

## CPP 52: Poster: Hydrogels, Microgels, Responsive Polymers

Time: Wednesday 18:30–21:00

Location: P3

CPP 52.1 Wed 18:30 P3

**H<sub>2</sub>O - D<sub>2</sub>O exchange kinetics in PNIPAM based block copolymer films followed with in-situ neutron reflectivity** — ●LUCAS KREUZER<sup>1</sup>, TOBIAS WIDMANN<sup>1</sup>, NURI HOHN<sup>1</sup>, KUN WANG<sup>1</sup>, JEAN-FRANÇOIS MOULIN<sup>2</sup>, VIET HILDEBRAND<sup>3</sup>, ANDRÉ LASCHEWSKY<sup>3</sup>, CHRISTINE PAPADAKIS<sup>1</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik-Department, Fachgebiet Physik weicher Materie/Lehrstuhl für Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching — <sup>2</sup>HZG at MLZ, Lichtenbergstr. 1, 85748 Garching — <sup>3</sup>Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Straße 24-25, 14476 Potsdam-Golm

Responsive polymers, especially in thin film morphology, are of great interest for a wide variety of applications where a strong change of volume is desired even for small changes of an external stimulus such as temperature. In this context the most prominent representative is poly(N isopropylacrylamide) (PNIPAM). We study a new block copolymer which comprises a PNIPAM block and a poly(sulfobetaine) (PSB) block. Thin films are prepared by spin coating on silicon substrates. We have followed the swelling of such films in water vapor atmosphere and found signature of H<sub>2</sub>O - D<sub>2</sub>O exchange in FT-IR data. We use neutron reflectivity to study the swelling behavior and the H<sub>2</sub>O - D<sub>2</sub>O exchange of PNIPAM-b-PSB films in more detail. In-situ neutron reflectometry enables to follow the kinetics and determine the underlying fundamental processes.

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**In-Situ Neutron Reflectivity on H<sub>2</sub>O - D<sub>2</sub>O Exchange Kinetics of Cross-Linked PNIPAM Microgel Thin Films** — ●TOBIAS WIDMANN<sup>1</sup>, LUCAS P. KREUZER<sup>1</sup>, NURI HOHN<sup>1</sup>, KUN WANG<sup>1</sup>, JEAN-FRANÇOIS MOULIN<sup>2</sup>, YVONNE HERTLE<sup>3</sup>, THOMAS HELLEWEG<sup>3</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching — <sup>2</sup>HZG at MLZ, Lichtenbergstr. 1, 85748 Garching — <sup>3</sup>Bielefeld University, Physical and Biophysical Chemistry, Universitätsstr. 25, 33615 Bielefeld

Strong volume shifts of polymer thin films due to small modifications of an external stimulus like temperature are desired for a number of applications such as thermoresponsive nanoswitches or drug delivery in medicine. In this context the polymer which received most attention so far is poly(N-isopropylacrylamide), PNIPAM. The volume shift arises due to the collapse transition of the polymer at a lower critical solution temperature (LCST) which manifests in a swelling or deswelling of the polymer with water from its surroundings. To further our understanding of the kinetics of water uptake, release and exchange and the induced changes of the polymer properties, microgel thin films from a PNIPAM homopolymer with varying amounts of N,N'-Methylenebisacrylamide cross-linkers are prepared. In-situ neutron reflectometry in time of flight (TOF) mode is used to investigate the uptake and exchange kinetics of H<sub>2</sub>O with D<sub>2</sub>O and vice-versa for these films at temperatures below the LCST of PNIPAM.

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**Polymer microgels in cell-free biotechnology** — ●MAX MÄNNEL, NICOLAS HAUCK, THOMAS HEIDA, IVAN RAGUZIN, ANIKA KAUFMANN, ANDREAS FERY, and JULIAN THIELE — Leibniz-Institut für Polymerforschung Dresden e. V., Leibniz Research Cluster, Germany

The formation of microemulsions in microfluidic flow cells, termed droplet microfluidics, has been established as highly modular method for the fabrication of polymer microgels. The microfluidic flow cells are commonly fabricated by a combination of photo- and soft lithography using poly(dimethylsiloxane) (PDMS). A promising alternative which is less expensive and time-consuming is additive manufacturing, also referred to as 3D printing, which allows the fabrication of flow cells in an affordable, high-resolution and fast single-step process. Our investigated polymer microgels are formed by crosslinking thiol-functionalized hyaluronic acid (HASH) and poly(ethylene glycol) diacrylate (PEGDA) via mild thiol-Michael addition. These microgels have various applications in cell-free biotechnology since they provide a controllable reaction environment. One topic of intense research in our group is the immobilization of enzymes for the production of novel, non-natural pharmaceuticals, e. g. polyketides. Another relevant process in biotechnology is the cell-free protein synthesis which can be re-

alized by attaching DNA to the same polymer microgels. Performing these reactions in microfluidic bioreactors with various reaction chambers and a continuous flow allow the production of seldom products which can not be fabricated by conventional processes.

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**Optimization of Planar Hydrogel-Based Micro-Valves for On-Chip Flow Control** — ●ANTHONY BECK, PHILIPP J. MEHNER, GEORGI PASCHEW, MARTIN ELSTNER, and ANDREAS RICHTER — Chair of Polymeric Microsystems, Technische Universität Dresden, Germany

A successful miniaturization and commercialization of fully integrated microfluidic systems are still under development due to the lack of reliable microfluidic components like micro-valves. Feasible hydrogel-based micro-valve concepts have been demonstrated and show a promising potential for high integration lab-on-chip applications. Due to the vast amounts of synthesis and design parameters an experimental development of reproducible, low-response micro-valves have only been done insufficiently. We propose a systematic investigation of a temperature triggered, hydrogel-based, planar micro-valve. Experimentally, the channel shapes, number and geometry of hydrogel elements have been evaluated to improve performance parameters. Furthermore, different MEMS compatible manufacturing techniques are assessed. Additional modifications allow the development of one-directional valves with a diode-like behavior. Computer aided models describes physical design parameters which are implemented in the current concepts. The proposed design changes improve the valve response time and break through pressures of up to 1 bar and formulate new design rules for next generation micro-valves.

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**In-situ soft X-ray analysis of various polymer-based microcontainers for theranostic and catalytic applications** — ●ANDREAS SPÄTH<sup>1</sup>, GAIO PARADOSSI<sup>2</sup>, GEORGE TZVETKOV<sup>3</sup>, and RAINER H. FINK<sup>1</sup> — <sup>1</sup>Friedrich-Alexander Universität Erlangen-Nürnberg, Lehrstuhl für Physikalische Chemie II and ICMM, Erlangen, Germany — <sup>2</sup>Universita di Roma Tor Vergata, Dipartimento di Scienze e Tecnologie Chimiche, Rome, Italy — <sup>3</sup>University of Sofia, Department of Inorganic Chemistry, Sofia, Bulgaria

Polymer-based microshells and microgel particles are versatile containers for the transport of drugs, theranostic gases or catalytically active molecules. They are in many cases biodegradable and fully compatible to in-vivo applications. During recent years we have investigated a broad range of such hybrid materials ranging from gas filled microbubbles and thermoresponsible microgel networks to magnetoresponsive particles with embedded iron nanoparticles and core-shell systems with various fillings, e.g., ionic liquids [1-3]. Soft X-ray microscopy is an excellent tool to study those systems in-situ in aqueous matrix with high-resolution and chemical sensitivity. We have analyzed shell thicknesses, swelling behaviors and responses to temperature increase to contribute better understanding on release mechanisms, have developed procedures to derive 3D representations of the particles from originally 2D transmission micrographs.

- [1] A. Späth et al., Ultramicroscopy, 2014, 144, 19.
- [2] A. Späth et al., RSC Advances, 2014, 4, 3272.
- [3] A. Späth et al., RSC Advances, 2016, 6, 98228.

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**Aggregation behavior of PNIPAM in dependence on temperature and pressure** — ●BART-JAN NIEBUUR<sup>1</sup>, KORA-LEE CLAUDE<sup>1</sup>, SIMON PINZEK<sup>1</sup>, KONSTANTINOS N. RAFTOPOULOS<sup>1</sup>, VITALIY PIPICH<sup>2</sup>, MARIE-SOUSAI APPAVOU<sup>2</sup>, ALFONS SCHULTE<sup>3</sup>, and CHRISTINE M. PAPADAKIS<sup>1</sup> — <sup>1</sup>Technische Universität München, Physik-Department, Fachgebiet Physik weicher Materie, Garching, Germany — <sup>2</sup>Jülich Centre for Neutron Science JCNS, Forschungszentrum Jülich GmbH, Outstation at MLZ, Garching, Germany — <sup>3</sup>University of Central Florida, Department of Physics and College of Optics & Photonics, Orlando, U.S.A.

The phase separation mechanism of poly(N-isopropylacrylamide) (PNIPAM) is still under debate. Instead of phase separating macroscopically, PNIPAM forms stable mesoglobules in the two-phase region at atmospheric pressure in aqueous solutions. We have investigated the

phase behavior in dependence on temperature and pressure using turbidimetry. The aggregates in the two-phase region are characterized using very small-angle neutron scattering, optical microscopy and Raman spectroscopy. At high pressure, the aggregates are larger than at atmospheric pressure. A possible reason is the decreased efficiency of the phase separation at high pressure because the chains stay hydrated even in the two-phase region. Thus, inducing the phase transition by applying high pressure and by combining a variety of methods, the nature of the transition can be related to the mesoscopic domain structure in the two-phase state.

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**Poly(NIPAm) can actuate to stable 3D forms: An experimental-numerical study on one component dual actuation** — ●ALI GHAEMI<sup>1</sup>, LI LIU<sup>2</sup>, STEPHAN GEKLE<sup>1</sup>, and SEEMA AGARWAL<sup>2</sup> — <sup>1</sup>Biofluid Simulation and Modeling, Fachbereich Physik, and Bayreuth Center for Colloids and Interfaces, Universität Bayreuth, Universitätsstraße 30, 95440 Bayreuth, Germany — <sup>2</sup>Macromolecular Chemistry II and Bayreuth Center for Colloids and Interfaces, Universität Bayreuth, Universitätsstraße 30, 95440 Bayreuth, Germany

Numerical analysis in combination with experimental results are applied in order to explain the complex behavior of a rare example of one-component dual actuators. The system of interest is a bilayer with aligned and randomly oriented poly(N-isopropyl acrylamide) fibers which displays irreversible change in shape by rolling in contact with water, and reversible size change in response to temperature changes. A combination of anisotropic Young's modulus and temperature dependent swelling/shrinkage was shown to be responsible for the actuators controllable unique folding.

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**Phase transition and aggregation behaviour of an UCST-type copolymer Poly(Acrylamide-co-Acrylonitrile) in Aqueous Media** — ASAD ASADUJJAMAN<sup>1</sup>, BEN KENT<sup>2</sup>, and ●ANNABELLE BERTIN<sup>1,3</sup> — <sup>1</sup>Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany — <sup>2</sup>Helmholtz-Zentrum Berlin (HZB), Hahn-Meitner-Platz 1, 14109 Berlin, Germany — <sup>3</sup>Freie Universität Berlin, Institut für Chemie und Biochemie, Takustr. 3, 14195 Berlin, Germany

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. 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 and its thermo-induced aggregation behavior in aqueous media was studied.[1,2] We propose a model for the temperature-induced aggregation behaviour of UCST-type poly(AAm-co-AN) copolymer in aqueous solution on the basis of turbidity measurements, SLS, DLS, SANS and cryo-TEM. [1] Asadujjaman A., Kent B., Bertin A., *Soft Matter*, 2016, accepted. [2] Asadujjaman A., Bertin A., Schönhals A., *Soft Matter*, 2016, submitted.

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**Functional polymers based on diaminopyridine motif with tunable UCST behavior in alcohol and water/alcohol mixtures** — ASAD ASADUJJAMAN<sup>1</sup>, VAHID AHMADI SOURESHJANI<sup>1</sup>, MERAL YALCIN<sup>2</sup>, NIELS TEN BRUMMELHUIS<sup>2</sup>, and ●ANNABELLE BERTIN<sup>1,3</sup> — <sup>1</sup>Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany — <sup>2</sup>Humboldt Universität zu Berlin, Department of Chemistry, Brook-Taylor-Str. 2, 12489 Berlin, Germany — <sup>3</sup>Freie Universität Berlin, Institute of Chemistry and Biochemistry, Takustr. 3, 14195 Berlin, Germany

Thermoresponsive polymers are of great importance in numerous applications such as bioseparation, drug delivery, diagnostic and microfluidic applications. 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 and green solvents such as water or ethanol have been reported. Indeed, polymers with UCST behavior below 60°C in alcohol or water/alcohol mixtures are extremely promising for the preparation of smart materials for sensing. In this work two novel functional polymers of based on a 2,6-diaminopyridine motif were synthesized by free radical polymerization. Their UCST-type transition temperature is tunable by varying either their concentration in solution or the type of solvent. Insights into this

phenomenon will be given based on turbidimetry and temperature dependent dynamic light scattering.

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**Smart Binary Polymer Brush Surfaces For Controlled Biocatalysis** — ●ALICE ROSENTHAL<sup>1,2</sup>, SEBASTIAN RAUCH<sup>1</sup>, KLAUS-JOCHEN EICHHORN<sup>1</sup>, MANFRED STAMM<sup>1</sup>, and PETRA UHLMANN<sup>1,3</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., PF 120411, 01005 Dresden — <sup>2</sup>Technische Universität Dresden, 01062 Dresden — <sup>3</sup>Department of Chemistry, Hamilton Hall, University of Nebraska-Lincoln, 639 North 12th Street, Lincoln, Nebraska 68588, United States

Polymer brushes represent smart surfaces due to their ability to respond to changes in the environmental conditions (e. g. temperature) by showing a reversible swelling-deswelling behavior. Moreover, polymers with functional groups offer a way to immobilize enzymes in an active manner. By combining polymers with opposite properties, switching between different states depending on the external conditions becomes feasible. We fabricated binary polymer brushes consisting of the Poly(N-isopropylacrylamide) (PNIPAAm) and Poly(ethylene glycol) (PEG). In contrast to PEG, PNIPAAm exhibits a lower critical solution temperature (LCST) close to the physiological range (31 °C). In-situ spectroscopic ellipsometry was used to investigate the temperature-responsive swelling behavior of the binary brushes in comparison to the respective homo-brushes. Horseradish Peroxidase conjugated Streptavidin (SA-HRP) was immobilized through accessible alkyne groups at the outer extremity of the PNIPAAm chains. For the enzyme modified binary PNIPAAm/PEG brushes, the enzymatic activity can be switched between an active state at 20°C and a less active state at 40°C in aqueous medium.

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**Mixed polymer brushes with complex pH- and temperature-sensitivity and tunable protein adsorption capability** — ●STEFAN ADAM<sup>1,2</sup>, KLAUS-JOCHEN EICHHORN<sup>1</sup>, FRANK SIMON<sup>1</sup>, MANFRED STAMM<sup>1,2</sup>, and PETRA UHLMANN<sup>1,3</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., 01069 Dresden, Germany. — <sup>2</sup>Technische Universität Dresden, 01062 Dresden, Germany. — <sup>3</sup>University of Nebraska-Lincoln, Lincoln, NE 68588, USA.

Responsive polymer coatings or hydrogels can change their structural and physical properties due to external stimuli (e.g. temperature or pH). When combining polymers responding to different triggers, systems with new properties such as dual- up to multi-responsiveness can be created. We investigated the complex pH- and temperature-sensitive swelling behavior of mixed polymer brushes comprising pH-responsive poly(acrylic acid) (PAA) and a thermo-responsive poly(2-oxazoline) (POX) in water using in situ spectroscopic ellipsometry. Mixed brushes of varying compositions were prepared via a \*grafting to\* approach by sequential anchoring of both polymers. All binary brushes exhibit an amplified pH-sensitivity compared to PAA brushes as well as a temperature-sensitivity at sufficient high POX content and at pH>4. Angle-resolved X-ray photoelectron spectroscopy measurements were performed to get deeper insights into changes in the vertical brush composition caused by differences in the external environment, the brush composition and the preparation sequence. Such dual-responsive mixed brushes are promising for tuning the protein adsorption, as it could be proven for bovine serum albumin as a model protein.

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**Electroactive silicone gel layers with tailor made actuation behavior for tunable mirrors** — ●MARKUS FRANKE<sup>1</sup>, IRMA SLOWIK<sup>2</sup>, PHILIPP MEHNER<sup>1</sup>, ULRICH MERKEL<sup>1</sup>, HARTMUT FRÖB<sup>2</sup>, KARL LEO<sup>2</sup>, and ANDREAS RICHTER<sup>1</sup> — <sup>1</sup>Institut für Halbleiter- und Mikrosystemtechnik, Technische Universität Dresden, D-01062 Dresden, Germany — <sup>2</sup>Dresden Integrated Center for Applied Physics and Photonic Materials, Technische Universität Dresden, George-Bähr-Strasse 1, D-01069 Dresden, Germany

The research field of electroactive polymers (EAP) enables varied applications in robotics, energy harvesting, sensing or even tunable optics. Here, a utilization of EAP actuators for tuning optical mirrors can be a cost- and process-efficient alternative to current membrane based MEMS. In this study we developed various silicone gel based EAP actuators for tuning highly reflecting mirrors. They consist of a thin and structured silver layer acting as a flexible top electrode, a compressible silicone layer and a fixed ground electrode. This capacitor setup allows a tailor made EAP actuation and mirror deflection in height or angle by varying processing parameters like crosslinking

density of the gel, surface activation or lateral dimension of the electrode. These aspects could be clarified by surface analysis as well as electrical and mechanical characterization of the EAP actuator. Furthermore, finite element simulation helps to understand the versatile

mirror deflection shapes depending on the mechanical strength or the electrical field distribution of the capacitor. Finally, the EAP actuator with a planar shaped mirror deflection is applied for a tunable optical micro cavity setup.