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Anomalous Temperature Behavior of Lamellar Microdomain Structures in Binary Blends of Polystyrene-*block*-polyisoprene Diblock Copolymers

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The control of morphology in microphase-separated block copolymers is an important research subject.[1] Block copolymers consisting of chemically different polymer chains form microphase-separated structures whose repeating distance is comparable to the dimension of the block chain. The simplest primary structure is a diblock copolymer where two chemically different polymer chains are connected by a covalent bond at the respective chain ends. Recently, block copolymers having more complicated primary structures are synthesized in order to investigate effects of the primary structures on the microdomain morphology. Triblock, multiblock, graft copolymer, star polymer, star block copolymer, ABC triblock, ABC star polymer, and so forth are examples.[1,2] Very interesting characters found in those individual systems clearly indicate infinite possibilities for the morphology control by chemically designing primary structures of the copolymers. On the other hand, there are other interesting approaches without using chemical modifications. One of the simplest techniques is a binary blend of two different diblock copolymers comprising the same monomers A and B but having different molecular weights and compositions (α: $(A-B)_1 + \beta$: $(A-B)_2$ system).[3−12] This system is a candidate to design uniform microdomain structures without macroscopic phase separation if the molecular weights and compositions of α and β are not very different. In this regard, the binary blend of diblock copolymers is much superior to a blend of diblock copolymer and homopolymer.[12]

In the course of our study for the morphology control using the binary blend of polystyrene-*block*-polyisoprene (SI) diblock copolymers, we found a very unusual temperature behavior of lamellar microdomains. That is, the unit size of lamellae increased with increasing temperature, which is quite contrary to the usual behavior that the size (D) decreases with the absolute temperature (T) as $D \sim T^{-1/3}$ for a pure SI diblock copolymer.[13] The usual behavior can be explained by the temperature dependence of the chain dimension in the direction normal to the lamellar interface. Since the interaction parameter between styrene and isoprene segments (χ_{SI}) decreases with an increase of T (UCST (upper critical solution temperature) type behavior), the segregation between polystyrene (PS) and polyisoprene (PI) block chains becomes weaker with an increase of T, causing the chain dimensions of both PS and PI blocks to be more compact in the direction normal to the interface. Thus, the lamellar repeating distance becomes smaller with an increase of T. This is the normal temperature dependence of D in the UCST type pure SI diblocks. On the other hand, the behavior for the $(SI)_\alpha + (SI)_\beta$ blends reported in the present paper is quite unusual, such that the behavior is apparently LCST (lower-critical solution temperature) type. This fact implies that even the simplest system of the binary blend of diblock copolymers has very curious features to be investigated.

Table 1. Sample Characteristics

code name	ϕ_{PS}[a]	$10^{-3}M_n$[b]	M_w/M_n[c]	Z[d]	microstructure of PI[e] (mol %) cis-1,4	trans-1,4	3,4
SIZ-1	0.14	37.3	1.09	469	70	23	7
SIZ-2	0.81	44.8	1.07	507	39	61	0
SIZ-3	0.65	26.1	1.06	302	61	33	6
SIZ-4	0.26	24.5	1.05	302	73	20	7

[a] Volume fraction of polystyrene, analyzed by NMR. [b] Number-average molecular weight measured by membrane osmometry. [c] Heterogeneity index of molecular weight, measured by GPC. (M_w denotes the weight-average molecular weight.) [d] Reduced value of total degree of polymerization, calculated with $Z = (\nu_{PS}\nu_{PI})^{-0.5}(\nu_{PS}N_{PS} + \nu_{PI}N_{PI})$, where ν_K and N_K designate molar volume of the K segment and the degree of polymerization for the K block, respectively (K = PS or PI). Note here that the values of ν_K used were 107.2 and 81.9 cm^3/mol for PS and PI, respectively, which were evaluated from the values of mass density 0.969 g/cm^3 for PS and 0.830 g/cm^3 for PI at 413K (from ref 17). [e] Analyzed by NMR.

We used four kinds of SI samples of which characteristics are listed in Table 1. SIZ-1 and SIZ-2 have similar molecular weights (see the values of Z in Table 1, which are the reduced degrees of polymerization by taking into account the difference in the segmental volumes for PS and PI), and also, SIZ-3 and SIZ-4 have similar molecular weights. Therefore, two pairs (SIZ-1/2 and SIZ-3/4) were chosen to construct binary blends having the total volume fraction of PS ($\overline{\phi}_{PS}$) at ca. 0.5, where the sample code SIZ-x/y designates the binary blend of SIZ-x and SIZ-y. Note that exact values of $\overline{\phi}_{PS}$ are 0.40 and 0.48 for SIZ-1/2 and SIZ-3/4, respectively. Given amounts of two kinds of SI samples were dissolved into toluene with a total polymer concentration of ca. 5 wt %. A tiny drop of the toluene solution was then placed onto the distilled water. Due to quick spreading of the drop on the water surface, toluene evaporates immediately to form a thin polymer film. Accumulating the film one by one and further thermal annealing at 150 °C for about 40 min, we obtained samples subjected to the small-angle X-ray scattering (SAXS) measurements. The SAXS measurements with synchrotron radiations were conducted at the BL-10C beam line of the Photon Factory in the Institute of High Energy Physics.[14] The X-ray beam from the synchrotron was monochromatized by a couple of Si(111) single crystals and the wavelength λ of the monochromatized X-ray was 0.149 nm. A position-sensitive proportional counter was used to detect the scattering intensity as a

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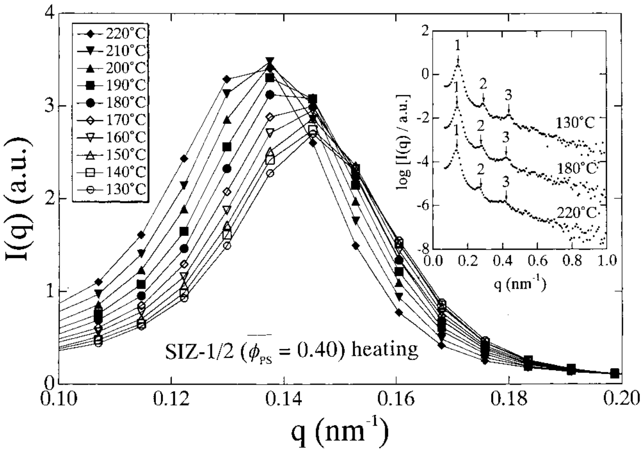

Figure 1. Change in SAXS profiles ($I(q)$ vs q) with temperature for the SIZ-1/2 blend, measured in the heating process. The heating rate was 2 °C/min. The inset shows SAXS profiles (log $I(q)$ vs q) as a function of temperature.

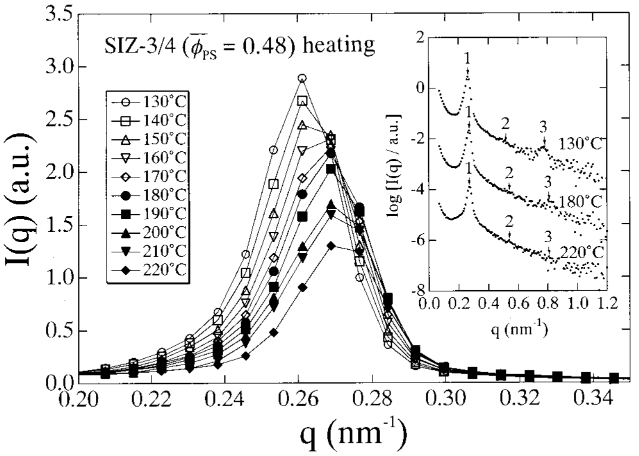

Figure 2. SAXS profiles for the SIZ-3/4 blend, similar to Figure 1.

function of the scattering angle θ. The sample-to-detector distance was about 1.9 m. For temperature dependence, time-resolved SAXS measurements were performed with 30 s time slices at 2 °C/min heating (or cooling) rate. The scattering intensity of an empty cell was subtracted from that of a sample by taking into account absorption due to the sample. The data were further corrected for the thermal diffuse scattering (TDS) due to density fluctuations. We assumed that the angle-independent TDS can be regarded as the average scattering intensity in the angular region of $1.3 < q < 1.4$ nm^{-1} (maximum q range of our SAXS measurements), where q is the magnitude of the scattering vector, defined as

$$q = (4\pi/\lambda)\sin(\theta/2) \tag{1}$$

The SAXS profiles (the scattering intensity $I(q)$ vs q) highlighting the first-order peaks are shown as a function of temperature in Figures 1 and 2 for SIZ-1/2 (heating process) and SIZ-3/4, respectively. The SAXS measurements were conducted with heating the sample from 120 to 220 °C at the heating rate of 2 °C/min. For SIZ-1/2, after maintaining the sample at 220 °C for about 4 min, the SAXS measurements were then made by cooling the sample to 150 °C (the cooling rate was 2 °C/min). The insets show the plot of the logarithm of the scattering intensity, log $I(q)$, vs q as a function of temperature. For both blends, the relative q values of the peaks can be assigned to 1, 2, and 3, indicating the existence of lamellar microdomain structures. This result confirms that two kinds of SI samples were mixed together at the molecular level and formed homogeneous microphase-separated domains without macrophase separation, while none of the SI samples used forms lamellar structures. As can be seen in the insets, no morphological transition occurred for those samples; i.e., the morphology was throughout lamellar, irrespective of temperature. The formation of such homogeneous lamellar structures is owing to the quick evaporation of the solvent in the procedure of sample preparation. Actually, we observed macroscopic phase separation for the sample prepared with an ordinary solution-cast method.[12,15] We discuss stability of the homogeneous lamellar structure in the following paragraph. For SIZ-1/2, the first-order peak shifts toward a smaller angle and its intensity increases with an increase of temperature. In the latter part of this paper, we present a model to explain the anomalous behavior by taking into account the UCST type interaction between styrene and isoprene segments. For SIZ-3/4, the first-order peak shifts toward a larger angle and its intensity decreases with increasing temperature, which is a normal UCST type behavior.

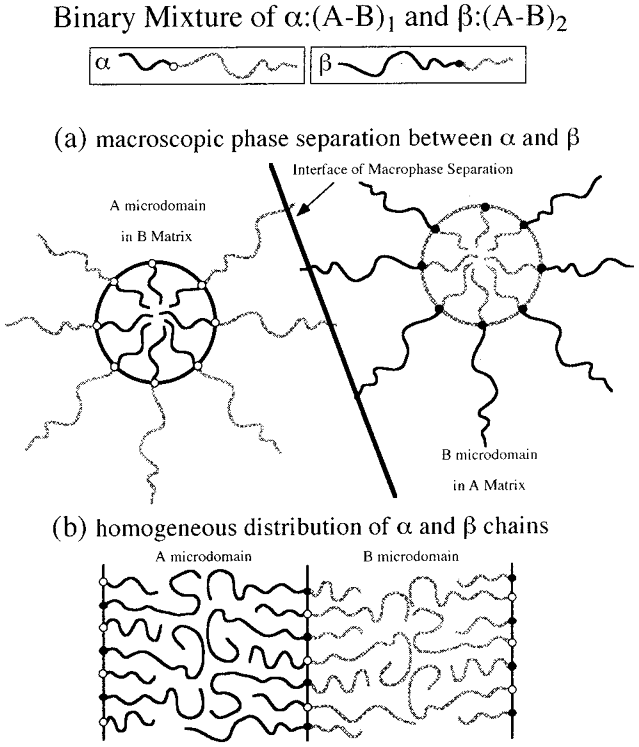

Figure 3. Schematic representation for mixing states in the binary blend of α, (A−B)$_1$, and β (A−B)$_2$. Macroscopic phase separation between α-rich and β-rich phases is illustrated in part (a), and a model for the homogeneous lamellar structures is sketched in part (b).

Concerning the structure cast quickly from a solution, we found vague morphological structures in the as-cast film. However, finally, we could get the homogeneous lamellar morphology by annealing this as-cast film. This fact can be interpreted as follows. Once the blocks are homogeneously mixed, the lamellar microdomain structure is thermodynamically stable due to the stabilization of interface between the PS and PI microdomains by packing alternatively the longer and shorter block chains in the respective microdomain space, as schematically shown in Figure 3b. Although the macroscopic phase separation is expected by the random phase

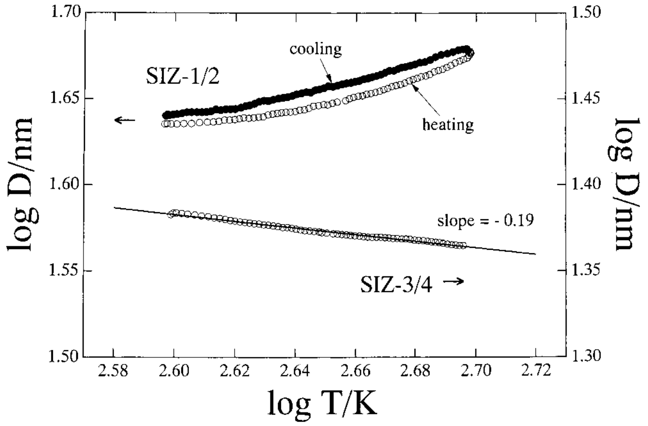

Figure 4. Double logarithmic plot of the lamellar repeating distance, D, vs absolute temperature, T. The values of D were evaluated from the position of the first-order peak in the SAXS profiles.

approximation calculation,[12,15] it increases unfavorable contacts between the longer PS and PI block chains in the interfacial region between α-rich and β-rich phases (Figure 3a). Thus, the schematic picture shown in Figure 3b is rather favored because of minimized unfavorable contacts between the PS and PI chains under this situation.

To discuss the temperature dependencies of the size of the lamellar microdomain, we evaluated the lamellar repeating distance, D, from the position of the first-order peak of the SAXS profiles as a function of temperature, where D is given by with q_1 being the q value of the

$$D = 2\pi/q_1 \qquad (2)$$

first-order peak. Double logarithmic plots of D vs absolute temperature, T, are shown in Figure 4. For the SIZ-3/4 blend, D decreased with an increase of T, which is the same temperature dependence (UCST type) as that for pure SI diblock copolymers. However, the exponent is quite small as compared to −1/3 for the pure blocks. The slope of the approximated straight line is −0.19, which indicates that the usual temperature dependence is suppressed, or in other words, the lamellar structures comprising the two different kinds of SI diblocks are insensitive to the change of temperature. The results for the SIZ-1/2 blend are much more striking. The lamellar repeating distance increased with an increase of T. This is completely opposite dependence to the usual case. At the same given temperature, the value of D is larger in the cooling process than the heating process. The differences were due to the measurement procedure employed. Namely, a thermodynamically stable state was not attained since the measuring temperature was changed constantly with a finite heating (or cooling) rate, and hence the indicated sample temperature does not reflect reality. If the structural response is retarded, then the state observed in the heating process may reflect the structure at the temperature lower than the apparent sample temperature. Similarly, in the cooling process, it is considered that the state corresponds to the temperature higher than the apparent sample temperature. Thus, we interpret the big differences of D in the heating and cooling processes. Although such results should be corrected by taking the zero limit of the heating (or cooling) rate, the important findings are that D increases in the heating process and decreases in the cooling process. If the increase of D in the heating process would imply that the homogeneous lamellar structure is not stable and undergoes macrophase separation, the fact that D decreases in the successive cooling process could not be explained. Again, it is emphasized that the anomalous temperature dependence was observed for the blend of SI diblocks having large compositional asymmetry.

Recently, Shi and Noolandi[8] have studied the phase behavior of a binary blend of diblocks by the self-consistent mean field theory. They examined binary blends consisting of identical amounts of the first component with the composition, f_1 (=f), and the second component with f_2 (=1 − f). Note that the overall composition was kept at 0.5. The degrees of polymerization Z for both components are 400. They found anomalous χ dependence of the domain spacing in the restricted f range ($0.82 \lesssim f \lesssim 0.83$; see Figure 10 in ref 8). Namely, the domain spacing increases when χ decreases from 0.2 to 0.05. Although the values of Z (=469 and 507 for SIZ-1 ($f_{PS} = 0.14$) and SIZ-2 ($f_{PS} = 0.81$), respectively) for our SI samples are larger than that discussed in their study ($Z = 400$), we converted the χ range of the anomalous behavior to the temperature range for our system with SIZ-1 and SIZ-2. Assuming that values for the product of χ and Z are constant, −126 and +145 °C are obtained for $\chi = 0.2$ and 0.05 ($\chi Z = 80$ and 20), respectively. Here, we employed the following temperature dependence of χ for the SI sample, which has been reported previously for a pure SI diblock copolymer[16] having $f_{PS} = 0.15$ and $M_n = 8.2 \times 10^4$,

$$\chi_{SI} = -0.0258 + 27.9/T \qquad (3)$$

Thus, it is found that the converted temperature range for the anomalous behavior roughly covers our experimental temperature range.

Starting with the picture shown in Figure 3b, let us consider what happens when the temperature is raised. As a more realistic model, the chain dimension is indicated by a circle in Figure 5a. As the temperature increases, the miscibility between the shorter PS and PI block chains is enhanced. Due to the miscibility enhancement, these shorter chains get closer and hence the interface between the PS and PI microdomains undulates. In the right-hand side of Figure 5b, chain overlapping of the longer PS and PI blocks is significant. In order to maintain a spatially homogeneous distribution of segments, such chain overlaps should be avoided. These can be avoided by stretching the longer block chains in a transverse direction (normal to the original interface), as illustrated in the left-hand side of Figure 5b. As a consequence, the repeating distance of the lamellae becomes larger at a higher temperature. Since no macroscopic phase separation is assumed in this scheme, the reversing change will take place when the temperature decreases. In other words, the anomalous behavior is governed by the miscibility enhancement between the shorter PS and PI block chains.

It is worth considering an extended scheme when the temperature is more raised. The longer block chains are more stretched in the transverse direction due to further enhancement of the miscibility between the shorter PS and PI block chains. However, the elastic force in this direction increases accordingly and this force may work to pull out the shorter block chains from the interfacial region. The occurrence of the chain pulling-out is determined by the balance of the elastic force and the interfacial tension. When the chain

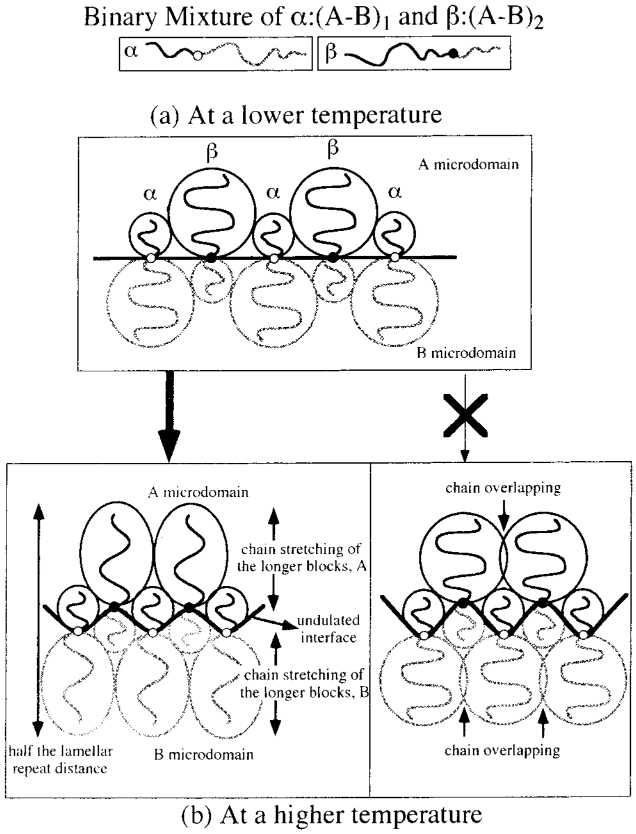

Figure 5. Models for the homogeneous lamellar structures at lower and higher temperatures, which are illustrated in (a) and (b), respectively. The circles stand for chain dimensions.

pulling-out occurs, this develops readily into macroscopic phase separation. When the temperature is reversely lowered from the macroscopically phase-separated state, the homogeneous lamellar microdomains are no longer spontaneously formed even if it is thermodynamically stable. The energy barrier is considered to be quite large. The situation is similar to the phase-separated polymer blends. In order to obtain a homogeneous mixing, an external force should be required. When casting the binary SI/SI mixtures, quick evaporation of the solvent is considered to work well to mix up two different kinds of SI samples.

In summary, uniform lamellar structures were obtained by evaporating the cast solvent very quickly for the total volume fraction of PS at ca. 0.5, even for the pairs (SIZ-1/2 and SIZ-3/4), for which the random phase approximation theory predicted macrophase separation.[12] For the blend sample having a large compositional asymmetry, SIZ-1/2, anomalous temperature dependence of the lamellar size was observed. The domain size increased with increasing temperature. This behavior is in good accord with the prediction of the self-consistent field theory, while the random phase approximation theory does not apply to our data. We assumed interface undulations by an increase of temperature, as shown in Figure 5b for an interpretation of the anomalous behavior. An experimental confirmation of the interface undulations should be elicited in the future work.

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