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Lamellar domain spacing of the ABB graft copolymers

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The molecular weight dependence of lamellar domain spacing of poly(2-vinylpyridine-*g*-styrene) was measured by small angle X-ray scattering (SAXS). The samples used are six three-arm star-shaped polymers having one polystyrene arm connected at the centre of a poly(2-vinylpyridine) chain. The volume fractions of grafted polystyrene chains, ϕ_s, of the samples range from 0.45 to 0.78, though all the samples were confirmed to have alternating lamellar structure by SAXS and transmission electron microscopy. It was found that the relationship between lamellar domain spacing, D, and the molecular weight, M, of the graft copolymers is given by $D = 0.015_3 \, M^{0.69}$ (nm) over the molecular weight range from 49 to 283 k irrespective of the difference in composition. The exponent 0.69 is quite close to 2/3, which is predicted for AB diblock copolymers by several different theories. However, the magnitude of the prefactor in the above relationship is apparently smaller than that for styrene–2-vinylpyridine diblock copolymers. This difference can be explained by considering the difference in structure between AB diblock copolymers and ABB graft copolymers. Copyright © 1996 Elsevier Science Ltd.

(Keywords: domain spacing; graft copolymer; lamellar structure; molecular weight dependence; block copolymer)

INTRODUCTION

Equilibrium morphologies of block copolymers have been extensively studied both experimentally and theoretically. It is well established that microphase-separated structures change with composition of block chains, i.e. from spherical structures with A spheres in a B matrix to cylindrical structures with A cylinders in a B matrix and successively to AB alternating lamellar structures with increasing volume fraction of A chains, ϕ_A, and then the reverse morphologies appear with further increasing ϕ_A for AB diblock copolymers [1–4]. In addition, recently, bicontinuous structures have been found in between cylindrical and lamellar structures for styrene–isoprene diblock copolymers [5].

Among these equilibrium morphologies, the molecular weight dependence of microdomain spacing has been quantitatively discussed for lamellar structures because the alternating lamellar structures are the simplest morphology over others. Meier[6], Semenov[7] and Ohta and Kawasaki[8] independently predicted the same simple 2/3 power for an exponent, ν, of domain spacing (D)–molecular weight (M) relationship:

$$D = KM^{\nu} \qquad (1)$$

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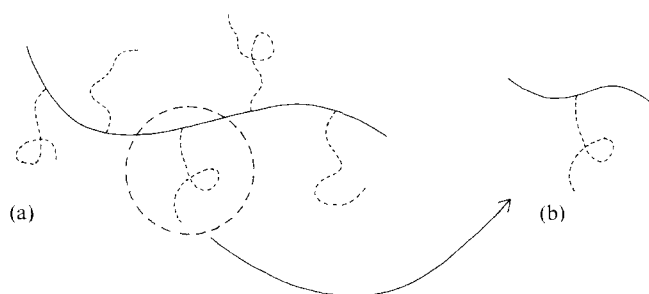† Present address: Tokai Rubber Industries Ltd, 360 Utazu, Kitatoyama, Komaki, Aichi 485, Japan

where K is a constant, while Helfand and Wasserman[9,10] gave $9/14 = 0.643$ for ν as an asymptotic value for a molecule with infinite molecular weight. On the other hand, Hashimoto et al.[11] experimentally examined the D–M relationship for styrene–isoprene diblock copolymers and obtained 2/3 as the exponent in equation (1). Moreover, Matsushita et al.[12] found 0.64 for the exponent by measuring domain spacings of styrene–2-vinylpyridine diblock copolymers over a wide range of molecular weight and reported that not only the exponent, but the magnitude of the experimental data are in good agreement with the theories of Helfand and Wasserman[9,10] and Semenov[7].

Graft copolymers are, in general, branched polymers which consist of backbone chains and many grafted chains, but a star molecule with one graft chain and two backbone chains connected at one point together can be considered as their basic unit as schematically shown in *Figure 1*. We regard this simple molecule as a model graft copolymer and call it ABB graft copolymer hereafter. This graft molecule has a structural feature of possessing asymmetry of number of block chains at the domain boundaries in bulk in contrast to block copolymers. In short, A and B chains of the graft copolymer have to be aligned one-to-two way at the interface in the microphase-separated structures, irrespective of their morphologies, while the chains of block copolymers are always aligned one-to-one way. Therefore, it is

Figure 1 Schematic drawings of (a) a graft copolymer chain and (b) its basic unit

Table 1 Molecular characteristics of SPP graft copolymers

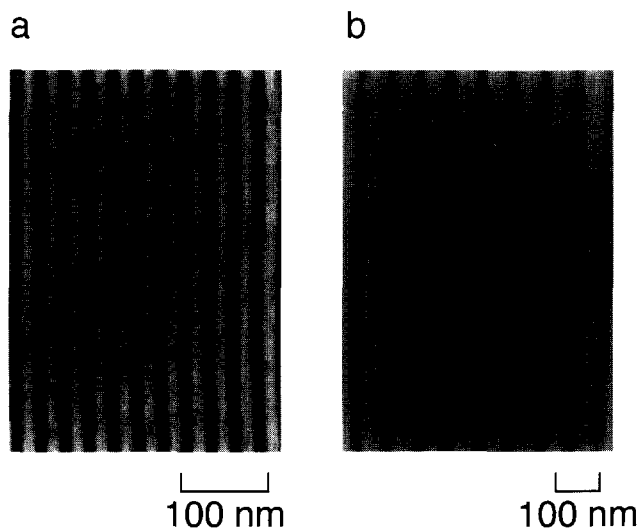| Sample code	$M_n \times 10^{-4}$ S	P	Graft	M_w/M_n	ϕ_s
SPP-6	2.52	1.12	4.94	1.02	0.55
SPP-3	5.35	2.49	9.52	1.03	0.58
SPP-5	9.25	2.54	14.2	1.05	0.67
SPP-4	9.25	5.65	20.6	1.04	0.45
SPP-9	17.5	2.70	23.0	1.02	0.78
SPP-8	17.5	6.90	28.3	1.02	0.58

Figure 2 Examples of TEM images of graft copolymers. Samples: (a) SPP-6; (b) SPP-9

worthwhile to study the microphase-separated structures of ABB graft copolymers focusing on this point.

Recently, the preparation methods and morphological features for two kinds of ABB graft copolymers were reported. One is styrene–isoprene–isoprene (SII) star molecules named 'miktoarm' polymers[13] and the other is styrene–2-vinylpyridine–2-vinylpyridine (SPP) star molecules[14]. However, no theoretical and experimental studies on the molecular weight dependence of microdomain spacing of graft copolymers have been reported so far.

The purpose of the present paper, therefore, is to examine the D–M relationship of these star molecules in comparison with those of AB diblock copolymers.

EXPERIMENTAL

The preparation and characterization methods were established and reported in previous papers[14,15]. Several procedures were improved to prepare samples with narrow molecular weight and composition distributions more effectively, and they will be reported elsewhere[16]. Six samples with different molecular weight and also different compositions were used in this work. Their molecular characteristics are listed in *Table 1*.

Film specimens for morphological observations were obtained by casting from dilute solutions of tetrahydrofuran, which is a common good solvent for the two constituent polymers, and the as-cast films were annealed at 150°C for one week. Microphase-separated structures were observed with a small-angle X-ray scattering (SAXS) apparatus and by transmission electron microscopy (TEM). Film specimens for TEM observations were stained with phosphotungstic acid (PTA). The details of these morphological observations were reported in previous papers[14,15].

RESULTS

Figure 2 shows microphase-separated structures of two samples. *Figure 2a* is a TEM image of the sample SPP-6, of which the volume fraction of polystyrene, ϕ_s, is 0.55, while *Figure 2b* is that of the sample SPP-9, whose ϕ_s is 0.78. The darker stripes correspond to poly(2-vinylpyridine) (P) phases while the brighter stripes correspond to polystyrene (S) phases, because the P phase can be stained with PTA preferentially. Apparently, both samples have alternating lamellar structures, though the relative thicknesses of P and S phases are different between *Figures 2a* and *2b* owing to the difference in composition between the samples.

SAXS diffraction patterns of six samples were compared in *Figure 3*. All the SAXS profiles have the integer-order diffraction peaks reflecting alternating lamellar structures, and the magnitude of the scattering vector q ($= 4\pi \sin\theta/\lambda$, where λ is the wavelength of the X-rays and 2θ is the scattering angle) of the first-order peaks decreases with increasing molecular weight of the samples from bottom to top as shown in this figure. Comparing all the patterns, however, we notice that several peaks are missing because of the particle scattering factors. They are the second- and the fourth-order peaks for SPP-4 whose ϕ_s is 0.45, the fifth-order one for SPP-8 whose ϕ_s is 0.58 and the third-order one for SPP-5 whose ϕ_s is 0.67. The reason for the disappearance of these diffraction peaks was briefly mentioned previously[5,16,17], but will be described in more detail in the Discussion section. The domain spacing, D, which expresses one repeating unit of a pair of lamellae was evaluated by using the Bragg condition:

$$D = 2\pi n/q_p \tag{2}$$

where n is the integer and q_ps are the magnitudes of wave vectors where the integer-order diffraction peaks appear. The D values thus obtained were double logarithmically plotted against the total molecular weight of the samples in *Figure 4*. The experimental data for styrene–2-vinylpyridine diblock copolymers are also plotted in this figure for comparison. *Figure 4* clearly shows that the domain spacing for SPP graft copolymers are
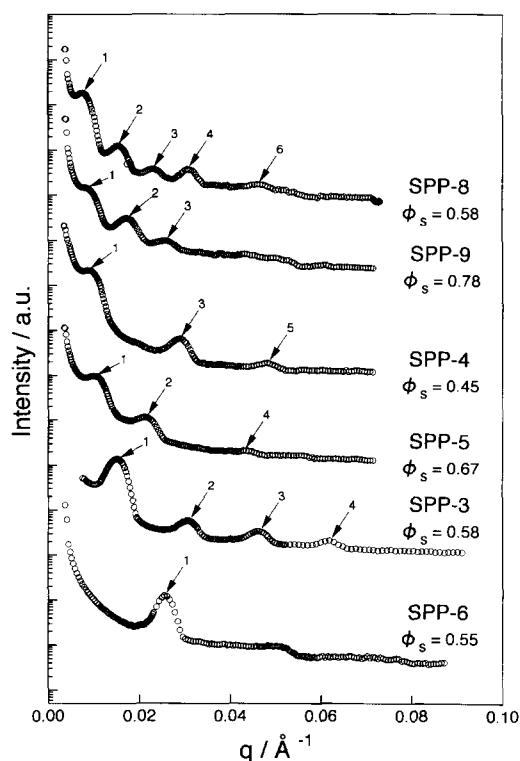
Figure 3 Comparison of SAXS diffraction patterns for samples with alternating lamellar structures
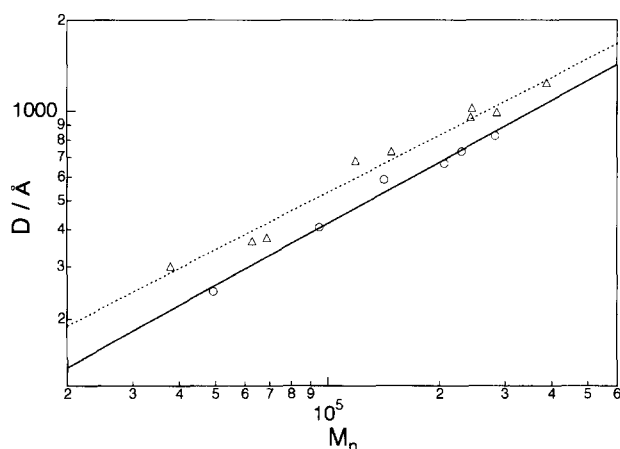

Figure 4 Domain spacing–molecular weight relationship of SPP graft copolymers in comparison with that of SP diblock copolymers. The circles represent SPP graft copolymers and the squares SP diblock copolymers. The dotted line is the observed D–M relationship for diblock copolymers determined in ref. 12, i.e. $D = 0.033_7 M^{0.64}$ (nm)

smaller than those for SP diblock copolymers beyond experimental errors. From this figure, moreover, we may conclude that the data for graft copolymers are well approximated by a straight line irrespective of the difference in composition of the samples. Thus, we have the following D–M relationship for the SPP graft copolymers:

$$D = 0.015_3 \, M^{0.69} \ (\text{nm}) \tag{3}$$

Equation (3) is expressed as a solid line in *Figure 4*. The exponent in equation (3), 0.69, is pretty close to the predicted value for diblock copolymers[6–8].
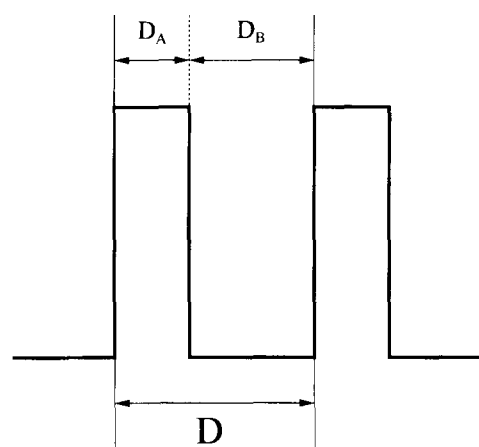

Figure 5 The most simplified square-wave model representing electron density profile for an alternating lamellar structure having a repeating period D with sub-thicknesses of D_A and D_B

DISCUSSION

It is very interesting that SPP graft copolymers with ϕ_s of 0.67 (SPP-5) and 0.78 (SPP-9) show alternating lamellar structure, while styrene–2-vinylpyridine (SP) diblock copolymers exhibit cylindrical structures at the same compositions. The reasons for the differences in microphase-separation structures between SP diblock copolymers and SPP graft copolymers at the same compositions were discussed briefly in a previous paper[14]. That is, the total chain dimensions of the backbone chains (P chains in the present samples) along the direction parallel to the lamellar interface could be larger than those of the linear block chains with the same molecular weight so that the interfaces tend to become convex toward the P domains to keep segment densities of each domain constant. They will be discussed in more detail elsewhere[16]. In this paper, therefore, we only discuss the reason for the disappearance of the specific peaks in SAXS diffraction patterns of SPP-5 ($\phi_s = 0.67$) and SPP-8 ($\phi_s = 0.58$) as well as the well known results for SPP-4 ($\phi_s = 0.45$), where the even number diffraction peaks are missing.

The Fourier transform of the form factors for the square wave with height L and period D $(= D_A + D_B)$ shown in *Figure 5* is expressed by

$$F(q) = (L/2)\sin(qD_A/2)/(qD_A/2) \tag{4}$$

where D_A and D_B are the thicknesses of components A and B. In equation (4), $F(q)$ vanishes if

$$qD_A/2 = m\pi \tag{5}$$

where m is the integer. Combining equations (2) and (5), we have the relationship:

$$nD_A = mD \qquad (m < n) \tag{6}$$

Equation (6) indicates the condition for disappearance of the nth-order diffraction peaks for alternating lamellar structures having domain spacing D and lamellar thickness of component A, D_A. Since the volume ratio is equal to the lamellar thickness ratio, the nth-order peaks disappear when $\phi_A = m/n$. In fact, the $\phi_A(\phi_s)$ values are 0.45 $(= 1/2)$, 0.58 $(= 3/5)$ and 0.67 $(= 2/3)$ for SPP-4, SPP-8 and SPP-5, respectively, and consequently the specific peaks corresponding to these ϕ_A disappear.
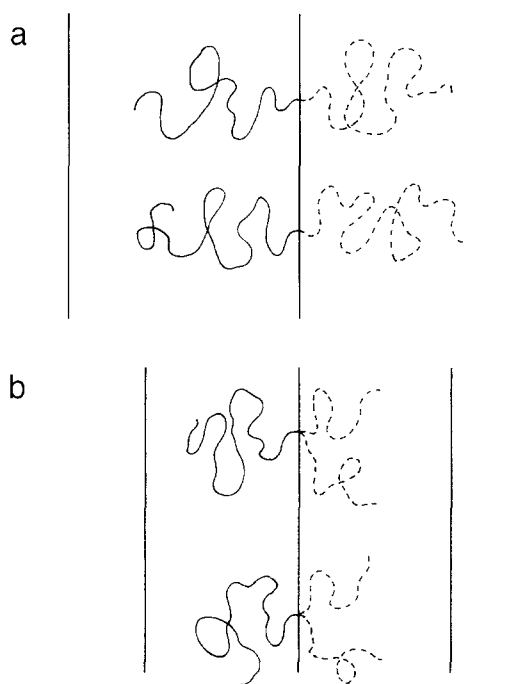
a

b

Figure 6 Schematic representations of chain conformations of (a) an AB diblock copolymer and (b) an ABB graft copolymer

Molecular conformations of SPP and SP chains are compared in *Figure 6* schematically. It can be seen from this figure that the domain spacings of SPP graft copolymers must be smaller than those of SP diblock copolymers with the same molecular weights and compositions because the P chains of SPP graft copolymers are divided into two arms.

Since there is no theoretical study on the domain sizes of graft copolymers in the strong segregation limit, we will extend the theory for block copolymers to graft copolymers to understand the difference quantitatively. Among the theories of microphase separation, the theory of Semenov is simple, but agrees well with the experimental data for diblock copolymers[7,12]. For simplicity, we assume that the statistical segment lengths and also the segment densities of polymer components are the same. These assumptions are almost valid for S and P pairs[12]. According to Semenov[7] the lamellar domain spacing of AB diblock copolymers is given by

$$D_{AB} = (4/6^{1/2})(3/\pi^2)^{1/3}\chi^{1/6}b\,N^{2/3} \qquad (7)$$

where χ is the Flory–Huggins interaction parameter, and b and N are the segment length and the total number of segments of block copolymers, respectively. Assuming that an ABB graft molecule can be divided into one A chain composed of N_A segments and two B chains composed of $N_B/2$ segments each and following the procedure in the theory of Semenov, we have the total free energy F for ABB graft copolymers to form the lamellar structures as

$$F = (1/D)\{(\pi^2/4b^2)[(d_A^3/N_A^2)$$
$$+ d_B^3/(N_B/2)^2] + (2b/6^{1/2})\chi^{1/2}\} \qquad (8)$$

where d_is are the half of the lamellar thickness of the i domain ($i = A$ or B). The first term of the right-hand side in equation (8) corresponds to the elastic energy of

polymer chains contracted and elongated in the microdomains while the second term expresses the surface energy. Since $N_A = \phi_A N$, $N_B = (1 - \phi_A)N$, $d_A = \phi_A D/2$ and $d_B = (1 - \phi_A)D/2$, equation (8) can be written as

$$F = (\pi^2/32b^2)(4 - 3\phi_A)D^2/N^2 + (2b/6^{1/2})\chi^{1/2}/D \qquad (9)$$

Minimizing the free energy with respect to D, we obtain the following equation for the lamellar domain spacing of ABB graft copolymers:

$$D_{ABB} = (4/6^{1/2})(3/\pi^2)^{1/3}(4 - 3\phi_A)^{-1/3}\chi^{1/6}b\,N^{2/3} \qquad (10)$$

It is clear from equation (10) that ABB graft copolymers have the same molecular weight dependence of D as AB diblock copolymers do, but that D_{ABB} weakly depends on ϕ_A, while D_{AB} is independent of ϕ_A. Comparing equations (7) and (10), the following relationship between D_{ABB} and D_{AB} is obtained:

$$D_{ABB} = (4 - 3\phi_A)^{-1/3}D_{AB} \qquad (11)$$

For example, the measured D_{SPP} for SPP-3, having $M = 95.2k$ and $\phi_s = 0.58$, is 40.7 nm, while the D_{AB} value for the SP diblock copolymer with M of 95.2 k is calculated to be 51.8 nm by using the experimental D–M relationship for SP diblock copolymers, i.e. $D = 0.033_7 M^{0.64}$ (nm)[12]. These values lead to the relationship $D_{SPP} = (40.7/51.8)D_{SP} = 0.78_6 D_{SP}$. On the other hand, if we introduce ϕ_A ($= \phi_s$) $= 0.58$ into equation (11), we have $D_{SPP} = 0.76_2 D_{SP}$, which agrees well with the observed value. Thus, the difference between the experimental domain spacings of SPP and SP block copolymers can be well explained by this theoretical consideration.

The average value of ϕ_s of the present six samples is 0.60 and consequently the average value of $(4 - 3\phi_s)^{-1/3}$ is 0.77. The ϕ_s value which most deviates from the average is 0.78 for SPP-9 and this leads to 0.84 for $(4 - 3\phi_s)^{-1/3}$. In the double logarithmic plots in *Figure 4*, this difference does not significantly affect the molecular weight dependence.

ACKNOWLEDGEMENTS

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