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Relation of Structural Change to Local Molecular Dynamics of Semi-Crystalline Block Copolymer During Crystallization

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Introduction

The crystallization of semi-crystalline block copolymer was affected by the stability of microdomain structures. When the stability of microdomain structures is enough low (*e.g.*, the molecular weight of the block copolymer is small), the morphological reorganization takes place from a microdomain structure into a lamellar morphology (*i.e.*, alternating structure composed of crystalline and amorphous layers) by a large driving force of crystallization. On the other hand, when the stability of microdomain structure is enough high, the crystallization proceeds within the microdomain structure without any morphological change to yield the *crystalline microdomain structure*. In the case of the crystallization in the spherical microdomain, very large supercooling was required to initiate the crystallization.

Here, we investigated the structure change of polybutadiene-*b*-poly(ε-caprolactone) (PB-*b*-PCL) by SAXS/WAXD measurements and the chain mobility of PCL by ESR. PB-*b*-PCL used forms spherical microphase separated structure, where PCL is minor component. We can obtain the two states of PCL by choosing crystallization/annealing temperature. One has no PCL crystalline in the sphere; the other includes the crystalline. The relation of chain mobility in amorphous region of PCL with the structure in the spherical microdomain was investigated

Experiment

The PB-*b*-PCL used in this study was synthesized by a sequential anionic polymerization. The polymerization was terminated by CO_2 and CH_3COOH to introduce a functional group of COOH at the chain end in order to spin-label. M_n of PB and PCL blocks and the polydispersity index (M_w/M_n) were 120,000 g/mol, 16,000 g/mol, and 1.1, respectively, which prescribed the volume fraction of PCL f_{PCL}=0.10. Small and wide-angle X-ray scattering (SAXS & WAXS) measurements were performed at beam line BL-9C and 15A in Photon Factory of KEK in Tsukuba, Japan. SAXS and WAXS detectors were one dimensional position sensitive proportional counter (PSPC) with an effective length of 10 cm. The wavelength of X-ray was 0.15 nm. The detector of the SAXS and WAXS was located at the distance of 100 cm and 70 cm, respectively. Collagen and tripalmitin were used as a standard specimen to calibrate SAXS and WAXS, respectively. The scattering intensities were corrected for the background scattering and sample absorption.

Result and Discussion

After PB-b-PCL was super cooled to 333 K to crystallize PCL block, SAXS/WAXS measurements were conducted on heating to 343 K and cooling. Figure 1 shows the SAXS profiles for the heating where sample includes crystalline) and cooling process (without crystalline) at 298K (below T_m). A slight change of scattering with crystallization was observed. For instance, the scattering peaks become broader and shift slightly to a large *q*. These facts indicate that a deformation of the spherical microdomain occurred with the crystallization. To clarify the detail of this deformation, we calculated the SAXS profile by using the shape factor. The spherical micriodomain was assumed to be deformed into ellipsoid-like objects. The resulting profiles (solid lines) are shown in the Figure. We independently investigated a chain mobility of PCL chain end located in the amorphous region of PCL. The PCL amorphous region was found to be mobile on cooling process, where PCL was completely amorphous, in comparison with on heating where PCL was partially crystallized). The density of amorphous region in each state can be calculated as assuming the PCL sphere and ellipsoid-like shapes which were determined by simulation of SAXS profiles. The estimation revealed the density of PCL amorphous was low on heating process, *i.e.*, when PCL was crystallized. The low density of PCL amorphous in PCL domain was related to the high mobility of PCL chain in amorphous region.

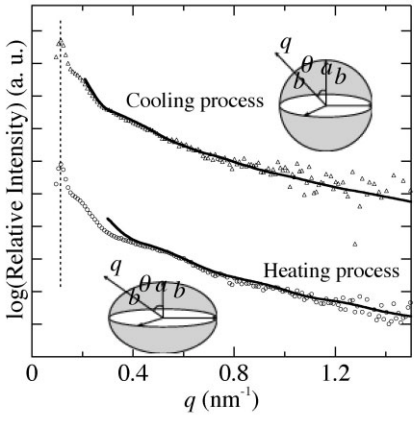

Figure 1. SAXS profiles on cooling (upper) and heating (bottom) measured at 298 K, where PCL was fully amorphous and partially crystallized, respectively.

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