

Crystal Orientation of Poly(ϵ -caprolactone) Blocks Confined in Crystallized Lamellar Morphology of Poly(ϵ -caprolactone)-*block*-Polyethylene Copolymers.

1. Experimental Results

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Introduction

Morphology formation in crystalline-amorphous diblock copolymers is extremely complicated due to the interplay between microphase separation and crystallization. When the glass transition temperature of amorphous blocks is sufficiently higher than the crystallization temperature of crystalline blocks (hard confinement) or two blocks are strongly segregated (soft confinement), crystallization occurs within this structure to yield the crystallized microdomain structure. In this study, we investigate the crystal orientation of poly(ϵ -caprolactone) (PCL) blocks spatially confined in the solid lamellar morphology formed by the crystallization of polyethylene (PE) blocks in PCL-*b*-PE copolymers.

Experimental Section

Samples Several PCL-*b*-PE copolymers were synthesized by anionic polymerization. The crystallizable temperature of PE blocks is sufficiently higher than that of PCL blocks, so that the PE blocks crystallize first to form the solid lamellar morphology (PE lamellar morphology), followed by PCL crystallization when PCL-*b*-PE is quenched from the microphase-separated melt into low temperatures.

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

Results and Discussion

We first obtained the morphology formed in the system using SR-SAXS. The SAXS curve at 120°C (where both blocks were amorphous) had a couple of sharp scattering peaks, the angular positions of which exactly corresponded to a ratio of 1 : 2 : 3, indicating the lamellar microdomain structure is formed. The SR-SAXS curve at 70°C (where PE was crystallized and PCL amorphous) had diffuse scattering peaks, the positions of which also corresponded to a ratio of 1 : 2 : 3, suggesting the PE lamellar morphology is formed. However, the primary peak position was significantly different between SR-SAXS curves at 120°C and 70°C, indicating that

morphological transition has occurred by the crystallization of PE blocks.

The uniaxial orientation of the PE lamellar morphology was carried out at 80°C by applying the rotational shear to the samples. Fig. 1 shows the 2D-SAXS patterns of sheared PCL-*b*-PE at 70°C. We find several diffraction spots on the meridian arising from parallel stacks of the PE lamellar morphology, showing the PE lamellar morphology is preferentially oriented parallel to the shear direction. These diffraction patterns did not change substantially after PCL crystallization, so that the uniaxial orientation of the PE lamellar morphology was preserved after crystallization.

Fig. 2 shows the typical 2D-WAXD patterns at 70°C. We find clear (110) and (200) diffractions of PE crystals. After cooling the samples into low temperatures (where both blocks were crystallized), we had combined 2D-WAXD patterns consisting of PE and PCL diffractions. The WAXD patterns can be analyzed to get information on crystal orientation of PCL blocks as a function of crystallization temperature and confinement size.

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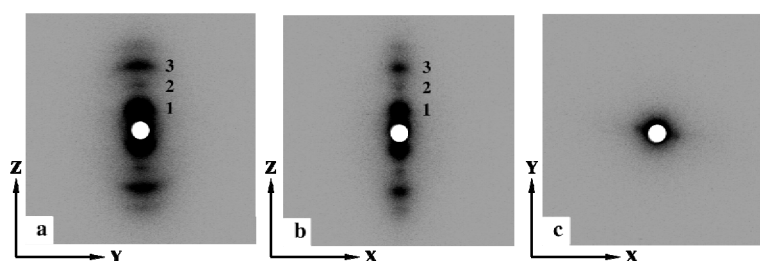


Fig. 1. 2D-SAXS patterns at 70°C for uniaxially oriented PCL-*b*-PE viewed from X (a, shear direction), Y(b), and Z (c) directions.

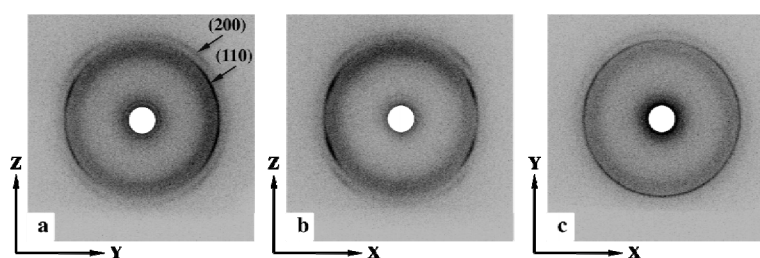


Fig. 2. 2D-WAXD patterns at 70°C for uniaxially oriented PCL-*b*-PE viewed from X (a, shear direction), Y(b), and Z (c) directions.