

CPP 11: Responsive and Adaptive Systems

Time: Monday 11:15–13:00

Location: C 230

CPP 11.1 Mon 11:15 C 230

Light-responsive azobenzene star with a flat core — ●MARKUS KOCH¹, MARINA SAPHIANNIKOVA¹, SVETLANA SANTER², and OLGA GUSKOVA¹ — ¹Institute Theory of Polymers, IPF Dresden, Germany — ²Institute of Physics and Astronomy, University of Potsdam

This study focuses on comparing physical properties of photoisomers of an azobenzene star with benzene-1,3,5-tricarboxamide core. Three azobenzene arms of the molecule undergo a reversible trans-cis isomerisation upon UV-vis light illumination giving rise to multiple states from the planar all-trans one, via two mixed states to the kinked all-cis isomer. To characterize the light-triggered switching of solvophilicity/solvophobicity of the star, the difference in solvation free energy is calculated for the transfer of an azobenzene star from its gas phase to implicit or explicit solvents. From the analysis of two contributions to the free energy of hydration, the non-polar van der Waals and the electrostatic terms, calculated using soft LJ and Coulomb potentials [1] we conclude that isomerization state largely determines the polarity of the molecule and the solute-solvent electrostatic interactions. This convertible hydrophilicity/hydrophobicity together with re-adjustable occupied volume and the surface area accessible to water, explains the physics of the self-assembly/disassembly of the azobenzene star with a flat core triggered by light.

This work was supported by DFG (Project No GU 1510/3-1 and SA 1657/13-1).

[1] M. Koch et al. *J. Phys. Chem. B* 2017, 121, 8854.

CPP 11.2 Mon 11:30 C 230

Photomigration in azo-polymer thin films probed by atomistic molecular dynamics simulations — ●MARCUS BÖCKMANN and NIKOS DOLTSINIS — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität, Münster, Germany

Photoresponsive polymers containing azobenzene (AB) as the photochromic unit are well known for allowing photopatterning and the fabrication of surface relief gratings (SRGs) [1,2]. In this contribution, we will report on recent results from our theoretical studies based on multiscale molecular dynamics (MD) simulation techniques [3,4] applied to the phenomenon of light-induced mass transport – also being termed photofluidity [5] – in an active layer slab of poly-disperse-orange-3-metacrylamide (PDO3M) [6].

[1] P. Rochon, E. Batalla, and A. Natansohn, *Appl. Phys. Lett.* **66**, 136 (1995).

[2] N.S. Yadavalli, F. Linde, A. Kopyshv, and S. Santer, *ACS Appl. Mater. Int.* **5**, 7743 (2013).

[3] M. Böckmann, D. Marx, C. Peter, L. Delle Site, 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] P. Karageorgiev, D. Neher, B. Schulz, B. Stiller, U. Pietsch, M. Giersig, and L. Brehmer *Nature Materials* **4**, 699 (2005).

[6] M. Böckmann and N. L. Doltsinis, *J. Chem. Phys.* **145**, 154701 (2016).

CPP 11.3 Mon 11:45 C 230

Smart Air/Water Interfaces with Arylazopyrazol Surfactants and their Role in Responsive Aqueous Foam — ●MARCO SCHNURBUS¹, LUCAS STRICKER², BART JAN RAVOO², and BJÖRN BRAUNSCHWEIG¹ — ¹Institute of Physical Chemistry — ²Organic Chemistry Institute, WWU Münster, 48149 Münster, Germany

A new light-switchable azo-surfactant arylazopyrazol tetraethylen glycol carboxylic acid (AAP-E₄) was used as a building block to functionalize macroscopic foams. AAP-E₄ was studied in the bulk with UV/Vis spectroscopy and at the interface with sum frequency generation as well as tensiometry. Foaming experiments were done with a dynamic foam analyzer in order to study the role of AAP-E₄ surfactants within macroscopic foam. In the bulk, it is possible to switch the AAP-E₄ surfactant reversibly from trans to cis configurations and vice versa using 380 nm UV and 520 nm green light. At the interface, we demonstrate excellent switching ability of AAP-E₄ surfactants. We show that the responsiveness of the interface is strongly influenced by lateral electrostatic interactions. Consequently, the disjoining pressure and thus the foam stability are highly dependent on the bulk pH and the charging state of the interface. For that reason, we have studied both the surface net charge and the surface excess as important pa-

rameters that determine foam stability in this system and show that neutral pH conditions lead to the best compromise between switching ability, surface excess and surface charging. Measurements on the foam stability demonstrated that foams under illumination with green light are more stable compared to foams illuminated with UV light.

CPP 11.4 Mon 12:00 C 230

Spiropyran ring opening reactions to measure forces on the molecular scale — ●OLIVER BRÜGNER and MICHAEL WALTER — FIT Freiburger Zentrum für interaktive Werkstoffe und bioinspirierte Technologien, Universität Freiburg

Spiropyran are mechanochromatic molecules which change color under the influence of force. These molecules can be integrated into polymers. By stretching the polymer, mechanical forces are transferred to spiropyran and lead to a ring opening reaction. Thereby the colorless spiropyran transforms into the colored merocyanine form. This reaction is reversible and the back reaction is already induced by thermodynamic excitations at room temperature [Kem]. Therefore spiropyran can be used as a molecular switch and belongs to the group of interactive materials.

In order to understand the molecular insides needed for using spiropyran as the responsive material in polymeric force sensors in the future, we investigated the energetics of spiropyran based on density functional theory and added entropic effects of the polymer. The model used is a combination of a relatively simple description of the polymer combined with an accurate description of the spiropyran ring opening reaction. We determine the dependence of the force on the polymer stretching length and find a very good agreement with experimental results from single molecule AFM experiments.

[Kem] Fabian Kempe, Oliver Brügger, Hannah Buchheit, Sarah N. Momm, Felix Riehle, Sophie Hameury, Michael Walter, and Michael Sommer, *Angew. Chem. Int. Ed.* **56** (2017) 1-5

CPP 11.5 Mon 12:15 C 230

Thermo-Responsive Foams from Aqueous Hydroxypropyl Cellulose Solutions — ●ERIC WEISSENBORN and BJÖRN BRAUNSCHWEIG — Institute of Physical Chemistry, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster, Germany

We have studied the ability of hydroxypropyl cellulose (HPC) with a molecular weight of 1 MDa to switch macroscopic foam reversibly from stable to unstable conditions. At 25°C room temperature, foams from 0.5 μM HPC are extremely stable with lifetimes of several hours. However, we can dramatically reduce the foam stability by increasing the temperature to 50°C which is well above the lower critical solution temperature (LCST) of 45°C. In order to clarify the underlying mechanism, we investigated the adsorption of HPC at the air/water interface by recording dynamic surface tensions using the pendant drop method. In addition, UV-VIS spectroscopy and dynamic light scattering indicate the formation of aggregates in the bulk for temperatures above the LCST. Bulk rheology of HPC dilutions shows that at these temperatures, the solutions viscosity is substantially decreased and as a consequence the foam drainage is increased. The latter decreases the foam stability, because foam drainage is one of the major destabilization mechanisms in this system. A fast reduction of temperature from 50°C to 25°C solubilizes the polymer reversibly and leads to a stabilization of the foam back to its initial stability.

CPP 11.6 Mon 12:30 C 230

Density and temperature dependence on supramolecular polymer morphology of polyethylene and polybutylene glycols with hydrogen bonding ends — ●EUNSANG LEE and WOLFGANG PAUL — Institut für Physik, Martin-Luther Universität Halle-Wittenberg, Halle, Germany

Rheological properties of supramolecular polymers depend on their structure including the size, the number, and the topology of aggregates. A polymer with a hydrogen-bonding motif at both ends is one widely used precursor to build the supramolecular polymers. In this work we investigate structures of supramolecular polyethylene glycol and polybutylene glycols with associating ends in wide range of temperature and density using a coarse-grained (CG) model via stochastic approximation Monte Carlo method. Our CG force field is constructed by Boltzmann inversion of the probability distributions of all-atom

polymer conformations. This work especially focuses on the transition from ring- to chain-dominated phases since the ring contaminant in a ring-linear blend melt is known to significantly influence its rheology. The phase diagram in a density-temperature space displays two continuous transition lines. One is the transition from ring- to chain-dominated phase with a coexistence between two phases at the transition temperature and the other is the transition from chain-dominated to free chain phase. For supramolecular polymers at melt-like density it turns out that chain aggregates dominate over rings at room temperature.

CPP 11.7 Mon 12:45 C 230

Single dendronized macromolecules as force probes for 2D interaction forces — •MOHAMMAD FARDIN GHOLAMI¹, JOSE D. COJAL GONZALEZ¹, SIMONE DELL'ELCE¹, VITALIJ SCENEV¹, NIKOLAI SEVERIN¹, BAOZHONG ZHANG², A. DIETER SCHLÜTER², and JÜRGEN P. RABE¹ — ¹Department of Physics & IRIS Adlershof, Humboldt-Universität zu Berlin — ²Department of Materials, Institute of Polymers, ETH Zürich

Graphene can replicate the topography of a substrate with a precision down to single macromolecules [1]. Here we use this capability and investigate the deformation of the macromolecules under graphene based 2D materials. We sandwiched cylindrically shaped dendronized polymers (denpols) between mica and graphene oxides (GO), reduced graphene oxides (rGO), and graphenes. The cross section of the denpols can be systematically varied through the dendron generation. The height of the molecular imprints in GO agrees with the height of those on bare mica while the height of molecular imprints in graphenes are smaller than the height of uncovered molecules, with the difference growing with the dendron generation. The heights of molecular imprints in rGO are in between those for graphene and GO. We attribute this to a larger interaction between those sheets and the mica, effectively squeezing the molecules as observed also in steered MD simulations. The combination of these experimental and theoretical results imply that it is possible to measure the interaction forces between 2D sheets and substrates by using the macromolecules as force sensors.

[1] N. Severin, *et al. Nano Lett.* 11 (2011) 2436.