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Characteristic Melting Behavior Observed in Crystalline-Amorphous Diblock Copolymers

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Introduction

The heating process of crystalline-amorphous diblock copolymers, polynorbornene-*block*-polynorbornene derivative (PNB-*b*-PNBX), has been investigated by time-resolved small-angle X-ray scattering with synchrotron radiation (SR-SAXS), where we observed a strong SAXS intensity appearing at small angles when PNB blocks melted during heating (Fig. 1 arrow). In this study, we investigate the condition to observe such strong SAXS intensity.

Experimental Section

Samples

The molecular characteristics of PNB-*b*-PNBX are shown in Table 1. All the samples were first annealed at 170 °C for 5 hours and cooled down to room temperature at a rate of 0.8°C /min before heating measurements. In addition, B68 was isothermally crystallized at 110 °C for 0 (quench), 7, and 14 hours to change the crystallized morphology formed in the system.

SR-SAXS Measurements

The time-resolved SR-SAXS experiment was performed at beam line BL-10C. The background scattering and Lorenz factor were taken into account, and finally the relative intensity was obtained as a function of wave number s (= $(2/\lambda)$ sin θ, 2θ: scattering angle and λ = 0.1488 nm).

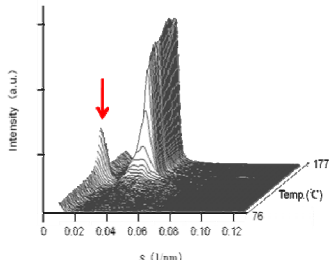

Fig. 1. Time-resolved SR-SAXS during heating from 76ºC to 177ºC.

Table 1. Molecular characteristics of PNB-*b*-PBBX used in this study

Sample	fPNB (vol.fra)	Mn	Mw/Mn	Tm (℃)	Tc (℃)	Tg (℃)
B12	0.12	20600	1.26	111.0	50.0	121
B18	0.18	28200	1.23	109.0	56.4	106
B25	0.25	24600	1.29	103.4	56.7	123
B30	0.30	25400	1.14	116.0	67.4	123
B33	0.33	25200	1.25	116.4	65.7	124
B49	0.49	22800	1.12	127.3	74.4	-*
B61	0.61	46300	1.20	131.2	108.2	125
B66	0.66	52200	1.21	133.8	111.4	126
B68	0.68	31000	1.13	135.0	108.8	125
B79	0.79	43900	1.09	143.6	123.2	133
B81	0.81	59900	1.13	143.0	115.0	136
PNB	1.00	9100	2.18	135.9	117.0	-
PNBX	0	14900	2.02	-	-	141

Results and Discussion

The strong intensity at small angles were observed only for PNB-*b*-PNBX with the volume fraction of PNB ϕ_{PNB} >0.30. This SAXS intensity increased with increasing ϕ_{PNB}. The temperature range in which this small-angle scattering appeared exactly corresponded to the melting temperature of PNB blocks measured by DSC (Fig. 2). The glass transition temperature of PNBX blocks was also close to this temperature range, but seemed not to be intimately related to the strong intensity. It is not clearly whether there was correlation between the glass transition and the scattering intensity at small angles.

We performed SR-SAXS measurements during heating of B68 with different thermal histories. When B68 was quenched from the microdomain structure, PNB blocks crystallized within the existing micriodomain. However, when B68 was annealed at *Tc* for 7 or 14 hours, a morphological transition occurred to yield the crystallized lamellar morphology. The strong SAXS intensity t small angle was confirmed for every sample, but the SAXS intensity at small angles increased with increasing annealing time. This means the crystallized lamellar morphology shows stronger SAXS intensity at small angles than the crystallized microdomain when PNB is melted during heating, suggesting that the small–angle SAXS intensity is related to the morphological transition from the lamellar morphology to the microdomain structure.

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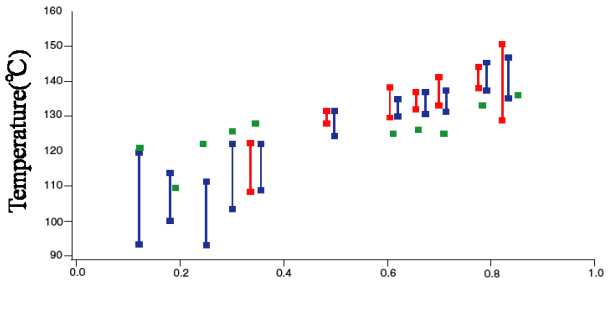

Fig. 2 melting temperature of PNB blocks (■), glass transition temperature of PNBX (■), and the temperature range of strong intensity at small angles (■) are plotted against ϕ_{PNB}