

Phase Morphology and Crystal Orientation Changes in Nano-Confined Lamellae of PEO-*b*-PS Block Copolymer

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Beamline: X27C

Introduction: The T_c -dependent crystals orientation changes had been found in low molecular weight PEO-*b*-PS block copolymer with a lamellar morphology [1]. Here, a high molecular weight PEO-*b*-PS block copolymer with a lamellar morphology is used to study the crystals orientation behaviors. With the molecular weight of PEO increasing, the layer thickness of PEO will also increase. The glassy PS layer will have less confinement on the crystallization of PEO, so the relationship between crystal orientation and T_c also changes.

Methods and Materials: The molecular weight of PS block was 26,100 g/mol and that of the PEO block was 23,100 g/mol, and the polydispersity is 1.05. The sample was subjected to large-amplitude oscillating shear (LAOS) under a dry argon atmosphere at 160 °C to achieve uniform, parallel alignment of the lamellar phase morphology. Simultaneous 2D SAXS and WAXS experiments were conducted at the synchrotron X-ray beamline X27C.

Results: Figure 1 shows 2D SAXS pattern on a shear-aligned sample when the X-ray beam is along shear direction. Up to four orders of scattering peaks can be observed, and $q/q^* = 1:2:3:4$ (q^* is the scattering vector of the first-order peak). This result indicates that the block copolymer lamellae are macroscopically aligned parallel to the shear direction. The first-order scattering peak corresponds to a Bragg spacing of 31.1 nm. Therefore, The thickness of the PEO and PS layers can be calculated to be 14.2 and 16.9 nm.

A relationship between the tilting angle and T_c for the PEO-*b*-PS block copolymer with different molecular weight is plotted in Figure 3. It can be seen that, compared with the low molecular weight diblock copolymer (9.2-8.7k), the temperature region of tilted PEO crystal orientation is much narrow for the high molecular weight diblock sample (26.1-23.1k). With the tilting angle increasing from the 0° to 90°, the temperature region for low molecular weight sample is 45°C (from -10°C to 35°C), that for high molecular weight sample is 20°C (from 0°C to 20°C). It may result from the less confinement of high molecular weight sample since its PEO layer thickness is much bigger than that of the low molecular weight sample. In addition, the crystal size, the crystal nucleation rate and growth rate will also affect the T_c -dependence crystal orientations.

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References:

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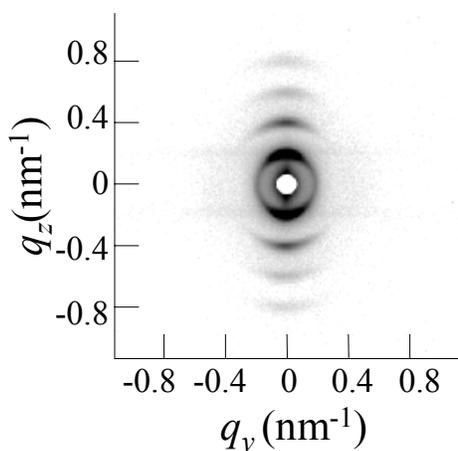


Fig. 1 2D SAXS obtained when the X-ray beam is parallel to shear direction.

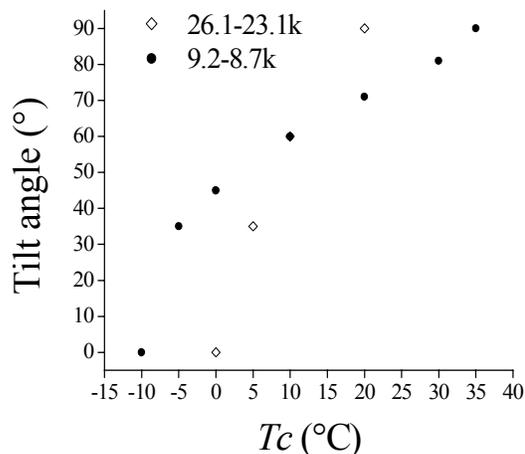


Fig. 2 The *c*-axis tilt angle (from the lamellar surface) dependence on T_c .