

CPP 88: Responsive and Adaptive Systems

Time: Thursday 9:30–11:30

Location: ZEU 114

CPP 88.1 Thu 9:30 ZEU 114

Orientation approach to directional deformations in glassy azopolymers — ●BHARTI YADAV, JAN DOMURATH, and MARINA SAPHIANNIKOVA — Leibniz-Institut für Polymerforschung Dresden e.V., PF 120411, 01069 Dresden

Glassy azopolymers deform in the presence of light even below the glass transition temperature, as the light induced stress is greater than the yield stress. The photodeformations are directional and depend on the polarization of light. For linearly polarized light the azopolymers elongate in the direction of polarization and for circularly polarized light in the plane perpendicular to the propagation vector. The cause of these directional deformations is the orientation potential which acts on each chromophore attached to the main chain and generates a light induced stress. We model the azopolymers as visco-plastic materials by implementing the stress in a finite element modelling software ANSYS. The true strains and elongations are calculated as a function of time for both linearly and circularly polarized light when the intensity of light is homogeneous [1]. Additionally, we implement the light induced stress corresponding to stripe-like Gaussian distributed light with polarization in the direction of intensity gradient to get the photodeformations and to compare with experimental results [2]. [1] B. Yadav, J. Domurath, K. Kim, S. Lee, M. Saphiannikova, J. Phys. Chem. B 122 (2019) 2001-2009 [2] A. Ambrosio, A. Camposeo, A. Carella, F. Borbone, D. Pisignano, A. Roviello, P. Maddalena, J. App. Phys. 107 (2010) 083110

CPP 88.2 Thu 9:45 ZEU 114

Deformation of Azo-Polymer Droplets by Light: Modeling the Effects of Light on Glassy Azobenzene Materials — ●MARKUS KOCH, MARINA SAPHIANNIKOVA, and OLGA GUSKOVA — Institute Theory of Polymers, IPF Dresden, Germany

Azobenzene (azo) is the most widespread light-responsive molecule due to its well-studied trans-cis photoisomerization mechanism. This compound has gained prominence due to the possibility to create surface relief gratings in azo-polymer materials using light interference patterns. However, it remains an open question how light induces mechanical stresses in the material. To study this process we consider a model system: a droplet composed of PMMA with azobenzene side chains, exposed to linearly polarized UV-Vis light. Experiments demonstrate, that such droplets deform along the polarization direction [1]. Here, using all-atom MD simulations two different approaches are applied: In the first case, the angle-dependent photoisomerization of azobenzene is simulated explicitly. In the second case, an effective orientation potential acts on the azo groups [2]. We demonstrate that both approaches lead to the reorientation of azobenzene in the polymer matrix and discuss the induced deformation of the droplet.

We thank the German Research Foundation (DFG) for financial support, project GU 1510/3-1.

- [1] Loebner, S. et al., J. Phys. Chem. B, 122 (6), 2001-2009 (2018)
 [2] Toshchevnikov, V. et al. J. Phys. Chem. Lett., 8 (5), 1094-1098 (2017)

CPP 88.3 Thu 10:00 ZEU 114

Photo-switchable surfactants for responsive air-water interfaces: Azo vs AAP amphiphiles — ●MARCO SCHNURBUS¹, RICHARD CAMPBELL², JÖRN DROSTE¹, CHRISTIAN HONNIGFORT¹, PHILIPP GUTFREUND³, MICHAEL HANSEN¹, and BJÖRN BRAUNSCHWEIG¹ — ¹Institute of Physical Chemistry, WWU Münster — ²Division of Pharmacy & Optometry, Manchester — ³ILL, Grenoble

Two photo-switchable ammonium bromide surfactants (Azo-TB and AAP-TB) were compared with respect to their switching ability. Both surfactants were studied with UV/Vis and NMR spectroscopy in the bulk and with sum-frequency generation (SFG), neutron reflectometry (NR) and tensiometry at the air-water interface. The surfactants undergo photo-isomerization reactions from their Z and E conformation when irradiated with 365 nm UV and 520 nm green light. NMR spectroscopy showed a higher photostationary state (PSS) for the E-isomer under green light irradiation for the AAP-TB, whereas the Z-isomer under UV light had a higher PSS for the Azo-TB. Tensiometry demonstrates the surfactants ability to reversibly change the surface tension with light irradiation, which yields a maximum change in surface ten-

sion of 12 mN/m and 8 mN/m for AAP-TB and Azo-TB surfactants, respectively. Furthermore, the surface excess from NR as well as the aromatic C-H band and the nonresonant contribution to the SFG spectra demonstrate higher switching abilities for the AAP-TB surfactant. In addition, analysis of SFG spectra from O-H and C-H stretching bands of Azo-TB and AAP-TB surfactants indicate surfactant desorption from the air-water interface when irradiated with UV light.

CPP 88.4 Thu 10:15 ZEU 114

Polarization controlled fine structure of diffraction spots from optically induced azo-polymer surface relief grating: In-situ atomic force microscopy and diffraction efficiency measurements — ●JOACHIM JELKEN, CARSTEN HENKEL, and SVETLANA SANTER — Institute of Physics and Astronomy, University of Potsdam, Potsdam, Germany

Here we present an experimental and theoretical study of an observed fine structure in the diffraction spot of an azo-polymer surface relief grating. This is achieved utilizing a homemade setup [1] which consists of three parts: a two beam interference setup for topography structuring, an atomic force microscope (AFM) for in-situ recording of surface morphology, and a diffraction efficiency (DE) setup which enables to obtain information about the birefringence grating at the same time. Our findings show that the fine structure is a result of a gaussian intensity profile of the recording interference pattern [2], which will create a gaussian amplitude modulation (envelope) of the surface and birefringence grating. A wide probe beam will average across the grating which results in the observed fine structure of the diffraction spot. The spatial profile of the diffraction spot is thereby converting from a gaussian, to a *donut* (dark spot in the center) and finally to a *Saturn* (bright ring with bright center) structure with an increase in the SRG height. We will show that we can switch between the different spatial profiles by changing the polarization of the probe beam. [1]J. Jelken and S. Santer, RSC Advances, 2019, 9, 20295-20305 [2]J. Jelken, C. Henkel and S. Santer, Appl. Phys. B, 2019, 125, 218

CPP 88.5 Thu 10:30 ZEU 114

Unexpected Monolayer-to-Bilayer Transition of Arylazopyrazol Surfactants Facilitates Superior Photo-Control of Fluid Interfaces — ●CHRISTIAN HONNIGFORT¹, RICHARD A. CAMPBELL², DANA GLIKMAN¹, MARCO SCHNURBUS¹, PHILIPP GUTFREUND³, BART JAN RAVOO¹, and BJÖRN BRAUNSCHWEIG¹ — ¹University of Münster, Germany — ²University of Manchester, United Kingdom — ³Institut Laue-Langevin, France

Interfaces that can change their chemistry on demand have huge potential for applications and are prerequisite for responsive or adaptive materials. We report on the performance of a newly designed n-butyl-arylazopyrazole butyl sulfonate (butyl-AAP-C₄S) surfactant that can change its structure at the air-water interface by E/Z photoisomerization in an unprecedented way. Large and reversible changes in surface tension ($\Delta\gamma \sim 27$ mN/m) and surface excess ($\Delta\Gamma > 2.9$ $\mu\text{mol}/\text{m}^2$) demonstrate superior performance of the butyl-AAP-C₄S amphiphile to that of existing ionic surfactants. Neutron reflectometry and sum-frequency generation spectroscopy reveal that these large changes are caused by an unexpected monolayer-to-bilayer transition. This exceptional behavior is further shown to have also dramatic consequences at larger length scales as highlighted by two application like the light-triggered collapse of aqueous foam which is tuned from high (>1h) to low (<10min) stabilities and light-actuated particle motion via Marangoni flows.

CPP 88.6 Thu 10:45 ZEU 114

Kinetics of phase separation in PNIPAM solutions after pressure jumps — BART-JAN NIEBUUR¹, LEONARDO CHIAPPISI^{2,3}, XIAOHAN ZHANG¹, FLORIAN A. JUNG¹, ALFONS SCHULTE⁴, and ●CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Fachgebiet Physik weicher Materie, 85748 Garching — ²Institut Laue-Langevin, Large Scale Structures Group, 38042 Grenoble, France — ³TU Berlin, Institut für Chemie, 10623 Berlin — ⁴University of Central Florida, Department of Physics and College of Optics and Photonics, Orlando, FL, U.S.A.

The thermoresponsive polymer PNIPAM in aqueous solution features lower critical solution behavior. Its cloud point depends on pressure

with the coexistence line being an ellipse in the temperature-pressure frame. Performing fast pressure jumps from the one-phase to the two-phase region along with time-resolved small-angle neutron scattering, we can follow the pathway of phase separation with a time resolution of 50 ms and over a wide range of length scales [1]. Since the hydration state of PNIPAM depends on pressure, pressure jumps at low and at high pressures allow addressing the role of dehydration for the aggregate growth [2]. Varying the target pressure gives insight into the role of kinetic and thermodynamic factors.

1. B.-J. Niebuur et al., *ACS Macro Lett.* **7**, 1155 (2018).

2. B.-J. Niebuur et al., *Macromolecules* **52**, 6416 (2019).

CPP 88.7 Thu 11:00 ZEU 114

Thermal behavior and co-nonsolvency of the amphiphilic diblock copolymers PMMA-*b*-PNIPAM in aqueous solution —

•CHIA-HSIN KO¹, CRISTIANE HENSCHL², GEETHU P. MELEDAM¹, MARTIN SCHROER³, PETER MÜLLER-BUSCHBAUM¹, ANDRÉ LASCHEWSKY^{2,4}, and CHRISTINE M. PAPADAKIS¹ — ¹Physics Department, Technical University of Munich, Garching, Germany — ²Institut für Chemie, University of Potsdam, Potsdam-Golm, Germany — ³European Molecular Biology Laboratory, Hamburg, Germany — ⁴Fraunhofer Institute for Applied Polymer Research IAP, Potsdam-Golm, Germany

Amphiphilic diblock copolymers having a hydrophobic poly(methyl methacrylate) (PMMA) block and a thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) block form core-shell micelles in aqueous solution. The PNIPAM blocks are not only sensitive to temperature, but also to the solvent composition. Adding methanol as a cosolvent causes these blocks to collapse which reduces the transition temperature, i.e. co-nonsolvency is observed. We focus on investigating (i) the structure of the self-assembled micelles and the changes upon collapse and aggregation with increasing temperature, and (ii)

the co-nonsolvency effect of PMMA-*b*-PNIPAM in pure D₂O and in different D₂O/CD₃OD mixtures using turbidimetry, differential scanning calorimetry (DSC), dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS). The results reveal the role of the nature of the thermoresponsive block on the thermal behavior and the morphology changes upon temperature and solvent composition.

CPP 88.8 Thu 11:15 ZEU 114

Untethered and ultrafast soft-bodied robots — •XU WANG¹, GUOYONG MAO², JIN GE¹, RICO ILLING¹, MICHAEL DRACK², GILBERT SANTIAGO CANON BERMUDEZ¹, JURGEN FASSBENDER¹, TOBIAS KOSUB¹, MARTIN KALTENBRUNNER², and DENYS MAKAROV¹ — ¹Helmholtz-Zentrum Dresden - Rossendorf — ²Johannes Kepler University Linz

Soft robots have been developed to fulfil demands of better deformability and adaptability to a changing environment.[1-4] The use of magnetic fields is appealing for diverse application scenarios (e.g. environmental, biological, medical), where the benefits stem from their long-range penetration, easy accessibility, and controllability.[1-4] There are numerous demonstrations of magnetically triggered miniaturized soft robots performing multimodal locomotion[3] and complex 3D actuations.[4]

Here, we present ultrathin (7-100 μm) and lightweight (1.2-2.4 g/cm³) soft robots that can be actuated in a small magnetic field of 2 mT reaching full actuation amplitude in 10 ms only. By programming the foils into different geometries, these soft robots are readily used for multifunctional motions with a magnetic coil or a permanent magnet, such as a quick fly gripper, and a complex non-linear cross-clapping mimicked motion.

1. Z. Ren et al., *Nat. Commun.* **10**, 2703 (2019). 2. Y. Kim et al., *Science Robotics* **4**, eaax7329 (2019). 3. W. Hu et al., *Nature*, **554**, 81(2018) 4. Kim. Y, et al., *Nature*, **558**, 274 (2018)