

CPP 10: Poster: Structure and Dynamics of Responsive Hydrogels

Time: Monday 16:30–18:00

Location: Poster C

CPP 10.1 Mon 16:30 Poster C

Temperature dependent switching kinetics and aging effects of gold coated end-capped PNIPAM thin films —

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Poly(N-isopropylacrylamide) (PNIPAM) is one of the prominent thermo-sensitive hydrogels for the construction of nanoscale electric switches which are sensitive to water and to water vapour (humidity). We choose PNIPAM end-capped with n-butyltrithiocarbonate (nbc-PNIPAM), a very short hydrophobic end group, to introduce an internal ordering and increase the mechanical stability in the films without sacrificing the swelling ability seriously. Two different gold layers with 0.4 nm and 5 nm thickness are coated on the nbc-PNIPAM surface by sputtering. The surface structures of the dry films before and after switching are characterized with AFM. The internal structures after each swelling-deswelling cycle are investigated by grazing incidence small angle x-ray scattering (GISAXS). The temperature dependent switching kinetics and aging effects in water vapour of such films is probed by in-situ neutron reflectometry. The real time water diffusion and thickness changes for the two different gold layer thicknesses are compared and discussed in the framework of electric switches applications

CPP 10.2 Mon 16:30 Poster C

Star-PEG-Heparin-Polyelectrolyte-Hydrogels- viscoelasticity and swelling behavior —

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We are studying a new class of biohybrid networks made of heparin (HEP), a highly charged glycosaminoglycan, and non-charged, elastic 4-star-shaped-polyethylene glycol (PEG) in solutions of various salt concentrations. We use a mean-field type model to understand the combined effects of counterions and a good solvent on the swelling properties of the gels. By changing the mole-fraction between HEP and PEG the effective degree of cross-linking can be controlled. The interplay between charge and excluded volume effects lead to nearly constant heparin concentration in the swollen gel under physiological conditions, independent of the mole-fraction at preparation while allowing large variations of the storage modulus and degree of swelling. This opens the possibility to synthesize gels which allow a constant release of heparin-binding signaling molecules while independently controlling the mechanical properties to optimize matrices with both mechanical and biomolecular cues for cell replacement-based therapies.

CPP 10.3 Mon 16:30 Poster C

The Self-assembly of Triblock Copolymers into Smart Hydrogels. Comparing PolyNIPAM with PolyMDEGA as Responsive Hydrophilic Block —

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Amphiphilic block copolymers, consisting of a hydrophilic A and a hydrophobic B block, self-assemble into a wealth of supramolecular structures. Depending on the concentration they are known to associate into micelles, followed by clusters, and finally into macroscopic hydrogels. For BAB-type triblock copolymers, the association deals with an even more complex situation. Instead of forming only core-shell micelles, an open association leading to branched structures with improved swelling properties may occur.

In this context, we are exploring symmetrical triblock copolymers of the BAB type. Copolymers were synthesised with long hydrophilic A and short styrenic B blocks that are directly soluble in water. Moreover, we implemented thermo-responsive "smart" A blocks in these block copolymers, enabling to switch the amphiphilic

behaviour "on" and "off". Poly(N-isopropylacrylamide) PolyNIPAM and poly(methoxy diethylene glycol) PolyMDEGA were chosen as hydrophilic blocks with a similar lower critical solution temperature. Characteristic differences are found between the two different "smart" blocks, as studied by dynamic light scattering (DLS) and rheology.

CPP 10.4 Mon 16:30 Poster C

Collapse behavior of thermo-responsive poly(2-oxazoline) copolymers —

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The poly(2-oxazoline) (POx) system offers the possibility to tune the water-solubility in a wide range. Moreover, using 2-isopropyl (iPr) as a side group results in a thermo-responsive polymer with a lower critical solution temperature (LCST) [1].

We have investigated the LCST behavior of an iPrOx homopolymers as well as a gradient copolymer with few n-nonyl-2-oxazoline (NOx) groups in aqueous solution. The LCST and the molecular aggregation behavior were studied using single molecule as well as ensemble characterization techniques (fluorescence correlation spectroscopy (FCS), turbidimetry and small-angle neutron scattering). We have found that iPrOx in aqueous solution shows mean-field temperature behavior and forms large aggregates above the LCST. In contrast, the collapse behavior of the gradient copolymer shows more complex behaviour. In addition to the large aggregates formed at the LCST, the polymers form small globules which gradually grow as temperature is increased.

[1] R. Jordan, C. M. Papadakis, et al., Colloid Polym. Sci. 282, 833 (2004); Macromol. Chem. Phys. 208, 1402 (2007); Colloid Polym. Sci. 285, 491 (2007); Macromol. Chem. Phys. 209, 2248, (2008).

CPP 10.5 Mon 16:30 Poster C

Structure and dynamics of thermoresponsive blockcopolymer gels —

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Thermoresponsive polymer gels display strong changes in volume when heated above the lower critical solution temperature (LCST). Therefore they are interesting candidates for applications in ultrafiltration or as drug delivery systems. We investigate triblock copolymers consisting of two hydrophobic polystyrene (PS) end blocks and a hydrophilic poly(N-isopropyl acrylamide) (PNIPAM) middle block. In aqueous solution they form core-shell micelles or micellar networks. The structure of the micelles and their correlation is determined using small-angle neutron scattering (SANS) and dynamic light scattering [1]. The micellar radius shows a sudden decrease at the LCST, i.e. the formerly hydrophilic shell shrinks. Above the LCST, the collapsed micelles form clusters, and water is released. The kinetics of the collapse transition is investigated in time-resolved SANS measurements. Neutron spin-echo spectroscopy is used to study the segmental dynamics of the hydrophilic block. The intermediate scattering function displays the fast PNIPAM segmental motion and the slow micellar diffusion.

[1] A. Jain, C. M. Papadakis et al., Macromol. Symp., accepted

CPP 10.6 Mon 16:30 Poster C

Hydrogels based on NIPAM —

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During the last decades microgels made of N-isopropylacrylamide (NIPAM) have attracted much interest and were studied by several techniques like microscopy and light scattering [1]. These polymer particles show thermoresponsive behaviour and can therefore be classified as "smart" materials.

One aim of our studies is the raise of the size of microgels which we build up to around 1 μm . In this case we follow two strategies of preparing these particles. On the one hand we use core-shell mi-

crogel with NIPAM and on the other hand we added a co-monomer into the core surrounded by a NIPAM shell. For both strategies microgel particles are synthesized by emulsion polymerization without using any surfactants at temperature about 70°C [2]. The size of microgels is determined by Dynamic Light Scattering and Atomic Force Microscopy. The prepared nanoparticles were used for investigation on silica surfaces. Here, the behaviour and the coverage of the surface are investigated by changing external parameter like temperature and salinity.

[1] *K. Kratz, T. Hellweg, W. Eimer, *Polymer* (2001), 42, 6531 [2]*R. Pelton, *Adv. Colloid Interface Sci.* (2000), 85, 1

CPP 10.7 Mon 16:30 Poster C

Thermoresponsive Behaviour of adsorbed P(NIPAM-co-AAc) Microgel Particles — ANNA BURMISTROVA, •MARCEL RICHTER, and REGINE VON KLITZING — Technische Universität Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany

During the last decades microgels made of N-isopropylacrylamide (NIPAM) have attracted much interest and were studied by several techniques like microscopy and light scattering [1]. These polymer particles show thermoresponsive behaviour and can therefore be classified as *smart* materials. Monodisperse PNIPAM microgels were synthesized by emulsion polymerisation without using surfactants. To receive the pH-sensitive microgels, acrylic acid (AAc) as a co-monomer was used. [2, 3]. The particles were adsorbed on the different substrates (silicon precoated with different polyelectrolytes and gold) [4, 5]. The thermo induced swelling/deswelling behaviour of adsorbed microgels was studied by Atomic Force Microscopy and Quartz Crystal Microbalance methods. The effect of co-monomer content (AAc), effect of pH and effect of ionic strength were investigated.

[1] K. Kratz, T. Hellweg, W. Eimer, *Polymer* (2001) 42, 6531 [2] S. Höfl, I. Zitzler, T. Hellweg, S. Herminghaus, F. Mugele, *Polymer* (2007) 48, 245 [3] S. Nayak, L.A. Lyon, *Angew. Chem.* (2005), 117, 7862 [4] S. Schmidt, T. Hellweg, R.v. Klitzing, *Langmuir* (2008), 24, 12595 [5] Stephan Schmidt, Hubert Motschmann, Thomas Hellweg, Regine von Klitzing, *Polymer* (2008), 49, 3, 749

CPP 10.8 Mon 16:30 Poster C

Characterization of PMDEGA based hydrogel films — •QI ZHONG¹, GUNAR KAUNE¹, MONIKA RAWOLLE¹, EZZELDIN METWALLI¹, ACHILLE M. BIVIGOU-KOUMBA², ANDRE LASCHEWSKY², CHRISTINE M. PAPADAKIS¹, ROBERT CUBITT³, and PETER MÜLLER-

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Stimuli-sensitive hydrogels exhibit interesting properties which attract increasing attention due to a large variety of applications such as drug delivery, sensors and bioseparation. A novel thermo-responsive poly(monomethoxy diethyleneglycol acrylate) (PMDEGA) exhibits a higher lower critical solution temperature (LCST) when compared to the frequently investigated thermoresponsive polymer poly(N-isopropylacrylamide) (PNIPAM). Thus PMDEGA can be an interesting alternative to PNIPAM in tropical countries where the temperature is above the LCST of PNIPAM. In order to create an internal ordering in the thin hydrogel films of PMDEGA, the homopolymer is replaced by a PMDEGA based tri-block copolymer with polystyrene as an end group, P(S-b-MDEGA-b-S). Thin films of homo- and tri-block polymer with different thickness are prepared by spin coating and characterized with X-ray reflectivity and white light interferometry. Neutron reflectivity is used to investigate the kinetic behaviour of the films in temperature jumps above LCST.

CPP 10.9 Mon 16:30 Poster C

Environment-friendly photolithography using poly-(N-isopropylacrylamide)-based thermoresponsive photoresists — •LEONID IONOV¹, NIKOLAY PURETSKIY¹, GEORGI STOYCHEV¹, SVETLANA ZAKHARCHENKO¹, STEFAN DIEZ², and MANFRED STAMM¹ — ¹Leibniz-Institut fuer Polymerforschung Dresden e.V., Dresden, Germany — ²Max-Planck-Institute of Molecular Cell Biology and Genetics, Dresden, Germany

We report a novel approach for the temperature-triggered development of water-soluble photoresists based on photocleavable poly-(N-isopropylacrylamide) copolymers. These copolymers are soluble in aqueous environment below their Lower Critical Solution Temperature (LCST). Upon UV irradiation, the photocleavable groups are deprotected resulting in an increased LCST. Thus, the illuminated parts of spin-coated copolymer layers dissolve at higher temperatures than the surrounding areas, leading to pattern development. The photoresist can finally be completely removed at low temperature. We demonstrate the applicability of this novel photolithographic approach by the patterning of fluorescent proteins.