Thin films of diblock copolymers with one crystalline block

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Block copolymers offer a wide range of surface morphologies in thin films due to their ability to microphase-separate into mesoscopic structures [1]. In thin films of diblock copolymers having one amorphous and one (semi-)crystalline block, the final structure formed depends on the competition between three transitions: the order-disorder transition of the diblock copolymer, the crystallization of the crystallizable block, and the vitrification of the amorphous block [2,3]. In the present study, we combine different techniques in order to relate crystal growth rate and the resulting surface textures to the orientation and spacings of the mesoscopic structures and the orientations within the films. By using grazing-incidence small-angle X-ray scattering (GISAXS), we have been able to characterize the mesoscopic structures within the thin films. Grazing incidence wide angle X-ray scattering (GIWAXS) provided detailed information on the orientation of the crystallites within the thin films as well as on the degree of crystallinity. This information about structures inside the film is complementary to the surface textures measured by atomic-force microscopy (AFM).

We have investigated a lamellae-forming poly(styrene-b-ethyleneoxide) (PS-b-PEO) diblock copolymer with the blocks having molar masses of 3,000 g/mol each. Samples were prepared by spin-coating from toluene solution onto Si wafers. The film thickness was ~760 Å. Crystallization of the PEO block was performed at different temperatures, \( T_x \), while monitoring the crystal growth by optical microscopy. In this way, we could ensure that the entire film was crystallized. The orientation of the PEO crystallites was studied by GIWAXS at BW2, Hasylab (incident angle \( \alpha_i = 0.16° \) and wavelength \( \lambda = 1.24 \) Å) and at Risø National Laboratory, Roskilde, Denmark (\( \alpha_i = 0.18° \) and \( \lambda = 1.54 \) Å). The lamellar orientation was monitored using GISAXS at BW4 [4] with the beam (\( \lambda = 1.38 \) Å) focused by Be lenses to a size of \( 78 \times 46 \) \( \mu \)m\(^2\), i.e. the length of the footprint was kept below 10 mm. The incident angles were chosen to be above the critical angle of total reflection of the polymer film (0.15°) so the beam penetrates the polymer film.

The surface morphology (Fig. 1) depended significantly on \( T_x \). At 25°C (Fig. 1a), crystallization resulted in a weakly textured morphology, whereas at \( T_x = 50°C \), large terraces having a height of 110 ± 5 Å were formed (Fig. 1b). The 2D GISAXS maps gave insight into the lamellar orientation and thickness (Fig. 1c and d). The
Bragg sheets were located at the positions expected from a DWBA model for parallel lamellae of thickness 160 ± 5 Å for \( T_x = 25 \, ^\circ C \) and 210 ± 5 Å for \( T_x = 50 \, ^\circ C \), respectively [5].

The 2D GIWAXS images showed a clear distinction of the crystalline texture in the two films (Fig. 2a, b). At \( T_x = 25 \, ^\circ C \) (fig. 2a), two strong and rather isotropic rings were observed: The first is due to the 120 reflection, whereas the second belongs to a group of reflections, namely 032, -132, -212, and 112. For films crystallized at \( T_x = 50 \, ^\circ C \) (fig. 2b), two peaks with a significantly narrower distribution were observed, which were assigned to the 120 and 032 reflections. Fig. 2c and d show simulated 2D GIWAXS images for films crystallized at \( T_x = 25 \, ^\circ C \) and \( T_x = 50 \, ^\circ C \), respectively. Using monoclinic unit cell parameters for the PEO crystals [6], simulations were obtained by varying both, the orientation angle of the unit cell c-axis with respect to the film normal and the width of the crystallite orientation. At \( T_x = 50 \, ^\circ C \), the c-axis of the unit cell is parallel to the film normal, whereas at \( T_x = 25 \, ^\circ C \), the c-axis is tilted by an angle of 35°. We note that the asymmetry in the intensities of figure 2b is due to the large size of the crystalline domains (Fig. 1b).

The degree of crystallinity was estimated from the high-resolution intensity profiles obtained at BW2. The percentage of crystalline domains in the films was found to be 62 and 98 % for \( T_x = 25 \) and 50°C, respectively (i.e. in the film plane) which suggest a more perfect PEO chain attachment at \( T_x = 50 \, ^\circ C \) than at \( T_x = 25 \, ^\circ C \). These findings are in consistency with the AFM images.

In summary, we have demonstrated that crystalline lamellae preferentially orient parallel to the film substrate for both crystallization temperatures, but the lamellar repeat distance increases with \( T_x \). At \( T_x = 25 \, ^\circ C \), the orientation of the PEO chain stems fluctuates around an average inclination angle of 35° with respect to the film normal, which is also causing the roughness of the film surface. For films crystallized at \( T_x = 50 \, ^\circ C \), the chain stems were found to be oriented mainly perpendicular to the film surface, promoting flat and terraced surfaces. This work is financially supported by DFG (Pa771/3), the Incentive Fund for Research Collaborations between TUM and Danish Technical University and the EU COST P12 program.

References