

CPP 8: Responsive and Adaptive Systems

Time: Monday 10:45–13:00

Location: ZEU 255

CPP 8.1 Mon 10:45 ZEU 255

Spreading drops of volatile oil induce long range thickness gradients in swelling hydrophobic polymer brush layers — ●ÖZLEM KAP¹, SIMON HARTMANN², HARMEN HOEK¹, IGOR SIRETANU¹, SISSI DE BEER³, UWE THIELE², and FRIDER MUGELE¹ — ¹University of Twente, Physics of Complex Fluids, PO Box 217, 7500 AE Enschede (NL) — ²Westfälische-Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 9, 48149 Münster (D) — ³University of Twente, Sustainable Polymer Chem., PO Box 217, 7500 AE Enschede (NL)

Polymer brush layers are responsive materials that swell in contact with good solvents and their vapors. We combined optical experiments and numerical calculations based on gradient dynamics of a free energy density to study how fluid flow and solvent diffusion control the macroscopic spreading of (weakly) volatile oil drops and the swelling kinetics of an underlying hydrophobic polymer brush layer. The macroscopic spreading dynamics follow algebraic law with an exponent of 1/6, yet the spreading drops are found to be surrounded by halos of partially swollen polymer brushes. The width of the halos reaches values of hundreds of micrometers wide within hours to days, with thickness variations ranging from the dry thickness up to a maximum swelling ratio of ~ 4 close to the contact line. The halo profiles display long-living non-equilibrium steady state configurations that are controlled by the competition of two transport mechanisms, solvent diffusion through the polymer brush layer and through the vapor phase.

CPP 8.2 Mon 11:00 ZEU 255

Effect of architecture in thermoresponsive hydrogels from PEG-based tri- and tetrablock terpolymers — ●FEIFEI ZHENG¹, WENQI XU¹, EIRINI MELAMPANAKI¹, ANNA P. CONSTANTINOU², THEONI K. GEORGIU², and CHRISTINE M. PAPADAKIS¹ — ¹TUM School of Natural Sciences, Technical University of Munich, Garching, Germany — ²Department of Materials, Imperial College, London, UK

Thermogels are an exciting class of stimuli-responsive materials with many promising applications ranging from the medical field to additive manufacturing. The mechanical properties in the gel state strongly depending on the architecture of the polymer [1]. Here, we address an ABC triblock terpolymer and a BABC tetrablock terpolymer consisting of the hydrophilic oligo(ethylene glycol) methyl ether methacrylate (OEGMA, A), hydrophobic *n*-butyl methacrylate (BuMA, B), and thermoresponsive di(ethylene glycol) methyl ether methacrylate (DEGMA, C). The results from dynamic light scattering on dilute solutions show that the hydrodynamic radii of the micelles formed by both, ABC and of BABC, increase strongly above 25 °C, and the solutions feature a cloud point, i.e. aggregation of the micelles sets in. By synchrotron small-angle X-ray scattering, we found that, ABC and BABC form elongated and spherical micelles, respectively. Forward scattering attributed to large aggregates is observed at temperatures above the cloud point for both terpolymers.

[1] A. P. Constantinou et al., *Macromolecules*, 2021, 54, 1943.

15 min. break

CPP 8.3 Mon 11:30 ZEU 255

Hydration Water Dynamics in a Thermoresponsive Polymer Solution Under Pressure — BART-JAN NIEBUUR¹, BAHAR YAZDANSHENAS¹, FEIFEI ZHENG¹, WIEBKE LOHSTROH², MARCELL WOLF², MARIE-SOUSAI APPAVOU³, MICHAELA ZAMPONI³, ALFONS SCHULTE⁴, and ●CHRISTINE M. PAPADAKIS¹ — ¹Technical University of Munich, TUM School of Natural Sciences, Garching, Germany — ²Technical University of Munich, Heinz Maier-Leibnitz Zentrum (MLZ), Garching, Germany — ³Jülich Centre for Neutron Science (JCNS) at MLZ, Garching, Germany — ⁴University of Central Florida, Department of Physics, Orlando FL, U.S.A.

The water dynamics is key to functionality and phase behavior of synthetic and biological polymers. We investigate the dynamic behavior of hydration water in a concentrated aqueous solution of the thermoresponsive polymer poly(*N*-isopropyl acrylamide) (PNIPAM) in dependence on temperature and pressure employing quasi-elastic neutron scattering (QENS) [1]. The susceptibility spectra reveal the relaxation peak of the hydration water in addition to the known dynamic processes of bulk water. We find that the dehydration process at the

phase transition depends strongly on pressure. Using perdeuterated PNIPAM along with QENS allows us to suppress the signal of the chain segments and to identify and characterize the behavior of the different types of bound water at the phase transition.

1. B.-J. Niebuur, W. Lohstroh, M.-S. Appavou, A. Schulte, C. M. Papadakis, *Macromolecules* 2019, 52, 1942.

CPP 8.4 Mon 11:45 ZEU 255

Topology Impact on nanoscale hydration of polymer brushes — ●APOSTOLOS VAGIAS¹, ANDREW NELSON², PEIXI WANG³, JULIJA REITENBACH³, CHRISTINA GEIGER³, LUCAS PHILIPP KREUZER^{1,3}, THOMAS SAERBECK⁴, ROBERT CUBITT⁴, EDMONDO MARIA BENETTI⁵, and PETER MÜLLER-BUSCHBAUM^{1,3} — ¹MLZ, TUM, Garching — ²ANSTO, Sydney, Australia — ³TUM School of Natural Sciences, Chair for Functional Materials, Garching — ⁴ILL, Grenoble, France — ⁵Polymer Surfaces Group, University of Padova, Padova, Italy

Polymer brushes have demonstrated growing interest during last years, in particular in combination with exposure to aqueous environment. By utilizing time-of-flight neutron reflectometry (ToF-NR), we correlate the swelling properties of hydrophilic cyclic grafted polymer brushes to their thermodynamics. Cyclic brushes exhibit more compact conformations with lower roughness compared to their linear analogues, due to the absence of dangling chain ends extending at the interface. In addition, due to increased interchain steric repulsions, cyclic brushes feature larger swelling ratios at the same composition and comparable molar mass. Moreover, the two topologies exhibit differences in ageing, upon repetitive swelling/drying cycles. We present a case where current Flory-like expressions breakdown in the explanation of the experimental observations.

CPP 8.5 Mon 12:00 ZEU 255

Spiropyran/Merocyanine Amphiphile in Various Solvents: A Joint Experimental-Theoretical Approach to Photophysical Properties — VLADYSLAV SAVCHENKO¹, NINO LOMADZE², SVETLANA SANTER², and ●OLGA GUSKOVA¹ — ¹IPF Dresden — ²University of Potsdam

This joint experimental-theoretical work explains the negative photochromism of spiropyran-containing (SP) amphiphile aqueous solutions. Experiments demonstrate that the orange-red merocyanine (MC) form becomes thermodynamically more stable in water, and both UV and vis stimuli lead to the partial or complete photobleaching of the solution. The explanation of this phenomenon is given on the basis of DFT calculations and MD simulations. The latter reveal that stabilization of MC in water proceeds with the energy of ca. 70 kJ/mol, and that the Helmholtz free energy of hydration of MC form is 100 kJ/mol lower. The explanation of such a difference lies in the molecular properties of the MC. The presence of three charged groups on the periphery of a flat MC backbone stimulates its self-assembly in water ending up with the formation of elongated associates with stack-like building blocks. Our quantitative evaluation of the hydrophilicity switching in SP/MC containing surfactants may prompt the search for new systems, including colloidal and polymeric ones, aiming at remote tuning of their morphology, which could give new promising shapes and patterns for the needs of modern nanotechnology. This work is supported by DFG, grant GU1510/5-1. [1] Savchenko V., et al. *Int. J. Mol. Sci.* 2022, 23(19), 11535

CPP 8.6 Mon 12:15 ZEU 255

Mechanochemistry: a theoretical and experimental interplay — ●MICHAEL WALTER, Wafa MAFTUHN, and POOJA BHAT — Albert-Ludwigs-Universität Freiburg, Freiburg i. Br., Germany

Mechanochromic polymers are intriguing materials that allow to sense force of specimens under load. The connection between macroscopic stress and the forces acting on the molecular level is still elusive and covalently incorporated molecular mechanochromophors promise to shed light on this connection. Most mechanochromic systems rely on covalent bond scission with optically distinct *on* and *off* states. Bond rupture is induced by temperature fluctuations involving force dependent barriers. We show that these barriers are fully determined by the dissociation energy and the maximal force the potential can withstand, which allows for a re-interpretation of the Eyring-Zhurkov-Bell length

Δx^{\ddagger} and the expressions going beyond.

We furthermore present and analyse the concept of mechanochromic donor-acceptor (DA) torsional springs that allows for a continuous mapping of molecular forces to photoluminescence wavelengths. The mechanically induced deflection from equilibrium geometry of the DA spring is theoretically predicted and reveals forces of 1 nN on the molecular level. Our theoretical analysis demonstrates a thiophene ring flip as the major part of the overall mechanochromic response within a related ansa-DAD spring at forces as low as 27 pN. Such micromechanical motion gives access to sensing of tiny forces and expands both sensitivity and the force range of conformational mechanochromophores.

CPP 8.7 Mon 12:30 ZEU 255

Humidity & Electrochemical Switching of Mixed Conducting Polymer Films — ●SABINE LUDWIGS — IPOC - Functional Polymers, Institute of Polymer Chemistry, University of Stuttgart

Though electrochemistry of conducting polymers is a rather old topic(1), only recently conducting polymers have received renewed attention as inherently mixed-ionic-electronic conductors for a number of emerging switchable technologies including actuators, wetting on surfaces and electrically switchable metasurfaces. One of the work-horses of the community remains poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). While typically known as synthetic metal with application as transparent flexible electrodes, the material is a mixed conductor and shows ionic conductivity which is strongly affected by humidity.(2) The humidity dependence of the PSS polyelectrolyte phase together with the electroactive nature of the PEDOT can be used to create multifunctional and multiresponsive materials and films. A recent example from my group is the preparation of intelligent humidity-triggered bilayer actuators whose bending behavior (curvature) can be explained by the humidity-dependent mechani-

cal behavior of the constituents.(3) In collaboration with the Giessen Group the electrochemical stimuli were further used to switch nanoantennas on and off between the metallic and the insulating state.(4)

Ref: (1) Chemical Reviews 2010, 110, 4724.(2) ACS Applied Materials & Interfaces, 2020, 12, 6742. (3) Advanced Materials 2021, 202007982. (4) Science 2021, 374, 612.

CPP 8.8 Mon 12:45 ZEU 255

Stimuli-responsive high aspect ratio surfaces for wetting studies — ●GISELA CONSTANCE¹, INDRA APSITE¹, PAUL AUERBACH², SEBASTIAN ALAND³, DENNIS SCHÖNFELD³, THORSTEN PRETSCH³, PAVEL MILKIN¹, and LEONID IONOV^{1,4} — ¹Uni Bayreuth, Bayreuth, Germany — ²HTW Dresden, Dresden, Germany — ³Fraunhofer IAP, Postdam, Germany — ⁴BPI, Bayreuth, Germany

The fabrication of switchable surfaces has been of interest in several fields such as biotechnology, industry, and others. The selection of materials and methods is crucial to provide proper control on the tunable surface. In this research, an exceptionally high aspect ratio lamellar surface topography was fabricated by melt-electrowriting of microfibers of a shape-memory thermo-responsive polyurethane. Two different types of stimuli: temperature and light exposition were applied to modify the mechanical properties and by it the deformation and recovery of the original surface. Wetting studies showed that the deformation of the high aspect ratio lamellar surface can be tuned not only manually, but as well by a liquid droplet. This behavior is controlled by variation of temperature conducted by direct heating/cooling or by exposure to light when the lamellae were stained with black ink. The liquid in combination with thermo-responsive topography presents a new type of wetting behavior. This feature opens the possibility to apply such topographies for the design of smart elements for microfluidic devices, for example, smart valves.