

## CPP 34: Poster: Elastomers and Gels

Time: Wednesday 17:00–19:00

Location: P2

CPP 34.1 Wed 17:00 P2

**Tailoring the near-surface composition profiles of pressure sensitive adhesive films and the resulting mechanical properties** — ●ALEXANDER DIERTHER<sup>1</sup>, KATHARINA ECKER<sup>1</sup>, YANA PEYKOVA<sup>2</sup>, NORBERT WILLENBACHER<sup>2</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik Department, LS Funkt. Mat., James-Franck-Str. 1, 85748 Garching, Germany — <sup>2</sup>KIT, Inst. f. Mech. Verfahrenstechnik und Mechanik, Kaiserstraße 12, 76131 Karlsruhe, Germany

Pressure sensitive adhesives (PSAs) are used for many different applications, such as for example adhesive foils or binding materials. A prominent class of PSA films is based on statistical copolymers. In the presented work we focus on the PSA model system P(EHA-stat-MMA) consisting of the tacky monomer ethylhexylacrylate and the glassy monomer methylmethacrylate.

Recently, we observed the existence of enrichment layers of one type of monomer near the sample surface having an influence on the tackiness [1]. We extend this work towards tailoring the near-surface composition. One route is to use selectivity by exposing the samples to an atmosphere with the appropriate relative humidity. As a result, the surface content of the more polar PMMA increases with increasing humidity. The effect gets less pronounced with increasing distance from the film surface.

[1] Diethert et al, ACS Appl. Mater. Interfaces 2, 2060-2068 (2010)

CPP 34.2 Wed 17:00 P2

**Computer simulation of Olympic Gels** — ●JAKOB FISCHER<sup>1,2</sup>, MICHAEL LANG<sup>1</sup>, and JENS-UWE SOMMER<sup>1,2</sup> — <sup>1</sup>Leibniz Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany — <sup>2</sup>Institut für Theoretische Physik, Technische Universität Dresden

A polymer gel formed by ring polymers that are connected exclusively through topologic entanglements is called "Olympic Gel", since it resembles the structure of the Olympic Rings. Olympic gels are interesting materials for theorists, since they have the potential to study the effect of entanglements directly. One of the goals of our work is to study the formation of such materials, in particular we want to investigate whether the idea of Raphael et al. [1] (step-wise creation using different chain lengths) or of Pickett [2] (selectively reactive end-groups) are more promising for an experimental study. For comparison, "ideal" model gels will be created in the simulations by allowing the polymer strands to freely cross each other. The structure of the gel will be investigated using tools of knot theory [3] and the gel point and elasticity of the material will be estimated based on the connectivity of the rings and tube models of entangled polymers.

[1] E. Raphael, C. Gay. P.G. De Gennes, JStatPhys. 89, 111 (1997).  
[2] G.T. Pickett, EuroPhysLett 76, 616 (2006).  
[3] M. Lang, W. Michalke, S. Kreitmeier, JCompPhys 185, 549 (2003).

CPP 34.3 Wed 17:00 P2

**Polymer dynamics and crosslink density of SBR nanocomposites containing fillers with different surface area** — ●ANAS MUJTABA, M. KELLER, S. ILISCH, H.-J RADUSCH, T. THURN-ALBRECHT, K. SAALWÄCHTER, and M. BEINER — Faculty of Natural Sciences II & Center of Engineering Sciences, Martin-Luther-University, 06099 Halle/Saale, Germany

Styrene butadiene rubber (SBR) samples filled with different amounts of silica nanoparticles or mixtures of high-surface silica and low-surface borosilicate particles are investigated by dynamic shear measurements and solid state NMR. Aim is to study the influence of filler surface area on the properties of the SBR matrix. Shear data shows that substituting high- with low-surface filler at constant volume fraction is not only affecting reinforcement and plateau modulus but also energy dissipation in the plateau range. Glass temperature and frequency-temperature position of the main transition  $\alpha$  of SBR matrix, however, are not much affected. Dynamic strain sweeps reveal the contribution of the filler network which breaks at large deformations. Double-quantum NMR data are used to determine crosslink densities. Absolute values for the crosslink densities of SBR composites are calculated using additional information from shear measurements on unfilled samples. The results imply that the effective crosslink density of the SBR matrix is slightly decreasing if filler content or filler surface

area increases. In general, our findings indicate a strong influence of filler surface area on the composite properties. The implications for the optimization of SBR based composites for tyre applications are discussed.

CPP 34.4 Wed 17:00 P2

**Switching Behavior of Thermoresponsive Poly(2-oxazoline) Copolymers** — ●SEBASTIAN JAKSCH<sup>1</sup>, JOSEPH ADELSBERGER<sup>1</sup>, ANITA SCHULZE<sup>4</sup>, STEPHAN SALZINGER<sup>2</sup>, STEPHAN HUBER<sup>2</sup>, RAINER JORDAN<sup>2,4</sup>, ZHENYU DI<sup>3</sup>, and CHRISTINE M. PAPADAKIS<sup>1</sup> — <sup>1</sup>TU München, Physikdepartment, Physik der weichen Materie, Garching — <sup>2</sup>TU München, Department Chemie, Lehrstuhl für Makromolekulare Chemie, Garching — <sup>3</sup>JCNS-FRM II, Garching — <sup>4</sup>TU Dresden, Department Chemie, Professur für Makromolekulare Chemie, Dresden

Amphiphilic copolymers in aqueous solution exhibit a wide range of morphologies ranging from micellar and other colloidal structures to hydrogels at high concentrations. Poly(2-oxazoline)s represent a very attractive class of materials as their properties can be tuned from hydrophilic via thermoresponsive to hydrophobic by changing the side group from methyl (MOx) over *iso*-propyl (*i*PrOx) and *n*-propyl (*n*PrOx) to nonyl (NOx) with the backbone being rather polar. We present here measurements on different chain architectures.

Temperature-dependent SANS measurements were carried out at KWS 2/FRM II around the lower critical solution temperature (LCST) for P*i*PrOx homopolymer and gradient copolymers with NOx monomers in dilute solution in D<sub>2</sub>O. P*i*PrOx is soluble with swollen chainconformations below the LCST. With increasing amount of NOx monomers, the chainconformation becomes more compact. The chain size grows when the LCST is approached from below and follows a power law, indicating a critical phase transition. In all cases large aggregates are present as well.

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**Cononsolvency in thermoresponsive PNIPAM-based block copolymers** — ●GABRIELE DE PAOLI<sup>1</sup>, SEBASTIAN JAKSCH<sup>1</sup>, ANNA MIASNIKOVA<sup>2</sup>, ANDRÉ LASCHEWSKY<sup>2</sup>, PETER MÜLLER-BUSCHBAUM<sup>1</sup>, and CHRISTINE M. PAPADAKIS<sup>1</sup> — <sup>1</sup>Physikdepartment, Physik Weicher Materie, TU München, Garching — <sup>2</sup>Institut für Chemie, Universität Potsdam, Potsdam

Thermoresponsive polymers are smart materials which have attracted great attention because of their potential applicability e.g. in controlled ultrafiltration [1]. Among these, poly(*N*-isopropyl acryl amide) (PNIPAM) exhibits in water a lower critical solution temperature (LCST) of ca. 32 °C. Interestingly, the insolubility can also be triggered by the addition of alcohols, which, in the pure state, are good solvents for PNIPAM [2]. This is the so-called cononsolvency phenomenon.

Herein, we report on the cononsolvency behavior of micelles formed by amphiphilic block copolymers having a long hydrophilic PNIPAM block and a short hydrophobic polystyrene block. Turbidity and dynamic light scattering experiments clearly show that methanol acts as a cononsolvent for these polymeric systems in water. Compared to the homopolymer, the amphiphilic block copolymers are unexpectedly more sensitive to the presence of methanol. Moreover, a control over the size of aggregates formed in solution is obtained by adjusting the amount of cononsolvent in the binary solutions.

[1] Y.S. Park et al., *Langmuir* 14, 910 (1998). [2] H.G. Schild et al. *Macromolecules* 24, 948 (1991).

CPP 34.6 Wed 17:00 P2

**Mechanical properties of the thermo-responsive hydrogel PNIPAM investigated by Brillouin spectroscopy** — ●JOHANNES WIEDERSICH, ANDREAS MEIER-KOLL, PETER MÜLLER-BUSCHBAUM, and WINFRIED PETRY — TU München, Physik Department, LS Funkt. Mat., James-Franck-Str. 1, 85748 Garching, Germany

Poly(*N*-isopropyl acrylamide) (PNIPAM) is a thermo-responsive polymer that shows a volume phase transition at the lower critical solution temperature (LCST) around 33 °C. Below the LCST the polymer incorporates water molecules into its network. At higher temperatures the polymer network collapses and precipitates.

We investigate high frequency sound propagation and attenuation of this hydrogel system by means of Brillouin spectroscopy, covering the

range from well below to well above the phase transition. We probe the structure and dynamics of the system on length scales close to the size of a solvated PNIPAM molecule and on timescales on the order of those of fluctuations of hydrogen bonds.

Both the sound velocity and acoustic attenuation increase with increasing concentration. This is attributed to a larger elastic modulus at higher concentrations and to a stronger damping of sound waves for more concentrated solutions, respectively. Deviations from purely exponential damping of sound waves are observed.

Above the LCST two phases coexist: One is water-like with respect to sound propagation, the other one displays a higher sound velocity than the homogeneous solution.

CPP 34.7 Wed 17:00 P2

**A comparison of the thermoresponsive switching behavior in thin films of cyclic and linear PNIPAM** — ●DAVID MAGERL<sup>1</sup>, XING-PING QIU<sup>2</sup>, FRANÇOISE WINNIK<sup>2</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik Department, LS Funkt. Mat., James-Franck-Str. 1, 85748 Garching, Germany — <sup>2</sup>Université de Montréal, Faculty of Pharmacy and Department of Chemistry, CP 6128 Succursale Centre Ville Montréal QC H3C 3J7, Canada

Stimuli-responsive hydrogels are of increasing interest because of their use in a variety of applications such as drug-delivery and sensors. Poly(N-isopropylacrylamide) (PNIPAM) is one of the most studied polymer in this context. There are very few studies of cyclic PNIPAM, although this topology is of great interest because of the absence of endgroups, which has a significant impact on the lower critical solution temperature (LCST), as reported in comparative studies of cyclic and linear PNIPAM [1].

In this study, we compare the properties of spin-coated thin films of cyclic and linear PNIPAM samples with similar molecular weights and a low polydispersity. The film thickness was varied and the films were characterized with x-ray reflectivity and optical microscopy. The swelling behavior of films exposed to water vapor was investigated as a function of film thickness in order to assess the influence of chain topography on the thin film behavior.

[1] Yuichi Satokawa et al., *Macromolecules*, 42(4), 1400-1403, (2009).

CPP 34.8 Wed 17:00 P2

**Quellungsverhalten von oberflächengebundenen Mikrostrukturen** — ●XIAOQIANG HOU<sup>1</sup>, TOBIAS KÖNIG<sup>1,2</sup>, OSWALD PRUCKER<sup>1</sup> und JÜRGEN RÜHE<sup>1</sup> — <sup>1</sup>IMTEK Institut für Mikrosystemtechnik, Universität Freiburg — <sup>2</sup>Institut für Experimentalphysik, Universität Potsdam

Oberflächengebundene Polymermikrostrukturen sind interessante Architekturen für Anwendungen in der Sensorik oder Aktorik, insbesondere im biomedizinischen Bereich. Besonders interessant sind solche Systeme, die durch externe Stimuli geschaltet werden, indem die Strukturen durch Lösungsmittel quellen oder schrumpfen. Bei Mikrostrukturen ist dabei zu beachten, dass das Quellungsverhalten (QV) von oberflächengebundenen 2D-Strukturen sich fundamental von dem von freien 3D-Strukturen unterscheidet. In unserer Studie untersuchen wir das QV von oberflächengebundenen Hydrogel-Mikrostrukturen. Die Hydrogele weisen Strukturbreiten zwischen 1 und 250µm und Strukturhöhen zwischen 10nm und 1µm auf und sind über photolithographische bzw. Zwei-Photonen-Lithographie-Prozesse hergestellt worden. Dabei wurden Copolymere mit Dimethylacrylamid (DMAAm) als Basiskomponente und benzophenongruppenhaltige Monomere als Vernetzkomponente eingesetzt. Unter UV-Licht vernetzen die Polymere und werden an die Oberfläche des jeweiligen Substrats angebunden. Das QV wird mit Hilfe der Rasterkraftmikroskopie untersucht (Wasser/Luft). Dabei wird der Einfluss des Aspektverhältnisses auf das Quellungsvermögen der Polymere untersucht.

CPP 34.9 Wed 17:00 P2

**Energy Transfer as a Probe for Studying the Phase Transition of Oligo(ethyleneglycol) based Thermoresponsive Hydrogels** — ●SAHIKA INAL<sup>1</sup>, JONAS DAVID KÖLSCH<sup>2</sup>, DIETMAR JANIETZ<sup>3</sup>, ANDRÉ LASCHEWSKY<sup>2</sup>, and DIETER NEHER<sup>1</sup> — <sup>1</sup>Uni. of Potsdam, Inst. of Physics and Astronomy, 14476, Golm, Germany — <sup>2</sup>Uni. of Potsdam, Applied Polymer Chemistry, 14476, Golm, Germany — <sup>3</sup>Fraunhofer Inst. for Applied Polymer Research, 14406, Golm, Germany

Since their discovery, the thermally induced phase transition of thermoresponsive polymers have been widely studied by various techniques. At the temperature known as lower critical solution temper-

ature (LCST), the polymer chains demonstrate a transition from a hydrated state to a collapsed structure, offering an excellent model to investigate molecular interactions at play. In the present study, we use energy transfer (RET) between a conjugated polymer nanoparticle (NP) and a dye labeled thermoresponsive polymer to monitor the coil globule transition of the polymer. The internal structure of this aqueous polymer solution is investigated by fluorescence spectroscopy and dynamic light scattering measurements. When the mixture is heated above LCST, the RET is more efficient, i.e. the ratio of acceptor to donor fluorescence intensity significantly increases. Simultaneously, the average size of the particles in the mixtures containing NPs undergoes a remarkable increase. We propose that the NPs become imbedded into the dehydrated globules of the collapsed chains of the polymer above LCST, forming larger globules and bringing the acceptor chromophores closer to the donor units attached to the polymer.

CPP 34.10 Wed 17:00 P2

**Preparation and characterization of pNIPAM/Au composite particles** — ●ADRIAN CARL and REGINE VON KLITZING — Stranski-Laboratorium, Institut für Chemie, Technische Universität Berlin

Microgels made of pNIPAM present a well known and characterized thermoresponsive material which is swollen by water. Gold nanorods are interesting because their optical properties are a function of shape and environmental parameters. It is appealing to combine both materials, each possessing remarkable properties, to investigate the structure and response of those composites, namely gold nanoparticle decorated polymer gels. In order to do so, two different microgel batches were prepared, using a weak acid or base as comonomer. Two comonomers were used in order to study the influence of net charge of the microgel particle on the morphology of the synthesized systems. Gold nanoparticles of ellipsoidal and rod shape were synthesized within the microgels. The inorganic nanoparticles were prepared in different sizes and shapes. In the scope of our studies the influence of synthetic conditions on the morphological features of the obtained gold nanoparticles and the structure of the microgel composites was investigated. The composite microgels were characterized by DLS, TEM, SAXS and UV-VIS spectroscopy. TEM measurements were supposed to give insight into the distribution of gold nanoparticles within the microgel particle which was a central question of these investigations. A model is proposed that gives qualitative information on the composites inner morphology.

CPP 34.11 Wed 17:00 P2

**Structural investigations of p-NIPAM microgels by incorporation of gold nanoparticles** — ●KORNELIA GAWLITZA<sup>1</sup>, MATTHIAS KARG<sup>2</sup>, ADRIAN CARL<sup>1</sup>, PAUL MULVANEY<sup>2</sup>, and REGINE VON KLITZING<sup>1</sup> — <sup>1</sup>Stranski-Laboratorium, Institut für Chemie, Technische Universität Berlin — <sup>2</sup>School of Chemistry & Bio21 Institute, University of Melbourne

Due to the reversible volume phase transition at around 32°C, poly-N-isopropylacrylamide (p-NIPAM) is interesting for applications like drug delivery and biocatalysis.[1] Due to the characteristic plasmon resonance of gold nanoparticles (NP) which is a function of the particle size and shape, another field of high research interest is owned by these metal NPs. One approach to receive information about the mesh size of p-NIPAM microgels is to incorporate metal NPs into the polymer network.[2] In our studies, we synthesized citrate stabilized spherical gold NPs with different diameters and different p-NIPAM microgels. Afterwards, we incorporated these NPs into the polymer by physical entrapment. Using transmission electron microscopy (TEM), we were able to observe different structures inside of the polymer network by changing the amount of crosslinker from 5% to 0.25%. Therefore, a model from previous studies was applied to get information of a 3D object from a 2D TEM image. The characterization of the synthesized gold NPs was done by TEM while the size of the p-NIPAM microgel particles was determined by Dynamic Light Scattering (DLS). [1] K. Kratz, T. Hellweg, W. Eimer, *Polymer* (2001), 42, 6531 [2] Kuang, M.; Wang, D.; Möhwald, H. *Adv Funct Mater* 2005, 15, 1611

CPP 34.12 Wed 17:00 P2

**Isotropic and uniaxial ferrogels with Ni nanorods as magnetic phase** — ●PHILIPP BENDER, ANDREAS TSCHÖPE, and RAINER BIRNINGER — Universität des Saarlandes, Saarbrücken, Deutschland

The present study focuses on the synthesis and characterization of gelatine-based ferrogels with Ni nanorods as magnetic phase. With diameters < 64 nm and aspect ratios > 3 the nanorods are uniaxial ferromagnetic single-domain particles. In the resulting ferrogels the

nanorods can rotate in field direction by applying a homogenous magnetic field, working against the mechanical torque, which is caused by the shear deformation of the gel matrix. The nanorods itself were synthesized by electro-deposition of Ni into porous alumina templates, released into aqueous dispersion by dissolution of the alumina layer and further processed to gelatine-based ferrogels. The nanorods are mechanically linked to the polymer network and exhibit - without further pretreatment - an isotropic orientation distribution. However, applying an external homogenous magnetic field during the gelation process enabled the preparation of magnetically textured ferrogels. In the current work angular-dependent static magnetization measurements were used to analyze the rotation of the nanorods in soft uniaxial ferrogels, using a hard uniaxial ferrogel as reference. The elastic properties of the corresponding isotropic ferrogel were characterized using a theoretical model, which is based on the Stoner-Wohlfarth-model.

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**Magnetic field dependent optical transmission of ferrogels with Ni nanorods as magnetic phase** — ●ETIENNE WAGNER,

PHILIPP BENDER, ANDREAS TSCHÖPE, and RAINER BIRNINGER —  
Universität des Saarlandes, Saarbrücken, Deutschland

Uniaxial ferromagnetic single-domain Ni nanorods with diameters  $< 64$  nm and aspect ratios  $> 3$  were synthesized by electrodeposition of Ni into porous alumina templates. They were released by dissolution of the alumina matrix in aqueous sodium hydroxide solution (NaOH) containing additionally polyvinyl-pyrrolidone (PVP) as surfactant. After a thorough washing procedure the nanorods were dispersed in bidistilled water, and mixed into gelatine solutions at  $60^{\circ}\text{C}$ . Applying a homogenous magnetic field while cooling down the solution to room temperature results in uniaxial ferrogels, where the nanorods are mechanically linked to the polymer network. When the surrounding gel matrix is soft enough, a magnetic torque enables the rotation of the nanorods in field direction. In the present study the elastic response of the Ni nanorods to an external homogenous magnetic field is analyzed via optical transmission. In particular, the rotation angle of the nanorods in field direction was determined dependent on the magnitude of the applied field for different particle densities, gelatine concentrations and gelation times.