

Crystallization Behavior of Double Crystalline Block Copolymer/Crystalline Homopolymer Blends

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1 Introduction

We have recently examined the crystalline morphology formed in binary blends of poly(ϵ -caprolactone)-*block*-polyethylene diblock copolymers (PCL-*b*-PE) and PCL homopolymers, and found that the morphology depended significantly on the miscible state between PCL-*b*-PE and PCL homopolymers before crystallization [1]. In this study, we investigate the crystallization behavior of PCL chains (i.e., PCL blocks in PCL-*b*-PE and PCL homopolymers), where the PCL homopolymer exists with different miscible states in the microphase-separated melt. From these results, we try to elucidate a substantial difference in the crystallization behavior of PCL chains on the basis of the miscible state of PCL homopolymers [2].

2 Experiment

Samples The PCL-*b*-PE and PCL homopolymers are the same samples used in our previous study [1]. We prepared two binary PCL-*b*-PE/PCL homopolymer blends, Blend 1 and Blend 2, where the PCL homopolymer was localized between PCL blocks in the lamellar microdomain structure in Blend 1, whereas it was homogeneously mixed with PCL blocks in Blend 2.

Measurements The isothermal crystallization behavior of PCL chains was examined using simultaneous SAXS/WAXD techniques with synchrotron radiation. The experiment was performed at beam line BL-10C in KEK-PF.

3 Results and Discussion

Figure shows the typical time-resolved SAXS (a) and

WAXD (b) curves for Blend 1 during isothermal crystallization at 38 °C. The SAXS curve at 120 °C has several scattering peaks arising from the lamellar microdomain structure (not shown in Figure a). By quenching to 38 °C, it turns into another one with diffuse scattering peaks (corresponding to the SAXS curve at $t = 0$ s in Figure a) due to the advance crystallization of PE blocks. This diffuse scattering peak grows remarkably by the subsequent crystallization of PCL chains (shown by an arrow). Two distinct scattering peaks (indicated by s^* and $2s^*$) can be observed after the complete crystallization of PCL chains (at $t = 1170$ s), the positions of which exactly correspond to a ratio of 1 : 2, suggesting a crystalline lamellar morphology is formed in the system. The WAXD curves have three appreciable diffraction peaks (Figure b). Because the diffraction pattern from PE crystals is extremely similar to that from PCL crystals, these peaks are combined diffractions arising from PE and PCL crystals.

The fundamental parameters characterizing the crystallization behavior were extracted from SAXS and WAXD curves, and we clarified the difference in the crystallization behavior of PCL chains between Blend 1 and Blend 2.

References

- [1] S. Gondo *et al.*, *Polymer* **54**, 6768 (2013).
[2] S. Gondo *et al.*, *Polym. J.*, in press (2015).

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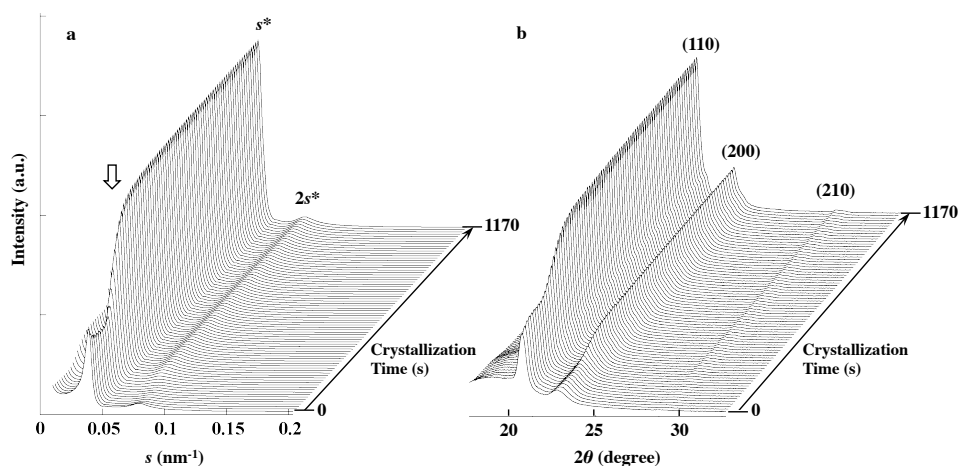


Figure. Typical time-resolved SAXS (a) and WAXD (b) curves for Blend 1 during isothermal crystallization at 38 °C. s^* in (a) represents the wavenumber of primary peak position and (110), (200), and (210) in (b) are the diffraction planes of PCL crystals.