Materials Science

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Orientation Structure of Semi-Crystalline Block Copolymer Polybutadiene-*b*-poly(ε-caprolactone) Induced by Crystallization

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Introduction

Crystallization behavior in confinement space such as microphase separation among some semicrystalline block copolymer has been often studied by many researchers, including study on structure development of crystalline in crystallizable component. In this study, the crystalline structure (orientation) of semi-crystalline block copolymer, polybutadiene-*b*-poly(ε-caprolactone) (PB-*b*-PCL), was investigated by small and wide-angle X-ray scattering (SAXS & WAXS) in oriented microphase separated structure.

Experimental

Sample Preparation

PB-*b*-PCL was synthesized by sequential anionic polymerization. Number averaged molecular weight, molecular weight dispersed index, and volume fraction of PCL were 9300, 1.7, and 63. PCL melting point T_m was 60 °C by obtained DSC. In molten state above T_m, the sample showed a lamellae microphase separated structure confirmed by SAXS measurement. The lamellar microdomain was oriented in the melt-state by application of an elongational flow field in a channel (10mm wide) die at 75 °C (above T_m of PCL) for 1 min, hold for 10 min, and the sample was crystallized isothermally at 40, 25, 0 °C and quenched to liquid nitrogen temperature. The sample thickness decreased from 2 to 1 mm by the orientation.

Result and Discussion

Figure 1 shows SAXS patterns of PB-b-PCL crystallized at 298K for an hour, which was measured at 298K, (a) edge view, (b) end view, and (c) through view. In the each view, y-direction corresponds to the flow direction, z-direction is a weighted direction and perpendicular to the y, x-direction is perpendicular to the both directions. In the edge view, scattering peaks were observed in equatorial and meridian direction, but the peaks in the meridian were weaker. Scattering position of the each direction was quite different. In the end view, the same tendency was obtained, but the peaks in the meridian were less observable than those in edge view. In the through view, a relatively weak ring (slightly oriented) pattern was observed. The domain spacing *d* corresponding to equatorial peaks in the end and edge views was calculated to be 28.2 nm. The *d* due to meridian peaks was 22.8 nm, which coincides with the *d* from the rings in the through view. From SAXS measurement indicates an anisotropic structure, the lamellae microdomain was considered to be oriented (parallel) to the flow direction. The rings in the through view can be assigned to the crystalline-amorphous alternative structure in the microdomain, no scattering from a lamellae microphase separation was observed.

To elucidate the orientation structure of microphase separation and crystalline, we measured 2D WAXS. As a result of WAXS measurements, c-axis of crystalline of PCL in the microdomain was predominantly oriented parallel to the lamellae microdomain plane. At lower crystallization temperature, a probability of the orientation of the *c*-axis perpendicular to the lamellae plane increased. Increasing T_c induced more dominant orientation parallel to the microdomain plane of the *c*-axis. The orientation of crystalline of PCL was opposite behavior reported previously in the semicrystalline block copolymers.[1] The mechanism of present study is still under investigation.

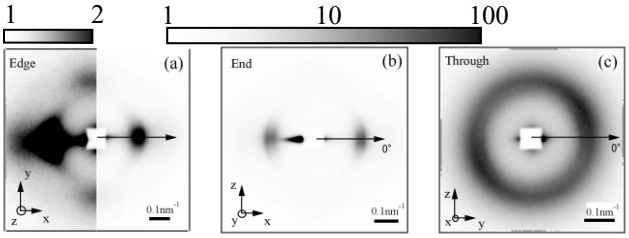

Figure 1. 2D SAXS patterns of PB-b-PCL crystallized at 298K.

References

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