

CPP 69: Focus: Polymers in Multi-Compartment and Aqueous Solutions I - organized by Jens-Uwe Sommer and Debasish Mukheri

Time: Thursday 15:00–18:30

Location: C 130

Topical Talk CPP 69.1 Thu 15:00 C 130

Biomimetic functions of hydrophobic-hydrophilic random copolymers — ●MONICA OLVERA DE LA CRUZ¹, TRUNG NGUYEN¹, BAOFU QIAO¹, and TING XU² — ¹Northwestern University, Evanston, IL, USA — ²University of California, Berkeley, CA, USA

Random copolymers with hydrophobic and hydrophilic groups are multicomponent systems with important functionalities for biomimetic applications. They can dissolve in organic solvents and in water and as such can be used to disperse and stabilize enzymes in unfavorable solvents. In this talk, we address the key factors that govern the ability of random copolymers to adsorb to biological substrates including proteins. Our findings show that for sufficiently strong solvent selectivity there exists an optimal value of the copolymer adsorbing fraction that maximizes the surface coverage. The existence of the optimal adsorbing fraction is shown to result from the balance between the entropic and energetic gains accompanying the adsorption process. Full atom and coarse-grained simulations show that there is a clear connection between substrate surface composition and fraction of copolymer adsorbed, and that the adsorption is highly sequence selective by the substrate composition. The results in this work set the stage for computational design of random copolymers for stabilizing and delivering enzymes across multiple media.

CPP 69.2 Thu 15:30 C 130

Precision Polymer Engineering through Biomolecular Templates — ●DAVID NG, SEAN HARVEY, YU TOKURA, and TANJA WEIL — Max Planck Institute for Polymer Research, Mainz, Germany

Nature provides a host of macromolecules that are both specific in their functions as well as sequence. The absolute atomic positioning in three dimensional space provides a precision scaffold unrivalled in the synthetic world even in the years to come. It is therefore intuitive that by combining the vast spectrum of knowledge on protein and DNA architectures with polymer chemistry, a new platform that allows the customization of nanoscale features can be evolved.

In the first part, we will discuss the conceptual design of using the protein structure as a backbone to position polymers. Depending on the chemistry and the strategy, materials ranging from anisotropic hybrid nanostructures to stimulus responsive hydrogels can be constructed. In the second part, DNA origami technology is used to provide true programmable features. Persistent shapes that do not exist in nature can be first templated by the origami by which polymers can be designated and grown in limitless possibilities in a three dimensional space. Collectively, we show that the incorporation of bioarchitectures into nanotechnology is multifold, with implications that impact the design as well as further application of such systems.

CPP 69.3 Thu 15:45 C 130

Entropic Segregation in Mixtures of Dendrimers and Linear Polymer Solutions — ●MARTIN WENGENMAYR^{1,2}, RON DOCKHORN^{1,2}, and JENS-UWE SOMMER^{1,2} — ¹Leibniz-Institut für Polymerforschung Dresden, Germany — ²Technische Universität Dresden, Germany

In mixtures of chemically compatible branched and linear polymers demixing effects are observed suggesting entropic forces caused by a difference in architecture only. For a better understanding of topological effects in mixtures of chemically identical polymers we investigate dendrimers of different sizes dissolved in a polymer solution of various chain lengths. We find that linear chains do always interpenetrate the volume of the dendrimer, whereas a collapsed state of the dendrimer known for poor solvent conditions, does not appear. Based on a scaling analysis of the dendrimer size we suggest that a thread length of the dendrimer, i.e. the longest path from the core to the terminal groups, is the relevant variable which should be compared with the chain length of the linear polymers. We can identify two scaling regions: When the chains are short compared to the length of the thread the dendrimer displays good solvent behavior, whereas longer chains lead to a θ -state of the dendrimer. Using umbrella sampling we observe an effective attraction between two dendrimers immersed in the solution of long linear chains. These insights are used to understand dendrimers used as processing aids in extrusion processes.

CPP 69.4 Thu 16:00 C 130

Orthogonally and doubly switchable diblock copolymers: Schizophrenic behavior — NATALYA S. VISHNEVETSKAYA¹, VIET HILDEBRAND², BART-JAN NIEBUUR¹, PETER MÜLLER-BUSCHBAUM¹, ANDRÉ LASCHEWSKY^{2,3}, and ●CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Garching, Germany — ²Universität Potsdam, Institut für Chemie, Germany — ³Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam-Golm, Germany

Doubly switchable diblock copolymers from blocks featuring lower and upper critical solution temperature behavior (LCST, UCST) may serve for advanced delivery purposes. We present results from diblock copolymers having a thermoresponsive LCST block and a zwitterionic UCST polysulfobetaine block, which is sensitive to ionic strength as well [1]. In aqueous solution, these diblock copolymers are expected to form core-shell micelles with the UCST block in the core and the LCST block in the shell or vice versa, i.e. so-called schizophrenic behavior. Depending on the values of the respective cloud points, the switching between these states may proceed via a molecularly dissolved state or via precipitation.

Using turbidimetry and small-angle neutron scattering, we investigate the phase behavior and the micellar structures in dependence on the choice of the two blocks and the block copolymer composition. Orthogonal and double switching behavior is identified and is found to depend crucially on these factors [1].

1. N. S. Vishnevetskaya et al., *Macromolecules* **49**, 6655 (2016) and **50**, 3985 (2017).

CPP 69.5 Thu 16:15 C 130

Kinetics of Mesoglobule Formation in Dependence on Pressure of Aqueous Poly(N-isopropylacrylamide) Solutions — ●BART-JAN NIEBUUR¹, LEONARDO CHIAPPISI², XIAOHAN ZHANG¹, FLORIAN JUNG¹, VITALIY PIPICH³, MARIE-SOUSAI APPAVOU³, ALFONS SCHULTE⁴, and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Garching, Germany — ²Institut Laue-Langevin, Grenoble, France — ³JCNS at MLZ, FZ Jülich, Garching, Germany — ⁴University of Central Florida, Department of Physics, Orlando, U.S.A.

Aqueous solutions of the thermoresponsive polymer Poly(N-isopropylacrylamide) form stable mesoglobules above their cloud point. Their size and degree of hydration depend strongly on pressure [1]. To elucidate the early stages of mesoglobule growth, time-resolved small-angle neutron scattering is applied during pressure jumps which induce phase separation. In this way, the phase-separated state is reached extremely fast within few ms. At low pressure, two different growth processes are observed. The early stage of aggregation is diffusion-limited, followed by the appearance of an energy barrier, hindering the growth during later stages. The time at which the energy barrier starts to dominate depends strongly on the target pressure of the jump. At high pressure, only one growth process is observed, and the energy barrier hindering the aggregation is much smaller than at low pressure. Thus, the growth behavior seems to be closely related to the hydration state of the polymeric chains [1].

[1] B.-J. Niebuur et al., *ACS Macro Lett.* **6**, 1180 (2017)

15 min. break

Topical Talk CPP 69.6 Thu 16:45 C 130

Soft matters in one-phase mixed solvents — ●TAKEAKI ARAKI — Department of Physics, Kyoto University, Kyoto, Japan

We numerically study charged polymers and colloids in solvent mixtures. Even when the solvent is mixed in the bulk, local concentration inhomogeneities cause the attractive interactions among the solutes. (1) The behaviors of polyelectrolyte chains in solvent mixtures are investigated, taking into account the concentration inhomogeneity and the ionization. When changing the interaction parameters between the solvent components, we found a first-order transition of the polymer conformation. In the mixing state far from the coexistence curve, the polymers behave as semi-flexible chains. In the phase-separated state, on the other hand, they show compact conformations included in the droplets. As the interaction parameters of the mixture are in-

creased, an inhomogeneous concentration field develops around the polymer and induces critical Casimir attractive interactions among the monomers. The competition between the electrostatic interactions and the critical Casimir ones gives rise to drastic changes in the conformation.⁽²⁾ We studied the behavior of colloidal suspensions in solvent mixtures under shear flows. Far from the phase-separation point, they are well dispersed and the suspension exhibits a Newtonian viscosity. When the mixture is close to the coexistence curve, the particles aggregate by attractive interactions due to the concentration inhomogeneity, and the viscosity of the suspension increases.

CPP 69.7 Thu 17:15 C 130

Drunken polymers: How does a polymer swell in poor solvent mixtures? — ●DEBASHISH MUKHERJI¹, CARLOS MARQUES², TORSTEN STUEHN¹, and KURT KREMER¹ — ¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz, Germany — ²Institut Charles Sadron, Université de Strasbourg, CNRS, 23 rue du Loess, 67034, Strasbourg Cedex 2, France

Macromolecular solubility in solvent mixtures often strikes as a paradoxical phenomenon [1]. In a standard poor solvent, chains can collapse due to increased monomer-solvent repulsion interactions that lead to an effective attraction between monomer units, also known as depletion induced attraction. While polymer collapse in poor solvent is well understood, polymer swelling at intermediate mixing ratios of two repulsive solvents still lacks a microscopic explanation. Here we combine computer simulations and theoretical arguments to unveil the microscopic, generic origin of this collapse-swelling-collapse scenario. We show that this phenomenon naturally emerges at constant pressure in mixtures of purely repulsive components when a delicate balance of the entropically driven depletion interactions is achieved [2].

[1] D. Mukherji, C. M. Marques, and K. Kremer, *Nature Communications* 5, 4882 (2014). [2] D. Mukherji, C. M. Marques, T. Stuehn, and K. Kremer, *Nature Communications* 8, 1374 (2017).

CPP 69.8 Thu 17:30 C 130

Polymer brush in competitive solvents — ●ANDRE GALUSCHKO and JENS-UWE SOMMER — Leibniz-Institut für Polymerforschung Dresden e. V. Germany

By means of molecular dynamics simulation we study the equilibrium properties of a single polymer brush layer immersed in two good solvents (solvent and cosolvent), which induces for a single chain a coil-globule-coil transition depending on the co-/solvent-composition^[1,2], called cononsolvency effect.

We extend the proposed simulation model in Ref.[2] to a homopolymer brush, where the solvent is treated implicitly and the cosolvent particles are simulated explicitly to mimic the concentration dependent composition. The attraction of cosolvent towards the monomer and the influence of grafting density are varied.

The recently developed theoretical description of an adsorption-attraction model for such scenario (Ref.[3]) is tested with our simulation results. We find very good agreement of our data and the proposed theory.

Additionally, we observe coexisting partially collapsed and swollen brush phases, which is coupled to a concentration-dependent Flory-Huggins mixing parameter as discussed in Ref.[3,4].

[1] Mukherji, Marques, Kremer, *Nat. Commun.* 2014, 5, p. 4882

[2] Heyda, Muzdalo, Dzubiella, *Macromolecules* 2013, 46, p. 1231

[3] Sommer, *Macromolecules*, 2017, 50, p. 2219

[4] Baulin, Zhulina, Halperin, *J. Chem. Phys.* 2003, 119, p. 10977

CPP 69.9 Thu 17:45 C 130

Lubrication by vapor-hydrated polymer brushes — JAN-WILLEM NIJKAMP, LUUK VAN DER VELDEN, ILSE DE VRIES, JURJEN REGENSPURG, SINEM TAS, HUBERT GOJZEWSKI, KRISTIANNE TEMPELMAN, NIECK BENES, JULIUS VANCISO, and ●SISSI DE BEER — University of Twente, Enschede, the Netherlands

Hydrophilic polymer brushes are well-known to be excellent lubricants when they are fully immersed in water. However, many applications require low-friction in air. We evaluate the water-distribution in hydrophilic polymer brushes in humid air and study the lubricating performance of these brushes as a function of the relative humidity using both molecular dynamics simulations and atomic force microscopy experiments. Our results show two characteristic maxima in the friction as a function of humidity, which indicates that there are multiple dynamic relaxations in the brush.

CPP 69.10 Thu 18:00 C 130

How robust is atomistic modeling of LCST of polyNIPAM? — VLADIMIR PALIVEC, DENIS ZADRAZIL, and ●JAN HEYDA — University of Chemistry and Technology, Prague, Czech Republic

Poly-N-isopropyl acrylamide (PNIPAM) serves as a role model of thermoresponsive polymers in vast majority of computational studies. Our community relies, almost exclusively, on the OPLS-AA parameterization of Vrabec et al. (DOI: 10.1016/j.fluid.2010.03.025). Despite its usage over almost a decade, our knowledge comes only from independent long simulation runs at set of temperatures. An important warning was raised by a recent work of Kang et al. (DOI: 10.1021/acs.jpcc.6b09165), where microsecond swollen-collapse-swollen transition times were reported even for chain as short as 30mer. Notably, there is no simulation study in which equilibrium thermodynamics and LCST of the PNIPAM model are determined. In this contribution, we invest 1 million CPU hours to shed light on this missing gap, and critically compare transition thermodynamics of available PNIPAM models.

CPP 69.11 Thu 18:15 C 130

Detailed calorimetric study on the collapse of poly(N-isopropylacrylamide) in aqueous sodium and guanidinium salts solutions — ●DANIEL ONDO, ADAM KOVALČÍK, JAKUB POLÁK, VLADIMÍR PALIVEC, and JAN HEYDA — University of Chemistry and Technology, Prague, Czech Republic

Poly(N-isopropylacrylamide) (pNIPAM) is a thermoresponsive polymer with a lower critical solution temperature (LCST) in pure water at 33 C. Addition of electrolytes, protein denaturants or organic cosolvents as a third component into aqueous pNIPAM mixtures, may change its solvation and balance between a collapsed hydrophobic and a swollen hydrophilic states hence alter the LCST and related thermodynamic quantities. In this work, employing the isothermal titration (ITC) and differential scanning (DSC) calorimetry, the LCST and total enthalpy of the collapse process of pNIPAM as a function of polymer and salt concentration (NaCl, Na₂SO₄, NaClO₄, NaSCN, GndCl, Gnd₂SO₄, GndSCN) were measured. Any effort to fit the calorimetric data by mass-action chemical binding or kinetic models failed. Nevertheless, the solvation of the collapsed polymer at 35 C is well described by Schellman's solvation model. The experimentally observed trends in LCST and total collapse transition enthalpy are in agreement with literature, verify the salt-polymer solvation model and are consistent with specifically designed dialysis measurements. Moreover, the microscopic details derived from the calorimetric measurements are in accord with performed μ -long atomistic simulations in the explicit solvent.