CPP 14: Elastomers and Gels

Time: Tuesday 10:30–13:00 Location: ZEU 114

Topical Talk CPP 14.1 Tue 10:30 ZEU 114

Network effects in nano-filled polymer systems — •Kay Saalwächter[1], Cornelius Franz[1], Kerstin Schäler[1], Salim Ok[2], Martin Steinhart[2], Aurelie Papon[3], Francois Lequeux[3], and Helene Montes[3] — [1]Institut für Physik - NMR, Martin-Luther-Univ. Halle-Wittenberg, Halle, Germany — [2]Institut für Chemie, Universität Osnabrück, Germany — [3]Physico-chimie des Polymères et Milieux Dispersés, ESPCI ParisTech, Paris, France

The effect of nanoscopic filler particles on the dynamics of linear and cross-linked chains above T_g is controversial. While often, an increase of the cross-link density in the particle vicinity was claimed, previous work of our group based on the use of low-field multiple-quantum (MQ) NMR has indicated that the homogeneity of the matrix is hardly ever affected by different types of filler [1]. However, in model-filled samples consisting of a dispersion of grafted silica particles, we found a (i) fraction of polymer with slower dynamics and (ii) a fraction with locally increased cross-link density, that both correlate with the silica specific surface. We further discuss related results for linear melt dynamics in nanoscopic model confinement provided by anodic aluminum oxide (AAO) membranes with channels of 20–400 nm diameter [2]. We consistently observe a fraction of chains with less isotropic dynamics on long time scales, behaving network-like. Our results are consistent with a layer thickness of a few nanometers at the non-interacting interface, where the geometric confinement modifies the chain modes.

[1] J. L. Valentín et al., *Macromolecules* **43**, 334 (2010).

[2] S. Ok et al., *Macromolecules* **43**, 4429 (2010).

CPP 14.2 Tue 11:00 ZEU 114

The distribution of segmental order in polymer networks — •Michael Lang[1] and Jens-Uwe Sommer[1,2] — [1]Leibniz Institut für Polymerforschung e.V., Hohe Straße 6, 01069 Dresden, Germany — [2]Institut für Theoretische Physik, Technische Universität Dresden

Recently we showed [1] that segmental order in entangled polymer networks is controlled by monomer fluctuations along the tube, which leads to a dependence $(N_eN)^{-1/2}$ for the average segment orientation of entangled chains of length $N > N_e$ in monodisperse networks, where N_e denotes the tube reorientation length. We extend this approach to derive the distribution of segmental order based on Gaussian chain conformations and randomly reorienting tubes for monodisperse samples. Furthermore, effects of polydispersity are discussed and we also include the effect of the most predominant network defects in our discussions.

[1] M. Lang, J.-U. Sommer, PRL 108, 177801 (2010).

CPP 14.3 Tue 11:15 ZEU 114

Switching kinetics of pMDEGA based thermo-responsive hydrogel films probed by in-situ neutron reflectivity — •Qi Zhong[1], Gunar Kaune[1], Monika Rawolle[1], Ezzeldin Metwalli[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 Funkt. Mat., James-Franck-Str. 1, 85748 Garching, Germany — [2]Universität Potsdam, Inst. Chemie, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany — [3]Institut Laue-Langevin, 6 rue Jules Horowitz, 38000 Grenoble, France

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. In order to create an internal ordering in thin PMDEGA hydrogel films, the homopolymer is replaced by a PMDEGA based tri-block copolymer with polystyrene as an end group, P(S-b-MDEGA-b-S). Homo- and tri-block polymer thin films, with thickness of 35.9 nm and 39.4 nm respectively, are prepared by spin coating. Neutron reflectivity is used to probe the kinetic behaviour of the thermo-responsive hydrogel films in temperature jumps above the LCST.

CPP 14.4 Tue 11:30 ZEU 114

Light-induced deformation of azobenzene elastomers: different molecular models — •Vladimir Toshchevikov[1,2], Marina Saphiannikova[1], and Gert Heinrich[1] — [1]Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany — [2]Institute of Macromolecular Compounds, Bolshoi pr. 31, 199004 Saint-Petersburg, Russia

Light-sensitive elastomers bearing azobenzene chromophores in network strands have a fascinating potential for technical applications (microrobots, micropumps, artificial muscles, smart materials) due to their ability to change the shape under light irradiation. In the present work, we extend the theory [1] devoted to light-induced deformation of amorphous azobenzene polymers consisting of short oligomers to azobenzene elastomers. Different molecular models are used: a regular cubic network model and a general network model with random orientation of end-to-end vectors of network strands. We show that similar to amorphous azobenzene polymers, azobenzene elastomers demonstrate either expansion or contraction with respect to the polarization vector of the light depending on their chemical structure. Increase of the degree of croslinking results in the decrease of the magnitude of the photo-induced deformation at the same light intensity. The results of the theory are compared with experimental data for azobenzene elastomers.

This work was supported by the DFG grant GR 3725/2-1.

[1] V.Toshchevikov, M.Saphiannikova, G.Heinrich. J. Phys. Chem. B 2009, 113, 5032.

CPP 14.5 Tue 11:45 ZEU 114

Mechanical moduli of magneto-sensitive elastomers in a homogeneous magnetic field — •Dmytro Ivaneyko[1,2], Vladimir Toshchevikov[1], Marina Saphiannikova[1], and Gert Heinrich[1] — [1]Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany — [2]Technische Universität Dresden, ECEMP, Marschner Str. 39, 01307 Dresden, Germany

Magneto-sensitive elastomers (MSEs) are a class of smart materials whose mechanical properties can be controlled by application of an external magnetic field [1]. Recently, MSEs have been used in mechanical systems and automobile applications such as stiffness tunable mounts and suspension devices. In the present work, we develop the theory of mechanical properties of MSEs which takes into account a non-linear elasticity of a polymer matrix. Different spatial configurations of magnetic particles within the matrix are considered: homogeneous, chain-like and plane-like. It is shown that interaction between the magnetic particles results in the contraction of an elastomer along the direction of uniform magnetic field. With increasing magnetic field the shear modulus for the shear deformation perpendicular to the magnetic field increases for all spatial configurations of magnetic particles. The Young modulus for the tensile deformation along the magnetic field decreases for the chain-like configurations and increases for the plane-like configurations with increasing magnetic field.

This work was supported by funds of Europe Union and the Free State of Saxony.

[1] Varga, Z.; Filipcsei, G.; Zrínyi, M., Polymer 2005, 46, 7779-7787.

CPP 14.6 Tue 12:00 ZEU 114

Magnetophoretic transport in thermoreversible ferrogels — •Tobias Lang[1], Marina Krekhova[2], Holger Schmalz[2], Reinhard Richter[1], and Ingo Rehberg[1] — [1]EP5, Universität Bayreuth — [2]MC1, Universität Bayreuth

The viscoelastic properties of thermoreversible ferrogels [1] can be tuned via the temperature, making such gels an exciting type of magnetic soft matter [2]. Preliminary studies with these materials showed a separation effect of gel and ferrofluid. So far magnetophoresis was studied by optical means, and limited to dilute magnetic fluids [3]. With our x-ray based technique [4], we are able to investigate magnetophoretic transport in any kind of magnetic fluid as well as in ferrogels.

Most recently, we were able to synthesize cobalt ferrite hydrogels [5]. These thermoreversible hydrogels have cubic and hexagonal mesophases which are tunable via the temperature. As a consequence, the magnetophoretic transport in different phases can be studied as a function of the viscoelasticity. For a further characterization of the samples, magnetometric and magneto-rheometric measurements have been carried out.

[1] G. Lattermann and M. Krekhova, Macromol. Rapid. Commun. 27. 1273 (2006) [2] C. Gollwitzer et al., Soft Matter 5, 2093 (2009) [3] A.S. Ivanov, A.F. Pshenichnikov, JMMM 322, 2575-2580 (2010) [4] R. Richter and J. Bläsing, Rev. Sci. Instrum. 72, 1729 (2001) [5] M. Krekhova et al., Langmuir (DOI: 10.1021/la1040823) (2010)

CPP 14.7 Tue 12:15 ZEU 114

Micro- to Mesoscale Simulation of Hydrogel Swelling Dynamics Based on a Phase field Model

— •Daming Li, Hongliu Yang, and Heike Emmerich — Materials and Process Simulation (MPS), University of Bayreuth

Hydrogels consist of three-dimensional charged polymer networks, mobile ions, and solvent, and they are usually synthesized by chemically cross-linking charged polymers. Hydrogels can swell or shrink by the absorption or squeeze of solvent if it is under the external stimuli, e.g., temperatures, pH, ionic strength, etc. Stimuli-response hydrogels have attracted much attention for their potential in wide range of applications, e.g. drug delivery, biosensors, tissue engineering etc.

Here we contribute to a precise understanding of the mechanisms responsible for the hydrogels' swelling kinetics as well as dynamics by proposing for the first time a model approach that can resolve the inherent short range correlation effects along the hydrogel-solution interface jointly with the long range ionic transport fields. To that end we investigate the swelling dynamics of hydrogels, which is a moving boundary problem, by a phase field model, which couples the Nernest-Planck like equation for the concentration of mobile ions, Poisson equation for the electric potential, mechanical equation for the displacement and an equation for the phase field variable. Simulation reveals that under the chemical stimulation the hydrogel will swell or shrink if the concentration of mobile ions inside bath solution decreases or increases. This is in agreement with the experimental results qualitatively.

CPP 14.8 Tue 12:30 ZEU 114

Kinetics of structural changes in concentrated thermoresponsive blockcopolymer solutions

— •Joseph Adelsberger[1], Ezzeldin Metwalli[1], Alexander Diethert[1], Achille Bivigou-Koumba[2], André Laschewsky[2], Isabelle Grillo[3], Peter Müller-Buschbaum[1], and Christine M. Papadakis[1] — [1]TU München, Lehrstuhl für funktionelle Materialien, Garching — [2]Universität Potsdam, Institut für Chemie — [3]Institut Laue-Langevin, Grenoble

Thermoresponsive polymers display strong changes in volume when heated above the lower critical solution temperature (LCST). Therefore they are interesting candidates for applications in ultrafiltration, in sensors or as drug delivery systems. We study triblock copolymers consisting of two hydrophobic polystyrene end blocks and a hydrophilic poly(N-isopropyl acrylamide) middle block. In aqueous solution they form core-shell micelles or micellar networks [1]. In order to elucidate the structural changes, occuring after rapid heating above the LCST, we have performed time-resolved small-angle neutron scattering experiments with measurement times down to 0.1 s at D22 at ILL in Grenoble. The micellar radius shows a sudden decrease immediately after the LCST is crossed, i.e. the formerly hydrophilic shell shrinks and releases water. Moreover collapsed micelles form small fractal aggregates, which become denser and grow to big clusters.

[1] A. Jain, C. M. Papadakis et al., *Macromol. Symp.* **291-292** (2010), 221; J. Adelsberger, C. M. Papadakis et al., *Macromolecules* **43** (2010), 2490

CPP 14.9 Tue 12:45 ZEU 114

Elasticity of Core-Shell Microgel particles determined by AFM Technique depending on the Temperature

— •Marcel Richter and Regine von Klitzing — Technische Universität Berlin

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

In special the mechanical properties these microgels are of great interest. Here, AFM is a suitable method for the determination of the Young‘s modulus [2]. We synthesised core-shell particles and investigate the change in stiffness according to the cross linker and comonomer amount. Due to the thermoresponsive behaviour of our particles the elasticity was determined in a temperature range for 20°C to 65 °C. These microgel particles are synthesized by emulsion polymerization without using any surfactants at temperature about 70°C [3]. The size of microgels is determined by Dynamic Light Scattering and Atomic Force Microscopy.

[1] K. Kratz, T. Hellweg, W. Eimer, Polymer (2001), 42, 6531 [2] E. K. Dimitriadis et al, Biophysical Journal, (2002), 82, 2798 [3] R. Pelton, Adv. Colloid Interface Sci. (2000), 85, 1