

## CPP 18: Interfaces and Thin Films II

Time: Tuesday 13:45–16:15

Location: H39

**Topical Talk**

CPP 18.1 Tue 13:45 H39

**Functional thin films based on polymer- and hybrid-nanostructures for photovoltaic applications** — ●PETER MÜLLER-BUSCHBAUM — TU München, Physik-Department LS E13, James-Franck-Str. 1, 85747 Garching

Conducting photoactive polymers offer fascinating new possibilities with respect to energy research applications such as photovoltaics (PV). In the organic photovoltaics (OPV) approach both parts of a thin film, the n- and p-type material, are made from such conjugated polymers. In a hybrid approach typically the p-type conducting polymer is in contact with a metal oxide as for example titania. For both types of PV systems, the tailoring of the interface morphology between n- and p-type materials is essential. The small exciton diffusion length in conducting polymers causes a need for domain sizes on that scale, thereby resulting in the bulk heterojunction approach. Grazing incidence small and wide angle scattering allow for a determination of this inner structure, which is the essential key for tailoring morphologies. In OPV model systems the influence of blend ration [1] and post production treatments [2] on both, device performance and morphology, are discussed.

[1] Ruderer, Müller-Buschbaum et al.; Chem. Phys. Chem. 10, 664-671 (2009)

[2] McNeill, Müller-Buschbaum, et al.; Adv. Funct. Mat. 19, 3103-3111 (2009)

CPP 18.2 Tue 14:15 H39

**Formation of lateral structures in thin diblock copolymer films by vapor treatment** — ALESSANDRO SEPE<sup>1</sup>, PETER CERNOCH<sup>2</sup>, PETR STEPANEK<sup>2</sup>, DETLEF-M. SMILGIES<sup>3</sup>, STEPHAN V. ROTH<sup>4</sup>, ANDREAS TIMMANN<sup>4</sup>, and ●CHRISTINE M. PAPADAKIS<sup>1</sup> — <sup>1</sup>TU München, Physikdepartment E13, Garching — <sup>2</sup>Inst. Macromolecular Chemistry, Prague, Czech Republic — <sup>3</sup>Cornell University, Ithaca NY, USA — <sup>4</sup>HASYLAB at DESY, Hamburg

Exposure of block copolymer thin films to solvent vapor allows to control the orientation of the mesostructure with respect to the film surface. Using real-time, in situ grazing-incidence small-angle X-ray scattering (GISAXS), we have investigated the structural changes in thin films of lamellae-forming poly(4-octylstyrene-*b*-butylmethacrylate) [1] during exposure to hexane and cyclohexane vapor.

We have varied the initial film thickness and have found that, in all cases, a lateral structure is created. However, both, the kinetics of structure creation and the final repeat distance depend strongly on the film thickness and on the solvent chosen. Instabilities are observed during the first few minutes of vapor exposure in the thicker films, whereas the behaviour is continuous in the thinner film.

1. P. Cernoch, P. Stepanek et al., Eur. Poly. J. 43, 1144 (2007)

CPP 18.3 Tue 14:30 H39

**Creating Nanostructures with Supramolecular Copolymers: A DFT-based Monte Carlo Approach** — ●KOSTAS DAOULAS<sup>1</sup>, ANNA CAVALLO<sup>2</sup>, ROY SHENHAR<sup>3</sup>, and MARCUS MÜLLER<sup>1</sup> — <sup>1</sup>Institut für Theoretische Physik, Georg-August-Universität Göttingen, Germany — <sup>2</sup>Dipartimento di Fisica "E.R. Caianiello", Università degli Studi di Salerno, Italy — <sup>3</sup>Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Israel

Designing assembling molecular systems capable of changing the morphology in response to external stimuli is important for nanotechnology related applications. We develop a density functional theory based Monte Carlo approach for studying assembling supramolecular, "living", copolymer systems in the bulk and in thin films. Here, we consider a system consisting of A and B monomers, where all A monomers are permanently bonded into n blocks, connected irreversibly at one end to a short B block so that irreversible AB diblocks are formed. The remaining B monomers can reversibly associate into linear chains, with each other as well as with the B terminus of the diblock; thus the spectrum of the different molecular species consists of B homopolymers, AB diblocks, and ABA triblocks. We discuss representative phase diagrams as a function of the A/B block ratio, the A/B monomer incompatibility, and the strength of the B-species association energy. The interplay between the morphology and system stoichiometry is highlighted. We conclude by considering the perspectives of directing

the assembly of living copolymers using patterned substrates.

CPP 18.4 Tue 14:45 H39

**Bundle Formation in Polyelectrolyte Brushes Caused by Divalent Ions** — ●HEIKO AHRENS<sup>1</sup>, JENS-UWE GÜNTHER<sup>1</sup>, STEPHAN FÖRSTER<sup>2</sup>, and CHRISTIANE A. HELM<sup>1</sup> — <sup>1</sup>Institut für Physik, Ernst-Moritz-Arndt Universität, Felix-Hausdorff-Str. 6, D-17489 Greifswald, Germany — <sup>2</sup>Institut für Physikalische Chemie, Universität Hamburg, Grindelallee 117, D-20146 Hamburg, Germany

Monolayers from amphiphilic block copolymers consisting of a fluid hydrophobic and a polyelectrolyte part are studied with X-ray reflectivity and Grazing Incidence Diffraction. The concentration of divalent cations (Ca<sup>2+</sup>, Sr<sup>2+</sup>) is varied between 0.001 and 1 mM. At 0.001 mM the brush thickness is almost constant resembling the osmotic brush phase (brush thickness almost 50 % of contour length), at 1 mM the brush shrinks and the thickness scales with the molecular area with an exponent -0.5 (brush thickness as small as 20% of the contour length). Always, between two and four chains form a bundle, independent of salt concentration. For concentrations between 0.003 and 1 mM, the peaks are very weak, suggesting only small fractions of the chains form bundles. At 0.001 mM, the peak is stronger, similar to findings with monovalent ions in solution. We conclude that the divalent ions form links between polyelectrolyte chains, which is very different from monovalent ions. For monovalent ions, the aggregation number varies due to a balance between long-ranged electrostatic repulsion, whose range and amplitude is decreased on salt addition, and a short-ranged attraction presumably due to hydrophobic forces (J.U. Günther et al., PRL 2008, 101 (2008) No. 258303).

CPP 18.5 Tue 15:00 H39

**Single polyelectrolyte layers adsorbed at high salt conditions: polyelectrolyte brush domains coexisting with flatly adsorbed chains** — ●STEPHAN BLOCK and CHRISTIANE A. HELM — Institut für Physik, Ernst-Moritz-Arndt Universität, Felix-Hausdorff-Str. 6, D-17489 Greifswald, Germany

AFM is used to measure the surface forces and to image sodium poly(styrene sulfonate) (PSS) layers physisorbed from 1 M NaCl solution on different length scales within one experiment. Domains of PSS brushes coexist with flatly adsorbed PSS. For degree of polymerization  $N = 380$ , the brush area fraction 6 %. With increasing degree of polymerization, brush area fraction and domain size increase, while the domain radii range from 50 nm up to 1500 nm. Laterally homogeneous brush layers are found for a degree of polymerization exceeding 1100. Colloidal probe technique reveals that the surface forces are a superposition of steric and electrostatic forces, their respective contribution is determined by the brush area fraction. A comparison with literature demonstrates that adsorbed PSS brushes show the same scaling behaviour as end-grafted PSS brushes. We develop a model for the adsorption of polyelectrolytes in which not the whole chain but only a fraction of the monomers adsorbs onto the surface. Thereby we show that partial adsorption can lead to stable conformations and calculate scaling laws for the fraction of adsorbed monomers and the distance between the chains dangling into solution.

CPP 18.6 Tue 15:15 H39

**Polyelectrolyte Solutions Confined between Two Solid Surfaces** — ●CAGRI ÜZÜM and REGINE V. KLITZING — Stranski-Laboratorium für Physikalische und Theoretische Chemie - Institut für Chemie TU Berlin, Sekr. TC 9 Strasse des 17. Juni 124 D-10623 Berlin

Thin liquid films play an important role in macroscopic colloidal systems. Stability of a colloidal suspension -in which particles are dispersed in a liquid- is mainly dominated by the stability of the thin films separating the dispersed particles.

In this contribution, liquid thin films of polyelectrolyte (PSS and PAMPS derivatives) solutions confined between two solid surfaces are studied. Colloidal Probe AFM is used to study the structure formation of aqueous polyelectrolyte solutions under geometrical confinement.

It was observed that AFM force measurements on the polyelectrolyte solutions lead to oscillatory force curves in a certain concentration range. These oscillatory curves can be used to study the interactions between the polyelectrolyte chains, which were described also by theo-

ritical models. Concentration, type of the monomers and charge fraction of the polyelectrolyte chains determine the structuring [1]. In addition to those, effect of surfactant in the system, molecular weight and architecture of the polyelectrolyte chains on the structuring were investigated. Viscosity and conductivity measurements were taken for a better understanding of the phenomena.

[1] D. Qu, J.S. Pedersen, S. Garnier, A. Laschewsky, H. Möhwald and R. v. Klitzing. *Macromolecules* 39, 7364 (2006).

CPP 18.7 Tue 15:30 H39

**Analysing the development of entanglements in spin coated films** — ●JULIA ZABEL and ALEXANDER BLUMEN — Albert-Ludwigs-Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg

As technological applications increasingly probe the nano scale and the importance of polymers in such devices rises, it becomes more and more important to understand the behavior of polymers confined to molecular lengthscales. Over the last years there has been a vast amount of experiments designed to understand the deviation of the properties of thin films from the bulk behavior. One can measure a film thickness dependence in such quantities as the glass transition temperature, the elastic modulus and relaxation times. But as varied as the experimental setups are the results. The often contradicting conclusions give rise to the suspicion that film preparation and annealing might play a large role in the outcome of the experiments. This is why we choose to research out-of-equilibrium films. In a toy model based on the spin coating process we simulate films of varying thickness and chain length. We then study their relaxation by analysing the polymers' conformation and entanglement over time. We discuss and compare different procedures to count entanglements, such as the determination of the self density, the so-called "packing model" and the Primitive Path Analysis. In this context we question whether reaching an equilibrium value for the polymer extension necessarily indicates that an equilibrium situation for the entanglements is reached.

CPP 18.8 Tue 15:45 H39

**Stress relaxation during polymer brush swelling** — SEBASTIAN LENZ<sup>1</sup>, ADRIAN RÜHM<sup>2</sup>, RÜDIGER BERGER<sup>1</sup>, and ●JOCHEN S. GUTMANN<sup>1,3</sup> — <sup>1</sup>Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz (Germany) — <sup>2</sup>Max-Planck-Institut für Metallforschung, ZWE FRM-II / N-REX+, Lichtenbergstr. 1, D-

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End-tethered polymer brushes can be used to create switchable surfaces. The properties of such surfaces are dependent on the solvent quality. We focused on the swelling behavior of poly-methyl-methacrylate (PMMA) brushes as a model system. The aim of the presented work was to relate structural brush features in the collapsed/swollen state, such as the brush thickness and the adsorbed solvent fraction, to mechanical properties.

The structure of the polymer brush was measured in situ with Neutron Reflectivity (NR) as a function of solvent quality. Using scaling theories the effective polymer-solvent interaction parameters could be estimated from the NR results.

Preparing the PMMA brush directly on nanomechanical cantilever sensor arrays allowed us to perform surface stress experiments and relate the obtained mechanical results to the results obtained from NR. It was concluded that attractive polymer/polymer interactions relax towards zero reaching theta solvent conditions.

CPP 18.9 Tue 16:00 H39

**Cross-linked Polymer Brushes** — ●MAX HOFFMANN<sup>1,2</sup>, MICHAEL LANG<sup>1</sup>, and JENS-UWE SOMMER<sup>1,2</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden, Hohe Strasse 6, 01069 Dresden, Deutschland — <sup>2</sup>Institut für Theoretische Physik, Technische Universität Dresden, 01069 Dresden, Deutschland

Cross-linked polymer brushes have gained increasing attention in recent years. However, up to now there is only little theoretical work done on this topic. Based on simulations of the bond fluctuation model, the cross-linking process will be introduced in detail. The simulation based percolation threshold induced by the cross-links is lower than the percolation threshold which is expected from the mean field gelation model. In order to understand the percolation behavior a new percolation model is developed which we call star-percolation model. As a coarse-grained model the star-percolation model contains core features of the cross-linking process of the polymer brush. Standard properties like the percolation threshold and the cluster size distribution as well as other static and dynamic properties of the cross-linked polymer brushes are discussed.