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Crystalline Morphology Formed in Binary Blends of Crystalline-Crystalline Diblock Copolymers and Crystalline Homopolymers

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1 Introduction

In binary blends of A-B block copolymers and A homopolymers, the A homopolymer takes different miscible states in the microdomain structure; A homopolymers are uniformly mixed with A blocks (wet brush) or localized between A blocks (dry brush) [1]. In this study, we examine the crystalline morphology formed in binary blends of crystalline-crystalline diblock copolymers, poly(ε-caprolactone)-*block*-polyethylene (PCL-*b*-PE), and PCL homopolymers, where the PE blocks crystallize first on quenching from a lamellar microdomain structure to set a hard lamellar morphology in the blend, followed by the crystallization of PCL chains (PCL blocks + PCL homopolymers). We discuss the effect of the advance crystallization of PE blocks on the subsequent crystallization of PCL chains for different miscible states of PCL homopolymers.

2 Experimental

Samples: PCL-*b*-PE copolymers and PCL homopolymers were synthesized using anionic polymerization. The blends with various volume fractions of PCL homopolymers φ_{homo} were prepared using a solvent-casting method with benzene as a common solvent.

Measurements: The morphology formed in the blends was investigated using synchrotron small-angle X-ray scattering (SR-SAXS), which was performed at beam line BL-10C in KEK-PF. The melting temperature of PCL chains was obtained using differential scanning calorimetry (DSC) at a heating rate of 10 °C/min.

3 Results and Discussion

Figure shows the SAXS curves of blends with φ_{homo} = 0 (neat copolymer), 0.19, and 1 (neat homopolymer) at 120 °C, 70 °C, and 30 °C. Several scattering peaks are observed at 120 °C, where PE blocks and PCL chains are amorphous. The angular positions of these peaks correspond exactly to a ratio of 1:2:3:4, indicating a lamellar microdomain structure is formed in the blends. Similar SAXS curves are observed for the blends with various φ_{homo}. When the blends are quenched to 70 °C to crystallize PE blocks, the primary SAXS peak shifts to smaller *s* and the higher-order peaks completely disappear. This fact clearly indicates that the lamellar microdomain structure formed at 120 °C is replaced with the hard lamellar morphology by the crystallization of PE blocks (PE lamellar morphology). When the blends are quenched further into 30 °C to crystallize PCL chains, the SAXS curves are almost similar to those observed at 70 °C, suggesting that the PCL homopolymers are not expelled from the PE lamellar morphology and crystallize there.

It is found from DSC measurements that the PCL chains form a mixed crystal in the PE lamellar morphology when the PCL homopolymers are uniformly mixed with PCL blocks in the lamellar microdomain structure (wet brush). However, the PCL chains form separate PCL crystals in the PE lamellar morphology when the PCL homopolymers are localized between PCL blocks (dry brush).

[1] S. Koizumi *et al.*, *Macromolecures* **27**, 6532-6540, 1994.

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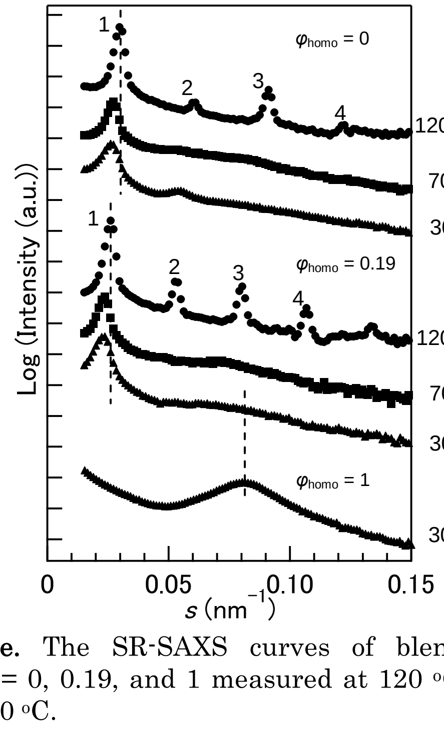

Figure. The SR-SAXS curves of blends with φ_{homo} = 0, 0.19, and 1 measured at 120 °C, 70 °C, and 30 °C.