

CPP 31: Thin Films

Time: Thursday 9:30–11:00

Location: C 264

CPP 31.1 Thu 9:30 C 264

Cylindrical phase of diblock copolymers in thin films — ●ROSA MARIANNE BREUER and BARBARA DROSSEL — Institut für Festkörperphysik, Hochschulstr. 6, 64289 Darmstadt

Diblock copolymers are polymers in which two chains of different monomers are covalently bound to one another. Because of their different chemical nature the blocks have a tendency to phase separate, but a macroscopic phase separation is prohibited by the chemical bond connecting the different blocks. Therefore such molecules have a tendency to separate on a microscopic scale forming a variety of ordered structures, called microphases. We investigate the microphases of diblock copolymers confined in a thin film with walls attracting one of the monomer types. We focus on the possible structures of copolymers that form cylindrical phases in the bulk. We employ both self-consistent field theory and strong segregation theory to obtain the concentration profile minimizing the free energy of the system and to compare the free energy of possible morphologies. We present a phase diagram showing the possible microphases for a diblock copolymer with fixed volume fraction and fixed segregation parameter in dependence of the film thickness and the affinity of the walls. We study the effects of numerical inaccuracies on the appearance of different morphologies and their free energies.

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3-Dimensional Control over lamella orientation in thick block copolymer films — ●VIOLETTA OLSZOWKA, LARISA TSARKOVA, and ALEXANDER BÖKER — Physikalische Chemie II, Universität Bayreuth, Germany

We present a novel route to produce thick films with long-ranged 3D ordered upstanding lamellae and a perfectly ordered nano-stripped surface pattern. Thick lamella polystyrene-*b*-poly(2-vinyl pyridine) diblock copolymer films are exposed simultaneously to a selective solvent vapor and to an in-plane electric field. The orientation of the lamellae was studied by combined scanning force microscopy, grazing incidence small angle x-ray scattering and transmission electron microscopy measurements. The lamellae orientation perpendicular to the film plane upon long-term selective solvent annealing was detected in a narrow window of the film thickness (about 17-22 lamella distances). In thicker and thinner films, lamellae were perfectly aligned parallel to the film plane due to the surface fields effects. Theoretical model is proposed to account for the thickness- and annealing time dependent reorientation of lamella domains. The observed phenomena presumably initiates in the interior of the film when the concentration fluctuations due to selective swelling overcome the suppression by the surface fields.

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Phase behaviour of ultra-thin polymer films grafted on Micro-Cantilever-Sensors (MCS) — ●SEBASTIAN LENZ¹, SEBASTIAN K. NETT^{1,2}, MINE MEMESA¹, RÜDIGER BERGER¹, JOCHEN S. GUTMANN^{1,2}, ANDREAS TIMMANN³, and STEPHAN V. ROTH³ — ¹Max-Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz (Germany) — ²Institute for Physical Chemistry, Johannes Gutenberg University, Jakob-Welder-Weg 10, D-55099 Mainz (Germany) — ³HASYLAB at DESY, Notkestr. 85, D-22603 Hamburg (Germany)

Phase behaviour of polymer films plays an important role to tailor surface properties of materials. Using a polymer blend mixture with a lower miscibility gap, we anticipate a phase transition from a one phase towards a two phase system upon changing temperature. As a suitable system a polymer blend composed of polystyrene (PS) and poly-vinyl-methyl-ether (PVME) [1] is chosen.

During phase transition, we want to correlate structural changes in the grafted polymer layer to surface stress induced curvature changes of the MCS over time. To study structural features in the nanometre scale and due to the small sample size of a polymer-coated cantilever we have to use recently developed characterization techniques. A combination of micro-focused Grazing Incident Small Angle Scattering (GISAXS) [2] and micro-focused X-Ray reflectivity was chosen to obtain structural information of the systems.

[1] Tanaka et al., *Macromolecules* 28, (1995) 934-938.[2] S.V. Roth et al., *Rrv. Sci. Instr.* 77, (2006) 085106.

CPP 31.4 Thu 10:15 C 264

Solvent content in thin spin-coated polymer films — ●JAN PERLICH¹, VOLKER KÖRSTGENS¹, EZZELDIN METWALLI¹, LEANDER SCHULZ¹, ROBERT GEORGI², and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department LS E13, James-Franck-Str. 1, 85748 Garching (Germany) — ²Forschungsneutronenquelle Heinz Maier-Leibnitz, TU München, Lichtenbergstr. 1, 85747 Garching (Germany)

The detection of remaining solvent in thin polymer films is important due to its effect on chain mobility and film homogeneity. It is essential for swelling experiments to define the initial state with respect to the amount of solvent included inside the film directly after preparation. Moreover, it gives an estimate on possible aging effects caused by the reduction of the solvent content. The investigation focuses on a well controlled model system, which consists of protonated polystyrene (PS) with different molecular weights, spin-coated out of protonated or deuterated solvent onto silicon substrates. Directly after spin-coating the thin films were investigated with neutron reflectometry at the MIRA instrument of the research neutron source FRM-II. A narrow qz range around the critical edge was probed with high resolution. Due to the high sensitivity of the position of the critical edge on the ratio of protonated PS and deuterated solvent, the exact position of the critical edge enables to determine the solvent content. Two different key parameters are addressed: the molecular weight of PS and the film thickness. In addition, annealing of the as-prepared films is discussed. We acknowledge financial support by project MU 1487/4-2.

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Temperature dependent swelling behavior of PNIPAM based block copolymer films — ●WEINAN WANG¹, PETER MÜLLER-BUSCHBAUM¹, KORDELIA TROLL¹, AMIT KULKARNI¹, CHRISTINE PAPADAKIS¹, ACHILLE M. BIVIGOU KOUMBA², and ANDRE LASCHEWSKY² — ¹TU München, Physik - Department E13, James-Franck-Str. 1, D-85747 Garching — ²Potsdam Universität, Inst. Chemie, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam-Golm

PNIPAM is one of the prominent stimuli-sensitive hydrogels because it has a relatively low collapse transition temperature at 32°C. To introduce an internal ordering and increase the mechanical stability in the films, the homopolymer is typically replaced by PNIPAM based block copolymers. We focus on how the internal structures depend on the temperature in the swollen state and how the transition temperature depends on the initial film thickness. The films are freshly made by spin coating. For the investigation of the morphologies of the films at different temperatures in the swollen state, especially the changes of internal structures, grazing incidence small angle X-ray scattering (GISAXS) and transmission X-ray scattering are performed. To detect the possible shift of the transition temperature with film thickness, in-situ ellipsometry is applied. It is observed that both the size and the ordering of internal structures are changed at the transition temperature. The transition temperatures of the films depend strongly on the initial film thickness and are significantly different from those of the bulk materials. In addition, atomic force microscopy (AFM) and X-ray reflectivity are also used for characterization.

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Glass transition and miscibility of polymer blends in ultra-thin films — ●DONGSHAN ZHOU^{1,2}, HEIKO HUTH¹, ALEXANDER MINAKOV¹, and CHRISTOPH SCHICK¹ — ¹Inst. Phys., Univ. Rostock, Germany — ²School. Chem. & Chemical Eng., Nanjing Univ., China

Glass transition and polymer blend miscibility in ultra-thin films is critical for their use as materials. Calorimetric studies can provide important information on finite size and interfacial effects on the phase separation. Here we use the recently developed differential alternating current chip calorimeter to study glass transition and miscibility of blend composed of equal mass ratio of polystyrene and poly(2,6-dimethyl-p-phenylene oxide) confined in thin film (5 ~ 320 nm). The step of heat capacity during the glass transition is well identified even for the thinnest film of c.a. 4.5 nm, showing the performance of the calorimeter to measure the change of heat capacity in the level of pJ/K [H. Huth, *J. Polym. Sci. B Polym. Phys.* 2006, 44, 2996]. Despite the remarkable change of thickness (from below 1/2 R_g to 13.5 R_g), both the glass transition temperature and the temperature range

of the transition keep unchanged in the frequency range available. The independence of the T_g with thickness in this work is in consistence with calorimetric measurements in thin films of single component polymers, but contrary to previous work on the same polymer blends based

on ellipsometry [J. H. Kim, *Macromolecules*, 2002, 35,311]. In the system under investigation we see only one glass transition, arguments on whether the miscibility is changed or not due to the confinement will be available after investigation on a wider range of compositions.