Versatile Controls of Microdomain Morphologies and Temperature Dependencies in Lamellar Spacing by Blending Diblock Copolymers Bearing Antisymmetric Compositions

Junji Fukuhara,† Akifumi Yasui,† Katsuhiro Yamamoto,‡,§ and Shinichi Sakura†,*,†,‡

1Department of Biobased Materials Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan
2Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
3Frontier Research Institute for Materials Science, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
4Institute of Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

ABSTRACT: The morphologies of the microphase-separated structures in the binary blends of diblock copolymers (AB/AB) have been studied intensively for the case of diblock copolymers bearing antisymmetric compositions with similar molecular weights. Here, the two diblock copolymers 1 and 2, of which compositions are 0.5 − x and 0.5 + x (0 < x < 0.5), respectively, were blended, and the morphology diagram was constructed in the plot of χZ vs the average composition of the A component, where χ is the interaction parameter between A and B segments and Z is the average degree of polymerization of the two AB diblock copolymers. The temperature-dependent morphologies were analyzed by synchrotron small-angle X-ray scattering (SAXS) measurements. It was found that the morphology diagram agrees in principle with the theoretical one for the neat AB diblocks by Matsen and Bates (Macromolecules 1996, 29, 1091–1098), although the disordered phase was a bit expanded in the experimentally determined morphology diagram. Anomalous temperature dependencies in the lamellar spacing have been also comprehensively studied for the binary blends of antisymmetric diblock copolymers as a function of the degree of compositional asymmetry by closely adjusting the average composition in the blend specimen at 0.50. For this purpose, more than 20 neat diblock copolymers have been synthesized with a wide range of compositions from 0.20 to 0.87 and a range of molecular weight of 12 000–33 800. The temperature dependencies of the lamellar spacing were also analyzed by synchrotron SAXS measurements. As a result, the following things were found. The scaling exponent α in D ∼ T−α was still negative but slightly larger than the usual value (i.e., α = −0.33) for the smaller degree of asymmetry in the composition (i.e., x is small), while α became positive for the higher degree of asymmetry. The latter result is very anomalous because the temperature dependence is opposite (i.e., the lamellar spacing increases with an increase of temperature). The value of α was found to be linearly rationalized with the degree of asymmetry τ (which is especially introduced in the current paper for this purpose), for the binary blends with the average composition of 0.50. Based on this result, one can prepare lamellar microdomains, of which spacing does not change with temperature, by blending two diblock copolymers with τ = 1.33 (corresponding to 0.3 and 0.7 of compositions) having similar molecular weights. This would be important for manufacturing materials with properties (for instance, the optical property) independent of temperature. From the current study, the binary blends of the antisymmetric diblock copolymers are concluded to be versatile such that the precise controls of the morphologies and the temperature dependencies of the lamellar microdomains are plausible.

INTRODUCTION

Precise control of morphologies of microphase-separated structures requires well-defined block copolymers with monodispersity in molecular weights and in compositions. However, polymer synthesis techniques (living polymerization) and a special chromatographic method of fractionation (two-dimensional HPLC fractionation) are required for this purpose. These are quite heavy tasks for general researchers and create a high barrier. On the contrary, binary blends of block copolymers provide a facile strategy of precise control of compositions. In this regard, two block copolymers with antisymmetric compositions are preferred, although the composition is not monodisperse for the case of the blends. Since the blending is much easier as compared to the case of synthesizing a well-defined neat block copolymer with the targeted composition, mimicking a phase diagram of the microphase-separated structures has been studied. The binary blends of diblocks, AB/AB, have been intensively examined both experimentally and theoretically since the 1980s, not only for the purpose of the morphology con-
but also for many other aspects, such as elucidation of the cosurfactant effects (mixtures of small amounts of short diblocks in the long diblocks), 3,5,8,9,13,16,17,26,28–31,33,35,36,38 anomalous temperature behavior of the domain spacing, elucidation of the cast solvent on the morphology in thin films, 34,35 and examination of the grain boundary structure between the macroscopically phase-separated grains of thick and thin lamellae. 6 For these many purposes, a variety of AB/ABA binary blends have been examined, such as [long symmetric AB]/[short symmetric AB] blends, 5–6,9,13,16,17,26,29,36 [long asymmetric AB]/[short symmetric AB] blends, 14,24,28,30,31,33,35,38 [asymmetric AB]/[symmetric AB] blends (with similar molecular weights), 12,25 and antisymmetric AB/AB blends (with similar molecular weights). 7,10–12,18–23,27,32–34,37,39 Furthermore, binary blends of AB/ABA 40–44 and ABA/ABA, 45–47 have attracted interest from the viewpoint of mechanical properties because the ABA triblock copolymers possess good elastomeric property due to the bridge conformation of the B midblock chains between the dispersed A microdomains. 50,45–47 As a matter of fact, the blends of SI/SIS are technologically applied to adhesive materials, 52–44 where SI and SIS denote a polystyrene-block-polysoprene diblock copolymer and a polystyrene-block-polysoprene-block-polystyrene triblock copolymer, respectively. For such AB/ABA blends, the Monte Carlo simulation has also been performed to study the microdomain structures in thin films. 41 As another notable report on the miscibility of binary blends, the miscibility between SI and SB (polystyrene-block-polybutadiene diblock copolymer) has been reported with similar molecular weights, but immiscibility between SI and (SI) 4 (a linear tetrablock copolymer with similar molecular weights to the SI diblock). 49 By noting good miscibility between SI and SIS (with similar molecular weights of an entire polymer chain), the above-mentioned miscibility/immiscibility results indicate a nice contrast in the fact that the dissimilarity in chemical structures of the chain segments does not matter, but the difference in the architecture of a polymer chain matters to the miscibility between two block copolymers.

As for the anomalous temperature dependence of the lamellar spacing in diblock copolymer blends, we have reported it for the first time for lamellar microdomains formed in binary blends of antisymmetric SI/SI of which compositions are 0.5 – x and 0.5 + x (0 < x < 0.5), respectively, with similar molecular weights. 19 That is to say, the domain spacing (D) increased with temperature, which is very different from the common knowledge that D decreases with temperature as D ∼ T−1/3 (T the absolute temperature in Kelvin), 50,51 for the UCST (upper critical solution temperature) type miscibility change with temperature; namely, the miscibility is increased when temperature increases. Such an anomaly has been first theoretically predicted by Shi and Noolandi 11,19 and later reported experimentally by many different groups 24,27,29,31,35,39 not only for the lamellar microdomain but also for the bicontinuous microdomain. 51 The increase of D at high temperature has been ascribed to delocalization (solubilization) of short diblock chains into both of the polystyrene (PS) and polysoprene (PI) lamellar phases, which has been evidenced by small-angle neutron scattering for the case of a [long asymmetric SI]/[short symmetric SI] blend. 24 As for the antisymmetric case, the delocalization mechanism would be applicable, as pointed out by Park et al. 19 However, this process is clearly the onset of the macroscopic phase separation. Our result previously reported 19 clearly indicated almost reversible temperature dependencies upon cooling from the highest temperature subsequently after heating. This fact clearly indicates that the anomalous temperature dependence cannot be ascribed to the macroscopic phase separation process. In other words, the anomaly cannot be ascribed to delocalization (solubilization) for the case of the antisymmetric blends.

In the current study, we will first provide a summary of the phase diagram by using SI/SI blends with appropriately adjusting the overall PS average volume fraction (ϕps) in the plot of χZ vs ϕps where χ and Z are the interaction parameter between A and B segments and the average degree of polymerization as defined in refs 21 and 22. Actually, this is the comprehensive version of the phase diagram as previously reported 22 based on our experimental results using SI samples with similar molecular weights, and it is compared with a theoretical phase diagram for the antisymmetric AB/AB blend (with the same molecular weights) by Matsen and Bates 12 and with a theoretical phase diagram for a neat diblock. 12

In this study, we intend to examine the temperature dependency of D for the lamellar morphology. Therefore, it is important to examine in advance whether the lamellar phase prevails in the average composition range of 0.4–0.6 at χZ ≈ 20, as in the case of the neat diblock copolymers. As a matter of fact, this can be clearly confirmed later (Figure 2). Thus, it is possible to examine the temperature behaviors not only for the average PS fraction of 0.50 but also for the case of not exactly being identical to 0.50. Since the latter case lacks the balance of the stoichiometric numbers of the antisymmetric AB/AB diblock chains, the latter possesses the significance to highlight a feature of the lamellar structure comprising stoichiometric numbers of the antisymmetric diblock copolymer chains, as shown in Figure 1. In this sense, Figure 2 plays an important role to examine in advance whether the lamellar morphology can be formed for the binary blend having the average composition not exactly being identical to 0.50.

We then examine the temperature dependence of the lamellar spacing in various binary blends of poly(methyl acrylate)-block-polystyrene (MS) diblock copolymers with the synchrotron small-angle X-ray scattering (SAXS) measurements. For this purpose, the antisymmetric binary blends were prepared by using MS diblock copolymers 1 and 2, with compositions of 0.5 – x and 0.5 + x (0 < x < 0.5), respectively. In this study, more than 20 samples have been synthesized with...
a wide range of compositions from 0.20 to 0.87 and the range of the molecular weight of 12 000–33 800 (Table 1). The significant point of using the MS specimens is that the segregation between PMA (poly(methyl acrylate); M) and PS (S) is much larger than that for the SI specimens. Using the following temperature dependencies of $\chi$ for the SI and the MS specimens in the literature, which reports the anomalous behavior of the temperature dependence of $\chi$ for the SI and the MS specimens (Table 1).

$$\chi = -0.0258 + 27.9/T \text{ for SI}$$

$$\chi = 0.0466 + 15.3/T \text{ for MS}$$

the values of $\chi$ at 150 and 180 °C for SI are 0.040 and 0.036, respectively, and those for MS are 0.083 and 0.080, respectively. Thus, the ratios of the $\chi$ values are 2.06 and 2.25 for 150 and 180 °C, respectively. This means that a lower molecular weight is required for the MS specimens to match the segregation power $\chi Z$. As a matter of fact, the molecular weights of the MS specimens listed in Table 1 are less than those of the SI specimens in the literature, which reports the anomalous temperature dependence of $\chi$. Since the lower molecular weight specimens have much lower viscosity, the required experimental time can be reduced for the examination of the equilibrium behavior of the temperature dependence of $D$, not only in the heating process (Figure 6) but also in the multiple cycles of the heating/cooling processes (Figure 10).

Table 1. Sample Characteristics

| specimen code | $M_a$ (Da) | $M_w/M_a$ | $\phi_{PS}$ | specimen code | $M_a$ (Da) | $M_w/M_a$ | $\phi_{PS}$ |
|---------------|------------|-----------|-------------|---------------|------------|-----------|-------------|
| MS1           | 16500      | 1.09      | 0.20        | MS12          | 19400      | 1.09      | 0.57        |
| MS2           | 12500      | 1.08      | 0.21        | MS13          | 14200      | 1.06      | 0.58        |
| MS3           | 12900      | 1.08      | 0.27        | MS14          | 19800      | 1.09      | 0.59        |
| MS4           | 14700      | 1.06      | 0.30        | MS15          | 16900      | 1.12      | 0.61        |
| MS5           | 20900      | 1.14      | 0.31        | MS16          | 33800      | 1.13      | 0.65        |
| MS6           | 14000      | 1.12      | 0.37        | MS17          | 20600      | 1.11      | 0.70        |
| MS7           | 21000      | 1.13      | 0.38        | MS18          | 14000      | 1.10      | 0.73        |
| MS8           | 15200      | 1.12      | 0.42        | MS19          | 14500      | 1.10      | 0.81        |
| MS9           | 16500      | 1.06      | 0.44        | MS20          | 13000      | 1.09      | 0.85        |
| MS10          | 12000      | 1.05      | 0.46        | MS21          | 13000      | 1.11      | 0.87        |
| MS11          | 17300      | 1.10      | 0.50        |               |            |           |             |

$^a$Determined by GPC (PS equivalent). $^b$Volume fraction of polystyrene determined by $^1$H NMR (200 MHz)

Figure 2 is a schematic illustration showing the concept of the packing condition of block chains in lamellar microdomains for the case of the antisymmetric binary blends (50/50). This kind of mutual-compensating chain packing in the lamellar microdomains has been supported experimentally by the neutron reflectivity measurements and by theoretical consideration. Since we found the temperature-independent $D$ for a particular case of the antisymmetric blend of diblock copolymers, it would be important for manufacturing materials with properties (for instance, the optical property) independent of temperature. Actually, based on our experimental results, one can prepare lamellar microdomains for which spacing does not change with temperature by blending two diblock copolymers.

## RESULTS AND DISCUSSION

Figure 2 is the result of the morphology diagram in the weak-segregation limit for the binary blends of SI diblock copolymers SIZ-3 and SIZ-4. Figure 2 also compares our experimental results with the theoretical result of Matsen and Bates for the neat diblocks, as indicated with red broken curves. It is noted here that Matsen and Bates have reported the morphology diagram for the antisymmetric AB/AB blend with 0.25/0.75 of the compositions, which should be more appropriate for comparison with our experimental results. However, their theoretical result (Figure 3 of ref 12 for 0.25/0.75 antisymmetric composition relevant to the SIZ-3/SIZ-4 blends) is found at a glance to be different from our experimental one. One of the major differences is that there is no double-gyroid phase existing in their theoretical phase diagram. Therefore, we decided to make a comparison with the theoretical result for the neat AB diblocks in Figure 2. Definitely good agreement between the experimental and theoretical morphology diagrams can be recognized, although it has been reported that the cylinder region expands while the lamellar region shrinks in the morphology diagram upon blending two diblocks. One important disagreement found in Figure 2 is that the experimental morphology diagram exhibits the wider region of the disordered state, such that the direct transitions to the disordered state were observed from the cylinders or from the gyroid phase upon heating without passing through the spherical (body-centered cubic) phase. However, this is a well-known phenomenon as the fluctuation effect reported by Khandpur et al. for the neat block copolymers. Therefore, the disagreement in the morphology diagram in Figure 2 is not ascribed to the blending. Thus, the mimicking of the
morphological phase diagram can be stated to be almost perfect for this particular pair of the SI diblocks.

Figure 3 shows the SAXS profiles measured at room temperature for MS5 and MS17 specimens. The specimens were thermally annealed at 150 °C for 24 h in advance.

![Figure 3. SAXS profiles measured at room temperature for MS5 and MS17 specimens. The specimens were thermally annealed at 150 °C for 24 h in advance.](image)

Changes in the SAXS profiles as a function of temperature for the (a) MSS/MS17 (50/50) (the antisymmetric binary blend of MSS and MS17) specimen and (b) MS11 (the neat block copolymer). These are the results of the in situ SAXS measurements in the course of the temperature ramp of 2.0 °C/min.

\[
\Delta q^2 = \left( \frac{2\pi}{D_G} \right)^2 + \left( \frac{2\pi g^2}{d} \right) m^4
\]

Figure 4. Changes in the SAXS profiles as a function of temperature for the (a) MSS/MS17 (50/50) (the antisymmetric binary blend of MSS and MS17) specimen and (b) MS11 (the neat block copolymer). These are the results of the in situ SAXS measurements in the course of the temperature ramp of 2.0 °C/min.

where \( \Delta q \) is the integral width of the reflection peaks (\( \Delta q = S/I_m \)), where \( S \) and \( I_m \) denote, respectively, the peak area (integrated intensity) and the scattering intensity at the peak top. \( D_G \) is the average grain size; \( d \) is the average spacing of the reflection planes; \( m \) is the order of the reflection peak; and \( g \) is the lattice distortion factor, as defined by

\[
g = \frac{\Delta d}{d}
\]

where \( \Delta d \) is the standard deviation of the distribution of the spacing \( d \). It should be noted here that the experimentally observed peak breadth contains an error due to the instrumental broadening. To correct for this effect, the following relationship should be used

\[
(\Delta q')^2 = (\Delta q)^2 - B^2
\]

where \( \Delta q' \) denotes the observed peak breadth (integral width). Note here that \( B^2 = 1.16 \times 10^{-4} \) (nm\(^{-2}\)) was estimated from the standard sample (chicken tendon collagen) according to the procedure provided in our previous paper.\(^5\) By conducting a computational peak decomposition of the 1d-SAXS profiles, the peak breadth, \( \Delta q' \), was evaluated for the first- and third-order reflections, respectively, as \( m = 1 \) and 3. After the correction according to eq 6, the \( (\Delta q')^2 \) values were obtained. Figure 5 shows the plots of \( (\Delta q')^2 \) vs \( m^4 \) for the neat MSS, MS11, and MS17 specimens and the MSS/MS17 (50/50) blend specimen. From the slope and the intercept of the approximated lines, values of the \( g \) factor and \( D_G \) were estimated, respectively, which are summarized in Table 2. At a glance of the SAXS profiles shown in Figure 4, the fact that the grain size in the blend was smaller as compared to that of the neat lamellar specimen (MS11) might be ascribed to blending. However, this is not appropriate because the grain sizes of the neat MS5 and MS17 specimens (before blending) are found to be as small as that of the blend. By examining the results shown in Table 2, it can be concluded that both the grain size and the \( g \) factor were almost unchanged upon blending.
We now examine the temperature dependence of the lamellar spacing. To clearly examine the unusual behavior, the exponent $\alpha$ in the relationship of $D \sim T^\alpha$ is evaluated with the scaling behavior between $D$ and $T$ in the short experimental range of 150–180 °C. Actually, this assumption can be confirmed in Figure 6 (the double logarithmic plots of the lamellar spacing $D$ and the absolute temperature $T$) for all of the antisymmetric blends (with similar molecular weights), although our previous result showed nonlinear dependence for much wider temperature range (120–220 °C).19

Note here that $D$ is evaluated by $D = 2\pi/q^*$ from the $q$ position ($q^*$) of the first-order peak in the SAXS profile. In order to accurately determine $q^*$, the computational peak fitting was performed on the first-order peak. As seen in the plot of Figure 6c (for the neat MS11 diblock copolymer), the usual behavior is observed with a slightly higher value of $\alpha$ than the usual one ($\alpha = -0.33$). On the other hand, unusual behaviors are seen for all of the blend specimens. Especially, completely opposite temperature dependence is observed for the MS1/MS19 blend specimen. Note here that the two diblock copolymers have fully symmetric compositions. The dependence of $\alpha$ on the degree of deviation in composition, $\Delta \phi$, is shown in Figure 7a. Here, $\Delta \phi$ is defined as

$$\Delta \phi = x_1 \phi_{PS,1} - 0.5l + x_2 \phi_{PS,2} - 0.5l$$

(8)

where $x_1$ and $x_2$ are the volume fraction of the diblock copolymers 1 and 2, respectively, in the binary blend ($x_1 + x_2 = 1$). $\phi_{PS,1}$ and $\phi_{PS,2}$ denote the volume fraction of PS in the diblock copolymers 1 and 2, respectively. It is clear that $\alpha$ increases with $\Delta \phi$ and that its dependency is accelerated as a function of $\Delta \phi$. Although it was possible to fit the data with a mathematic equation, it is more convenient to obtain a linear dependence. For this purpose, we introduce the degree of

$$\alpha = d \log V^{1/3}/d \log T = \beta T/3$$

(7)

For the temperature range of the examination of the scaling behavior in Figure 6 (150–180 °C), the scaling exponent due to the thermal expansion can be estimated using eq 7 as 0.072–0.091, which is quite a bit smaller than $\alpha = 0.42$ at most experimental values found by this study.

Such unusual temperature dependence of $D$ ($D$ increases with temperature) has been reported already in our previous publication19 for the case when the two blended diblock copolymers have biased compositions. The dependence of $\alpha$ on the degree of deviation in composition, $\Delta \phi$, is shown in Figure 7a. Here, $\Delta \phi$ is defined as

$$\Delta \phi = x_1 \phi_{PS,1} - 0.5l + x_2 \phi_{PS,2} - 0.5l$$

(8)

where $x_1$ and $x_2$ are the volume fraction of the diblock copolymers 1 and 2, respectively, in the binary blend ($x_1 + x_2 = 1$). $\phi_{PS,1}$ and $\phi_{PS,2}$ denote the volume fraction of PS in the diblock copolymers 1 and 2, respectively. It is clear that $\alpha$ increases with $\Delta \phi$ and that its dependency is accelerated as a function of $\Delta \phi$. Although it was possible to fit the data with a mathematic equation, it is more convenient to obtain a linear dependence. For this purpose, we introduce the degree of

Figure 6. Double logarithmic plots of the lamellar spacing $D$ and the absolute temperature $T$ for the binary blends of MS diblock copolymers having antisymmetric compositions with respect to the volume fraction of 0.50. (a) MS1/MS19 (50/50), (b) MS5/MS17 (50/50), (c) MS11 neat diblock, (d) MS3/MS18 (50/50), and (e) MS8/MS13 (50/50) specimens. Note here that the two diblock copolymers in each blend specimen have similar molecular weights. 

Table 2. Results of the Hosemann Analysis

| specimen      | morphology | grain size (nm) | $g$ factor |
|---------------|------------|----------------|------------|
| MS5           | cylinder   | 141            | 0.0350     |
| MS11          | lamella    | 432            | 0.0250     |
| MS17          | cylinder   | 132            | 0.0379     |
| MS5/MS17 (50/50) | lamella   | 175            | 0.0343     |

Figure 5. Hosemann plots ($\Delta q^2$ vs $m^3$) for the neat MS5 (cylinder), MS11 (lamella), and MS17 (cylinder) specimens and MS5/MS17 (50/50) blend specimen (lamella).
range of 0.4–0.6 at \( \chi Z \approx 20 \). Therefore, it was also possible to check the relationship between \( \alpha \) and \( \tau \) as shown in Figure 7c for the cases of the average PS fraction of 0.40 and 0.60 (not exactly identical to 0.50). On the contrary to Figure 7b, the linearity is poor. As for the blend of homopolymers 1 and 2, the relationship between \( \alpha \) and \( \tau \) is the same as the approximated line in Figure 7b but the broken line is shifted to set the origin of this broken line at \( (\alpha, \tau) \approx (-0.25, 0.5) \). Interestingly, the good linearity is only found for the average PS fraction of 0.50 (Figure 7b), while the linearity is poor for the case of the average PS fraction being not exactly identical to 0.50 (Figure 7c). This fact clearly indicates that the temperature behavior of the lamellar microdomain spacing can be controlled almost perfectly by means of \( \tau \) for the case of the lamellar structure comprising the antisymmetric AB/AB diblock copolymer chains, as shown ideally in Figure 1.

Moreover, a slight breaking of the balance of the antisymmetric compositions in the two kinds of the AB diblocks (namely, those compositions do not meet \( \phi_{PS,1} = 1 - \phi_{PS,2} \)) can be allowed for the precise controlling of \( \alpha \) by means of \( \tau \) as long as the average composition is maintained at 0.50. On the contrary, the precise controlling of \( \alpha \) by means of \( \tau \) is difficult when the average composition is not identical to 0.50 (namely, the lamellar structure is not like that shown in Figure 1). Thus, the illustration in Figure 1 is considered to give a good physical insight into recognizing the anomalous temperature behavior (namely, the lamellar spacing increases with temperature).

Figure 8 explains the reason for the unusual behavior of \( D \) for the case of the antisymmetric binary blend of diblock copolymers forming the lamellar morphology, as compared with the case of the neat diblock copolymers. Here, the UCST-type behavior is assumed. As shown in Figure 8a, the repulsive interaction between A and B block chains deforms the polymer coils in the direction perpendicular to the lamellar interface. Therefore, the degree of the deformation of the polymer coil is decreased when the repulsive interaction is decreased at higher temperature. This explains qualitatively the decrease in \( D \) with the increase in \( T \) for the neat diblock copolymers (enhancement of miscibility results in \( D_1 < D_c \)). As for the case of the antisymmetric binary blend of diblock copolymers forming the lamellar morphology (Figure 8b and 8c), the strong segregation between the longer A and the longer B chains is screened by the shorter A and the shorter B chains. Due to the screen effect, the longer chains of A and B cannot feel their existence, and therefore the longer chains are not necessarily stretched in the direction perpendicular to the lamellar interface (the longitudinal direction). On the contrary at higher temperature, the miscibility between the shorter A and the shorter B chains is increased because the value of \( \chi Z \) (segregation power) is lower for the lower molecular-weight components. Therefore, the shorter A and B chains can be more or less partially mixed, resulting in interdigitation of the interface, as shown in Figure 8b and 8c. The mixed shorter A/B chain interface can be formed, if the molecular weights of the shorter chains are small enough to meet the condition of the miscibility (i.e., the \( \chi Z \) value is lower than the critical value of the complete miscible state). In such condition, the lateral distance between the two neighboring longer chains is decreased so that the chance of chain overlapping is increased. To avoid the chain overlaps, the longer chains tend to be stretched. Due to this effect the longer chains are more or less stretched in the longitudinal direction even at higher temperature (as schematically illustrated in

Figure 7. (a) Dependence of the exponent \( \alpha \) on the degree of deviation in composition, \( \Delta \phi \), for the average PS fraction of 0.50 (antisymmetric MS/MS blends). Note here that the exponent \( \alpha \) denotes the scaling relation between \( D \) and \( T \) as \( D \sim T^{\alpha} \). The definition of \( \Delta \phi \) is given by eq 8 in the text. (b) Dependence of \( \alpha \) on the degree of asymmetry \( \tau \) of the composition for the blends with the average PS fraction of 0.50 (not only for the antisymmetric cases but also for the nonantisymmetric cases). The definition of \( \tau \) is given by eq 9 in the text. (c) The same plot as (b) but for the average PS fraction of 0.40 and 0.60.

\[
\tau = \frac{x_1\left(1 - \phi_{PS,1}\right)}{\phi_{PS,1} - \phi_{PS,2}} + x_2\left(1 - \frac{\phi_{PS,2}}{\phi_{PS,1}}\right) - 1
\]  

where \( \phi_{PS,1} < 0.5 \) and \( \phi_{PS,2} > 0.5 \). For the neat diblock copolymer with the composition of 0.50, \( \tau \) is so defined to be zero. As for the blend of homopolymers 1 and 2, \( \tau \) becomes infinity. For the MS1/MS19 specimen exhibiting the unusual behavior as shown in Figure 6a, \( \tau \) is quite large (\( \tau = 3.13 \)). Thus, it is considered that the unusual behavior is more intensively observed (namely, the exponent \( \alpha \) becomes positive and larger) for the larger value of \( \tau \). We now examine the relationship between \( \alpha \) and \( \tau \) quantitatively in Figure 7b for the blends with the average PS fraction of 0.50 (not only for the antisymmetric cases but also for the nonantisymmetric cases). In Figure 7b, good linearity can be confirmed. This clearly indicates that \( \tau \) is a good measure of the unusual behavior of \( D \). As shown in Figure 2, the blends of two diblock copolymers can form the lamellar morphology in the average composition (namely, the lamellar structure is not like that shown in Figure 1). Thus, the illustration in Figure 1 is considered to give a good physical insight into recognizing the anomalous temperature behavior (namely, the lamellar spacing increases with temperature).
Based on the result shown in Figure 7, the values of the spacing $D$ at 150 °C were plotted in Figure 9a against the summation of $M_n$ of the PMA block in the MS diblock 1 having $\phi_{PS,1} (>0.5)$ and $M_n$ of the PS block in the MS diblock 2 having $\phi_{PS,2} (>0.5)$. Note here that the labels a–e indicate the data points for the blend specimens shown in Figures 6a–6e, respectively. It is very clear that the linearity of the data points in Figure 9a is much better as compared to the plot shown in Figure 9b as a function of the average $M_n$ of the two diblocks blended, although the values of the spacing for the points at a and b and those at c and d are not appropriately in a good order as a function of $M_n$ (PMA,1) + $M_n$ (PS,2). However, the plots in Figure 9a still show satisfactorily the good linearity as it is.

Figure 10 shows the results in the double logarithmic plots of $D$ and $T$ for the MSS/MS17 (50/50) blend specimen. The temperature ramp-up rate was 2.0 °C/min, and the cooling rate was also 2.0 °C/min. The hysteresis of the changes in $D$ is clearly observed, and then it can be stated that the temperature-independent $D$ in the first heating process was not permanent. It is interestingly found that $D$ is almost constant not only in the first heating but also in the second heating, although the level of $D$ increased. Furthermore, the usual behavior with the exponent $\alpha$ being equal to $-0.33$ (which is also usual) was found in the second cooling process. The illustration presented in Figure 8b is considered irreversible, and it may be speculated that the arrangement of the shorter chains giving rise to the screening compositions our experimental result of the anomaly in the temperature dependence of the domain spacing ($D$ increases with $T$) is theoretically supported.

It is important to recognize that the spacing $D$ can be scaled by the total lengths of the longer block chains A and B, according to the molecular model as illustrated in Figure 1. To examine this insight, the values of the spacing $D$ at 150 °C were plotted in Figure 9a against the summation of $M_n$ of the PMA block in the MS diblock 1 having $\phi_{PS,1} (>0.5)$ and $M_n$ of the PS block in the MS diblock 2 having $\phi_{PS,2} (>0.5)$. Note here that the labels a–e indicate the data points for the blend specimens shown in Figures 6a–6e, respectively.
The invariance in the arrangement of the chains can easily rearrange positions as compared to the longer and shorter B chains when heated again because the shorter macroscopic phase separation, the blend specimen is the rearrangement of the shorter chains promotes also the process, and then the usual behavior appeared in the third heating process, and then the usual behavior appeared in the third heating process. Therefore, it is considered that the rearrangement of invariant behavior is no longer the case in the third heating temperature-invariant concluded that such anomalous behavior (including the optical property) independent of temperature. Nevertheless, it was found that such anomalous behavior (including the temperature-invariant D behavior) is only transient (not permanent), taking place along the course of the macroscopic phase separation between the diblock copolymers 1 and 2, as it may be theoretically predicted by Shi and Noolandi.12 As for the application for the utilization of the temperature-invariant properties (for instance, the optical properties due to the form birefringence of microdomains20,61), cross-linking of constituent block chains may work for the robustness of temperature-invariant properties in many repeated cycles of heating and cooling.

■ CONCLUSIONS

The morphologies of the microphase-separated structures in the binary blends of diblock copolymers (SI/SI) have been studied intensively for the case of diblock copolymers bearing antisymmetric compositions with similar molecular weights. Here, the two diblock copolymers 1 and 2, of which compositions are 0.5 − x and 0.5 + x (0 < x < 0.5), respectively, were blended, and the morphology diagram was constructed in the plot of \( \chi \Delta Z \) vs \( \phi \). The temperature dependencies of the morphologies were analyzed by synchrotron SAXS measurements. It was found that the morphology diagram agrees in principle with the theoretical one by Matsen and Bates, although the disordered phase was a bit expanded in the experimentally determined morphology diagram.

The antisymmetric binary blends of MS diblock copolymers having oppositely biased compositions were prepared to study anomalous temperature dependence of the lamellar spacing. For this purpose, more than 20 specimens have been synthesized with a wide range of compositions from 0.20 to 0.87 and the range of the molecular weight of 12000–33800. Note that the molecular weights of the blended diblock copolymers were chosen almost the same as each other and that the compositions of the blended diblock copolymers 1 and 2 are \( \phi_{PS,1} = 0.5 − x \) and \( \phi_{PS,2} = 0.5 + x \) (0 < x < 0.5), respectively. By closely adjusting the average PS volume fraction in the blend specimen at 0.50, it was possible to form the lamellar morphology without macroscopic phase separation, as speculated something like the illustration shown in Figure 1. As a result of the SAXS analyses, the following things were found. The scaling exponent \( \alpha \) in \( D \sim T^\alpha \) was still negative but slightly larger than the usual value (i.e., \( \alpha = −0.33 \)) for the smaller degree of asymmetry in the composition (i.e., x is small), while \( \alpha \) became positive for the higher degree of asymmetry. The latter result is very anomalous because the temperature dependence is opposite (i.e., the lamellar spacing increases with an increase of temperature). The value of \( \alpha \) was found to be linearly rationalized with the degree of compositional asymmetry \( \tau \) (which is especially introduced in the current paper for this purpose), including nonantisymmetric binary blend cases (however, with the average PS composition being set rigorously at 0.50). Based on this result, one can prepare lamellar microdomains of which spacing does not change with temperature by blending two diblock copolymers with \( \tau = 1.33 \) (corresponding to \( \phi_{PS,1} = 0.3 \) and \( \phi_{PS,2} = 0.7 \)) having similar molecular weights. This would be important for manufacturing materials with properties (for instance, the optical property) independent of temperature. Nevertheless, it was found that such anomalous behavior (including the temperature-invariant D behavior) is only transient (not permanent), taking place along the course of the macroscopic phase separation between the diblock copolymers 1 and 2. Cross-linking of constituent block chains may work for the robustness of temperature-invariant properties in many repeated cycles of heating and cooling. From the current study, the binary blends of the antisymmetric diblock copolymers were concluded to be versatile such that the precise controls of the morphologies and the temperature dependencies of the lamellar microdomains were possible.

■ EXPERIMENTAL SECTION

Specimens. Two SI diblock copolymers, SIZ-3 and SIZ-4, were synthesized by living anionic polymerization. The molecular characteristics are \( \phi_{PS} = 0.65 \) and \( M_n = 26.1 \times 10^3 \) for SIZ-3 and \( \phi_{PS} = 0.26 \) and \( M_n = 24.5 \times 10^3 \) for SIZ-4. These are the same specimens used in our previous studies.19,21,22

The MS diblock copolymers were synthesized by atom transfer radical polymerization (ATRP) under reduced pressure, according to the previous method.22,62,63 Inhibitors of radical polymerization (or antioxidants) in styrene (Extra Pure Reagent, Nacalai Tesque Co., Ltd.), methyl acrylate (Extra Pure Reagent, Nacalai Tesque), anisole (Extra Pure Reagent, Nacalai Tesque), and toluene (Extra Pure Reagent, Nacalai Tesque) were removed by adsorption on granulated
alumina. \(N,N',N'' N''\)-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich Chemical Co., Ltd.), methyl 2-bromopropionate (MBBr, 98%, Aldrich), and CuBr (98%, Aldrich) were used as received. As a first component, PMA was synthesized. The initiator (MBBr), CuBr(I), and the ligand (PMDETA) with their molar ratio 2:1:1 were added to a given amount of the methyl acrylate monomer. Finally, the solvent anisole was poured into the system with the concentration of 25 wt % with respect to the monomer amount. The solution was added in a round-bottomed flask. After degassing by freeze-and-thaw cycles three times, the flask was sealed in vacuum. The sealed flask was immersed into an oil-bath at 368 K to conduct polymerization. After the polymerization, the solution was diluted with toluene. Activated alumina powders were used to remove the catalysts. Subsequently, synthesized PMA was precipitated into a large amount of methanol from the toluene solution. The PMA was dried under vacuum at 323 K for 24 h and subjected to the gel permeation chromatography (GPC) measurements to determine \(M_n\) and its distribution \((M_w/M_n)\). The radical can be reproduced at the PMA chain ends and was used as a macroinitiator in the successive stage of the chain extension reaction of PS chains. This polymer was chain-extended with PS via the ATRP at 383 K using the CuBr(I) (or CuCl(I)) and PMDETA. The PMA macroinitiator, CuBr(I) (or CuCl(I)), and the ligand with 1:1:1 molar ratio were added to a given amount of the styrene monomer. Finally, the solvent anisole was poured into the system with the concentration of 25 wt % with respect to the monomer amount and then polymerized at 383 K. The catalysts were removed by the same procedure mentioned above. After the chain extension reaction, the reaction mixture was purified by the precipitation from toluene solution into excess methanol. Then, the total \(M_n\) and \(M_w/M_n\) were determined by the GPC measurement. To evaluate the composition, nuclear magnetic resonance (NMR) measurements were performed on AVANCE (Bruker) operated at 200 MHz at room temperature. The deuterated chloroform \((\text{CDCl}_3)\) was used as a solvent. Using the densities \(\phi_{PS}\) was eventually evaluated. The characteristics of MS samples thus synthesized are summarized in Table 1.

Preparation of the Blend Specimens. It is very important to prepare the blend specimens without undergoing the macroscopic phase separation. As a matter of fact, there would be a large chance of the macroscopic phase separation if the general solution casting would be conducted for the binary blend of diblock copolymers 1 and 2 for which compositions are very much different. Therefore, the special solution casting protocol was employed in the current study according to the method, which was already reported in our previous publication.59 In principle, this method utilizes blow drying of the casting solution developed on the water surface to quickly evaporate the cast solvent. First, the MS diblock copolymers were independently weighed to make a blend with a given ratio, and then they were altogether dissolved in toluene. The casting solution was prepared with 8 wt % of the total polymer concentration by stirring for more than 12 h. A small amount of an antioxidant (\(\text{tert-}\text{butyl catechol}\)) was added to set the final concentration at 0.2 wt % of the antioxidant in the polymer specimen. Then, the casting solution was developed on the surface of distilled water by using a syringe. Then, it was dried drop by drop by using a hair dryer, and the dried specimen was gathered. This treatment was repeated many times to obtain a large enough amount of the specimen. Finally, the specimens were thermally annealed at 150 °C for 24 h in an oven purged with the dried nitrogen gas in order to fabricate a regular lamellar morphology without the macroscopic phase separation, as schematically shown in Figure 1.

Note here that the molecular weights of the blended diblock copolymers were chosen almost the same as each other. Actually the molecular weights of the blended specimens, which are used for the examination of the temperature dependence of \(D\) as shown in Figure 6, are similar to each other, as MS1/ MS19 (16500/14500; the ratio is 1.14), MS5/MS17(20900/ 20600; the ratio is 1.01), MS3/MS18 (12900/14000; the ratio is 1.09), and MS8/MS13 (15200/14200; the ratio is 1.07).

SAXS Measurements. The SAXS measurements were carried out at the BL-10C beamline of the Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan, by using X-ray with a wavelength of 0.1488 nm. This beamline provides a quasi point-focused beam by using a toroidal mirror, and the beam size was measured at the detector position, which was 850 μm in the vertical direction and 1000 μm in the horizontal direction. A standard slit system with widths of 0.7 × 0.7 mm was used for the SAXS collimation. The sample-to-detector distance was set at 1.9 m. A position-sensitive-proportional counter was used as a one-dimensional detector to measure the scattering-angle-dependent X-ray intensity (one-dimensional SAXS profile) at once. The scattering intensity of an empty cell was subtracted from that of a specimen by taking into account of absorption due to the specimen. For the measurements of the temperature-dependent SAXS profiles, the time-resolved measurements were performed with the heating of the specimen at 2 °C/min in a narrow temperature range of 150–180 °C.

**Author Information**

**Corresponding Author**

*E-mail: shin@kit.ac.jp.*

**ORCID**

Shinichi Sakurai: 0000-0002-5756-1066

**Notes**

The authors declare no competing financial interest.

**Acknowledgments**

The SAXS experiments were performed under the approval of the Photon Factory (High Energy Research Organization, Tsukuba, Japan) Program Advisory Committee (Proposal No. 2005G187).

**References**

1. Matsen, M. W.; Bates, F. S. Unifying Weak- and Strong-Segregation Block Copolymer Theories. *Macromolecules* 1996, 29, 1091–1098.
2. Park, S.; Kwon, K.; Cho, D.; Lee, B.; Ree, M.; Chang, T. Phase Diagram Constructed from the HPLC Fractions of a Polystyrene-b-polyisoprene Prepared by Anionic Polymerization. *Macromolecules* 2003, 36, 4662–4666.
3. Hadziioannou, G.; Skoullos, A. Structural Study of Mixtures of Styrene/Isoprene Two- and Three-Block Copolymers. *Macromolecules* 1982, 15, 267–271.
4. Hashimoto, T.; Yasamaki, K.; Koizumi, S.; Hasegawa, H. Ordered Structure in Blends of Block Copolymers. I. Miscibility Criterion for Lamellar Block Copolymers. *Macromolecules* 1993, 26, 2895–2904.
5. Shi, A.-C.; Noolandi, J. Effects of Short Diblocks at Interfaces of Strongly Segregated Long Diblocks. *Macromolecules* 1994, 27, 2936–2944.
(6) Hashimoto, T.; Koizumi, S.; Hasegawa, H. Ordered Structure in Blends of Block Copolymers. 2. Self-Assembly for Immiscible Lamella-Forming Copolymers. Macromolecules 1994, 27, 1562–1570.

(7) Koizumi, S.; Hasegawa, H.; Hashimoto, T. Ordered Structure in Blends of Block Copolymers. S. Self-Assembly in Blends of Sphero- or Cylinder-Forming Copolymers. Macromolecules 1994, 27, 4371–4381.

(8) Spontak, R. J. Self-consistent Field Theory of Ordered Block Copolymer Blends. I. (AB)$_n$/[(AB)$_m$ Blends. Macromolecules 1994, 27, 6363–6370.

(9) Shi, A.-C.; Noolandi, J.; Hoffmann, H. Diblock Copolymer Blends as Mixtures of Surfactants and Cosurfactants. Macromolecules 1994, 27, 6661–6664.

(10) Vilesov, A. D.; Floudas, G.; Pakula, T.; Melenevskaya, Y. E.; Birshtein, T. M.; Lyatskaya, Y. V. Lamellar structure formation in the mixture of two cylinder-forming block copolymers. Macromol. Chem. Phys. 1994, 195, 2317–2326.

(11) Shi, A.-C.; Noolandi, J. Binary Mixtures of Diblock Copolymers: Phase Diagrams with a New Twist. Macromolecules 1995, 28, 3103–3109.

(12) Matsen, M. W.; Bates, F. S. One-Component Approximation for Binary Diblock Copolymer Blends. Macromolecules 1995, 28, 7298–7300.

(13) Matsen, M. W. Immiscibility of large and small symmetric diblock copolymers. J. Chem. Phys. 1995, 103, 3268–3271.

(14) Zhao, J.; Majumdar, B.; Schulz, M. F.; Bates, F. S.; Almdal, K.; Mortensen, K.; Hajduk, D. A.; Gruner, S. M. Phase Behavior of Pure Diblocks and Binary Diblock Blends of Poly(ethylene)-Poly(ethylacrylate). Macromolecules 1996, 29, 1204–1215.

(15) Spontak, R. J.; Fung, J. C.; Braunfeld, M. B.; Sedat, J. W.; Agard, D. A.; Kane, L.; Smith, S. D.; Satkowski, M. M.; Ashraf, A.; Hajduk, D. A.; Gruner, S. M. Phase Behavior of Ordered Diblock Copolymer Blends: Effect of Compositional Heterogeneity. Macromolecules 1996, 29, 4494–4507.

(16) Lin, E. K.; Gast, A. P.; Shi, A.-C.; Noolandi, J.; Smith, S. D. Effect of Short Diblock Copolymers at Internal Interfaces of Large Diblock Copolymer Mesophases. Macromolecules 1996, 29, 5920–5925.

(17) Kane, L.; Satkowski, M. M.; Smith, S. D.; Spontak, R. J. Phase Behavior and Morphological Characteristics of Compositionally Symmetric Diblock Copolymer Blends. Macromolecules 1996, 29, 8662–8870.

(18) Yamaguchi, D.; Hashimoto, T.; Han, C. D.; Baek, D. M.; Kim, J. K.; Shi, A.-C. Order-Disorder Transition, Microdomain Structure, and Phase Behavior in Binary Mixtures of Low Molecular Weight Polystyrene-block-polysoprene Copolymers. Macromolecules 1997, 30, 5832–5842.

(19) Sakurai, S.; Umeda, H.; Yoshida, A.; Nomura, S. Anomalous Temperature Behavior of Lamellar Micromdomain Structures in Binary Blends of Polystyrene-block-polysoprene Diblock Copolymers. Macromolecules 1997, 30, 7614–7617.

(20) Sakurai, S.; Nomura, S. Phase behaviour in binary mixtures of diblock copolymers as analysed by the random phase approximation calculations. Polymer 1997, 38, 4103–4112.

(21) Sakurai, S.; Umeda, H.; Furukawa, C.; Irie, H.; Nomura, S.; Lee, H. H.; Kim, J. K. Thermally induced morphological transition from lamella to gyroid in a binary blend of diblock copolymers. J. Chem. Phys. 1998, 108, 4333–4339.

(22) Sakurai, S.; Irie, H.; Umeda, H.; Nomura, S.; Lee, H. H.; Kim, J. K. Gyroid Structures and Morphological Control in Binary Blends of Polystyrene-block-polysoprene Diblock Copolymers. Macromolecules 1998, 31, 336–343.

(23) Koneripalli, N.; Levicky, R.; Bates, F. S.; Matsen, M. W.; Satija, S. K.; Ankner, J.; Kaiser, H. Ordering in Blends of Diblock Copolymers. Macromolecules 1998, 31, 3498–3508.

(24) Yamaguchi, D.; Bodycomb, J.; Koizumi, S.; Hashimoto, T. Ordered Structure in Blends of Block Copolymers. 4. Location of the Short Diblock. Macromolecules 1999, 32, 5884–5894.

(25) Lipic, P. M.; Bates, F. S.; Matsen, M. W. Non-equilibrium phase behavior of diblock copolymer melts and binary blends in the intermediate segregation regime. J. Polym. Sci., Part B: Polym. Phys. 1999, 37, 2229–2238.

(26) Yamaguchi, D.; Shiratake, S.; Hashimoto, T. Ordered Structure in Blends of Block Copolymers. 5. Blends of Lamella-Forming Block Copolymers Showing both Microphase Separation Involving Unique Morphological Transformations and Macrophase Separation. Macromolecules 2000, 33, 8258–8268.

(27) Yamaguchi, D.; Takenaka, M.; Hasegawa, H.; Hashimoto, T. Macro- and Microphase Transitions in Binary Blends of Block Copolymers with Complementarily Asymmetric Compositions. Macromolecules 2001, 34, 1707–1719.

(28) Court, F.; Hashimoto, T. Morphological Studies of Binary Mixtures of Block Copolymers. 1. Cosurfactant Effects and Composition Dependence of Morphology. Macromolecules 2001, 34, 2536–2545.

(29) Yamaguchi, D.; Hasegawa, H.; Hashimoto, T. A Phase Diagram for the Binary Blends of Nearly Symmetric Diblock Copolymers. 2. Parameter Space of Temperature and Blend Composition. Macromolecules 2001, 34, 6506–6518.

(30) Court, F.; Hashimoto, T. Morphological Studies of Binary Mixtures of Block Copolymers. 2. Chain Organization of Long and Short Blocks in Lamellar Microdomains and Its Effect on Domain Size and Stability. Macromolecules 2002, 35, 2566–2575.

(31) Court, F.; Yamaguchi, D.; Hashimoto, T. Morphological Studies of Binary Mixtures of Block Copolymers: Temperature Dependence of Cosurfactant Effects. Macromolecules 2006, 39, 2596–2605.

(32) Chen, Y.; Wang, Z.; Gong, Y.; Huang, H.; He, T. Solvent-Induced Novel Morphologies in Diblock Copolymer Blend Thin Films. J. Phys. Chem. B 2006, 110, 1647–1655.

(33) Chen, F.; Kondo, Y.; Hashimoto, T. Control of Nanostructure in Mixtures of Block Copolymers: Curvature Control via Cosurfactant Effects. Macromolecules 2007, 40, 3714–3723.

(34) Guo, R.; Huang, H.; Chen, Y.; Gong, Y.; Du, B.; He, T. Effect of the Nature of Annealing Solvent on the Morphology of Diblock Copolymer Blend Thin Films. Macromolecules 2008, 41, 890–900.

(35) Court, F.; Yamaguchi, D.; Hashimoto, T. Morphological and Scattering Studies of Binary Mixtures of Block Copolymers: Cosurfactant Effects Observed in the Parameter Space of Temperature, Blend Composition, and Molecular Weight Ratio. Macromolecules 2008, 41, 4828–4837.

(36) Wu, Z.; Li, B.; Jin, O.; Ding, D.; Shi, A.-C. Microphase and Macrophase Separations in Binary Blends of Diblock Copolymers. Macromolecules 2011, 44, 1680–1694.

(37) Spiro, J. G.; Illy, N.; Winnik, M. A.; Vavasour, J. D.; Whittmore, M. D. Theory of Lamellar Superstructure from a Mixture of Two Cylindrical PS–PMMA Block Copolymers. Macromolecules 2012, 45, 4280–4294.

(38) Padmanabhan, P.; Martinez-Veracoechea, F. J.; Araque, J. C.; Escobedo, F. A. A theoretical and simulation study of the self-assembly of a binary blend of diblock copolymers. J. Chem. Phys. 2012, 136, 234905.

(39) Park, S.-B.; Ha, J.-G.; Hahn, S. K.; Zin, W.-C. Temperature-dependent location of a weakly segregated block copolymer in binary blends of block copolymers. J. Polym. Sci., Part B: Polym. Phys. 2014, 52, 470–476.

(40) Kane, L.; Norman, D. A.; White, S. A.; Matsen, M. W.; Satkowski, M. M.; Smith, S. D.; Spontak, R. J. Molecular, Nanostructural and Mechanical Characteristics of Lamellar Triblock Copolymer Blends: Effects of Molecular Weight and Constraint. Macromol. Rapid Commun. 2001, 22, 281–296.
Morphology and Adhesion Property of Polystyrene Block Copolymer. *J. Adhesion Sci. Technol.* 2011, 25, 869–881.

(44) Nakamura, Y.; Adachi, M.; Ito, K.; Kato, Y.; Fuji, S.; Sasaki, M.; Urahama, Y.; Sakurai, S. Effects of Compatibility between Tackifier and Polymer on Adhesion Property and Phase Structure: Tackifier-added Polystyrene-based Triblock/Diblock Copolymer Blend System. *J. Appl. Polym. Sci.* 2011, 120, 2251–2260.

(45) Sakurai, S.; Isobe, D.; Okamoto, S.; Nomura, S. Control of Mechanical Properties via Morphological Control through Blending of Elastomeric Polystyrene-block-polybutadiene-block-polystyrene Tri-block Copolymers. *Zairyo* 2001, 225–228.

(46) Lach, R.; Weidisch, R.; Knoll, K. Morphology and Mechanical Properties of Binary Triblock Copolymer Blends. *J. Polym. Sci., Part B: Polym. Phys.* 2005, 43, 429–438.

(47) Thunga, M.; Satapathy, B. K.; Staudinger, U.; Weidisch, R.; Abdel-Goad, M.; Janke, A.; Knoll, K. Dynamic Mechanical and Rheological Properties of Binary S-(S/B)-S Triblock Copolymer Blends. *J. Polym. Sci., Part B: Polym. Phys.* 2008, 46, 329–343.

(48) Vaidya, N. Y.; Han, C. D. Temperature-Composition Phase Diagrams for Binary Blends Consisting of Chemically Dissimilar Diblock Copolymers. *Macromolecules* 2000, 33, 3009–3018.

(49) Spontak, R. J.; Fung, J. C.; Braunfeld, M. B.; Sedat, J. W.; Agard, D. A.; Ashraf, A.; Smith, S. D. Architecture-Induced Phase Immiscibility in a Diblock/ Multiblock Copolymer Blend. *Macromolecules* 1996, 29, 2850–2856.

(50) Shibayama, M.; Hashimoto, T.; Kawai, H. Ordered structure in block polymer solutions. 1. Selective solvents. *Macromolecules* 1983, 16, 16–28.

(51) Hashimoto, T.; Shibayama, M.; Kawai, H. Ordered structure in block polymer solutions. 4. Scaling rules on size of fluctuations with block molecular weight, concentration, and temperature in segregation and homogeneous regimes. *Macromolecules* 1983, 16, 1093–1101.

(52) Miwa, Y.; Yamamoto, K.; Sakaguchi, M.; Sakai, M.; Tanida, K.; Hara, S.; Okamoto, S.; Shimada, S. A Site-Specific ESR Spin-Labeling Study of Molecular Motion in Microphase-Separated Polystyrene-block-poly(methyl acrylate) with Lamellar Morphology. *Macromolecules* 2004, 37, 831–839.

(53) Khandpur, A. K.; Förster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. Polyisoprene-Polystyrene Diblock Copolymer Phase Diagram near the Order-Disorder Transition. *Macromolecules* 1995, 28, 8796–8806.

(54) Hashimoto, T.; Kawamura, T.; Harada, M.; Tanaka, H. Small-Angle Scattering from Hexagonally Packed Cylindrical Particles with Paracrystalline Distortion. *Macromolecules* 1994, 27, 3063–3072.

(55) Matsushita, Y.; Momose, H.; Yoshida, Y.; Noda, I. Lamellar domain spacing of the ABB graft copolymers. *Polymer* 1997, 38, 149–153.

(56) Hosemann, R.; Lemm, K.; Wilke, W. The Paracrystal as a Model for Liquid Crystals. *Mol. Cryst.* 1967, 1, 333–362.

(57) Ohnogi, H.; Sasaki, S.; Sakurai, S. Evaluation of Grain Size by Small-Angle X-Ray Scattering for a Block Copolymer Film in Which Cylindrical Microdomains Are Perpendicularly Oriented. *Macromol. Symp.* 2016, 366, 35–41.

(58) Brandrup, J.; Immergut, E. H., Ed., *Polymer Handbook*, 3rd ed.; John Wiley & Sons: New York, 1989; p V/81.

(59) Simha, R.; Boyer, R. F. On a General Relation Involving the Glass Temperature and Coefficients of Expansion of Polymers. *J. Chem. Phys.* 1962, 37, 1003–1007.

(60) Folkes, M. J.; Keller, A. The birefringence and mechanical properties of a ‘single crystal’ from a three-block copolymer. *Polymer* 1971, 12, 222–236.

(61) Sakurai, S.; Yoshida, H.; Fukuoka, R.; Mouri, M.; Yamamoto, K.; Okamoto, S. Spontaneous Perpendicular Orientation of Cylindrical Microdomains in a Block Copolymer Thick Film. *Macromolecules* 2009, 42, 2115–2121.

(62) Miwa, Y.; Tanida, K.; Yamamoto, K.; Okamoto, S.; Sakaguchi, M.; Sakai, M.; Makita, S.; Sakurai, S.; Shimada, S. Dynamic Heterogeneity in Interfacial Region of Microphase-Separated Poly-