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Chain Dimensions of the Mid-Blocks of ABA Triblock Copolymers with Lamellar Structures in Bulk

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It is well-established that block copolymer chains are deformed in the microphase-separated bulk state in the strong segregation regime.[2−11] In a previous work, we found that polystyrene (S) mid-blocks of PSP triblock copolymers with alternating lamellar structure were shrunk in the direction parallel to the lamellar interface to compensate for the elongation in the perpendicular direction so as to keep their volumes constant, though the manner of chain deformation depends on the compositions.[12] Further, recently we reported that PSP have alternating lamellar structures in the composition range $0.27 \le \phi_s \le 0.58$, where ϕ_s is the volume fraction of S.[13] In this study, therefore, chain dimensions of S blocks of PSP triblock copolymers having two extreme compositions of the lamellar region were measured by small-angle neutron scattering (SANS) to clarify the composition dependence of single chain conformations of the mid-blocks of triblock copolymers.

Samples were anionically polymerized monodisperse block copolymers. Two sets of PSP and deuterium-labeled PDP, where D denotes polystyrene-d_8, triblock copolymers were used; their overall ϕ_s are 0.27 and 0.58, being lower and higher extremes, therefore, named blends L_e and H_e, respectively. Their molecular characteristics are in Table 1. Films were obtained by solvent casting from dilute solutions of THF. After the films were dried and annealed at 150 °C for a week, microphase separation structures were observed by transmission electron microscopy(TEM) by staining ultrathin sections with OsO_4. TEM images for two blends are shown in Figure 1, demonstrating the lamellar structures with brighter stripes of S phase and the darker ones of P phase.

Several blend films with slightly different mixing ratios were prepared for both the L_e and H_e samples to search for the contrast matching point between S and P phases in SANS experiments. The PDP/PSP blend ratios are between 10/90 and 13/87 by weight,[12] and the experimentally determined matching ratios are given in Table 1. The geometric relationship between a sample film and the SANS neutron beam is drawn schematically in Figure 1 of ref 12. Two geometries were used. One is the "through" orientation in which the direction of the neutron beam was normal to the lamellar interfaces, and the other is the "edge" orientation in which the neutrons were incident parallel to the lamellar planes. Measurements were carried out using the SANS-U spectrometer of the Institute for Solid State Physics, the University of Tokyo. The experimental details and data analysis methods were described previously.[12]

Table 1. Molecular Characteristics of Samples

blends	samples	ϕ_s	$M \times 10^{-3}$ P − S(D) − P	$w(D)^a$	X^b
L_e	PDP-7	0.23	41.2 − 24.6 − 41.2	0.130	0.106
	PSP-24	0.28	46.5 − 32.0 − 46.5		
H_e	PDP-6	0.55	40.3 − 90.2 − 40.3	0.116	0.106
	PSP-12	0.58	28.9 − 72.3 − 28.9		

[a] Weight fractions of the labeled copolymer in the blends. [b] Volume fractions of the labeled segment in polystyrene phases.

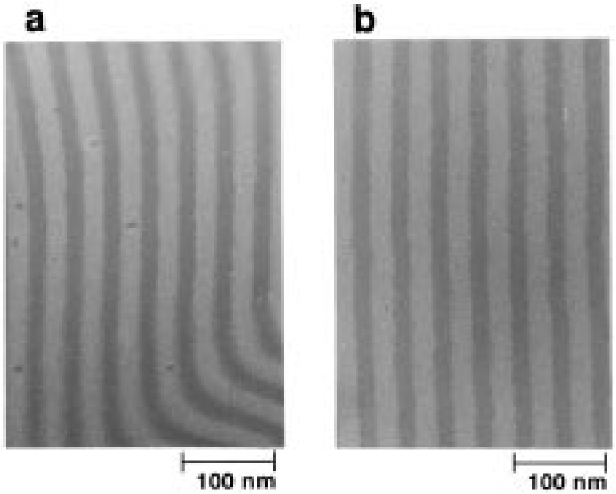

Figure 1. Transmission electron micrographs of two blend samples from labeled and unlabeled block copolymers with two extreme compositions of lamellar region. Samples are (a) PDP-7/PSP-24, whose weight ratio is 0.130/0.870, and (b) PDP-6/PSP-12, whose weight ratio is 0.116/0.884.

Three R_g components, $R_{g,k}$'s(k = x, y, or z), were evaluated from the coherent scattering intensity as a function of q_k, $I(q_k)$, according to eq 1,[11]

$$I(q_k) = I(0)\exp(-q_k^{\,2}R_{g,k}^{\,2}) \quad (k = x, y, \text{or } z) \qquad (1)$$

where q_k ($=4\pi(\sin\theta_k)/\lambda$) is the scattering vector along the k-axis (k = x, y, or z) with wavelength λ of the neutrons and the scattering angle $2\theta_k$. Figure 2 compares the Guinier plots of sector-averaged edge-view intensities from blend Le which give two R_g components. The top curve of Figure 2 gives the R_g component of the S block in the direction parallel to lamellar interface, $R_{g,z}$, while the R_g component perpendicular to lamellar interface, $R_{g,y}$, can be estimated from the bottom curve in Figure 2 (cf. figure caption). These curves were obtained from the blend film whose diffraction peaks were most surpressed by contrast-matching. The R_g component estimated from the circularly averaged through view data was defined as $R_{g,x}$, though the experimental data were not shown here.

$R_{g,k}$'s (k = x, y, z) thus obtained were compared in Table 2 together with the data, which have previously been reported, for the other two blends whose ϕ_s values are 0.32 and 0.50, respectively.[12] M_{nor}'s in Table 2 are the normalized molecular weight of S blocks.[14] Though the mismatch in the molecular weight of the labeled and

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Table 2. Chain Dimensions of Polystyrene Block in PSP Triblock Copolymers

blends	$M_{nor}(S) \times 10^{-3}$	ϕ_s[b]	$R_{g,k}$ (nm) $R_{g,x}$	$R_{g,y}$	$R_{g,z}$	R_{g,k_0}[c]	$R_{g,y}/R_{g,x}$
L_e	31.0	0.27	2.07 ± 0.03	5.10 ± 0.35	2.06 ± 0.06	2.91	2.46
I[a]	30.6	0.32	2.48 ± 0.03	4.11 ± 0.13	2.48 ± 0.05	2.89	1.66
IV[a]	44.3	0.50	3.12 ± 0.06	3.85 ± 0.05	3.25 ± 0.08	3.47	1.23
H_e	73.5	0.58	3.75 ± 0.05	5.41 ± 0.45	3.83 ± 0.09	4.47	1.44

[a] Blend code used in ref 12; the data came from Table 3 in the same reference. [b] Volume fractions of polystyrene phases. [c] One-dimensional unperturbed chain dimensions obtained by using the relationship $R_{g,k_0} = 0.0165\ M^{1/2}$.

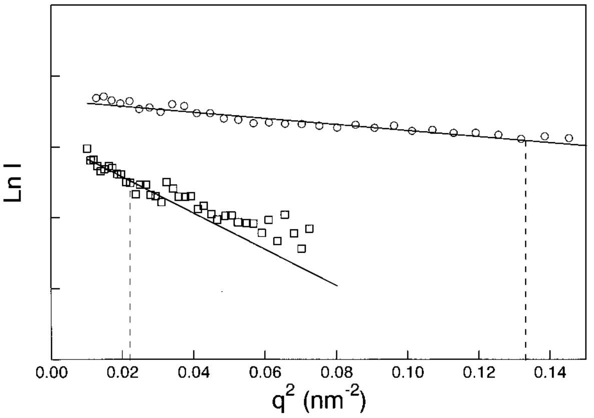

Figure 2. Comparison of Guinier plots of SANS edge view intensities for blend L_e. *I* are the coherent scattering intensities and q ($=4\pi(\sin\theta)/\lambda$) is the scattering vector, where λ is the wavelength of neutrons and 2θ is the scattering angle. The circles are the sector-averaged data at around $\psi = 90 \pm 5°$ and $\psi = 270 \pm 5°$, whereas the squares are the data at around $\psi = 0 \pm 5°$ and $\psi = 180 \pm 5°$ on the two-dimensional detector. The former values were obtained from the measurements whose sample-to-detector (S−D) distance was 4m, while the S−D distance for the latter values was 8m. The maximum q values where Guinier's approximation can be held were designated as the vertical broken lines.[11]

unlabeled molecules are considerable in both L_e and H_e, it was confirmed that it affects the measured apparent radii of gyration less than 1.5%.[15] Table 2 also includes R_{g,k_0}, which denotes the *k*-componet ($k = x$, y, or z) of the unperturbed radius of gyration, R_{g_0}, obtained by using the relationship, $R_{g_0} = 3R_{g,k_0}$, and $R_{g,y}/R_{g,x}$ columns for comparison. From this table we notice the tendency that the $R_{g,y}/R_{g,x}$ value of the S mid-block is decreasing with increasing ϕ_s.

To derive the general conclusion concerning the composition dependence of the degree of chain deformation, we have to pay attention to the fact that it also depends on the molecular weight of polymers. The experimental data of styrene-*b*-2-vinylpyridine (SP) diblock copolymers were used to discuss this point. According to our previous work,[11] $R_{g,x}$ and $R_{g,y}$ of S blocks in SP can be scaled as

$$R_{g,x} \propto M^{0.43} \tag{2}$$

$$R_{g,y} \propto M^{0.64} \tag{3}$$

where *M* is the molecular weight of the S block. If we assume that the $R_g - M^{\nu}$ proportionalities in eqs 2 and 3 can be also applied to the S block of PSP, we can reduce $R_{g,k}$'s to a certain molecular weight and compare them. The assumption on $R_{g,y}$ may be reasonable since the domain spacing of PSP has essentially the same molecular weight dependence as that of SP irrespective of the composition,[12] whereas the assumption on $R_{g,x}$ may be poorer because the molecular weight dependence of *x*- or *z*-components of R_g could be composition dependent.

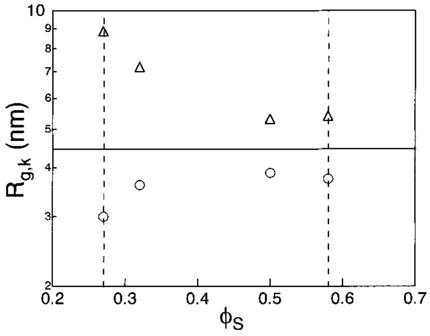

Figure 3. Reduced radii of gyration of S blocks as a function of volume fraction of S in triblock copolymers. The circles denote $R_{g,x}$, while triangles are for $R_{g,y}$. The solid line corresponds to the *k*-component ($k = x$ or y) of the unperturbed chain dimension, R_{g,k_0}, of S chain with molecular weight of 73.5K.[11] The vertical two broken lines indicate the composition limits for PSP triblock copolymers to form alternating lamellar structures.

Using eqs 2 and 3 and the data of blend L_e and also those of two blends I and IV in Table 2, $R_{g,x}$ and $R_{g,y}$ values were calculated by reducing to the molecular weight of S in blend H_e, 73.5K, and plotted against ϕ_s in Figure 3. From this figure, we can derive the conclusion that $R_{g,y}/R_{g,x}$ values are decreasing with increasing ϕ_s but they tend to level off around $\phi_s = 0.5$.

It is actually not facile to distinguish between *loop* and *bridge* conformations from the present scattering experiments;[16] however, from the present results we can speculate with more confidence than those of the previous paper[12] that the mid-blocks of PSP tend to have more *bridges* when ϕ_s is low and that the fraction of *loops* increases with increasing ϕ_s. This hypothesis is consistent with the data since one would expect the mid-block to be more stretched when its two ends are anchored at opposites sides of the S lamella than it would be when its two ends are tethered to the same boundary.

References and Notes

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