Macromolecules 1990, *23*, 4317–4321

Chain Conformation of a Block Polymer in a Microphase-Separated Structure

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Received July 13, 1989; Revised Manuscript Received March 7, 1990

ABSTRACT: The radii of gyration of a polystyrene block along the directions parallel and perpendicular to the lamellae in the lamellar structure of poly(styrene-*b*-2-vinylpyridine) were measured by small-angle neutron scattering. It was found that the block polymer is extended along the perpendicular direction, while it is contracted along the parallel direction. The extension is in accord with the theories of microphase-separated structure, but no theory predicts the contraction. From the molecular weight dependences of the radius of gyration along the directions parallel and perpendicular to the lamellae, it is concluded that the block polymer is contracted along the parallel direction to keep the volume occupied by the block chain constant when the microphase separation occurs.

Introduction

Studies on chain conformations of polymers are important to the understanding of their physical properties at the molecular level. It was found by small-angle neutron scattering (SANS) that the chain conformation is Gaussian in concentrated solutions and in melts as predicted by Flory.[2-4] In microphase-separated structures, however, the block polymers are confined anisotropically so that their conformations should be distorted as suggested by the molecular weight dependence of the domain spacing, D; i.e., $D \propto M^{2/3}$.[5-11] Therefore, it is of interest to study the conformation of a block polymer chain not merely because it could lead to the understanding of the microphase-separated structure at the molecular level but because it could clarify the difference between conformations of polymer chains in isotropic and anisotropic domains.

Typical microdomain morphologies of block copolymers are lamellar, cylindrical, and spherical structures, of which the first one is the most suitable for the study of a single-chain conformation. This is not only because the lamellar structure is the basic and simplest microdomain but because its domain spacing can be assumed to be very close to the equilibrium one in contrast to other structures, such as the spherical structure, of which the domain spacing is affected by nonequilibrium factors encountered in the domain formation process.[10,11] Since the lamellae of the present sample are predominantly oriented along the direction parallel to the surface of film specimen as reported previously,[15,16] moreover, the dimensions of a block chain along the directions parallel and perpendicular to the lamellae can readily be measured.

Several experimental works have been published so far on the conformation of block polymers in lamellar structures.[12-14] Using styrene–isoprene diblock copolymers, Hadziioannou et al.[12] reported that the block polymer chain is contracted along the parallel direction, while Hasegawa et al.[13] observed the extension of the block chain along the perpendicular direction as well as the contraction along the parallel direction. Moreover, Quan et al.[14] reported on the extension of the midblock of the styrene–butadiene–styrene triblock copolymer along the perpendicular direction. The extension of a block polymer along the perpendicular direction can be predicted by the theories by microphase-separated structures.[5-9] However, the reason for the contraction along the parallel direction remains unknown.

To have a definite conclusion on this problem, the molecular weight dependence of the chain dimensions of block polymer in microphase-separated structures should be studied. In this work, therefore, we prepared diblock copolymers of deuterated styrene and 2-vinylpyridine with different molecular weights and studied the molecular weight dependence of the radii of gyration of the polystyrene block along the directions parallel and perpendicular to the lamellae by SANS. These samples are suitable for the chain conformation study by SANS, because the scattering length density of poly(2-vinylpyridine) is between those of deuterated and hydrogenated polystyrenes. In principle, therefore, the single-chain scattering could be measured without interference from the scattering due to microdomain structure or the domain scattering by blending an appropriate amount of the deuterated polystyrene blocks to equalize the scattering length densities in the two domains, if the deuterated and hydrogenated polystyrene blocks would be randomly mixed. Moreover, it is noted that the statistical segment lengths of both block polymers are almost the same.[17]

As reported in a previous paper,[15] a contrast matching between domains is required to extract the single-chain scattering of a block polymer along the perpendicular direction, while it is not required along the parallel direction since the lamellae are predominantly oriented along the direction parallel to a film surface. However, we could not achieve the contrast matching except for one low molecular weight sample. Hence, we measured the radius of gyration along the perpendicular direction only for the low molecular weight sample and we assumed that the radii of gyration along the perpendicular direction are proportional to their domain spacings[16] measured by small-angle X-ray scattering for the other samples.

Table I
Molecular Characteristics of Block Copolymers of Styrene and 2-Vinylpyridine

blend no.	sample code	$M_n \times 10^{-3}$ [a]	M_w/M_n (GPC)	Φ_s [b]
I	DP-22	**21**-19	1.01	0.50
	SP-22	20-18	1.02	0.51
II	DP-33	**34**-32	1.04	0.49
	SP-33	37-26	1.03	0.53
III	DP-77	**92**-75	1.09	0.50
	SP-77	77-72	1.02	0.53
IV	DP-15	**162**-131	1.10	0.49
	SP-15	119-124	1.06	0.50

[a] Numbers written in boldface denote the molecular weights of deuterated blocks. [b] Φ_s is the volume fraction of polystyrene determined by elemental analysis.

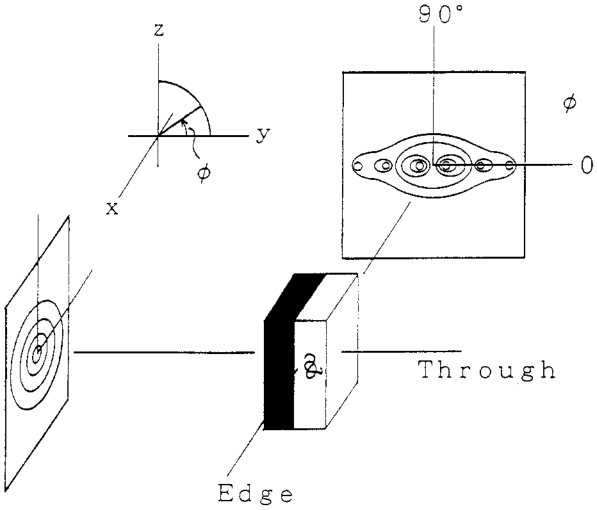

Figure 1. Geometrical relationship between sample specimen and two-dimensional position-sensitive detector. The azimuthal angle, ϕ, on the detector is also defined in the figure.

Experimental Section

Four pair of deuterated and hydrogenated styrene-2-vinylpyridine diblock copolymers were prepared for this study by an anionic polymerization technique. The preparation and characterization methods were reported previously.[15,18] In Table I the molecular characteristics of the block copolymers having deuterated polystyrene chains are listed together with the corresponding hydrogenated samples. The letters D and S in the sample code denote deuterated and hydrogenated polystyrene blocks, while P denotes the poly(2-vinylpyridine) block. The number-averaged molecular weight, M_n, of each block is listed in the table in the same order as the letters in the corresponding sample code. As shown in the table the molecular weight distributions of all samples are narrow and the volume fraction of styrene blocks, Φ_s, is around 0.5.

The film specimens for SANS were prepared by solvent-casting from 3 to 4% solutions of tetrahydrofuran, which is a good solvent for both blocks as reported previously.[15] With a transmission electron microscope we observed that all the film specimens have a lamellar microdomain morphology, which is predominantly oriented to the direction parallel to the film surface as mentioned before.[15,16]

Conformation measurements were carried out at room temperatures with a SANS spectrometer[19] at the National Institute of Standards and Technology equipped with a two-dimensional position-sensitive detector. The wavelength, λ, was 6.0 Å, and the width of the distribution, $\Delta\lambda/\lambda$, was 0.25. The range of magnitude of the scattering vector q ($=(4\pi/\lambda)\sin\theta$) was 0.007–0.13 Å^{-1}, where 2θ is the scattering angle. The geometric relationship between sample and detector is illustrated schematically in Figure 1. The scattering intensities were measured with two sample orientations, that is, the edge and through views defined here, in which film specimens are set perpendicular and parallel to neutron beam, respectively. The azimuthal angle on the detector is also defined as shown in Figure 1. The degree of orientation of the lamellae to the film surface was confirmed to be very high for every film specimen by comparing the contour maps in the edge and through views shown in Figures 2 and 3 in a previous paper.[15]

Since the strong domain scattering would obscure the single-chain scattering in the edge view, we attempted to eliminate the domain scattering using the blends of deuterated and hydrogenated samples, of which the deuterated block contents were varied around the calculated value (ca. 11 wt %) where the scattering length densities between the two domains are equal. For this purpose we prepared seven film specimens with the

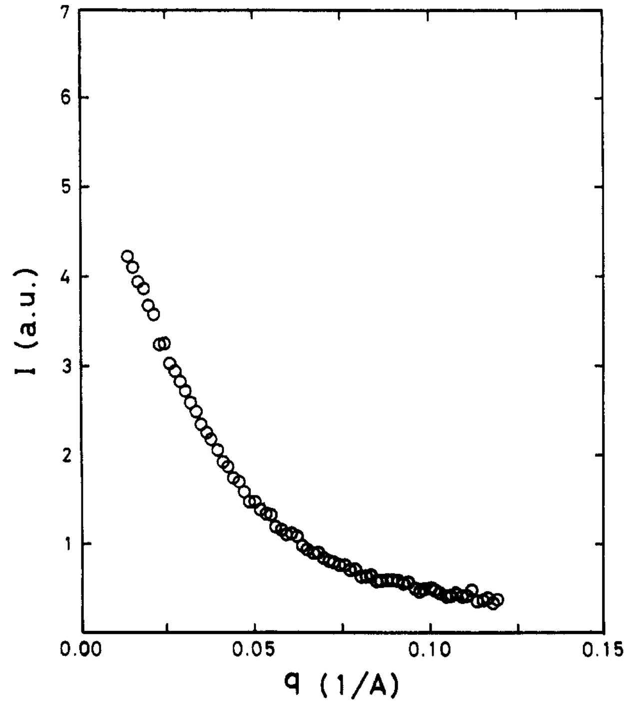

Figure 2. Example of coherent scattering intensity vs q for a blend sample at the through view. Intensities were obtained by a circular average of the two-dimensional data: sample, blend II; mixing ratio, 12/88 by weight.

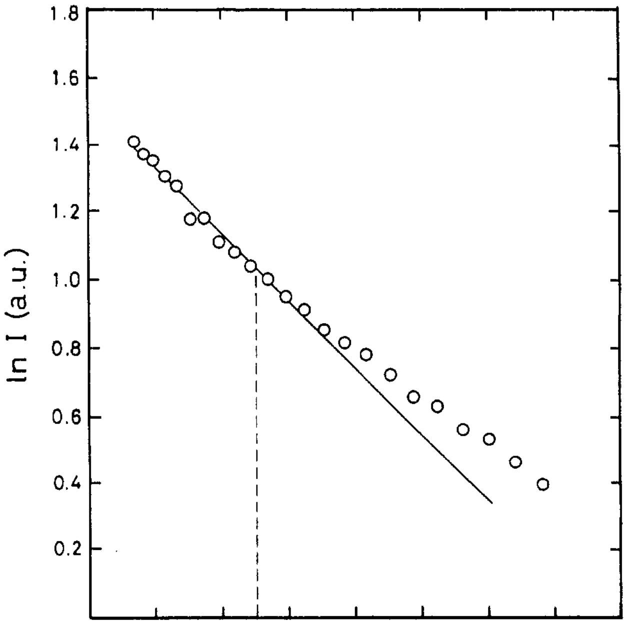

Figure 3. Guinier plot of the data in Figure 2. The dotted vertical line indicates the upper limit of Guinier's range described in the text.

different deuterated block contents for blend sample II, three for blend sample III, and five for blend sample IV.[15] As mentioned before, however, we succeeded in contrast matching only for the blend sample II. The molecular weights of blend sample I were too low to prepare the film specimen, which could be successfully cut and piled up for measurements in the edge view. Therefore, we measured the single-chain scattering in both views only for blend sample II, while only the through-view measurements were carried out for the other blend samples.

Scattering intensities on the two-dimensional detector were circularly averaged at equal q values for the through-view experiments, while sector averages were taken in the angle range of ±5° around 0° and 90° of azimuthal angle for the edge-view experiments of the blend sample II. The scattering intensity from a film specimen made of a hydrogenated sample was measured at high angles to evaluate the incoherent scattering intensity.

Results

The single-chain scattering function, $I(q)$, of an anisotropic and oriented polymer chain in the Guinier range is given by[12,20]

$$I(q) = I(0)\exp(-q^2 R_{g,k}^2) \qquad (1)$$

where $R_{g,k}$ is the radius of gyration of a chain along the k axis ($k = x$ or y or z).

Only the single-chain scattering is observed in the through view, so that we can evaluate directly the radius of gyration of a block chain along the direction parallel to the lamellae. The scattering intensities are circularly symmetric around the y axis on the x–z plane in the coordinate defined in Figure 1. Since the radius of gyration along the z axis, $R_{g,z}$, is evaluated from scattering data at $\phi = 90°$ in the edge view, we call the dimension evaluated from the circularly averaged scattering data in the through view the radius of gyration along the x axis, $R_{g,x}$, for convenience. They should be equal in the present geometry. Figures 2 and 3 show an example of a single-chain scattering and the corresponding Guinier plot in the through view, respectively, after the incoherent scattering intensity was subtracted.[15] Since the shape of the block polymer is not spherical but is still isotropic in the through view, we evaluated the radius of gyration along the x axis, $R_{g,x}$, from the initial slope of Guinier plot in the q range, which corresponds to the Guinier range for a spherical particle having the same radius of gyration; that is, $q^2R_g^2 < 1.3^2$ or $q^2R_{g,k}^2 < 1.3^2/3$, since $R_{g,k}^2 = R_g^2/3$.[20] The upper limit of this range is shown by the broken line in Figure 3.

In blend sample II the contrast matching was practically achieved at two deuterated block contents, where the DP/SP ratios are 10.1/89.9 and 10.5/89.5 by weight.[15] Figures 4a and 5a show the single-chain scatterings of the blend sample II with 10.5/89.5 at the azimuthal angles of 0° and 90° or along the y and z axes, respectively, in the edge view. The data points in these figures scatter more than those in Figure 3 because of the sector average. Figures 4b and 5b show the Guinier plots of the same data as those in Figures 4a and 5a, respectively. The upper limits of the Guinier range are also shown by the broken lines in Figures 4b and 5b, assuming that $q^2R_{g,k}^2 < 1.3^2/3$, although the range for the single-chain scattering in Figure 4b is different, owing to the anisotropic shape of the block polymer along the y axis as discussed later.

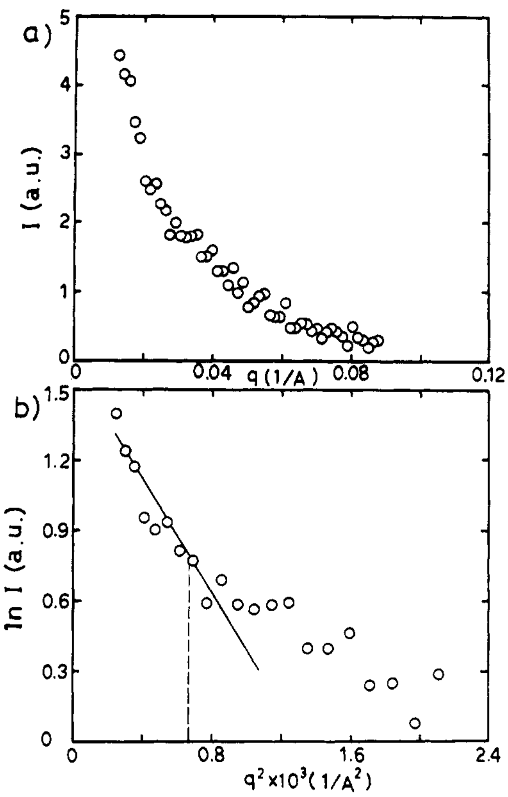

Figure 4. (a) Sector-averaged coherent scattering intensity vs q at the azimuthal angle of 0 ± 5° for the edge-view measurement: sample, blend II; mixing ratio, 10.5/89.5 by weight. (b) Guinier plots of the data in (a). The dotted vertical line indicates the upper limit of Guinier's range described in the text.

Tables II and III summarize $R_{g,x}$, $R_{g,y}$, and $R_{g,z}$ for the polystyrene block in blend sample II and the molecular weight dependence of $R_{g,x}$ of the polystyrene blocks, respectively. $R_{g,x}$ in blend samples II–IV and $R_{g,y}$ and $R_{g,z}$ in blend sample II were evaluated by averaging the observed values for the respective blend samples with the different deuterated block contents as mentioned before. Here the observed radii of gyration are obtained by assuming that the chain lengths of deuterated and hydrogenated block polymers are equal, since the corrections for the radius of gyration due to the difference in the chain length are about 2% even for blend sample IV, of which the length difference is largest (ca. 20%) as shown in Table I, when the fraction of deuterated chain is low (ca. 0.1).[21,22] The errors were estimated by taking into account both the standard deviation of the slope in the linear least-squares fit of Guinier plots and the deviation of the observed values with different deuterated block contents from the average value. The unperturbed radii of gyration of the block chains and the ratios of the observed values to them are also listed. Here, the unperturbed radius of gyration along any axis, $R_{g,k0}$ was evaluated by

$$R_{g,k0} = 0.159M^{1/2}\ (\text{Å}) \qquad (2a)$$

where eq 2a was obtained from the following radius of gyration–molecular weight relationship for deuterated polystyrene in bulk[4] by using $R_{g,0}^2 = 3R_{g,k0}^2$.

$$R_{g,0} = 0.275M^{0.5} \qquad (2b)$$

Table II shows that $R_{g,x}$ is equal to $R_{g,z}$ as it must be and that the block chain in blend sample II is extended along the direction perpendicular to the lamellae, while it is contracted along the direction parallel to the lamellae. Moreover, Table III shows that the contraction ratio increases with increasing molecular weight.

Discussion

Figure 6 shows the molecular weight dependence of the radius of gyration of the block polymer along the direction

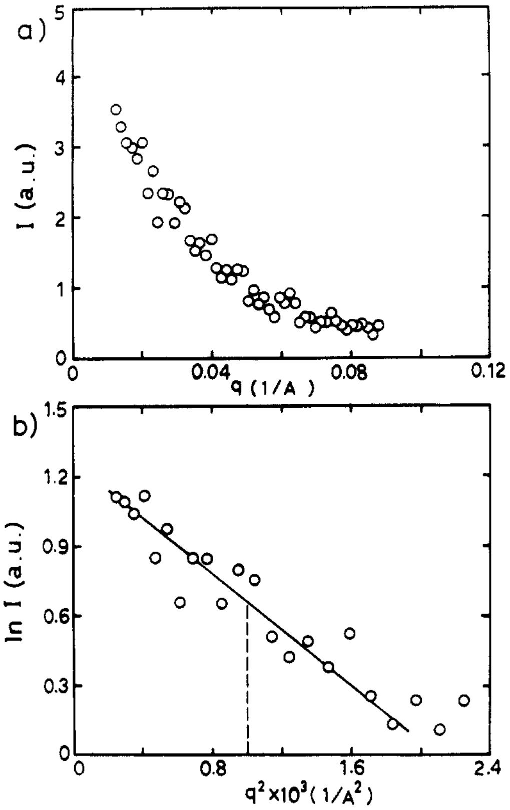

Figure 5. (a) Sector-averaged coherent scattering intensity vs q at the azimuthal angle of 90 ± 5° for the edge-view measurement. The sample is the same as that in Figure 4. (b) Guinier plots of the data in (a). The dotted vertical line indicates the upper limit of Guinier's range described in the text.

Table II
Radius of Gyration of a Polystyrene Block in Lamellar Structure of Blend Sample II

M (D) × 10^{-3}	$R_{g,k0}$, Å		$R_{g,k}$, Å	$R_{g,k}/R_{g,k0}$
34	29.3	x	23.8 ± 0.9	0.81 ± 0.03
		y	36.0 ± 2.0	1.23 ± 0.07
		z	23.7 ± 1.5	0.81 ± 0.05

Table III
Molecular Weight Dependence of $R_{g,x}$ of Polystyrene Block in Lamellar Structures

blend no.	M (D) × 10^{-3}	$R_{g,x}$, Å	$R_{g,x}/R_{g,x0}$	$\langle \cos^2 \phi \rangle^{1/2}$
I	21	21.6 ± 0.7	0.95 ± 0.03	
II	34	23.8 ± 0.9	0.81 ± 0.03	0.943
III	92	40.4 ± 2.0	0.84 ± 0.04	0.953
IV	162	49.1 ± 1.8	0.77 ± 0.03	0.938

parallel to lamellae $R_{g,x}$ or $R_{g,z}$ and along the direction perpendicular to lamellae $R_{g,y}$, together with eq 2a for the unperturbed chain. Here, we assumed that $R_{g,y}$ increases with increasing molecular weight according to the same power law as the molecular weight dependence of the domain spacing, D, which is in good agreement with the theories of microphase-separated structure[16]

$$D = 0.33_7 M_n^{0.64} \text{ (Å)} \tag{3}$$

where M_n is the number-average molecular weight of the block copolymer. With this assumption we drew the straight line with a slope of 0.64 through the experimental value of the radius of gyration for blend sample II. This assumption may be reasonable since eq 3 is in good agreement with the theoretical prediction in the strong segregation limit where the domain spacing is determined by the radius of gyration of the block polymer along the direction perpendicular to the lamellae as reported previously.[16] From Figure 6 we have the molecular weight dependences of $R_{g,x}$, $R_{g,y}$, and $R_{g,z}$ of a block polymer in the lamellar structure as

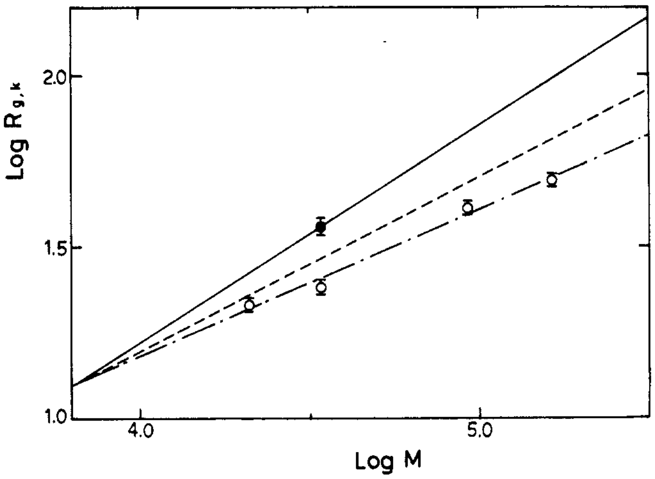

Figure 6. Double-logarithmic plots of $R_{g,x}$ (○) and $R_{g,y}$ (●) vs the molecular weight of polystyrene block in the lamellar structure. The solid, dashed-dotted, and broken lines denote eqs 5, 4, and 2a, respectively.

$$R_{g,x} = R_{g,z} = 0.28_9 M^{0.43 \pm 0.03} \text{ (Å)} \tag{4}$$

$$R_{g,y} = 0.045_3 M^{0.64 \pm 0.03} \text{ (Å)} \tag{5}$$

Comparing eqs 2a, 4, and 5, we find that the contraction ratio along the parallel direction is lower than the extension ratio along the perpendicular direction.

All the theories of microphase-separated structure in the strong segregation limit[5-9] predict the extension of the block chain along the perpendicular direction, but only the theory of Meier[5] explicitly gives the extension ratio to the unperturbed dimension of the block chain along the perpendicular direction. According to his theory, the extension ratio, α_y, is evaluated from the domain spacing, D, by using the equations

$$D = T_A + T_B \tag{6a}$$

$$T_i = 1.4 \alpha_y \langle r^2 \rangle_{0i}^{1/2} \tag{6b}$$

where T_i is the thickness of the i phase and $\langle r^2 \rangle_{0i}$ is the mean-square unperturbed end-to-end distance of polymer i (=A or B). Using the molecular weight and composition of blend sample II in Table I and also the bulk densities of their components, i.e., 1.13 g/cm³ for D, 1.05 g/cm³ for S, and 1.14 g/cm³ for P, we have 63K and 0.52 for the number-average molecular weight and the volume fraction of polystyrene block, respectively, when the weight fraction of the deuterated block chain in the blend sample is 0.105 where the contrast matching is achieved as reported previously.[15] Introducing this molecular weight into eq 6, we have D = 398 Å and hence T = 207 Å for the polystyrene domain. Moreover, we have 124 Å for $\langle r^2 \rangle_0^{1/2}$ of the polystyrene block by using eq 2b and the relationship between the mean-square end-to-end distance and mean-square radius of gyration for the Gaussian chain, $\langle r^2 \rangle_0/6 = R_{g,0}^2$. Introducing the values of $\langle r^2 \rangle_0^{1/2}$ and T into eq 6b, we have α_y = 1.19, which is in good agreement with the experimental value (1.23) listed in Table II. The lamellar domain spacings predicted by the theories of Meier and Helfand–Wasserman agree with each other,[10] and the latter is in good agreement with the experimental data of lamellar structures as described in an accompanying paper.[16] Therefore, these results imply that these theories of microphase-separated structure can explain not only the molecular weight dependence of the domain spacing but also the chain conformation of the block copolymer along the direction perpendicular to the lamellae. However, they do not predict the contraction of block polymer along the direction parallel to the lamellae.

If we assume that the shapes of a deformed polymer chain in a lamellar structure and an undeformed polymer chain in a disordered state are an ellipsoid of revolution and a sphere, respectively, according to the above results, and that their radii are proportional to the corresponding radii of gyration, the volumes of the ellipsoid of revolution V_e and the sphere V_s can be given by

$$V_e \propto (4\pi/3)R_{g,x}R_{g,y}R_{g,z} = 0.016M^{1.5} \tag{7}$$

$$V_s \propto (4\pi/3)R_{g,0}{}^3 = 0.017M^{1.5} \tag{8}$$

Comparing eq 7 with eq 8, we can see that not only the molecular weight dependences but also the prefactors of the volumes occupied by a single chain are almost the same in the disordered state and in the lamellar structure. That is, the volume occupied by a block polymer does not vary, when the microphase separation occurs. This result implies that the block polymer is contracted along the direction parallel to the lamellae to preserve the same degree of coil overlapping or the same intermolecular interaction in the lamellar structure as in the disordered state.

In the above discussion we assumed that the lamellae are perfectly parallel to the surface of the film specimen. However, the actual orientation cannot be expected to be perfect. Expermentally, the degree of orientation of the lamellae can be estimated from the edge-view data by[12]

$$\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi,\theta) \cos^2 \phi \sin \phi \, d\phi}{\int_0^{\pi/2} I(\phi,\theta) \sin \phi \, d\phi} \tag{9}$$

where $I(\phi,\theta)$ is the coherent domain scattering intensity at an azimuthal angle ϕ and a scattering angle θ. We choose the angle where the first diffraction peak appears in SANS as the scattering angle θ in the present evaluation. Since the observed total scattering intensity consists of both the domain scattering and the single-chain scattering, the domain scattering intensity $I(\phi, \theta)$ was evaluated by subtracting the single-chain scattering or the scattering intensity $I(90, \theta)$ at $\phi = 90°$ from the observed total intensity at ϕ. Then, the orientation $\langle \cos^2 \phi \rangle$ was evaluated by using the summation in eq 10 in place of the integration in eq 9

$$\langle \cos^2 \phi \rangle = \frac{\sum_{n=0}^{17} (I(5n, \theta) - I(90, \theta)) \cos^2 (5n) \sin (5n)}{\sum_{n=0}^{17} (I(5n, \theta) - I(90, \theta)) \sin (5n)} \tag{10}$$

where $I(5n, \theta)$ and $I(90, \theta)$ are the sector-averaged total coherent scattering intensities around $\phi = 5n \pm 5°$ and the sector-averaged single-chain scattering around $90 \pm 5°$, respectively. The calculated values are listed in the last column of Table III. As shown in the table the orientation $\langle \cos^2 \phi \rangle^{1/2}$ is around 0.94, which is very close to the perfect orientation, irrespective of molecular weight. This result indicates that the absolute values of the radii of gyration of block polymers may be slightly different from the values listed in Tables II and III, but the molecular weight dependences are similar to the data in Figure 6. Therefore, the above conclusion still holds, though quantitative modifications are necessary.

Acknowledgment. We acknowledge a partial support of this work by the Japan Society for Promotion of Science and the National Science Foundation under the Japan–U.S. Cooperative Science Program.

References and Notes

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