CPP 37: Focus: Smart Hydrogels and Hydrogel Based Devices II - organized by Gerald Gerlach, Walter Richtering and Thomas Hellweg

Time: Wednesday 9:30–13:00 Location: C 130

Topical Talk CPP 37.1 Wed 9:30 C 130

Enzyme-functionalized polymer microgels for drug building block synthesis — •Julian Thiele — Leibniz-Institut für Polymerforschung Dresden e.V. / Leibniz Research Cluster, Dresden, Germany

In an attempt to close the current innovation gap in antibiotics research, we utilize highly specific, genetically engineered enzymes for drug synthesis in cell-free biotechnology. These enzymes require tailored experimental platforms that maintain enzyme activity, enhance the enzyme*s shelf life, and allow for extraction of valuable enzymes from reaction mixtures for recycling purposes. Being part of the Leibniz Research Cluster - an interdisciplinary network of five young investigator groups - we perform enzymatic reactions in polymer microgels with tailored size, porosity and functionalization. As material basis, we employ hyaluronic acid, which is cross-linked by mild [4+2]cycloaddition or thiol-Michael addition, and functionalized with Ni-NTA linker molecules to capture His-tagged enzymes. By loading these microgels into microreactors with active components (e.g. heating pads and valves), we tailor reaction conditions down to the micrometer scale and extract samples for in situ analytics by HPLC-MS and CARS as well as colorimetric assays, which are designed towards individual reaction intermediates and products. We show the capability of this approach using the example of malonate-to-Malonyl CoA conversion, which is a key intermediate in the synthesis of polyketide-based drugs.

CPP 37.2 Wed 10:00 C 130

Vapor-deposited Thin Hydrogel Coatings for Controlled Drug Release — Stephan Tumphart[1,2], •Paul Christian[1], Anna Coclite[1], and Oliver Werzer[2] — [1]Inst. f. Solid State Physics, Graz University of Technology, Austria — [2]Pharm. Tech. & Biopharmacy, University of Graz, Austria

Polymers can have a wide range of applications in the field of pharmaceutical formulation but are most often employed for controlled release behavior. "Smart polymers", meaning polymers that change chemical and physical properties depending on the environment they are in, are particularly interesting as they allow for a targeted release. However, the preparation of thin & defined polymer coatings atop of drug layers is usually difficult by common solution techniques. Initiated Chemical Vapor Deposition (iCVD), a solvent-free polymerization technique, is a powerful tool to conformally prepare thin polymer layers even on delicate substrates. In this study, the release behavior of model pharmaceuticals such as Indomethacin and Clotrimazole is investigated when coated either with a hydrogel or with a thermally-responsive polymer (NIPAAm). Depending on mesh size, polymer and temperature, the release behavior could be varied between several orders of magnitude.

CPP 37.3 Wed 10:15 C 130

Mechano-responsive Coiled Coil-based Hydrogels as Extracellular Matrix Mimics — •Alberto Sanz de Leon, Melis Goktas, Patricia Lopez Garcia, and Kerstin Blank — Max Planck Institute of Colloids and Interfaces, Mechano(bio)chemistry, Potsdam-Golm Science Park, 14424 Potsdam, Germany

Coiled coils (CCs) are protein motifs consisting of at least two α-helices wound into a superhelix. Besides providing structural support, CCs are also involved in different biomechanical signaling processes as they possess a well-defined response to mechanical loads. Considering their natural function as mechano-responsive building blocks, we have synthesized biomimetic hydrogels, using different CC sequences as dynamic, reversible crosslinks. These hydrogels can be fully disassembled and reassembled, showing well-defined self-healing properties. Observing their frequency-dependent behavior at different temperatures and strain rates, we are able to quantify thermodynamic and mechanical processes within these hydrogels. Their bulk mechanical response is well described by the Maxwell model for viscoelastic liquids. Using the Bell-Evans model, we are able to extract molecular parameters that describe CC rupture in the hydrogels. Comparing with single molecule force spectroscopy experiments, we show that this approach is sufficiently accurate to quantitatively extract molecular information from bulk viscoelastic parameters. These results lay the foundation for the future application of these hydrogels as smart mechano-responsive ECM mimics for dissecting local and global factors that determine the process of cellular mechanosensing.

CPP 37.4 Wed 10:30 C 130

Gene expression in NTA-hyaluronan hydrogel particles: A strategy for in situ separation and purification of His-tagged proteins — •THOMAS HEIDA, TONY KÖHLER, ANDREAS FERY, and JULIAN THIELE — Leibniz Institut für Polymerforschung e.V., Dresden, Germany

We present the synthesis and characterization of nitrilotriacetic acid (NTA)-modified hydrogel particles as well as their application in in vitro transcription/translation (IVTT), to selectively catch and separate expressed proteins in situ. Droplet microfluidics is employed to fabricate hydrogel particles based on furan-functionalized hyaluronic acid and maleimide-modified poly(ethylene glycol) (PEG) crosslinkers. As a proof of principle, we show selective conjugation and release of His-tagged green fluorescent protein (GFP) within the particles by reversible binding via Ni(II)-complexation. Thereafter, we utilize these particles as experimental platform in in vitro transcription/translation (IVTT) by additional functionalization with DNA encoding for His-GFP. In situ formed proteins are selectively separated from the complex IVTT reaction mixture and controllably released from the gel matrix after purification. Our NTA-hyaluronan microgels serve as robust experimental platform for cell-free synthesis and purification of His-tagged proteins.

15 min. break

Topical Talk CPP 37.5 Wed 11:00 C 130

Microgel-functionalized membranes — •Matthias Wessling — DWI Leibniz Institute for Interactive Materials, Aachen, Germany

Microgels are interactive soft colloids that can be triggered and tuned. They change size, charge, and density. This presentation explores the use of microgels to functionalize synthetic membranes. Examples will demonstrate that (a) temperature modulation tunes size exclusion (b) charge control influences electro-static repulsion of charged organic dye molecules while passing uncharged molecules of an even larger size (c) monolayers of microgels tune the monovalent/bivalent ion selectivity of synthetic ion exchange membranes (d) printed dotlike patterns of microgel monolayers effectively actuate chaotic electro-convection at polarized ion exchange membrane.

CPP 37.6 Wed 11:30 C 130

Smart membranes by electron beam cross-linking of copolymer microgels — •Johannes Bookhold and Thomas Hellweg — Universität Bielefeld, Bielefeld, Deutschland

The aim of this contribution is the preparation of free-standing, transferable microgel layers from cross-linkable microgels. The approach is based on the deposition of microgels, containing aromatic moieties, by spincoating on a sacrificial gold layer. During this work NIPAm has been copolymerized with N-Benzylhydrylacrylamide (BHAm) in order to manufacture novel cross-linkable microgels. After confirmation of the incorporation of the copolymer via PCS and IR-spectroscopy measurements into the polymer network, monolayers of the microgels were spin-coated onto gold coated silicon-wafers. Afterwards the incorporated aromatic comonomers were irradiated using an electron beam leading to a cross-linking of the microgels. The cross-linked microgel-monolayer was detached from the wafer through the dissolving of the gold coating in an acidic environment. In order to perform temperature dependent diffusion measurements the detached membrane was transferred onto a silica-nitrate chip with a pinhole. In a microfluidic device the diffusion through the covered pinhole was determined using conductivity measurements.

CPP 37.7 Wed 11:45 C 130

Influence of the surface confinement on the structural properties of adsorbed microgel particles — •Tetyana Kyrey[1,2], Judith Witte[1], Regine von Klitzing[3], Stefan Wellert[1], and Olaf Holderer[2] — [1]Technische Universität Berlin, Berlin, Germany — [2]JCNS at MLZ, Garching, Germany — [3]Technische Universität Darmstadt, Darmstadt, Germany

In the last few decades a lot of work was devoted to investigate stimuli-responsive *smart* polymer systems. The main feature of such sys-

tems is their ability to rapidly react to an external stimulus such as temperature, light or solvent quality. Of special interest are stimuli responsive polymer systems at interfaces. Due to surface confinement their ability to dramatically change the characteristic sizes is limited. In the current work, the structural properties of adsorbed individual poly(N-isopropylacrylamide)(PNIPAM) microgel particles on Si-blocks by means of AFM, neutron reflectometry and grazing incidence small-angle neutron scattering (GISANS) are investigated. We discuss PNIPAM microgel particles in dependence on the crosslinker content (N,N-methylenebisacrylamide, 0.5 and 5%) at temperatures below and above the volume phase transition temperature (VPTT). The influence of the surface confinement on the swelling process and possibility to form individual particles on the surface at the different crosslinker content are presented.

CPP 37.8 Wed 12:00 C 130

Hydrogels for Microsensors - Mechanical Properties and Swelling Forces of Microgel Particles — •Maximilian Seuss[1], Willi Schmolke[2], Sebastian Seiffert[2], Astrid Drechsler[1], Ivan Raguzin[1], Julian Thiele[1], and Andreas Fery[1] — [1]Leibniz Institut für Polymerforschung Dresden e.V., Dresden, Germany — [2]Institute of Physical Chemistry, Johannes Gutenberg-Universität, Mainz, Germany

Hydrogels have drawn the focus of engineers to be applied in microsensors since many hydrogels exhibit a volume phase transition reacting to an external stimulus, e.g. changes in the pH, temperature or concentration of specific molecules. Here we present an approach for core-shell microgel particles which are responsive to temperature while the surface adhesion stays unaltered. This is achieved by encapsulating a pre-prepared poly(N-isopropylacrylamide) (pNiPAAm) microgel particle with a poly(acrylamide) shell in a microfluidic reactor. Combining optical microscopy and colloidal probe AFM measurements we demonstrate that the responsiveness as well as the accompanied changes in mechanical properties can be detected on the per-se unresponsive shell.[1] Furthermore, the colloidal probe technique is applied to directly measure the exerted swelling force of single confined model pNiPAAm hydrogel particle. Combining the network architecture with the changes in volume, mechanical compliance and resulting swelling forces may provide important parameters for novel sensor designs.

[1] M. Seuss, W. Schmolke, A. Drechsler, A. Fery, S. Seiffert, ASC Appl. Mater. Interfaces, 2016, 8, 16317

CPP 37.9 Wed 12:15 C 130

Properties and internal structure of thermoresponsive acrylamide based core-shell microgels — •Marian Cors[1,2], Oliver Wrede[1], Julian Oberdisse[2], and Thomas Hellweg[1] — [1]Bielefeld University, Bielefeld, Germany — [2]Laboratoire Charles Coulomb, Université de Montpellier, Montpellier, France

A gel is a dispersed system which consists of at least two different components: a solid or flexible mesh and a fluid (water in the present case). Microgels are gels in the size range of 10 nm to 1 μm and can be used in a wide range of applications like drug delivery and smart surface coatings. If the microgel consists of acrylamides like N-isopropylmethacrylamide (NIPMAM) or N-n-propylacrylamid (NNPAM) as network component, they show a volume phase transition (VPT) at a certain temperature, the volume phase transition temperature (VPTT). An increase in temperature above the VPTT leads to an abrupt decrease in size and a decrease in temperature leads to an abrupt increase in size. The VPTT is specific for each monomer. To use microgels in sensors or for nanoactuators the thermoresponse has to be precise. That is why we investigated microgels with a core-shell architecture containing NIPMAM and NNPAM. These particles show a tunable linear change in size between 22 °C and 43 °C. Furthermore, we deposited these microgels on surfaces and investigated the properties of the coating. The properties of these particles and coatings can be adjusted by selecting specific synthesis conditions. We then did small angle neutron scattering (SANS) to determine the internal structure of the core-shell microgel.

CPP 37.10 Wed 12:30 C 130

Feringa Type Engines in Polymer Model Systems: Folding, Coiling, Molecular Stirling Engines, and Active Gels — •Cornelia Schuster[1,2], Michael Lang[1], Ron Dockhorn[1,2], Martin Wengenmayr[1,2], and Jens-Uwe Sommer[1,2] — [1]Institut Theorie der Polymere, Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany — [2]Technische Universität Dresden, Institute for Theoretical Physics, Zellescher Weg 17, 01069 Dresden, Germany

We use the bond fluctuation model to study the contraction process of different polymeric model systems with attached Feringa engines, where the top part of the molecule rotates unidirectional with respect to the bottom part upon irradition with light. For a figure of 8 shaped model system, a contraction process is observed that consists of two steps: folding followed by coiling. Double stranded polymers are studied in a slit geometry where either both strands connected to bottom and top of engine are connected to the bottom and top wall respectively (X geometry) or always only one strand connects to a particular wall (H-geometry). The different attachment causes distinct work cycles that allows to consider a Stirling machine that is either efficient at a small (H-geometry) or at a large wall separation (X-geometry). Insertion of the engines as centers of 4-functional stars in star polymer nano-gels leads to gel shrinkage upon irradiation with light as a function of the quantity of adsorbed light. The results of the first two model systems are used to elucidate the effectiveness of the engines inside the gel.

CPP 37.11 Wed 12:45 C 130

Silo outflow of soft frictionless hydrogel spheres — •Ahmed Ashour[1], Torsten Trittel[1], Tamás Börzsönyi[2], and Ralf Stannarius[1] — [1]Institute of Experimental Physics, Otto von Guericke University, Magdeburg, Germany — [2]Institute for Solid State Physics and Optics, Wigner Research Center for Physics, Hungarian Academy of Sciences, Budapest, Hungary

The outflow of hard grains with different shapes and types in 2D and 3D silos has been extensively studied. The availability of incompressible but deformable hydrogels in recent years opened the door to study the effects of softness and nearly zero friction on the outflow of grains from silos with small aperture under the influence of gravity. We conduct a quasi-2D silo experiment with hydrogel spheres. This material shows new qualitative and quantitative features as compared to hard grains: The silo does not clog even when the orifice size is only slightly larger than two spheres in diameter. By decreasing the orifice size below two sphere diameters, intermittency of the flow rapidly increases, followed by a permanently clogged state. The soft spheres clog at a certain container fill height, unlike hard grains which flow out practically independent of the container fill level. The Janssen effect, a saturation of the pressure in a silo with fill height, is obviously ineffective for the soft frictionless material, the pressure at the silo bottom increases linearly with fill height (hydrostatic). On the other hand Beverloo's equation that describes the mass flow rate remains valid. Another important difference to hard grain silo discharge is that above a certain height respective to the orifice, the spheres above move in plug flow.