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Crystallization of Poly(ε-caprolactone) Blocks Confined in Crystallized Lamellar Morphology of Poly(ε-caprolactone)-*block*-Polyethylene Copolymers: Effects of Polyethylene Crystallinity and Confinement Size

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1 Introduction

In crystalline-crystalline diblock copolymers with separate melting temperatures, poly(ε-caprolactone)-*block*-polyethylene (PCL-*b*-PE), crystal orientation of PCL blocks depended significantly on the size of spatial confinement provided by the crystallized lamellar morphology of PE blocks (PE lamellar morphology) [1]. In this study, we investigated the crystal orientation of PCL blocks spatially confined in the PE lamellar morphology with different crystallinities of PE blocks χ_{PE} and layer thicknesses of PCL blocks d_{PCL}, and elucidated the combined effects of χ_{PE} and d_{PCL} on the subsequent crystallization of PCL blocks.

2 Experiment

Samples PCL-*b*-PE copolymers with several χ_{PE} were synthesized using anionic polymerization. PE blocks crystallize first on quenching to form the crystallized lamellar morphology (PE lamellar morphology), followed by the crystallization of PCL blocks spatially confined in the PE lamellar morphology. E07 and E23 are PCL-*b*-PE copolymers with similar and smaller d_{PCL} (8.3 ~ 8.8 nm) and different χ_{PE} (χ_{PE} ~ 7 % for E07 and χ_{PE} ~ 23 % for E23). The uniaxial orientation of the PE lamellar morphology was carried out at 70 °C by applying the rotational shear to the samples in order to investigate the internal crystal orientation of PCL blocks.

Measurements The morphology formed in the system was investigated using two-dimensional synchrotron small-angle X-ray scattering (2D-SAXS), which was performed at beam line BL-10C in KEK-PF. The crystal orientation of PCL blocks was observed using two-dimensional conventional wide-angle X-ray diffraction (2D-WAXD).

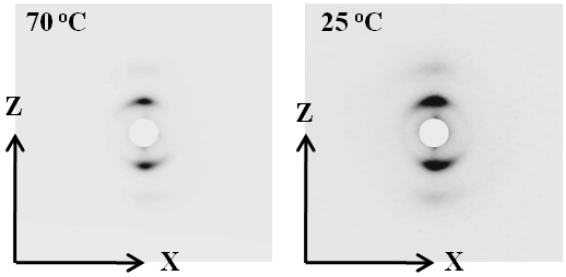

Fig. 1. 2D-SAXS patterns of uniaxially oriented E07 when viewed from the Y direction, which is perpendicular to the shear direction (X).

3 Results and Discussion

Fig. 1 shows the 2D-SAXS patterns of sheared PCL-*b*-PE at selected temperatures indicated. We find a couple of scattering spots on the meridian arising from parallel stacking of PE lamellae at 70 °C, showing that the PE lamllar morphology is preferentially oriented parallel to the shear direction. It is also found that these scattering patterns are maintained at 25 °C, where PCL blocks have already crystallized, indicating that PCL blocks crystallize within the oriented PE lamellar morphplogy.

Fig. 2 shows the diffraction intensity from the (110) plane of PCL crystals plotted against azimuthal angle φ evaluated from 2D-WAXD patterns at selected temperatures. At 0 °C, E07 has two distinct peaks at φ ~ 90 ° and 270 °, and E23 seems to have no peaks. At 45 °C, on the other hand, E07 still has two peaks similar to those at 0 °C, but E23 has four peaks at φ ~ 65 °, 115 °, 245 °, and 295 °. Fig. 2 indicates that the c-axis of PCL crystals in E23 changes almost random to perpendicular to the lamellar surface normal with increasing crystallization temperature T_c. The c-axis of PCL crystals in E07, however, is independent on T_c. These results suggest that when d_{PCL} is smaller, the PE lamellar morphology with higher χ_{PE} plays as hard confinement similar to glassy microdomains and that with lower χ_{PE} does as soft confinement similar to rubbery microdomains.

References

[1] T. Higa *et al.*, *Polymer* **51**, 5576-84, 2010.

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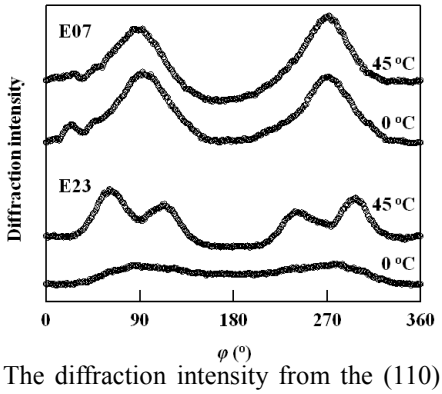

Fig. 2. The diffraction intensity from the (110) plane of PCL crystals plotted against azimuthal angle φ at T_c = 0 °C and 45 °C. φ = 0 ° and 180 ° correspond to the meridian.