Morphology formation in crystalline-crystalline diblock copolymers

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Introduction

It is well-known from recent studies that the morphology formed in crystalline-amorphous diblock copolymers is determined by a delicate balance among the driving force of crystallization (crystallization temperature), stability of microdomain structure (order-disorder transition temperature of microdomain structure), and mobility of constituent blocks (glass transition temperature of the amorphous block) [1,2]. In the crystalline-crystalline diblock copolymers, more complicated morphology formation will be expected, because the constituent block with higher melting temperature crystallizes first from the microdomain structure, followed by the crystallization of the lower melting block. In this study, the crystallization process of the lower melting block is mainly examined, where the lamellar morphology exists in the system by the crystallization of higher melting blocks.

Experimental

The crystalline-crystalline diblock copolymers used in this study are poly(ε-caprolactone)-*block*-polyethylene (PCL-*b*-PE) with various molecular characteristics, which were obtained by the hydrogenation of PCL-*block*-polybutadiene diblocks in the presence of the Adams catalyst PtO_2 (Table 1.). The melting temperature of the PE block (higher melting block) is *ca.* 100 °C and that of the PCL block (lower melting block) is *ca.* 60 °C. The PE block crystallizes quickly during quenching, so that we can observe the crystallization process of PCL blocks within the lamellar morphology formed by the crystallization of PE blocks.

Table 1. Characterization of samples

Notation	M_n[1]	M_w/M_n[2]	PCL:PE (vol.%)[3]
A1	8400	1.13	42:58
A2	11000	1.09	69:31
A3	18000	1.18	51:49
A4	29000	1.20	64:36

1) Determined by MO. 2) Determined by GPC.
3) Calculated from ^{1}H-NMR.

We quenched the sample from the microphase-separated melt into various crystallization temperatures T_c, and the crystallization process of PCL blocks was pursued by small-angle X-ray scattering with synchrotron radiation (SR-SAXS) at BL-10C. The SAXS intensity was collected as the sum of the scattered intensity during a period of 10 s.

Results

Figure 1 shows the time-resolved SAXS profile of A3 after quenching into 42°C. At $t = 0$, a shape scattering peak is observed, which arises from the microdomain structure in the melt. This peak disappears just after quenching and simultaneously the diffuse scattering peak appears at lower angle, for which the lamellar morphology of PE blocks is responsible. That is, the crystallization of PE blocks brings about morphological rearrangement from the microdomain structure into the lamellar morphology during quenching.

At $t \sim 2000$ s, the peak intensity gradually increases, suggesting that PCL blocks start to crystallize from the pre-existing lamellar morphology. Simultaneously the peak position shifts slightly to smaller angle, indicating that the alternating period of the lamellar morphology increases further with the crystallization of PCL blocks. This fact suggests that the lamellar morphology of PE blocks might be distorted by the crystallization of PCL blocks.
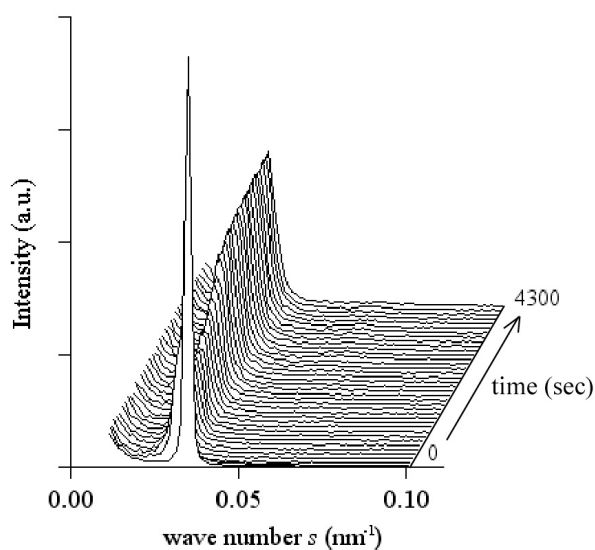

Figure 1. Time-resolved SAXS profile for A3 after quenching into 42°C.

References

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