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Time-Resolved Small- and Wide-Angle X-ray Scattering Studies on Structure Formation in Crystalline Graft Copolymers

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Introduction

Semi-crystalline block copolymers can exhibit considerable morphological richness, arising from the two forces which can drive structure development microphase separation between unlike blocks in the melt, which favors the formation of nanometer length scale domains (e.g., spheres, cylinders, lamellae), and crystallization of one block, which favors the formation of alternating amorphous and crystalline layers. In addition, a glass transition temperature of amorphous blocks is an important key to understand the crystallization behavior of crystalline-amorphous block copolymers. In this study we synthesized well-defined semi-crystalline polymers, by sequential anionic polymerization. Crystallization behavior of these polymers was investigated using wide and small angle X-ray scattering (WAXS and SAXS).

Experimental

All precursors, polybutadiene homopolymer (PB), polybutadiene-*b*-polystyrene (BS), and polybutadiene-*b*-polystyrene-*b*-polyisoprene (BSI), were synthesized via sequential anionic polymerization in toluene. Synthesized polymers have a narrow molecular weight distribution ($M_w/M_n < 1.1$). Semi-crystalline polymers, PE, HBS, and HBSI, were obtained by hydrogenation of PB, BS, and BSI, respectively. Table 1 shows characteristics of semi-crystalline polymers. The measurement was performed at beam line BL9C and 15A. The SAXS detector was one-dimensional position sensitive proportional counter (PSPC) located at a distance of 1.0 m (BL9C) and 2.3 m (BL15A) from the sample position. The WAXS detector (PSPC) was located at a distance of 0.7 m (BL9C) and 0.3 m (BL15A) from the sample position. Collagen and tripalmitin were used as standard specimens to calibrate the SAXS and WAXS detectors, respectively. The experimental data were corrected for the background and sample absorption. Isothermal crystallization experiments were performed as following procedure: the samples were annealed at 423K for 20 min and then quenched to crystallization temperatures to isothermally crystallize PE. Date acquisition time was 28 sec.

Table 1. Characteristics of semi-crystalline polymers

Sample	$M_{n,\,total}$ (kg/mol)[a]	ϕ_E[b]	ϕ_{PS}[b]
HBSI	42000	0.31	0.53
HBS	42000	0.54	0.46
PE	20000	1	-

[a] determined by GPC PS standard. [b] volume fraction.

Result and Discussion

The crystallization rate R_c for PE decreased as T_c increased. On the other hand, the R_c for HBSI had little dependence of T_c and was slower than for PE. This behavior suggested immobile glassy PS restricted the mobility of PE chain in the microdomain. The change in intensity of the primary peak arising from microphase-separated lamellar structure was well-described by the Avrami equation. Figure shows Avrami plots during isothermal crystallization of (a) HBSI and (b) PE. The Avrami exponent (n) for HBSI was constant (n=1.5) without reference to T_c and very different from those for PE (n=3.0). This result reflected that the crystallization of PE in the HBSI was confined within lamella microdomain structure. In diblock copolymer, small exponent was also obtained.

In semi-crystalline diblock copolymer, HBS, crystallization rate R_c slightly decreased in comparison with triblock copolymer HBSI. The glass transition temperature of PS block in HBSI was considered to be lower than that of HBS because soft segments, polyisoprene, attached to the PS in triblock polymer. In general, soft component in block copolymer reduce a glass transition temperaure of hard component. The R_c of crystalline polymer surrounded by soft segments is proposed to be reduced by other researchers. In this case, the R_c depression can be interpreted by this effect. And the stability of microdomain structure may affect this phenomenon. The triblock may have more stable structure under the crystalline temperatures.

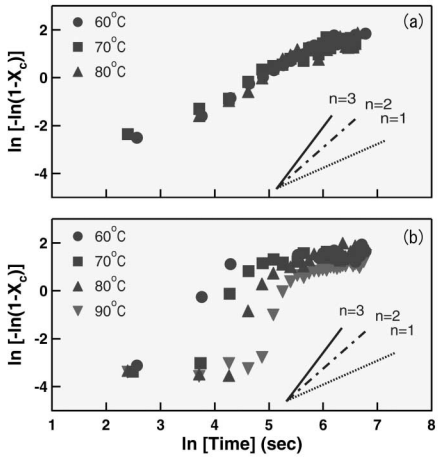

Figure 1. Avrami plots during isothermal crystallization of (a) HBSI and (b) PE.