



Crystallization of double crystalline block copolymer/crystalline homopolymer blends: 1. Crystalline morphology



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ABSTRACT

The crystalline morphology formed in binary blends of poly(ϵ -caprolactone)-*block*-polyethylene (PCL-*b*-PE) copolymers and PCL homopolymers has been examined using synchrotron small-angle X-ray scattering (SR-SAXS) and differential scanning calorimetry (DSC) as a function of the homopolymer fraction in the blend. The PE block crystallized first on quenching from a lamellar microdomain structure to set a hard lamellar morphology (PE lamellar morphology) in the blend, followed by the crystallization of PCL chains (*i.e.*, PCL homopolymers + PCL blocks). Two binary blends were studied by considering the miscible state of PCL homopolymers in the microdomain structure: when the PCL homopolymers were uniformly mixed with PCL blocks, they formed a mixed crystal. When the PCL homopolymers were localized between PCL blocks in the microdomain structure, DSC results suggested the possible formation of separate PCL crystals in the PE lamellar morphology. The effect of the advance crystallization of PE blocks on the subsequent crystallization of PCL chains was discussed as compared with the crystalline morphology formed in PCL-*block*-polybutadiene copolymer/PCL homopolymer blends, where the crystallization of PCL chains started directly from a microdomain structure without forming the hard lamellar morphology.

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1. Introduction

The crystallization of weakly segregated crystalline–crystalline diblock copolymers is extremely complicated because two different blocks crystallize from a microdomain structure existing in the melt to replace it with a new morphology [1–3]. Many studies are reported on such crystallization behavior and resulting morphology, where two crystallizations occur simultaneously [4–17] or separately [18–33] depending on the crystallizable temperatures T_c of constituent blocks. When T_c values of both blocks are close enough, we expect a simultaneous crystallization, that is, an interactive crystallization of both blocks [4–10,14,16,17] to show a characteristic morphology formation. In contrast, when T_c of one block is sufficiently higher than that of the other block, the higher- T_c blocks crystallize first to yield a hard lamellar morphology, an alternating structure consisting of thin lamellar crystals and amorphous layers, and subsequently the lower- T_c blocks crystallize within this morphology. For example, we investigated the crystallization behavior and resulting morphology of poly(ϵ -caprolactone)-*block*-polyethylene (PCL-*b*-PE) copolymers [21–27], where the PE blocks

crystallized first on quenching to form a hard lamellar morphology (PE lamellar morphology), followed by the crystallization of PCL blocks within this morphology. In this morphology formation, each crystallization process is substantially independent because the crystallizable temperatures of both blocks are largely separated.

Two kinds of crystallization starting from a microdomain structure are also achieved by blending crystalline A homopolymers into crystalline-amorphous A-B copolymers, because the crystallization behavior of A homopolymers would be slightly different from that of A blocks. Several experimental results are reported on the morphology formation in such binary blends [34–39], where the miscible state of A homopolymers in the microdomain structure (*i.e.*, uniformly mixed, localized, or macrophase-separated) significantly affects the subsequent crystallization behavior and resulting morphology. For example, we investigated the crystalline morphology formed in binary blends of PCL-*block*-polybutadiene (PCL-*b*-PB) copolymers and PCL homopolymers [34]. When the PCL homopolymer was uniformly mixed with the PCL block in the lamellar microdomain they formed a mixed crystal after crystallization, whereas two separate lamellar morphologies, one consisting of PCL blocks and the other PCL homopolymers, were formed when the PCL homopolymer was localized between PCL blocks (Fig. 1). In these systems, the microdomain structure is completely replaced with the lamellar morphology by the

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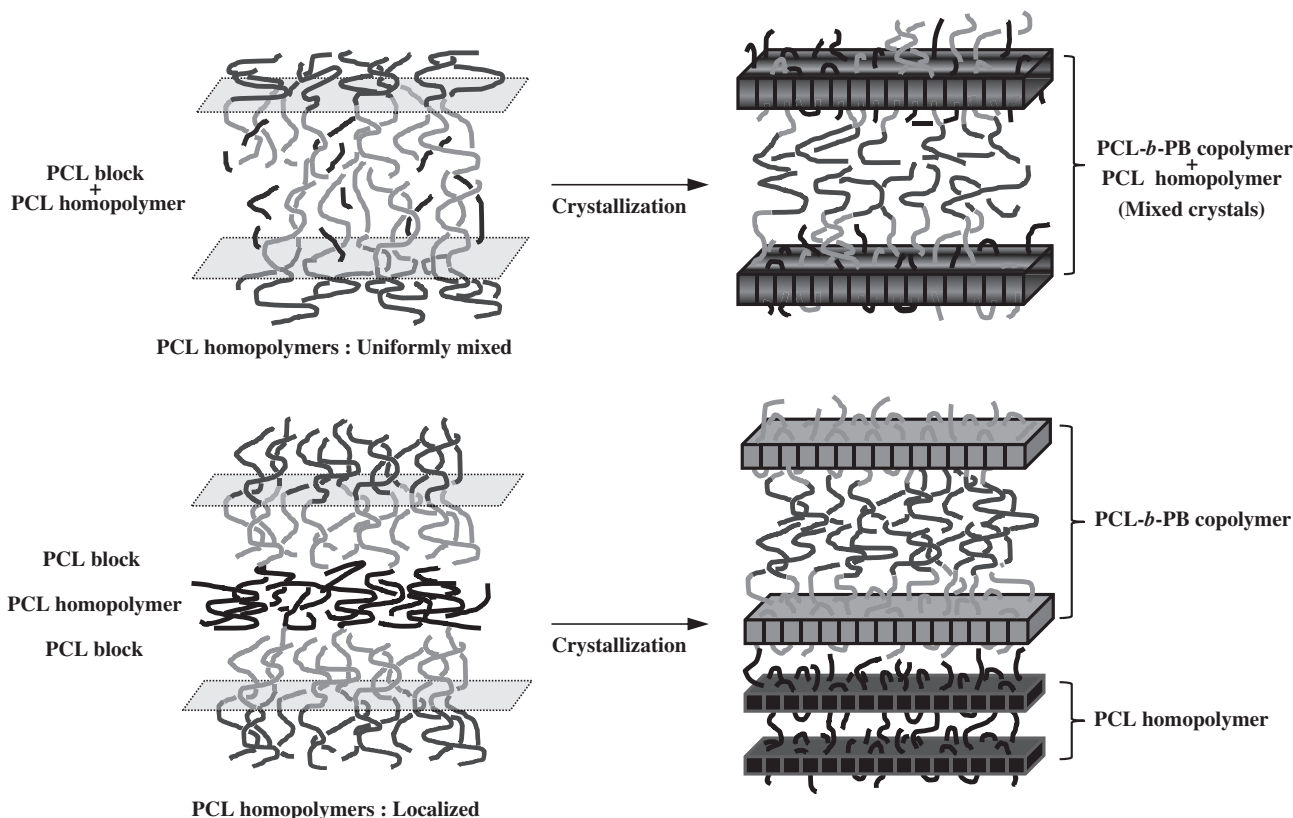


Fig. 1. Illustration showing the morphological transition occurring in PCL-*b*-PB copolymer/PCL homopolymer blends by the crystallization of PCL chains. Before crystallization, the PCL homopolymer is uniformly mixed with PCL blocks within the lamellar microdomain in the upper panel, whereas it is localized between PCL blocks in the lower panel.

crystallization of constituent blocks and homopolymers (*i.e.*, break-out crystallization). Therefore, it is intuitively anticipated that the PCL homopolymer has a chance to move extensively during crystallization to form a separate lamellar morphology.

In this study, we examine the crystalline morphology formed in binary blends of PCL-*b*-PE copolymers and PCL homopolymers, where the crystallizable temperature of PE blocks is sufficiently higher than that of PCL chains (*i.e.*, PCL blocks + PCL homopolymers). Consequently, the PCL chains are spatially confined in a hard lamellar morphology formed by the crystallization of PE blocks and forced to crystallize there, where the PCL homopolymer localized between PCL blocks can not move extensively to form a separate lamellar morphology. This is substantially different from the crystallization of PCL-*b*-PB copolymer/PCL homopolymer blends (Fig. 1), and a new point of the present study. We try to obtain a relationship among the miscible state of PCL homopolymers in the microdomain structure, PE lamellar morphology, and final morphology after the crystallization of PCL chains.

2. Experimental

2.1. Samples and sample preparation

The crystalline–crystalline diblock copolymer used in this study is poly(ϵ -caprolactone)-*block*-polyethylene (PCL-*b*-PE) and the crystalline homopolymer is poly(ϵ -caprolactone) (PCL). The synthesis method of PCL-*b*-PE copolymers was already described in our previous publications [21–26]. We synthesized two PCL-*b*-PE copolymers (denoted PCL-PE1 and PCL-PE2 in Table 1), and prepared two blends (Blend 1 and Blend 2) using an identical PCL homopolymer, which was synthesized in toluene by the ring-

opening polymerization of ϵ -caprolactone monomers with *n*-butyllithium as an initiator. The molecular characteristics of PCL-*b*-PE blocks and PCL homopolymer in Blend 1 and Blend 2 are shown in Table 1, where the specific volume of amorphous PCL homopolymers [40] and PE homopolymers [41] was used to evaluate the volume % of each block in PCL-*b*-PE. The two blends are different in the miscible state of PCL homopolymers within the microdomain structure, which was achieved by controlling the molecular weight ratio of PCL blocks and PCL homopolymers. Actually, we find later that the PCL homopolymer is localized between PCL blocks in the lamellar microdomain structure in Blend 1, whereas it is homogeneously mixed with PCL blocks in Blend 2.

The blends with various volume fractions of PCL homopolymers ϕ_{PCL} were prepared using a solution-casting method with benzene as a common solvent. First, the PCL-*b*-PE copolymer and PCL homopolymer were dissolved uniformly in benzene and the solution was cast on a glass plate. The solvent was gradually evaporated under vacuum at 120 °C for more than 12 h to remove the last trace of benzene.

2.2. Synchrotron small-angle X-ray scattering measurements

The morphology formed in the blends at 120 °C (PE blocks and PCL chains melted), 70 °C (PE blocks crystallized and PCL chains melted), and 30 °C (both crystallized) was examined using small-angle X-ray scattering with synchrotron radiation (SR-SAXS), which was performed at Photon Factory in High Energy Accelerator Research Organization, Tsukuba Japan, with a small-angle X-ray equipment for solution installed at BL-10C beam-line. Details of the equipment and the instrumentation are already described elsewhere [42–44]. The scattered intensity from the samples was

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