

CPP 2: Focus: Field Controllable Functional Polymers I

Time: Monday 9:30–12:30

Location: C 264

Invited Talk

CPP 2.1 Mon 9:30 C 264

Polymer films with optically controlled shape and functionality on a nanometer scale — ●SVETLANA SANTER — Universität Potsdam

When azo-modified photosensitive polymer films are irradiated with light interference patterns, topographic variations in the film develop that follow the field vector distribution resulting in the formation of surface relief gratings (SRG). In my talk I plan to address two major points concerning the experimental efforts to understand SRG formation in azobenzene containing thin polymer films: (i) how is the orientation of the electric field vector within the interfering electromagnetic fields related to the topographical pattern within the SRG; (ii) how can one measure locally the opto-mechanical forces emerging during topography change. In the first part, I will present a new set-up combining an atomic force microscope (AFM) and two-beam interferometry, with which it is possible to track the topography change in-situ while at the same time changing polarization and phase of the impinging interference pattern. In the second part of my talk I will present how graphene can be utilized as a nanoscopic probe in order to characterize local opto-mechanical forces generated within photosensitive azobenzene containing polymer films. Based upon our experimental results we can deduce that internal stresses within the film due to grating formation can exceed 1 GPa. To demonstrate the strength of the opto-mechanical forces generated within the polymer film in the last part of my talk I will report on opto-mechanical scission of polymer chains in photosensitive polymer brushes.

CPP 2.2 Mon 10:00 C 264

Light-induced deformation of azobenzene-containing LC networks — ●VLADIMIR TOSHCHEVIKOV¹, TATIANA PETROVA^{1,2}, and MARINA SAPHIANNIKOVA¹ — ¹Leibniz-Institut für Polymerforschung Dresden e.V. — ²Cheremovets State University, Russia

Azobenzene containing polymer networks belong to a class of smart materials, which are able to change their shape under light illumination. The photomechanical behavior of these materials is very sensitive to their chemical structure [1, 2]. In the present study we develop a theory of light-induced deformation of two-component polymer networks, which contain azobenzene chromophores and liquid crystalline (LC) mesogens. It is shown that preferential reorientation of chromophores perpendicular to the polarization direction leads to the reorientation of the mesogens due to LC interactions between the components. Reorientation of the chromophores and mesogens results in the light-induced deformation of the polymer network. The magnitude of deformation increases with increase of the volume fraction of chromophores and the strength of LC interactions between the components. Influence of the dilution of azobenzene networks by the bent cis-isomers of the chromophores on the light-induced deformation is discussed.

[1] V. Toshchevnikov et al. *J. Phys. Chem. B* 116 (2012), 913; 118 (2014) 12297.

[2] V. Toshchevnikov et al. *J. Chem. Phys.* 137 (2012), 024903.

CPP 2.3 Mon 10:15 C 264

Towards Understanding Photoswitchable Materials: Molecular Dynamics Simulation Studies of Azobenzene-Containing Polymers — ●MARCUS BÖCKMANN and NIKOS DOLTSINIS — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität Münster, Münster, Germany

A large number of photoresponsive materials are made from polymers or liquid crystals that contain azobenzene (AB) as photochromic unit [1]. In this contribution, we will report on results from our theoretical studies based on multiscale molecular dynamics (MD) simulation techniques [2-4] applied to helical foldamers [4], artificial muscles [5], liquid crystals [3], and the phenomenon of photofluidity [6] yielding surface relief gratings (SRGs) in an active layer of poly-disperse-orange-3-metacrylamide (PDO3M).

[1] Y. Zhao and T. Ikeda, eds., *Smart Light-Responsive Materials: Azobenzene-Containing Polymers and Liquid Crystals* (Wiley-VCH, Weinheim, 2009). [2] M. Böckmann, N. L. Doltsinis, and D. Marx, *J. Phys. Chem. A* 114, 745 (2010). [3] M. Böckmann, D. Marx, C. Peter, L. DelleSite, K. Kremer, and N. Doltsinis, *Phys. Chem. Chem. Phys.* 10, 1039 (2011). [4] M. Böckmann, S.

Braun, N. L. Doltsinis, and D. Marx, *J. Chem. Phys.* 139, 084108 (2013). [5] D. Bléger, T. Liebig, R. Thiermann, M. Maskos, J. P. Rabe, and S. Hecht *Angew. Chem. Int. Ed.* 50, 12559 (2011). [6] P. Karageorgiev, D. Neher, B. Schulz, B. Stiller, U. Pietsch, M. Giersig, and L. Brehmer *Nature Materials* 4, 699 (2005).

CPP 2.4 Mon 10:30 C 264

Aggregation behaviour of doubly thermo-responsive poly(sulfobetaine-b-(N-isopropylmethacrylamide) diblock copolymers — ●NATALYA VISHNEVETSKAYA¹, VIET HILDEBRAND², MARTINE PHILIPP¹, ANDRÉ LASCHEWSKY^{2,3}, PETER MÜLLER-BUSCHBAUM¹, and CHRISTINE PAPADAKIS¹ — ¹TU München, Physik-Department, Physik weicher Materie — ²Universität Potsdam, Institut für Chemie — ³Fraunhofer Institut für Angewandte Polymerforschung IAP, Potsdam-Golm

Diblock copolymers consisting of non-ionic poly(N-isopropylmethacrylamide) (PNIPMAM block) and a zwitterionic poly(sulfobetaine) (PSB block) feature both a lower and an upper critical solution temperature (LCST and UCST) in aqueous solution. Accordingly, P(SB-b-NIPMAM) is expected to form (i) micelles with PNIPMAM shell and PSB core or vice versa at low and high temperatures and (ii) unimers or large aggregates in the intermediate temperature range, depending on the chemical structure and the molar mass of the PSB block as well as on the presence of electrolyte.

The phase transition temperatures in dependence on the electrolyte concentration are investigated via turbidimetry. The aggregation behavior modulated by dual stimuli (temperature and electrolyte concentration) is studied by temperature-resolved small-angle X-ray and neutron scattering (SAXS, SANS). Aggregation of P(SB-b-NIPMAM) in deuterated water was found to occur above LCST and below UCST. The structures formed depended markedly on the blocks lengths, whereas the salt-induced structural changes were only minor.

CPP 2.5 Mon 10:45 C 264

Reversible thermosensitive biodegradable polymeric actuators driven by confined crystallization in thin films — ●VLADISLAV STROGANOV and LEONID IONOV — Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Deutschland

Polymer actuators are materials capable of changing their shape in response to variation of environmental conditions, thus performing mechanical work. They have been used for many applications such as: controlling the liquid flow in microfluidical devices actuators, designing of swimmers, walkers, sensors, imaging devices, and 3D microfabrication. One of the promising fields of applications of polymeric actuators is the design of biomaterials such as stents, sutures as well as bio-scaffolds. For such kind of applications, polymeric actuators must be both biocompatible and biodegradable.

In this work we report design of biodegradable thermoresponsive polymeric films with reversible actuation based on polycaprolactone-gelatin bilayers. The films are unfolded at room temperature, fold at temperature above polycaprolactone melting point and unfold again at room temperature. The actuation is based on reversible switching of the structure of the hydrophobic polymer (polycaprolactone) upon melting and crystallization. We found that the origin of this completely unexpected behavior is the orientation of polycaprolactone chains parallel to the surface of the film, which is retained even after melting and crystallization of the polymer - *crystallization memory effect*. We also demonstrated potential application of such reversible biodegradable thermo-sensitive actuators for reversible encapsulation.

15 min. break**Invited Talk**

CPP 2.6 Mon 11:15 C 264

Field Responses of Magnetic Gels — RUDOLF WEEBER¹, SOFIA S. KANTOROVICH², and ●CHRISTIAN HOLM¹ — ¹Institut für Computerephysik, Universität Stuttgart, Stuttgart, Germany — ²Universität Wien, Sensengasse 8, 1090 Wien, Austria

Ferrogels are hydrogels that additionally contain magnetic single-domain particles and whose properties can be controlled by using external magnetic fields. We will present recent results on the microstructure, the magnetic behavior, and the mechanical and viscoelastic properties of 2D and 3D magnetic gels on the basis of 2

microscopic particle models. In the first model the nano-magnets are part of the chain monomers, whereas in the second model the magnetic particles are restricted to the network nodes. We will focus on the magnetic field-actuated changes in the microstructure of the gel and correspondingly on the change in elastic behavior, magnetic response, and viscoelastic properties. We first summarize 2d computer models for the deformation by a change in the interaction between magnetic nano-particles [1]. Then we will present results for the second model where the deformation of the gel is triggered by torque transmission. In these systems, the polymer network is cross-linked by magnetic node particles. If time permits we will also present recent results on dipolar shifted particles [2].

[1] R. Weeber, S. Kantorovich, C. Holm, *Soft Matter* 8 (2012) 9923-9932. [2] R. Weeber, M. Klinkigt, S. Kantorovich, C. Holm, *Journal of Chemical Physics* 139 (2013) 214901.

CPP 2.7 Mon 11:45 C 264

Electro-optics in fast switching polymer-stabilized liquid crystals of high chirality — ●ALEXANDER LORENZ¹, DAMIAN J. GARDINER², RACHEL HYMAN², STEPHEN M. MORRIS³, and TIMOTHY D. WILKINSON² — ¹Stranski-Laboratorium, Sek. TC 9, Technische Universität Berlin, Str. des 17. Juni 124, 10623 Berlin, Germany — ²Centre of Molecular Materials for Photonics and Electronics, Department of Engineering, University of Cambridge, 9 JJ Thomson Avenue, Cambridge CB3 0FA, United Kingdom — ³Department of Engineering Science University of Oxford, Parks Road, Oxford OX1 3PJ, United Kingdom

The electro-optic performance of a fast (< 1 ms) switching polymer-stabilized hyper-twisted chiral nematic LC [1] was rigorously analyzed with experiments and simulations: The induced birefringence was quantitatively traced back to both flexoelectro-optic switching and dielectric coupling [1]. In addition, a polymer-stabilized wide temperature blue phase LC [2] (based on well-known LC E7 and chiral dopant R5011) was generated in reflective test cells that possessed structured aluminum electrodes on a silicon wafer. A diffraction experiment revealed continuous, polarization independent optical phase modulation (maximum phase modulation depth of π) in the thin (4 microns) polymer-stabilized LC layer [2]. 1. A. Lorenz et al., *Applied Physics Letters* 104, 071102 (2014). 2. R. M. Hyman et al., *Applied Optics* 53, 6925 (2014).

CPP 2.8 Mon 12:00 C 264

Viscoelastic properties of magneto-sensitive elastomers — ●DMYTRO IVANEYKO, VLADIMIR TOSHCHÉVIKOV, and MARINA SAPHIRNIKOVA — Leibniz-Institut für Polymerforschung Dresden e.V.

Magneto-sensitive elastomers (MSEs) are smart materials which consist of micron-sized magnetic particles dispersed within a non-magnetic elastomeric matrix. Mechanical properties of MSEs change considerably under external magnetic field [1]. In the present study we consider viscoelastic properties of isotropic MSEs using a coarse-grained cubic network model, which describes the network dynamics in the low-frequency regime [2]. Equations of motion for magnetic particles take into account topology of the elastic network and magnetic interactions between the particles. We show that the application of uniform magnetic field leads to the splitting of the relaxation spectrum into two branches for the motions of the particles parallel and perpendicular to the field. The shear dynamic moduli G' and G'' of MSEs are calculated as functions of the frequency. The values of G' and G'' are shown to depend on the direction of the shear deformation with respect to the magnetic field. For instance, both G' and G'' increase if the shear is applied perpendicular to the direction of the magnetic field. This prediction is in a qualitative agreement with existing experimental data.

[1] D. Ivaneyko et al., *Soft Matter* 10 (2014), 2213.

[2] V.P. Toshchevnikov et al., *Macromolecules* 42 (2009), 3417.

CPP 2.9 Mon 12:15 C 264

Mesoscopic modeling of ferrogels and magnetic elastomers — PEET CREMER¹, GIORGIO PESSOT¹, MITSUSUKE TARAMA^{1,2}, ELSHAD ALLAHYAROV¹, HARTMUT LÖWEN¹, and ●ANDREAS M. MENZEL¹ — ¹Heinrich-Heine-Universität Düsseldorf, Düsseldorf, Germany — ²Kyoto University, Kyoto, Japan

Ferrogels and magnetic elastomers consist of colloidal magnetic particles embedded in a crosslinked polymer matrix. Tunable elastic moduli that can be switched by an external magnetic field represent one of their outstanding features. Our goal is to understand and identify such controllable material properties on the magnetic particle level using both particle-matrix and simplified dipole-spring models.

We studied how the particle arrangement and orientation of the magnetic moments can influence the elastic moduli when the strength of the magnetic interaction is controlled. In one case, we used the particle distribution of a real experimental sample as an input. Here, the convenient technical assumption of affine deformations must be dropped. Furthermore, we demonstrated that the relaxation dynamics of the materials can be tuned by the particle arrangement, by external magnetic fields, and by an orientational memory. Apart from that we showed that a pronounced switchable nonlinear stress-strain behavior is found under suitable circumstances.

In the future, we aim at a connection of our characterization to more microscopic and to macroscopic scales. We have already taken the first steps into these directions by comparing to minimum Monte-Carlo simulations and by performing a simplified coarse-graining procedure.