG.[1] This specific coupling reaction is already well applied for the ligation of proteins with lipids, nucleic acids, sugars, solid surfaces, small molecules and other proteins.[2] Here, we demonstrate that Sortase A can also be applied to link purely artificial chemical structures. Two synthetic building blocks, A and B, were equipped with the peptide recognition motifs. The concept will be shown with silica nanoparticles and different polymer blocks as A and B (Figure 1). In future, this enzymatic linkage strategy provides an attractive alternative tool for cases in which traditional chemical approaches are limited.

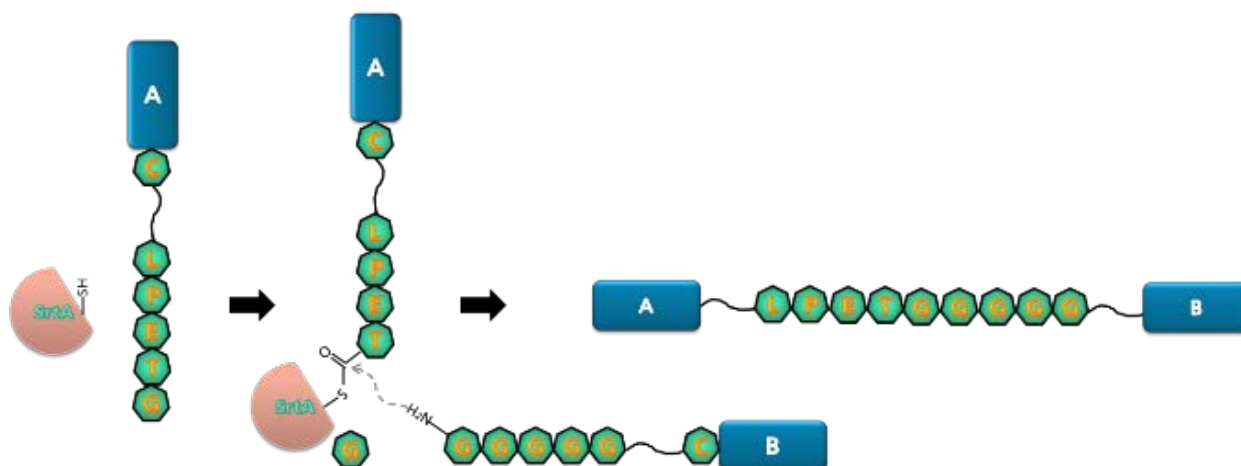


FIGURE 1. The SrtA reaction. SrtA recognizes the synthetic block A by its attached -LPETG motif and forms a thioester intermediate. This intermediate is resolved by the attack of the amine from the G oligomer from B, thus covalently linking A to B and regenerating SrtA.

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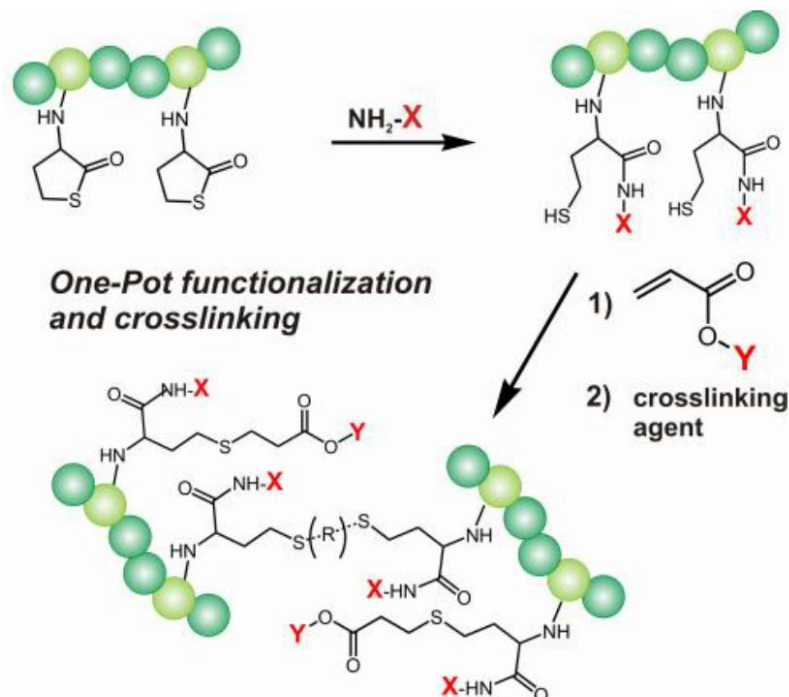
A thiolactone based one-pot double functionalization protocol for the synthesis of multiresponsive polymers and hydrogels

Stefan Reinicke^{*a}, Pieter Espeel^b, Milan M. Stamenovic^b, Filip E. Du Prez^b

^a *Fraunhofer Institute for Applied Polymer Research, Department of Life Science and Bioprocesses, Geiselbergstraße 69, 14476, Potsdam-Golm, Germany*

^b *Department of Organic Chemistry, Polymer Chemistry Research Group, Ghent University Krijgslaan 281 S4-bis, B-9000 Ghent, Belgium*

δ -Butyrolactone as latent and stable thiol functionality has proven to be a very useful building block in synthetic macromolecular chemistry as it allows for the usage of efficient conjugation chemistries such as the well-known thiol-ene “click” reaction without having to face the typically occurring problems when working with thiol containing structures [1]. Thiol groups can be released *in situ* by reacting the respective thiolactone structure with a ring opening amine (Scheme 1) followed by direct conversion of the generated thiol groups with another reactant such as an acrylate. As not only the thiol converting acrylate can introduce new functions to the structure but also the ring opening amine, the whole protocol qualifies as an easy to perform one-pot double functionalization procedure.



Scheme 1. A one-pot double functionalization protocol of thiolactone containing polymers for the synthesis of multifunctional polymer and hydrogel structures.

In this contribution, we show, how to synthesize multifunctional, responsive polymers [2] and hydrogels [3] via such a double functionalization protocol starting from thiolactone containing poly(*N*-isopropyl acrylamide) (pNIPAAm) precursors. Those precursors are easily accessible from copolymerization of NIPAAm with the respective thiolactone acrylamide using the RAFT technique.

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Green modification of a cellulose II gel to tailor surface functionality and particle size

Marco Beaumont^a, Hubert Hettegger^a, Tiina Nypelö^a, Martina Opietnik^b,
Antje Potthast^a, Thomas Rosenau^a

^a University of Natural Resources and Life Sciences Vienna (BOKU), Department of Chemistry, Division of Chemistry of Renewable Resources, Konrad-Lorenz-Str. 24, A-3430 Tulln, Austria.

^b Lenzing AG, Werkstr. 2, A-4860 Lenzing, Austria.

Keywords: Cellulose II gel, spherical nanoparticles, green chemistry, click chemistry

Nanostructured cellulose gels, such as cellulose nanofibrils or bacterial cellulose, feature an open-porous structure and a fibrillar nanohierarchy, and have high surface areas. In addition to that, they are biodegradable, biocompatible, renewable and environment-friendly. In order to influence their properties and to increase functionality by chemical means, it is mandatory to introduce new functional groups onto the cellulose surface. However, it is a major challenge to achieve this goal without causing reactivity losses and undesired changes of the nanostructure. Appropriate functionalization procedures have to be mild, heterogeneous and should be in agreement with the principles of sustainable and green chemistry. In this contribution, we demonstrate two different approaches to functionalize a nanostructured cellulose II gel in order to tune its particle size[1] and surface functionality[2]. First, the particle size was tailored from the micro range to the nano range – to obtain spherical nanoparticles decorated with carboxylate groups. Second, we present a recent procedure to introduce azide groups onto the cellulose surface to act as a click synthon, proceeding by silanization only in water as reaction medium without the need of the usually required curing step. The silanization protocol can be also applied to other cellulosic materials and is an elegant and sustainable avenue to a variety of functionalized nanostructured celluloses.

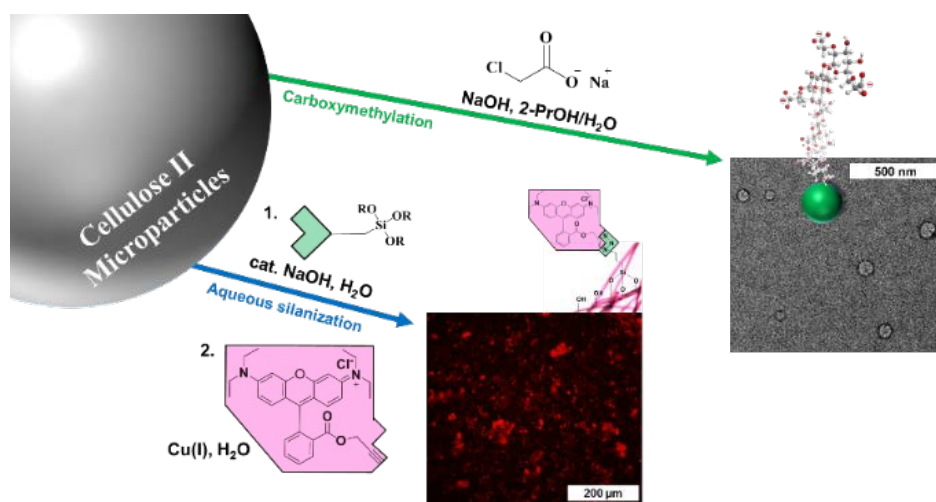


FIGURE 1. Functionalization of cellulose II microparticles through aqueous silanization to introduce a click synthon[1] and through carboxymethylation to control particle size and surface charge[2].

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Modification of Oleic Acid Ester with Polymerizable Functional Groups for Photoinitiated and Thermal Initiated Polymerization

S. Walther^a, B. Strehmel^a and V. Strehmel^a

^aInstitute for Coatings and Surface Chemistry, Niederrhein University of Applied Sciences, Adlerstrasse 32, D-47798 Krefeld, Germany

Keywords: renewable resources, photopolymerization, unsaturated fatty acid esters

Oleic acid represents an interesting and efficient alternative for petroleum based monomers in industry. In this work, the rather unreactive double bond of oleic acid was modified resulting in polymerizable (meth)acrylates. This occurred by either a two step (esterification[1], reaction with NBS/(meth)acrylic acid[2]) or a three step synthesis (esterification[1], epoxidation[3], ring opening with (meth)acrylic acid[4]). The functionalized materials were thermally polymerized using AIBN or photoinitiated by UV light. Ivocerin[®] served as photoinitiator. In particular, factors such as polymerizability, reactivity, and oxygen inhibition of the individual monomers were investigated in comparison with commercial available lauryl(meth)acrylate. The measured glass transition (T_g) was low for the polymerized modified oleic esters ($R_1 = \text{OH}$, $R_2 = \text{H}$: $T_g = -53^\circ\text{C}$ (photopolymerization) / -46°C (thermally by AIBN); $R_1 = \text{Br}$, $R_2 = \text{H}$: $T_g = -56^\circ\text{C}$ (photopolymerization); $R_1 = \text{OH}$, $R_2 = \text{CH}_3$: $T_g = -20^\circ\text{C}$ (photopolymerization) / -31°C (thermally by AIBN); $R_1 = \text{Br}$, $R_2 = \text{CH}_3$: $T_g = -50^\circ\text{C}$ (photopolymerization)). No polymer was obtained by thermal initiation with AIBN using Br-substituted monomers.

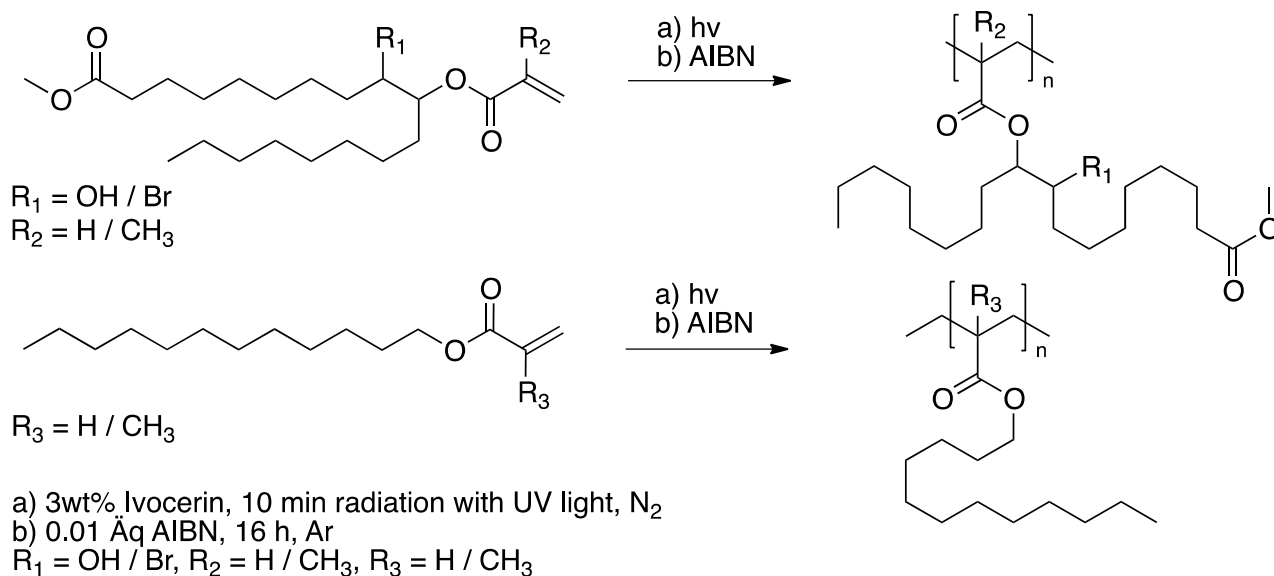


FIGURE 1: Photo- and thermal initiated polymerizations

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Photopolymerization of Ionic Liquid Methacrylates

Pia Borchert^a, Bernd Strehmel^a, Veronika Strehmel^a

^a*Institute for Coatings and Surface Chemistry, Department of Chemistry,
Niederrhein University of Applied Sciences, Adlerstr. 32, D-47798 Krefeld*

Keywords: photopolymerization, ionic liquid methacrylates, glass transition temperature

Ionic liquids containing a polymerizable functional group have received increased interest due to the fact that they combine polymerizability with the superior properties of ionic liquids – such as negligible vapor pressure, nonflammability and high ion conductivity[1]. This leads to high application potential of such monomers.

Bis(4-methoxybenzoyl)-diethylgermanium[2] was used to start a radical photoinitiated polymerization of ionic liquid methacrylates (**1**) upon exposure to UV light ($\lambda = 320\text{--}380\text{ nm}$). The polymerization rate (R_p^{\max}) and the needed time to reach the polymerization rate (t_{\max}) were determined using Photo-DSC measurements. These parameters describe the reactivity of the compounds. Polymerization rate (R_p) was obtained as function of time for all ionic liquid monomers. The time taken to reach the maximum of the polymerization rate (t_{\max}) lies between 3 and 6 seconds, whereas R_p^{\max} does not differ significantly.

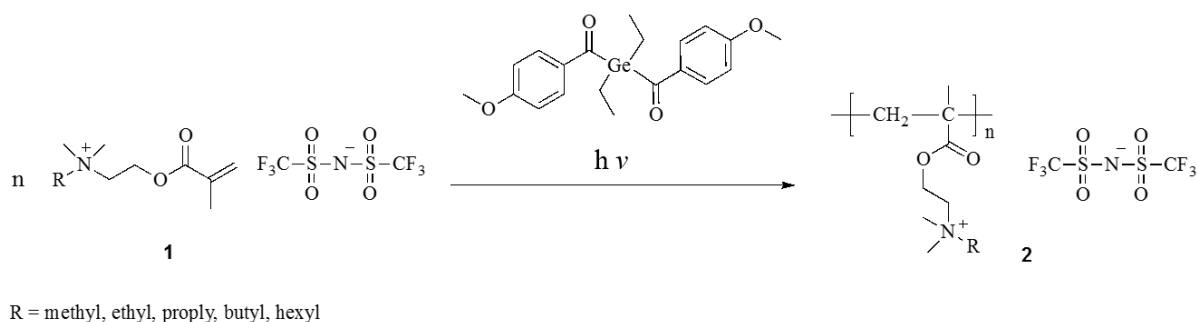


FIGURE 1. Photoinitiated polymerization of **1** in the presence of bis(4-methoxybenzoyl)-diethylgermanium.

NMR spectroscopic analysis of the polymers after completing the kinetic experiments showed conversion of double bonds between 85 % and 98 %. T_g of all monomers lies well below the temperature selected for polymerization. And increases during polymerization because the polymer formed possesses a T_g higher than room temperature.

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Post-Polymerization Modification of Functional Polymethylenes

T. Krappitz, P. Theato*

*Institute for Technical and Macromolecular Chemistry, University of Hamburg,
Bundesstraße 45, D-20146 Hamburg, Germany.
Email: theato@chemie.uni-hamburg.de*

Keywords: post-polymerization modification, C1 polymerization, polymethylenes, rhodium catalysis

Nowadays, many synthetic materials are based on polyolefins and are produced on large scale and in a huge variety annually. However, there is still a lack in polymers with a high functional density attached to the polymer backbone due to issues regarding conventional olefin polymerization by radical or transition-metal catalyzed approaches. Therefore, a recently developed polymerization technique by the group of *de Bruin* is highly promising to avoid these limitations.[1] In our group we are utilizing a novel approach by post-polymerization modification (**Figure 1**) and investigating the limits of *click-chemistry* and variability of monomers for rhodium-mediated C1 polymerization in particular.[2,3]

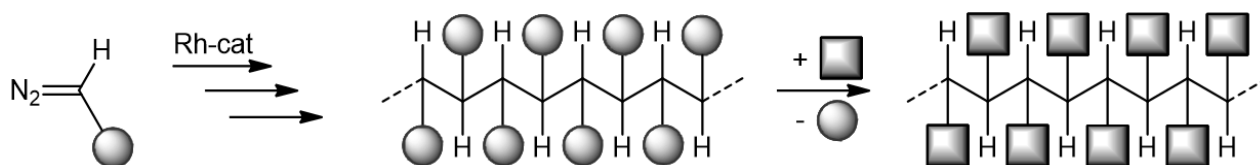


FIGURE 1. Polymerization of diazo compounds via transition-metal catalysis, followed by post-polymerization modification at every main chain carbon atom.

We are investigating and comparing the effects and characteristics between conventional olefin (C2) polymerization and novel C1 polymerization of α -diazocarbonyl based monomers. Our research sheds light on the scope of C1 polymerization as well as the influence of side chain density on post-polymerization modification.

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Towards “Ultimate Control”: Functionalized MOF Environments for Controlled Polymerization

Hui-Chun Lee, Markus Antonietti, Bernhard V.K.J. Schmidt

Max Planck Institute of Colloids and Interfaces, Research Campus Golm,
14424 Potsdam, Germany

Keywords: ARGET ATRP, MOFs, tacticity control, one-pot controlled polymerization

This research aims for a facile approach towards the synthesis of well-defined polymers, such as molecular weight, composition and tacticity. Biology demonstrates that an universal strategy towards well defined polymers is the proper design of confined environment as reaction center via specific molecular interaction. Consequently, an approach combining confined porous textures and controlled polymerization is proposed to advance synthetic polymer chemistry, i.e. a connection of metal-organic frameworks (MOFs) and activators regenerated by electron transfer-atom transfer radical polymerization (ARGET-ATRP). Taking advantage of the self-catalytic property, the ATRP-oriented MOFs, initiator-functionalized MOFs, are designed and fabricated to facilitate realize an all-embraced MOF system for versatile polymerization and application. Combining the concept of biological processes that are based on confined space with controlled polymerization processes, a significant step towards ultimate control on polymer synthesis can be taken.

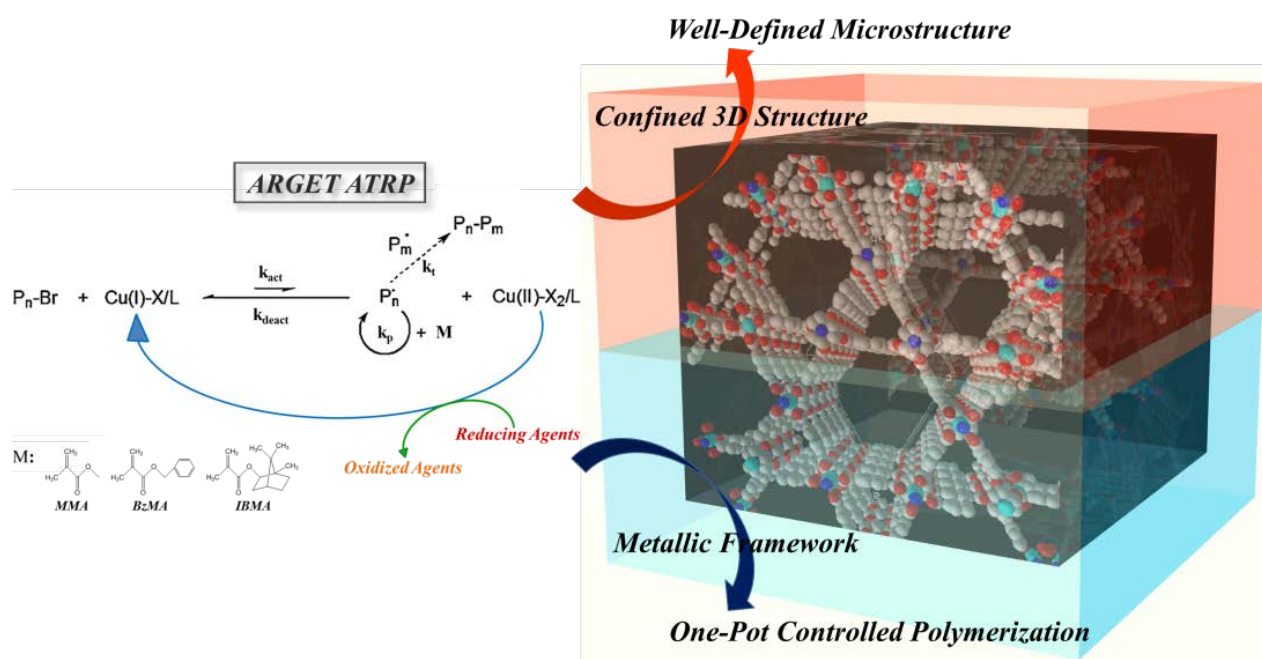


FIGURE 1. Schematic illustration of the ARGET-ATRP process and functionalized MOFs equipped with confined structure and catalytic property for one-pot controlled polymerization.

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Synthesis and self-assembly of protein-polymer conjugates

Shuhao Zhang^a, Stefan Reinicke^a, Alexander Böker^a

^a Fraunhofer Institute for Applied Polymer Research, Geiselbergstraße 69, 14476 Potsdam

Keywords: 2-deoxy-ribose-5-phosphate aldolase, NIPAAm, ATRP, RAFT

Aldolases catalyze the reversible aldol reaction between an electrophilic and a nucleophilic carbonyl compound[1], with 2-deoxy-ribose-5-phosphate aldolase (DERA) being a particularly interesting in that respect as it can be used in principle for the synthesis of cholesterol-lowering drugs[2]. However, DERA exhibits a limited stability towards the industrial relevant substrates, therefore we aim to immobilize DERA in thin membrane layers to allow for the efficient process control of aldolase-catalyzed reactions.

Two different approaches were followed to design polymer-protein conjugates for the preparation of the functional membranes. In the 'grafting-from'-approach poly(*N*-isopropylacrylamide) chains were grown from a protein macroinitiator which was previously synthesized by modifying DERA with an ATRP initiating fragment. The 'grafting-to'-method on the other hand aimed on first synthesizing pNIPAAm chains with a protein-reactive end group by RAFT, followed by reaction of the resulting polymers with DERA to form the targeted conjugates.

Varies of conjugates with different molecular weight and molecular weight distribution were prepared to study the properties and self-assembly behavior of the conjugates.

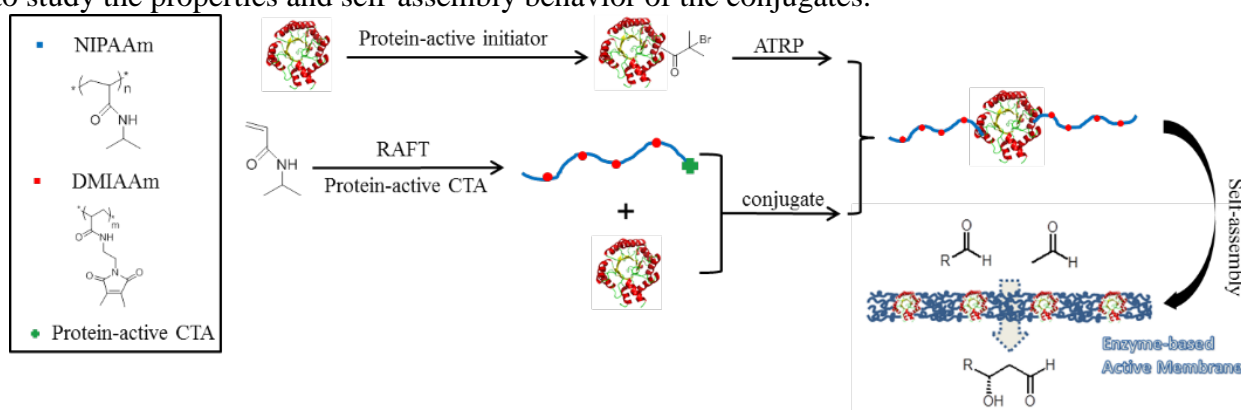


FIGURE 1. Preparation of the protein-polymer conjugate and membrane

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Effect of metallo-polymer chain extension on the morphology and release kinetics of microparticles composed of terpyridine-capped polylactides and their stereocomplexes

Marek Brzeziński^{a,b}, Anna Kacprzak^b,
Marcelo Calderon^a and Sebastian Seiffert^{a,c}

^a Freie Universität Berlin, Institute of Chemistry and Biochemistry,
Takustr. 3 D-14195 Berlin, Germany.

^b Department of Polymer Chemistry, Centre of Molecular and Macromolecular Studies,
Polish Academy of Sciences, Sienkiewicza 112, 90-363, Lodz, Poland

^c Johannes-Gutenberg-Universität Mainz, Institute of Physical Chemistry,
Duesbergweg 10–14, D-55128 Mainz, Germany.

Keywords: controlled release, metallo-polymers, polylactide, stereocomplexation

Controlled assembly of supramolecular building blocks is a promising strategy for the fabrication of degradable “smart” drug delivery systems in the form of microparticles [1]. Therefore, monodisperse biodegradable microparticles were fabricated from terpyridine (TPy) and bisterpyridine (bisTPy) end-functionalized PLAs that were transiently extended by chain association through strong complexation to different metal cations, namely, Ni^{2+} , Co^{2+} , or Fe^{2+} . Moreover, we took additional advantage of stereocomplexation between enantiomeric L- and D-PLAs, thereby combining hydrogen-bonding cross-linking with metal-complexation chain extension in one polymeric material. This synthetic building block concept enables us to tune the particles porosity and as a result drug release kinetics from our microcapsules (Figure 1).

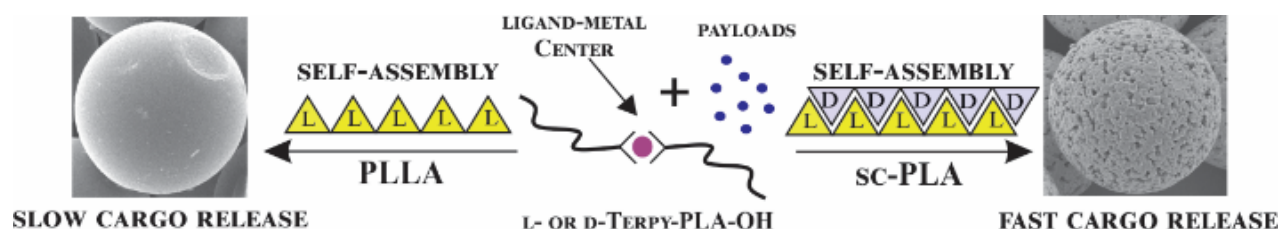


FIGURE 1. The scheme of self-assembly of terpyridine-functionalized PLAs and their stereocomplexes. The more porous stereocomplex particles exhibit faster cargo release.

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Aqueous self-assembly of amphiphilic poly(D-/L-lactide) based block copolymers

Sebastian Noack^a, Anna Bogomolova^b, Helmut Schlaad^a

^aUniversity of Potsdam, Institute of Chemistry, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany. ^bMax Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, Research Campus Golm, 14424 Potsdam, Germany

Keywords: polylactide; stereocomplexation; self-assembly

Poly(D-lactide) and poly(L-lactide) are biodegradable, hydrophobic polymers which are known for their ability to form well-defined 1:1 stereocomplexes. Stereocomplexation is also observed for polylactide-based block copolymers, for instance poly(ethylene glycol)-*block*-polylactide, and can be applied to produce stable polymer particles for drug delivery applications.[1]

Herein we present a systematic study of the time-resolved aggregation process of a series of amphiphilic poly(ethylene glycol)-*block*-poly(D-/L-lactide) copolymers in aqueous solution. The influence of the length of the hydrophilic poly(ethylene glycol) block, the position to which the poly(ethylene glycol) block is attached to the polylactide chain (either to C- or O-terminus), and the sample preparation method (direct dissolution or solvent exchange) was investigated by dynamic and static light scattering (DLS/SLS) as well as by differential scanning calorimetry (DSC).

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DNA Complexes with Acetate bis(1,10-phenanthroline)silver(I) Monohydrate in Solution and Metallization of Resulting Structures

Zhang Qiushi, Mikhail Osolodkov, Eugenii Tolstyko,
Viktor Demidov, Nina Kasyanenko

*Faculty of Physics, St. Petersburg State University,
198504, Ul`janovskaja street 1, Petrodvoretz, Saint-Petersburg, Russia*

Keywords: DNA metallization, phenanthroline, silver nanoparticles

Complexes with metal ions have a great potential for applications in medicine. Phenanthrolines as bidentate ligands, binding to silver ions, are able to generate coordination polymers. These coordination complexes are thought to act as cross-links for DNA in tumor cells. Phenanthroline is also known as antimicrobial and antitumor agent. The investigation of DNA interaction with these compounds in a solution can propose the molecular model of their biological activity. The interaction of this complex with DNA is interesting from a medical point of view. In addition, using phenanthroline compounds with metal ions, especially silver ions, it is possible to link them to DNA molecule. The reduction of silver ions on DNA strands results in creation of conductive structures based on DNA. This technology offers great opportunities in the field of nanoelectronics.

In this work, we have studied the interaction of acetate bis(1,10-phenanthroline)silver(I), further Ag-phen, with thymus DNA using UV spectroscopy, CD, viscometry, flow birefringence methods. The DNA melting in the presence of Ag-phen was also studied, and the results were compared with the effect of free silver ions and free phenanthroline ligand. We have obtained a technique of creation of thread-like DNA structures with reduced metal and studied obtained structures by SEM and AFM. The presence of metallic silver in their composition is confirmed. We have also compared this structures with complexes of DNA with silver nanopareicles. In addition, the data on the mechanical properties of DNA-phenanthroline-silver structures was obtained. The electrochemical properties of these structures were also investigated.

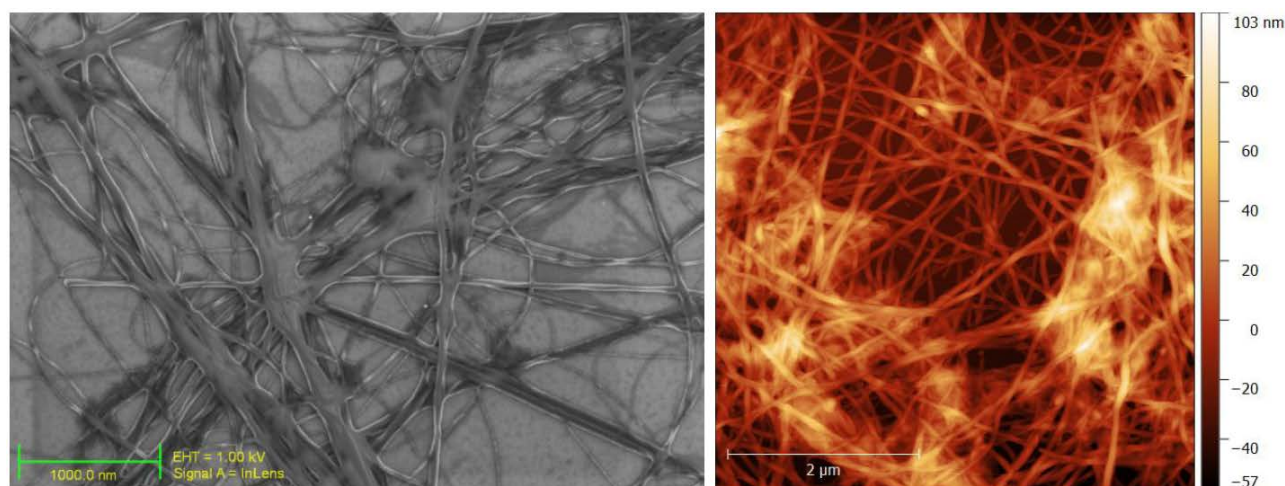


FIGURE 1. DNA-phenanthroline-silver structures (left – SEM, right – AFM).

Investigation of modified chitosan - alkylethoxy carboxylate based complexes

Bin Dai^a, Michael Gradzielski^a

^a*Stranski Laboratory for Physical und Theoretical Chemistry, Department of Chemistry, Technical University of Berlin, Straße des 17. Juni 124, 10623, Berlin*

Keywords: chitosan quaternization, vesicle, scattering methods

Polyelectrolyte - surfactant complexes are always interesting for their potential structural transitions which arise from their mutual interaction. Chitosan - alkylethoxy carboxylate complexes studied by L. Chiappisi et al in our group [1,2] demonstrated multilamellar/-faceted structures to be present at pH 4.0, where the number of correlated bilayers is controlled by the mixing ratio of surfactant and polymer. Such systems are interesting as potential “smart” biofriendly carrier system. In more recent work we modified the chitosan to a permanently charged polycation in order to extending the application pH range to pH 7 or above. In this work, methylation quaternized [3] chitosan with substitution degree up to 92% was prepared and complexes formed with the surfactant at acidic and neutral pH. The structure of the ionically assembled complexes was investigated with different methods e.g. UV spectroscopy, static and dynamic light scattering, and small-angle neutron scattering (SANS). Our results revealed that the complex structures now survives at higher pH. Possible structures are illustrated in figure 1. At lower polycation concentration, the vesicle encapsulated chitosan complex transitioned to micelle screened chitosan complexes. At higher polycation concentration, the chitosan screened vesicle complex transformed to micelle decorated polymer network.

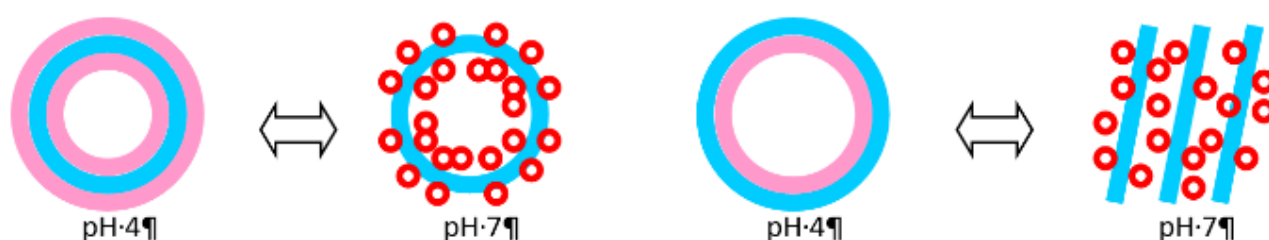


FIGURE 1. Suggested polyelectrolyte – alkyl ethylene oxide carboxylate complex structure in aqueous solution at different pH and concentration. Modified chitosan is shown in blue, surfactant vesicle bilayers are shown in pink, surfactant micelles are showed in red. Left: at lower chitosan concentration; right: at higher chitosan concentration.

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Aggregation behavior of hydrophobically modified polyacrylate – Variation of alkyl chain length

Sven Riemer^a, Michael Gradzielski^a

^a*Stranski-Laboratorium, Technische Chemie Berlin, Straße des 17. Juni 124, 10623 Berlin*

Keywords: hydrophobically modified polyacrylates, SANS, self-aggregation

The aggregation behaviour in aqueous solution of hydrophobically modified polyacrylates, synthesized by Atomic Transfer Radical Copolymerisation (ATRP) of mixtures of alkyl acrylate and t-butyl acrylate and subsequent hydrolysis of the t-butyl acrylate, was investigated by a combination of static and dynamic light scattering with small-angle neutron scattering (SANS). The degree of amphiphilicity was varied by the percentage of alkyl chains and the length of the alkyl chain (butyl to dodecyl), and, in addition, depends strongly on pH via the ionization of the polyacrylate backbone. SANS shows the formation of hydrophobic domains whose size scales with the length of the alkyl chain. The tendency for domain formation increases with the length of the alkyl chains and is much more pronounced for lower pH, while at high pH the electrostatic charging suppresses the formation of hydrophobic domains for chains shorter than octyl. Then only relatively large and loosely connected aggregates are formed. These hydrophobically modified copolymers show a pronouncedly pH dependent aggregation behaviour that is controlled by the length and percentage of hydrophobic modification [1] and this widely tuneable aggregation behaviour could be interesting for the transport and controlled release of hydrophobic cargo molecules.

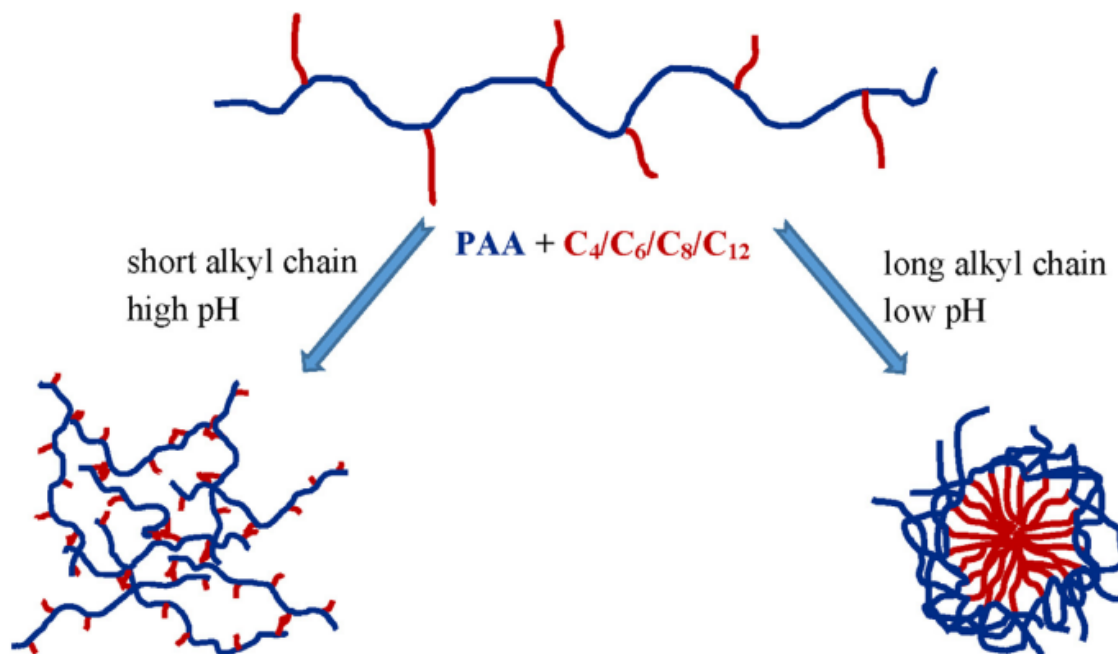


FIGURE 1. Scheme of different aggregation behaviour for the differently long hydrophobic side chain and at different pH.

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Combination of fiber optical methods for monitoring dynamic changes during the switching process of PNIPAM particles

Peter Werner, Roland Hass, Oliver Reich

University of Potsdam, Institute of Chemistry, Physical Chemistry-innoFSPEC, Potsdam/Germany

Keywords: PDW, PAT, PNIPAM, LCST

Smart polymers like Poly(*N*-isopropylacrylamide) (PNIPAM) have great potential for diverse applications like drug delivery systems, protein separation, biosensors, or catalyst carriers. According PNIPAM is one of the most investigated polymers within recent decades. PNIPAM exhibits a reversible coil-to-globule and globule-to-coil transition induced by a temperature change around the lower critical solution temperature (LCST). However, the complete mechanism behind these effects is not fully understood so far.

To determine more details about the mechanism and the structural changes of PNIPAM particles around the LCST, new measurement techniques may be helpful. With the implementation of different inline process analytical techniques (PAT), dynamic changes during the transition process of PNIPAM are detectable.

In this contribution a combination of different PAT in an automated lab reactor for the analysis of the coil-to-globule and globule-to-coil transition of a highly concentrated PNIPAM suspension is presented. One of these techniques is Photon Density Wave (PDW) spectroscopy. This is a method to characterize independently the absorption and scattering properties of highly turbid liquid suspensions. Another PAT applied is Focused Beam Reflectance Measurement (FBRM). This technique measures the chord length distribution of the particles and provides size information during the transition process. With the different PAT (PDW spectroscopy, FBRM, turbidity probe and particle vision measurement) the influence of different heating and cooling rates on the coil-to-globule and globule-to-coil transition could be measured. It could be found out that the whole transition process starts and ends far under and above the LCST. Also, with different heating and cooling rates a direct influence on the LCST and a change in the typical hysteresis could be seen. In addition, an inverse hysteresis is observed by PDW spectroscopy and turbidity measurement for the PNIPAM transition process.

Temperature Sensitive Aggregation Behavior of Poly(Acrylamide-co-Acrylonitrile) in Aqueous Media

Asad Asadujjaman^a, Annabelle Bertin^{*a,b}

^a Federal Institute for Materials Research and Testing (BAM),

Unter den Eichen 87, 12205, Berlin Germany.

^b Freie Universität Berlin, Institut für Chemie und Biochemie, Takustr. 3, 14195 Berlin, Germany.

Keywords: Thermoresponsive polymer, UCST, Copolymer, RAFT

Thermoresponsive polymers have shown great potential in applications such as bioseparation, drug delivery and diagnostic.[1,2] Only few thermoresponsive polymers that present an upper critical solution temperature (UCST), i.e. phase separate from solution upon cooling, in a relevant temperature range have been reported so far. Moreover, the most studied UCST type polymers namely polybetaines are difficult to use under physiological conditions, which significantly restricts their potential applications.[3] Therefore, UCST polymers with sharp and robust phase transition in physiological conditions (in the presence of salts, ions etc.) are highly needed in order to extend the range of applications of this class of polymers.[4]

Herein, a robust UCST-type copolymer of acrylamide (AAm) and acrylonitrile (AN) (poly(AAm-co-AN)) was prepared by reversible addition fragmentation chain transfer (RAFT) polymerization[4] and its thermo-induced aggregation behavior in aqueous media was studied. At temperature below the UCST, the copolymer chains were aggregated together. The aggregate size was found to be larger with increasing AN contents and became smaller upon dilution of the copolymer solutions. While above the UCST, the copolymer chains were expanded and weakly associated in solution. The association between the copolymer chains formed smaller aggregates with increasing the AN contents or the dilution of the solutions. A model is proposed to explain such aggregation behavior (Fig. 1).

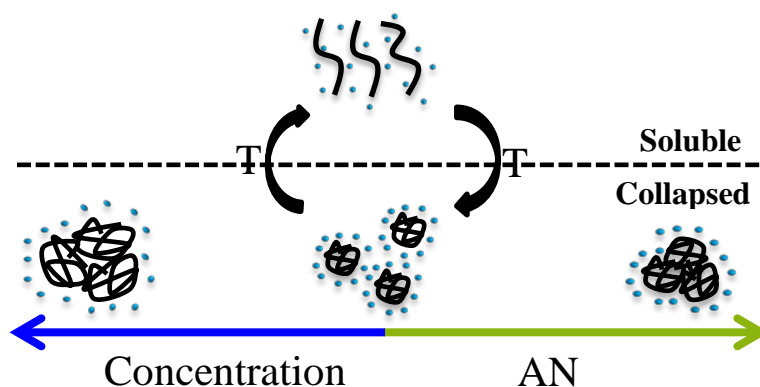


FIGURE 1. Schematic illustration of the possible aggregation behavior.

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Reversible Bidirectional Shape-Memory Effect of Crosslinked Thermoplastic Polymer Blends

Muhammad Farhan,^{a,b} Karl Kratz^a, Andreas Lendlein^{a,b,c}

^a *Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies, Helmholtz-Zentrum Geesthacht, 14513 Teltow, Germany*

^b *Institute of Chemistry, University of Potsdam, 14476 Potsdam, Germany*

^c *Institute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany*

Keywords: shape-memory effect, crosslinked thermoplastics, polymeric actuators

Polymer networks based on crosslinked thermoplastics, having broad melting transitions were recently introduced as actuators exhibiting a reversible bidirectional shape-memory effect (rbSME). Such materials reversibly change their shape upon repetitive heating and cooling, whereby moderate reversible strains below 10% could be obtained [1, 2]. The underlying working principle of these polymeric actuators utilizes lower melting crystallites of the broad melting transition as actuation domains (ADs), while higher melting crystallites act as skeleton forming domains determining the actuators' shape and ensuring the orientation of the ADs.

In this study, we explored whether crosslinked blends of poly(ethylene-*co*-vinylacetate) with a vinyl acetate content of 18 wt% and poly(ϵ -caprolactone) (cPEVA/PCLs) can provide rbSME with larger reversible strains in the temperature interval between ambient temperature and 70 °C.

Two partially overlapping melting transitions with a first peak maximum around 54 ± 1 °C related to the PCL crystals and a second one around 81 ± 1 °C attributed to the polyethylene crystals were observed in dynamic scanning calorimetry experiments for the cPEVA/PCLs. A pronounced rbSME with reversible strains up to 25% was achieved for all copolymer networks as quantified by cyclic, thermomechanical tensile tests, when repetitively heated to 70 °C and cooled to 25 °C. The obtained large reversible strains of cPEVA/PCLs can be attributed to a higher amount of ADs in the crosslinked blends, when compared to the crosslinked homopolymers, cPCL and cPEVA.

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Novel synthetic approach for thermoresponsive nanogels facilitate the *in situ* encapsulation and triggered release of bio-macromolecules

M. Giulbudagian^a, G. Yealland^b, S. Hönzke^b, S. Hedtrich^b, M. Calderón^{a,*}

^aFreie Universität Berlin, Institute for Chemistry and Biochemistry,
Takustrasse 3, 14195 Berlin, Germany

^bFreie Universität Berlin, Institute for Pharmaceutical Sciences,
Königin-Luise-Strasse 2 and 4, 14195 Berlin, Germany

* marcelo.calderon@fu-berlin.de

Keywords: bio-macromolecules, nanogels, nanoprecipitation, thermoresponsive

This study presents a modular approach for the synthesis of thermoresponsive nanogels by thermo-nanoprecipitation. By taking advantage of the polymers inherent thermoresponsiveness, the developed method does not require the use of organic solvents or surfactants. The mild reaction conditions allow for the encapsulation of bio-macromolecules during synthesis, without loss of structural integrity.

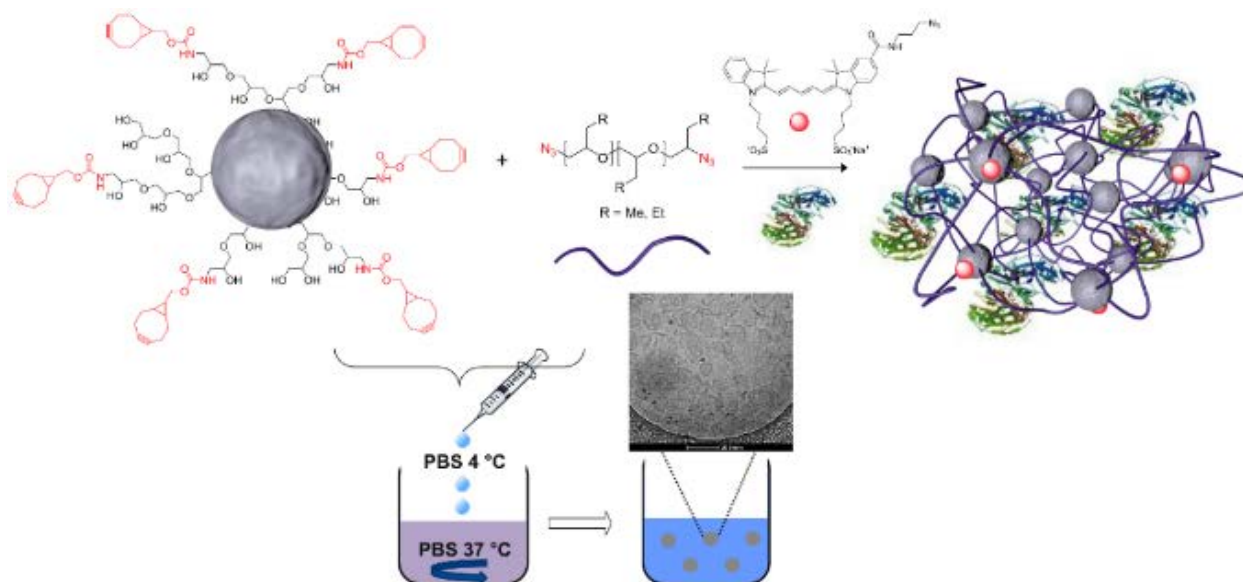


FIGURE 1. The functionalized polymeric precursors are dissolved in PBS at 4°C and precipitated into PBS above the transition temperature of the polymer. Proteins are encapsulated during nanogels formation. Unreacted alkynes are quenched with azide functionalized fluorescent dye.

We acknowledge the support from Deutsche Forschungsgemeinschaft (DFG)/German Research Foundation via SFB1112, Projects A04, C04. We gratefully acknowledge financial support from the Bundesministerium für Bildung und Forschung (BMBF) through the NanoMatFutur award (13N12561).

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Nano- and Micro- Patterning of Poly(Ethylene Glycol) Hydrogels with Gold Nanoparticles

Cigdem Alkan and Marga Lensen

*Technische Universität Berlin, Institut für Chemie, Nanostrukturierte Biomaterialien,
Sekt. TC 1, Straße des 17. Juni 124, 10623 Berlin, Germany
* e-mail: cigdem.alkan@tu-berlin.de, Lensen@chem.tu-berlin.de*

Poly(ethylene glycol) (PEG) hydrogels are well known to be non-toxic, non-fouling, non-immunogenic and are therefore widely used in industry, medicine and cell biological research.[1] While they effectively prevent interactions with proteins and cells, modifications on the surface properties, such as applying nano- or micro-sized topography, changing the elastic property or (bio)chemical surface patterning, allow cell adhesion on the modified areas.[2,3]

Gold nanoparticles (Au NPs) are minimally toxic, can be easily synthesized with different sizes and shapes, equipped with desired functionalities and have special optical properties, such as the size-dependent surface plasmon resonance in the visible region.[4]

Hence particularly due to the interesting characteristics of Au NPs and PEG, the combinations of PEG hydrogels with Au NPs (PEG – Au NPs composites) represent promising biomaterials which can be applied in many fields like biosensors, tissue engineering or for studying of the fundamental cell-biomaterial interactions.

In this work different sizes and shapes of Au NPs are decorated on PEG-based hydrogels in nano- or micro-patterned lines or rectangular island structures and interactions of the cells (L929 fibroblasts) with these PEG – Au NPs composites are investigated. The cells adhere and spread selectively and specifically on the nano- and micro-patterned Au NPs areas. For this purpose different patterning methods are developed, mostly based on concepts from soft lithography, exploiting the unique and tailor-made properties of our polymeric hydrogels (e.g. crosslinking density, elasticity, swelling degree, hydrophilicity and chemical functionality). Our work tool for the hydrogel synthesis ranges from linear UV-crosslinked PEG575 prepolymers to multifunctional star shaped 8PEG precursors, which are crosslinked via amine-Michael type addition reactions.[5] For micro-patterning of Au NPs on PEG hydrogels our **Fill-Molding in Capillaries (FIMIC)**[3] and our novel **micro-contact wet deprinting (μ -CwdP)** methods and for the nano-patterning wrinkled PDMS stamps[6] are used.

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Thermo-responsive Nanogels Cross-linked by Gold Nanoparticles for Drug Delivery

Emanuel A. Glitscher^a, Julián Bergueiro^a and Marcelo Calderón^a

^a*Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany, e.glitscher@fu-berlin.de*

Keywords: Gold nanoparticles, thermoresponsive nanogels, drug delivery

Nanogels (NGs) are highly cross-linked polymeric networks which combine excellent water solubility, biocompatibility, and access for easy chemical modification. These properties along with high capacities for the encapsulation of bioactive molecules introduce nanogels as ideal candidates for biomedical applications like drug delivery. Especially thermo-responsive NGs can respond to varying temperatures by swelling and deswelling. Taking advantage of this physical transition, the release of encapsulated molecules can be triggered.[1] Herein, we report the synthesis and characterization of thermoresponsive nanogels cross-linked by anisotropic gold nanoparticles (AuNPs) exploiting a modified thermo-nanoprecipitation technique.[2] Anisotropic AuNPs show the ability to efficiently convert near infra-red (NIR) light into heat and therefore trigger the phase transition of the polymeric material when integrated into the nanogels.[3] The presented gold-based nanogels are currently under investigation by our research group regarding their potential for temperature-controlled drug release and additional photothermal therapy.

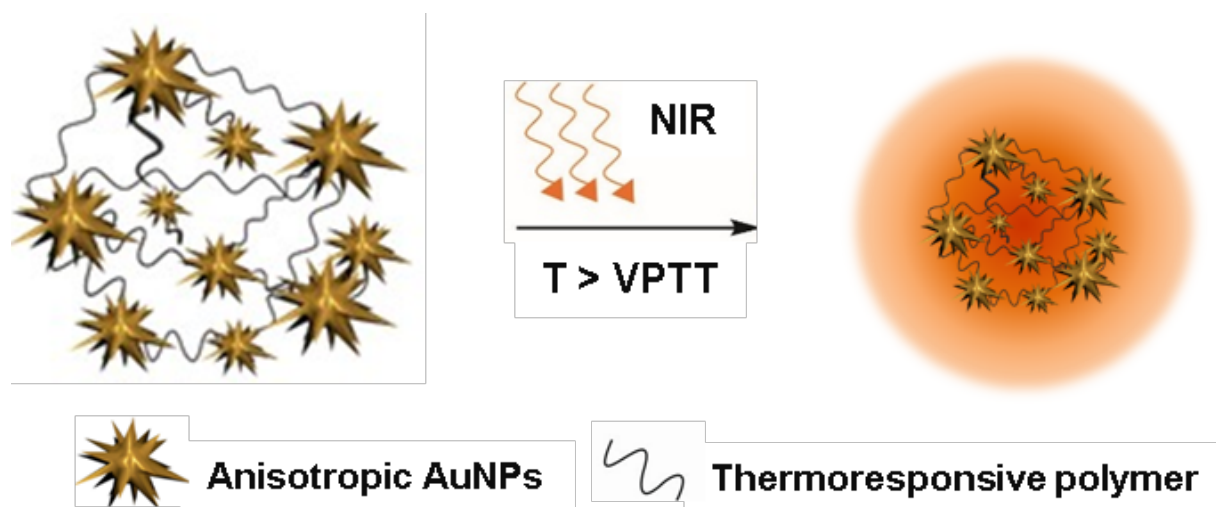


FIGURE 1. Schematic representation of thermo-responsive nanogels cross-linked by AuNPs and their temperature-induced volume-phase transition when irradiated with NIR light.

Acknowledgements: The authors gratefully acknowledge financial support from the Bundesministerium für Bildung und Forschung (BMBF) through the NanoMatFutur award (Thermonanoge, 13N12561).

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Polyethyleneimine Functionalized Oligo[(ϵ -caprolactone)-*co*-glycolide] ABA Block Copolymers and Their Formation into Polycationic Micelles

Maria Balk^a, Marc Behl^a, Christian Wischke^a, Jing Yang^b, Qian Li^b,
Yakai Feng^b, Andreas Lendlein^{a*}

^a *Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies, Helmholtz-Zentrum Geesthacht, Kantstraße 55, Teltow, Germany*

^b *School of Chemical Engineering and Technology, Collaborative Innovation Center of Chemical Science and Chemical Engineering, Tianjin University, Weijin Road 92, Tianjin, China*

Keywords: Self-Assembly, Micelles, Degradable Copolymers

The reduction of the inherent cytotoxicity of polyethylenimine (PEI) based nucleic acid delivery vectors is a major challenge in gene therapy. Cationic polymeric micelles obtained by self-assembly of amphiphilic block copolymers including PEI moieties enable the condensing of polyanionic molecules and provide low cytotoxicity.[1,2] The gene condensing capacity can be adjusted by a co-assembly agent providing a shielding effect of the surface charge. In addition, micelles comprising a degradable core, e.g. poly(lactide-*co*-glycolide), enabled the hydrolytic degradation of the micelles after gene transfection.[3] However, these micellar structures exhibited a stability of less than two days at a pH of 7.4, resulting in a limited time period accessible for transfection, as the release of polyanionic molecules should only occur after uptake of the micelle in early endosomes with a pH = 5.5.

Here, we explored whether polycationic micelles can be created, which would provide a controlled degradation in an acidic pH range. Degradable and amphiphilic ABA block copolymers from hyperbranched PEI A blocks and B blocks based on the hydrophobic oligoesters oligo[(ϵ -caprolactone)-*co*-glycolide] (CG) were prepared. Cationic micellar structures with particle sizes between 19 ± 1 nm and 43 ± 2 nm were obtained by self-assembly of the ABA block copolymers in PBS solution (pH = 7.4). The properties of micelles, e.g. the zeta potential could be controlled by the chain length of B blocks and/or the integration of poly(ethylene glycol) (PEG) functionalized CG oligoester as a co-assembly agent. The sizes of cationic micelles were stable at pH 7.4 for a time period of more than two weeks. At pH = 5.5, as present in early endosomes, an increase of micelle sizes above ten times was observed within two weeks attributing to an accelerated degradation. In this way, the tailored cationic micelles might act as an environmentally triggered delivery system for condensed macromolecules after particle uptake in early endosomes.

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Functional polymer patchy microparticles

Fatemeh Naderi Mehr^{a, b}, Alexander Böker^{a, b}

^aFraunhofer Institute for Applied Polymer Research IAP,
Geiselbergstr. 69, 14476 Potsdam-Golm, Germany

^bLehrstuhl für Polymermaterialien und Polymertechnologie, Universität Potsdam,
14476 Potsdam-Golm, Germany

Keywords: Patchy particles, ERO (epoxide ring opening reaction), μ cp (micro contact printing)

Polymer microparticles with functionalized reactive “patches” on their surfaces are getting more and more attractive in recent studies and colloidal systems. These patchy particles assemble in solution to superstructures similar to DNA and RNA strands.[1]

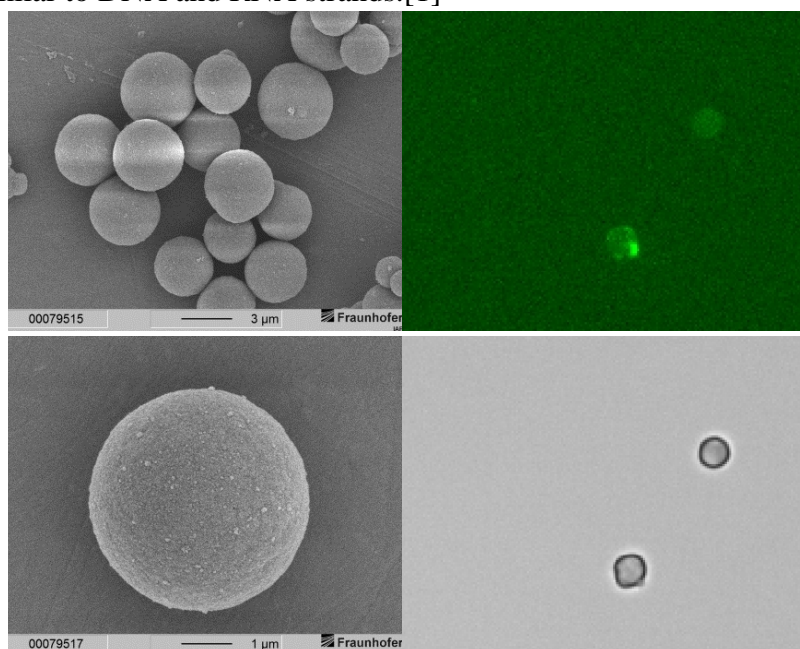


FIGURE 1. SEM micrographs of poly(GMA-*co*-DVB) particles (left) and fluorescence microscopy images of a labeled patchy particle (right)

We introduce the preparation of poly(glycidylmethacrylate-*co*-divinylbenzene) (PGMA-*co*-DVB) microspheres via precipitation poly-merization with a concentration of DVB 75 mol% in a mixture of acetonitrile toluene (8:2) yielding an average size of $\sim 4.5 \mu\text{m}$. [2]

The covalent modification of polymer beads was done using microcontact printing (μ cp) via one type of click chemistry called “epoxide ring opening” (ERO). [2] Polyethyleneimine (PEI) was used as ink reagent, which was labeled after attachment to bead surface with fluorescein isothiocyanate (FITC) to make a clear visualization of the patches by fluorescence microscopy.

The effect of time, temperature and pressure as well as the concentration of PEI on the patch size was studied.

Because of the anisotropic character of self-assembly patchy particles they can be applied in various fields e.g. as biosensor by cell targeting and also bar-coded detection. [3]

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Depsipeptide submicron particles of different sizes as drug delivery systems

Nadia Brunacci^{a,b}, Toufik Naolou^a, Christian Wischke^a,
Axel T. Neffe^{a,b}, Andreas Lendlein^{a,b}

^a *Institute of Biomaterial Science and Berlin-Brandenburg Centre for regenerative Therapies, Helmholtz-Zentrum Geesthacht, 14513 Teltow, Germany.*

^b *Institute of Chemistry, University of Potsdam, Potsdam, Germany.*

Keywords: submicron particles, depsipeptide, surfactants, dexamethasone

Polymeric particulate carriers are explored for potential delivery of drugs into the skin. Submicron particles of larger sizes (300-900 nm) are required to target hair follicles as uptake pathway, while smaller particles might directly enter the stratum corneum. Poly- or oligo[*rac*-lactide)-*co*-glycolide] (PLGA/OLGA) suffer from low drug loadings of dexamethasone (DXM) [1], an antiinflammatory drug relevant for skin applications. We hypothesized that oligodepsipeptides (ODP) may be more efficient drug carriers, as in contrast to OLGA hydrogen bond donor and acceptor groups are displayed, which may increase the interaction with a cargo. Here, it was investigated whether the formation of submicron particles of different sizes from oligo[3-(*S*)-sec-butylmorpholine-2,5-dione]diols (OBMD-diol) with a M_n of 4-6 kDa is possible. In a first step, particle preparation by emulsion solvent evaporation as well as nanoprecipitation was studied, comparing star-shaped oligo(ethylene glycol) of 10 kDa functionalized with desamino-tyrosine (sOEG-DAT) [2] to the commonly employed surfactants polyvinylalcohol (PVA), polyoxyethylen-(20)-sorbitanmonolaurat (Polysorbate 20), and D- α -tocopherol polyethylene glycol succinate (VIT E-TPGS) regarding their suitability for OBMD-diol particle formation. It could be shown that sOEG-DAT enabled the tailoring of particle size (160-900 nm), while the other surfactants either gave only one size or did not result in particle formation. Furthermore, sOEG-DAT could be employed at low concentrations (0.1 wt.%). The encapsulation of DXM as model drug molecule in 160 nm OBMD-diol particles could be achieved with a drug loading (DL) of 2 wt.%, which was up to 16 times higher than the DL reached in the widely used OLGA carrier of similar sizes prepared for comparison. It has been, therefore, demonstrated that OBMD-diol particle size can be tailored by changing either surfactant/oligomer concentration or preparation method and that DXM-loaded OBMD-diol particles have a much higher DL compared to the widely used OLGA carriers.

Acknowledgements: This work was partially financed via the Collaborative Research Centre 1112 “Nanocarriers”, subproject A03, by the DFG. We thank H. Schmidt for technical support.

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Insights in interaction and phase transition behavior of bio-inspired poly(2-oxazoline) coated Laponite hybrid nanoparticles

Ina Dambowsky^a, Igor Zlotnikov^b, Barbara Aichmayer^b, Helmut Cölfen^c, Helmut Schlaad^a

^aUniversity of Potsdam, Institute of Chemistry,
Karl-Liebknecht-Straße 24-25, 14476 Potsdam, Germany.

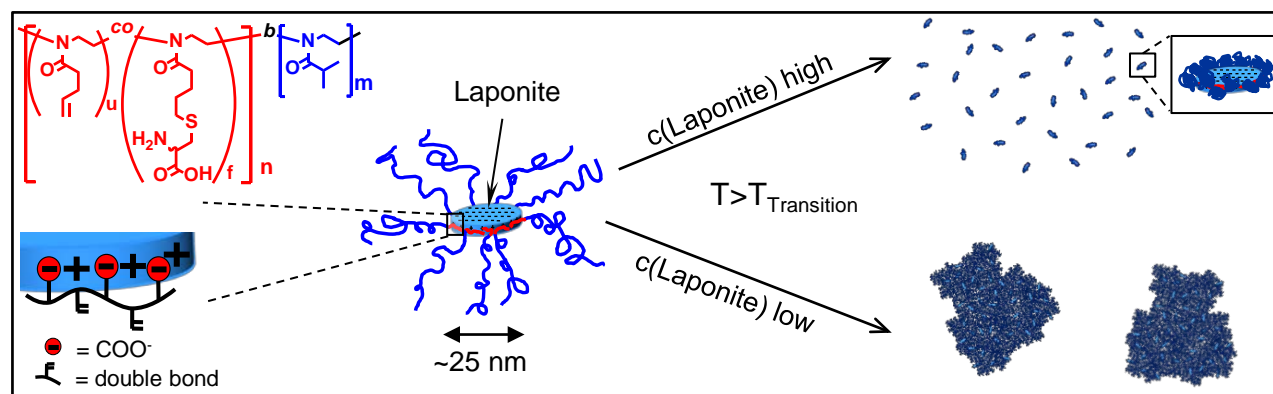
^bMax Planck Institute of Colloids and Interfaces, Department of Biomaterials,
Research Campus Golm, 14424 Potsdam, Germany.

^cUniversity of Konstanz, Physical Chemistry,
Universitätsstraße 10, 78457 Konstanz, Germany.

Keywords: organic-inorganic nano hybrid material, self-assembly, phase transition

Natural composite materials, such as nacre or bone, possess a well controlled coupling between their components. In addition to the hierarchical structuring of these materials, the interfacial interaction between the inorganic particles and the organic matrix is a determining factor for their superior mechanical properties.[1]

In the present study, we present the fabrication of bio-inspired nano hybrid particles based on poly(2-oxazoline) block copolymer and Laponite. The block copolymer consists of an amino acid-functionalized “gluing” block, interacting with inorganic Laponite nanoplatelets, and a thermo-responsive solvating block (Scheme 1). We were able to reveal structure-property relationships within the formed aqueous hybrid dispersions using analytical ultracentrifugation, zeta potential, phototurbidimetry, and dynamic light scattering measurements. Furthermore, we were able to show that the phase transition behavior of the dispersions was strongly affected by the content of the Laponite nanoplatelets.



SCHEME 1. Interaction of amino acid-functionalized poly(2-oxazoline) block copolymer with Laponite nanoplatelets and the phase transition behavior of their aqueous dispersions.

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Polymeric submicron vesicular structures via self-assembly of double hydrophilic Pullulan-polyacrylamide block copolymers in aqueous solution

Jochen Willersinn^a, Markus Antonietti^a, Bernhard V.K.J. Schmidt^a

^aMax-Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, Am Mühlenberg 1, 14476 Potsdam, Germany

Keywords: Self-assembly, DHBC, vesicles

The synthesis of novel carrier systems bearing a water permeable shell with pores of adjustable sizes is of a high interest in biomedical and polymer science. Core shell particles synthesized by amphiphilic block copolymers lack of this ability due to the particle shells hydrophobic character. In contrast to amphiphilic particles, the use of double hydrophilic block copolymers (DHBCs) enables an access to the desired particle features. However, the self-assembly of these block copolymers to particles in aqueous media is strongly dependent on the miscibility of the different blocks and yet only few examples of self-assembly of purely hydrophilic block copolymers were reported. [1,2] Here, we present an access to purely hydrophilic submicron particles based on Pullulan-*b*-poly(dimethylacrylamide) (Pullulan-*b*-PDMA) and Pullulan-*b*-poly(ehtylacrylamide) (Pullulan-*b*-PEA). Polyacrylamides were synthesized with reversible deactivation radical polymerization (RDRP) starting from an azide functionalized initiator and conjugated to alkyne functionalized Pullulan via copper catalyzed azide-alkyne cycloaddition (CuAAC). Block copolymers self-assembled into spherical structures with apparent hydrodynamic diameters of 250 nm. The structures were investigated via DLS, cryo SEM and LSCM techniques.

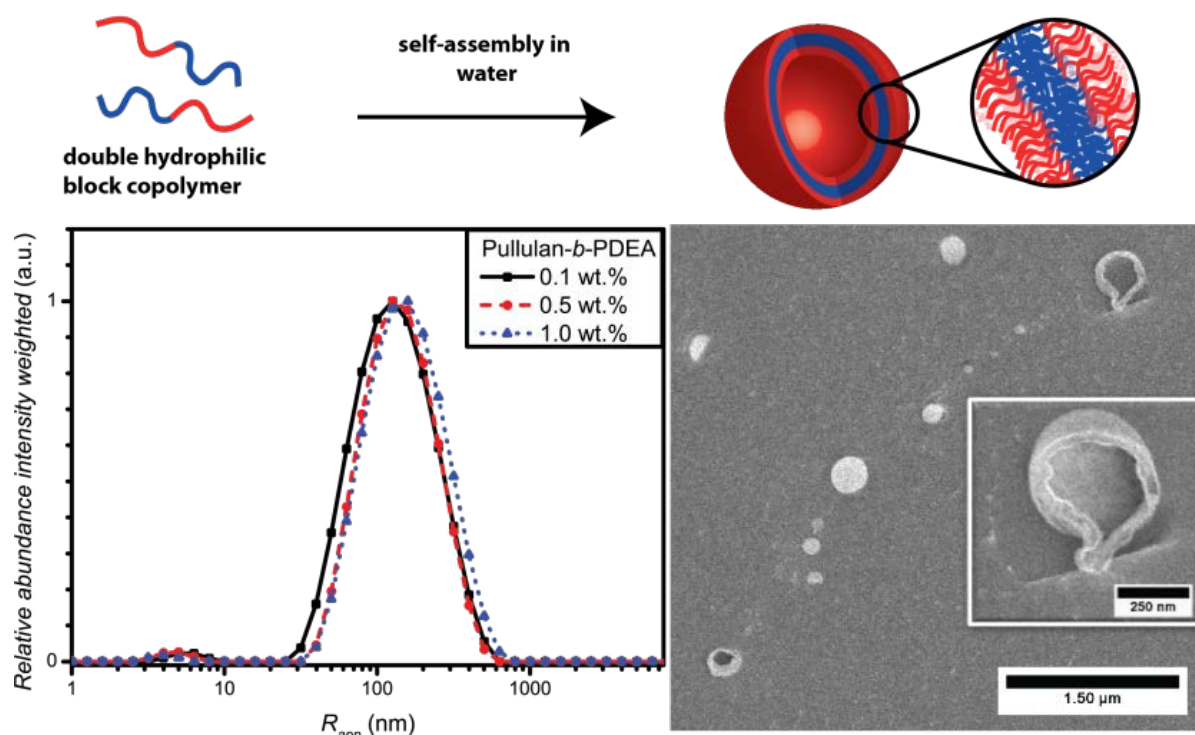


FIGURE 1. Self-assembly scheme of DHBCs in water. Apparent particle size distribution curves of Pullulan-*b*-PEA determined via DLS and cryo SEM micrographs of the afforded vesicular structures.

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Formation and Control of Vesicle Templated Polymer Nanocapsules

Hacer Yalcinkaya^a, Michael Gradzielski^a

^a*Technische Universität Berlin, Stranski-Laboratorium
für Physikalische Chemie und Theoretische Chemie*

Keywords: Polymer nanocapsule, self aggregation, vesicle

Hollow polymer nanocapsules are particularly appealing structures with their increasing usage in nanomedicine based on their structural advantage as having an empty core for encapsulating drugs, proteins or enzymes [1]. Nanocapsules were studied and developed formerly with utilization of self-aggregated templates through the stabilization of vesicle structures especially via polymerization within the bilayer [2]. As a well-defined vesicle system with a polydispersity of 5% spontaneously formed from mixing of micellar TDMAO (tetradecyldimethylamine oxide) and LiPFOS (lithium perfluorooctylsulfonate) solutions was studied before and controlled by the addition of the Pluronic type of copolymers ($\text{EO}_n\text{-PO}_m\text{-EO}_n$) via the mechanism of vesicle formation [3]. These kinetically stabilised vesicles are convenient to be used as templates by fixing with polymerisation in order to form polymer nanocapsules. Therefore monomeric precursors (styrene, alkylacrylates) were incorporated into the vesicle bilayer and ultimately these structures were stabilized by UV induced radical polymerization. Structural alteration of the vesicles upon incorporation of the different monomers and the cross-linkers as well as the effect of subsequent polymerization in the membrane have been investigated by light scattering, small angle neutron scattering, electron microscopy and turbidity measurements. SANS analyses signify an evident transition from monomer loaded micellar system to vesicle structure and the polymerization process shows that the initial structures can be successfully used as templates (Fig.1). Based on these results the potential of this approach to produce well-defined nanocapsules starting from a self-assembled system and following polymerization is critically evaluated.

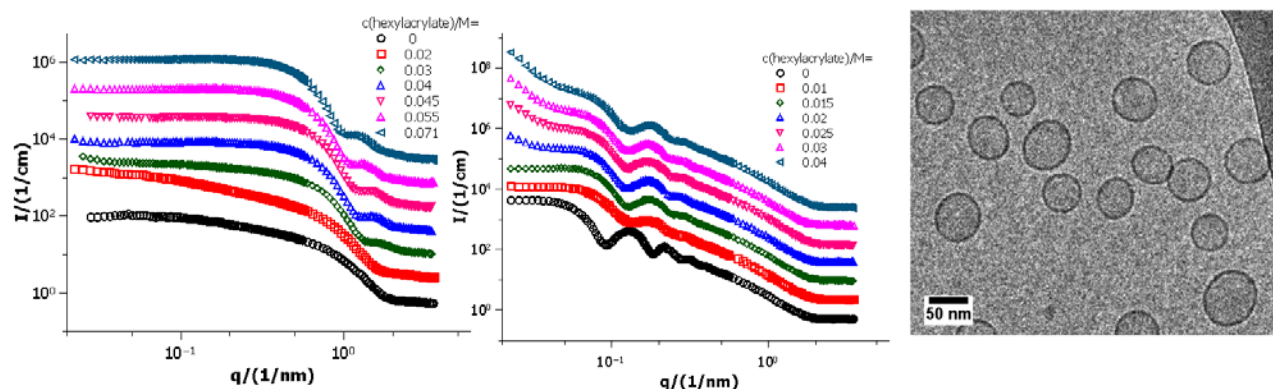


FIGURE 1. a) SANS intensity patterns of monomer loaded micelles b) SANS intensity patterns of vesicles containing increasing amount of monomer c) Cryo-TEM images of cross-linked polymerized vesicles.

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To transmembrane protein-polymer conjugates and beyond: Moving from proof-of-principles to applications

Himanshu Charan^{a, b}, Ulrich Glebe^{a, b}, Alexander Böker^{a, b}

^a Fraunhofer Institute for Applied Polymer Research IAP,
Geiselbergstr. 69, 14476 Potsdam, Germany.

^b Lehrstuhl für Polymermaterialien und Polymertechnologie, Universität Potsdam,
14476 Potsdam, Germany

Keywords: Protein-polymer conjugates; FhuA; ultra-thin self-assembled membranes

Protein-polymer conjugates have been known for around 50 years now and have gained significantly more prominence in the last decade.[1,2] With the advent of controlled radical polymerization (CRP), very sophisticated polymer architectures can now be synthesized on proteins. While many proteins have been targeted for making conjugates, membrane proteins remain untouched. Ferric Hydroxamate Uptake protein component A (FhuA) is a membrane protein from *E. Coli*'s outer cell membrane. The amine groups from the lysine residues of the protein FhuA were first converted into an initiating site for CRP and polymer chains subsequently grown from them. We proved, for the first time, that it is possible also to target this class of proteins using MALDI-ToF MS, SDS-PAGE, and analytical ultracentrifugation. These conjugates were then utilized for generation of ultra-thin functional membranes by first allowing them to self-assemble at the air-water interface, and subsequent cross-linking (Figure 1). The protein channels form the most ideal pores, having universally fixed size and the predetermined functionality. Additionally, by combining the tailoring afforded by genetic engineering tools for proteins with the variety of properties afforded by polymer blocks such as temperature and pH responsivity, a range of smart functions can be added to the membranes in not so distant future.

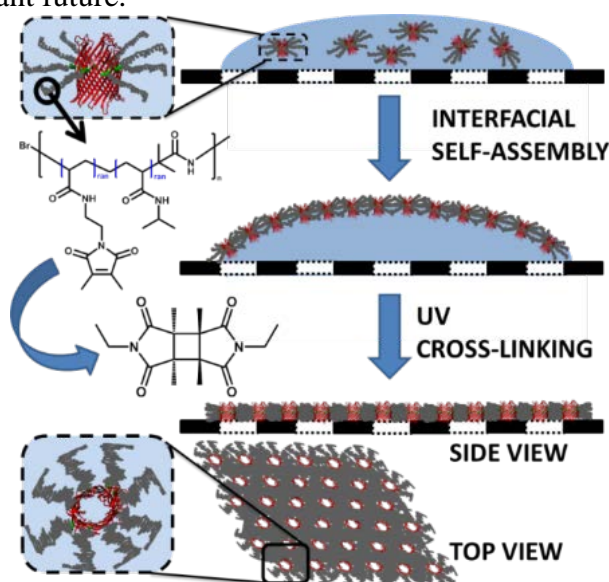


FIGURE 1. FhuA-polymer conjugates were self-assembled at the air-water interface and then UV cross-linked to generate stable membranes.

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Functionalized graphene as extracellular matrix mimics: toward well-defined 2D nanomaterials for multivalent virus interactions

M.F. Gholami^a, D. Lauster^b, K. Ludwig^c, J. Storm^b, B. Ziem^c, N. Severin^a,
C. Böttcher^c, J.P. Rabe^a, A. Herrmann^b, R. Haag^c, M. Adeli^c

^a *Institut für Physik & IRIS Adlershof,
Humboldt-Universität zu Berlin*

^b *Institut für Biologie, Humboldt-Universität zu Berlin*

^c *Institut für Chemie und Biochemie, Freie Universität Berlin*

Keywords: Multivalency, Hyperbranched Polyglycerols, Functionalization, Graphene, viral interactions

Multivalency is widely used by nature to control biological interactions. Therefore, we also considered it for the design of a new generation of anti-viral drugs. Two-dimensional materials are promising carriers for multivalency. Graphene, in particular, is very robust yet chemically rather inert and therefore it is difficult to control the density distribution of its functionalization. We employed Scanning Force Microscopy (SFM) in quantitative imaging mode to investigate the functionalization of thermally reduced graphene oxide sheets and further used the sheets for the inhibition of the vesicular stomatitis virus (VSV) as a model virus. The functionalization of the sheets was carried out using a [2+1] nitrene cycloaddition reaction at ambient conditions. SFM imaging reveals a high density and homogenous distribution of the functionalization, depending on reaction conditions. Moreover, it allows to gain insight into the interaction of the multivalently functionalized sheets with VSV depending on the type and density of the functionalization.

Functionalization of surfaces using Diazoesters and CHic reaction

Philip Kotrade^a, Oswald Prucker^a, Jürgen Rühe^a

^aDepartment of Microsystems Engineering (IMTEK)
University Freiburg, Georges-Köhler-Allee 103, 79110 Freiburg

Keywords: CHic reaction, diazoester, surface modification

The introduction and control of surface functionalities is an important part of material science. Since polymers possess a broad variety of properties, the use of such materials as coatings is a smart way to generate desired surface properties. Next to those material properties, existing techniques for film deposition make polymers a powerful tool for the modification of surfaces. A major challenge for polymer films on surfaces is the long term stability as well as the introduction of further functionalities. To address this issue we developed a crosslinker system which is based on the C,H insertion crosslinking (CHic) reaction of a reactive intermediate. Those intermediates may be ketyl-radicals, nitrenes and carbenes¹⁻³. The here presented system consists of a diazoester which generates a carbene upon thermal or photochemical activation. First tests show that the crosslinker inserts into any C,H bond present in the vicinity, allowing for the simple modification of basically all polymeric surfaces. Furthermore this approach holds the ability to introduce functionalities to the surface, by for example immobilizing biomolecules in a surface-attached polymer network³, which then in turn can be used as smart surface devices. Such water swellable hydrogels are interesting for biomedical applications^{4,5}. The presented method for surface modification holds great promise to become a standard way of surface modification for polymeric substrates.

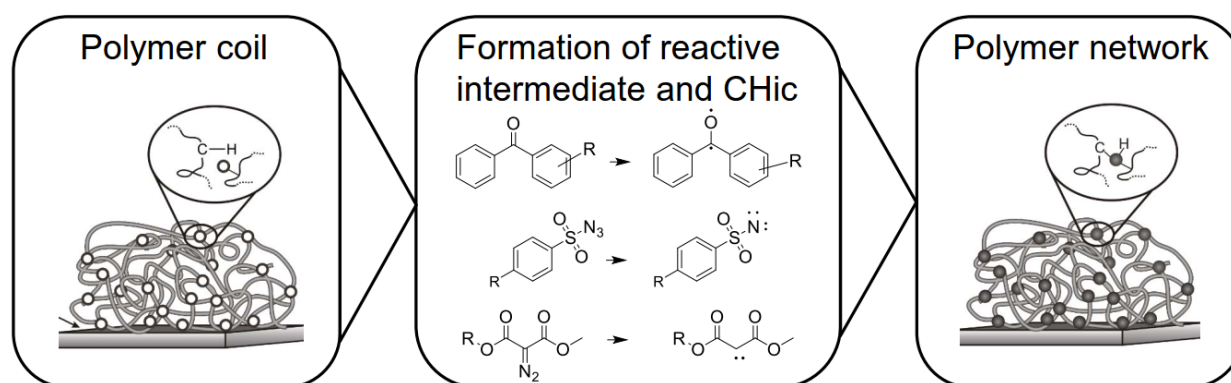


FIGURE 1. Formation of a surface-attached polymer network using the CHic reaction.

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Catecholate-Based Photocurable Materials for Bioinspired Coatings for Osteoconduction of Titanium Implants

Kathleen Hennig, Wolfdietrich Meyer

Fraunhofer Institute for Applied Polymer Research IAP, Geiselbergstr. 69, D-14476 Potsdam

Keywords: adhesive polymers, catechol functionality, dopamine, gelatine, hydroxyapatite

A complete biological integration into the surrounding bone is a critical step for clinical success of an implant. Titanium and its alloys have an excellent biocompatibility but are not integrated into the bone. The bone formation in the near proximity of the surface of the implant *named osteoconduction*[1] is a crucial factor in this respect.[2]

We investigate an biomimetic adhesive material compounded by a building block system consisting of three different substances, each responsible for a certain functionality of a bone like material that covers a titanium implant surface. The material is achieved with methacrylated gelatine as scaffold matrix[3] and hydroxyapatite (HA) for bone mineralization[4], both prerequisites for cell based ossification processes.

The third component is the special interest in this work. We develop a biomimetic adhesive photopolymer primer that enables the compound not only to adhere permanently to the implant surface, but also gives cohesive stability within the bone-like material itself.

Currently, catecholates like dopamine have received considerable interest as anchor groups for biomedically relevant metal surfaces and nanoparticles.[5] We synthesized several photoreactive monomers based on the dopamine residue functionalized with acrylic and methacrylic groups. Structural characterization of the monomers was performed by ¹H-NMR and FT-IR. The photocurability of the monomers were investigated by (photo)-DSC and FT-IR. A setup was developed to measure the mechanical adhesion forces of the corresponding photopolymers from the above described compound system to the titanium surface.

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Active Surfaces Based on Temperature-Sensitive Polymers

Yi Jiang^{a,b}, Yue Liu^{a,b}, Liang Fang^{a,#}, Karl Kratz^a, Andreas Lendlein^{a,b}

^a*Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies, Helmholtz-Zentrum Geesthacht, Kanstr. 55, 14513 Teltow*

^b*Institute of Chemistry, University Potsdam, 14476 Potsdam, Germany*

[#]*Present address: State Key Laboratory of Materials-Oriented Chemical Engineering, College of Material Science and Engineering, Nanjing Tech University, 210009, Nanjing, China.*

Keywords: shape-memory effect, temperature-memory effect, microstructure surfaces

Temperature-memory polymers (TMP) can memorize the temperatures where they have been deformed into a temporary shape by recovering their permanent shape at temperatures equivalent to the applied deformation temperatures.

In the current study we explored whether the response temperature where micro/nano-topographical shape changes occur in microstructured polymeric substrates can be controlled by cold, warm or hot deformation. Crosslinked poly[ethylene-*ran*-(vinyl acetate)] (cPEVA) was selected as TMP material of hydrophobic nature having a broad melting transition (T_{trans}) which is capable to memorize the deformation temperature.[1,2] The cPEVA substrate had a permanent microstructure design of micro-cylinder arrays with a height of 10 μm and a diameter of 25 μm resulting in a “superhydrophilic” wetting behavior as confirmed by dynamic contact angle measurements via captive bubble method. By vertical compression with a Si-Wafer at different temperatures the microstructured substrate was transformed into a temporary nano-smooth surface, which showed hydrophobic wetting behavior. Upon heating to 100 °C the temporary even substrates showed micro as well as nano-level topographical changes, which occurred at temperatures close to the applied deformation temperatures, as characterized by atomic force microscopy experiments. The fully restored microstructures showed again a hydrophilic wetting behavior. In this way the response temperature characterizing the shape change as well as the change in wettability of the polymeric substrate could be systematically adjusted in a broad temperature range from 38 ± 1 °C to 81 ± 1 °C, demonstrating the applicability of the presented surface functionalization technology.

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Adsorption of solutes on a thermoresponsive PNIPAM polymer

Matej Kanduč^a, Richard Chudoba^{a,b}, Karol Palczynski^a,
Won Kyu Kim^a, Rafael Roa^a and Joachim Dzubiella^{a,b}

^a *Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany*

^b *Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, D-12489 Berlin, Germany*

Keywords: nanocarriers, polymers, adsorption, MD simulations

Thermoresponsive hydrogels, such as Poly(N-isopropylacrylamide) (PNIPAM), are recently becoming very popular as ‘smart’ carriers in modern nanoscience. By changing the temperature, the PNIPAM hydrogel structure can undergo a sharp transition from a swollen into a collapsed state, which alters the selectivity for the solute particles that diffuse through the hydrogel. Catalytic model reactions of the reduction of p-nitrophenol and nitrobenzene nicely demonstrate such a selectivity, where the reaction rates of both reactants dramatically change after the transition [1]. In order to gain insights into the nanoscale structure and binding details in such systems, we employ Molecular Dynamics simulations of PNIPAM polymer in explicit water. We model an extended PNIPAM polymer chain in the presence of various solutes dissolved in water, which mimics the hydrogel in the swollen state. We put particular attention to aromatic molecules and explore the influence of temperature, polymer stretch, and polymer tacticity on the solute binding affinities. We find that, quite general, an adsorption raises with the size of a molecule. Moreover, nitrated aromatic molecules exhibit profound adsorption. On the other hand, the presence of polar hydroxyl groups do not alter the adsorption much.

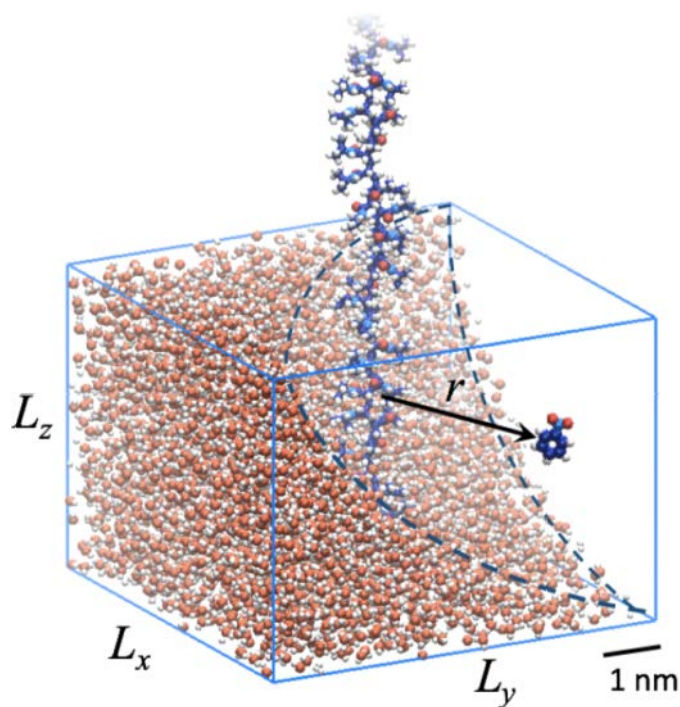


FIGURE 1. Simulation snapshot: Periodically replicated isotactic PNIPAM chain composed of 20 monomers in the presence of a single nitrobenzene molecule.

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Description of Catalytic Rates in Stimuli-Responsive Nanoreactors

Rafael Roa^a, Stefano Angioletti-Uberti^b, and Joachim Dzubiella^{a,c}

^a*Institute for Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin, Berlin, Germany*

^b*International Center for Soft Matter Research, Beijing University of Chemical Technology, Beijing, China*

^c*Institute for Physics, Humboldt-Universität zu Berlin, Berlin, Germany*

Keywords: nanoreactors, stimuli-responsive polymers, catalysis, diffusion-influenced reactions

In recent years, the use of stimuli-responsive polymer coatings has come out as a possible new way to control the catalytic activity of colloids and nanoparticles [1-3]. The polymer coating not only prevents particles from coagulation or aggregation, but actively participates in the catalytic process by changing the local environment for the reactants. The catalytic rate can be thus flexibly tuned and switched, e.g., by the temperature [1-3], ionic strength, or pH.

In this work we present a comprehensive theoretical framework that, by extending concepts from the Debye-Smoluchowski theory of diffusion [3,4], allows to qualitatively and quantitatively describe the influence of all major experimentally tunable parameters on the nanoreactors' catalytic rate. We pay special attention to the case of multicomponent systems by analyzing the temporal and spatial distribution of reactants and products. Besides, we study the effect of electrostatic interactions on the catalytic rate. This theoretical framework is also useful to find out what parameters most sensitively tune such rate, therefore providing theory-guided design principle for stimuli-responsive nanoreactors' synthesis.

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**Properties of poly(sebacic acid) monolayers
at the air-water interface**

Falko O. Rottke^{a,b}, Burkhard Schulz^{a,b}, Sascha Eidner^a,
Michael U. Kumke^a, Abraham Domb^c and Andreas Lendlein^{a,b}

^a University of Potsdam, Institute of Chemistry,
Karl-Liebknecht-Straße 24 – 25, 14476 Potsdam, Germany

^b Institute of Biomaterial Science, Helmholtz-Zentrum Geesthacht,
Kantstraße 55, 14513 Teltow, Germany

^c School of Pharmacy- Faculty of Medicine, The Hebrew University of Jerusalem,
Jerusalem 91120, Israel

Keywords: Kelvin technique, Langmuir technique, polyanhydrides, polymer crystallization

Biodegradable aliphatic polyanhydrides are interesting materials for medical applications, requiring a short-term degradation like drug delivery systems [1]. Such polymers are considered to undergo surface erosion and in this way understanding of molecular interactions between polymer and environment plays a key role to tailor their degradation behavior. For this purpose poly(sebacic anhydride)[2] (PSA) is investigated by Langmuir technique allowing to generate monomolecular layers of certain samples at the air-water interface. The mechanical film properties were controlled by variation of surface pressure π , and simultaneously occurring changes inside the layer were monitored *via* Brewster angle microscopy (BAM) and Kelvin technique. A pronounced influence of subphase composition towards the monolayer's packing and surface pressure-induced crystallization of PSA was revealed: On phosphate buffer saline (PBS) the investigated PSA layers were more compressible up to $5 \text{ mN}\cdot\text{m}^{-1}$ in contrast to $3 \text{ mN}\cdot\text{m}^{-1}$ on water and able to exhibit higher surface potential values (310 mV vs 260 mV). Both findings indicate a denser packing of PSA on PBS. Moreover, the crystallite's habitus observed on water were with a diameter of 5.5 nm more compact in contrast to PBS ($\sim 2 \text{ nm}$), but in any case of fibroid nature. Sum frequency generation (SFG) spectroscopy was applied to elucidate the molecular basis for the influence of subphase composition, as this technique allows to monitor molecular vibrations, e.g. CH_2 -stretching or OH (water) vibrations, at interfaces. The SFG data revealed that the subphase composition affects the interaction of interfacial water molecules with PSA units in a way that the water surface is differently ordered.

A combination of Langmuir and Kelvin technique as well as BAM and SFG spectroscopy represents here an unique approach to study polymeric Langmuir layers on a molecular level and evaluate microscopic interactions at the material-environment interface.

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Enzymatic degradation of oligo(ϵ -caprolactone) based Langmuir films adjusted by variation of polymer structure

Anne-Christin Schöne^{a,b}, Burkhard Schulz^{a,b}, and Andreas Lendlein^{a,b}

^a*Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany*

^b*Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies, Helmholtz-Zentrum Geesthacht, Kantstraße 55, 14513 Teltow, Germany*

Keywords: oligo(ϵ -caprolactone), polyesterurethanes, Langmuir films, degradation

A detailed knowledge of degradation is essential for application of polymers in medical devices. Most analytical methods investigating degradation processes concentrate on the characteristics of bulk 3D samples. The Langmuir techniques enable the preparation of polymer films and allow a time-saving investigation of both, the polymer degradation behavior and the polymer-enzyme interactions at an interphase. In those studies the polymer degradation is related to the reduction of the required surface area for a polymer layer under constant surface pressure conditions when water-soluble degradation fragments are formed.[1]

The interactions of monolayers from oligo(ϵ -caprolactone) based copolyesterurethanes (P(OCL-U)) linked with urethane junction units derived from 2, 2 (4), 4-trimethyl-hexamethylene-diisocyanate (TMDI), hexamethylene diisocyanate (HDI) or lysine ethylester diisocyanate (LDI) with the lipase from *Pseudomonas cepacia* are evaluated. The influence of the macromolecular architecture and of the chemical structure on the scission process of the polymer chains is studied in comparison to linear OCL. The enzymatic degradation behavior of P(OCL-U)s containing OCL segments with the same molecular weights than the pristine OCL-diol is investigated at 37 °C on a phosphate buffer saline (PBS) subphase.

P(OCL-U)s films exhibit an at least five times lower degradation in comparison to linear OCL independent on the molecular weight of the copolymers and on the film packing density.[2] The induced intramolecular interactions between the urethane junction units in the macromolecular chains and the enzyme molecules in the subphase lead to a lag time preceding to the initiation of the formation of water-soluble degradation fragments.

The Langmuir technique allows the fast investigation of polymer-enzyme interactions and their impact on degradation processes, which enable the tuning of polyesterurethane based devices for enhanced medical applications.

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Sulfobetaine Methacrylate Homo- and Block Copolymers as Versatile Components for Multi-responsive Systems

Noverra M. Nizardo^a, Viet Hildebrand^a, Eric Schönemann^a, André Laschewsky^{a,b}

^a *Inst. Chemie, Universität Potsdam, Karl-Liebknechtstr.24-25, 14476 Potsdam-Golm, Germany*

^b *Fraunhofer Institute for Applied Polymer Research IAP, 14476 Potsdam-Golm, Germany*

Keywords: polyzwitterions, self-assembly, smart materials, protein mimics

Zwitterionic compounds are wide-spread in nature, and are found for instance as lipids, osmolytes and proteins. Zwitterionic polymers, such as polysulfobetaines (PSBs), are thus attractive, offering, e.g., good biocompatibility and anti-fouling behavior [1,2]. Moreover, many polysulfobetaines exhibit an upper critical solution temperature (UCST) in aqueous media, which can be modulated efficiently by adding low molar mass electrolytes. All these properties render PSBs interesting materials, especially for biomedical applications. In this general context, we have synthesized various sulfobetaine-based methacrylate (co)polymers via controlled radical polymerizations, namely by reversible addition fragmentation transfer (RAFT) and by atom transfer radical polymerization (ATRP), and studied their UCST behavior.[3] With the final goal to establish PSB as responsive block for controlled delivery purposes, we are exploring two kinds of block copolymers of sulfobetaines: on the one hand, PSB blocks are combined with hydrophilic blocks, such as PEG [4]; on the other hand, PSB blocks are combined with hydrophobic blocks. We shall present the synthesis of such responsive copolymers and discuss their temperature- and ion-responsive behavior and the resulting self-assembly.

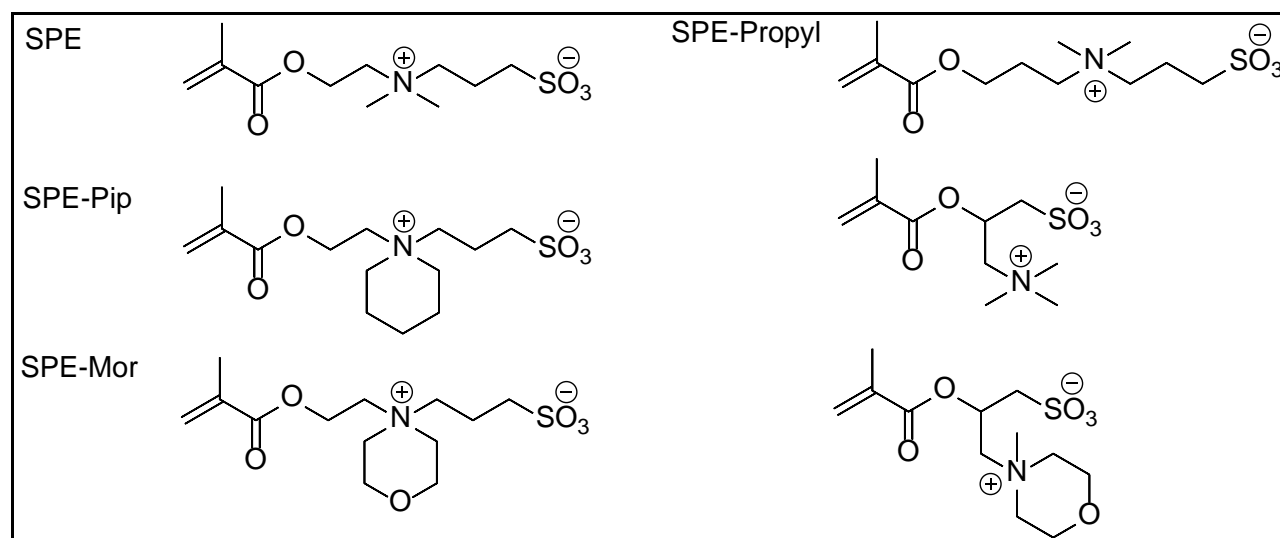


FIGURE 1. Examples of sulfobetaine methacrylates explored.

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Insights in the shape-memory mechanism of multiblock copolymers having crystallizable as well as glassy switching domains

Wan Yan,^{a, b} Marc Behl,^a Karl Kratz,^a Andreas Lendlein^{a, b}

^a *Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies, Helmholtz Zentrum Geesthacht, Kantstr. 55, D-14513, Teltow, Germany*

^b *Institute of Chemistry, University Potsdam, 14476 Potsdam, Germany*

Keywords: Multiblock copolymer, shape-memory effect, crystallinity

A multiblock copolymer consisting of crystallizable poly(ϵ -caprolactone) (PCL) and crystallizable poly[oligo(3*S*-iso-butylmorpholine-2,5-dione)] (PIBMD) named PCL-PIBMD is capable of a shape-memory effect, whereby PIBMD crystals determine the permanent shape and both PCL crystals and PIBMD amorphous domains, having similar transition temperatures, can act as switching domains stabilizing the temporary shape. [1,2]

In the current study, we explored the nano-structural changes occurring in PCL-PIBMD during programming via uniaxial deformation when different deformation strains were applied. For distinguishing the relative contribution of crystalline PCL and PIBMD amorphous phases to the fixation of the temporary shape a toluene vapor treatment of programmed PIBMD-PCL samples was applied. Here toluene was selected as solvent selectively dissolving PCL crystallites, while PIBMD amorphous and crystalline domains should not be affected.

The shape-memory properties were quantified by cyclic, thermomechanical tensile tests, where different strains in the range from 50% - 900% were applied for programming PCL-PIBMD films at 50 °C. The nano-structural changes were examined by atomic force microscopy (AFM) measurements and in-situ wide and small angle X-ray scattering experiments (WAXS, SAXS).

With increasing the programming strain, the higher degrees of orientation were observed in the amorphous PIBMD domains and the level of fragmentation of existing large PIBMD crystals was found to increase. By increasing the deformation strain from 50 to 900% resulted in an increase of the shape fixity ratio from 93 \pm 1% to 96 \pm 1%, while the recovery ratio decreased from 92 \pm 1% to 84 \pm 1%. Toluene vapor treatment experiments could demonstrate that the temporary shape was fixed by both crystalline PCL and glassy PIBMD domains, whereby the contribution of PIBMD to fixation was found to increase with increasing programming strain.

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Shape-memory effect of electrospun copolyesterurethanes microparticles and hollow microfiber-meshes

Quanchao Zhang^{a,b}, Karl Kratz^a, Andreas Lendlein^{a, b}

^a Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies, Helmholtz-Zentrum Geesthacht, 14513 Teltow, Germany;

^b Institute of Chemistry, University Potsdam, 14476 Potsdam, Germany;

Keywords: Shape-memory effect, hollow microfibers, microparticles

Copolyetheresterurethanes consisting of oligo(p-dioxanone) (OPDO) hard and crystallizable oligo(ϵ -caprolactone) (OCL) switching segments named PDC exhibiting a phase-segregated morphology have been reported as multifunctional materials combining a shape-memory function with a tailorable degradation behavior. While the previous investigations concentrated on macroscopic shaped bodies like films or fibers, in the current work we explored the shape-memory capability of electrospun microscaled objects i.e. microparticles and hollow microfiber-meshes. PDC microfiber meshes composed of single hollow fibers with an outer diameter of $1.4 \pm 0.4 \mu\text{m}$ and a wall thickness of 0.5 ± 0.2 or $0.3 \pm 0.2 \mu\text{m}$ as well as solid fibers with the same diameter were prepared by coaxial electrospinning using poly(ethylene glycol) (PEG) as sacrificial core material, which was removed by exposure to water. Solid almost spherical PDC microparticles with a diameter of $3.9 \mu\text{m}$ were prepared via electrospraying.

Differential scanning calorimetry experiments and tensile tests revealed an increase in degree of crystallinity of the OCL switching domains from $37 \pm 1\%$ to $52 \pm 1\%$ as well as an increase of the fiber-meshes' Young's modulus from 4.6 ± 0.7 to 11.8 ± 1.3 with decreasing wall thickness of the single hollow fibers. Cyclic, thermomechanical uniaxial tensile tests showed a pronounced shape-memory effect for all fiber-meshes, whereby meshes composed of hollow microfibers with a wall thickness of $0.3 \pm 0.2 \mu\text{m}$ exhibited the highest shape recovery ratio, while the shape fixity ratio was found to decrease with reducing wall thickness. These findings can be attributed to higher degrees of macromolecular chain orientation in the electrospun meshes with thinner wall thickness in the single hollow microfibers. PDC microparticles were obtained and deformed by compression at 55°C and different programming pressures of 0.2 MPa and 100 MPa. The shape recovery of programmed single particles during heating to 60°C was analyzed online and offline by optical and scanning electron microscopy. Here a pronounced SME with a shape recovery ratio 80% was achieved when low programming pressure was applied. Finally, by programming an array of PDC microparticles a temporary film could be generated, which disintegrates into particles by heating to 60°C . Here it was demonstrated that microscaled PCD objects can be equipped with a thermally-induced shape-memory effect, and in this way shape changes on macro as well as micro level can be realized.

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High-strain shape-memory effect of poly(carbonate-urea-urethane) networks

M. Mazurek-Budzyńska^{a,b}, M. Y. Razzaq^a, K. Tomczyk^b,

G. Rokicki^b, M. Behl^a, A. Lendlein^a

^a *Helmholtz-Zentrum Geesthacht, Institute of Biomaterial Science,
Kantstr. 55, 14513 Teltow, Germany*

^b *Warsaw University of Technology, Department of Chemistry,
Noakowskiego 3, 00-664 Warszawa, Poland*

Keywords: Poly(carbonate-urea-urethane)s, oligo(alkylene carbonate) diols, one-way high-strain shape-memory effect.

A challenge in the design of the shape-memory polymers (SMPs) is to achieve high deformability with simultaneous high shape recovery. SMPs can be realized as thermoplastic phase-segregated materials with netpoints based on physical interactions or as covalent polymer networks. Thermoplastic materials provide a high deformability, but exhibit low shape recovery ratios. In contrast, SMPs based on covalent networks have shown great shape recovery ratios but limited capacity of deformations.[1] In this study we explore whether SMPs capable of high strain deformations and high shape recovery ratio can be created by polymer networks providing two kinds of netpoints – covalent bonds and physical interactions. Poly(carbonate-urea-urethane)s (PCUUs) synthesized by a precursor route were selected as a model system.[2]

In the first step diisocyanate telechelics were obtained by reacting oligo(alkylene carbonate) diol with isophorone diisocyanate. Afterwards a curing process was performed, in which water vapor was added to hydrolyze the isocyanate to amine groups. Subsequent reaction of the amine and isocyanate groups resulted in polymer chain extension with urea bonds formation. Hard domains containing urea and urethane groups acted as physical cross-links through the hydrogen bonds. Due to the excess of diisocyanate present in the system, small amounts of covalent bonds acting as permanent cross-links were created in form of allophanate and biuret groups.

The influence of the programming-deformation ($\varepsilon_{\text{prog}}$), M_n of oligo(alkylene carbonate) diol as well the length of the hydrocarbon chain in its' repeating unit on one-way shape-memory properties was investigated. The PCUU networks exhibited excellent shape fixity ratios ($R_f = 92\text{--}97\%$) and shape recovery ratios ($R_r \geq 99\%$) with $\varepsilon_{\text{prog}}$ up to 1000%. The switching temperature (T_{sw}) varied in the range from 36 to 68 °C. The high-strain capacity and the high Young's modulus as well as the improved resistance to hydrolysis in comparison to poly(ester-urethane)s, make obtained PCUUs interesting candidate for applications in long-term medical devices.

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Two Level Shape Changes of Cuboidal Polymeric Microparticles

Yue Liu ^{a,b}, Muhammad Yasar Razzaq^a,
Karl Kratz ^a, Andreas Lendlein ^{a,b}

^a*Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies,
Helmholtz-Zentrum Geesthacht, Kanstr. 55, 14513 Teltow*

^b*Institute of Chemistry, University Potsdam, 14476 Potsdam, Germany*

Keywords: thermo-sensitive polymer, shape-memory effect, microparticles

The controlled deformation and quantification of shape changes in polymeric micro-objects represents a major technological challenge. [1]

In this work shape-memory polymer micro-cuboids were utilized as model system for exploring their shape-memory capability on the microscopic geometry level as well as on the nanoscale roughness changes on the top surface of the cuboidal particles.

Polymeric micro-cuboids having an edge length of 25 μm and a height of 10 μm were prepared from crosslinked poly[ethylene-co-(vinyl acetate)] (cPEVA) [2] with different vinyl acetate contents of 18 or 40 wt% using a poly(dimethylsiloxane) based soft mold approach. The shape recovery of single micro-cuboid during heating was monitored online by optical microscopy (OM) and quantified by the related changes in the projected area (PA). The temperature-induced changes height (H) as well as in nano-roughness were investigated by in-situ atomic force microscopy (AFM). Programming by compression resulted in various deformed micro-cuboids exhibiting compression ratios ranging from $23 \pm 3\%$ to $74 \pm 1\%$ for cPEVA18 and from $42 \pm 0\%$ to $79 \pm 1\%$ for cPEVA40. Excellent shape-memory properties, characterized by a complete recovery of the original micro-cuboid dimensions, including their nano-roughness, were achieved in AFM heating experiments independent from the compression ratio. All investigated micro-cuboids exhibited similar switching temperatures in the range from $T_{\text{sw}} = 80 \pm 2\text{ }^{\circ}\text{C}$ to $85 \pm 2\text{ }^{\circ}\text{C}$ for cPEVA18, while cPEVA40 micro-cuboids exhibited lower switching temperatures of $T_{\text{sw}} = 63 \pm 2\text{ }^{\circ}\text{C}$ and $68 \pm 2\text{ }^{\circ}\text{C}$.

Finally, it could be demonstrated that an array of micro-cuboids can be compressed into a temporary stable film, which can disintegrate gradually into individual cuboids upon heating to $100\text{ }^{\circ}\text{C}$, illustrating the applicability of the presented technology.

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Protein Absorption on Nanoparticles for Biomedical Applications

Enrico Miceli^{a,b}, Ernesto Rafael Osorio-Blanco^a, Loryn Fechner^a,
Mrityunjoy Kar^a, Chris Weise^a, Marcelo Calderón^{a,b}

^a *Institut für Chemie und Biochemie, Freie Universität Berlin, Takustrasse 3, 14195 Berlin.*

^b *Helmholtz Virtuelles Institut – Multifunctional Biomaterials for Medicine,
Helmholtz-Zentrum Geesthacht, Germany.*

Keywords: thermoresponsive nanogels, protein corona, drug delivery

Introduction

Thermoresponsive, dendritic polyglycerol (dPG)-based nanogels have shown potential applications in nanomedicine as efficient drug delivery systems. Such polymeric nanogels allow the controlled release of drugs upon collapsing of their structures activated by a thermal stimulus [1]. Nano-sized materials have extremely high surface area to volume ratio which promotes various non-specific binding of proteins on their surface in contact with biological fluids. The obtained nanoparticle-protein corona complex determines the fate of the nanoparticles in biological systems by interacting with various cell surface receptors [2]. Hence, it is of fundamental interest and important to characterize the protein corona formed on nanoparticles to predict their *in vivo* behaviour. Herein, we report the analysis of competitive protein absorption on the surface of dPG-based thermoresponsive nanogels.

The nanogels of our interest were incubated with human serum at 37°C for 24h. The separation of the protein corona from the unbound proteins was performed via filtration (MWCO = 1 MDa). A qualitative screening of the protein corona of the nanogels was done via SDS-PAGE. The full corona was digested by lysyl endopeptidase and trypsin, then screened via LC-MS/MS to obtain its semiquantitative composition.

Results and Discussion

Preliminary results showed that thermoresponsive dPG-based nanogels form a soft protein corona in presence of human serum, with a composition of mainly human serum albumin (HSA) regardless of the incubation time. The presence of a HSA corona increases the blood retention and prevents the opsonisation of the nanogels [3]. It was found that, at T = 37°C, an increasing amount of dPG in the nanogels reduced protein absorption, when NGs were hydrophobic (dPG-PNIPAM, LCST = 33°C). In turn, for NGs in their hydrophilic state (dPG-PNIPMAM, LCST = 46°C) no influence on the protein absorption was found for increasing dPG amounts. Overall, these features are strongly supporting the possibility for an *in vivo* application of thermoresponsive dPG-based nanogels.

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Following Cellular Uptake and Internal Drug Release of Polymer-Drug Conjugates by Fluorescent Turn-on Probes

Gregor Nagel, Harald R. Krüger, Stefanie Wedepohl, Marcelo Calderón

Institut für Chemie und Biochemie, Freie Universität Berlin. Takustrasse 3, 14195 Berlin, Germany.

E-mail: gregor.nagel@fu-berlin.de. Homepage: <http://www.bcp.fu-berlin.de/chemie/calderon>

Keywords: Fluorescent turn-on probe, polymer-drug conjugate, linker design

In the field of polymer therapeutics valuable *in vitro* characterization of drug delivery systems (DDS) is crucial before performing expensive *in vivo* studies. The main tools nowadays are cytotoxicity assays and confocal microscopy but these assays do not allow the correlation of DDS performance with their cellular uptake and drug release. Here, we present the a series of polyglycerol-based fluorescent turn-on probes that contain a quenched donor moiety whose fluorescence can be regained by linker cleavage (Fig. 1). Those system enable the study of the intracellular drug/dye release triggered by e.g. acidic environment or enzyme overexpression. The probes were investigated by fluorescence life time imaging microscopy (FLIM), life cell imaging[1], and cell-based microplate assay[2] giving real time information by recovery of fluorescence after linker cleavage. Due to the modular synthesis strategy, we suggest that such functional probes can be applied to test the performance of other polymer-drug conjugates as well as the implication of the linker design on drug toxicity.

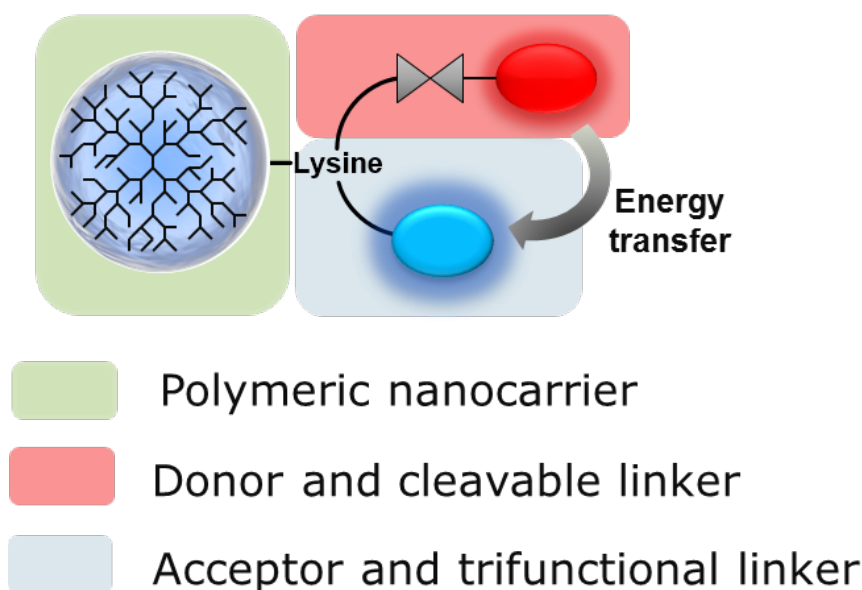


FIGURE 1. Modular approach followed for the synthesis of dendritic polymer imaging systems.

The authors would like to thank the financial support from the Bundesministerium für Bildung und Forschung (BMBF) through the ThermoNanoge NanoMatFutur award (13N12561) and the Freie Universität Focus Area Nanoscale.

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Rapid Identification of tailored Peptide-Polymer Transporters for Therapeutic Agents via Microscopy coupled MALDI TOF/TOF MS

Dario Remmler^a, Timm Schwaar^a, Anna Grafl^a and Hans G. Börner^a

^a*Department of Chemistry, Laboratory for Organic Synthesis of Functional Systems, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, Berlin*

Keywords: Combinatorial Chemistry, Solubilizer, Peptide-Polymer Transporter

One-bead-one-compound peptide libraries are powerful tools to select high affinity binders. This combinatorial methodology proved to be valuable for a large variety of applications. However, library design as well as the selection of positive hits and sequencing of peptides on identified beads is tedious and highly challenging. One of the major limitations results from the desired size of the library to identify excellent binders. Although common polymer beads of 500 μm are easy to handle, a high diversity of e.g. 10^9 particles requires ~ 66 kg of particles, which renders the approach impractical. Since the mass of beads exponentially increases with the radius, the use of customized 10 μm particles is planned. This requires screening of only 0.5 g of particles in respect to the same diversity. An analytical high-throughput platform was developed using microscopy coupled MALDI TOF/TOF MS to screen and identify high affinity binders. Figure 1 shows the experimental setup with peptide-loaded resin beads immobilized on a MALDI plate.

Furthermore, the presented approach will be used to develop a screening method to obtain peptide-polymer transporters for hydrophobic systems, e.g. skin. This is a highly challenging research area, since the stratum corneum layer of the epidermis does not enable absorption of foreign materials with a molecular weight exceeding 1000 Da. Above mentioned transporters may act as penetration enhancers, promoting the drug uptake through the skin. The aim is to demonstrate the applicability to realize specific drug transporters [1] by selecting high affinity binders for high potential drugs, where solubility causes currently undesired pharmacological profiles [2].

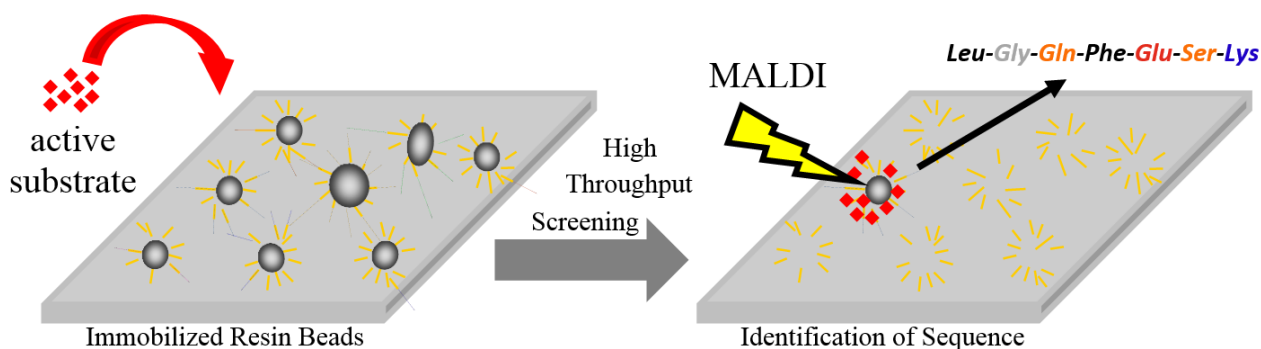


FIGURE 1. Schematic presentation of the method to identify high affinity binders by microscopy coupled MALDI TOF/TOF MS.

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Delivery Systems for siRNA and DNA molecules

Ivan Unksov^a, Alexands Slita^b, Alexandra Petrova^b, Igor Pereviazko^a,
Vladimir Bakulev^a, Svetlana Santer^c, Nina Kasyanenko^a

^a*Faculty of Physics, St. Petersburg State University, Ul`janovskaja street 1,
Petrodvoretz, Saint-Petersburg, 198504, Russia*

^b*Research Institute of Influenza, Molecular Virology Department, 15/17,
Prof. Popova str., St. Petersburg, 197376 Russia,*

^c*Potsdam University Am Neuen Palais 10, 14469 Potsdam,*

Keywords: DANN delivery systems, siRNA, transfection

The interaction between cationic agents with nucleic acids DNA and RNA has been studied extensively. The transition of the rigid and highly charged macromolecule (DNA) to the compact form induced by azobenzene containing surfactant AzoTAB in NaCl salt aqueous solutions was investigated. The compact nanoparticles, formed upon the interaction of nucleic acids with some agents, are employed for biomedicine as carriers for the delivery of nucleic acids into cells. The delivery of small interfering RNAs (siRNAs) is regarded as a powerful therapeutic tool as a posttranslation gene regulation process and has been extensively studied since the demonstration of RNA interference (RNAi). Naked siRNA molecules are not able to efficiently enter cells to bind with the mRNA target.

At the first step two nucleic acids, macromolecular DNA and small interfering RNA (siRNA), were examined upon the interaction with the surfactant. It was shown that the binding of surfactant with DNA and siRNA is accompanied with the formation of micelle-like structures. For DNA macromolecules of high molecular weight we also carried out a combined viscometry/flow birefringence study to examine DNA conformational changes upon binding with trans- and cis-isomers of the surfactant. For siRNA + surfactant systems we aimed to determine the conditions of gene vectors' creation by AFM observation and by testing the delivery on MDCK cell line.

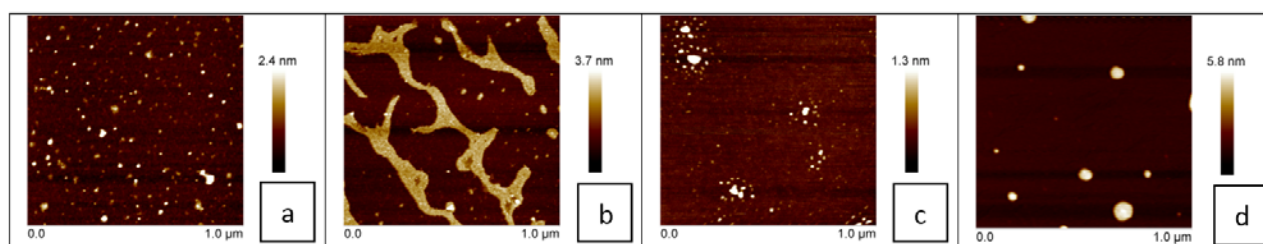


Figure 1. AFM images of siRNA complexes with surfactant at molar ratio of surfactant to molar ratio of DNA phosphates (z). a – without surfactant; b – at $z=0.6$; c – at $z=1.6$; d – at $z=8$

Glycopolymer brushes - a powerful tool for the analysis of glycan-mediated interaction

Christine Schulte¹, Uwe Schnakenberg², Lothar Elling³,
Alexander Böker¹, Ruben R. Rosencrantz¹

¹ *Fraunhofer-Institut für Angewandte Polymerforschung, Geiselbergstraße 69, 14476 Potsdam, Germany, ruben.rosencrantz@iap.fraunhofer.de*

² *Institute of Materials in Electrical Engineering 1, RWTH Aachen University, Sommerfeldstr. 24, 52074 Aachen, Germany*

³ *Laboratory for Biomaterials, Institute for Biotechnology and Helmholtz-Institute for Biomedical Engineering, RWTH Aachen University, Pauwelsstr. 20, 52074 Aachen, Germany*

Keywords: Glycopolymers, Microcontact printing, Lectin binding, Biosensors

Glycans are recognition sites on cell surfaces, where they act as antennas to exchange information between cells and their surroundings. They are involved in cell adhesion, signal transduction and regulation. These recognition processes are induced by a selective, specific and avidity-driven interaction with proteins called lectins. The avidity of proteins towards lectins is modulated by the number of presented glycans and may be increased dramatically by presenting multivalent ligands.

We make protein-glycan interactions accessible to bioanalytical platforms by developing polymers that show an extraordinary high affinity towards lectins. Our glycopolymers are polymers with carbohydrate side chains as functional groups. The pendant carbohydrates can specifically interact with lectins. These polymers are synthesized as polymer brushes on different surfaces like gold, silicone or glass. For controlling the polymer layer thickness we apply surface-initiated atom transfer radical polymerization (SI-ATRP) for maintaining high control over the polymerization process. To establish an intrinsic negative control we bind the initiator via microcontact printing on the surface. With this we produce micro-patterned glyco-chips with highest lectin affinity. The glycopolymer brushes that we develop present a high number of carbohydrate pendants which increases the affinity of lectins in orders of magnitude. We achieve K_D values in the low nanomolar range, which is very uncommon for glycan-mediated interaction and normally only found for antibodies. Another advantage of our polymeric layer is the low unspecific adsorption of proteins, which makes additional blocking steps obsolete. It is possible to change thickness, density or functionality of the glycopolymer brush layer, altering avidity and binding mode of lectins.

Glycopolymer brushes represent a novel class of polymers, which can be used in biology, pharmacy and biomedicine. The prepared surfaces are shown to be compatible with bioanalytical methods. These newly generated surfaces will be used as biosensors and in medical diagnostics of cancer or microbe contamination.

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Mechanical characterization of high-density polyethylene in contact with diesel and biodiesel fuels

Maren Erdmann, Ute Niebergall, Martin Böhning

*Bundesanstalt für Materialforschung und -prüfung,
Unter den Eichen 87, 12205 Berlin, Germany*

Keywords: PE-HD, diesel, biodiesel, oxidation

Renewable resources become more and more relevant to maintain energy demands for an increasing global population. Biosynthetic fuels like biodiesel might replace conventional petrochemical fuels, such as diesel. However, more research is needed to characterize the interaction between the different fuels and polymeric materials widely used in the fuel infrastructure as well as for automotive parts. Especially changes in the structural properties and mechanical behavior of the polyethylene (PE-HD) have to be addressed.

The presented work comprises the direct interaction of high density polyethylene (PE-HD) with diesel and biodiesel, resulting in swelling and plasticization. Also long-term degradation phenomena will be discussed [1-3].

The chosen PE-HD types are typical thermoplastic resins for container and storage tank applications. The impact of diesel and biodiesel in PE-HD is investigated by changes in the mechanical properties with emphasis on the Charpy impact strength [2]. Furthermore, structural and dynamic influences on the polymeric material induced by diesel and biodiesel are proven in Dynamic Mechanical Analysis (DMA). Both methods, Charpy impact strength and DMA, reveal softening effects due to the migration of diesel and biodiesel into the amorphous regions of PE-HD.

Since biodiesel is more prone to oxidative degradation compared to diesel [3], the fuel/air/polymer-interaction is studied for partly immersed tensile test specimens. Main focus of the evaluation is the co-oxidation. Here, the accelerated deterioration of PE caused by the sorption of the facile oxidation of biodiesel into the solid polymer might be a major degradation mechanism in this context.

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2-(Dimethylamino)acridone – A Versatile New Fluorescence Label for Polymers in the Investigation of Mesoscopic Honeycomb Structures

Dirk Schanzenbach^a, Olaf Karthaus^b, André Laschewsky^{a,c},
Masatsugu Shimomura^b

^a Universität Potsdam, Institute of Chemistry, Potsdam-Golm, Germany

^b Chitose Institute of Science and Technology (CIST), Faculty of Photonics Science,
Dept. of Bio- and Material Photonics, Chitose-shi, Hokkaido, Japan

^c Fraunhofer Institute of Applied Polymer Research (IAP), Potsdam-Golm, Germany

Keywords: Honeycomb Structures, Polymer Labeling, Acridones, Fluorescence Microscopy

Honeycomb (HC) films with highly ordered mesoscopic structures are known since two decades. A common method to produce such films is the dewetting technique, by casting a polymer solution containing a stabilizing polyion complex on a substrate under a highly humid atmosphere. In order to investigate the mesoscopic structures by fluorescence microscopy, HC films labeled with solvatochromic fluorescent dyes were developed. The new, small solvatochromic fluorophore 2-(dimethylamino)acridone (DMA) was employed for activating the HC film for fluorescence microscopy without affecting the HC films. Two methods of DMA-labeling were investigated: 1) post-polymerization labeling, by formation of the HC film from a reactive polymer followed by reaction with a suitably derivatized acridone, and 2) formation of HC films from various copolymers containing an acridone-functionalized monomer. We studied properties of the HC films via SEM, fluorescence microscopy and contact angle measurements, comparing labeled and non-labeled films. The results demonstrate that DMA is a suitable label that, while not interfering with HC film formation and properties, not only effectively visualizes the HC films, but also detects sensitively defects and structural irregularities in the HC patterns.

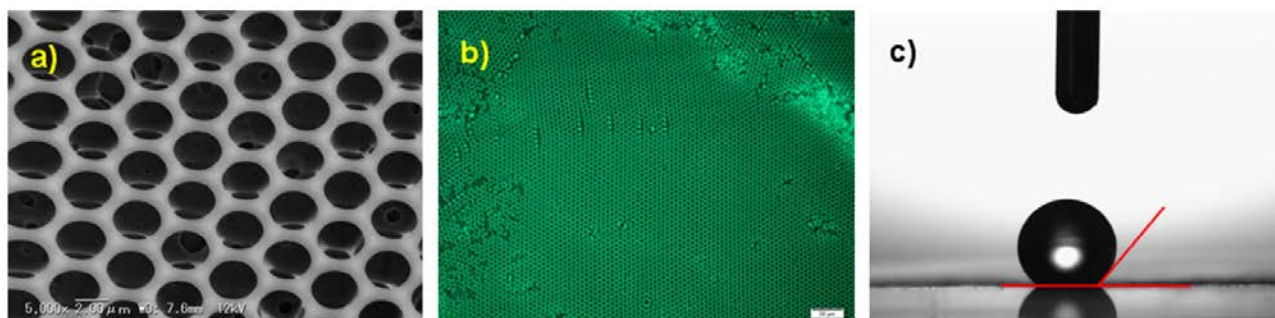


FIGURE 1. a) Scanning electron micrograph of a HC film; b) fluorescence microscopy of an acridone-labeled HC film, showing irregularities; c) contact angle measurement of a water drop on a HC film

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**Environmental stress cracking (ESC) of PE-HD induced by liquid media -
Validation and verification of the Full-Notch-Creep Test (FNCT)**

Markus Schilling^a, Martin Böhning^a, Harald Oehler^b, Ingo Alig^b, Ute Niebergall^a

^a*Bundesanstalt für Materialforschung und –prüfung (BAM),*

Unter den Eichen 87, 12205 Berlin, Germany,

markus.schilling@bam.de, martin.boehning@bam.de, ute.niebergall@bam.de,

^b*Fraunhofer-Institut für Betriebsfestigkeit und Systemzuverlässigkeit LBF,*

Schlossgartenstraße 6, 64289 Darmstadt, Germany, harald.oehler@lbf.fraunhofer.de,

ingo.alig@lbf.fraunhofer.de

Keywords: Full-Notch Creep Test (FNCT), PE-HD, environmental stress cracking, biodiesel

The Full-Notch-Creep Test (FNCT) is widely used to characterize the slow crack growth (SCG) behavior of polyolefinic materials in “inert” media as well as effects of environmental stress cracking (ESC) in which the medium has decisive influence on damage mechanism and time to failure. The test is of greatest importance for pipe and blow molding types of PE-HD - especially for transport and packaging of dangerous goods but also for most other high-performance applications.

Usually the FNCT is applied as a standardized testing method (ISO 16770) using a few universal liquid media, such as solutions of Arkopal N 100.

In our study, selected relevant PE-HD materials are investigated also in real media – practical formulations as well as representative pure chemicals – and influences of temperature and geometry of specimen and notch are explicitly addressed. Furthermore, the investigations comprise also the ESC behavior of PE-HD in media that are sorbed to a significant extent – one example are fuels, such as diesel and biodiesel – based on comparison with samples previously saturated with those media. Thus, also the underlying diffusion controlled sorption process has to be assessed before.

The investigations were performed using a FNCT-device with 12 individual sub-stations, each equipped with individual electronic stress and temperature control and continuous online monitoring of the specimen elongation.

Isolation of Lignin from Birch Wood and Bark Using Ionic Liquids

David Strunk, Veronika Strehmel

*Institute for Coatings and Surface Chemistry, Department of Chemistry,
Niederrhein University of Applied Sciences, Adlerstr. 32, D-47798 Krefeld, Germany*

Keywords: lignin, wood, bark, ionic liquid

Silver birch is a widespread tree species in northern Europe comprising about 25 % lignin [1, 2]. Some ionic liquids have gained a remarkable interest due to their capability to dissolve lignocellulosic biomass and lignin, respectively [3].

Rasped and sieved birch interior wood and birch bark were extracted with methanol at first, followed by extraction with an ionic liquid at elevated temperatures. Examples for ionic liquids used were 1-butyl-3-methylimidazolium acetate (BMImAcO), 1-butyl-3-methylimidazolium chloride (BMImCl), 1-ethyl-3-methylimidazolium tosylate (EMImTsO) and 1-ethyl-3-methylimidazolium mesylate (EMImMsO). The solubility of birch interior wood and birch bark in the ionic liquid was between 3 wt % and 29 wt % and increased as follows: EMImTsO \approx EMImMsO < BMImCl < BMImAcO.

Addition of AlCl₃ to BMImCl resulted in an increase in solubility. In this way, 94 wt % of interior wood and 72 wt % of bark were dissolved in the ionic liquid.

Precipitation and purification of lignin resulted in different amounts of lignin obtained from bark (up to 8 wt %) and interior wood (up to 1 wt %) depending on the structure of the ionic liquid and the temperature used. The selectivity (mass of lignin relative to the sum of masses of lignin and carbohydrates) was between 23 wt % and 90 wt % for extraction of lignin from interior wood and bark, respectively. It increased in the order: BMImAcO < BMImCl < EMImTsO \approx EMImMsO.

Acetylation of purified wood lignin resulted in a completely THF soluble product, although only 30 wt % of the acetylated bark lignin was soluble in THF. SEC analysis of lignin showed a relative low molecular weight in case of the BMImCl / AlCl₃-System.

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Effect of Cononsolvency: Comparing PNIPAM-Based Microgels in Water/Ethanol-Mixtures in Bulk to Different Surfaces

Sebastian Backes, Weronika Nasiłowska, Patrick Krause,
Marcus Witt, Regine von Klitzing

^aInstitut für Chemie, Technische Universität Berlin, Germany

Keywords: Cononsolvency, PNIPAM, Microgels

Microgels made of water-soluble poly(N-isopropylacrylamide) (PNIPAM) show a volume phase transition temperature (VPTT) around 32°C in water above which they shrink considerably. Additionally, the polymer is sensitive to the composition of the solvent, shrinking in intermediate mixing ratios of water and ethanol, while swelling in the respective pure solvents (cononsolvency). In the presented work the combination of these two effects on microgels has been studied. The microgel volume is measured as function of temperature and ethanol/water ratio in bulk with DLS and after adsorption at different surfaces (polycation (PAH) and gold coated Silicon surfaces) with AFM. The minimum microgel volume occurs in bulk at around 20% ethanol content while at PAH surfaces it is shifted to higher ethanol contents[1]. The VPTT decreases with increasing ethanol content up to 30%, but this shift is more pronounced in bulk than on a PAH surface, corresponding to the results reported in [1] (see Figure 1). The results on a gold surface resemble those in bulk. At higher ethanol content beyond 30%, no VPTT is observed in the measuring range (10-60°C), but a reswelling of the particles can be observed for high ethanol content. Additionally to pure PNIPAM microgels, gels with acrylic acid as a comonomer have been analyzed. They show a broader transition, but a similar trend in the shift of the VPTT. Simulations of this problem are in progress.

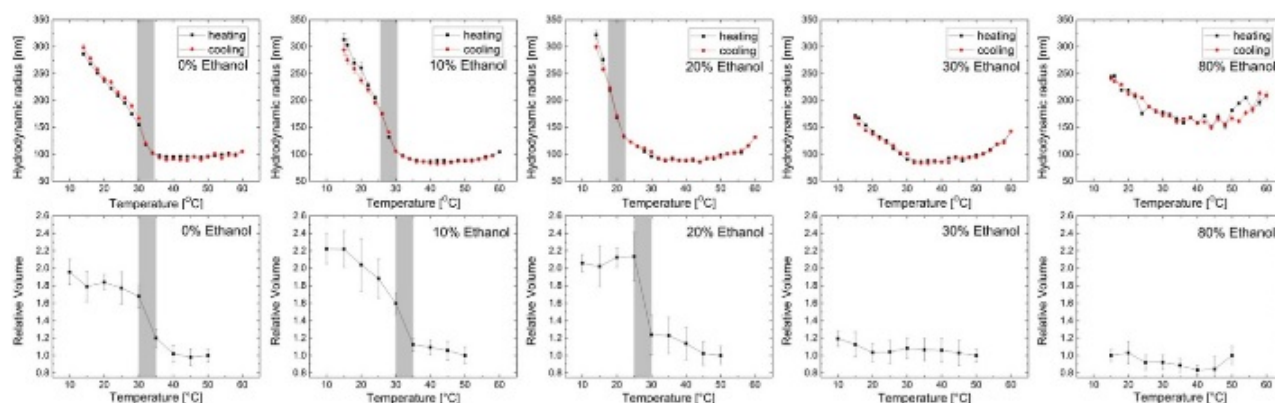


FIGURE 1. Hydrodynamic radius (upper row, measured by DLS) in bulk and relative volume (lower row, measured by AFM) on PAH surface of PNIPAM microgels against temperature in different water/ethanol mixtures. Grey bar indicates volume phase transition.

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Molecular p-doping of semiconducting polymers with the strong Lewis acid tris(pentafluorophenyl)borane

Malavika Arvind^a, Patrick Pingel^b, Silvia Janietz^b, Dieter Neher^a

^a *University of Potsdam, Soft Matter Physics,
Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany*

^b *Fraunhofer Institute for Applied Polymer Research (IAP),
Geiselberg Str. 69, 14476 Potsdam, Germany*

Keywords: molecular doping, optical spectroscopy, charge transfer mechanism, conductivity

Electronic devices such as solar cells, field-effect transistors, light-emitting diodes with organic (polymeric) active layers have many advantages over the existing inorganic electronics, primarily with respect to ease of processing, and device flexibility. However, traditional inorganic devices are still far superior to organic systems in terms of device performance due to efficient charge transport and high carrier mobility in the inorganic semiconductors. A simple way of improving the intrinsic charge carrier density and conductivity of semiconducting polymers is by doping with small molecules that are strongly electron withdrawing (p-doping) or electron donating (n-doping). One of the most commonly studied organic p-dopants is tetrafluorotetracyanoquinodimethane (F4TCNQ). This material however, is known to have poor solubility[1] in most organic solvents, and also diffuses easily through the layers[2].

In this work, we employ tris(pentafluorophenyl)borane (BCF) – a well soluble, strong Lewis acid, which was shown recently to serve as a dopant[3] for the well known semiconducting polymer poly(3-hexylthiophene) (P3HT). Analysis of the sub-band gap signals in the UV-Vis-NIR spectra of BCF doped P3HT solutions and thin films indicates a doping process that is very similar to that in F4TCNQ-P3HT systems, despite the obvious structural dissimilarity between the two dopants. Moreover, at similar doping concentrations, BCF doped P3HT layers show superior conductivities that are nearly 3 times higher than that of F4TCNQ doped layers. This, and the fact that BCF is highly soluble in many organic solvents unlike F4TCNQ, indicates that BCF could be an effective p-dopant for use in organic electronics.

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Synthesis of Donor-Acceptor polymers by direct arylation

Diana Zimmermann,^a Jonas Schröder,^a Silvia Janietz,^a Christian Sprau,^b Alexander Colsmann,^b Hartmut Krüger^a

^a *Department Organic Materials for Electronics, Fraunhofer Institute for Applied Polymer Research, Geiselbergstraße 69, 14476 Potsdam, Germany.*

^b *Karlsruhe Institute of Technology, Light Technology Institute, Engesserstraße 13, 76131 Karlsruhe, Germany.*

Keywords: Synthesis, organic photovoltaics, direct arylation

Donor-acceptor polymers for organic photovoltaics are usually synthesized by STILLE coupling. However, this method has disadvantages such as additional steps to introduce the stannyl endgroup in monomer synthesis, and the stannyl monomers exhibit moderate stability, making their purification challenging.[1] Furthermore, with respect to safety regulations, toxic stannyl compounds are difficult to handle in industrial processes and in larger quantities. A new synthetic approach, i.e., the direct arylation where stannyls are not required and bromoarenes are coupled directly to activated H-arylenes shall avoid these problems.[2] The biggest challenge in direct arylation polymerization is the inhibition of undesired linking by competitive C-H-bonds of the monomers as they cause structural defects like crosslinking, branching and homocoupling, all known to affect the photovoltaic performance. There are two possibilities of yielding defect-free polymers. The first option is change of the monomer structure allowing only one reactive site. Alternatively, the reaction conditions can be optimized.[3]

In this work, at first, various reaction conditions were adjusted. The catalytic system (consisting of catalyst, ligand and base), the solvent, the use of additives as well as the temperature are the most important handles to control the reactivity of the different monomers.[4] For the general adjustment 4,7-dibromobenzo-[1,2,5]thia-diazole (BT) as acceptor and (4,8-bis((2-ethylhexyl-oxy)benzo[1,2-b:4,5-b']dithiophene) (BDT) as donor were employed. The optimal conditions were transferred to a modified monomer system where the free β -protons on the BDT were substituted by methyl groups and subsequently to an efficient conjugated copolymer comprising BDT and quinoxaline monomers which was previously synthesized by STILLE coupling only. In the corresponding organic solar cells, a power conversion efficiency (PCE) of 4.6%, i.e., a relative PCE of about 60% (versus the STILLE polymer), was achieved.

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Charge Recombination in Polymer Solar Cells

Pietro Caprioglio^a, Steffen Roland^a, Liang Yan^b, Wei You^b and Dieter Neher^a

^a *Institute of Physics and Astronomy, Soft Matter Physics, University of Potsdam,
D-14476 Potsdam, Germany*

^b *Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill,
North Carolina 27599, United States*

Solar cells comprising organic semiconductors have become capable of generating charge with high efficiency over the entire visible spectrum. In these cells, the performance is only limited by non-geminate recombination of free charge. The mechanism of this recombination is still under debate. It is yet not fully understood what determines recombination of charges in these cells and what are the possible channels for this process. Here, we investigated four different polymer-fullerene bulk heterojunction solar cells. As donor polymer we used either the fluorinated or the non-fluorinated version of a block copolymer (FTAZ, HTAZ). As acceptor we chose the fullerene derivatives PCBM or ICBA which differ in their lowest unoccupied molecular orbital (LUMO) energy. By using two different charge extraction methods TDCF (Time Delayed Collection Field) and BACE (Bias Assisted Charge Extraction), with TDCF we are able to probe the transient (time-dependent) charge recombination and steady state recombination rate under the very same conditions. We are able to describe both, transient and steady state measurements, consistently in a picture that indicates that recombination is governed totally by thermalized charges, meaning that hot carriers are not relevant for this type of mechanisms. Additionally, a detailed analysis of the recombination mechanism as function of carrier density suggests that recombination in organic solar cells is dominated by thermalized CT states in the mixed donor acceptor phase, and that the energetics of the pure phases have no influence on the recombination current.

Monodisperse Conjugated Polymer Particles - Synthesis, Polymerization Kinetics and Photonic Applications

S. Ciftci, A. Mikosch, A. J. C. Kuehne

*DWI – Leibniz Institute for Interactive Materials
RWTH Aachen University, Forckenbeckstraße 50, 52076 Aachen*

Keywords: conjugated polymer particles, self-assembly, photonic crystals

The production of particles, which spontaneously self-assemble into colloidal crystals with a photonic band-gap, opens pathways towards laser resonators without using time-consuming and costly micro- and nanofabrication techniques. Here, we present novel dispersion polymerizations yielding monodisperse particles of conjugated polymers with an electronic bandgap (Fig. 1b).[1] Such hard sphere conjugated polymer particles produced by a cross-coupling dispersion polymerization self-assemble into photonic crystals and at the same time act as a laser gain medium. Furthermore, seeding of this dispersion polymerization with dielectric particles facilitates the generation of core shell particles, which act as whispering gallery mode resonators (Fig. 1c). To elucidate the mechanism of our cross-coupling dispersion polymerization, we investigate the kinetics of the underlying particle formation. We find that nucleation of oligomeric species takes place in the pseudo linear kinetic regime followed by a classical growth mechanism. During growth, also limited solid-state coupling occurs leading to fully polymerized particles. The self-assembled colloidal crystals as well as the whispering gallery mode resonators exhibit laser emission at low thresholds.

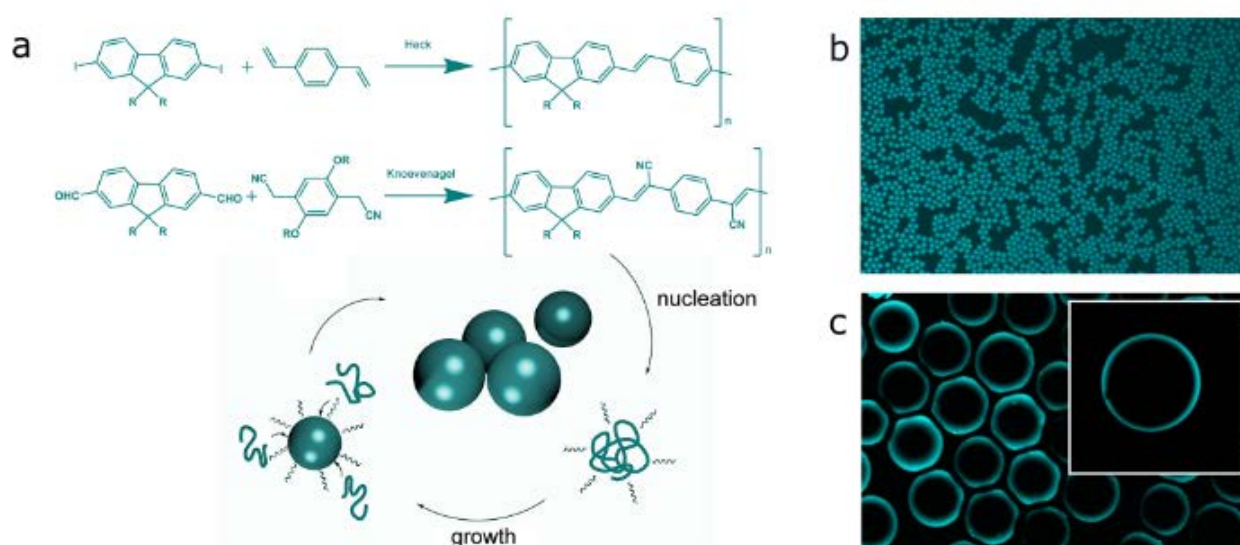


FIGURE 1. (a) Reaction schemes and dispersion polymerization mechanism for the formation of monodisperse conjugated particles. (c) Conjugated hard sphere particles self assembled into crystals. (e) Confocal microscopy image of silica core- conjugated polymer shell particles.

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Electrochemical functionalization of spin-coated PEDOT:PSS layers on glass towards biosensing by use of diazonium compounds

Jörg Rappich^a, Felix Rösicke^{a,b}, Matthias Zellmeier^a,
Silvia Janietz^c, Karsten Hinrichs^d

^a Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institut für Silizium-Photovoltaik, Kekuléstr. 5, 12489, Berlin, Germany

^b Humboldt-Universität zu Berlin, School of Analytical Sciences Adlershof (SALSA), Office: IRIS-Building, Unter den Linden 6, 10099 Berlin, Germany.

^c Fraunhofer-Institut für Angewandte Polymerforschung, Geiselbergstraße 69, 14476 Potsdam-Golm, Germany

^d Leibniz-Institut für Analytische Wissenschaften - ISAS e.V., Schwarzschildstraße 8, 12489, Berlin, Germany

Keywords: Electrochemical functionalization, diazonium ions, infrared spectroscopies

Functional polymers like polymer brushes, electro polymerized pre-functionalized thiophene and molecularly imprinted polymers are more and more in the focus of nowadays research for sensing applications [1-3]. Hereby one way of functionalization is the introduction of specific groups that serve as linkage elements to a variety of biomolecules. In this study poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), PEDOT:PSS, spin-coated on glass substrates was electrochemically functionalized by 4-nitro-, 4-amino-, and 4-maleimidobenzene using their respective diazonium compounds [4]. The electrochemical processing was controlled by the applied potential, solution composition, and the electrical conductivity of the PEDOT:PSS layer. The functionalized surfaces were investigated by infrared spectroscopic ellipsometry, X-ray photoelectron spectroscopy, and optical spectroscopies. The measurements revealed the presence of the functional groups (i.e. amino, maleimide, and nitro) on the polymer surfaces.

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Dynamics of Azobenzene Dimer Photoisomerization: Electronic and Steric Effects

E. Titov^{ab}, G. Granucci^c, I. V. Malyar^d, J. P. Götze^a, M. Persico^c,
S. Santer^b, and P. Saalfrank^a

^a*Institute of Chemistry, University of Potsdam,
Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany*

^b*Institute of Physics and Astronomy, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany*

^c*Department of Chemistry and Industrial Chemistry,
University of Pisa, via Moruzzi 13, 56124 Pisa, Italy*

^d*Department of Nano- and Biomedical Technologies, Saratov State University,
Astrakhanskaya 83, 410012 Saratov, Russia*

Keywords: azobenzene, dimer, photodynamics, surface hopping, self-assembled monolayer

The photoswitching of azobenzene-containing molecules, which can be utilized to induce photoresponse of polymers, *e.g.*, DNA [1,2], is easily reachable in solution, but can be drastically suppressed in densely packed environments, such as self-assembled monolayers (SAMs) [3]. Reasons for this have been proposed to be steric hindrance and/or large exciton coupling [3,4] between azobenzene chromophores. In this work by means of nonadiabatic molecular dynamics with trajectory surface hopping [5], we investigate the isomerization of an isolated azobenzene dimer and a dimer embedded in a SAM-like environment of additional azobenzene molecules, after excitation into the $\pi\pi^*$ absorption band, thus accounting for electronic coupling between chromophores and steric hindrance. Our simulations reveal that in comparison to the single molecule the quantum yield of the *trans* \rightarrow *cis* photoisomerization is only slightly different for the isolated dimer, but greatly reduced in the sterically constrained situation. Other implications of dimerization and steric constraints as well as the relation to the experimental results obtained for the azobenzene-containing monolayers on a silicon surface are also discussed.

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Azobenzene-Containing End-Grafted “Polymer Mushrooms” in the Dark: A Full-Atomistic Molecular Dynamics Simulations

Markus Koch^{a,b}, Olga Guskova^{a,c}

^a*Institute Theory of Polymers, IPF Dresden, Hohe Str. 6, 01069 Dresden, Germany*

^b*Institute of Theoretical Physics, TU Dresden, Zellescher Weg 17, 01069 Dresden, Germany*

^c*Dresden Center for Computational Materials Science, TU Dresden, 01062 Dresden, Germany*

Keywords: azobenzene chromophore, polymer brush, equilibrium, computer simulation

The reversible *cis-trans* photoisomerization of azobenzene (azo) chromophores underlies the light-controllable self-assembling of soft matter, for instance the formation of optical surface gratings in thin azo polymer films. Polymer brushes either mixed with photosensitive azo functions or chemically decorated by azo pendants provide specific benefits as compared to thin non-grafted spin-casted films [1, 2].

Here we present the results of all-atom molecular dynamics (MD) simulations aiming at investigation of structural properties of a test system: a single polymer chain in “mushroom” regime being tethered to the solid substrate. This polymer chain is functionalized with azobenzene chromophores covalently bonded as side chains. Two types of azo moieties are modelled: monomeric unit (Figure 1) and three-arm unit with 1,3,5-benzene-tricarboxamide core.

The simulations are carried out at equilibrium (in the dark), i.e. all azobenzenes are considered to be in *trans*-isomerization state. The equilibrium geometries and partial atomic electrostatic potential charges of azos are calculated using DFT/B3LYP/6-31G(d,p) method as implemented in Gaussian 09 Rev A01. The force-field NVT-MD simulations of the end-grafted PMAA backbone with length up to 100 monomeric units are performed for different content of azo side chains in BIOVIA Materials Studio v8.0.

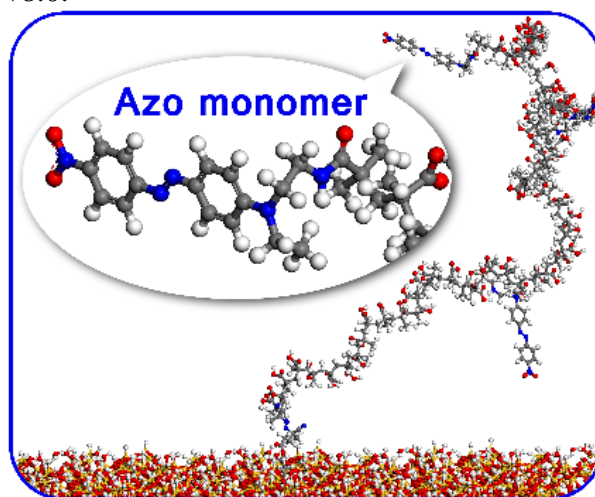


FIGURE 1. Azo-PMAA “mushrooms” tethered to silica surface; the content of *trans*-azo moieties per chain is 5%.

The funding received from the German Research Foundation (DFG) for the Project GU 1510/3-1 “Bridging molecular orientation and isomerisation state with macro-deformation in photoactive azobenzene-containing materials” is highly appreciated.

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Light-Switchable Polymers of Intrinsic Microporosity

Daniel Becker^a, Nora Konnertz^b, Martin Böhning^b, Johannes Schmidt^a,
Arne Thomas^a

^a Technische Universität Berlin, Institute of Chemistry, Functional Materials,
Hardenbergstraße 40, D-10623 (Germany)

^b Bundesanstalt für Materialforschung und -prüfung
Unter den Eichen 87, D-12205 (Germany)

Keywords: light-switchable porosity, diarylethenes, polymers of intrinsic microporosity

Diarylethenes (DAEs) are photochromic molecules that perform cyclisation and cycloreversion in a reversible manner triggered by electromagnetic stimuli. Upon isomerisation, the molecule's stiffness as well as its electronic properties experience vast changes. This work demonstrates how these properties can be exploited by showing that DAEs can be made a constituent part of the backbone of a polymer of intrinsic microporosity (PIM). Resulting microporous DAE-PIM shows light-induced isomerisation in both dissolved and solid state with concomitant alterations in the compound's gas sorption properties such as nitrogen uptake and affinity to e.g. carbon dioxide. Moreover, owing to the excellent solubility of DAE-PIM a composite material in conjunction with Matrimid could be produced as free-standing gas-permeable membrane the properties of which such as gas permeability and diffusivity could be altered by virtue of light stimuli.

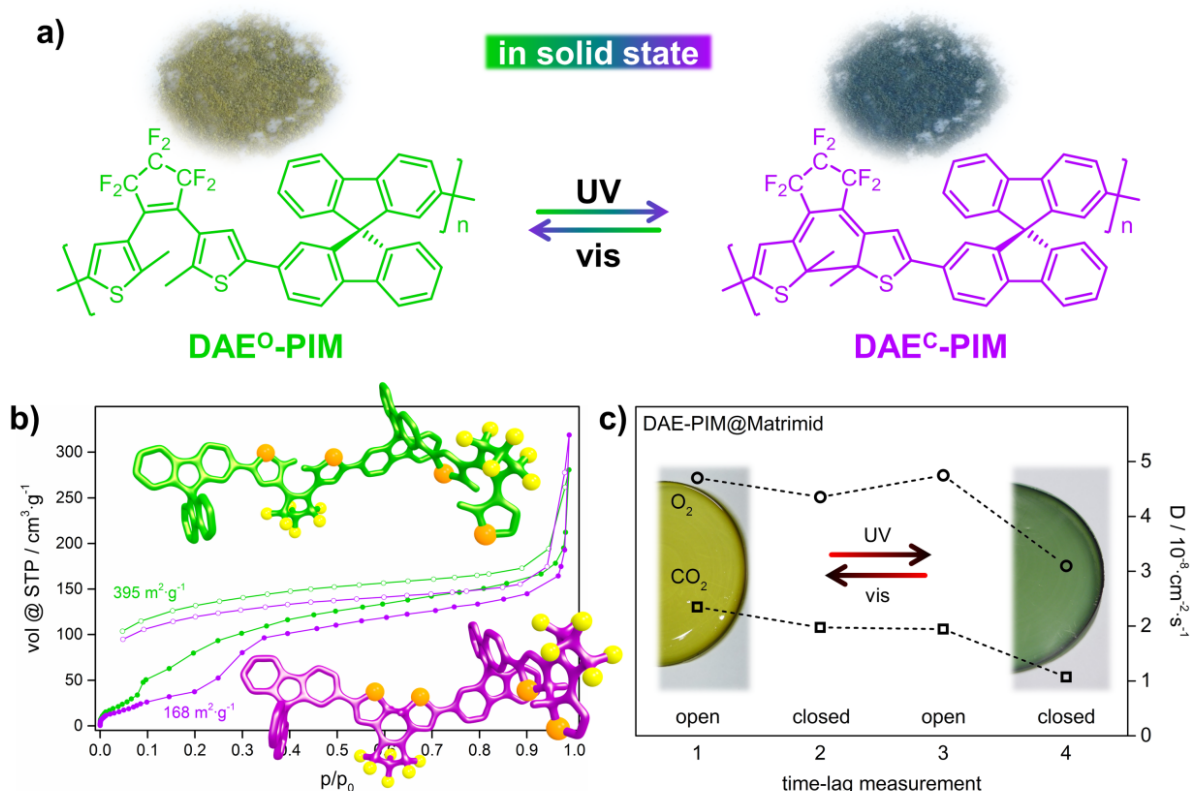


FIGURE 1. a) Sketch of isomerisation event in DAE-PIM. Superscripts ^O and ^C refer to open and closed isomer, respectively. b) Isotherms derived from nitrogen sorption at 77 K for open and closed isomer of DAE-PIM. c) Diffusion coefficient (D) for a composite membrane of DAE-PIM in a matrix of Matrimid. Open and closed state show different values for D with respect to oxygen and carbon dioxide.

Photosoap: light-controlled particle assemblies through diffusio-osmotic flows

David Feldmann,¹ Salim Maduar,² Nino Lomadze,¹ Alexey Kopyshv,¹
Olga I. Vinogradova,^{2,3,4} Svetlana Santer¹

¹ Institute of Physics and Astronomy, University of Potsdam, 14476 Potsdam, Germany

² A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russia

³ Department of Physics, M. V. Lomonosov Moscow State University, 119991 Moscow, Russia

⁴ DWI-Leibniz Institute for Interactive Materials, Aachen, Germany

Here we report on light generated local hydrodynamic flow for manipulation of micro-particles trapped at solid/liquid interface. To induce local hydrodynamic flow, a photo-soap consisting of a charged head group and a hydrophobic tail modified with azobenzene group has been utilized. Under illumination, azobenzene undergoes a reversible photo-isomerization reaction from a *trans*- to a *cis*-state accompanied by a change in the hydrophobicity of the surfactant [1-4]. Microparticles, trapped at a glass/liquid (aqueous solution of the photo-soap) interface, can be moved along the solid surface when illuminated with focused UV light. The velocity of the particles depends strongly on the photo-soap concentration and ionic strength and is ca. 1 $\mu\text{m}/\text{sec}$ at maximum. The direction of particles motion can be reversed by applying irradiation with green light: particles gather at the center of the beam. Particle motion can be explained by diffusio-osmotic flow which is induced close to the surface carrying microparticles (Figure 1 I). Using this flow, we can clean surfaces out of micro-dust, gather objects or structure particle assemblies (Figure 1 II). On patterned surfaces objects can be guided in a certain direction (see Figure 1 IId).

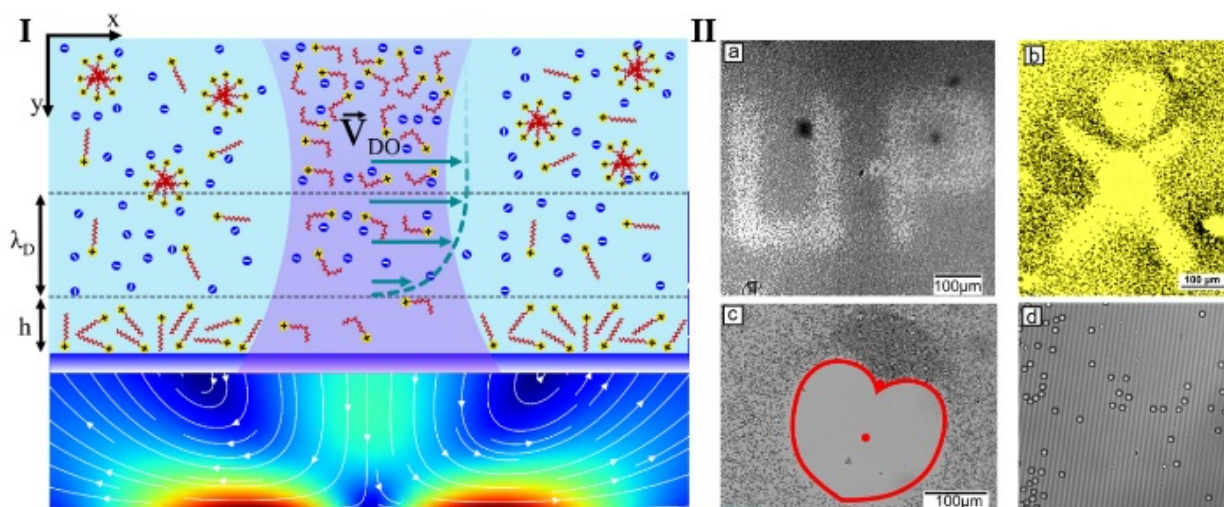


FIGURE 1. I.) Schematic of light induced outward flow. Local UV irradiation creates a concentration gradient driving a diffusio-osmotic flow in the interfacial area. Below: calculated stream lines of the resulting flow. II.) (a, b) Logo of the University of Potsdam and “happy man” inscribed in a densely packed layer of Si micro-particles ($d = 2\mu\text{m}$). c) Simultaneous UV and green irradiation results in a “heart-shaped” void. d) Directed particle motion on patterned surface.

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Conditional repair by locally switching the thermal healing capability of dynamic covalent polymers with light

Anne Fuhrmann^a, Robert Göstl^a, Robert Wendt^a, Julia Kötteritzsch^b,
Martin D. Hager^b, Ulrich S. Schubert^b, Kerstin Brademann-Jock^c,
Andreas F. Thünemann^c, Ulrich Nöchel^d, Marc Behl^d, and Stefan Hecht^a

^a Laboratory of Organic Chemistry and Functional Materials, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin (Germany), anne.peter.1@chemie.hu-berlin.de

^b Friedrich-Schiller-Universität Jena, Humboldt-Str. 10, 07743 Jena (Germany)

^c Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin,.

^d Helmholtz-Zentrum Geesthacht, Kantstr. 55, 14513 Teltow (Germany).

Keywords: programmable self-healing materials, dynamic covalent polymer networks, photoswitches

Healable materials[1] have the potential to reduce the environmental footprint of our technological society through extending the life cycles of consumer products and constructions. However, as most healing processes are carried out by heat alone, the ability to heal damage generally sacrifices the parent material's thermal and mechanical properties. Here, we present a dynamic covalent polymer network[2] whose thermal healing ability can be switched 'on' and 'off' by light, thereby providing a new level of control while retaining the advantageous properties of global static polymer networks. We employ a photoswitchable furan-substituted diarylethene crosslinker, reacting with maleimide-containing copolymers via the Diels-Alder reaction (DAR) forming strong covalent bonds while simultaneously allowing for the reversible, spatiotemporally resolved control over thermally induced de- and re-crosslinking.

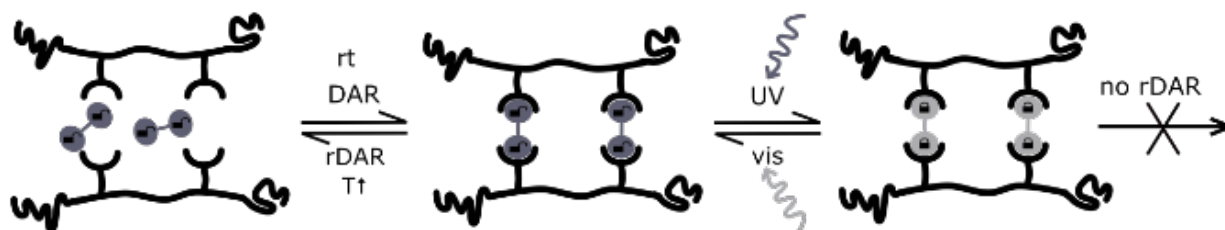


FIGURE 1. Aim of this work: Thermally induced crosslinking via the Diels-Alder reaction (DAR) and decrosslinking via the retro Diels-Alder reaction (rDAR) of photoresponsive polymers allowing for a reversible, spatiotemporally resolved control by different colours of light.

By tuning this de- and re-crosslinking via the equilibrium of the Diels-Alder (DA) and retro Diels-Alder reaction (rDAR) with light[3], we demonstrate a control of the local healing of scratches in thin polymeric films. We reason that our system has the potential to make an important contribution to responsive coatings, photolithography, and microfabrication.

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Photocontrolling Imine Exchange Kinetics to Modulate Inherent Characteristics of Self-healing Polysiloxane Networks

Michael Kathan^a, Petr Kovaříček^a, Christoph Jurissek^a, Antti Senf^a,
Andre Dallmann^a, Andreas F. Thünemann^b, Stefan Hecht^a

^aDept. Chem. & IRIS, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin

^bFederal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin

Keywords: Adaptive Materials • Dynamic Covalent Chemistry • Photochromism • Self-Healing

Materials that respond to the environment by changing their properties are critical for developing autonomously adaptive systems. However, to reversibly influence a material's inherent characteristics, such as its ability to self-heal, from distance without continuously expending energy, remains a challenging task. Herein, we report on the modulation of imine exchange kinetics by light, manifested in a remote controllable dynamic covalent polymer network.[1] Simple mixing of a commercially available amino-functionalized polysiloxane with small amounts of a photoswitchable diarylethene cross-linker, carrying two aldehyde groups, yields a rubbery material. Its viscoelastic and self-healing properties can be reversibly tuned with everyday light sources, such as sunlight. Our two-component system offers the unique advantage that self-healing takes place continuously without any additives at ambient conditions and is neither dependent on continuous illumination nor does it require recent damage. Overall, our approach allows for the local amplification of intrinsic material properties in a permanent yet reversible fashion. The availability of the inexpensive starting materials on a multi-gram scale, the easy synthesis of the polymer network, and its convenient handling paired with high versatility make our approach highly applicable to create custom-tailed adaptive materials.

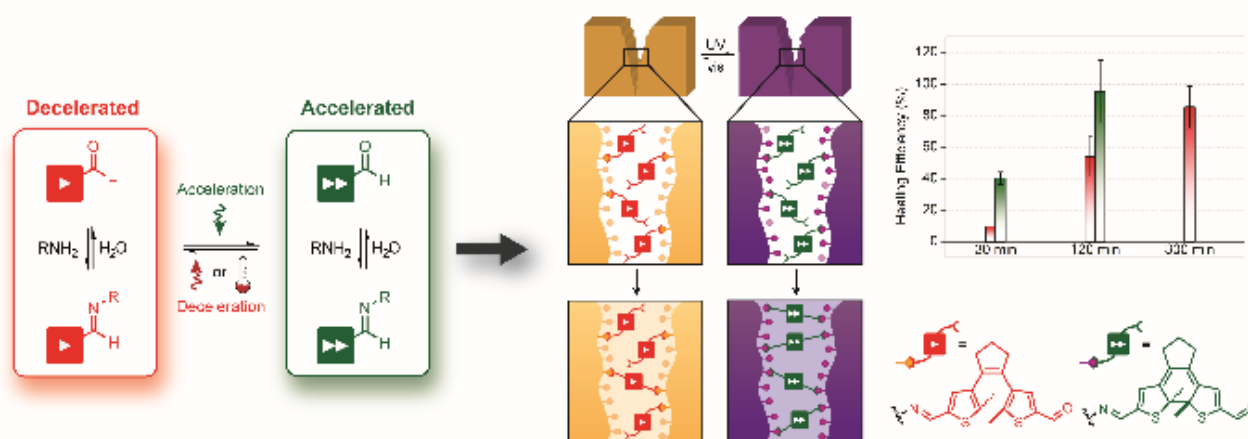


FIGURE 1. Photocontrolling the electrophilicity of carbonyl/imine groups (left) enables adaptive materials with remote-controllable, intrinsic properties, such as self-healing (right).[1]

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Photosensitive microgels containing azobenzene surfactants

S. Schimka^{a,b}, A.M. Rumyantsev^c; E. Yu. Kramarenko,^c M. Lehmann^d,
N. Lomadze^a, R. von Klitzing^d, S. Santer^a

^aUniversity of Potsdam, Institute of Astronomy and Physics, Potsdam-Golm, Germany

^bMax Plank Institute of colloids and Interfaces, Potsdam-Golm, Germany

^cLomonosov Moscow State University, Faculty of Physics, Moscow, 119991, Russia

^dTechnical University Berlin, ^dInstitute of Chemistry, 10623 Berlin, Germany

The interest on stimuli-sensitive microgel particles consisting of cross-linked polymers has attracted an enormous attention, due to their ability to encapsulate and/or release compounds upon changing of external triggers. The origin of the process is the change of microgels size induced by variations in pH, temperature, chemical composition of the solvent as well as application of light or static magnetic fields [1].

Here we report on the experimental and theoretical investigation of light sensitive microgel particles that can change their volume reversibly in response to illumination with light of different wavelengths [2-4]. The 8-fold change in volume under light exposure takes place within seconds and can be conducted reversibly many times. To make the anionic microgels photosensitive we add azobenzene containing surfactants with a positively charged polyamine head group and a hydrophobic tail with an azobenzene moiety. We have studied four photosensitive surfactants differing in the number of charges at the head group to be 1+, 1.5+, 2+ and 3+, while the hydrophobic tail is kept similar. Under illumination, azobenzene undergoes a reversible photo-isomerization reaction from a *trans*- to a *cis*-state accompanied by a change in the hydrophobicity of the surfactant. Depending on the isomerization state, the surfactant molecules are either accommodated within the microgel (*trans*-state) resulting in its shrinkage or desorbed back into water (*cis*-isomer) letting the micogel to swell. The properties of the complexes were investigated using UV-visible spectroscopy supplemented by dynamic light scattering, Zeta-sizer and SEM measurements. We have found experimentally and theoretically that the surfactant concentration needed for microgel compaction increases with decreasing number of charges of the head group.

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A Comparative Study of Photoinduced Deformation in Azobenzene Containing Polymer Films

Sarah Loebner^a, Alexey Kopyshchev^a, Nino Lomadze^a, Nataraja Sekhar Yadavalli^b, Elena Sava,^c Nicolae Hurduc,^c and Svetlana Santer^a

^a Experimental physics, Institute of Physics and Astronomy, University of Potsdam, Germany

^b Present address: Nanostructured Materials Laboratory, The University of Georgia, Georgia, USA

^c Technical University of Iasi, Department of Natural and Synthetic Polymers, Romania

Here we report on light induced structuring and deformation of three photosensitive polymers differing in their glass transition temperature. To inscribe surface relief gratings, the polymer films were irradiated with interference pattern of different polarization: intensity interference pattern (IIP) and polarization interference pattern (PIP). The irradiation was conducted in-situ while simultaneously acquiring the topography change with AFM. The polymers show comparable kinetic of topography change and maximally attainable grating height under irradiation with IIP. The illumination with PIP results in larger grating height for all three polymers, but more pronounced topography change was found for the polymers of larger glass transition temperature.

We have also performed experiments where a rectangular piece of polymer film was cut out of the film using AFM lithography and irradiated with homogeneous light of linear polarization. For all three polymers we have found that the rectangular piece elongates along the electrical field vector and contracts in perpendicular direction.

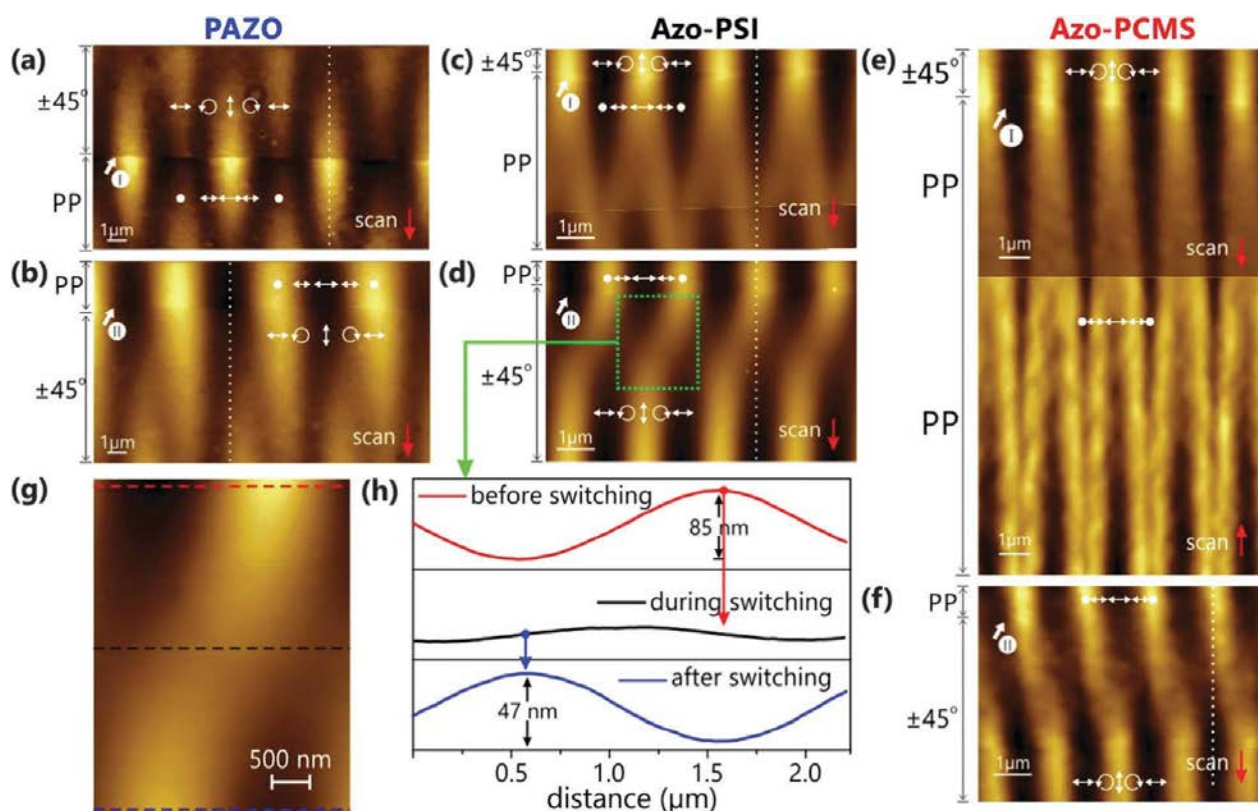


Figure1. [1] Switching experiments: comparison of SRG formation in PAZO (a, b), azo-Psi (c, d) and azo-PCMS (e, f) films using irradiation with $\pm 45^\circ$ and PP.

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Near field induced structuring of photosensitive polymer films: SNOM and AFM measurements

Joachim Jelken, Burkhard Stiller, Carsten Henkel, Svetlana Santer, Dieter Neher

Institute of Physics and Astronomy, University of Potsdam, Potsdam, Germany

Here we report on structuring of photosensitive polymer films by near field intensity pattern. The near fields were generated at a nano-groove fabricated within a thin metal layer. It is well known that when the nano-groove is irradiated, a surface plasmon wave is generated within the nano-groove, that as commonly expected should propagate along the metal surface. We have found, that instead of propagating SP mode, a standing EM-wave is generated at the metal/dielectric interface as a result of constructive interference between propagating SP mode and transmitted light. We have investigated two different sets of the nano-antennas consisting of either gold or silver thin films of 60nm in thickness patterned with nano-grooves of 100nm in width and 10 μ m in length using focused ion beam (FIB) technique and/or AFM nano-lithography.

We have analyzed this phenomenon using photosensitive azobenzene containing polymer film placed above the metal surface [1-4]. The polymer films deform following the intensity distribution of light only in case of stationary distribution of the intensity or polarization pattern. We have analyzed the system theoretically and have found that the standing wave exist even in the absence of the polymer film. This was also supported by SNOM measurements [5].

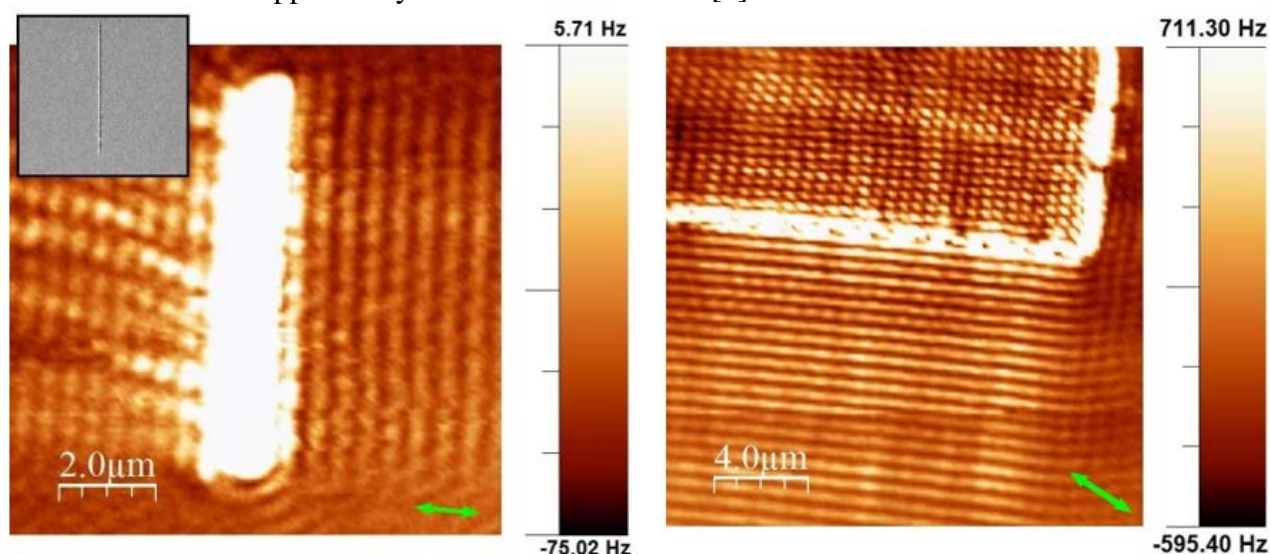


FIGURE 1. Surface plasmons at a FIB nano-groove in silver (left) and at a nanostructure made by an AFM nano-lithography (right). Inside the rectangular structure the plasmons interfere and form a chessboard-pattern. The green arrow indicates the direction of polarization of the incoming light.

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Tunable distributed feedback (DFB) dye lasers based on elastomer polymers

Alex Berdin^{a,b}, Oksana Sakhno^a, Michael Wegener^a

^aFraunhofer IAP, ^bUniversity of Potsdam

Keywords: Elastomer Polymers, Laser, Tunability, Single-Mode

Distributed feedback (DFB) dye lasers are a topic of research and development due to their properties to enable a narrow band, single-mode emission applicable e.g. in spectroscopic devices.[1] If such DFB dye lasers are processed with elastomeric polymers they offer possibilities to tune their properties due the flexibility and stretchability of the elastomers. Here, the fabrication of the polymeric device is demonstrated, starting with the holographic preparation of a master surface relief grating (SRG), the replication of the SRG into elastomeric polymers as well as the formation of the laser cavity by covering the SRG with laser dyes. The in this way constructed DFB dye laser is stretchable which offers the possibility to adjust its emission range. In detail, we demonstrate that it is possible to cover an emission range between 575 nm and 700 nm by adjusting the grating period, the polymer matrix and the laser dye. Current research is related to the combination of several gratings with different periods and different dyes onto a single elastomeric substrate. This would result in a tunable emission range of over 100nm by stretching the DFB dye lasers mechanically, e.g. by means of an electromechanical actuator. This concept is discussed in detail.

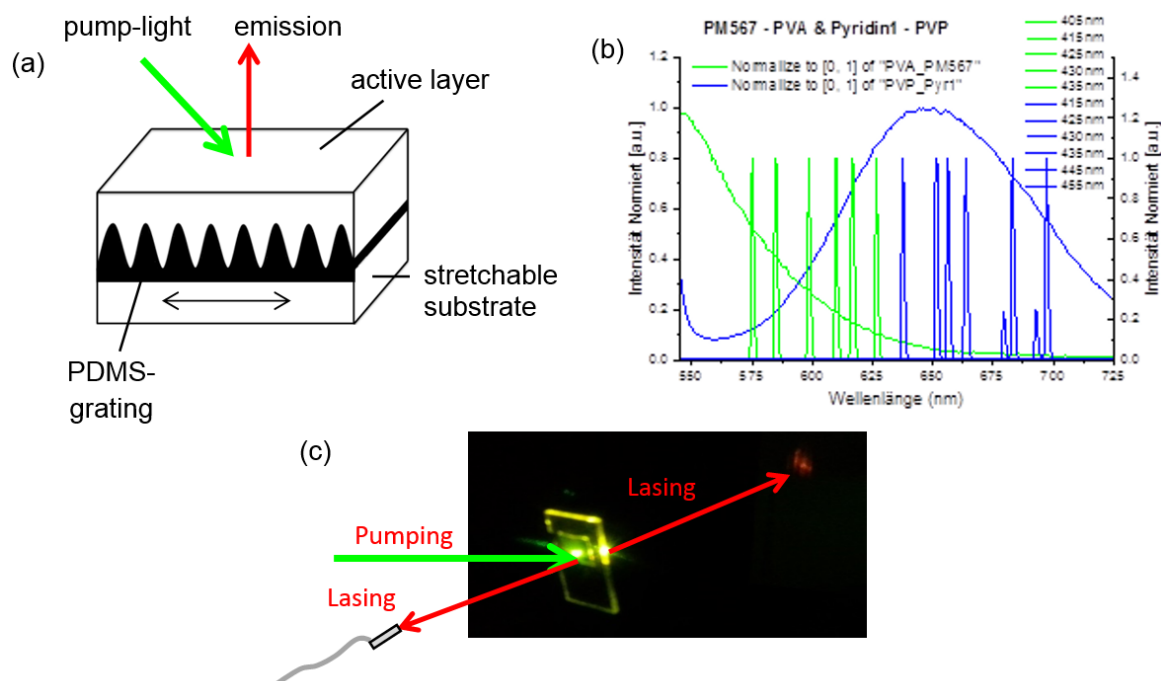


FIGURE 1. (a) DFB-Laser model, (b) emission spectra with two different elastomers and laser dyes, (c) fabricated DFB Dye Laser

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High throughput fabrication of single use microfluidic devices using hydrophilic polymers designed for roll-to-roll UV nanoimprint lithography

Manuel W. Thesen^a, Mirko Lohse^a, Maren Schiersch^a, Dieter Nees^b, Stefan Köstler^b, Anja Haase^b, Nerea Briz Iceta^c, Ana M. Ayerdi Izquierdo^c, Gabi Grützner^a

^a *micro resist technology GmbH, Köpenicker Str. 325, 12555 Berlin, Germany, m.thesen@microresist.de*

^b *Joanneum Research Materials, Franz-Pichler-Str. 30, 8160 Weiz, Austria*

^c *Tecnalia, Parque Científico y Tecnológico, E-20009 Donostia-San Sebastián, Spain*

Keywords: UV-Nanoimprint lithography (UV-NIL), roll-to-roll, microfluidics, surface biofunctionalization

Standard manufacturing technologies for microfluidic chips are mainly conventional photolithography, soft lithography, or molding techniques [1]. Most of the applied materials are generic ones like conventional elastomeric polydimethyl-siloxane (PDMS), thermoplastic materials like polymethyl methacrylate (PMMA) or polystyrene (PS), or even photoresists like SU-8 [1,2]. If a certain surface function is needed for the final application, e.g. reactive side moieties at the top surface of the microfluidic channels for subsequent biofunctionalization and cell adhesion, additional cost intensive process steps are obviously essential. In contrast to such standard manufacturing methods UV-nanoimprint lithography (UV-NIL) is a nano-fabrication method providing the possibility of a direct structuring of functional materials. For high throughput and HVM, roll-to-roll UV-nanoimprint lithography (R2R UV-NIL) is proposed to be an alternative low cost manufacturing technology for such microfluidic devices in one single step [3]. In this contribution we will demonstrate the development status of a photo-curable and biocompatible NIL resist especially designed for the application in R2R UV-NIL mass prototyping featuring selected material characteristics for microfluidic device fabrication. Furthermore, we will show preliminary results of the covalent biofunctionalization of the resist top surface using different biomolecules. Preliminary high throughput manufacturing applying the newly developed formulations in a roller NIL process will be shown and characterized, finally.

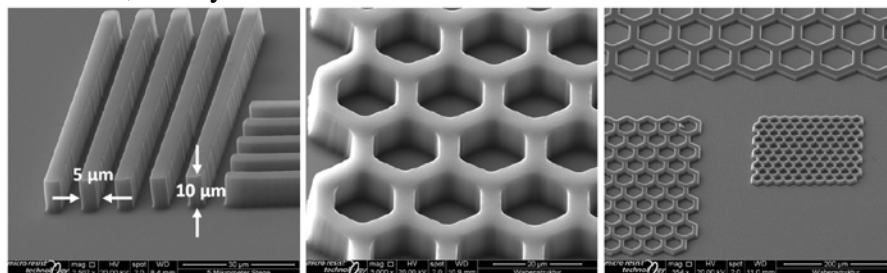


FIGURE 1. SEM images of batch fabricated UV-NIL imprints using the herein presented newly developed biocompatible resist prototypes.

Acknowledgement

Parts of this work have been performed within the H2020 EU-funded project “R2RBiofluidics”, Grant Agreement number 646260

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Tailor-made functional materials for UV-NIL and direct fabrication of microfluidic chips

Mirko Lohse^a, Manuel W. Thesen^a, Maren Schiersch^a, Nerea Briz Iceta^b,
Ana M. Ayerdi Izquierdo^b, Gabi Grützner^a

^a *micro resist technology GmbH, Köpenicker Str. 325, 12555 Berlin, Germany,*

^b *Tecnalia, Parque Científico y Tecnológico, E-20009 Donostia-San Sebastián, Spain*

Keywords: UV-NIL, microfluidics, biofunctionalization, functional materials

For the fabrication of microfluidic devices mainly conventional elastomers like polydimethylsiloxane (PDMS), thermoplastic materials like polymethyl methacrylate (PMMA) or polystyrene (PS), photoresists like SU-8, or even inorganic materials like rigid silicon and glass are commonly used [1,2]. If a surface modification by biomolecules is needed for the final application, e.g. cell adhesion for drug or disease screening, especially a hydrophilic surface including reactive moieties of the fabricated nanochannels are beneficial for in-situ surface biofunctionalization and subsequent single cell attachment. But most state-of-the-art materials, like PDMS, suffer from intrinsic hydrophobicity, requiring post treatments, that especially in the case of PDMS, hydrophilizes the surface only temporally. We will show first results of photo-curable NIL resists featuring the relevant material characteristics for fast imprint processes as well as for cell attachment: excellent biocompatibility after curing, high optical transmission in the visible range of the spectrum, high hydrophilicity beside low hygroscopicity, fast curing rate during photo-radiation, good adhesion to several plastic films like PET or PC, without any surface treatment. Specific concentration of carboxylic acid moieties at the cured resist top surface allows subsequent biofunctionalization of these material surfaces using different biomolecules like covalently bonded collagen, fibronectin, and polylysine. In addition, PC12 cell adhesion tests will be explained and the resulting simultaneous differentiation to neuronal-like-cells on the artificial resist surfaces will be discussed.

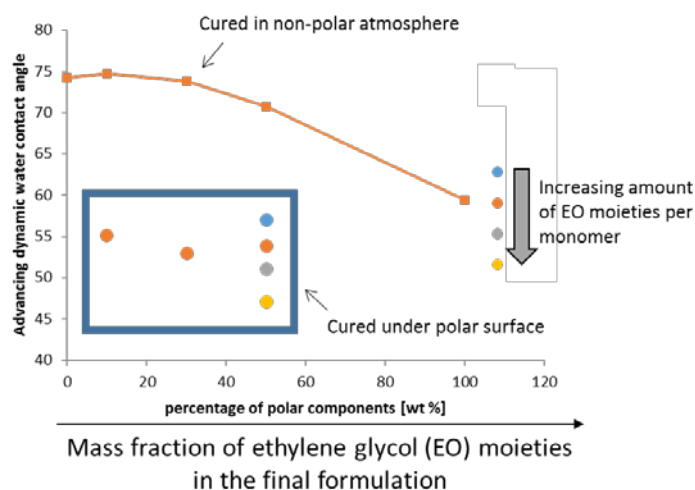


FIGURE 1. Dependence of the adv. dynamic contact angle of water on the degree of ethoxylated monomer within the formulation according to different curing conditions.

Acknowledgement

Parts of this work have been performed within the H2020 EU-funded project “R2RBiofluidics”, Grant Agreement number 646260

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UV-induced Crosslinking in Polymers at the near visible area

Simon Zunker, Oswald Prucker^a, Jürgen Rühle^a

^a*Department of Microsystems Engineering (IMTEK), Georges-Köhler-Allee 105, University of Freiburg, 79110 Freiburg*

Keywords: CHic reaction, lamination, crosslinking

The lamination of polymer foils is a well-known process in industry and has a wide variety of applications such as the sealing of food bags or the coating of sensitive materials.[1] Conventional lamination is limited on chemically identical polymers and relies on the interdiffusion of chains across the interface. Incompatible materials cannot be laminated in this way. This is a major problem for example for the generation of polymer based micro-optical systems as they require the generation multilayer foils of often very different polymers. Therefore, we developed a reactive lamination process that uses crosslinker systems to connect the polymer foils covalently to each other. We use polymers with photoreactive sulfonyl azide-groups or aromatic carbonyl compounds such as benzophenone or anthraquinone that can be coated onto the polymer foils to form a compatibilizing layer between them. Upon activation C,H-insertion reactions are triggered and chemical connections across the interfaces are generated. We call this process C,H insertion crosslinking (CHic).[1,2]

A major challenge for this process is the strong UV absorption found in commercial polymer foils due to additives. We have now developed thioxanthenes that show good absorption properties near the visible light if combined with amines to increase their reactivity. First tests show high reactivity and a fast network formation which is strongly influenced by the amount of amine inside the polymer chain. The presented process for lamination holds great promise for the manufacturing of polymer based optronic systems as it connects protecting properties with good optical behavior for nearly any combination of polymer foils and even introduces the possibility to produce multilayer systems.

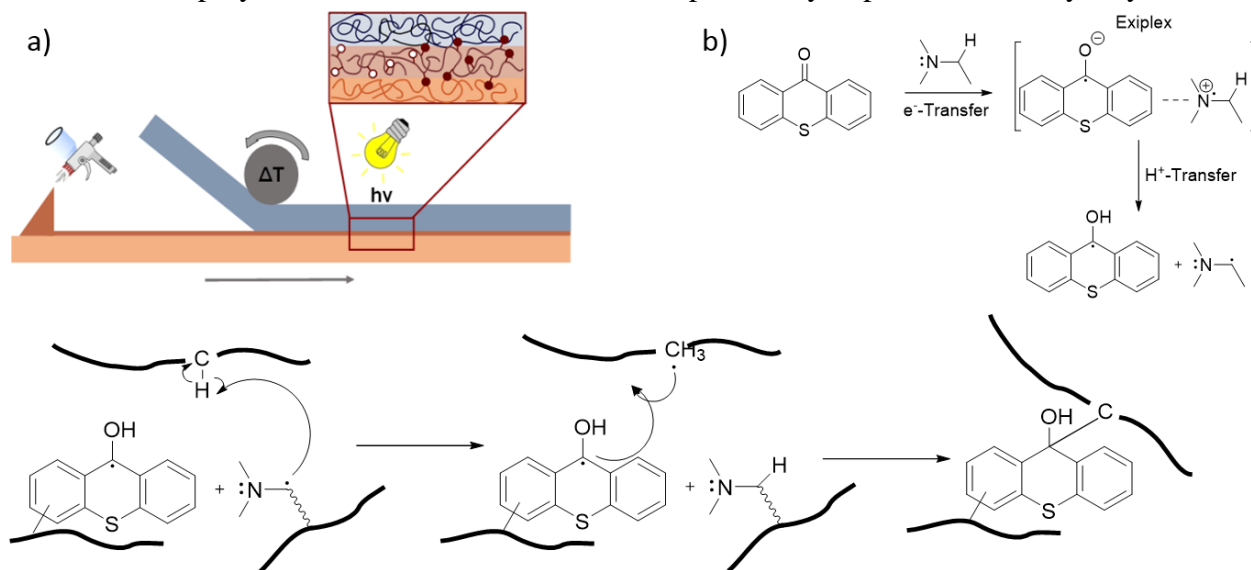


FIGURE 1 **a).** Image of the reactive lamination prozess; **b).** Amine supported activation of thioxanthone; **c).** assumed mechanism for the amine supported crosslinking of thioxanthone.

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Modification of Silica Particles via Micro Contact Printing

Marc Zimmermann^a, Daniela John^a, Alexander Böker^a

^a Fraunhofer Institute for Applied Polymer Research, Geiselbergstraße 69, 14476 Potsdam-Golm

Keywords: Silica Microparticles, Micro Contact Printing, PDMS, Self-assembly

The precise and selective modification of silica microparticles is a challenging task, which led to very different approaches over the years reaching from dip coating, etching processes and interface reactions in two phase systems [1 – 3].

While there are several studies concerning the preparation of patchy or janus-like polymer particles with micro contact printing (μ CP), only very few studies use this technique to create patchy silica particles. A great stability concerning temperature and various solvents and a broad selection of alkoxy silanes for surface modification make these silica particles very attractive for further investigations.

Our group works with PDMS as a substrate for μ CP. Using air plasma treatment with the right parameters (time, pressure, power) during the elongations of PDMS substrates, wrinkles with defined amplitudes and wavelength, can be produced on the surface [4]. These structures are useful for the alignment of colloids and function as structured stamps for the preparation of multivalent patchy particles. Most methods creating multivalent patchy particles are constrained to a high symmetry of the patches (e. g. 60° angle), which we can bypassed using our μ CP approach with structured substrates. After printing, these patches can be modified with reversible (supramolecular) or irreversible crosslink chemistry (click reactions) to achieve the possibility of switchable colloidal assemblies.

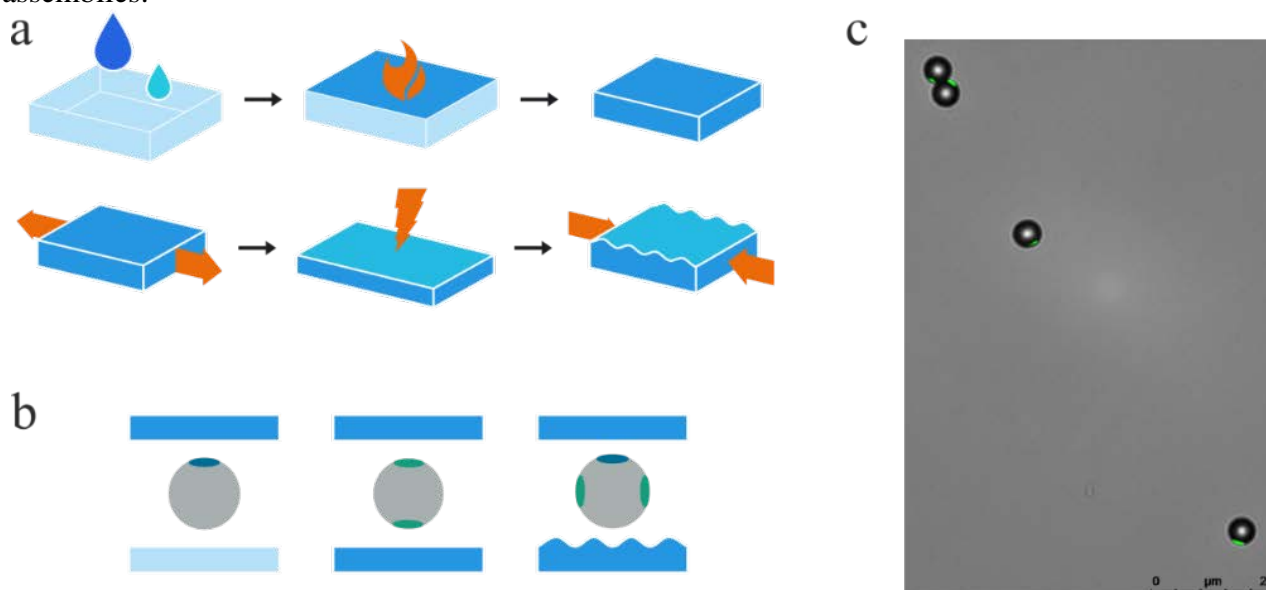


FIGURE 1. (a) Mixing and curing of the PDMS stamp with subsequent elongation and air plasma treatment producing wrinkles. (b) Scheme of the μ CP process leading to mono-, bi- and trivalent silica particles. (c) Fluorescence microscope image of patchy silica particles.

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Nano-mechanical imaging reveals heterogeneous cross-link distribution in sulfur-vulcanized butadiene-styrene rubber comprising ZnO particles

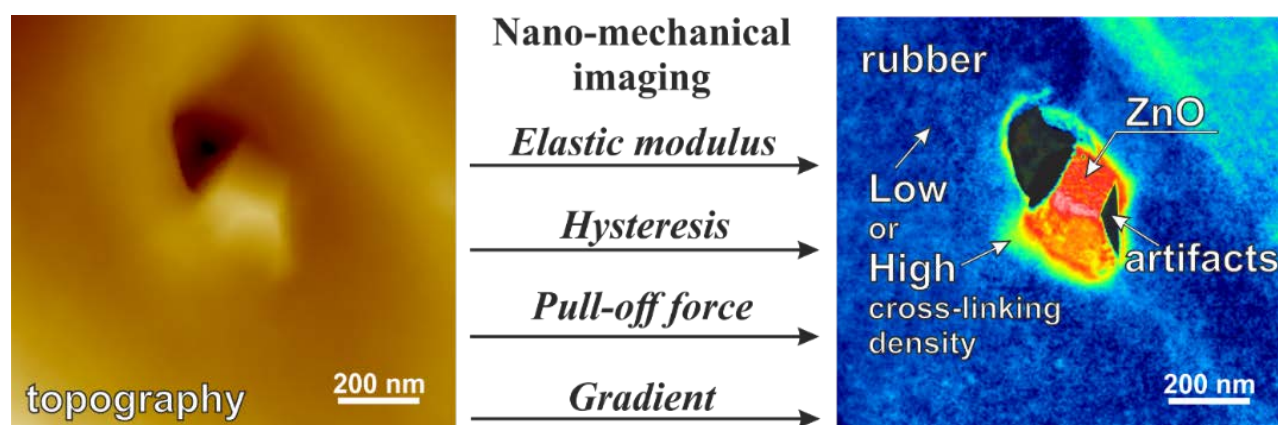
Yulia Glebova^{1,2}, Valentin Reiter¹, Sari Suvanto³, Tarmo Korpela³,
Tuula T. Pakkanen³, Nikolai Severin¹, Vladimir Shershnev², Jürgen P. Rabe¹

¹*Department of Physics & IRIS Adlershof, Humboldt-Universität zu Berlin, Germany*

²*Moscow State University of Fine Chemical Technologies, Russia*

³*Department of Chemistry, University of Eastern Finland, Finland*

The addition of zinc oxide (ZnO) to sulfur (S-) vulcanized rubbers is known to accelerate the cross-linking kinetics and to increase the heterogeneity of the cross-link density. However, the spatial distribution of cross-links is hardly known and two different mechanisms and their relative contributions to the ZnO influence on the cross-linking process are still disputed. One suggests that the Zn^{2+} ions diffuse from ZnO into the rubber matrix accelerating cross-linking reactions. However, to the best of our knowledge, the correlation of cross-link density heterogeneity with locations of ZnO particles has not been investigated so far. The second mechanism argues that the surface of ZnO accelerates cross-linking. We therefore investigated S-vulcanized butadiene-styrene rubber comprising ZnO particles. The samples were fractured and then investigated employing the nano-mechanical mapping mode (NM) of scanning force microscopy (SFM), supported by scanning electron microscopy (SEM). We find that rubber around the ZnO particles exhibits a higher Young's modulus in a shell with a width up to about 200 nanometers (Figure). Furthermore, the extension and retraction curves on these shells exhibit a smaller hysteresis than on the rubber further away from the ZnO particles. We attribute the higher Young's modulus and the smaller hysteresis to a higher cross-link density in rubber surrounding the ZnO particles and explain this with the activity of the particles' surfaces.



Topography image of fractured rubber surface reveals occasional angular particles (left). Mapping of elastic modulus, hysteresis, pull-off force and gradient of height image allows us to argue that the angular particles are ZnO surrounded by a rubber shell with higher cross-linking density (right).

Synthesis and Self-assembly of Responsive Cobalt Nanoparticles

Li Tan^{a, b}, Bing Liu^c, Ulrich Glebe^{a, b}, Alexander Böker^{a, b}

^a Fraunhofer Institute for Applied Polymer Research IAP,
Geiselbergstr. 69, 14476 Potsdam-Golm, Germany.

^b Lehrstuhl für Polymermaterialien und Polymertechnologie, Universität Potsdam,
14476 Potsdam-Golm, Germany

^c Institute of Chemistry Chinese Academy of Sciences, 100864, Beijing, China

Keywords: Cobalt nanoparticles; ATRP; Poly(NIPAM); Self-assembly

Ferromagnetic nanoparticles (NPs) are able to self-assemble into one- and two-dimensional nanostructures [1] such as nanochains, nanorings and nanoplates. However, tuning the self-assembly of ferromagnetic NPs is a challenging task. Atom-transfer radical polymerization (ATRP) is an effective “graft-from” method, which can be used to coat nanoparticles with an environment-responsive polymer shell. The responsive behavior is expected to also tune the self-assembly process of ferromagnetic NPs. For example, poly(*N*-isopropylacrylamide) (PNIPAM) can undergo a reversible sharp phase transition at a lower critical solution temperature (LCST) near 32 °C in aqueous solution[2], which typically induces a change of hydrodynamic radius of colloidal particles. In this project, we synthesized Co@PNIPAM core-shell nanoparticles and are exploring their temperature-responsive assembly behavior, as illustrated in Figure 1.

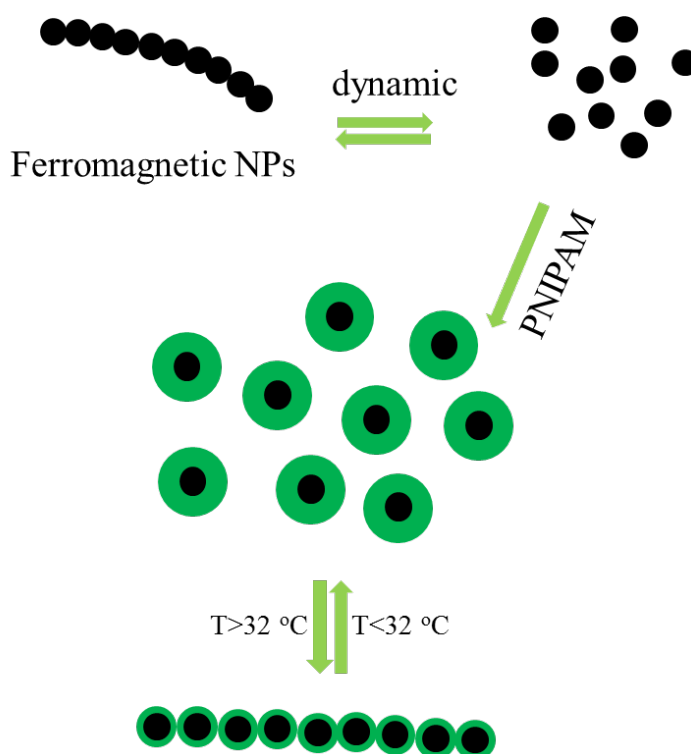


FIGURE 1. Overview of the self-assembly of the Co@PNIPAM.

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Thermoresponsive Magnetic Nanogels in Anticancer Applications

Julian Bergueiro^a, Catalina Biglione^b, Miriam Strumia^b, and Marcelo Calderón^a

^aFreie Universität Berlin, Institut für Chemie und Biochemie, Takustrasse 3, 14195 Berlin Germany

^bLAMAP Departamento de Química Orgánica Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Haya de la Torre y Medina Allende X5000HUACórdoba, Argentina

Keywords: Thermoresponsive, Magnetic, Nanogels, Bioapplication

In the recent years, several systems have been developed for drug delivery, specially in the cancer treatment [1]. One of the potential systems are the stimuli responsive nanometric systems also known as smart nanogels.[2] On then, several stimuli can be utilized, such as pH, temperature, ionic strength, light irradiation, etc[3]. Between then, thermoresponsive nanogels have gained great interest in the last years. The incorporation of magnetic nanoparticles (MNPs) into the polymer matrix presents several advantages since this way the systems can be used as contrast agents, for guiding therapy, and for hyperthermia[3]. The present work investigates for the first time the covalent incorporation of MNPs in OEG-based nanogels using 2-hydroxymethylmethacrylate as comonomer as a potential binding site for a drug. We describe herein a new robust strategy for the thermoresponsive magnetic nanogels (tMNGs) synthesis based on an ultrasound assisted thermo-precipitation/polymerization approach. In addition, the application of these tMNGs in nanomedicine is being tested as drug delivery systems, an magnetic resonance imaging contrasting agent as well as for cancer cell sorting.

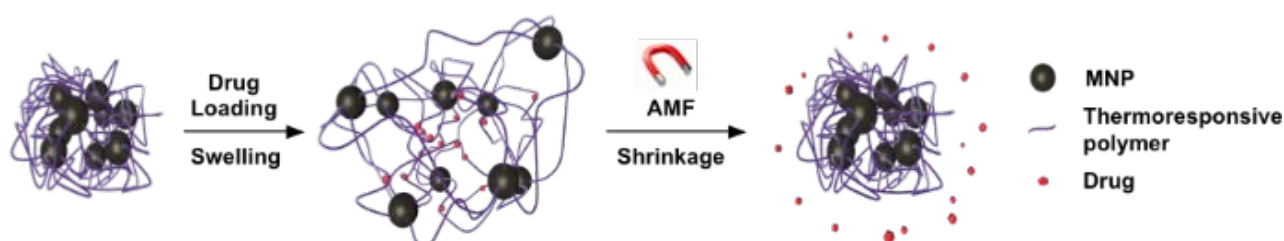


FIGURE 1. tMNGs drug loading and alternate magnetic field (AMF) triggered release.

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Nano-structural evolution and self-healing of micellar hydrogels followed with scanning force microscopy

V. Reiter², V. Can¹, Z. Kochovski², N. Severin², M. Siebenbürger¹,
B. Kent¹, J. Just¹, J. P. Rabe², M. Ballauff^{1,2}, O. Okay^{1,3}

¹*Helmholtz-Zentrum Berlin, Soft Matter and Functional Materials;*

²*Humboldt-Universität zu Berlin, Department of Physics & IRIS Adlershof;*

³*Istanbul Technical University, Department of Chemistry*

Understanding the nanoscale structure and dynamics of supramolecular hydrogels is essential for exploiting their self-healing mechanisms. Here we investigate the response of a micellar hydrogel to damage and its self-healing mechanism with scanning force microscopy (SFM) [1]. The hydrogel consists of worm-like sodium dodecyl sulfate (SDS) micelles and *in-situ* synthesized hydrophilic-hydrophobic block copolymers. Imaging of a cut made on the gel surface with an SFM tip reveals terraced structure with step heights between 4 and 5 nm, which is attributed to layers of SDS micelles. Self-healing of the damaged hydrogel under ambient conditions begins by reshaping of the cut into circular holes (Figure 1). The self-healing process is facilitated by elevated temperatures and high humidities and finally leads to complete healing of the gel surface.

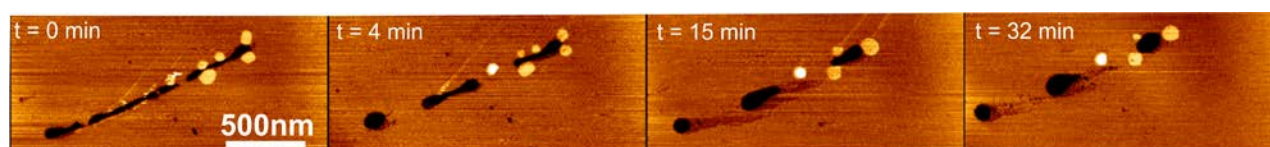


FIGURE 1. Sequence of SFM topography images of a gel surface cut with an SFM tip. The initially elongated cut becomes first dumbbell-like and eventually relaxes into circular holes. Imaging is performed under ambient conditions.

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In-situ Investigation of the Polydopamine (PDA) Structure in Different Buffer Solutions by Infrared Spectroscopic Ellipsometry (IRSE)

Guoguang Sun^{1,*}, Jörg Rappich² and Karsten Hinrichs¹

¹*Leibniz-Institut für Analytische Wissenschaften - ISAS e.V.,
Schwarzschildstraße 8, 12489, Berlin, Germany*

²*Helmholtz-Zentrum Berlin für Materialien und Energie GmbH,
Institut für Silizium Photovoltaik, Kekuléstr. 5, 12489, Berlin, Germany*

Keywords: polydopamine (PDA), in-situ IRSE, Polymer Structure, Buffer solution

Bio-inspired surfaces like polydopamine (PDA) are of high technological interest for fabrication of biosensors or bio-related devices [1-2]. Specific biomolecular adsorption properties are depending on chemical structure and morphology of the PDA. The experimental parameters of PDA deposition (*e.g.*, pH value, concentration, reaction time, additional ions; etc.) are crucial for the final structural properties and growth mechanisms of the PDA film [3]. In this work, thin PDA films achieved under different buffer solutions (Tris and PBS) were studied in a multi-method approach. The time-dependent deposition of PDA films in different buffer solutions was in-situ monitored by infrared spectroscopic ellipsometry (IRSE). The in-situ and ex-situ IR spectra showed that a more quinoid structure was obtained in PDA films deposited in PBS buffer solution. Also a rougher film surface was achieved using PBS buffer solution which was confirmed by AFM imaging. The chemical homogeneity of the films was studied by AFM-IR with nanometer resolution.

Acknowledgement

The financial support of the Deutsche Forschungsgemeinschaft (DFG, GZ: SU 894/2-1) is gratefully acknowledged.

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Unveiling the Dynamics of Self-Assembled Layers in Ultra-Thin Films of PVME and PVME/PS Blend Using Nano-Relaxation Spectroscopy

Sherif Madkour, Paulina Szymoniak, Andreas Schönhals

*Bundesanstalt für Materialforschung und –prüfung (BAM),
Unter den Eichen 87, 12205 Berlin, Germany*

Keywords: Broadband dielectric spectroscopy, AC-chip calorimetry, Ultrathin films, Dynamic glass transition.

In the course of miniaturizing modern technology down to the molecular scale, much remain unknown about the materials behavior and the deviations from the bulk that might arise from confinement effects. Here, a combination of nano-sized relaxation spectroscopies (Broadband dielectric spectroscopy (BDS) and Specific heat spectroscopy (SHS); employing AC nanochip calorimetry) were utilized to investigate the glassy dynamics of ultra-thin films of Poly (vinyl methyl ether) (PVME) and of blends PVME / Polystyrene (PS) 50:50 wt-%., which are miscible in bulk (thicknesses: ca. 8 nm – 160 nm, film thickness was controlled by ellipsometry, film topography by AFM). Both methods are sensitive to different probes; where SHS senses entropy fluctuations while BDS measures dipole fluctuations. For BDS measurements, a recently developed nano-structured electrode sample arrangement is employed, where ultra-thin films are spin-coated on an ultra-flat highly conductive silicon wafer, sandwiched between a wafer with nanostructured SiO₂ nano-spacers with heights between 35 nm and 70 nm. For PVME films, two thickness independent processes were observed and interpreted to be the α -processes of a bulk-like layer and a process due to an adsorbed layer to the substrate. This adsorbed layer further undergoes a confinement effect that results in the localization of the segmental dynamics, which results in an Arrhenius-like temperature dependence. A detailed analysis of the dielectric strengths of both processes reveals that the thickness of the adsorbed layer decreases with increasing temperature, while that of the bulk-like layer increases. For the blend system, by measuring the dynamic T_g in dependence of the film thickness, SHS showed that the T_g of the whole film was strongly influenced by a nanometer-thick surface layer at the polymer/air interface due to a self-assembling process [1]. The dynamic T_g obtained from the SHS measurements decreased with decreasing film thickness. On the other hand, BDS measurements showed a completely different behavior. At high temperatures, the temperature dependence of the relaxation times of the films follows that of bulk-like PS/PVME; obeying the VFT-law. With decreasing temperature, the temperature dependence deviates from the VFT to an Arrhenius law; where the apparent activation energy decreases with decreasing film thickness. This is the first example where confinement induced changes were observed by BDS for ultra-thin films. All results were analyzed in detail in a comprehensive discussion.

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Study of the Confinement Effect in Hyperbranched Polyamine Ester /Kaolinite Nanocomposites by Broadband Dielectric Spectroscopy and Specific Heat Spectroscopy

Shereen Shabaan Omara^{a,b}, Mona H. Abdel Rehim^c, Ahmed Ghoneim^b,
Sherif Madkour^a, Andreas F. Thünemann^a,
Gamal Turkey^b and, Andreas Schönhals^a

^a*Bundesanstalt für Materialforschung und –prüfung (BAM),
Unter den Eichen 87, 12205 Berlin (Germany)*

^b*Microwave Physics and Dielectrics Dept.,*

^c*Packing and Packaging Materials Dept. of National Research Centre,
33 El Behooth St., Dokki, Giza, Egypt*

Keywords: Hyperbranched polymers, Nanocomposites, Confinement and Dynamic Glass Transition Temperature.

Recently, Hyperbranched polymers (HBP) / nanocomposites have drawn much attention and obtained dense research activities from both industry and academia. For the different potential applications, an understanding of the molecular mobility of molecules and the mechanism of charge transport in HBPs and in HBPs/nanocomposites is required. Here, hyperbranched polyamine ester (HPAE) /kaolinite (Ka) nanocomposites were prepared by two different methodologies. Firstly, an in situ polymerization process was employed where diethanolamine is inserted as monomer between the Ka-layers and polymerized with methyl acrylate to prepare HPAE/Ka-DEA nanocomposites. Secondly, an ex situ method is applied where Ka is modified with dodecylamine and solution-blended with pure HPAE. The morphology of both sets of nanocomposites was investigated by SAXS and TEM. The results showed that in situ polymerization led to more or less intercalated morphology while the ex situ method yielded exfoliated structures. Differential Scanning Calorimetry (DSC) and Broadband Dielectric Relaxation (BDS) were used to investigate both kinds of nanocomposites in detail. The segmental dynamics (α -relaxation) could not be observed directly by BDS because the conductivity masks the dielectric response above the glass transition temperature T_g . By using Specific Heat Spectroscopy (SHS), utilizing AC-chip calorimetry, the segmental dynamics for pure HPAE and its nanocomposites were investigated. A comparison of the temperature dependencies of the dynamic glass transition measured with AC-chip calorimetry and that of DC-conductivity measured by dielectric spectroscopy reveals a decoupling in their dynamic temperature dependencies which becomes weaker with decreasing fragility.

Effect of fluctuations on tracer diffusion in networks

Won Kyu Kim^a, Rafael Roa^a, Matej Kanduc^a, Joachim Dzubiella^{a,b}

^a *Institut für Weiche Materie und Funktionale Materialien, Helmholtz-Zentrum Berlin, Berlin, Germany*

^b *Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany*

Keywords: tracer diffusion, network, thermosensitive hydrogels, modeling and theory

We study the tracer diffusion in simple Lennard-Jones fluids and semi-flexible chain networks, using coarse-grained molecular dynamics computer simulations. For the fluid system, we find that various dynamic regimes are nontrivially dependent on inter-(tracer-fluid) and intra-(fluid-fluid) interactions, where fluctuations arising in the system largely affect the tracer diffusion. We compute the tracer diffusivities spanning a wide range of the interaction strengths, and reveal that an abrupt diffusivity shift signifies the gas-liquid phase transition. For the network system, we further extend the model towards tracer-hydrogel diffusion by imposing connectivity and semi-flexibility between the fluid particles that constitute the hydrogel network. Depending on the network–network and the tracer–network couplings, the network structure reveals a non-monotonic behaviour, and we discuss how the tracers diffusion and transport show a variety of dynamic regimes in conjunction with the network rigidity and fluctuations.

QCM System for the Characterization of Gas Sorption and Physical Aging of Membrane Polymers for Gas Separation Applications

Nora Konnertz, Martin Böhning

Bundesanstalt für Materialforschung und –prüfung (BAM), Unter den Eichen 87, 12205 Berlin

Keywords: Quartz Crystal Microbalance QCM; Gas Sorption; thin Films; high Pressure

Polymers are favorable materials for gas separation membranes. In general, gas transport experiments are performed with films in the range of 100 μm thickness. However, in large-scale processes very thin selective polymer layers in the range of 100 nm to 1 μm are used. Moreover, it was shown that thin films behave different compared to thick films with respect to gas transport properties and physical aging as well. Thus, for fundamental research it is important to realize gas transport experiments with thin films. The Quartz Crystal Microbalance (QCM) is a very sensitive method to detect mass changes in the range of nanograms. Therefore, this method enables sorption experiments with thin films or layers attached to the QCM crystal (100 nm up to 1 μm). Here, we present the experimental set-up for using the QCM technique for characterizing the gas sorption behavior of thin polymer films in a temperature controlled pressurized environment (up to 50 bar) (Fig. 1b) - also quartz crystals and crystal holders were optimized (Fig. 1a). The study aims for the characterization of long-term behavior and physical aging of high-performance polymers for gas separation membranes - such as polyimides and polymers of intrinsic microporosity (PIMs) and respective nanocomposites. Especially the differences of the behavior of thin films compared to films with thicknesses up to 100 μm as well as nanofiller induced-effects are addressed.

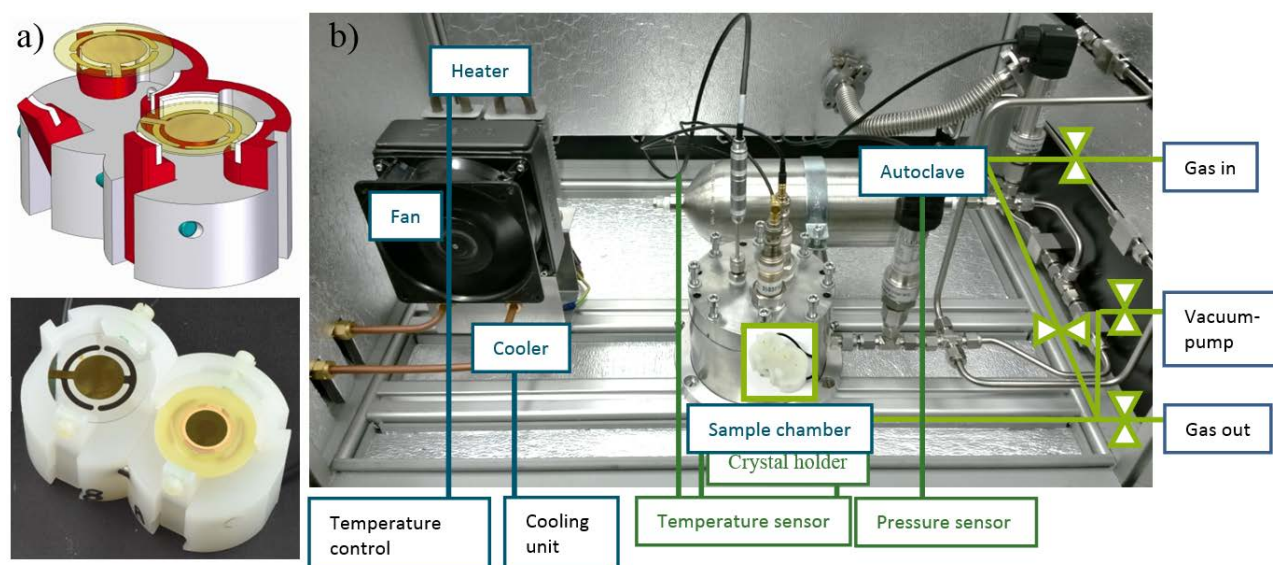


FIGURE 1. a) CAD model of the QCM crystal holder and fabricated crystal holder made of PVDF with two types of quartz crystals. b) Image and scheme of the QCM set-up.

Enhanced Gas Separation Performance of Nanocomposites based on a Polymer with Intrinsic Microporosity PIM-1 and Phenethyl-POSS

Nora Konnertz, Andreas Schönhals, Martin Böhning

Bundesanstalt für Materialforschung und –prüfung (BAM), Unter den Eichen 87, 12205 Berlin

Keywords: Polymer of Intrinsic Microporosity, PIM-1, POSS, Gas Permeation

In times of the energy revolution, the need for energy efficient separation processes promotes the advancement of new high performance materials for use as highly selective separation membranes. Most promising materials in this field, especially for gas separation, are polymers with intrinsic microporosity (PIMs) which were firstly introduced by Budd and McKeown [1]. In this study the permeability of PIM-1 was increased by 439 % by formation of nanocomposites with only 1 wt% of polyhedral oligomeric phenethyl-silsesquioxane (PhE-POSS) within the polymer matrix (Figure 1a). As the CO_2/CH_4 selectivity is fully retained, this leads to a shift in the Robeson plot towards the upper bound (Figure 1b). The Robeson plot describes the current state of the art trade-off relation between selectivity and permeability of all known membrane polymers. As molecular mobility is a key factor for gas transport as well as the often observed physical aging of such polymers, our study also includes for the first time, molecular dynamics and conductivity of pure PIM-1 and PIM-1 nanocomposites as investigated by broadband dielectric spectroscopy (BDS) [2].

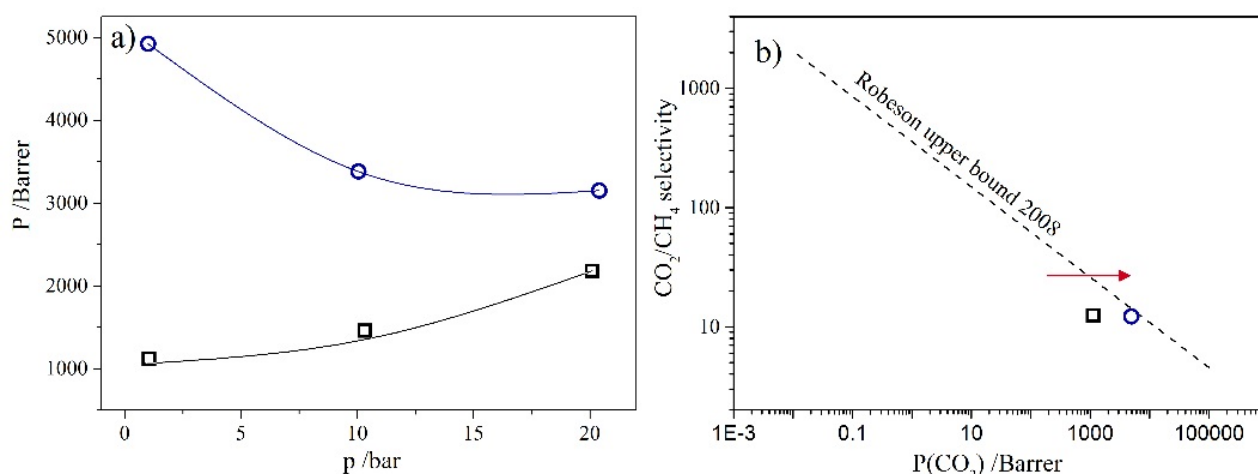


FIGURE 1. a) Permeability vs. CO₂ –pressure and b) CO₂/CH₄ selectivity vs. CO₂ permeability of PIM1-00 (□) and PIM1-01 (○) at 35°C.

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Advancement in Dielectrics-Reading on Kremer's View

Gamal M.Turky

Microwave Physics and Dielectrics Dept, NRC, Bohoos Str., Dokki, Cairo, Egypt

Keywords: BDS, Double Layer, Ionic Liquids, Charge Transport

Broadband Dielectric spectroscopy is one of the major tools in molecular physics. It plays an essential role in the characterization of advanced material such as Liquid Crystals or Ionic Liquids and the electrochemical double layer at the interface between it and the surface of the metal electrode in addition to the design of low-loss dielectric-materials.

Lately, many novel models have arisen in order to interpret the new systems and related phenomena among these novel views those of Friedrich Kremer. In the light of his novel views, new understanding of the dielectric spectroscopy and its interpretations has prevailed.

Unexpected Swelling of Polyelectrolyte Brush/Multilayer Composites in Humid Conditions

Oliver Löhmann^a, Samantha Micciulla^b, Olaf Soltwedel^c, Regine von Klitzing^a

^a*Technische Universität Berlin, Straße des 17. Juni 124, 12063 Berlin, Germany*

^b*Max Planck Institut für Kolloid- und Grenzflächenforschung Golm, Am Mühlenberg 1, 14476 Potsdam, Germany*

^c*Max Planck Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany*

Keywords: Polyelectrolyte multilayers, polymer brushes, neutron reflectometry, humidity

Introduction: Polymer coatings open a wide range of smart and active surfaces. Among possible preparation methods, the Layer-by-layer technique is an easy and versatile tool to functionalize a charged surface with a polyelectrolyte multilayer (PEM) with a thickness ranging from few nanometers up to micrometers¹. The large variety of polyelectrolytes opens different fields of applications for PEMs, for example antireflective coatings, antifouling coatings or carrier systems for specific target molecules.

Besides multilayers, polymer brushes can be also applied for surface functionalization. In contrast to physisorbed PEMs, brushes are covalently bound the surface. In particular, the grafting-from approach opens the opportunity to prepare well defined end-grafted polymer brushes with high grafting density and low polydispersity². From this, robust coatings with specific functionality can be prepared, which can be applied as coatings for implants, nanostructured surfaces or surfaces with specific hydrophobicity. The combination of both, multilayers and brushes, leads to a robust and multifunctional coating³. The study of the response to external stimuli is of crucial importance for many technical applications.

Presented work: Here, we present the swelling behavior of a composite consisting of a PEM-coated brush in humid conditions. PEM and brushes show a different swelling behavior during increasing relative humidity (RH). Ellipsometry data show that the swelling degree for PEM-coated brushes is between the two bare systems. A defined contrast between both compartments of the composite cannot be investigated by ellipsometry due to the very similar refractive index. Therefore, we used neutron reflectometry to investigate PMETAC brushes coated with dPSS/PDADMAC PEM of different layer numbers. The study demonstrates that PEM diffuses into the brush during the layer deposition and diffuses inside the brush by increasing the RH. At high RH the PEM diffuses towards the film/air interface, while the brush beneath the PEM absorbs reversibly more water than the PEM on top, which is counterintuitive. Possible explanations will be given.

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Temperature-induced F4TCNQ desorption from *p*-doped P3HT films

Hannes Hase,^a Andreas Opitz,^a Norbert Koch,^{a,b,c} Ingo Salzmann^a

^a*Humboldt-Universität zu Berlin, Department of Physics - Supramolecular Systems,
Brook-Taylor-Straße 6, D-12489 Berlin, Germany*

^b*Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Bereich Solarenergieforschung,
Albert-Einstein-Straße 15, 12489 Berlin, Germany*

^c*Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of
Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou 215123, P.R. China*

Keywords: annealing, diffusion, dopant, polymer

Typically, after solution processing, functional conjugated polymer (CP) films are thermally treated with great application-related success, e.g., in organic photovoltaic cells. In a number of studies, the same approach is being followed also for *p*-doped CPs, where doping by strong electron acceptors aims at improving the electrical properties of the films. The dopants employed are typically conjugated organic molecules of low-molecular weight like, e.g., tetrafluoro-tetracyanoquinodimethane (F4-TCNQ). Such materials are, however, expected to be prone to diffusion caused by the thermal annealing. Interestingly, the temperature-dependent diffusion/desorption behavior of molecular dopants from CP films has hitherto been largely disregarded in pertinent literature.

In the present study, we explore to which extent different annealing temperatures (at constant annealing times) influence poly(3-hexylthiophene-2,5-diyl) (P3HT) thin films doped with F4-TCNQ, where integer-charge transfer between the *p*-dopant and the CP occurs as fundamental doping process. We determined the electrical conductivity before and after the annealing process and investigated the amount and the nature of the remaining dopants (anionic or neutral) by optical absorption spectroscopy (UV/Vis/NIR) and Fourier-transform infrared spectroscopy (FTIR). Annealing-induced changes in the morphology and structure of the films were assessed by atomic force microscopy (AFM) and grazing-incidence X-ray diffraction (GIXD).

We found that thermal annealing up to a sample temperature of 60 °C enhances the electrical conductivity only insignificantly and leaves the concentration of ionized dopants unchanged. However, by increasing the annealing temperature beyond, a significant reduction in the dopant concentration is observed and the conductivity is severely reduced. Therefore, either a treatment temperature should be chosen that leaves the doping concentration intact, or the latter should be adjusted in order to compensate for losses due to dopant desorption upon thermal treatment at higher temperatures, if needed in practical applications.

University of Potsdam
Campus Golm
Karl-Liebknecht-Str. 24/25
14476 Potsdam-Golm
Germany

Lectures & Posters: Building 27

