Crystallographic Studies of Crystalline Polymers within Nanoscale Confined Environments

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Microphase-separated lamellar microdomains (MDs) having various periodic dimensions were obtained from the self-assembly of a series of poly(4-vinylpyridine)-*b*-poly(ε-caprolactone) (P4VP-*b*-PCL) diblock copolymers having a variety of molar masses under a strong segregation limit. Crystallization of PCL segments in block copolymers was carried out within vitrified P4VP layers so as to create one-dimensional (1D) nanoscale confinement for PCL crystallization. Two effective confined sizes, which are employed to manipulate PCL crystallization, are 8.8 (69/46) and 11 (VP/CL 146/91) nm. The crystallographic geometry of PCL crystals in block copolymers was studied by combined small-angle and wide-angle X-ray experiments.

Crystal Orientation in Nanostructure. After melt-crystallization at 20 ^{o}C, the SAXS patterns along X and Y for VP/CL 146/91 are nearly identical, while there are no discernable Bragg arcs along the Z direction (Figure 1 (a)~(c)). Again, the strong anisotropy in 2D SAXS pattern indicates that the macroscopically aligned melt microphase-separated lamellar MDs, with its normal parallel to Z direction, is preserved after the crystallization process. As for the WAXS patterns the observed reflections could be indexed as (011), (200), (210) and (020) with the orthorhombic crystalline structure of PCL with a=0.7096 nm, b=0.4974 nm, c=1.7297 nm, and $\alpha=\beta=\gamma=90^{o}$[35-36]. Fig. 1 (d)~(e) shows a fiber-pattern-like pattern while Fig. (f) shows powder rings. The corresponding azimuthal profiles of these reflections in the 2D WAXD pattern along X (Fig. 1(d)) are shown in Fig. 1(g). The maximum intensities of all the observed reflections locate at the azimuthal angle, Φ = 90 and 270°. These results indicate that in PCL crystals the chain (c-axis) is oriented parallel to the microphase-separated lamellar surface normal (ñ) while the a and b axes are in the X-Y plan (Fig. 1(h)).

Next, we analyze what crystal orientation may be generated when the confining size is reduce below 8.8 nm. Decreasing the confined space to 8 nm, combined 2D SAXS (Figure 2 (a)~(c)) and WAXD (Figure 2 (d)~(f)) patterns for VP/CL 69/46 melt-crystallized at 20 ^{o}C indicates that the c-axis of the PCL crystals is oriented perpendicular to the normal ñ of the microphase-separated lamellae (i.e., parallel to the lamellar surface). The corresponding azimuthal profiles of these reflections in the 2D WAXD pattern along X (Fig. 2(d)) are shown in Fig. 2 (g). It is seen that the maximum diffraction intensity of the (110) reflection locates at the azimuthal angle, Φ = 53, 125, 231 and 300°; that of the (200) reflection is at Φ = 0 and 180°; that of the (210) reflections is at Φ = 34, 125, 217 and 321°; and that of the (020) reflection is at Φ = 90 and 270°. Indeed, the patterns display two meridional (200) reflections, two equatorial (020) reflections and two sets of quadrantal (110) and (210) reflections as shown in the schematic of the 2D WAXD pattern (Fig. 2 (h)).

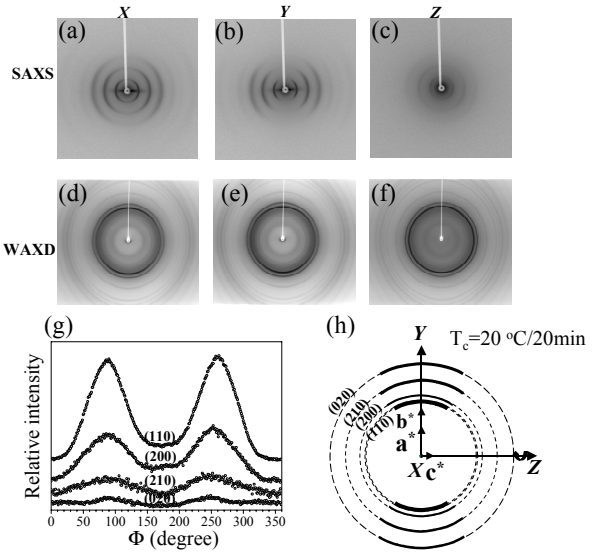

Figure 1. X-ray patterns of oriented VP/CL 146/91 samples isothermally crystallized at 20 ^{o}C from an ordered melt at 80 ^{o}C: 2D SAXS patterns with the beam parallel to the X- (a); Y- (b) and Z-direction (c); 2D WAXD patterns along the X- (d); Y- (e) and Z-direction (f) and (g) Azimuthal profiles for the 2-D WAXD pattern in Fig.1(d). (h) Corresponding reflections are indicated as shown in schematic of the 2D WAXD pattern.

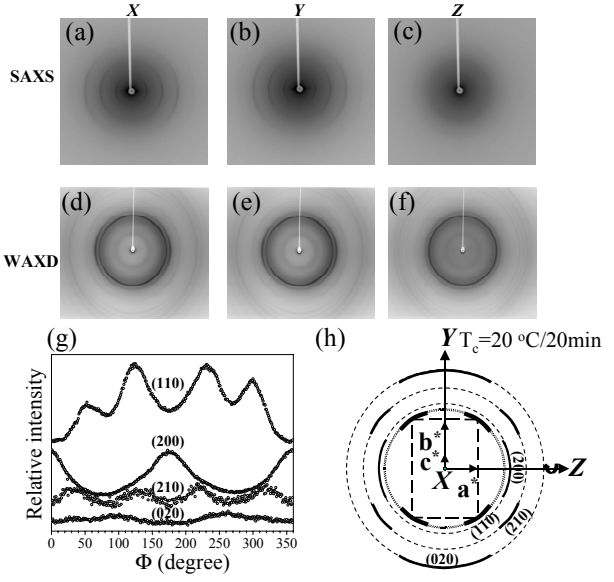

Figure 2. X-ray patterns of oriented VP/CL 69/46 samples isothermally crystallized at 20 ^{o}C from an ordered melt at 80 ^{o}C: 2D SAXS patterns with the beam parallel to the X- (a); Y- (b) and Z-direction (c); 2D WAXD patterns along the X- (d); Y- (e) and Z-direction (f) and (g) Azimuthal profiles for the 2-D WAXD pattern in Fig.2(d). (h) Corresponding reflections are indicated as shown in schematic of the 2D WAXD pattern.