Kinetics Studies of Block Copolymer Thin Films using Small-angle X-ray Scattering under Grazing Incidence
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Polymer thin films have numerous technical applications as functional coatings. Polymer blends and block copolymers can be tailored for specific mechanical, optical, electrical, and chemical properties. The structure and properties of block copolymer thin films can be significantly different from the bulk: the presence of two interfaces, the air-film interface and the film-substrate interface, can induce preferential ordering in the films, particularly if the film thickness is on the order of the typical length scale of the block copolymer microstructure [1]. In Monte Carlo simulations of symmetric diblock copolymers, which form a lamellar phase in the bulk, it was shown that the lamellae orient parallel to the interface if interfacial energies of the blocks differ considerably, whereas for similar interfacial energies of the blocks a perpendicular orientation of the lamellae with respect to the interface is favorable [2].

We have studied the symmetric diblock copolymer system polystyrene-polybutadiene (PS-PB). Samples were prepared by spin-coating polymer solution onto silicon wafers covered with the native oxide. Using a combination of atomic force microscopy (AFM) and grazing-incidence small-angle x-ray scattering (GISAXS), we have found that the lamellae orient perpendicular to the substrate surface for films with a molecular weight of 183 kg/mol [3]. Fig. 1 shows an AFM image and the corresponding GISAXS intensity map of such a film. The lamellar period corresponds to the bulk lamellar period [4]. In the following we will describe how the kinetics of such a film can be studied during exposure to solvent vapor with in-situ GISAXS.

Fig. 1 AFM and GISAXS images of symmetric PS-PB films with a molecular weight of 183 kg/mol. The scan range of the AFM image is 3 μm × 3 μm with height variations of up to 80 nm. The GISAXS image shows scattering rods in the direction perpendicular to the sample. The rods occur at in-plane positions corresponding to the bulk lamellar thickness. The intense intensity at low qz is blocked by a rod-like beam stop. Both images indicate the formation of perpendicular lamellae. The film thickness is ~2300 Å in both cases.
The information contained in a GISAXS intensity map is shown schematically in Fig 2: the intense x-ray beam from CHESS D station impinges under grazing incidence onto the sample and the scattered intensity is recorded with an area detector [5]. The intensity in the scattering plane is determined by the specular and diffuse reflectivity and contains information on the laterally averaged density profile normal to the substrate surface [6]. Parallel to the surface, small-angle scattering features indicative of lateral ordering inside the film can appear. The weak scattering signals are measured at low incident angles slightly above the critical angle, so that the film is still fully penetrated by the x-ray wave. Why did we choose the grazing-incidence geometry? Typical and technically interesting substrates such as silicon wafers or glass have thicknesses on the order of 1 mm and would require rather hard x-ray beams for a transmission experiment. Furthermore, the weak scattering from a film of typically 200 Å to 2000 Å thickness can be obscured by diffuse scattering from the substrate, whereas in grazing-incidence geometry the penetration of the x-ray photons into the substrate is limited, if the angle of incidence is close to the substrate critical angle.

Spin-coating is a fast process and may lead to non-equilibrium structures. A method of probing the stability of such prepared films is to expose them to solvent vapor. Toluene is an almost non-selective solvent for the two blocks, and was used both as the solvent for spin-coating and for the vapor treatment. The sample cell consisted of an aluminum cylinder with 6 μm Kapton windows and a solvent reservoir below the sample holder. The solvent could be injected into the cell with a syringe and a long Teflon capillary from outside the hutch. In order to limit radiation damage of the films, the cell was shifted laterally before each measurement, to expose a fresh part of the sample to the beam. This way up to 30 pristine spots could be examined on a single sample.

We found that with 10 sec exposures and about 30 sec read-out time we could follow changes in the film morphology on a time scale of minutes. Before solvent exposure, the GISAXS image was characterized by straight scattering rods as shown in Fig 1. After only 1 min of solvent exposure these scattering rods started to curve inwards to form a partial ring (Figure 3a). This indicates that the previously perpendicular lamellae were starting to tilt or curve. After about 15 min of vapor exposure, the spread of the scattering intensity perpendicular to the surface was reduced, indicative of the swelling of the polymer film to about twice its original thickness. When the solvent vapor was removed, the film became thinner on a time scale of only a few minutes, and the scattering intensity again revealed straight scattering rods. Interestingly, during swelling and drying the lamellar period stayed approximately the same.

We investigated a total of 7 samples which all showed consistent results. AFM images taken after the vapor treatment showed ordered regions with a lamellar texture as well as micron-size blobs without any apparent structure. This indicates formation of inhomogeneities during swelling and subsequent drying; however, judging from the GISAXS images, the transformation was partially reversible. Hence the investigated spin-coated films seem to be relatively stable.

In summary, the GISAXS technique can be employed to investigate the lateral structure of polymer thin films with mesoscopic periods of up to ~1000 Å. The GISAXS scattering signal at D-line was strong enough to allow in-situ studies of the film kinetics on a time-scale of...
minutes, even for a low-contrast system like PS-P2B [1]. It is foreseen to include a GISAXS set-up for the new ultra-high flux CHESS G1 station presently under construction.

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Fig. 4 Action at D station: Peter Busch at keyboards and Tune Bonné at log book preparing for a vapor series.

Fig. 3 Time-evolution of the GISAXS pattern of the sample shown in Fig. 1 during exposure to toluene vapor: (a) 1 min, (b) 4 min, (c) 17 min, (d) 33 min after toluene injection into the sample chamber. Already after 1 min of exposure, the rods started to curve. After 17 min the film swelled to about twice its initial thickness, as estimated from the decrease of the vertical spread of the Bragg rod. After 33 min, no more significant changes were observed: the film appeared to have taken up the equilibrium toluene concentration at ambient temperature.

References