

CPP 11: Interfaces and Thin Films I

Time: Monday 16:30–18:30

Location: ZEU 114

CPP 11.1 Mon 16:30 ZEU 114

Guiding Reorganization in Block Copolymer Thin Films on the Nanoscale by Judicious Control of Solvent Vapor Exposure — ALESSANDRO SEPE¹, DORTHE POSSELT², JIANQI ZHANG¹, JAN PERLICH³, DETLEF-M. SMILGIES⁴, ANDREY A. RUDOV⁵, IGOR I. POTEKIN⁵, and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Garching — ²Roskilde University, Denmark — ³DESY, Hamburg — ⁴Cornell University, Ithaca, NY, USA — ⁵Lomonosov Moscow State University, Russian Federation

A perfect alignment of nanostructured block copolymer thin films is mandatory for their applications. Solvent vapor annealing is a method to improve order in films prepared by spin-coating. We investigate thin films of lamellar poly(styrene-*b*-butadiene) (P(S-*b*-B)) in cyclohexane vapor. The rates of swelling in solvent vapor and drying as well as the maximum degree of swelling of the film are controlled. The structural changes are monitored in-situ using time-resolved grazing-incidence small-angle X-ray scattering (GISAXS). Good alignment of the lamellar nanostructure is achieved for a sufficiently high degree of swelling and is even further improved during drying, provided the rate of drying is sufficiently low. A second swelling/drying cycle shows that equilibrium has been achieved. During swelling, the lamellar stack rearranges as soon as T_g of PS is crossed, and additional lamellae are formed. During (slow) drying, this new structure is conserved. Computer simulations confirm this mechanism [2].

1. A. Sepe et al., submitted.

2. A.A. Rudov et al., *Macromolecules* **46**, 5786 (2013)

CPP 11.2 Mon 16:45 ZEU 114

Diblock-copolymer thin films under shear — LENIN S. SHAGOLSEM^{1,2}, TORSTEN KREER¹, and JENS-UWE SOMMER^{1,2} — ¹Leibniz Institute of Polymer Research Dresden — ²TU Dresden

By employing molecular dynamics simulations we study the behavior of copolymer thin films under shear. In particular, we consider symmetric diblock-copolymer melts confined by two non-selective walls. Since there is no preferential interaction between the walls and the components of the diblock-copolymer a vertically oriented lamellar structure is formed. We investigate the response of the system to transverse and perpendicular modes of shear and study shear deformation of the lamellae, reorientation transition in transverse shear, and flow behavior. We find that the inclined lamellae state (observed for transverse shear below a critical shear rate) is stabilized by a cyclic motion of chains. Above a critical shear rate, the lamellae orient along the direction of flow. Furthermore, the macroscopic response is investigated by kinetic friction coefficient and shear viscosity. We observe that the critical shear rate, at which the lamellae reorientation occurs, coincides with the onset of shear-thinning.

CPP 11.3 Mon 17:00 ZEU 114

Structural evolution of perpendicular lamellae in diblock copolymer thin films during solvent vapor treatment investigated by GISAXS — JIANQI ZHANG¹, DORTHE POSSELT², ALESSANDRO SEPE¹, XUHU SHEN¹, JAN PERLICH³, DETLEF-M. SMILGIES⁴, and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Garching — ²IMFUFU, Roskilde University, Denmark — ³DESY, Hamburg — ⁴Cornell University, Ithaca, NY, USA

Drastic structural rearrangements in block copolymer thin films occur during solvent vapor treatment. Their understanding is mandatory for the use of solvent vapor treatment for annealing defects otherwise hampering applications. We investigate the structural evolution in poly(styrene-*b*-butadiene) (P(S-*b*-B)) diblock copolymer thin films featuring perpendicular lamellae. The changes during solvent vapor treatment are studied in-situ using time-resolved grazing-incidence small-angle X-ray scattering (GISAXS) [1]. The swelling of the film is one-dimensional along the substrate normal. During swelling, the initially perpendicular lamellae tilt within the film to be able to shrink, as confirmed by computer simulations [2]. In contrast, at the film surface, the lamellae stay perpendicular, and eventually vanish at the expense of a thin PB wetting layer. During the subsequent drying, the perpendicular lamellae reappear at the surface, and finally, PS blocks protrude. By modeling, the time-dependent height of the protrusions can be quantitatively extracted.

1. J. Zhang et al., *Macromol. Rapid Commun.* **34**, 1289 (2013)2. A.A. Rudov et al., *Macromolecules* **46**, 5786 (2013)

CPP 11.4 Mon 17:15 ZEU 114

Highly enhanced ordering dynamics in solvent-annealed block-copolymer films supported by a polymer network — ANJA STENBOCK-FERMOR¹, LARISA TSARKOVA¹, ALEXANDER BÖKER¹, and ARMIN KNOLL² — ¹DWI at RWTH-Aachen University, Forckenbeckstraße 50, 52074 Aachen — ²IBM Research GmbH, Säumerstrasse 4, CH-8803 Rüschlikon Switzerland

We studied the solvent driven ordering dynamics of block copolymer films supported by a densely cross-linked organic hard mask (HM) designed for lithographic fabrication. We found that the ordering of microphase separated domains on the HM layer proceeds significantly faster as compared to similar films on silicon wafers. Both the dynamics of terrace-formation as well as the long-range lateral ordering of the microdomains is greatly enhanced. The effect is independent on the chemical structure and volume composition (cylinder-/ lamella-forming) of the studied block copolymers. Importantly, enhanced ordering is achieved even at a reduced degree of swelling corresponding to an intermediate to strong segregation regime, when similar films on conventional substrate show very limited ordering. In-situ ellipsometric measurements of the swollen films revealed an insignificant increase by 1-3 vol. % in the solvent up-take by HM-supported films. Therefore we attribute the enhanced dynamics to reduced interactions at the block copolymer/HM-support interface. Apart from immediate technological impact in block copolymer-assisted nanolithography, our findings convey novel insight into effects of molecular architecture on polymer-solvent interactions.

CPP 11.5 Mon 17:30 ZEU 114

Tuning the Monolayer Properties of Liquid Crystalline Septithiophenes — KHOSROW RAHIMI¹, WIM DE JEU¹, ULRICH ZIENER², MARTIN MÖLLER¹, and AHMED MOURRAN¹ — ¹DWI Interactive Materials Research at RWTH Aachen, Germany — ²Institute of Organic Chemistry III, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany

Conjugated molecules including oligothiophenes are promising materials for organic electronic devices due to the combination of low-cost solution processing and charge transport mobility. The conduction in thin polycrystalline films is limited by the degree of crystallinity and the extent of the crystalline domains. To optimize single crystal devices in monolayers, crystal growth involves the delicate point of decoupling of lateral (two-dimensional) growth from that perpendicular to the substrate. The growth kinetics of molecular thin films will be influenced by possible liquid crystal (LC) order due to anisotropy in molecular structure. New terminally substituted oligothiophenes have been synthesized, that exhibit thermotropic LC phases. They consist of a conjugated thiophene backbone to which long flexible alkyl chains are attached that incorporate a bulky -Si(CH₃)- group. Varying the position of -Si(CH₃)- in the linear alkyl chain, we find that the temperature window of LC phase is larger when -Si(CH₃)- is situated away from the thiophene core. As a result the monodomain size is enhanced. However, this trend is vice versa when the Si group is very close to the core. We conclude that deposition and formation of monolayer and its monodomain size is controlled with LC phase.

CPP 11.6 Mon 17:45 ZEU 114

FTIR Imaging of PFSA Membranes for Fuel Cells — PAWEŁ GAZDZICKI¹ and MARTINA CORASANITI² — ¹German Aerospace Center (DLR), Institute of Technical Thermodynamics, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany — ²Solvay Specialty Polymers, viale Lombardia 20, 20021 Bollate (MI), Italy

In our presentation we provide an attenuated total reflection (ATR) Fourier transform infrared (FTIR) imaging study of perfluorosulfonic acid (PFSA) membranes. These materials are typically used as ion conductors in electrochemical energy converters such as low temperature fuel cells. The spectroscopic images have been measured using a focal plane array detector allowing for a lateral resolution of 1 μ m. Thanks to this superior resolution it is possible to detect statistically distributed areas with increased hydrophobicity which exhibit a reduced concentrations of sulfonic acid groups and an increased concentration of the polytetrafluoroethylene (PTFE) backbone. For

Aquivion® the diameter of the individual regions of $-\text{SO}_3^-$ depletion is found to be 5 - 15 μm ; the overall percentage of area with reduced SO_3^- occurrence is about 1.5 - 2% of the analysed surface area. Additionally, we compare FTIR transmission and ATR spectra that provide bulk and surface specific information, respectively.

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for Fuel Cell and Hydrogen Joint Technology Initiative under Grant No. 303452 (Impact).

CPP 11.7 Mon 18:00 ZEU 114

Gas permeation of carbon nanomembranes — ●VAHE CHINARIAN¹, MIN AI¹, SERGEY SHISHATSKIY², JAN WIND², XIANGHUI ZHANG¹, CHRISTOPH T. NOTTBOHM¹, NILS MELECH¹, ANDREAS WINTER¹, HENNING VIEKER¹, JUN QIU³, KARL-JOSEF DIETZ⁴, ARMIN GÖLZHÄUSER¹, and ANDRE BEYER¹ — ¹Physics of Supramolecular Systems, University of Bielefeld, 33615 Bielefeld, Germany — ²Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, 21502 Geesthacht, Germany — ³Performance Materials-Chemistry & Technology, DSM, 6160 MD Geleen, The Netherlands — ⁴Plant Biochemistry and Physiology, University of Bielefeld, 33615 Bielefeld, Germany

Gas permeation characteristics of carbon nanomembranes (CNMs) from self-assembled monolayers are reported for the first time. The assembly of CNMs onto polydimethylsiloxane (PDMS) support membranes allows determination of gas permeation characteristics. Single layer and triple layer CNMs with thicknesses of 1 nm and 3 nm were investigated in respect to permeation of hydrogen, helium, carbon dioxide, oxygen, nitrogen, argon, methane and ethane. In addition,

the CNM-PDMS composites were characterized by X-ray photoelectron spectroscopy, helium-ion microscopy as well as atomic force microscopy. A careful analysis about the contribution of the PDMS support membranes to the gas permeation allowed an estimate of the intrinsic CNM permeances. These values indicate a molecular sieve-like property of CNMs which is attributed to molecular-sized channels in CNMs.

CPP 11.8 Mon 18:15 ZEU 114

Perfluorinated compound rigidifies model lipid membrane — ●BEATE-ANNETTE BRÜNING¹ and BELA FARAGO² — ¹Soft Matter and Functional Materials, Helmholtz Zentrum Berlin, Berlin, Germany — ²Time-of-Flight and High Resolution, Institut Laue-Langevin, Grenoble, France

We report a combined dynamic light scattering (DLS) and neutron spin-echo (NSE) study on vesicles composed of the phospholipid 1,2-dimyristoyl-sn-glycero-3-phosphatidylcholine (DMPC) under the influence of varying amounts of perfluorooctanoic acid (PFOA). Mechanical properties of a model membrane and the corresponding bilayer undulation dynamics can be specifically influenced by changing its composition. We have performed DLS on vesicles composed of DMPC/PFOA mixtures to investigate changes in their respective size and corresponding center-of-mass diffusion. We study bilayer undulation and bulk diffusion dynamics using NSE, on time scales up to 200 ns. We calculate the bilayer bending rigidities κ for varying ratios of the perfluorinated compound, and obtain a bilayer stiffening for increasing amounts of the perfluorinated surfactant. Similar to the effect evoked by cholesterol, we attribute the observed stiffening to a condensing effect of the perfluorinated compound on the lipid bilayer.