CPP 27: Poster: (Hydrogels) and Elastomers

Time: Wednesday 11:00–13:00 — Location: Poster A

CPP 27.1 Wed 11:00 Poster A
Cononsolvency in aqueous solutions of P(S-*b*-NIPAM) diblock copolymers — •Konstantinos Kyriakos[1], Martine Philipp[1], Joseph Adelsberger[1], Sebastian Jaksch[1], Anna Miasnikova[2], Andre Laschewsky[2], Isabelle Grillo[3], Peter Müller-Buschbaum[1], and Christine M. Papadakis[1] — [1]TU München, Physik Department, Physik weicher Materie, Garching — [2]Universität Potsdam, Institut für Chemie — [3]ILL, Grenoble

Thermoresponsive hydrogels have attracted a lot of attention as switches. PNIPAM exhibits a lower critical solution temperature (LCST) of 32 °C. Moreover, PNIPAM exhibits the cononsolvency effect, i.e. a miscibility gap upon addition of a second polar solvent, e.g. methanol. Diblock copolymers consisting of a long thermoresponsive PNIPAM block and a short hydrophobic polystyrene block (P(S-*b*-NIPAM)), are of great interest regarding their tendency to form core-shell micelles in aqueous solution.

We report here on a stopped-flow experiment with time-resolved SANS on P(S-*b*-NIPAM) diblock copolymers in micellar solution in D_2O to which d-MeOH was added in various mixing ratios. The focus is on the micellar structure and the correlation between the micelles. For all chosen solvent ratios, the growth of clusters with final sizes between 40 nm and 50 nm is observed.

CPP 27.2 Wed 11:00 Poster A
Rate Theory of Cyclic Structures in Polymer Model Networks — •Michael Lang[1], Konrad Schwenke[1,2], and Jens-Uwe Sommer[1] — [1]Leibniz Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany — [2]Institut f. Baustoffe (IfB), ETH Zürich, Schafmattstrasse 6, 8093 Zürich, Switzerland

A rate theory of the homo- and co-polymerization of f-functional molecules is developed, which contains the formation of short cyclic structures inside the network. The predictions of this model are compared with Monte-Carlo simulations of network formation. We find that homo-polymerizations are well captured by mean-field models at concentrations larger than one quarter of the geometrical overlap concentration. A comparison with the simulation data reveals that correlations among multiply connected molecules can be neglected for these samples. Co-polymerizations are considered in the case of a strict A-B reactions, where all reactive groups of individual molecules are either of type A or type B . For these systems we find a strong influence of density fluctuations of both species for all concentrations investigated. The effect of fluctuations is more than compensated by the lack of ring structures containing an odd number of molecules as compared to homo-polymerizations. Therefore, network formation is readily possible at concentrations one order of magnitude below the overlap concentration. Based on our data we conclude that fluctuation effects are important for co-polymerizations and that mean-field models are less appropriate for their description.

CPP 27.3 Wed 11:00 Poster A
Interaction of Au-NPs with p-NIPAM microgel particles — •Kornelia Gawlitza[1], Matthias Karg[2], Paul Mulvaney[3], and Regine von Klitzing[1] — [1]Stranski-Laboratorium, Institut für Chemie, Technische Universität Berlin, Germany — [2]Physical Chemistry I, University of Bayreuth, Germany — [3]School of Chemistry & Bio21 Institute, University of Melbourne, Australia

In the last decades, gold nanoparticles (Au-NPs) have been used for the preparation of hybrid materials that combine organic and inorganic components.[1] Due to the thermoresponsibility of poly-N-Isopropylacrylamide (p-NIPAM) microgel particles they are of interest for a lot of applications. In the literature, the usage of Au-NPs to investigate the structure of p-NIPAM microgel particles is discussed.[2] In the present study, Au-NPs with a diameter of 18 nm were synthesized and incorporated within p-NIPAM microgel particles with a varying crosslinker content of 0.25%, 5% and 10%. By using Transmission Electron Microscopy (TEM), cryo-TEM and UV-VIS-spectroscopy, the location of the Au-NPs within the polymer network was determined. As result, the Au-NPs are only located in the outer shell of the polymer network. Additionally, an increase in temperature above the lower critical solution temperature (LCST) leads to a Plasmon-coupling which can be shown by a red shift of the absorption maximum. [1] *R. Contreras-Cáceres, A. Sánchez-Iglesias, M. Karg, I. Pastoriza-Santos,

J. Pérez-Juste, J. Pacifico, T. Hellweg, A. Fernández-Barbero, L. M. Liz- Marzán, Adv. Mater. 2008, 20, 1666. [2]*M. Kuang, D. Wang, H. Möhwald, Adv. Funct. Mater. 2005, 15, 1611.

CPP 27.4 Wed 11:00 Poster A
Thermoresponsive microgels prepared using a semi-batch emulsion polymerization — •Sarah T. Turner and Regine von Klitzing — Stranski Laboratory, Dept. of Chemistry, TU Berlin, Germany

The ability to reversibly switch between a collapsed and expanded state in response to an external stimulus, such as temperature or pH-value, makes microgels attractive for applications such as sensoric and drug delivery systems. Thermoresponsive microgels prepared using a batch emulsion polymerization are known to contain inhomogeneities in the crosslinking density distribution due to the variation in the monomer and crosslinker reactivities [1]. A semi-batch emulsion polymerization is a versatile alternative to a batch polymerization for the preparation of microgels that provides a more homogeneous internal crosslinking distribution, compared to the batch emulsion polymerization, when the feed rate is set to the consumption rate of the various monomer components [2]. Here, we present the results of kinetic and morphological studies on microgels prepared by batch and semi-batch methods. Moreover, the preparation and response of hybrid microgels containing metallic nanoparticles implementing the semi-batch method are studied.
[1] X. Wu et al. *Coll. Polym. Sci.* **272**, 467 (1994). [2] R. Acciaro et al. *Langmuir* **27**, 7917 (2011).

CPP 27.5 Wed 11:00 Poster A
Star-PEG-Heparin-Polyelectrolyte-Hydrogels - Network Structure — •Ron Dockhorn[1,2] and Jens-Uwe Sommer[1,2] — [1]Leibniz Institute of Polymer Research Dresden, D-01069 Dresden, Germany — [2]Technische Universität Dresden, Institute for Theoretical Physics, D-01069 Dresden, Germany

We are studying a new class of biohybrid hydrogels made of heparin, a rod-like highly charged glycosaminoglycan as a highly functionalized cross-linker, and non-charged, elastic 4-star-shaped-polyethylene glycol. We focus on the network structure by using the bond-fluctuation simulation method and determine the defects, the topological arrangement, and percolation threshold of the gels. Also, we investigate the influence of the initial molar ratio, the variations of functionalized groups, and the concentration dependence of the reaction mixture. We developed a mean-field type model to understand the combined effects of counterions and a good solvent on the swelling properties of the gels [1]. It has been shown that this interplay leads to nearly constant heparin concentration in the swollen gel under physiological conditions, while large variations of the degree of swelling and the storage modulus are accessible. This gels allow a constant release of heparin-binding signaling molecules while independently controlling the mechanical properties to optimize matrices with both mechanical and biomolecular features for cell replacement-based therapies.
[1] Sommer, J.-U., Dockhorn, R. et al., Swelling Equilibrium of a Binary Polymer Gel, Macromolecules 2011 44 (4), 981-986

CPP 27.6 Wed 11:00 Poster A
Structure-Function-Relationships in Biomimetic Hydrogels — •Valentin Hagel, Seraphine Wegner, Yvonne Schoen, Isabell Nuss, Tamas Haraszti, Heike Boehm, and Joachim Spatz — Max Planck Insitute for Intelligent Systems, Department New Materials and Biosystems, Stuttgart, Germany & University of Heidelberg, Department of Biophysical Chemistry, Heidelberg, Germany

Hydrogels are extensively studied as matrices for tissue engineering applications. The importance of these materials comes from their chemical versatility that allows for the design of a broad range of gels with tunable properties and their excellent biocompatibility due to their physical similarity to the native extracellular matrix. Engineering the mechanical and structural properties of hydrogels allows to design feasible materials for tissue repair implants. We present the analysis of hyaluronan-based hydrogels formed with a new type of biomimetic cross-linker. For the characterization of the polymer morphology and transport phenomena within the gels FRAP is used and a diffusion model is derived from the obtained data. Mechanical

and rheological analyses are done on a mechanical testing system and a rotational rheometer. The results from both the mechanical and the diffusion analysis are correlated in order to establish structure-function-relationships.

CPP 27.7 Wed 11:00 Poster A

Tracer diffusion in hydrogels — •Peter Kosovan, Olaf Lenz, and Christian Holm — Institute of computational physics, University of Stuttgart, Germany

In this work we consider the diffusion behaviour of a simple spherical tracer particle in polymer networks of hydrogels. There have been hints detained via Fluorescence Correlation Spectroscopy on anomalous diffusion of FCS tracer particles in a hydrogel. We investigate by means of MD simulation the diffusion properties of a tracer particle in the presence of polymer chains with which it interacts. With a sufficiently strong tracer-polymer interaction, subdiffusive behaviour is observed on intermediate time scales and normal diffusive on long time scales. The observation is rationalised via a simple two-state model.

CPP 27.8 Wed 11:00 Poster A

MD simulations of charged hydrogels under external pressure: perspective for seawater desalination — •Tobias Richter, Peter Kosovan, and Christian Holm — Institute of computational physics, University of Stuttgart, Germany

Recent experiments show that application of mechanical pressure on charged hydrogels can be utilised to extract water with a lower salt content than the original solution in which the gel was swollen. It has been suggested to utilise this for an inexpensive method of obtaining desalinated water. We performed a series of MD simulations systematically investigating equilibrium between charged hydrogels under compression and a salt solution. In particular, we investigate the influence of chain length, degree of charging of the hydrogel and concentration of the original salt solution on the salt concentration in the obtained desalinated water.

CPP 27.9 Wed 11:00 Poster A

Microscopic modelling of magneto-sensitive elastomers: lattice approaches — •Dmytro Ivaneyko[1,2], Vladimir Toshchevikov[2], Marina Saphiannikova[2], and Gert Heinrich[1,2] — [1]Institute of Materials Science, Technical University of Dresden, 7 Helmholtz Str., 01069 Dresden, Germany — [2]Leibniz Institute of Polymer Research Dresden, 6 Hohe Str., 01069 Dresden, Germany

We propose a theory which describes the mechanical behaviour of magneto-sensitive elastomers (MSEs) under a uniform external magnetic field. We focus on the MSEs with isotropic spatial distribution of magnetic particles. A mechanical model is used in which magnetic particles are arranged on the sites of three regular lattices: simple cubic, body-centered cubic and hexagonal close-packed lattices. By this we extend our previous approach [1] which used only the simple cubic lattice for describing the isotropic spatial distribution of the particles. The magneto-induced deformation and the Young's modulus of MSEs are calculated as functions of the strength of the external magnetic field. We show that the magneto-mechanical behaviour of MSEs is very sensitive to the spatial distribution of the magnetic particles. MSEs can demonstrate either uniaxial expansion or contraction along the magnetic field and the Young's modulus can be an increasing or decreasing function of the strength of the magnetic field depending on the spatial distribution of the magnetic particles.

[1] Ivaneyko, D.; Toshchevikov, V.P.; Saphiannikova, M.; Heinrich, G., Macromolecular Theory & Simulations 2011, 20, 411-424

CPP 27.10 Wed 11:00 Poster A

Switching Behavior of Thermoresponsive Poly(2-oxazoline) Copolymers — •Sebastian Jaksch[1], Stephan Salzinger[2], Stephan Huber[2], Joseph Adelsberger[1], Peter Busch[3], Rainer Jordan[4], and Christine M. Papadakis[1] — [1]TU München, Physikdepartment, Physik der weichen Materie, Garching — [2]TU München, Department Chemie, Lehrstuhl für Makromolekulare Chemie, Garching — [3]JCNS-FRM II, Garching — [4]TU Dresden, Department Chemie, Professur für Makromolekulare Chemie, Dresden

Thermoresponsive polymers in aqueous solution exhibit a strong change in solubility and volume when heated above their cloud point. Especially interesting polymers of this class of materials are poly(2-oxazoline)s (POx) which are biocompatible. We investigate poly[(iso-propyl-2-oxazoline)-grad-(n-nonyl-2-oxazoline)] gradient copolymers where the fraction of the hydrophic nonyl moieties is var-

ied. These moieties are found to lower the cloud point from 41°C to 23°C. In order to elucidate the aggregation behavior around the cloud point we performed small-angle neutron scattering experiments. The unimer radii increase upon heating towards the cloud point which is consistent with an onset of aggregation. Above the cloud point, we first encounter an intermediate regime, where, instead of the expected collapse, the small aggregates formed below the cloud point, dominate. Large aggregates are only formed a few Kelvin above the cloud point.

[1] S. Salzinger, S. Jaksch, C.M. Papadakis et al., Coll. Polym. Sci. accepted

CPP 27.11 Wed 11:00 Poster A

Swelling and switching behavior of thermo-responsive P(S-b-MDEGA-b-S) hydrogel films under vapor atmosphere — •Qi Zhong[1], Ezzeldin Metwalli[1], Monika Rawolle[1], Gunar Kaune[1], Achille M. Bivigou-Koumba[2], Andre Laschewsky[2], Christine M. Papadakis[1], Robert Cubitt[3], and Peter Müller-Buschbaum[1] — [1]TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching, Germany — [2]Potsdam Universität, Inst. Chemie, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany — [3]ILL, 6 rue Jules Horowitz, 38000 Grenoble, France

By a change of temperature below or above the lower critical solution temperature (LCST), thermo-responsive hydrogels switch between a swollen and a collapsed state. The thermo-responsive poly(monomethoxy diethyleneglycol acrylate) (PMDEGA) exhibits a higher LCST (39.6 oC) as compared to the frequently investigated poly(N-isopropylacrylamide) (PNIPAM), which can be advantageous for many applications. To introduce an internal ordering, a tri-block copolymer with hydrophobic polystyrene end-blocks is under investigation. P(S-b-MDEGA-b-S) films are successfully prepared by spin-coating. The response of P(S-b-MDEGA-b-S) films to a sudden thermal stimulus is probed. To study this switching behaviour, in-situ neutron reflectivity is used. P(S-b-MDEGA-b-S) films subjected to different thermal stimuli are under investigation.

CPP 27.12 Wed 11:00 Poster A

Elastic anomalies at the volume phase transition of PNIPAM solutions — •Martine Philipp[1], Ulrich Müller[2], Olga Astasheva[2], Jan Krüger[2], and Peter Müller-Buschbaum[1] — [1]TU München, Physik-Department, LS Funktionelle Materialien, Garching, Germany — [2]Université du Luxembourg, Laboratoire de physique des matériaux avancés, Luxembourg, Luxembourg

The molecular collapse of poly(N-isopropyl acrylamide) (PNIPAM) in aqueous solution at the lower critical solution temperature has been intensively investigated in basic and applied research. On a macroscopic scale, this phase transition is reflected in an anomalous behavior of the mass density and elastic properties. Particularly in case of chemical PNIPAM hydrogels, the longitudinal elastic modulus is considered as the order parameter susceptibility of the highly complex volume transition. In the current contribution the evolution of elastic anomalies at the discontinuous volume transition of PNIPAM solutions is presented in dependence of temperature and PNIPAM concentration. Brillouin spectroscopy permits a novel and unique perspective on the static, dynamic and kinetic aspects of the phase separation occurring at about 32°C. In particular the qualitative changes of the acoustic phonon spectrum at the phase transition reflect the formation of macroscopic PNIPAM-rich agglomerates embedded in the PNIPAM-poor phase.

CPP 27.13 Wed 11:00 Poster A

On the structure of Star Polymer Networks — •Michael Lang[1], Konrad Schwenke[1,2], and Jens-Uwe Sommer[1] — [1]Leibniz Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany — [2]Institut f. Baustoffe (IfB), ETH Zürich, Schafmattstrasse 6, 8093 Zürich, Switzerland

Using the bond fluctuation model we study polymer networks obtained by end-linking of symmetric 4-arm star polymers. We consider two types of systems. Solutions of one type (A) of star polymers and solutions of two types (A,B) of star polymers where A-type polymers can only crosslink with B-type polymers. We find [1] that network defects in A networks are dominated by short dangling loops close to overlap concentration c^*. AB networks develop a more perfect network structure, since loop sizes involving an odd number of stars are impossible, and thus, the most frequent dangling loop with largest impact on the phantom modulus is absent. The analysis of the pair-correlation and scattering function reveals an amorphous packing of A and B type stars in contrast to the previously suggested crystalline like order of A

and B components at c^*. Furthermore, we derive the vector order parameters associated with the most frequent network structures based on the phantom model. In particular for AB networks we can show that there is a dominating cyclic defect with a clearly separated order parameter that could be used to analyze cyclic network defects.

[1] K. Schwenke, M. Lang, J.-U. Sommer, Macromolecules, *in press.*

CPP 27.14   Wed 11:00   Poster A

Static, dynamic and kinetic property changes around the collapse transition of PNIPAM solutions as seen by Temperature Modulated Optical Refractometry — •Ralitsa Aleksandrova[1], Ulrich Müller[1], Martine Philipp[1,2], Roland Sanctuary[1], Peter Müller-Buschbaum[2], and Jan-Kristian Krüger[1] — [1]Université du Luxembourg, Faculté des Sciences, de la Technologie et de la Communication 162 A, avenue de la Faïencerie L-1511 Luxembourg — [2]Technische Universität München, Physik-Department E13, Lehrstuhl für Funktionelle Materialien, 85747 Garching, Germany

The collapse transitions of aqueous PNIPAM solutions are investigated by the novel technique of Temperature Modulated Optical Refractometry (TMOR) as a function of temperature and time. In addition to the refractive index, TMOR yields information about the real and imaginary part of the thermo-optical coefficient and the volume coefficient of thermal expansion. Since all these physical quantities couple rather directly to the order parameter of the collapse or volume phase transition, they are able to shed new light on the structure formation during the collapse phase of aqueous PNIPAM solutions on a mesoscopic and macroscopic scale.

CPP 27.15   Wed 11:00   Poster A

Visualization of the Coil-Globule Transition of a Thermoresponsive Polymer in Mixtures with a Conjugated Polyelectrolyte — •Sahika Inal[1], Jonas D. Kölsch[2], Dietmar Janietz[3], André Laschewsky[2], Ullrich Scherf[4], and Dieter Neher[1] — [1]Inst. of Physics and Astronomy, Uni. of Potsdam, Germany — [2]Department of Chemistry, Uni. of Potsdam, Germany — [3]Fraunhofer Inst. for Applied Polymer Research, Germany — [4]Macromolecular Chemistry Group, Bergische Uni. Wuppertal, Germany

Changes in the physical environment of smart polymers alter the intermolecular interactions that stabilize their chains in water, which translates into macroscopic responses such as coil to globule transition. Here, we present a scheme to optically visualize the temperature-induced coil to globule transition of a smart polymer using Förster resonance energy transfer (FRET). The aqueous mixtures of a cationic conjugated polymer electrolyte and a dye-labeled nonionic thermoresponsive polymer at room temperature exhibit reduced fluorescence intensity from the responsive polymer, accompanied by an enhanced emission from the polyelectrolyte, indicative of FRET mechanism. Heating this mixture above the cloud point of the smart polymer strongly reduces the efficiency of FRET. We propose that the two macromolecules form mixed aggregates at room temperature, and that these aggregates are disrupted upon the coil-globule transition. As a consequence, temperature-induced structural changes in these macromolecular complexes are detected as well visible variations of fluorescence signal. This visualization scheme shall be well applicable to biochemical sensors.

CPP 27.16   Wed 11:00   Poster A

Phase-transition actuator — •Roland Altmueller, Reinhard Schwoediauer, Siegfried Bauer, and Ingrid Graz — Soft Matter Physics, Institute for Experimental Physics, J. Kepler University, Altenbergerstrasse 69, 4040 Linz, Austria

Dielectric elastomers have widespread applications in sensing, for energy harvesting and actuation. By applying a sufficiently large voltage the elastomer in between two compliant electrodes deforms and complex shapes such as grippers or walkers are realized. However, the required driving voltages are large, often in the kilovolt range, so the reduction of the driving voltage has been identified as a key challenge in the field.

Here we present phase-transition actuators where an elastomeric frame undergoes large deformations caused by the phase transition of an embedded liquid from the liquid to the gaseous state. The phase transition in the liquid is simply induced by electrical Joule heating. A very large deformation is feasible on the base of the huge volume changes upon the liquid gaseous phase transition. Low voltage operation is guaranteed, since the deformation relies on liquid heating, albeit with larger power consumption in comparison to DEAs.

Biaxial deformations of up to 120 % are achieved in a 9 mm wide liquid reservoir within a PDMS elastomer at a driving voltage of 10 V and an input power of 1 W, with a large blocking force of 5-6 N. The proposed actuator concept is easily prone to miniaturization, potentially useful in Braille readers.

CPP 27.17   Wed 11:00   Poster A

Local stress distributions in strained elastomers by low-field NMR — •Maria Ott[1], Martin Schiewek[1], Horst Schneider[1], Paul Sotta[2], and Kay Saalwächter[1] — [1]Martin-Luther-Universität Halle-Wittenberg, Faculty of Natural Science II, Betty Heimann Str 7, 06120 Halle, Germany — [2]Laboratoire de physique des solides, Université Paris-Sud, Bât. 510, 91405 Orsay Cedex, France

Macroscopic strain applied to elastomeric networks induces reorientations of the constituent polymer chains. In this way, heterogeneities of the polymer matrix become apparent, reflecting a potentially non-trivial and complex distribution of local stresses, which is particulary relevant for elastomers with nanofillers. We present a general NMR approach [1] which enables to study the molecular-level effect of macroscopic strain by revealing the absolute values and the distributions of the average segmental residual dipolar couplings. These reflect the time-averaged orientation of the polymer backbone and are directly related to the local stress [2]. We demonstrate this approach using natural rubber of different cross-link densities and amounts of filler particles. We found new fractions of highly coupled (stressed) chain segments which increase with the applied strain. However, a large discrepancy of the overall increase reveals the limits of the well-established Gaussian model [3], and a new theoretical approach is discussed.

[1] K. Saalwächter, Prog. Nucl. Magn. Reson. 51, 1-35 (2007)
[2] J.-U. Sommer et al., Phys. Rev. E 78, 051803 (2008)
[3] P. Sotta, B. Deloche, Macromolecules 23, 1999-2007 (1990)