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Molecular Weight Dependence of the Lamellar Domain Spacing of ABC Triblock Copolymers and Their Chain Conformations in Lamellar Domains

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ABSTRACT: The molecular weight dependence of the lamellar domain spacing of isopren–styrene–2-vinylpyridine triblock copolymers in bulk was studied over the molecular weight range from 40K to 280K by using a small-angle X-ray scattering (SAXS) method. It was found that the lamellar domain spacings of the triblock copolymers are larger than those of styrene–2-vinylpyridine diblock copolymers with the same molecular volumes. This result can be interpreted by theories of microphase separation at the strong segregation limit, taking into account the fact that the number of boundaries in the repeating structure of triblock copolymers is twice as large as that of diblock copolymers. Moreover, small-angle neutron scattering (SANS) studies imply that the middle block chain of triblock copolymers is contracted along the direction parallel to lamellae in almost the same manner as the block chain of the diblock copolymers.

Introduction

Studies on the molecular weight dependence of the domain spacing of microphase-separated structures and the chain conformation of block polymer in the microdomains are important not only to understand the microdomain structures at the molecular level but also to clarify the chain conformations of polymers in anisotropic and confined spaces.

The microphase-separated structures of AB diblock copolymers and the chain conformation of block polymer in the microdomains have been extensively studied. Among typical morphologies of microdomains lamellar structures were most examined, because they can be assumed to be in equilibrium in contrast to other morphologies and we can determine the dimensions of the block chain along the directions parallel and perpendicular to lamellae.[2] The molecular weight dependence of the lamellar domain spacing of styrene–2-vinylpyridine (SP) diblock copolymers[3] is in good agreement with theories of microphase separation at the strong segregation limit, particularly the theories of Helfand–Wasserman[4] and Semenov[5] as reported previously. Moreover, it was found that the block chain of diblock copolymer is extended along the direction perpendicular to lamellae in accordance with the theories, but it is contracted along the direction parllel to lamellae in contrast to the theoretical prediction. As described in a previous paper the block chain is contracted along the parallel direction to keep the volume occupied by the block polymer coil constant when the microphase separation occurs.

The remarkable feature of microphase-separated structures of ABC triblock copolymers at the molecular level is the fact that the ends of the middle B-block chain are held at different boundaries, or the B-chain has a "bridge" conformation, while one end of the block chain of diblock copolymers is free. Therefore, it is very interesting to study microphase-separated structures of ABC triblock copolymers at the molecular level in comparison with those of diblock copolymers. It is to be noted that the chain conformation of ABC triblock copolymers is simpler than that of ABA triblock copolymers, though the morphologies of the former microdomains might be more complicated than those of the latter, since the former has only the bridge conformation for the middle B-block chain, while the latter has a "loop" conformation as well as the bridge conformation.

In a previous work[6] we studied the variation of the morphology of isoprene–styrene–2-vinylpyridine (ISP) triblock copolymers with the composition of the middle styrene block, keeping the volume fraction of both end blocks the same, and found that the triblock copolymers have three-phase four-layer lamellar structures around the composition of I:S:P = 1:1:1. In the present work, therefore, we prepared the triblock copolymers having almost the same composition of 1:1:1 but various molecular weights to study the molecular dependence of the lamellar domain spacing with SAXS. Moreover, we prepared triblock copolymers with deuterated styrene blocks having almost the same chain lengths as the ordinary ones to study the chain conformation of the middle block polymer in the lamellar structure of the triblock copolymer by SANS.

Experimental Section

Samples used here were 11 poly(isoprene-*b*-styrene-*b*-2-vinylpyridine)s with ordinary and deuterated styrene blocks (ISP and IDP triblock copolymers) for SAXS listed in Table I and the three pairs of ISP and IDP triblock copolymers having the middle block chains with almost the same chain length for SANS in Table II. As shown in these tables they have narrow distributions of molecular weight and composition. The preparation and characterization methods are the same as in a previous paper.[6]

Film specimens for transmission electron microscopy (TEM), SAXS, and SANS were prepared by solvent-casting from 4% solutions of tetrahydrofuran which is a good solvent for all the components of the triblock copolymers, drying at room temperatures *in vacuo* for a week, and annealing at 120 °C *in vacuo* for 10 days as reported previously.[6] We observed morphologies of film specimens stained by OsO_4 with a JEOL transmission

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Table I. Molecular Characteristics of Samples for SAXS and Their Lamellar Domain Spacings

			volume fraction				degree of polymerization				
sample code	$M_n \times 10^{-3}$	M_w/M_n	Φ_I	Φ_S	Φ_P	$V_m \times 10^{-3}$ (cm^3/mol)	N_I	N_S	N_P	N	D (nm)
IDP-4	36.0[a]	1.06	0.27	0.34	0.40	34	124	117	147	388	28
ISP-21	55	1.06	0.34	0.34	0.32	52	245	182	184	612	42
ISP-5	58	1.04	0.32	0.35	0.32	55	245	199	196	641	41.5
ISP-4	61	1.04	0.36	0.31	0.33	58	288	184	211	684	41.5
ISP-9	80	1.03	0.32	0.25	0.43	76	332	192	356	880	52
ISP-2	94	1.05	0.30	0.42	0.28	91	369	384	275	1029	57
ISP-8	99	1.03	0.34	0.27	0.39	95	439	259	402	1100	55.5
IDP-6	103.8[a]	1.03	0.21	0.41	0.37	98	283	409	399	1091	60
ISP-16	152	1.04	0.35	0.34	0.31	147	699	504	495	1698	83
ISP-22	216	1.11	0.32	0.35	0.33	205	904	734	744	2382	120
ISP-17	279	1.04	0.36	0.32	0.32	267	1321	872	937	3130	135

[a] Calculated value as ISP.

Table II. Molecular Characteristics of Samples for SANS and Its Data

blend no.	sample code	$M_n \times 10^{-3}$	M_w/M_n	Φ_S	N_S	$R_{g,x}$ (nm)	$R_{g,x}/R_{g,x0}$[a]	$\langle \cos^2 \phi \rangle^{1/2}$
I	ISP-21	55	1.06	0.38	183	1.98 ± 0.08	0.88 ± 0.04	0.916
	IDP-7	49	1.06	0.36	179			
II	ISP-2	94	1.05	0.42	346	3.04 ± 0.20	0.93 ± 0.07	
	IDP-6	107	1.03	0.41	375			
III	ISP-22	216	1.11	0.32	673	3.83 ± 0.70	0.73 ± 0.14	0.888
	IDP-8	273	1.09	0.33	964			

[a] The unperturbed radius of gyration of polystyrene along the axis is evaluated by using $R_{g,x0} = 0.0159M^{1/2}$ (nm).[2]

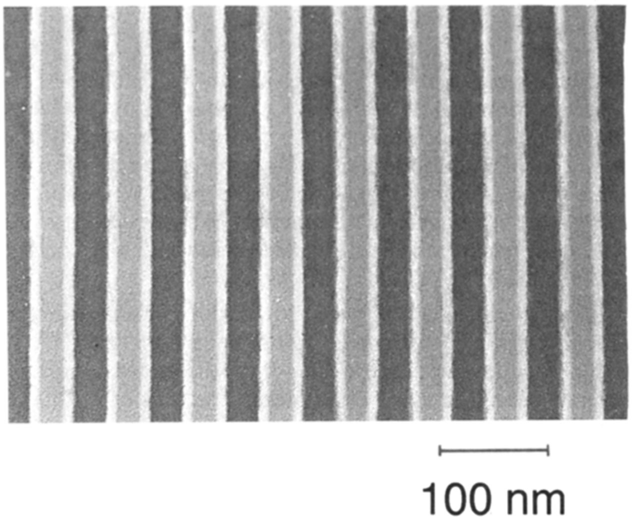

Figure 1. Typical electron micrograph of the three-phase four-layer lamellar structure of poly(isoprene-*b*-styrene-*b*-2-vinylpyridine) (ISP-16).

electron microscope Model 2000 FX[12] to confirm that all the specimens have three-phase four-layer structures as shown in Figure 1.

SAXS measurements were performed at room temperatures (~25 °C) with a Kratky U-slit camera of Anton Paar Co., equipped with a step scanner and a scintillation counter, using Cu Kα line (0.154 nm). The distance between the sample and the plane of registration was 210 mm. The scattering intensities were measured at the edge view where X-ray incidents parallel to the film surface as shown in Figure 2. The correction for finite slit width and length was carried out by using the procedure of Strobl[7] to yield the desmeared scattering intensity for a pinhole source for comparison.

SANS measurements were carried out at room temperatures (~22 °C) with a SANS spectrometer at the National Institute of Standards and Technology (NIST) equipped with a two-dimensional position-sensitive detector and a D$_2$O–ice cold source. The wavelength λ was 0.90 nm, and the width of the distribution $\Delta\lambda/\lambda$ was 0.25. The range of magnitude of scattering vector q $(=(4\pi/\lambda)\sin\theta)$ was 0.062–0.87 nm^{-1}, where 2θ is the scattering angle. The film specimens were blends of ordinary and deuterated samples listed in Table II. The measurements for chain conformation were performed only at the through view where the neutron beam incidents perpendicular to the film surface as shown in Figure 2, because contrast matching, which is necessary to extract a single-chain scattering at the edge view, is difficult in the case of a triblock copolymer with three different components. The measured intensities were averaged circularly at the same q values on the two-dimensional position-sensitive detector. The coherent scattering intensities were evaluated by subtracting the incoherent scattering intensities obtained for the ISP sample from the measured intensities.

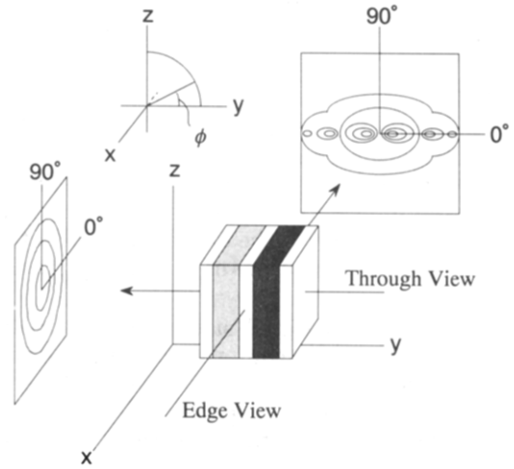

Figure 2. Geometrical relationship between the incident beam and film specimen. The azimuthal angle, ϕ, on the two-dimensional detector is defined in the figure.

Results

Figure 3 shows a triangle diagram for morphology and the composition of triblock copolymers to indicate the region of lamellar structures, where some new data are added to the previous ones.[6] From this figure we can see that the triblock copolymers do not have lamellar structures in the range of $\Phi_S \geq 0.45$ where $\Phi_I = \Phi_P$ (– · –), in the range of $\Phi_I \geq 0.4$ where $\Phi_S = \Phi_P$ (- - -), and in the range of $\Phi_P \geq 0.4$ where $\Phi_S = \Phi_I$ (· · ·). Here, Φ_K denotes the volume fraction of the K-block (K = I, S, or P). Thus, all the samples in Tables I and II have three-phase, four-layer lamellar structures as shown in Figure 1.

Figure 4 shows an example of semilogarithmic plots of SAXS intensity against the magnitude of scattering vector q for an ISP triblock copolymer together with that of an SP diblock copolymer at the edge view. The difference

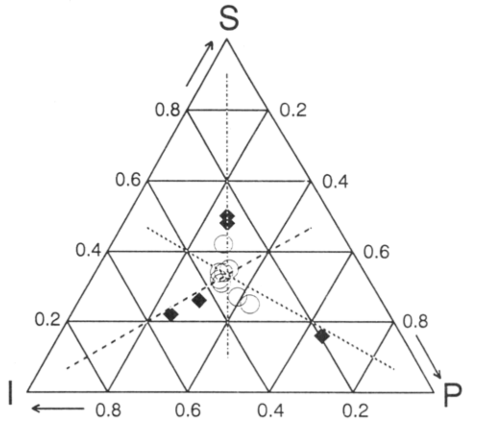

Figure 3. Triangle domain demonstrating the variation of morphology with the volume fraction of each block polymer for ISP triblock copolymers. The symbols ○ and ◆ denote three-phase, four-layer lamellar structures and other morphologies, respectively. The chain, broken, and dotted lines denote $\Phi_I = \Phi_P$, $\Phi_S = \Phi_P$, and $\Phi_S = \Phi_I$, respectively.

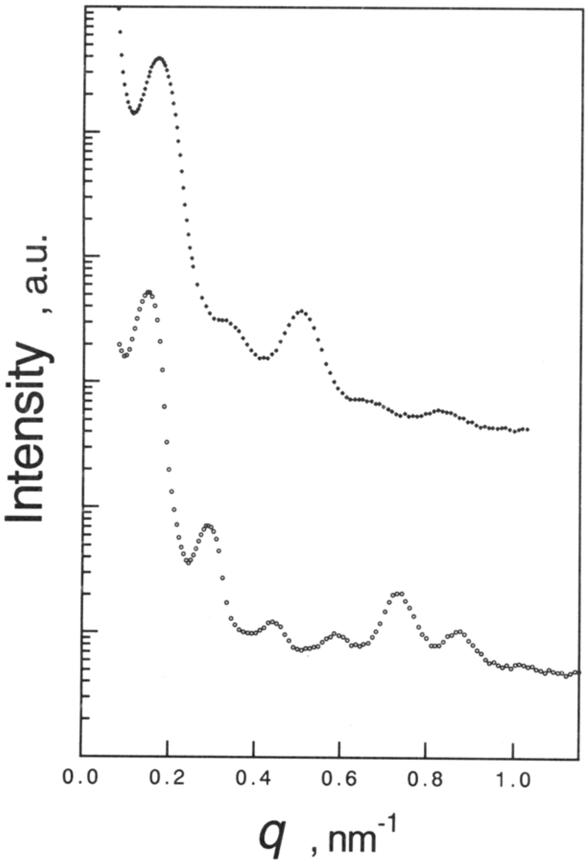

Figure 4. Examples of SAXS data of ISP triblock (ISP-5) (○) and SP diblock (SP-20) (◆) copolymers at the edge view.

between the diffraction profiles of di- and triblock copolymers is due to the difference between their particle scattering factors caused by the density profiles shown in Figure 5. The strong diffractions observed at the edge view as well as the TEM observation described above indicate that the lamellae are highly oriented to the direction parallel to film surface as well as reported for SP diblock copolymers previously.[3] Since there is no difference between the q values at the diffraction peaks, q_{max}, in the original and desmeared data within experimental error, the q_{max} values were determined from the original data.

The lamellar domain spacings D of the triblock copolymers were evaluated by using the Bragg equation, $D = 2n\pi/q_{max}$ where n is the order of diffraction. The D values in Table I are the averages of D evaluated from q_{max} of different orders. The diffraction peaks result from the period of electron density of lamellar structures as shown in Figure 5. The periods of ABC triblock and AB diblock copolymers consist of two molecules along the direction perpendicular to lamellae of both block copolymers, though the former is A–B–C–A and the latter is A–B. It is to be noted that the period of the ABA triblock copolymer is A–B, but it consists of one molecule along the direction perpendicular to lamellae.

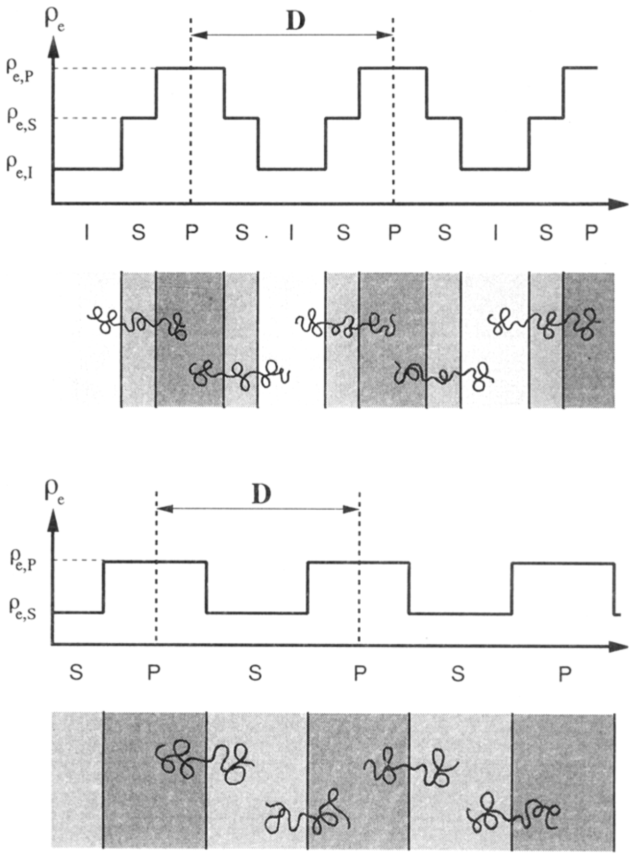

Figure 5. Electron density profiles for the lamellar structures of SP diblock and ISP triblock copolymers. D is the intensity period, and $\rho_{e,I}$, $\rho_{e,S}$, and $\rho_{e,P}$ are the electron densities of polyisoprene, polystyrene, and poly(2-vinylpyridine), respectively.

Figure 6 shows double-logarithmic plots of the experimental D (nm) values against the number-average molecular weight M_n. Using a least-squares method, we obtain the following empirical equation over the molecular weight range from 40K to 280K:

$$D = 0.085_5 M_n^{0.77\pm0.03} \qquad (1)$$

Hadziioannou et al. reported that the molecular weight dependence of the domain spacing for styrene–isoprene (SI) diblock copolymer is given by $D = 0.006M_n^{0.79}$ (nm).[9] Their result looks similar to our result of ISP triblock copolymers in terms of the high exponents, but the sample specimens used in their work were prepared by a "shearing technique", which is special and different from our preparing method. Recently, we found that the lamellar domain spacings of SP diblock copolymers are almost the same before and after annealing.[10] Therefore, we compare the data of an ISP triblock copolymer with those of SP diblock copolymers which were prepared by solvent-casting. Figure 7 shows the comparison between the D values of ISP triblock and SP diblock copolymers, where the molecular volumes V_m (cm^3/mol) are employed instead of molecular weights, because the domain spacings are considered to be determined by the molecular volumes

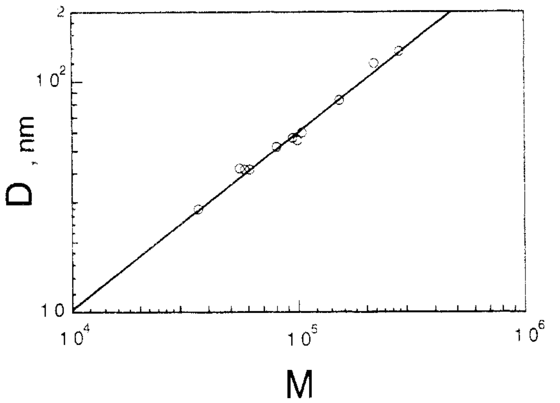

Figure 6. Double-logarithmic plots of lamellar domain spacing, D, against M_n for ISP triblock copolymers.

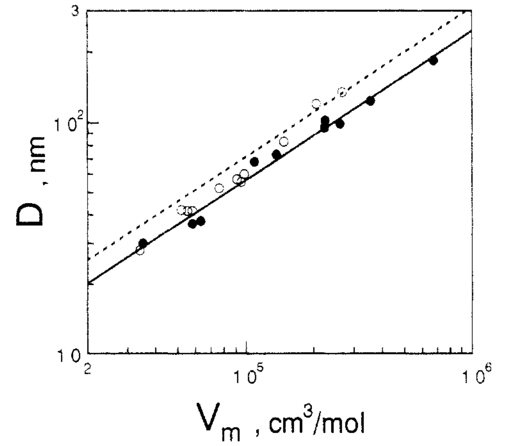

Figure 7. Double-logarithmic plots of lamellar domain spacing, D, against the molar volume, V_m, of di- (●) and triblock (○) copolymers. The full line denotes the empirical equation for SP diblock copolymers reported previously, and the broken line denotes the theoretical line which is $2^{1/3}$ times larger than the full line.

rather than the molecular weights when the species of block polymers are different. From this figure we can see that the lamellar domain spacings of ISP triblock copolymers are larger than those of SP diblock copolymers at least for the high molecular weight samples.

If lamellae are predominantly oriented along the direction parallel to the film surface, no diffraction is observed so that a single-chain scattering is measured at the through view without contrast matching in SANS as reported for SP diblock copolymers.[2] For the present triblock copolymers, however, diffraction peaks were observed even at the through view. This result imply that the orientation was not predominant, so that we estimated the degree of orientation listed in the last column in Table II by using the diffraction data at the edge view as reported for diblock copolymer previously.[2] The $\langle\cos^2\phi\rangle^{1/2}$ values are not very close to 1 in contrast to diblock copolymers (~0.94). The diffraction from lamellae at various directions causes the peaks at the through view, which may correspond to the circularly-averaged intensities at the edge view because the shapes of diffraction peaks at the through and edge views are very similar. To extract the single-chain scattering data at the through view as shown in Figure 8, therefore, we subtract the circularly-averaged scattering intensity at the edge view of the same specimen from the scattering data at the through view so as to minimize the diffraction peaks by adjusting the former scattering intensity because the diffraction is much stronger than the single chain scattering at the edge view. The radii of gyration, $R_{g,x}$, evaluated from the Guinier plot thus obtained are listed together with the ratio to the unperturbed radius of gyration $R_{g,x0}$ in Table II, and they are plotted against the molecular weight of middle block polymers together with the data of diblock copolymers in Figure 9.

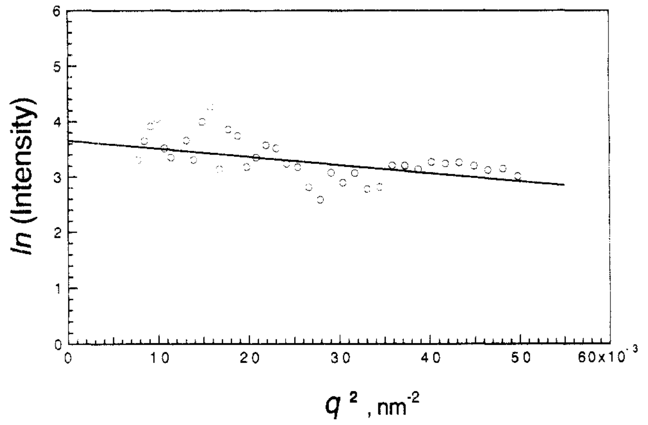

Figure 8. Guinier plots of the single-chain scattering intensity of the polystyrene block of a triblock copolymer in lamellar structure at the through view. The sample is blend III.

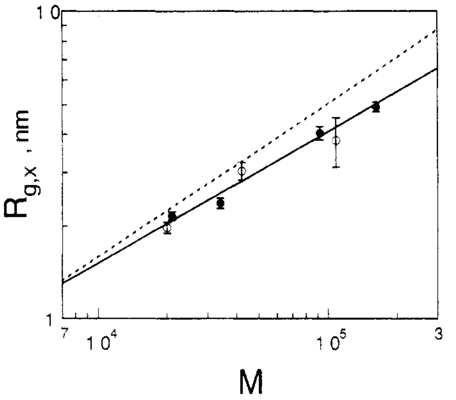

Figure 9. Double-logarithmic plots of $R_{g,x}$ against the molecular weight of the polystyrene block in the lamellar structures of ISP triblock (○) and SP diblock (●) copolymers. The broken line denotes the unperturbed radius of gyration along any axis, $R_{g,x0}$.

Discussion

Assuming that the free end of the block chain is located in the middle of the domain, Semenov presented a theoretical equation of molecular weight dependence of the lamellar domain spacing of symmetrical diblock copolymers, in which the numbers of segments, segment lengths, and densities of both block components are the same, at the strong segregation limit as

$$D = (4/6^{1/2})(3/\pi^2)^{1/3}\chi^{1/6}bZ^{2/3} \qquad (2)$$

where Z is the total number of segments of diblock copolymer, b is the Kuhn segment length, and χ is the Flory–Huggins interaction parameter. As reported in a previous paper,[3] this theory is in good agreement with the experimental results of SP diblock copolymers.

Since the conformation of the block chain of which the free end is located in the middle of the domain of diblock copolymers is similar to the bridge conformation of the middle B-block chain of ABC triblock copolymer, the same procedure in the theory of Semenov can be applied to the calculation of conformational entropy for the lamellar structure of ABC triblock copolymers. For the "symmetrical triblock copolymer" that the numbers of segments, segment lengths, and densities A, B, and C block polymers of triblock copolymers are the same, therefore, we have

$$D = (4/6^{1/2})(6/\pi^2)^{1/3}\chi^{1/6}bZ^{2/3} \qquad (3)$$

Here, we assume that the χ values between A and B and between B and C are the same. Comparing between eqs 2 and 3, we predict that the domain spacing of triblock copolymers is $2^{1/3}$ (=1.26) times larger than that of diblock copolymers. As shown in Figure 7 the experimental results are in good agreement with the theoretical prediction at least for the high molecular weight samples. The difference results from the fact that the number of boundaries in the repeating structure of triblock copolymers is twice as large as that of diblock copolymers as mentioned above. It was reported that lamellar domain spacings of SIS triblock copolymers are almost equal to those of SI diblock copolymers having the same composition but half the molecular weight of triblock copolymer as predicted by the theory of Helfand–Wasserman.[9,11] It is to be noted that the repeating unit of ABC triblock copolymers includes the two molecules (A–B–CC–B–A) but that of ABA triblock copolymers includes the one molecule (A–B–A), as mentioned above. The difference between ABC and ABA copolymers will be described in detail elsewhere.[10]

With decreasing molecular weight the contribution of free energy of the localization of the junction points, which is neglected in the theory of Semenov, increases. Assuming that the conformational entropy of the B-chain is the same as that of the A- or C-chain as used in the derivation of eq 3 from the theory of Helfand–Wasserman, we have the following equation for ABC triblock copolymers:

$$\frac{-2(\gamma_{\rm AB}+\gamma_{\rm BC})}{kT}\times\left(\frac{Z_{\rm A}}{\rho_{0\rm A}}+\frac{Z_{\rm B}}{\rho_{0\rm B}}+\frac{Z_{\rm C}}{\rho_{0\rm C}}\right)+2D+0.353\times \frac{({Z_{\rm A}}^{1/2}/\rho_{0\rm A}b_{\rm A})^{2.5}+({Z_{\rm B}}^{1/2}/\rho_{0\rm B}{\rm b}_{\rm B})^{2.5}+({Z_{\rm C}}^{1/2}/\rho_{0\rm C}{\rm b}_{\rm C})^{2.5}}{[(Z_{\rm A}/\rho_{0\rm A})+(Z_{\rm B}/\rho_{0\rm B})+(Z_{\rm C}/\rho_{0\rm C})]^{2.5}}\times D^{3.5}=0 \quad (4)$$

with

$$\gamma_{KJ}=kT{\alpha_{KJ}}^{1/2}\left[\frac{(\beta_K+\beta_J)}{2}+\frac{(\beta_K-\beta_J)^2}{6(\beta_K+\beta_J)}\right]$$

$$\alpha_{KJ}=\chi_{KJ}(\rho_{0K}\rho_{0J})^{1/2}$$

$$\beta_K=(\rho_{0K}{b_K}^2/6)^{1/2}$$

where Z_K is the number of segments in the K-block chain, ρ_{0K} is the number density of the K-segment in pure K-polymer, b_K is the Kuhn statistical segment length of the K-chain, and χ_{KJ} is the Flory–Huggins parameter between K- and J-polymers. If the contribution of the free energy of the localization of the junction points, that is, the second term in eq 4, is neglected, eq 4 corresponds to eq 3 and both equations are practically the same for the symmetrical triblock copolymer, though the front factors and exponents are slightly different. As reported previously[2] the statistical segment lengths of polystyrene and poly(2-vinylpyridine) are the same, so that the relationships between Z and the degree of polymerization N are the same. Therefore, using $b_{\rm I} = 5.9 \times 10^{-10}$,[8] $b_{\rm S} = b_{\rm P} = 6.8 \times 10^{-10}$ (m),[2] $b_{\rm I}{Z_{\rm I}}^{1/2} = 0.683{N_{\rm I}}^{1/2}$,[8] $b_{\rm S}{Z_{\rm S}}^{1/2} = 0.594{N_{\rm S}}^{1/2}$, $b_{\rm P}{Z_{\rm P}}^{1/2} = 0.594{N_{\rm P}}^{1/2}$,[2] $\rho_{\rm I} = 1.38 \times 10^4$,[8] $\rho_{\rm S} = 1.02 \times 10^4$, and $\rho_{\rm P} = 1.10 \times 10^4$ (mol/m^3)[2] and assuming $\chi_{\rm IS} = \chi_{\rm SP} = 0.1$ where the subscripts I, S, and P denote polyisoprene, polystyrene, and poly(2-vinylpyridine) blocks, we evaluated theoretical values for ISP triblock copolymers from eq 4 with and without the second term. In Figure 10 they are plotted against N together with a theoretical line of Helfand and Wasserman for an SP diblock copolymer.[3] As expected the theoretical line from eq 4 without the second term agrees with the experimental data at the high molecular weights. With decreasing the molecular weight the data deviate from this line and follow the theoretical line with the second term. Qualitatively speaking, however, the empirical molecular weight dependence given by eq 1 is somewhat stronger than the theoretical prediction, though the contribution of the localization of the junction points is larger for ABC triblock copolymers than for AB diblock copolymers, because the number of boundaries of the former is twice as large as that of the latter.

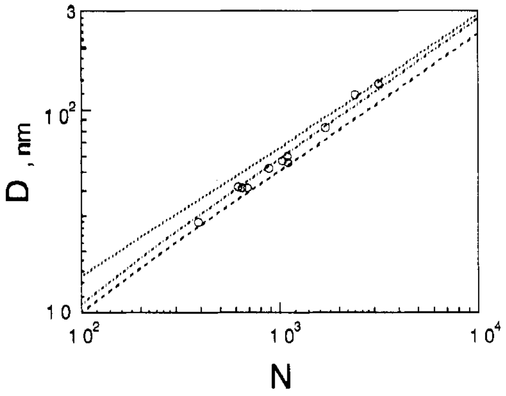

Figure 10. For comparison between the experimental D data of ISP triblock copolymers (○) and theoretical equations. The chain, dotted, and broken lines denote eq 4 with and without the second term for ISP triblock copolymer and the theory of Helfand and Wasserman for SP diblock copolymers, respectively. The number on the abscissa indicates the degree of polymerization, N of the block copolymer.

Figure 9 implies that the middle block chain is contracted along the direction parallel to lamellae at almost the same amount as the block chain of diblock copolymers. As reported previously the block chain of the diblock copolymer is contracted along the direction parallel to lamellae to keep the volume occupied by the block polymer coil constant. This may be the case for the triblock copolymer because the triblock copolymer may be extended along the direction perpendicular to lamellae at almost the same amount as the diblock copolymer as inferred from the domain spacing data. However, we do not have a definite conclusion, since the experimental erros are fairly large due to the imperfect orientation of lamellae.

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