Molecular Weight Dependence of Lamellar Domain Spacing of Diblock Copolymers in Bulk

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ABSTRACT: The molecular weight dependence of lamellar domain spacing of styrene–2-vinylpyridine diblock copolymers in bulk was measured by means of small-angle X-ray scattering and compared with theories of microphase-separated structure. It was found that the lamellar domain spacing–molecular weight relationship of the diblock copolymer in bulk is given by $D = 0.33_7 M^{0.64}$ over the molecular weight range from 38K to 740K. The experimental result is in good agreement with the theories on the basis of Gaussian chain statistics in a confined space, particularly the theory of Helfand–Wasserman.

Introduction

Studies on the molecular weight dependence of lamellar domain spacing are important to the understanding of microphase-separated structures at the molecular level, since the lamellar domain is the basic and the simplest morphology and, moreover, its domain spacing can be assumed to be very close to the equilibrium one in contrast to other microdomains such as a spherical structure, of which the domain spacing is due to a nonequilibrium effect encountered in the domain formation process.

Meier,[2,3] Helfand et al.,[4-6] Semenov,[7] and Kawasaki et al.[8-10] have presented theories of microphase-separated structure. Although they used different theoretical approaches, all the theories predict that the molecular weight dependence of lamellar domain spacing is given by a power law as

$$D \propto M^a \tag{1}$$

where the exponent a is $^2/_3$ or very close to $^2/_3$ in the narrow interphase approximation or in the strong segregation limit, where the interfacial thickness between two domains is sufficiently small compared with the domain spacing.[5,7,8,10] This approximation becomes more favorable at high molecular weights, because the block chains become incompatible if $\chi N \gg 10$ where χ is the Flory–Huggins interaction parameter and N is the degree of polymerization of block copolymer[11] and because the interfacial thickness is considered to be almost independent of molecular weight.[5,12] In experimental studies, on the other hand, it was reported that the lamellar domain spacings of the styrene–isoprene diblock copolymer are in good agreement with the above theoretical prediction over the molecular weight range from 20K to 110K,[12] while the other data of styrene–isoprene block copolymers containing the higher molecular weight samples show the larger exponent than $^2/_3$ in eq 1.[13] Therefore, it is worthwhile to study the molecular weight dependence of lamellar domain spacing over a high molecular weight range by using another well-defined diblock copolymer sample. Then, in the present work we used styrene–2-vinylpyridine diblock copolymers with the molecular weights from 38K to 740K. The present diblock copolymer can be considered as a "model" block copolymer because the molecular weight and composition distributions are fairly narrow[14,15] and the statistical segment lengths of polystyrene and poly(2-vinylpyridine) are practically the same,[16] yet they are incompatible. Thus, the diblock copolymer with a polystyrene content of 50 vol % can be regarded as a symmetrical block copolymer in which the molecular parameters of both blocks are equal and, hence, the theoretical treatment is simplified.

The present data on lamellar domain spacing of styrene–2-vinylpyridine diblock copolymers can also serve to estimate the molecular weight dependence of the radius of gyration along the direction perpendicular to the lamellae, which provides useful information about the conformation of block chains in lamellar structures as described in an accompanying paper.[17]

Experimental Section

Styrene–2-vinylpyridine diblock copolymer samples were prepared by an anionic polymerization technique and were characterized as reported previously.[14,15] Their molecular characteristics are listed in Table I. Film specimens for transmission electron microscopy (TEM) and small-angel X-ray scattering (SAXS) measurements were prepared by solvent-casting from dilute solutions of tetrahydrofuran, which is a good solvent for both blocks, followed by drying for 4–5 days in vacuo. The details of the preparation were also described previously.[18]

SAXS measurements were performed at room temperatures (~25 °C) with a Kratky U-slit camera from the Anton Paar Co., equipped with a step scanner and a scintillation counter using an X-ray beam with a wavelength (λ) of 1.54 Å. Two sets of entrance and counter slits were used to measure scattering intensities over the range of scattering vectors suitable to domain spacings. The widths of the two sets of entrance and counter slits were 60 and 150 μm and 100 and 250 μm, respectively. The distance between the sample and the plane of registration was 21 cm. The SAXS intensities were measured with two sample orientations, called edge and through views, in which the film specimens were set parallel and perpendicular to the X-ray beam, respectively. The correction for finite slit width and length was carried out according to Glatter's program[19] to yield the desmeared scattered intensity for a pinhole source for comparison.

Results

Figure 1 shows an example of a plot of the observed scattered intensity vs the magnitude of scattering vector q, where $q = (4\pi/\lambda) \sin \theta$ and 2θ is the scattering angle. Strong diffraction peaks are observed in the edge view, while no distinct peak is observed in the through view, though a small shoulder appears to exist. This result confirms that the lamellae are not perfectly but predominantly oriented along the direction parallel to the film surface as observed by TEM.[14] Thus, X-ray beams are considered to be incident to the directions almost parallel and perpendicular to the lamellae in the edge and

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

sample code	$M_n \times 10^{-3}$	M_w/M_n (GPC)	Φ_s[a]
SP-22	38	1.01	0.51
SP-33	63	1.03	0.52
SP-20	69	1.03	0.54
SP-34	119	1.03	0.51
SP-77	149	1.02	0.53
SP-15	243	1.06	0.50
SP-4	245	1.11	0.52
SP-21	286	1.08	0.50
SP-12	388	1.03	0.52
SP-24	739	1.11	0.51

[a] Φ_s is the volume fraction of polystyrene determined by elemental analysis.

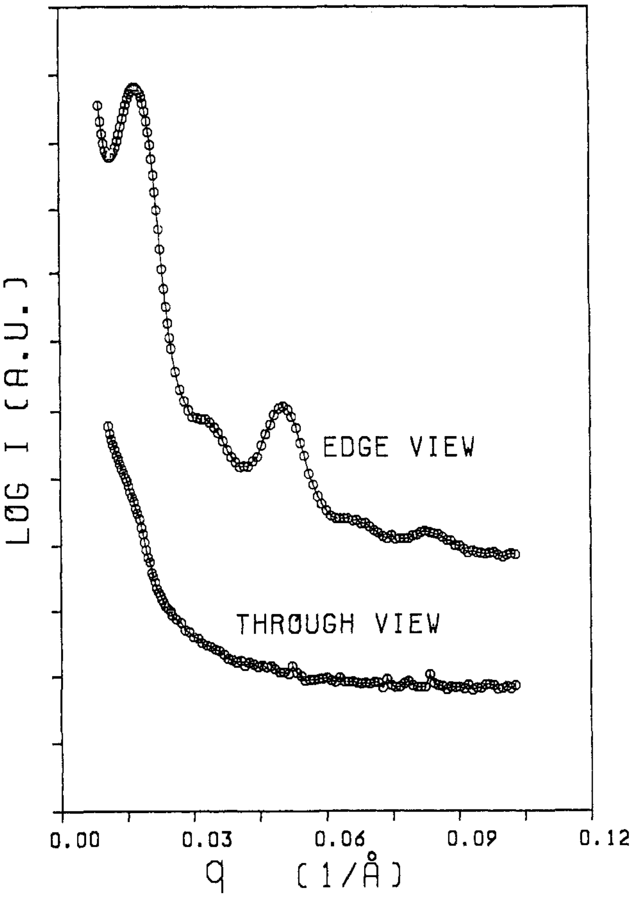

Figure 1. Example of SAXS data from a film specimen of diblock copolymer of styrene and 2-vinylpyridine in the through and edge view. The sample is SP-20.

through views, respectively. The desmearing could not yield the correct scattering data for a pinhole source if the lamellae would not be perfectly oriented. In the present data, however, the diffraction peaks in the corresponding desmeared data appear at the same scattering angle within experimental errors due to the predominant orientation of lamellae. All the prominent peaks are identified as diffractions corresponding to odd number orders because the thicknesses of the adjacent phases are almost equal to each other so that even number-order reflections are practically absent.[20]

The domain spacings, D, of the samples were evaluated from the Bragg equation, $D = 2\pi n/q_m$, where q_m is the magnitude of scattering vector at the maxima and n is the odd number. The D values evaluated from the peaks at all the odd number-order reflections were averaged to yield the experimental D values listed in Table II. Figure 2 shows a double-logarithmic plot of the experimental D values vs the number-averaged molecular weights, M_n, of the diblock copolymers. Using the least-squares method, we obtain the following empirical equation over the molecular weight range from 38K to 740K.

$$D = 0.33_7 M_n^{0.64\pm0.03} \tag{2}$$

Discussion

According to Helfand–Wasserman,[5] the domain spacing of a lamellar structure of a symmetrical diblock copolymer in the strong segregation limit is given by

$$-(2/6^{1/2})\chi^{1/2}bN + D + (0.353/2^{1/4})D^{3.5}/(bN^{1/2})^{2.5} = 0 \tag{3}$$

where b is the segment length. Since the second term can be neglected in comparison with the first and third terms when $N \gg 1$, we have

$$D = \{2^{3/2}/[(0.353^2)(3)]\}^{1/7}\chi^{1/7}bN^{9/14} = 1.34\chi^{1/7}bN^{9/14} \tag{4}$$

The interfacial thickness of an A–B diblock copolymer, t, can be defined by

$$t = 1/(\mathrm{d}\rho(r)/\mathrm{d}r)_{\rho(r)=1/2} \tag{5}$$

where $\rho(r)$ is the excess density of the A (or B) block at the interface. In the theory of Helfand–Wasserman the interfacial thickness, t, for a symmetrical diblock copolymer is given by

$$t = 2b/(6\chi)^{1/2} \tag{6}$$

According to Semenov,[7] the lamellar domain spacing in the strong segregation limit is given by

$$D = (4/6^{1/2})(3/\pi^2)^{1/3}\chi^{1/6}bN^{2/3} = 1.10\chi^{1/6}bN^{2/3} \tag{7}$$

Introducing his excess density at the interface into eq 5, we have the same equation as eq 6 for the interfacial thickness in the theory of Semenov.

Ohta and Kawasaki[8] presented the theoretical equation of lamellar domain spacing in the strong segregation limit as

$$D/\xi = [(16)(2^{1/2})/3]^{1/3}(R_g/\xi)^{4/3} \tag{8}$$

where R_g is the radius of gyration of block copolymer at an unperturbed state and ξ is the interfacial thickness defined in the theory of Ohta–Kawasaki, given by

$$\xi = b/(6\chi - 21.6/N)^{1/2} \tag{9}$$

If $N \gg 1$, eq 9 reads

$$\xi = b/(6\chi)^{1/2} \tag{10}$$

Substituting eq 10 in eq 8, we have

$$D = (2/3^{5/6})\chi^{1/6}bN^{2/3} = 0.80\chi^{1/6}bN^{2/3} \tag{11}$$

By introduction of their excess density at the interface into eq 5, the interfacial thickness, t, is given by

$$t = 2^{3/2}\xi = 2b/(3\chi)^{1/2} \tag{12}$$

By using eq 12, eq 8 is rewritten as

$$D/t = (2^2/3^{1/3})(R_g/t)^{4/3} = 2.77(R_g/t)^{4/3} \tag{13}$$

When $N \gg 1$, similarly, the theory of Helfand–Wasserman (eq 4) can be rewritten by using eq 6 as

$$D/t = 2(3^{5/2}/0.353^2)^{1/7}(R_g/t)^{9/7} = 3.99(R_g/t)^{9/7} \tag{14}$$

The theory of Semenov (eq 7) is also rewritten by using

Table II
Comparison between Observed and Theoretical Lamellar Domain Spacings

			D, Å				
sample code	$M_n \times 10^{-3}$	N	obsd	HW[a]	HW$_r$[a]	S[a]	OK[a]
SP-22	38	365	300	240	282	251	183
SP-33	63	606	365	343	391	352	256
SP-20	69	663	375	365	414	374	272
SP-34	119	1140	680	529	587	537	391
SP-77	149	1430	730	617	679	625	454
SP-15	243	2340	950	859	932	868	631
SP-4	245	2360	1020	864	937	873	635
SP-21	286	2750	990	958	1030	966	703
SP-12	388	3730	1240	1170	1260	1180	861
SP-24	739	7110	1850	1800	1900	1820	1324

[a] HW, HW$_r$, S, and OK denote the theoretical values of Helfand–Wasserman, its reduced form, Semenov and Ohta–Kawasaki, respectively.

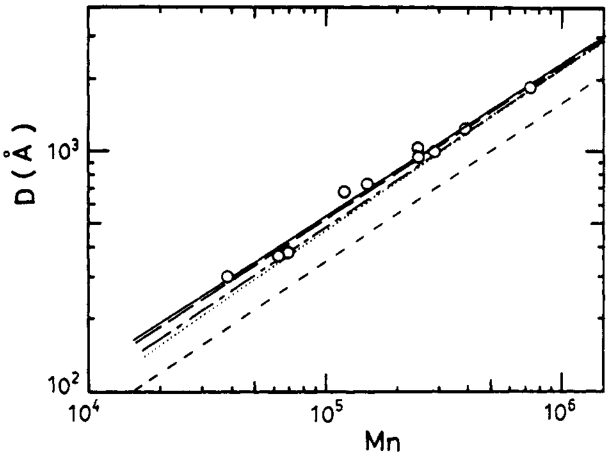

Figure 2. Double-logarithmic plots of domain spacing, D, vs M_n: (—) eq 2; (···) theory of Helfand–Wasserman (eq 3); (– –) reduced form of the theory of Helfand–Wasserman (eq 4); (–·–) theory of Semenov (eq 7); (- - -) theory of Ohta–Kawasaki (eq 11).

eq 6 as

$$D/t = [(2^7)(3)/\pi^2]^{1/3}(R_g/t)^{4/3} = 3.39(R_g/t)^{4/3} \quad (15)$$

Thus, the theories of Helfand–Wasserman and Semenov are expressed by reduced forms similar to the theory of Ohta–Kawasaki, eq 13, though the exponents and the coefficients are different.

The domain spacings evaluated from the theories of Helfand–Wasserman, Semenov, and Ohta–Kawasaki are listed in Table II. Figure 2 shows a comparison between the experimental data of styrene-2-vinylpyridine diblock copolymer and the theories. Since it was reported that the lamellar domain spacings predicted from the theories of Meier and Helfand–Wasserman agree with each other,[12] the former was not examined here. In the evaluation of the theoretical values, we used 1.04×10^{-2} mol/cm^3 and 6.8 Å for the density and statistical segment length of the diblock copolymer, respectively. The former value is the geometric average of the densities of polystyrene (1.01×10^{-2} mol/cm^3) and poly(2-vinylpyridine) (1.09×10^{-2} mol/cm^3), and the latter value was evaluated from the unperturbed dimension of polystyrene,[21] taking account of the fact that the unperturbed dimensions of polystyrene and poly(2-vinylpyridine) are almost the same.[16] Moreover, $M/N = 104.5$ was used as the average molecular weight of the monomers. For the Flory–Huggins interaction parameter, χ, between polystyrene and poly(2-vinylpyridine) we used 0.08 evaluated by applying the equation of Leibler[11] to small-angle neutron-scattering data from styrene-2-vinylpyridine diblock copolymer with a low molecular weight (12K) at a disordered state in bulk at 100 °C, since the temperature dependence of χ is very low ($\sim 10^{-4}$/deg). The details will be reported elsewhere.[22] As shown in Figure 2 the theories of Helfand–Wasserman and Semenov are in good agreement with the present data, while the magnitudes of D predicted by the theory of Ohta–Kawasaki are much smaller than the observed ones, though the observed exponent in eq 2 coincides with the theoretical value $^2/_3$ within experimental errors.

Since the theoretical equations for the molecular weight dependence of lamellar domain spacing can be expressed in terms of the interfacial thickness as shown above, the validity of the theories can be examined without using the χ parameter, which might have a large ambiguity, if we would have the experimental data of interfacial thickness. Unfortunately, however, it was difficult to measure the interfacial thickness of the present sample by SAXS, because the difference between electron densities of polystyrene and poly(2-vinylpyridine) is not large enough to give reliable scattering data at high scattering angles. Then, we examine the theories using the data of domain spacings and interfacial thickness (18 Å) of lamellar structures of styrene–isoprene diblock copolymers.[12] If we use $b = 6.3$ Å and $M/N = 84$ for the hypothetical symmetric styrene–isoprene diblock copolymer, since the errors in the symmetrical assumption are small,[12] we have $D/t = 3.52(R_g/t)^{9/7}$ and $D/t = 3.42(R_g/t)^{4/3}$ where the exponents are assumed to be $^9/_7$ and $^4/_3$, respectively. These results also indicate that the experimental data are in good agreement with the theories of Helfand–Wasserman (eq 14) and Semenov (eq 15) but do not agree with the theory of Ohta–Kawasaki (eq 13).

The free energy controlling the domain spacing mainly consists of the interfacial free energy, F_I, and the chain conformational free energy, F_C. In the theory of Helfand–Wasserman[5] $F_C \propto (D/N^{1/2})^{2.5}$, while in the theories of Semenov[7] and Ohta–Kawasaki[8] $F_C \propto (D/N^{1/2})^2$, but their prefactors are different. In all these theories, on the other hand, $F_I \propto \chi^{1/2}N/D$, though the prefactor in the theory of Ohta–Kawasaki is different from the others. The theory of Ohta–Kawasaki is formulated in terms of the local deviation of the monomer density, which is the local order parameter familiar in the theory of phase transition, and the free energy is obtained by neglecting the higher terms than the two-body interactions in its power series. Hence, the disagreement between their theory and the data is considered to be due to the poor convergence of the power series.[9,10] On the other hand, the theory of Helfand–Wasserman explicitly relies on the conformational characteristics on the basis of Gaussian chain statistics, and the differential equation of the chain propagator is solved to obtain F_C by decomposing the propagator into the normal mode.[5] Recently, solving the differential equation of chain propagator directly, Kawasaki and Kawakatsu[10] found that there is a crossover from the free energy of Helfand–Wasserman to that of Semenov around $D/bN^{1/2} = 5.7$, which corresponds to a very high molecular weight ($M > 10^7$) for the present diblock copolymer. Therefore, we must see a crossover between D and M from the theoretical equation of Helfand–Wasserman to that of Semenov at the very high molecular weight, because the interfacial free energy is the same in both theories.

From the above discussion we can conclude that the experimental results are well explained by the theories on the basis of Gaussian chain statistics in a confined space,[2,5,7,10] particularly, the theory of Helfand–Wasserman, taking into consideration that the molecular weights of the present diblock copolymers as well as those of the styrene–isoprene diblock copolymers discussed above[12] are much lower than the crossover molecular weights pointed out by Kawasaki and Kawakatsu.[10]

According to small-angle neutron-scattering studies reported in an accompanying paper,[17] the block chain in the lamellar domain is contracted along the direction parallel to the lamellae. It is very interesting that the theory of Helfand–Wasserman well explains the magnitude of lamellar domain spacing as well as its molecular weight dependence but does not predict the contraction.

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References and Notes

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