*Macromolecules* **2005,** *38,* 4371−4376

# Effect of Molecular Weight Distribution on Microphase-Separated Structures from Block Copolymers

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*Received January 7, 2005; Revised Manuscript Received February 16, 2005*

ABSTRACT: The effect of molecular weight distribution on microphase-separated structures for both AB diblock and BAB triblock copolymers was investigated in comparison with that of composition distribution. Monodisperse poly(styrene-*b*-2-vinylpyridine) (SP) and poly(2-vinylpyridine-*b*-styrene-*b*-2-vinylpyridine) (PSP) parent block copolymers were synthesized by living anionic polymerizations whose volume ratios were all designed to be 0.5/0.5. Three parent copolymers were blended variously with both number-average molecular weight and composition kept constant but having different molecular weight distribution. Microphase-separated structures of sample films obtained by solvent-casting followed by annealing were observed by transmission electron microscopy and small-angle X-ray scattering. It has been found that both SP and PSP block copolymers show simple lamellar structures even when the molecular weight distribution is relatively wide and that lamellar domain spacing increases with increase in polydispersity index of the blend system. Furthermore, the increment for PSP triblock is larger than that for SP diblock as was the result for the study on composition distribution. The microdomain expansion can be caused by the localization of polydisperse block chains in both phases, which was commonly observed for both the composition distribution system and the molecular weight distribution system.

## Introduction

Microphase-separated structures of block copolymers have been extensively studied for nearly four decades. In early days, it was the morphological transition with composition that was treated.[1−3] The dependence of molecular weight on microdomain size has been investigated precisely from the experimental viewpoint,[4−6] while theoretical studies were also made.[7,8] Chain connectivity has been recognized as another important molecular parameter of block copolymers and investigated systematically by observing microphase-separated structures made from various kinds of block copolymers such as ABA (BAB) linear,[9−12] ABB graft,[13−15] AB ring,[16−19] ABC linear,[20−23] ABC star,[24,25] and so on. Studies on systematic blending are also made for the purpose of generating a variety of complex systems, such as AB diblock copolymer/A homopolymer blends[26−29] and AB diblock copolymer/AB diblock copolymer blends.[30,31]

In most of these studies, block copolymer molecules with both narrow molecular weight and composition distribution have been used so as to make scientific achievements clear. On the other hand, however, block copolymers used in application fields possess, in general, both wide molecular weight and composition distribution, and hence it may affect the structures and properties of copolymers considerably. Therefore, some systematical studies were done concerning the distribution of block copolymers,[32,33] though two effects have not been evaluated quantitatively since it is hard to separate one effect from the other.

Recently, we have succeeded in evaluating the composition distribution dependence on microphase-separated structures made from polystyrene-*block*-poly(2-vinylpyridine) (SP) diblock copolymers of the AB type and poly(2-vinylpyridine)-*block*-polystyrene-*block*-poly(2-vinylpyridine) (PSP) triblock copolymers of the BAB type quantitatively by blending several monodisperse block copolymers. In previous papers we defined the “composition distribution” index by using $M_w(S)/M_n(S)$ values for blends made from monodisperse SP and PSP block copolymers but with various compositions, where $M_w(S)$ and $M_n(S)$ denote weight-average and number-average molecular weights of polystyrene blocks therein.[34,35] There we found that the blends with “composition distribution” indices smaller than the critical one show homogeneous and very periodic structures and that the microdomain spacing monotonically increases with “composition distribution”. However, the blend system phase-separates macroscopically into at least two microphase-separated structures if the composition distribution index exceeds the critical one, this phenomenon being more favorable for the triblock system than for the diblock one.

In this work, as the following step of the study on the effect of distribution of copolymers, the effect of molecular weight distribution on microphase-separated structures for both SP diblock and PSP triblock copolymers was investigated by using blend samples with the constant volume ratio of almost 0.5/0.5 and also with constant number-average molecular weight.

## Experimental Section

Each of the three parent block copolymers for both SP and PSP was synthesized in tetrahydrofuran (THF) at −78 °C by sequential living anionic polymerizations where cumyl potassium and naphthalene potassium as initiators were used, respectively.[34,35] These copolymers were purified by reprecipitating into hexane and were dried enough in vacuo followed by freeze-drying to remove remaining hexane or THF.

To determine the molecular weight distribution of parent block copolymers, the gel permeation chromatography (GPC) system, HLC-8020 of Tosoh Corp. with three G4000$H_{HR}$ columns, was used. The effect of homopolymer on microphase-separated structures should be fairly large in the present

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10.1021/ma050040t CCC: $30.25

**Table 1. Molecular Characteristics of Parent Block Copolymers**

| sample | $M_w{}^a/10^4$ | $M_w/M_n{}^b$ | $\phi_S{}^c$ |
|---|---|---|---|
| SP-S | 1.73 | 1.05 | 0.548 |
| SP-M | 7.33 | 1.03 | 0.527 |
| SP-L | 12.9 | 1.06 | 0.512 |
| PSP-S | 4.96 | 1.05 | 0.538 |
| PSP-M | 10.2 | 1.02 | 0.531 |
| PSP-L | 15.6 | 1.05 | 0.496 |

[a] Weight-average molecular weights measured by multiangle laser light scattering. [b] Apparent molecular weight distribution determined by gel permeation chromatography. [c] Volume fractions of polystyrene blocks measured by pyrolysis-gas chromatography.

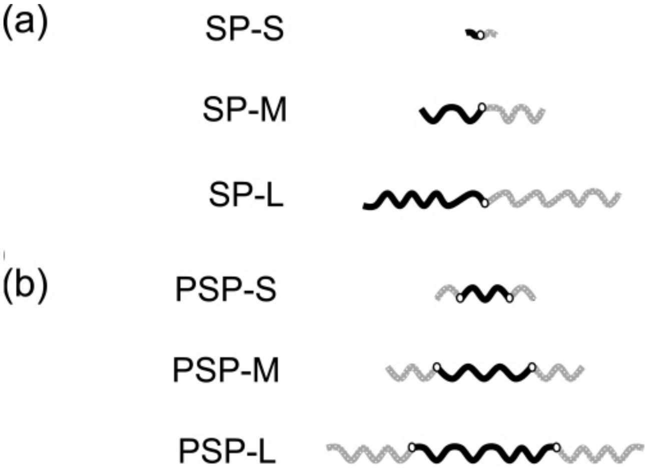

**Figure 1.** Schematic pictures of parent block copolymers used in this study.

study.[26−29] Therefore, the purity was determined carefully by temperature gradient interaction chromatography (TGIC) by using a typical isocratic HPLC system equipped with a $NH_2$-bonded silica gel column (Hypersil APS-1, 100 Å pore, 150 × 4.6 mm, 3 $\mu$m particle size). The details of TGIC experiments were described in a previous paper.[36] All parent block copolymers for both SP and PSP contain less than 1.0% precursor homopolymers, so that the effect of homopolymers was ignored in this work.

Absolute weight-averaged molecular weights of block copolymers were measured by multiangle laser light scattering (MALLS) by using the DAWN EOS enhanced optical system of Wyatt Technology. Volume fractions of polystyrene block for each copolymer were measured by pyrolysis−gas chromatography (pyrolysis−GC), GC-2010, of Shimadzu equipped with a PY-2020s pyrolyzer of Frontier Laboratory having an ultra alloy column and a FID detector. The experimental details were described elsewhere.[34,35]

Table 1 summarizes molecular characteristics of parent block copolymers thus obtained. The molecular weight ratio for SP diblock copolymers is 1.0:4.2:7.4, where the middle value is just the simple average of the small and the large ones, while it is 1.0:2.0:3.0 for PSP triblock copolymers. Namely, molecular weights of medium-size parent copolymers are designed to be the average of the other two copolymers for both systems. Polydispersity indices of all parent copolymers are less than 1.06, and volume fractions for two component polymers of all copolymers are almost 0.5. Schematic pictures of SP and PSP block copolymers are displayed in Figure 1.

These parent block copolymers are blended in several manners for both SP and PSP. The mole fractions of the smallest parent copolymer were set equal to that of the largest one to keep number-average molecular weights of blend samples constant. Several blend codes were defined as follows. Mole fractions, for three parent copolymers with corresponding $M_n$, following the Gaussian distribution functions $x_G(M_n,\sigma)$, are defined as shown in eq 1, with several squares of standard deviation value, $\sigma^2$, accordingly blend code **G($\sigma^2$)** are used, while those following the modified Gaussian distribution functions, $x_{MG}(M_n, A)$, are defined as shown in eq 2, with constant squares of standard deviation value, 2.55, but with a different floating parameter, $A$, accordingly blend code **MG-(A)** are used.

**Table 2. Molecular Weight Distribution and Domain Spacing of All Blend Samples for SP Diblock**

| code | $M/10^4\,{}^a$ | $M_w/M_n$ | $D$/nm | $D/D_0{}^b$ |
|---|---|---|---|---|
| G(4.5) | 7.32 | 1.16 | 41.2 | 1.04 |
| G(7.5) | 7.31 | 1.25 | 42.3 | 1.07 |
| G(20) | 7.31 | 1.34 | 43.5 | 1.10 |
| E3 | 7.31 | 1.39 | 44.2 | 1.12 |
| MG(0.22) | 7.30 | 1.46 | 44.8 | 1.13 |
| MG(0.09) | 7.30 | 1.53 | 45.5 | 1.15 |
| E2 | 7.29 | 1.59 | 45.8 | 1.16 |

[a] The calculated average molecular weights using $M_w$ values in Table 1. [b] $D_0$, 39.5 nm, is lamellar domain spacing for SP-M.

**Table 3. Molecular Weight Distribution and Domain Spacing of All Blend Samples for PSP Triblock**

| code | $M/10^4\,{}^a$ | $M_w/M_n$ | $D$/nm | $D/D_0{}^b$ |
|---|---|---|---|---|
| G(0.25) | 10.2 | 1.06 | 30.1 | 1.03 |
| G(0.50) | 10.2 | 1.12 | 31.1 | 1.06 |
| E3 | 10.1 | 1.19 | 32.2 | 1.10 |
| MG(0.20) | 10.1 | 1.22 | 33.0 | 1.13 |
| MG(0.09) | 10.1 | 1.25 | 33.5 | 1.14 |
| E2 | 10.1 | 1.27 | 34.4 | 1.17 |

[a] The calculated average molecular weights using $M_w$ values in Table 1. [b] $D_0$, 29.3 nm, is lamellar domain spacing for PSP-M.

$$x_G(M_n,\sigma) = (2\pi)^{-1/2}\sigma^{-1}\exp\{-(M_n - M_m)^2/2\sigma^2\} \quad (1)$$

$$x_{MG}(M_n,A) = A - (2\pi)^{-1/2}(2.55)^{-1/2}\exp\{-(M_n - M_m)^2/5.10\} \quad (2)$$

In these equations $M_m$ is the constant value which actually expresses the molecular weight of a medium-size parent copolymer. The blends with equal mole fractions of three parent copolymers were also prepared, and they were named **E3**. Blends with binominal mole fractions were additionally made from the largest copolymer and the smallest one, and they were named **E2**. Tables 2 and 3 show characteristics of blend samples and the corresponding codes. The molecular weight distribution of the parent block copolymers was assumed to be unity to simplify the calculation for $M_w/M_n$ value. This assumption does not lead to essential errors because polydispersity indices of all parent block copolymers are very small, less than 1.06. All the blend manners for SP diblock copolymers are compared in Figure 2a, where the horizontal axes denote the number-average molecular weight and the vertical ones the mole fraction, $x(M_n)$. In reality, the vertical axes have been converted into weight fraction, $w(M_n)$, for practical use, and they are displayed in Figure 2b. Almost the same blending manners were applied for PSP triblock copolymers, though they are not shown to avoid duplicated information.

Blended sample films were cast from THF solutions and dried enough in vacuo, followed by annealing at 150 °C for 4 days. These films were used for small-angle X-ray scattering (SAXS) measurements. SAXS apparatus used is the one installed in the beamline 15 A at Photon Factory in Tsukuba, Japan. Imaging plates (IP) were used as the detectors for the scattered X-rays. The wavelength of the incident X-ray is 0.1502 nm, and the camera length is 2401 mm. Transmission electron microscopy (TEM) was also carried out to confirm microphase-separated structures. Ultrathin sections were prepared from annealed films and stained with osmium tetroxide, and observations were performed by a Hitachi H-800 under an acceralation voltage of 100 kV.

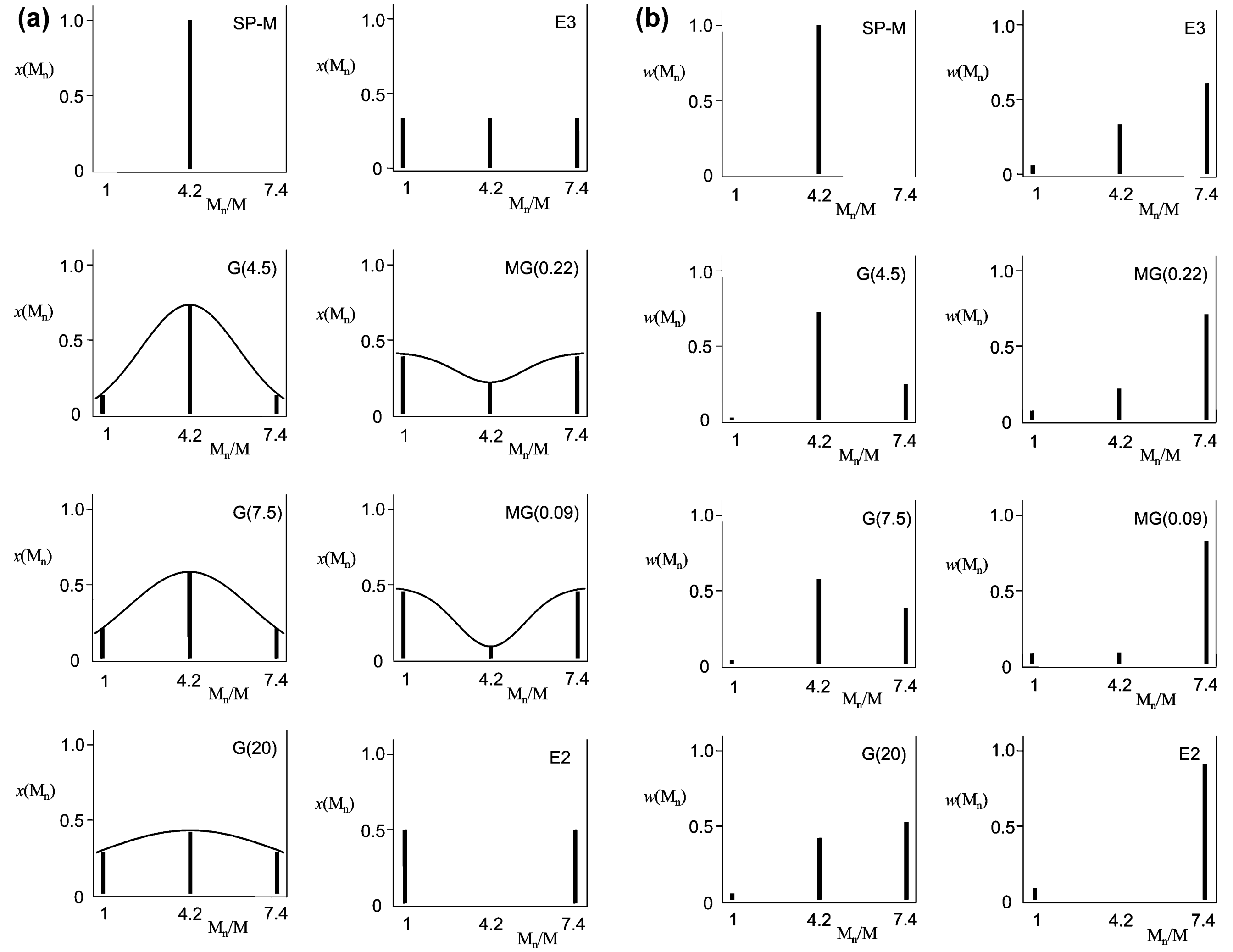

**Figure 2.** Blend manners prepared from parent SP diblock copolymers. Horizontal axes are number-average molecular weights while vertical axes for (a) are mole fractions and those for (b) denote weight fractions. $M$ is the constant value which denotes the molecular weight of the smallest size parent copolymer.

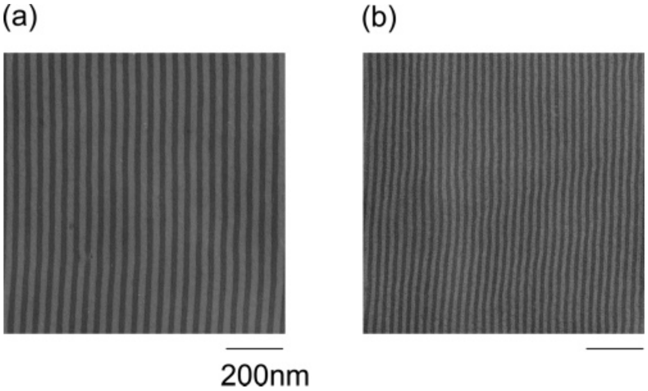

**Figure 3.** Typical transmission electron micrograph images of blend **E3** for both SP and PSP: (a) blend **E3** from SP diblock and (b) blend **E3** from PSP triblock. The brighter phase is polystyrene while the darker phase represents poly(2-vinylpyridine).

## Results

Figure 3 compares TEM images for **E3** of both SP and PSP. These two images are simple and homogeneous lamellar structures with flat interfaces, and all the other blend samples also show similar lamellar ones, though they are not shown. Thus, it has been found that blend samples form periodic lamellar structures within the $M_w/M_n$ range adopted in this study. SAXS diffraction profiles are compared in Figure 4; the observed results for SP diblock are shown in Figure 4a, while those for PSP triblock are shown in Figure 4b. The top profiles are for pure block copolymers, SP-M and PSP-M, and the scattering curves were arranged in the order of the magnitude of $M_w/M_n$ from top to bottom. Vertical axes of these figures are arbitrary, but logarithmic scale and horizontal axes show the magnitude of the scattering vector $|q|(=4\pi \sin\theta/\lambda)$, where $2\theta$ is the scattering angle and $\lambda$ is the wavelength. In Figure 4a,b all the curves have integer ordered peaks, where even number ordered peaks are considerably weak, indicating that the composition of one component is almost 0.5. In addition, one notices that diffraction peaks shift to lower $|q|$ value from top to bottom, with increase in $M_w/M_n$, representing the increase in lamellar domain spacing $D$ systematically.

Lamellar domain spacings, $D$s, were evaluated precisely by adopting the simple relationship $|q_p| = 2\pi n/D$, where $|q_p|$ denotes the magnitudes of scattering vector at diffracted peaks located, and $D$ satisfies Bragg's condition, $2D \sin\theta = n\lambda$. $D$s thus estimated are listed in Tables 2 and 3 for SP and PSP, respectively. To normalize the lamellar domain spacings, $D$s were divided by domain spacing $D_0$ of pure parent block copolymers, i.e., SP-M for the SP system and PSP-M

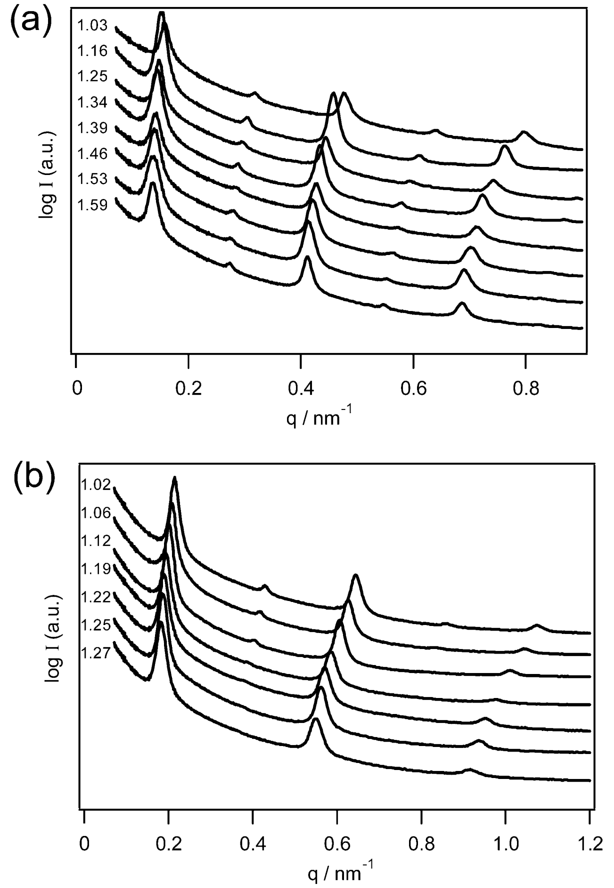

**Figure 4.** Comparison of SAXS diffraction patterns for all blends: (a) SP diblock; (b) PSP triblock. The top profiles are for pure block copolymers, SP-M and PSP-M, respectively, and the other profiles in both figures are displayed in the order of the magnitude of molecular weight distribution from top to bottom; the curves are shifted arbitrarily along the vertical axes to make clear the comparison. Molecular weight distribution values are referred to in Tables 2 and 3.

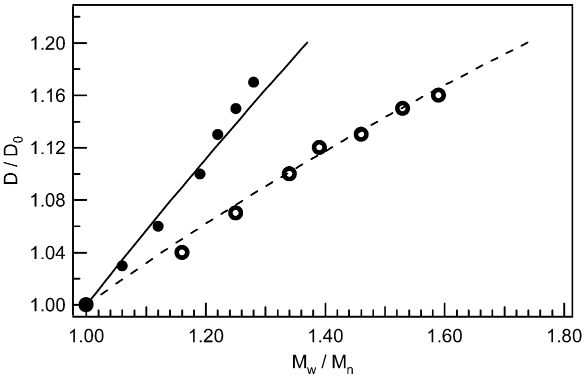

**Figure 5.** Molecular weight distribution dependence of the reduced domain spacing, $D/D_0$, for both SP and PSP. $D_0$ for SP, 39.5 nm, is the domain spacing of the medium-size parent copolymer, SP-M, while $D_0$ for PSP, 29.3 nm, is that of PSP-M. Open circles are for SP diblock system, while filled circles are for PSP triblock one. A broken line and a solid line are drawn just as guide for eyes for diblock copolymers and triblock copolymers, respectively.

for the PSP one. Thereby, $D/D_0$ values indicate the relative increase of domain spacings, and they are also displayed in Tables 2 and 3 and are plotted against $M_w/M_n$ in Figure 5. From this figure it is evident that (i) domain spacings increase with increase in polydispersity index monotonically for both SP and PSP and (ii) the increment of PSP is much larger than that of SP.

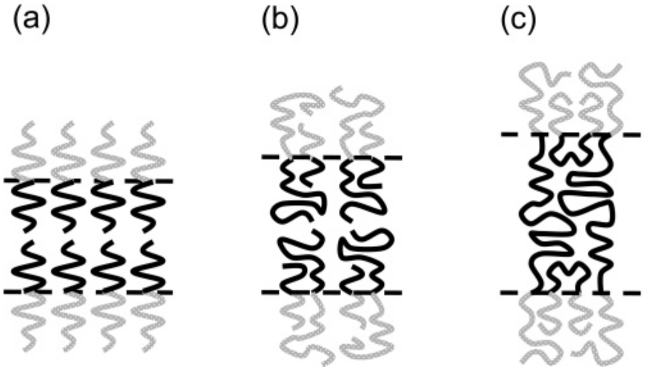

**Figure 6.** Schematic drawings comparing domains composed of three different systems: (a) monodisperse diblock copolymer system, (b) polydisperse diblock system, and (c) polydisperse triblock system.

## Discussion

The reasons for two major results (i) and (ii) raised in the previous section are discussed in this section. First, the result (i) is considered. Figure 6a,b schematically compares domains having a very small $M_w/M_n$ value and with a relatively large one for AB diblock copolymers. When $M_w/M_n$ is small, each block chain with the same length possesses essentially the same dimension. When $M_w/M_n$ is relatively large, however, shorter chains have to be localized near the interfaces of the domains. Accordingly, the chain segments on the tails of the longer chains could be squeezed so that they tend to localize at the centers of the domain to keep segment density constant. This phenomenon resembles the one observed for block copolymer/homopolymer blend systems[27,29] and must be the reason for the increase in domain spacing.

The other finding (ii) is explained below. Schematic pictures in Figure 6b,c compare lamellar microdomain for AB diblock copolymers with that for BAB triblock copolymers, both with a relatively large $M_w/M_n$ value. As the reason for (i) we described localization phenomenon of longer chains at the center of domain. For blend samples of BAB triblock copolymers with relatively large $M_w/M_n$, which have the mid-blocks with no ends and thereby adopt bridge or loop conformations, the very short mid-blocks must adopt loop conformation because of their shortness. Those short mid-blocks can be recognized to localize near the interfaces more severely than blocks of AB diblock copolymers.[19] This larger localization effect of short mid-blocks with loop conformation may induce the higher degree of localization of the central segments on long mid-blocks at the centers of the domains than that for both blocks of AB diblock copolymers. The larger increment of $D/D_0$ for PSP than SP can be conceived owing to this factor.

The effects of molecular weight distribution, i.e., (i) the increase in domain spacing and (ii) the larger increment of $D/D_0$ for PSP, obtained in the present work are qualitatively the same as the effects of the "composition distribution" system. Figure 7 compares plots of two series of $D/D_0$ for both SP and PSP systems. One consists of $D/D_0$ data plotted against overall "composition distribution" index, i.e., $M_w/M_n$(block), defined as the arithmetic averages of molecular weight distribution

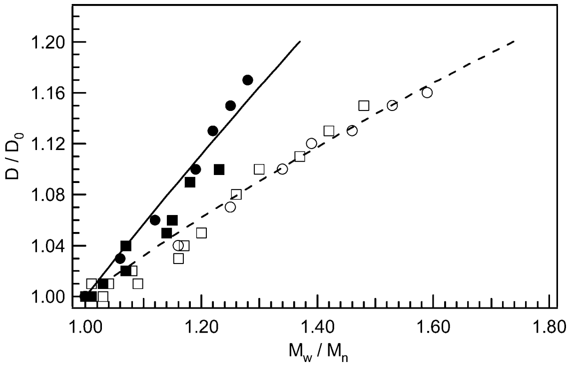

**Figure 7.** Comparison of *D*/*D*$_0$ values for two systems, i.e., composition distribution (squares) and molecular weight distribution (circles). A broken line is drawn for SP diblock copolymers, while a solid line is drawn for PSP triblock just as a guide for eyes. The circles are the data in the present study while the squares are those in previous studies.[34,35] The open symbols are for SP diblock system, whereas the closed ones are for PSP system.

of the two component blocks, $M_w/M_n$(block) (= ($M_w$(S)/$M_n$(S) + $M_w$(P)/$M_n$(P))/2), assuming S and P block chains form their individual domains independently;[34,35] the other one consists of the given data in this work plotted against $M_w/M_n$. A broken line is drawn just as a guide for eyes for SP diblock copolymers while a solid line is drawn for PSP triblock. It is clear from this figure that the data points for SP diblock copolymers (open symbols) are close to each other and those for PSP triblock copolymers (closed symbols) as well. Agreement of these inclinations seems to be derived from the common effect. If the connections of A blocks and B blocks at the domain interface were ignored, block chains with molecular weight distribution, expressed by circles, would be analogically identical with those having a composition distribution, expressed by squares. Therefore, the distribution effect for both molecular weight and composition distribution seems to be generated from the localization of polydisperse block chains in each phase, and it can be summarized by the viewpoint of "chain length distribution (CLD)" of each block chain.

As was reported in previous papers, block copolymers with large dispersity indices tend to macrophase-separate easily.[34,35] This trend is more evident for PSP triblock copolymer system than for SP diblock one. However, the threshold is not observed for both diblock and triblock in the present system, and some more extension might be observed. In other words, the data points, expressed by squares, are truncated at lower $M_w/M_n$ values than the data obtained in this work shown as circles in Figure 7. These results are quite reasonable if we compare the strength of interaction among molecules between composition and molecular weight distribution system. Namely, the repulsion potential between a S-rich molecule and a P-rich molecule having the same molecular weight is much larger than that between a short block copolymer molecule and a long molecule having the same composition. Thus, macrophase separation takes place more easily for the former system than the latter to lower total free energy of domain forming.

In summary, we conclude that (1) all blend samples made from three parent block copolymers whose A/B composition ratio is 0.5/0.5 form uniform lamellar structures within the range of molecular weight distribution adopted in this experiment, (2) the domain spacing increases monotonically with increase in polydispersity indices of blends for both AB and BAB, and (3) the increment of BAB is much larger than that of AB. Furthermore, by comparing the results on molecular weight and composition distribution, (4) the expansion phenomena of microdomains comes from the common feature of the localization of polydisperse block chains in both phases.

**Acknowledgment.** The authors thank Dr. S. Arai and Mr. Y. Yoshida at the Ecotopia Science Institute in Nagoya University for their help in taking transmission electron micrographs. We also thank Dr. J. Suzuki at the Center of Calculation in High Energy Accelerator Organization and Mr. T. Hikage at High Intensity X-ray diffraction Laboratory in Nagoya University for their help in measuring small-angle X-ray scattering. This work was partially supported by the Ministry of education, science, sports, and culture, Glant-in-Aid program #12450383 and #13031040 and also supported by the 21st century COE Program entitled "The Creation of Nature-Guided Materials Processing". The authors are thankful for their financial assistance.

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MA050040T