

## CPP 32: Poster Session II

Topics: Smart Hydrogels and Hydrogel-Based Devices (32.1-32.5), Hydrogels and Microgels (32.6-32.13).

Time: Tuesday 14:00–16:00

Location: Poster B

CPP 32.1 Tue 14:00 Poster B

**Structural investigations of multi-responsive physical hydrogels** — ●FLORIAN JUNG<sup>1</sup>, PANAYIOTA A. PANTELI<sup>2</sup>, CONSTANTINOS TSITSILIANIS<sup>3</sup>, COSTAS S. PATRICKIOS<sup>2</sup>, and CHRISTINE M. PAPADAKIS<sup>1</sup> — <sup>1</sup>Technical University of Munich, Physics Department, Garching, Germany — <sup>2</sup>University of Cyprus, Department of Chemistry, Nicosia, Cyprus — <sup>3</sup>University of Patras, Department of Chemical Engineering, Patras, Greece

Stimuli-responsive physical hydrogels strongly change their properties upon a small change of the environment and may be used as fast sensors or for drug delivery.

In the present work, we investigate the structure of a multiresponsive, CBABC type pentablock terpolymer. The end blocks are statistical copolymers of the hydrophobic *n*-BuMA and the thermoresponsive TEGMA, the intermediate middle blocks are the weak cationic polyelectrolyte PDMAEMA, and the middle block is the hydrophilic PEG. In aqueous solution, either flower-like micelles or a physical network, with the hydrophobic end blocks acting as crosslinks, are expected. The dynamics of the network may be tuned by varying the temperature around the cloudpoint. pH allows stretching of the intermediate blocks and thus tunes the gelation behavior. Concentration-, pH- and temperature-dependent structural information was obtained from dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS) investigations. The results show that there is an interplay between different responses in these multiresponsive systems.

CPP 32.2 Tue 14:00 Poster B

**Poisson-Boltzmann Cell Model for Swelling of Macroscopic Polymer Gels** — ●JONAS LANDSGESELL, PATRICK KREISSL, and CHRISTIAN HOLM — Institute for Computational Physics Universität Stuttgart Allmandring 3 70569 Stuttgart Germany

Polymer gels can swell tremendously when exposed to aqueous solutions. Recent experiments and theoretical work showed that polymer gels can even be used to desalinate sea water. In this context adequate modeling of the free energy is important for predicting e.g. the energetic costs for desalinating sea water. For an improved energetic description we developed a Poisson-Boltzmann (PB) model for polymer gels. This model allows e.g. the prediction of the swelling equilibrium of charged polyelectrolyte gels via solving numerically the PB cell model in the presence of salt. We compare the results of the cell model with previous results of Molecular Dynamics simulations.

CPP 32.3 Tue 14:00 Poster B

**Sophisticated Techniques to Implement Hydrogel Components into Microsystems** — ●ANTHONY BECK, PHILIPP JAN MEHNER, PHILIPP FRANK, SEBASTIAN HÄFNER, GEORGI PASCHEW, and ANDREAS RICHTER — Technische Universität Dresden, Institute of Semiconductors and Microsystems, Chair of Microsystems, 01062 Dresden, Germany

The successful miniaturization and commercialization of fully integrated microfluidic systems with monolithic active-material components is still under development. For example, feasible micro-valve concepts have been demonstrated that show promising potential for high integration on lab-on-chips and other applications. Due to the wide range of synthesis procedures, design parameters and the challenge to develop reproducible hydrogel-based components, the high degree of integration of hydrogels still cannot accomplish the expectations which were made by many researches.

We propose a reliable, systematic investigation on lithographical structuring hydrogels and MEMS-compatible fabrication techniques which make it possible to simultaneously and quickly integrate many different hydrogel-based components in one system. In the field of microfluidics, the channel shapes, number and geometry of various hydrogel-based valves and diodes have been evaluated experimentally to improve performance parameters. The proposed designs extend the application possibilities with back pressures of up to 1 bar. Important design rules for next generation highly integrated microfluidic components are formulated.

CPP 32.4 Tue 14:00 Poster B

**Janus emulsions and Janus gels stabilized by polyelectrolyte complexes** — ●RAJARSHI ROY RAJU, SABINE KOSMELLA, and JOACHIM KOETZ — Institut für Chemie, Universität Potsdam, Karl-Liebknecht-Strasse 24-25, D-14476, Potsdam, Germany

Janus emulsion is a special kind of emulsions which contains emulsion droplets composed by two hemispheres of immiscible oils surrounded by water. Our research activities deal with the formation of Janus emulsions through moderate-energy vibrational emulsification of olive oil and silicone oil in presence of polyelectrolytes, polyelectrolyte complexes and metallic nanoparticles stabilizing the individual oil droplets. Therefore, we have investigated the pH dependence of polyelectrolytes, e.g., chitosan, Na-carboxymethylcellulose (NaCMC), gelatin and N-polyacrylate (NaPAA), and their possibility to form well defined polyelectrolyte complexes. By using chitosan one can find a pH-dependent fine-tuning of the Janus droplet size. By adding gelatine/NaPAA complex particles, varying in the particle size between 200 and 400 nm, it was possible to tune the Janus emulsion droplet diameter between 50 and 200  $\mu\text{m}$ . Cryo-SEM images of the Janus droplets confirm the adsorption of complex particles on olive oil interface leading to a substantial decrease of the interfacial tension. Furthermore, Janus emulsion turns into a long-term stable Janus gel in presence of gelatine/NaCMC composites. In this case, Janus droplets remain embedded in the gel network and show elastic rheological behaviour along with noticeable thixotropic properties.

CPP 32.5 Tue 14:00 Poster B

**Modified Network Description Model of a Hydrogel-based Microvalve with Static and Transient Material Behavior for Parameter Variation Studies** — ●PHILIPP J. MEHNER, ANTHONY BECK, DAI ZHONGKE, ANDREAS VOIGT, UWE MARSCHNER, and ANDREAS RICHTER — Chair of Microsystems, Technische Universität Dresden, Germany

A hydrogel-based microvalve is a device which can be used for flow control in microfluidic systems either by an external source like heat or by fluidic stimuli like concentration levels or pH value. These microvalves show a transistor-like behavior and, comparable to the microelectronics field, open the possibility for highly integrated chips. This creates the need for a design environment to model the fluid behavior of microfluidic chips and requires furthermore a description of the behavior of the hydrogel in the valve as well as its interaction with the trigger domain.

We propose an updated network description model which is capable of efficiently computing an arbitrary number of hydrogel-based microvalves. The benefit is, that trigger interactions and swelling rates are included within the model and flow results can be probed for every individual microvalve. Hydrogel material behavior is implemented for the transient as well as the quasistatic swelling regime. Efficient parameter studies are now feasible and demonstrated. With this tool, it is possible to model highly integrated microfluidic circuits, such that design ideas can be tested first and can then be verified experimentally.

CPP 32.6 Tue 14:00 Poster B

**Spectroscopic investigation of periodic plasmonic superstructures** — ●EKATERINA PONOMAREVA and MATTHIAS KARG — Heinrich-Heine-University Düsseldorf, Physical Chemistry I, Düsseldorf, Germany

Nanoparticles with a plasmonic metal core and a soft cross-linked hydrogel shell spontaneously self-assemble at an air/liquid interface forming periodic monolayers [1]. These layers can be transferred on glass substrates yielding substrate-supported superstructures with hexagonally arranged plasmonic nanoparticles at inter-particle distances of a few hundred nm. Due to the spatial proximity and the periodicity of the array, localized surface plasmons of metal cores can couple to diffractive modes and thus support surface lattice plasmon resonances [2]. By embedding the monolayer into a gain-medium these resonances can be enhanced.

Here we will demonstrate the angular-dependent optical behavior of periodic plasmonic monolayers. UV-vis measurements show different optical properties for dilute particles in aqueous dispersion, the assembled monolayers and the monolayers upon embedding in a gain

matrix. A home-made laser-spectrometer was used to investigate the collective optical response of the plasmonic lattices in dependence on the detection and incident angle. With the set-up it is possible to observe the near-field and radiative plasmonic coupling effects in colloidal monolayers.

[1] K. Volk et al., *Adv. Mater.* 24 (2015), 7332

[2] K. Volk et al., *Adv. Optical Mater.* 5 (2017), 1600971

CPP 32.7 Tue 14:00 Poster B

**Ugi four-component reaction as versatile tool for multi-functional polysaccharide microgel fabrication** — ●NICOLAS HAUCK<sup>1</sup>, NALIN DE SEIXAS BORGES<sup>2</sup>, LUDGER WESSJOHANN<sup>2</sup>, ANDREAS FERY<sup>1</sup>, and JULIAN THIELE<sup>1</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany — <sup>2</sup>Leibniz-Institut für Pflanzenbiochemie, Halle, Germany

Polysaccharide-based microgels are of special interest in cell biology, tissue engineering, drug delivery, and cell-free biotechnology. However, hydrogel synthesis from polysaccharides often requires pre-functionalization of respective building blocks for subsequent crosslinking as well as for introducing other functionalities. In this context, it is particularly disadvantageous that conventional polymer-analogous coupling reactions often cannot simply be applied on polysaccharides due to an insufficient degree of functionalization. Thus, additional, time-consuming synthesis steps have to be afforded, before polysaccharide-based materials can be processed into defined microgels.

To address these challenges, we utilize multicomponent reactions, which allow for functionalization, e.g. with bioactive compounds or fluorescent dyes, and crosslinking of hydrogel precursors in parallel without time-consuming pre-modifications of precursors. Especially, the Ugi four component reaction is well suited for that purpose. Based on carboxylic acid-rich hyaluronic acid and a diamine as bifunctional crosslinker, hydrogels can be crosslinked with different functional aldehydes and isocyanides in situ to yield multifunctional microgels.

CPP 32.8 Tue 14:00 Poster B

**UV-Rheo-Raman: Chemo-mechanical monitoring of UV-cross-linking of polymers** — ●MORITZ STROBEL, ROBERT GERSTMAYR, MILAN KRACALIK, and SABINE HILD — Johannes Kepler University, Institute for Polymer Science, Linz, Austria

Hydrogels are rising up to meet requirements of many different fields and are of increasing interest in various applications, such as soft contact lenses, wound dressing or stretchable electronics. Many studies have focused on the different areas of applications but fewer investigate the connection between mechanical and chemical properties of these polymers and the influence of different curing parameters on the obtained product. In our approach we investigate simultaneously the chemical and mechanical properties at the different stages of curing of the hydrogels. This allows us to recognize correlations between for example the reaction turnovers and the gel point. Aim of this study is to investigate the influence of the intensity and the exposure time of the UV-light initiating the curing process on the obtained hydrogel. Therefore, mechanical properties are obtained by shear rheology measurements analyzing the storage and the loss modulus. An installed UV-laser enables us to perform in-situ rheo-Raman-measurements while curing the hydrogel. Chemical information regarding the cross-linking of the polymers while initiating the curing with UV-light is obtained by adding Raman spectroscopy to this set-up.

CPP 32.9 Tue 14:00 Poster B

**Enzymatic synthesis of stimuli-responsive microgels** — ●ELISABETH GAU<sup>1,2</sup>, FRANZISKA FLECKEN<sup>1,2</sup>, AGNIESZKA NATALIA KSIĄZKIEWICZ<sup>1,2</sup>, and ANDRIJ PICH<sup>1,2</sup> — <sup>1</sup>DWI - Leibniz-Institute for Interactive Materials e.V., Forckenbeckstraße 50, 52074 Aachen — <sup>2</sup>Functional and Interactive Polymers, Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Worringerweg 2, 52074 Aachen

Aqueous microgels are highly crosslinked, polymer colloids exhibiting promising properties for many applications in the biomedical field, like softness and stimuli-responsiveness depending on the incorporated monomers.[1,2] The most frequently used method for microgel synthesis is precipitation polymerization. For initiation, mainly thermic initiators like azo- or peroxide-based compounds are used, limiting the possible reactants to thermo stable substances.[2] Enzymatic initiation is a promising alternative to enable the incorporation of thermo instable biomolecules into polymers by decreasing the reaction temperature. Herein, we present the use of a glucose oxidase-based initiator system

for the synthesis of aqueous microgels.[3] Glucose oxidase catalyzes the oxidation of  $\beta$ -D-glucose with molecular oxygen to D-glucono-lactone and hydrogen peroxide. Through the addition of ferrous ions ( $\text{Fe}^{2+}$ ), the hydrogen peroxide is cleaved into hydroxyl radicals. These radicals act as initiators for the polymerization reaction.[4]

[1]: Pich et al., *Adv. Polym. Sci.* 2011, 234, 1-37. [3]: Gau et al., *Green Chemistry* 2017, accepted. [4]: Johnson et al., *Biomacromolecules* 2009, 10, 3114-3121.

CPP 32.10 Tue 14:00 Poster B

**Expandable and tough hydrogels for gel-embodied soft machines** — ●ROBERT GERSTMAYR<sup>1</sup>, MORITZ STROBEL<sup>1</sup>, DANIELA WIRTHL<sup>2</sup>, ROBERT PICHLER<sup>2</sup>, FLORIAN HARTMANN<sup>2</sup>, SABINE HILD<sup>1</sup>, SIEGFRIED BAUER<sup>2</sup>, and MARTIN KALTENBRUNNER<sup>2</sup> — <sup>1</sup>Institute of Polymer Science-JKU, Linz, Austria — <sup>2</sup>Soft Matter Physics-JKU, Linz, Austria

Natural hydrogel hybrids inspired scientists to develop wide ranging classes of soft hydrogel-based electronic, ionic and photonic devices based on soft and soft-to-hard hybrid architectures. For these applications tough hydrogels have proven to be a superior material due to their high flexibility and adequate strength. The tough gels we produced are full simultaneous interpenetrating polymer double networks, physically interlaced and inseparable. The materials show an advanced flexibility introduced by the energy dissipating reload mechanism of the second network. To obtain a prominent level of complexity a combination of several materials is needed. Which is achieved by bonding several layers consisting of various materials. A challenging task is to overcome the low interfacial toughness when bonding diverse substances to water-rich hydrogels. Cyanoacrylate adhesives, which rapidly polymerize in the presence of hydroxyl groups of water mixed with branched alkanes, form an easy-to-use colloidal glue suspension with tailorable properties. Raman spectroscopy was used for the characterization of the bonding interface. The diffusion behaviour and the thickness of the resulting moisture curing cyanoacrylate adhesive layer were analysed. Cyclic tensile tests were performed to examine the Mullins effect.

CPP 32.11 Tue 14:00 Poster B

**The Electrostatic Expansion of Ionic Microgels** — CARLOS G. LOPEZ, THOMAS LOHMEIER, ●JOHN E. WONG, and WALTER RICHTER — RWTH Aachen University

We report dynamic light scattering data for the hydrodynamic radius of a weakly charged PNIPAM based microgel as a function of temperature and added salt concentration.

Incorporation of 2% ionic co-monomers leads to an increase in the volume phase transition temperature of the microgel, which can be partially suppressed by addition of salt.

The charge induced swelling data are interpreted within the framework of the Flory-Rehner model, modified to include a Donnan term to account for the additional osmotic pressure arising from entropy of dissociated counterions. This model strongly under-predicts microgel swelling at all temperatures and added salt concentrations.

Our results suggest that repulsion between charged polymer segments plays a leading role in microgel expansion. Mean field theories for polyelectrolyte gels do not quantitatively capture this feature.

CPP 32.12 Tue 14:00 Poster B

**Degradable Microgels by Radical Ring Opening Polymerization (RROP) in Miniemulsion** — LARISSA HUSSMANN<sup>1,2</sup> and ●ANDRIJ PICH<sup>1,2</sup> — <sup>1</sup>DWI Leibniz Institute for Interactive Materials, Aachen, Germany — <sup>2</sup>RWTH Aachen University, Aachen, Germany

Due to their porous structure, water absorption and swelling capability, microgels have been applied in tissue engineering, release systems and coating devices. Especially Poly (N-vinylcaprolactam) (PVCL) microgels are interesting candidate for application in biomaterials due to their biocompatibility. However, in order to synthesize PVCL microgels that are able to release molecules or degrade in controlled way, degradable units need to be integrated into the microgel structure. In this work we follow a new approach that allows incorporation of degradable units into the PVCL chains of the microgel network. In our approach we focus on the copolymerization of VCL and a cyclic ketene acetal, to incorporate a degradable ester function in the polymer backbone, after radical ring opening polymerization (RROP)[1]. Obtained microgels may be suitable to a variety of bio-medical applications, due to their degradability as well as ability to solubilize hydrophobic molecules [2]. Also by varying the copolymer structure of microgel chains, it is expected to control the volume phase transition temperature (VPTT) and swelling of the microgels in aqueous

solutions.

[1] Bailey, W.J., Z. Ni, and S.-R. Wu, *Journal of Polymer Science: Polymer Chemistry Edition*, 1982. 20(11): p. 3021-3030. [2] Shi, Y. and S. Agarwal, *e-Polymers*. 2015. p. 217.

CPP 32.13 Tue 14:00 Poster B

**Optical properties of FePt-nanoparticle loaded microgels** —  
•ALEXANDER NEDILKO<sup>1</sup>, KATHARINA WIEMER<sup>2</sup>, ULRICH SIMON<sup>2</sup>, and  
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<sup>2</sup>Inst. of Inorganic Chemistry, RWTH Aachen

Microgels are polymer networks of micrometer or submicrometer dimensions. Suspended in a liquid, e.g., water, microgels are sensitive to ambient conditions such as temperature or pH. Good biocompatibility makes the microgels particularly interesting due to their potential use

for the controlled delivery of drugs or in biotechnology. By loading the microgels with iron-platinum nanoparticles (FePt NPs), which are good absorbers of light in the UV-vis spectral range, it is possible to create hybrid materials with interesting optical properties. The volume phase transition (VPT) of the microgels can be triggered by thermal and photothermal heating. We investigate the optical properties of FePt-NP loaded poly(N-vinylcaprolactam)-based microgels during the volume phase transition. For this purpose, we use an integrating sphere to separate from each other the parts of the incident light that are absorbed and scattered by the hybrid structures. The measurements show that the scattered part experiences a pronounced increase during the VPT of the microgel whereas the absorbed part remains almost at the initial value. The increase of the scattered part is caused by a change in the refractive index of the microgel material that results from the VPT.