Effect of Polyisoprene Molecular Weight on Morphological Transition in Binary Blends of Styrene−Isoprene Diblock Copolymer and Polyisoprene

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Diblock copolymers self-assemble into a variety of microstructures such as lamellae (L), hexagonally ordered cylinders (HEX), and body-centered-cubic (bcc) spheres.[1] In recent studies, a number of so-called complex phases, such as gyroid (G) with $Ia\bar{3}d$ symmetry and hexagonally perforated phase (HPL), have also been observed in a narrow region of composition between L and HEX phases.[2−5]

When a homopolymer is homogeneously mixed with a diblock copolymer, various structures similar to those observed with pure block copolymer can be formed as the volume fraction of one block.[6−9] In recent experimental studies, Yang et al.[8] observed HPL phase in blends of styrene−isoprene graft block copolymer and polystyrene (PS) homopolymer in a narrow volume fraction region between L and HEX. Lee et al.[9] also found a morphology similar to HPL phase during the thermally induced transition from L to HEX in blends of asymmetric styrene−isoprene−styrene triblock copolymer (S−I−S)/PS homopolymer. Recent self-consistent mean-field theory by Matsen suggested that the HPL phase is stabilized by the addition of homopolymer to a diblock copolymer at certain compositions in contrast to the case of pure block copolymer.[10,11] However, the relative stability of the HPL phase in diblock copolymer/homopolymer blend has not been known exactly until now. In this paper, we investigate the effect of homopolymer molecular weight on the formation of HPL phase in the intermediate transition from L to G phase.

Styrene−isoprene diblock copolymer (PSI67) was synthesized by living anionic polymerization using high-vacuum techniques. The polyisoprenes (PI) were obtained from Polysicences Co. and Daelim Industry Ltd. The molecular characteristics of diblock copolymer and homopolymers are listed in Table 1. Blends were prepared by solution-casting in toluene (∼10 wt % solid) in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group), and then the solvents were slowly evaporated. After complete removal of the solvent, the samples were annealed at 120 °C for 10 h. To observe morphological transitions, the weight fraction of homopolymer PI in the blend was designed to be 2.5 wt % (the total volume fraction of isoprene in blends = 0.35). The characteristics of microdomain structure for neat block copolymer and its binary blends are given in Table 2. Neat PSI67 copolymer has a gyroid morphology, while its binary blends has a lamellar morphology at room

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Table 1. Characteristics of Polymers Used

| sample code | M_w | M_w/M_n | composition (wt %)[c] | | |
| | | | | unsaturation | |
			styrene	cis 1, 4	trans 1, 4
PSI67	34000[a]	1.02[b]	70	68.3	26.4
PI1K	1060	1.20		62.9	30.7
PI3K	3000	1.08		69.6	23.8
PI7K	7000	1.05		65.3	28.2

[a] By low-angle laser light scattering (LALLS). [b] By GPC calibrated with PS standard. [c] By ^{1}H NMR.

Table 2. Characteristics of Microdomain Structures for Neat Block Copolymer and Its Binary Blends

sample	q^* (nm^{-1})[a]	interdomain dist D (nm)	phase[b] transitions
PSI67/PI7K	0.2693	23.33	L $\xrightarrow{185}$ G $\xrightarrow{225}$ Dis
PSI67/PI3K	0.2732	23.00	L $\xrightarrow{130}$ HPL $\xrightarrow{185}$ G $\xrightarrow{220}$ Dis
PSI67/PI1K	0.2782	22.59	L $\xrightarrow{130}$ HPL $\xrightarrow{175}$ G $\xrightarrow{215}$ Dis
PSI67	0.2786	22.55	G $\xrightarrow{220}$ Dis

[a] By SAXS measurements. [b] Numbers above arrows indicate the phase transition temperature in °C as determined from SAXS measurements.

temperature, which the lamellar microdomain spacings of blends increase with increasing PI molecular weight. SAXS measurements were performed on the 4C1 beamline using synchrotron X-ray radiation sources at the Pohang Accelerator Laboratory, Korea. The X-ray source wavelength was 1.608 Å. The experimental details were presented elsewhere.[12]

Figure 1a shows the SAXS patterns for unsheared PSI67/PI1K blend at each temperature during the heating process. Below 100 °C, the specimen has a lamellar (L) microstructure having peaks at positions of q^*, $2q^*$, and $3q^*$. At 120 °C, the scattering profile shows the splitting of the first-order peak as indicated by open triangle and arrow, which implies that the mixture begins to transform from L to a new morphology. After subsequent heating to 140 °C, the SAXS pattern clearly exhibits three strong peaks at $0.92q^*$, q^*, and $1.08q^*$, which is consistent with the scattering patterns of HPL shown in previous work,[5] indicating the completion of morphological transition. Therefore, it means that L and HPL morphologies coexist between 120 and 140 °C because a morphological transition from L to HPL occurs at this temperature range. At temperatures between 170 and 175 °C, the first-order peak at the position of $0.92q^*$ disappears, and the position of the third peak jumps from $1.08q^*$ to $1.15q^*$, indicating a morphological transition from HPL to G at this temperature range. It also means that the two-phase region of HPL and G exists in a narrow range of temperatures. Therefore, it is concluded that the blend transforms from HPL to G phase between 170 and 175 °C. Finally, at 215 °C, the SAXS profiles shows a single broad peak which indicates a disordered state. Thus, the SAXS profiles for PSI/PI1K indicate the OOT from L through HPL to G and the ODT from G to the disordered phase.

To confirm the thermodynamic stability of HPL phase, the blend was annealed at 150 °C for 48 h. After
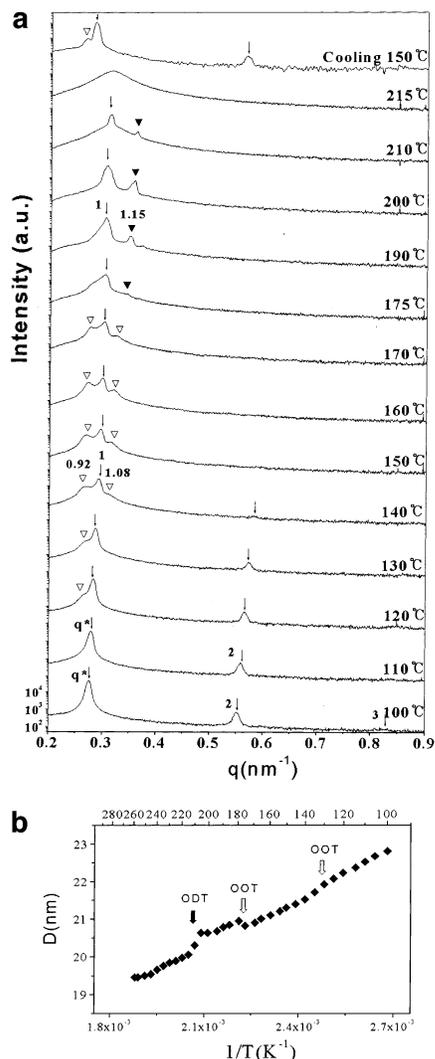
Figure 1. (a) SAXS profiles of unsheared PSI67/PI1K blend as a function of temperature at the rate of 2 °C/min. SAXS pattern observed during heating process was not much different from that after extended isothermal annealing. (b) Plot of interdomain distance $D (=2\pi/q^*)$ vs $1/T$. The T_{ODT} and T_{OOT} are indicated by filled and open arrows, respectively.

extended isothermal annealing, the SAXS pattern indicates only the scattered peaks characteristic of the HPL morphology without showing the indication of a partial transformation to the G phase. To provide further evidence for the equilibrium nature of the HPL phase, the blend was cooled to 150 °C where only HPL phase was clearly observed after heating to 180 °C where the G phase was observed. SAXS measurement after annealing for 5 h at 150 °C only shows the diffraction characteristic of HPL without the appearance of G phase, as shown in Figure 1a. However, even if the sample was annealed at 150 °C for several hours, there were some difference between cooling and heating patterns. The primary peak position on cooling is not consistent with that on heating. On cooling, the peak at $q = 0.57$ nm^{-1} characterizing a L phase is much developed, and two peaks at $0.92q^*$ and $1.08q^*$ characterizing a HPL phase are much weaker (especially, the peak at $1.08q^*$ almost disappeared). As judged from these results, the sample shows more characteristics of the L phase than those of the HPL phase on cooling and that the development of HPL from the G phase on cooling is more difficult process than that of HPL from
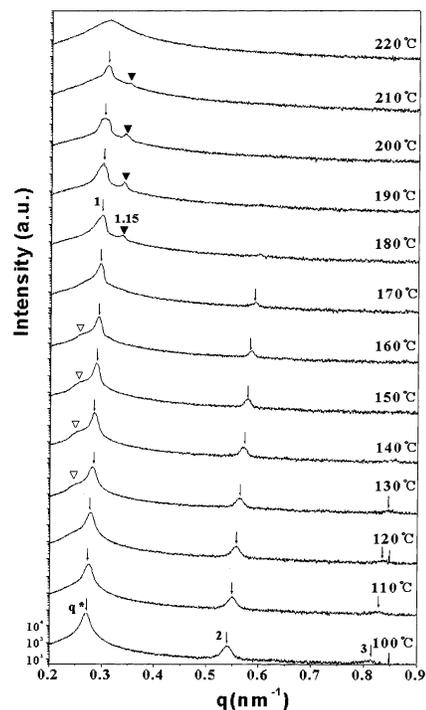

Figure 2. SAXS profiles of unsheared PSI67/PI3K blend as a function of temperature at the rate of 2 °C/min.

the L phase on heating. From these data, we may draw an inference as follows: the HPL phase may be either an unattainable stable morphology or a metastable intermediate phase between L and G phases and is more easily developed on heating than on cooling. Also, these experimental results show that the addition of homopolymer to block copolymer improves the development of the HPL phase which occurs hardly in pure block copolymer.

To view the morphological transition during heating, the interdomain distances, $D (=2\pi/q^*)$, are shown in Figure 1b as a function of temperature. The D vs $1/T$ plot shows a discontinuity at 215 °C, which indicates an ODT. The discontinuous changes in D occur at 130 and 175 °C as indicated by open arrows. These transition temperatures are consistent with the OOT temperatures from L to HPL and from HPL to G phases.

The SAXS profiles obtained in the PSI67/PI3K blend are shown in Figure 2. Below 100 °C, the specimen has lamellar microdomains having scattered peaks at positions of q^*, $2q^*$, and $3q^*$. At 140 °C, the broad peak marked by the open triangle indicates the existence of HPL phase. However, one can see that the broad peak and relatively few higher-order peaks indicate a lack of long-range order. The SAXS profiles obtained at 180 °C show the scattered peaks at q^* and $1.15q^*$, indicative of the presence of G phase. Finally, at 220 °C, the SAXS profiles show a single broad peak which indicates a disordered state. Thus, the SAXS profiles for PSI/PI3K indicate the OOT from L through HPL to G and the ODT from G to the disordered phase.

Figure 3 shows the SAXS profiles obtained from the PSI67/PI7K blend. At $T < 160$ °C, the SAXS profiles indicate that the specimen has an L phase with scattered peaks at positions of q^*, $2q^*$, and $3q^*$. When the sample was subsequently heated to the region where the HPL phase was previously observed, no diffraction associated with the HPL phase was observed. The HPL phase was also not observed after extended isothermal
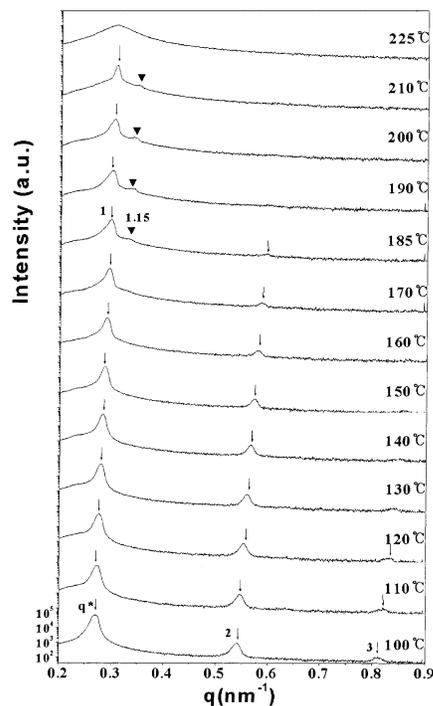
Figure 3. SAXS profiles of unsheared PSI67/PI7K blend as a function of temperature at the rate of 2 °C/min.

annealing at 150 °C for 24 h. At 185 °C, a side peak near the position of $1.15q^*$ indicative of the presence of the G phase is observed, and the second-order peak of the L phase also remains distinct. This implies that a morphological transition from L to G occurs at this temperature. At 200 °C, the SAXS profiles show only the peaks of G phases at positions of q^* and $1.15q^*$ without showing the second-order peak of the L phase. This fact indicates that the PSI67/PI7K blend undergoes direct transitions from the L to G phase without forming the HPL phase, in contrast to the two other blends.

It is important to note here that the increase in PI molecular weight causes the intermediate phase, HPL, to disappear during transition from the L to G phase. Hajduk et al. reported that, in the pure block copolymer system, transition kinetics depend on the system composition and that the direct transition from L to G can occur in the HPL phase-forming systems once the mean size of the G domains exceeds a certain critical size.[13] In this study, we found that the morphological transitions of block copolymer/homopolymer blends depend not only on system composition but also on the molecular weight of homopolymers. As seen in PSI67/PI1K and PSI67/PI3K blends, the addition of relatively lower molecular weight PI to a diblock copolymer leads to the formation of the HPL morphology at the intermediate region between the L and G phases. On the other hand, in PSI67/PI7K blends having higher molecular weight PI, a direct transition from L to G is observed without the appearance of the HPL structure. For asymmetric block copolymer such as the present case, a packing frustration effect has been known to play a role in phase stability.[11,14] Matsen et al. reported that the addition

of a homopolymer to the majority component of HEX phase relieves the packing frustration imposed on the block copolymer since the added homopolymer fills the corners of Wigner–Seitz cells.[11,14] Even though the effect of adding homopolymer to the minority domain is not yet clearly understood, the relief of packing frustration in HPL phase can be explained as a mechanism closed to that in HEX phase. In the HPL phase, the major component material forms the hexagonally packed channels which extended through the minor component layer and which form shapes similar to cylinders of the minor components in the HEX phase. Therefore, in the HPL phase, adding homopolymer to a minor component may reduce some of the packing frustration imposed on copolymers in the same manner as for the HEX phase, and the relief of packing frustration by homopolymers may play an important role in the stability of the HPL phase. In the PSI/PI7K blend, the HPL phase may be not observed in the intermediate transition region from L to G because the relatively high molecular weight PI cannot effectively fill the corners of Wigner–Seitz cells and cannot relieve some of the packing frustration.

In conclusion, the morphological transitions from L to HPL, from HPL to G, and from L to G during the heating process could be determined by SAXS. It was observed that the morphological transitions of the blend depend on the molecular weight of the homopolymer, and the relief of packing frustration by homopolymer may play an important role in the formation of the HPL morphology in the intermediate transition region from L to G.

References and Notes

(1) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(2) Förster, S.; Khandpur, A. K.; Zhao, J.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W. *Macromolecules* **1994**, *27*, 6922.
(3) Khandpur, A. K.; Förster, S.; Bates, F. S.; Zhao, J.; Ryan, A. J.; Bras, W.; Hamley, I. W. *Macromolecules* **1995**, *28*, 8796.
(4) Vigild, M. E.; Almdal, K.; Mortensen, K.; Hamley, I. W.; Faiclough, J. P. A.; Ryan, A. J. *Macromolecules* **1998**, *31*, 5702.
(5) Ahn, J.-H.; Zin, W.-C. *Macromolecules* **2000**, *33*, 641.
(6) Winey, K. I.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1992**, *25*, 2045.
(7) Bodycomb, J.; Yamaguchi, D.; Hashimoto, T. *Macromolecules* **2000**, *33*, 5187.
(8) Yang, L.; Gido, S. P.; Mays, J. W.; Pispas, S.; Hadjichristidis, N. *Macromolecules* **2001**, *34*, 4235.
(9) Lee, S.-H.; Cha, K.; Kim, G. *Macromolecules* **2000**, *33*, 7072.
(10) Matsen, M. W. *Phys. Rev. Lett.* **1995**, *74*, 4225.
(11) Matsen, M. W. *Macromolecules* **1995**, *28*, 5765.
(12) Ahn, J.-H.; Sohn, B. H.; Zin, W.-C.; Noh, S. T. *Macromolecules* **2001**, *34*, 4459.
(13) Hajduk, D. A.; Ho, R. M.; Hillmyer, M. A.; Bates, F. S.; Almdal, K. *J. Phys. Chem. B* **1998**, *102*, 1356.
(14) Matsen, M. W.; Bates, F. S. *Macromolecules* **1996**, *29*, 7641.