The structural rearrangements in block copolymer thin films have attracted considerable interest since vapor treatment is frequently used for annealing defects hampering applications. In-situ, real-time grazing-incidence small-angle X-ray scattering (GISAXS) is a very powerful method to determine the structural changes of block copolymer thin films with high time resolution and statistical relevance [1].

In the present work, we focus on poly(styrene-b-butadiene) (P(S-b-B)) diblock copolymers having a molar mass of 216 kg/mol which shown perpendicular lamellar orientation. Compared with parallel lamellae, perpendicular lamellae have severe geometrical constraints because the normal of the lamellar interfaces lies in the film plane and changes of the lamellar thickness are not easily accommodated. To investigate the structural changes during vapor treatment and drying, two different incident angles, one below and one above the critical angle of the polymer, were used in the GISAXS experiments. This way, we could discriminate surface-near order from the one in the bulk of the film. Cyclohexane was used to treat the samples; it is a good solvent for PB and a theta solvent for PS. Time-resolved GISAXS was performed at beamline BW4, HASYLAB at DESY. VIS interferometry was used to determine the film thickness during the vapour treatment. The time resolutions of GISAXS and VIS interferometry are 30 s and 1 s, respectively.

The presence of solvent in the microphase-separated, lamellar morphology not only lowers $T_g$ but also screens the repulsive interaction between the PS and the PB blocks. In the absence of solvent, $\chi_N = 190$; the diblock copolymer is deep in the strong-segregation regime. For a non-selective solvent, $N$ of the copolymer is decreased to $\chi_{\text{eff}}N$ with $\chi_{\text{eff}} = \phi\chi$ where $\phi$ is the volume fraction of polymer, calculated by $\phi = D_{\text{dry}}/D_{\text{film}}$, where $D_{\text{dry}}$ and $D_{\text{film}}$ are the film thicknesses of the as-prepared film and during vapor treatment, respectively. Using this assumption in spite of the slight selectivity of CHX, $\chi_{\text{eff}}N$ is estimated to decrease to 138 and 148 during the swelling, respectively, which is still significantly higher than 30; i.e., the block copolymer remains in the strong-segregation regime [2].
The variation of $D_{\text{lam}}$ was obtained by following the peak positions of the Bragg rods (BRs) in the 2D GISAXS images. The reduced lamellar thicknesses, defined as the ratio of the $D_{\text{lam}}$ values during the swelling and drying to the values of the as-prepared films, are plotted in Figure 1. Comparing with the behavior of the film thickness, we conclude that the swelling of the film is one-dimensional along the normal of the film surface, which is due to the geometrical confinement.

**Figure 2:** 2D GISAXS images during swelling (top row) and drying (bottom row). a) $\alpha_i = 0.18^\circ$ with rod beamstop as seen in the middle of each 2D image. Drying was started after 2480 s. b) $\alpha_i = 0.10^\circ$ without rod beamstop. The times after the beginning of the vapor treatment are indicated. Drying was started after 3000 s. The intensity scale is given on the right.

At $\alpha_i = 0.18^\circ$, the scattering signal is an average over the entire film thickness. The BRs bent inwards during the swelling (Figure 2a top). We attribute this bending to tilting of the lamellae away from the purely perpendicular orientation. During drying, the straight BRs reappeared (Figure 2a bottom) in such a way that, initially, they were very long along $q_z$ with very weak intensity; then, their intensity increased while their length decreased. Thus, we propose that the purely perpendicular orientation is lost due to the solvent uptake during swelling, while it is reinstalled during drying. At the end of the drying, the BRs became short again. At $\alpha_i = 0.10^\circ$, during swelling (Figure 2b, top row) the intensity of the BRs became weaker and weaker, which may be attributed to a loss of lamellar order near the film surface. During drying, a modulation appeared in-plane, i.e. at $q_y = 0$. Both the narrow and elongated DBRs and the modulation appeared during the drying are due to the protrusion of one block at the film surface. Since the solvent is slightly selective for the PB domains, the PS domains are more quickly depleted of the solvent and turn solid earlier than the PB domains. This means a characteristic time is passed after which there is practically no solvent left in the PS domains, while the PB domains are still swollen with solvent. Further evaporation leads to a collapse of the swollen PB domains to a level below the interface of the already rigid PS domains. This way, the protrusion structure is formed during drying.

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**References**
