

CPP 16: Interfaces and Thin Films II (joint session with DECHEMA and VDI)

The session is a joint session with ProcessNet "Grenzflächenbestimmte Systeme und Prozesse" of DECHEMA and VDI.

Organizers: Thomas Danner (BASF), Leo Nick (DECHEMA) and Regine v. Klitzing.

Time: Tuesday 9:30–13:00

Location: H40

Invited Talk CPP 16.1 Tue 9:30 H40

Functional nanolayers made from colloidal building blocks — ●ANDREAS FERY — University Bayreuth, Physical Chemistry II and Bayreuth Center for Colloids and Interfaces, Universitaetsstr. 30, 95444 Bayreuth, Germany

Colloidal particles are attractive building blocks for forming functional nanolayers. Already at the single particle level, even multiple functionalities like optical functionality or stimulus sensitivity can be established. These functionalities can be easily integrated into nanolayers, as particle immobilization typically does not require sophisticated specific coupling chemistry, but in many cases, physisorption relying on unspecific interactions is sufficient. Finally, multi-layer formation and/or lateral patterning can unlock novel properties, which arise from synergistic functional, as well as local or long range coupling effects.

We illustrate this concept with examples from the area of stimulus responsive layers using microgel- or block-copolymer building blocks. The stimulus sensitivity of those can be used for controlling the interaction of cells with surfaces, allowing for novel concepts in switchable cell culture surfaces or anti-fouling. As well, we discuss how non lithographic patterning of metallic colloidal particles can be used for controlling plasmonic coupling effects, leading to applications in sensorics and plasmonics.

CPP 16.2 Tue 10:00 H40

Vapor treatment of diblock copolymer thin films with perpendicular lamellar structure — ●JIANQI ZHANG¹, ALESSANDRO SEPE², DORTHE POSSELT³, JAN PERLICH⁴, XUHU SHEN¹, DETLEF-M SMLIGIES⁵, and CHRISTINE PAPADAKIS¹ — ¹TU München, Physikdepartment, Fachgebiet Physik weicher Materie, Garching, Germany — ²University of Cambridge, Department of Physics, UK — ³Roskilde University, IMFUFA, Denmark — ⁴HASYLAB at DESY, Hamburg, Germany — ⁵Cornell University, CHESS, Ithaca NY, USA

Solvent vapor treatment results in complex swelling kinetics in self-assembled thin films. We have investigated the structural changes of P(S-b-B) diblock copolymer thin films with perpendicular lamellar structure using in-situ, real-time grazing-incidence small-angle X-ray scattering. Cyclohexane (CHX), which is slightly selective for the PB block, was used to vapor-treat the films. For the as-prepared film, the image displays straight diffuse Bragg rods (DBRs), which indicate the perpendicular lamellar orientation. During vapor treatment, the DBRs bend inwards which we attribute to tilting of a fraction of the lamellae away from the purely perpendicular orientation. Upon subsequent drying, straight DBRs reappear, i.e. the perpendicular orientation is recovered. Additional narrow and elongated DBRs appear during the final stage of the drying process. This finding points to the protrusion of PS domains at the film surface because the PB domains dry more slowly.

CPP 16.3 Tue 10:15 H40

Internal structure and dynamics of microgel films at solid interfaces — ●STEFAN WELLERT¹, YVONNE HERTLE², MARCEL RICHTER¹, PETER MÜLLER-BUSCHBAUM³, THOMAS HELLMWEG², and REGINE VON KLITZING¹ — ¹Stranski Laboratorium, Inst.f. Chemie, TU Berlin, 10623 Berlin — ²Fakultät f. Chemie, Physikalische Chemie III, Universität Bielefeld, 33615 Bielefeld — ³Physikdepartment E13, TU München, 85747 Garching

The physico-chemical properties of stimuli-responsive polymers attract great interest in basic research and lead to a lively discussion of potential technical applications. A prominent example are microgel systems, which undergo a temperature induced phase transition corresponding to a discontinuous shrinking with increasing sample temperature. Microgel particles can be organized as ultra-thin films at solid surfaces, e.g. silicon single crystal surfaces. This leads to changes in the shrinking behaviour and the LCST. For example, the LCST is reduced between 1°C and several °C with respect to the bulk phase. These findings raise the question how the interactions with the solid surface affect the internal structure and dynamics of the microgel particles. In a series of surface sensitive scattering experiments we addressed this

question mainly focussing on the correlation length in the polymer network. Here, we present GISANS measurements investigating a microgel containing the monomer NIPAM, cross-linked with BIS (2 mol-% with respect to the mass of NIPAM). Additionally, first measurements addressing the internal dynamics in this system using neutron spin-echo spectroscopy under grazing incidence (GINSE) are discussed.

CPP 16.4 Tue 10:30 H40

Determination of the inner morphology of organic solar cells with grazing incidence small angle neutron scattering — MATTHIAS A. RUDERER¹, ROBERT MEIER¹, LIONEL PORCAR², ROBERT CUBITT², and ●PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik Department, LS Funktionelle Materialien, James-Frank-Str. 1, 85748 Garching, Germany — ²Institut Laue Langevin (ILL), 6 Jules Horowitz, 38042 Grenoble, France

Organic photovoltaic devices based on conducting polymers are of increasing interest. The device efficiency of an organic solar cell is determined by the inner morphology of the active layer. However, such inner morphologies are not easily detectable by real space imaging methods such as electron microscopy. In contrast, grazing incidence small angle neutron scattering (GISANS) is a unique tool for the characterization of the active layer morphology, in particular for donor-acceptor systems with polymer donor and small molecule acceptor blends. The scattering length density contrast in such blends is typically large, which makes special deuteration dispensable and real systems can be studied. For the example of P3HT:PCBM bulk heterojunction thin films the inner morphology is determined with GISANS. The phase separation structure and the amount of molecular intermixing are investigated as a function of the overall PCBM content. For the symmetric P3HT:PCBM ratio, which is typically highly efficient in photovoltaic devices, a structure size in the range of the exciton diffusion length, the largest PCBM phases and 18 vol% dispersed PCBM in the amorphous P3HT phase are found.

CPP 16.5 Tue 10:45 H40

Investigation of structure and molecular nature of the conjugated polymer films by hard and soft x-ray reflectivity and XAFS in reflection mode — ●ARMAN DAVTYAN, SOUREN GRIGORIAN, DMITRY KSENZOV, and ULLRICH PIETSCH — University of Siegen, Siegen, Germany

Structural and optical properties of the conjugated polymers were measured close and outside the K- absorption edge of carbon. Hard and soft x-ray reflectivity measurements are characterizing samples made of P3AT (poly(3-alkylthiophene)) thin films covered onto SiO₂ coated silicon substrates. The general structures of films were determined by combined fitting of hard and soft x-ray reflectivity curves. Additional chemical information was taken from the shape of curves taken by ReflEXAFS in the energy range of the Carbon K-edge (275-340 eV). It turns out that structural properties depend on the preparation technique used. Considering all information a three-layer model was appropriate to simulate the hard and soft x-ray reflection curves and the C K-edge ReflEXAFS profiles of the spin coated thin films.

CPP 16.6 Tue 11:00 H40

Hierarchical multiscale modelling of polymer-solid interfaces — ●KAREN JOHNSTON¹ and VAGELIS HARMANDARIS² — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²Department of Applied Mathematics, University of Crete, Greece

Polystyrene films sandwiched between two parallel gold surfaces were studied using hierarchical multiscale modelling. Classical all-atom polymer-surface interface potentials were developed based on density functional theory calculations that account for van der Waals forces [1]. All-atom molecular dynamics simulations were then used to study the structure and dynamics of 10mer polystyrene thin films up to 10 nm thick [2]. To study longer chains and thicker films a coarse-grained model was used [3] and the coarse-grained surface potentials were developed based on all-atom potential of mean force calculations. The results of the coarse-grained and all-atom simulations were compared

for a 5 nm film of 10mer polystyrene and the results were in good agreement. The coarse-grained model was used to simulate 10 and 20 nm films for chain lengths of up to 200mer and the dependence of the structure, dynamics and interphase width on chain length were investigated.

- [1] Johnston and Harmandaris, *J. Phys. Chem. C* 115, 14707 (2011)
- [2] Johnston and Harmandaris, *Soft Matter*, 8, 6320 (2012)
- [3] Fritz et al. *Macromolecules*, 42, 7579 (2009)

15 min. break

CPP 16.7 Tue 11:30 H40

Relaxation of non-equilibrium chain entanglement networks in thin polymer films — PAUL D. FOWLER, JOSHUA D. MCGRAW, MELISSA L. FERRARI, and KARI DALNOKI-VERESS — Department of Physics & Astronomy and the Brockhouse Institute for Materials Research, McMaster University, Hamilton, ON, Canada

It is well established that polymer films, prepared by spincoating, inherit non-equilibrium chain conformations which can affect macroscopic film properties. Here we present the results of crazing measurements [1] that elucidate the non-equilibrium chain configurations in spin-cast films. Furthermore, we find that the entanglement network equilibrates on a time scale comparable to one reptation time. In a second set of experiments, we confine polymers to films with thickness comparable to the molecular size. By stacking two such films at room temperature, a glassy bilayer film with a buried entropic interface is created. According to Silberberg's reflection principle, such an interface has an entropic cost associated with the restricted configurations of molecules that cannot cross the mid-plane of the bilayer. In the melt, the interface heals as chains from the two layers mix and entangle with one another. Crazing measurements reveal that it takes less than one bulk reptation time for a bilayer to become indistinguishable from a single film.

- [1] McGraw et al., *EPJE* (2012 - submitted).

CPP 16.8 Tue 11:45 H40

Nano-scale Roughness of Phase Boundaries in Heterogeneous Polymers: The rigid-mobile Interphase — MATTHIAS ROOS and KAY SAALWÄCHTER — Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany

Many macroscopic features of polymers rely on microscopic and nano-scale characteristics, so their morphology, in particular nano-scale dynamic heterogeneities, is of great importance. Based on the possible distinction of differently mobile parts of the sample by proton NMR, we use an effect called spin diffusion (i.e. transport of spin magnetization among the nuclei) to investigate neighborhood relations between rigid and mobile (below or above T_g , respectively) components in semi-crystalline polymers and block copolymers. In addition, a phase of intermediate mobility can be identified.

If there is a selective magnetization of the rigid phase, first the magnetization induced signal of the interphase rises, followed by the magnetization of the mobile phase. That is to say, the magnetization diffuses from the rigid phase to the mobile one but must cross the respective interphase. Contrary to this, if a selective magnetization of the mobile phase is created, the rigid phase will gain its magnetization simultaneously with the interphase.

It was possible to replicate this effect by simulating the diffusive behavior of magnetization when taking into account a thickness variation of the rigid phase, where the interphase is mainly situated in "depressions" of the rigid phase, i.e., in regions that are less exposed to the mobile phase.

CPP 16.9 Tue 12:00 H40

Glassy dynamics of densely packed semi-isolated polymer chains — MARTIN TRESS, EMMANUEL MAPESA, and FRIEDRICH KREMER — Universität Leipzig, Leipzig, Germany

The glassy dynamics of randomly distributed, densely packed semi-isolated poly(2-vinylpyridine) (P2VP) polymer chains is studied by means of Broadband Dielectric Spectroscopy (BDS). Therefore, a recently developed nano-structured electrode arrangement is refined to achieve an electrode-to-electrode distance of only 40 nm. On one of the ultra-flat, highly conductive silicon electrodes semi-isolated polymer coils are deposited. Atomic Force Microscopy scans of the identical sample before and after the BDS measurement reveal that, even for different molecular weights, the mean volume of the coils resembles 5 to 10 times the volume expected for a single chain. Accordingly,

the dynamics of coils on average consisting of 5 to 10 (therefore semi-isolated) polymer chains is measured and it compares well with that of bulk though the mean relaxation rate is slowed down by up to half a decade. This is attributed to attractive interactions of the P2VP segments with the supporting silica surface.

CPP 16.10 Tue 12:15 H40

Electric polarization in thin films of polyvinylidene fluoride doped with the ionic liquid 1-ethyl-3-methylimidazolium nitrate — ALEXANDER LACK, PETER FRÜBING, FEIPENG WANG, and REIMUND GERHARD — Applied Condensed-Matter Physics Group, Department of Physics and Astronomy, Faculty of Science, University of Potsdam, Karl-Liebknecht-Strasse 24-25, 14476 Potsdam, Germany

Dielectric properties of spin-coated polyvinylidene fluoride (PVDF) films containing a small amount (0.01 - 10 wt%) of the ionic liquid (IL) 1-ethyl-3-methylimidazolium nitrate $[EMIM^+][NO_3^-]$ and sandwiched between aluminium electrodes are investigated. Films with more than about 1 wt% IL exhibit pronounced current-voltage hysteresis which indicates the existence of a ferroelectric polarization. The dielectric spectra show pronounced charge-carrier polarizations with huge permittivities. In films with more than 0.1 wt% IL electrode polarization dominates. From its signatures the DC conductivity is estimated: for films with 1 wt% IL values of 10^{-7} and 10^{-4} S/cm are found at room temperature and 100 °C, respectively. The relaxation associated with the glass transition in PVDF tends to disappear for samples containing more than 1 wt% IL, though the crystallinity is only moderately enhanced. These findings refer to an ordered crystalline structure where ions are immobilized by Coulomb interaction with molecular dipoles within the polymer chain. The details of this interaction have still to be understood.

CPP 16.11 Tue 12:30 H40

Segmental and chain dynamics in thin layers of poly(cis-1,4-isoprene) — EMMANUEL URANDU MAPESA¹, MARTIN TRESS¹, MANFRED REICHE², and FRIEDRICH KREMER¹ — ¹University of Leipzig, Linnestraße 5, 04103 Leipzig, Germany. — ²Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle an der Saale, Germany.

Broadband Dielectric Spectroscopy (BDS) - in combination with a nanostructured electrode arrangement - is used to study thin layers of poly(cis-1,4-isoprene) (PIP). Being a Type A polymer, PIP enables the investigation of two distinct relaxation modes taking place at two different length scales: the segmental motion which involves structures of about one nanometer in size and the normal mode which represents the global dynamics of the chain. For molecular weights ($M_w = 24.5, 44.5, 53$ and 75 kg/mol) much greater than M_c (the critical molecular weight, $M_c = 10e+04$), down to thicknesses comparable to the respective radii of gyration, it is observed that: (i) the segmental mode as a local relaxation process is unaltered by the confinement in thin layers; (ii) the normal mode becomes faster with decreasing layer thickness, and (iii) this change in the normal mode is molecular-weight dependent. For M_w approximately equal to M_c , both the segmental and normal modes remain unaffected by changes in layer thickness.

CPP 16.12 Tue 12:45 H40

Azo-propellers as nanoscopic actuators in light-induced deformation of azobenzene polymer films — MARINA SAPHIANNIKOVA¹, VLADIMIR TOSHCHEVIKOV¹, and JAROSLAV ILNYTSKYI² — ¹Leibniz-Institut für Polymerforschung Dresden e.V. — ²Institute for Condensed Matter Physics, Lviv, Ukraine

We present the theoretical and MD simulation studies of thin azobenzene polymer films based on side-chain azo-oligomers having a stiff backbone and short spacers. Up to the glass transition temperature T_g the polymer backbone can be considered as a rigid prolate ellipsoid with a number of azobenzenes attached to it. Polar and azimuthal distributions of chromophores were studied at different temperatures and laser intensities. Their analysis was done in terms of nematic order parameters calculated in respect to the backbone. These parameters served then as input into a theoretical expression for the striction stress [1], which was found to be positive and above the yield stress. This explains irreversible elongation of the illuminated thin films below T_g , as found previously in experiment and MD simulations [2].

The light-induced reorientation of typical propeller-like structures is shown to be a microscopic reason of the sample elongation. Thus, molecular azo-propellers work as nanoscopic actuators which convert the light energy into material deformation. This finding opens a way for prediction of photomechanical properties of glassy azo-compounds

directly from their chemical structure.

[1] V.Toshchevnikov et al., J. Phys. Chem. B 113, 5032 (2009).

[2] J. Ilytskyi et al., J. Chem. Phys. 135, 044901 (2011).