CPP 13: Polymer Physics IV: Thin Films

Time: Tuesday 14:30–17:15 Location: H40

CPP 13.1 Tue 14:30 H40

Graphitizing polyimide surfaces — •Irina Lazareva, Yuri Koval, M. Alam, Stefan Strömsdörfer, Slava Dremov, and Paul Müller — Physikalisches Institut III, Universität Erlangen-Nürnberg Erwin-Rommel Str. 1, 91058 Erlangen, Germany

Various polymers can be converted to conducting state by ion irradiation. Recently we demonstrated that irradiation with Ar+ ions of energies even as low as 150 eV is effective. In contrast to high-energy ion bombardment, low-energy ion irradiation transforms only a thin surface layer. Depending on the irradiation conditions, the conducting layer can be partly or completely graphitized. We present our experimental results of graphitization of polyimide by Ar+ ions with energies between 150 eV and 1000 eV. The surface of the irradiated polyimide was investigated by atomic force and scanning tunneling microscopy. The atomic structure of the irradiated polyimide surface confirms the graphitic nature of the conducting layer. Transport properties of the graphitized layers were studied in the temperature range between 4.2 and 300 K. For high resistive films, the conductivity is provided by variable-range hopping. At high electric fields, the conductivity of the graphitized polyimide can be described by a Poole-Frenkel model. At temperatures below 10 K, tunneling becomes the main process of ionization, and a crossover to Fowler-Nordheim emission was observed. For higher radiation fluencies and higher process temperatures, the conductivity increased significantly and we observed semi-metallic behavior.

CPP 13.2 Tue 14:45 H40

Reversible charge storage and modification of thin polymer films investigated by electrostatic force microscopy — •Andreas Kleiner[1], Othmar Marti[1], Armin Knoll[2], Bernd Gotsmann[2], and Urs Dürig[2] — [1]Institute of Experimental Physics, Ulm University, 89069 Ulm, Germany — [2]IBM Research GmbH, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

Atomic force microscope (AFM) modes like force curve measurements, Pulsed Force Mode or intermittent contact techniques apply certain amounts of normal and lateral forces to the sample. In most cases this creates surface charges, similar to the macroscopic contact electrification of insulators. These charges can be imaged by Kelvin Probe or Electric Force Microscopy (KPFM / EFM). The quantity of charge depends on parameters like contact time, applied force or scanning velocity. By adjusting the tip voltage during contact, the amount and polarity can be controlled and charges can be erased and overwritten without change in the polymer structure. High voltages between tip and sample lead to raised topographic features due to the large non-uniform electric field. The height of these structures reaches several nanometers, depending on tip shape and applied voltage, and is reversible. Long-term measurements of these surface charges on different polymers at various temperatures will lead to a better understanding of charge storage and transport mechanisms on thin films.

CPP 13.3 Tue 15:00 H40

Assembly of diblock copolymers on patterned substrates: A "Single-Chain-in-Mean-Field-Simulation" study — •Marcus Muller and Kostas Daoulas — Institut fuer Theoretische Physik, Georg-August Universitaet, Goettingen

The directed assembly of diblock copolymers on patterned substrates is a way to create nanoscopically structured materials. We study the structure and kinetics of diblock copolymers on patterned substrates by simulating a large ensemble of independent chains in an external field. This external field depends on the density created by the ensemble of molecules and it is frequently updated as to mimic the instantaneous interactions of a molecule with its neighbors. This approximate, particle-based self-consistent field method allows to (i) incorporate arbitrary chain architecture (ii) includes fluctuations and (iii) the explicit propagation of the chain conformations in time permits us to study the kinetics of structure formation. The factors that control the accuracy of the method are quantitatively discussed [1] and the reconstruction of the soft morphology at substrate patterns that deviate from the periodic morphology of the diblock in the bulk are illustrated [2].

[1] K. Ch. Daoulas and M. Muller, J. Chem. Phys. 125, 184904 (2006); [2] K. Ch. Daoulas et al, Phys. Rev. Lett. 96, 036104 (2006)

CPP 13.4 Tue 15:15 H40

Demixing and dewetting in films of binary mixtures — •Santiago Madruga and Uwe Thiele — Max Planck Institute for the Physics of Complex Systems, Noethnitzer Str. 38, 01187 Dresden

Thin polymer films are often used in advanced technological applications either as homogeneous coatings or as structured functional layers. Their stability and therefore potential usage is mostly determined by the wettability properties of the substrate and is rather well understood for single component liquids.

However, in various applications the film consists of a binary mixture such as a polymer blend. Then the dynamics of the decomposition in the film and of dewetting of the film couple. This allows for new pathways of structuring like decomposition induced dewetting [1]. We complete the bulk description of the dynamics of a binary mixture (model-H) [2] with boundary conditions for the evolving free surface.

The model is used to analyse the spinodal decomposition of a film of a binary mixture. The composition gradients give rise to a solutal Marangoni effect that modifies the dynamics deeply. Linear results obtained with the full transport equations for (a) purely diffusive transport described by the Cahn-Hilliard equation and (b) diffusive and convective transport described by model-H between parallel plates are compared to the case of a free surface.

We acknowledge support by the EU under grant MRTN-CT-2004-005728. [1] R. Yeushalmi-Rozen, T. Kerle, and J. Klein. Science. 285, 1254-1256 (1999); [2] D.M. Anderson, G.B. McFadden, and A.A.Wheeler. Ann. Rev. Fluid Mech. 30, 139-165 (1998).

CPP 13.5 Tue 15:30 H40

Molecular-dynamics simulations of thin films with a free surface — •Simone Peter, Hendrik Meyer, and Joerg Baschnagel — Institut Cahrles Sadron, Strasbourg, France

We present results [1,2] from molecular-dynamics simulations for a model of non-entangled short polymer chains in a free standing and a supported film geometry. We investigate the influence of confinement on static and dynamic properties of the melt. We find that the relaxation at the surfaces is faster in comparison to the bulk. We perform a layer-resolved analysis of the dynamics and show that it is possible to associate a gradient in critical temperatures Tc(y) with the gradient in the relaxation dynamics. This finding is in qualitative agreement with experimental results on supported polystyrene (PS) films [Ellison et al, Nat. Mater. 2, 695 (2003)].

Furthermore we show that the y-dependence of Tc(y) can be expressed in terms of the depression of Tc(h), the global Tc for a film of thickness h, if we assume that Tc(h) is the arithmetic mean of Tc(y) and parameterize the depression of Tc(h) by Tc(h)=Tc/(1+h0/h), a formula suggested by Herminghaus et al [Eur. Phys. J E 5, 531 (2001)] for the reduction of the glass transition temperature in supported PS films. We demonstrate the validity of this formula by comparing our simulation results to results from other simulations and experiments.

[1] S. Peter, H. Meyer and J. Baschnagel, J. Polym. Sci. B, 44, 2951 (2006)

[2] S. Peter, H. Meyer, J. Baschnagel and R, Seemann, J. Phys: Condens. Matter (2007)

30 min. break

CPP 13.6 Tue 16:15 H40

Investigation of Polymer Surfaces by Dynamic Force Spectroscopy — •Jan-Erik Schmutz[1,2] and Hendrik Hölscher[1,2] — [1]CeNTech, Heisenbergstr. 11, 48149 Münster — [2]University of Münster, Wilhelm-Klemm-Str. 10, 48149 Münster

The atomic force microscope (AFM) is often used in dynamic modes to enhance the resolution compared to the conventional contact mode. The tapping mode where the cantilever is oscillating with a fixed frequency near the sample surface is the standard mode used in air and liquids. With a slight modification of the excitation it is possible to gain more information about the sample surface. This so-called constant-excitation mode (CE-mode) enables the direct and continous determination of conservative and dissipative tip-sample interactions [1]. Recently, we demonstrated the application of this technique to self-organizing DPPC films [2] which are frequently used as model systems

for biological membranes. Beside a comparable resolution to the tapping mode this technique also gives quantitative information about the material properties like adhesion force and contact stiffness. Here we apply this technique to the copolymers acrylonitrile butadiene styrene (ABS) and styrene butadiene styrene (SBS). The advantages of the CE-mode compared to the tapping mode will be discussed.
[1] H. Hölscher, B. Anczykowski, Surf. Sci. 579, 21 (2005)
[2] J.-E. Schmutz, M.M. Schäfer, H. Hölscher (submitted)

CPP 13.7 Tue 16:30 H40

Thin Films of Semifluorinated Liquid Crystalline Side Chain Block Copolymers — •Peter Busch[1,2,3], Sitaraman Krishnan[2], Marvin Paik[2], Gilman Toombes[4], Sol Gruner[3,4], and Christopher Ober[2] — [1]JCNS-FRMII, Lichtenbergstr. 1, TU München, 85747 Garching — [2]Department of Materials Science and Engineering, Cornell University, USA — [3]Cornell High Energy Synchrotron Source (CHESS), Cornell University, USA — [4]Department of Physics, Cornell University, USA

Fluorinated materials are interesting as coatings because of their low surface free energies. One possible approach to increase processability is the incorporation of semifluorinated alkenes as side chains to a polymerbackbone, which is part of a diblock copolymer.[1] The side chains arrange into liquid-crystalline, smectic layers, which increases the structural complexity compared to block copolymers with two amorphous blocks.

We present an X-ray study of a thin film of a diblock copolymer consisting of a polystyrene block and a semifluorinated, liquid-crystalline (LC) block. The focus will be the interplay between the self organization of the side chains into smectic layers and the mesoscopic arrangement of the polystyrene blocks with respect to the LC-block, which is strongly related the surface properties of the films.

[1] S. Krishnan, Y.-J. Kwark and C. K. Ober, The Chemical Record, 2004, 4, 315.

CPP 13.8 Tue 16:45 H40

Manipulation of smectic layers thickness in smectic elastomers by means of uniaxial stretching — •Victor Aksenov[1], Martin Rössle[2], Ralf Stannarius[1], and Rudolf Zentel[2] — [1]Otto-von-Guericke-Universität Magdeburg, Institut für Experimentelle Physik, Universitätsplatz 2, D-39106 Magdeburg — [2]Universität Mainz, Institut für Organische Chemie, Duesbergweg 10-14, D-55099 Mainz

The deformations of thin oriented films of smectic liquid crystal elastomers (LCE) have been studied on macroscopic and microscopic levels by small angle x-ray scattering (SAXS), optical reflectometry and polarized Fourier transform infrared (FTIR) spectroscopy [1, 2, 3] The polymeric network couples the microscopic characteristics such as director orientation and order parameter to the macroscopic dimensions of LCEs. For the material investigated in this work, it has been found that during stretching of free standing films with smectic layers parallel to the film surface, the optical thickness of the sample changes [1]. Small angle X-ray scattering (SAXS) measurements revealed the compression of the smectic layers in the SmA and SmC* phases [1]. The deformation induced tilt measured by polarized FTIR spectroscopy [3] is too small to explain the compression of the smectic layers.

[1] V. Aksenov, J. Bläsing, R. Stannarius, M. Rössle, and R. Zentel, 2005, Liquid Crystals, 32, No. 7, 805-813. [2] R. Stannarius, V. Aksenov, J. Bläsing, A. Krost, M. Rössle and R. Zentel, Phys. Chem. Chem. Phys., 2006, 8, 2293-2298. [3] V. Aksenov et al. 2008, Liquid Crystals (In press).

CPP 13.9 Tue 17:00 H40

Orientation and structural changes upon uni- and biaxial drawing of polyamide 6 — •Hussein Shanak[1], Karl-Heinz Ehses[1], Jan Lion[1], Peter Leibenguth[2], and Rolf Pelster[1] — [1]FR 7.2, Experimentalphysik, Universität des Saarlandes, Postfach 151150, 66041 Saarbrücken — [2]Lehrstuhl für Funktionswerkstoffe, Universität des Saarlandes, Postfach 151150, 66041 Saarbrücken, Germany

The influence of drawing on orientation, crystallinity, structural properties and anisotropy of polyamide 6 films was investigated. The samples were uniaxially and biaxially stretched. Their crystallinity as well as size and orientation of the crystallites were evaluated using X-ray diffraction. The orientation was analyzed using pole figures and hermans functions. In case of uniaxial drawing, the crystallinity increases and the films show strong orientation with increasing drawing ratio. The orientation of the biaxially drawn films is high and it is inhomogeneous, depending on the position on the film. The structural data is correlated with dielectric anisotropy that was measured at microwave frequencies.