Macromolecules **1993**, *26*, 6346–6349

Localization of a Homopolymer Dissolved in a Lamellar Structure of a Block Copolymer Studied by Small-Angle Neutron Scattering

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Received April 6, 1993; Revised Manuscript Received August 23, 1993[⊛]

ABSTRACT: The localization of deuterated styrene homopolymer dissolved in a lamellar structure of a styrene–2-vinylpyridine diblock copolymer was studied in comparison with that of the end part of the block copolymer by observing diffraction from the styrene and 2-vinylpyridine microdomains of deuterated styrene homopolymer/styrene–2-vinylpyridine diblock copolymer blends by small-angle neutron scattering (SANS). Even when the average scattering lengths of both domains were equal, that is, "phase contrast matching" was theoretically achieved, diffraction was definitely observed. From the diffraction profiles in SANS and the dependence of domain spacing on the volume fraction of the styrene homopolymer, it was found that the homopolymers are isolated in the middle of the polystyrene domain, though they are concentrated less than the end parts of the block chains.

Introduction

The microphase-separated structures of AB diblock copolymers have been well studied so that the variation of morphology with the composition,[1–3] the molecular weight dependence of domain sizes,[4–7] and the chain conformation of block polymers in the microdomains[8–12] are elucidated. To understand the microphase-separated structures of block copolymers in more detail at the molecular level, it is worthwhile to study the microdomains formed by block copolymer/homopolymer blends. In this subject, theoretical studies[13,14] on the phase diagram of homopolymer/block copolymer blends, and experimental studies on the molecular weight effects of homopolymer on the order–disorder transition,[15] the solubilization of low molecular weight homopolymers[16] and the chain dimension of homopolymer in microdomains[17,18] have been reported so far. Although these works imply that A homopolymers do not always mix uniformly in the A microdomain of AB diblock copolymers, direct evidence for the localization of homopolymers in microdomains has not been presented.

If the average scattering lengths of A and B domains of diblock copolymer could be equal by randomly distributing the deuterated A polymer segments in A domains, "phase contrast matching" could be achieved in small-angle neutron scattering (SANS).[19–24] In that case, the diffraction from the lamellar domains would disappear[12,22,23] even for the edge view where the primary beam is incident along the direction parallel to lamellae as shown in Figure 1. Conversely, we can study the localization of polymer segments in lamellae by measuring the diffraction from the edge view by SANS when the deuterated polymer segments are mixed. Recently, we studied the localization of deuterated ends of block polymer in lamellae by this method and found that the free ends of a block polymer are located in the middle of the lamellae.[24]

In this work, we studied the localization of homopolymer dissolved in the lamellar structure of block copolymer when the deuterated homopolymers are mixed in comparison with that of the end part of a block polymer by measuring diffraction at the edge view by SANS.

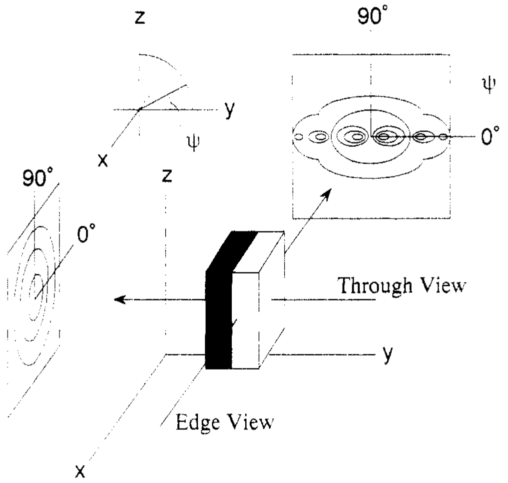

Figure 1. Schematic representation of the geometrical relationship between the sample specimen and the two-dimensional position-sensitive detector.

Experimental Section

Samples used are poly(styrene-d_8) (TUN-01), styrene-h_8–2-vinylpyridine diblock copolymer (SP-15), and styrene-d_8–styrene-h_8–2-vinylpyridine triblock copolymers (DSP-1). These three polymers were synthesized by two different methods. TUN-01 was polymerized with *sec*-butyllithium as an initiator in benzene,[25] while SP-15 and DSP-1 were prepared with cumylpotassium in tetrahydrofuran (THF).[26] Their molecular characteristics are listed in Table I. The volume fractions of a polystyrene block of SP-15 and DSP-1 are designed to be 0.5 so as to give lamellar structures in bulk. Film specimens for TUN-01/SP-15 and DSP-1/SP-15 blends called DHL and ELB, respectively, were obtained by solvent-casting from dilute solutions of THF which is a common good solvent for the two polymer species. As-cast films were dried in a vacuum oven at room temperature for several days and then annealed at 120 °C for 10 days under vacuum. Five film specimens of DHL and ELB blends with different mixing ratios and a film specimen of pure SP-15 were prepared. The mixing ratios of the blends are shown in Tables II and III.

Transmission electron micrographs show that all the film specimens have alternating lamellar structures whose lamellae

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[⊛] Abstract published in *Advance ACS Abstracts*, October 15, 1993.

0024-9297/93/2226-6346$04.00/0

Table I. Molecular Characteristics of Samples

	$M_n \times 10^{-3}$				
sample code	D	S	P	M_w/M_n	ϕ_S[a]
TUN-01	27			1.05	
SP-15		119	124	1.06	0.50
DSP-1	31	97	106	1.04	0.50

[a] Volume fraction of a polystyrene block determined by elemental analysis.

Table II. Characteristics of TUN-01/SP-15 Blends

blend code	ω_H[a]	x[b]
DHL-1	0.0419	0.078
DHL-2	0.0558	0.103
DHL-3	0.0696	0.127
DHL-4	0.0913	0.163
DHL-5	0.1150	0.201

[a] Weight fraction of deuterated homopolymer (TUN-01) in the blends. [b] Volume fraction of deuterated homopolymer (TUN-01) in the polystyrene domain.

Table III. Characteristics of DSP-1/SP-15 Blends

blend code	ω_L[a]	x[b]
ELB-1	0.326	0.069
ELB-2	0.379	0.080
ELB-3	0.430	0.092
ELB-4	0.483	0.103
ELB-5	0.529	0.112

[a] Weight fraction of end-labeled block copolymer (DSP-1) in the blends. [b] Volume fraction of the deuterated segment in the polystyrene domain.

are predominantly aligned parallel to the film surface. The small-angle X-ray scattering (SAXS) measurements were performed at room temperature with a Kratky U-slit camera of Anton Paar Co., equipped with a step scanner and a scintillation counter. [Disclaimer: Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST nor does it imply necessarily the best available for the purpose.] The widths of entrance slits and counterslits were 60 and 150 μm, respectively. The measured intensities were corrected to give desmeared data by Strobl's method.[27] The SANS instrument used was the 8-m SANS spectrometer at the National Institute of Standards and Technology with a two-dimensional position-sensitive detector. The distance from sample to detector was 3.5 m, and the wavelength of the incident beam was 0.6 nm. Both SAXS and SANS were measured using the edge view. Details of the scattering measurements were described previously.[23,28]

Results

SAXS and SANS profiles are compared for SP-15 and DHL-1 in Figures 2 and 3, respectively. In these figures SANS intensities were evaluated by averaging the data in the sector around $\Psi = 0 \pm 5°$ at the edge view, where Ψ is the azimuthal angle on the detector as shown in Figure 1. The odd-order peaks only appear for SP-15 in both SAXS and SANS as shown in Figure 2, indicating that the thicknesses of the polystyrene (S) and poly(2-vinylpyridine) (P) lamellae are equal. Figure 3 compares the SAXS and SANS diffraction profiles of DHL-1. This figure shows that the odd-order peaks only appear in the SAXS profile, while the distinct second-order peak is observed in addition to the first- and the third-order peaks in the SANS profile. The distinct second-order peak still exists for DHL-2, where the volume fraction of deuterated polystyrene is 0.103, even though this volume fraction corresponds to the condition of the phase contrast matching where the average scattering lengths of a P lamella and an S lamella containing styrene-d_8 homopolymer are equal. The same phenomena were observed for ELB blends, as shown in Figure 2 of a previous paper.[24] Thus, the appearance of the second-order peaks in SANS profiles can be interpreted by the scattering length profiles which involve the localization of a homopolymer chain in the middle of S lamellae like the end part of a polystyrene block as reported previously,[24] despite the molecular weight of the styrene homopolymer being lower than that of the polystyrene block of diblock copolymer.

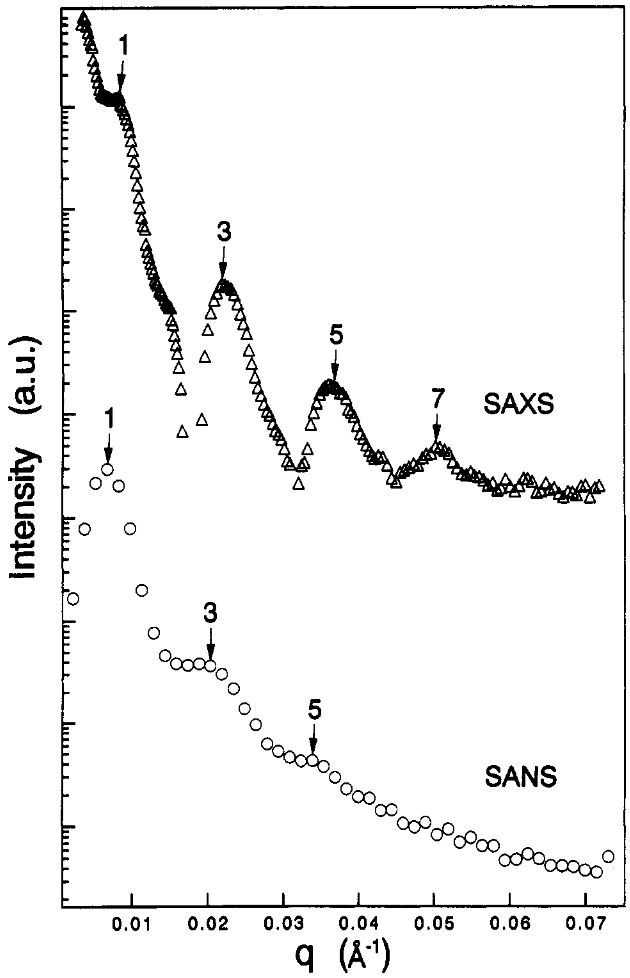

Figure 2. Comparison between SAXS and SANS data in the edge view for sample SP-15.

From the diffraction peaks in SAXS profiles, we evaluated the domain spacings, D, of DHL blends of SP-15, which were plotted against the volume fraction, x, of the deuterated styrene homopolymer in the S domain in Figure 4. From this figure, it is clear that D increases monotonically with increasing x.

Discussion

The contrast factor, R, for diffraction from S and P domains in SANS is given by[20,23]

$$R = \frac{[\beta_P - x\beta_{SD} - (1-x)\beta_{SH}]^2}{(\beta_P - \beta_{SH})^2} \qquad (1)$$

where β_{SH}, β_{SD}, and β_P denote the coherent scattering length densities of hydrogenated polystyrene, deuterated polystyrene, and poly(2-vinylpyridine), respectively, and x is the volume fraction of the deuterated segment in the S domain. The solid curve in Figure 5 was evaluated by using 6.47, 1.41, and 1.95 × 10¹⁰ cm⁻² for β_{SD}, β_{SH}, and β_P in eq 1. The data points in the figure were obtained from

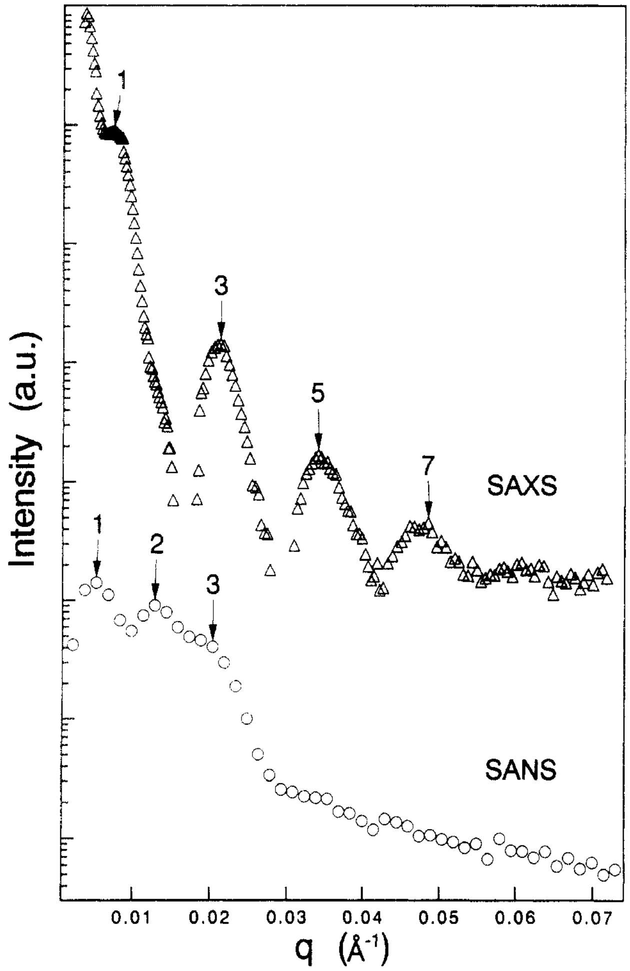

Figure 3. Comparison between SAXS and SANS data in the edge view for sample DHL-1.

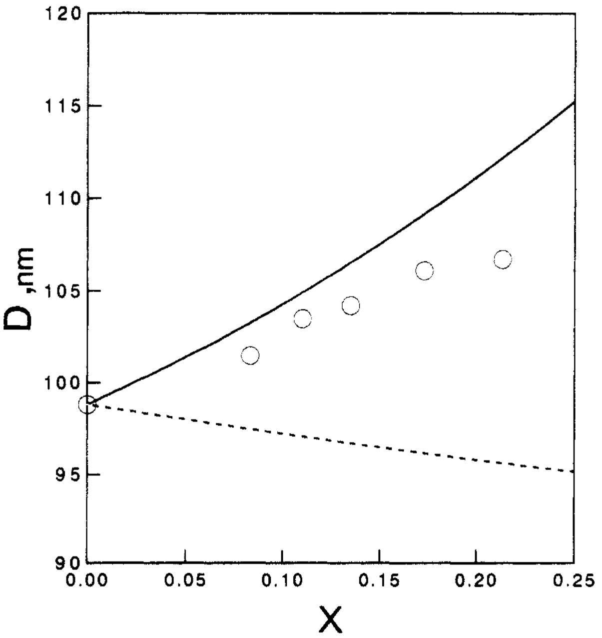

Figure 4. Domain spacings of blend samples as a function of volume fraction x of deuterated homopolymer in an S domain. The solid line is obtained from eq 3, while the dotted line is obtained from eq 4.

the edge view diffraction intensities by using[23]

$$\mathrm{Re} = \frac{[I_0(2) - I_{90}(2)]_x}{[I_0(2) - I_{90}(2)]_0} \qquad (2)$$

where $I_0(2)$ and $I_{90}(2)$ are the diffraction intensities of the

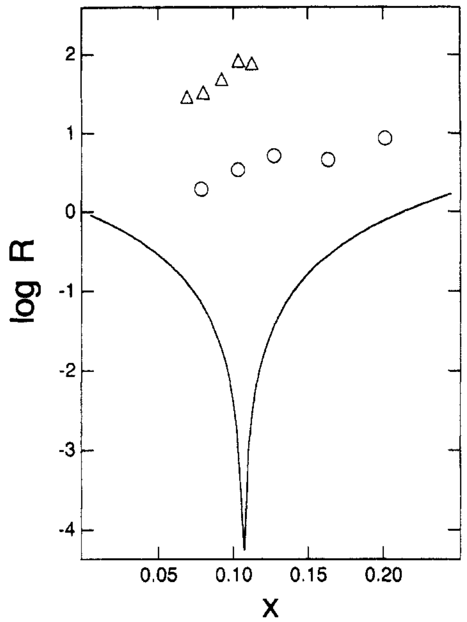

Figure 5. Variation of contrast factor R as a function of x for DHL (○) and ELB (△) blends. The solid line is obtained from eq 1.

second-order peak at the azimuthal angles 0° and 90° on the detector. The subscripts x and 0 refer to the blend sample with the volume fraction x of deuterated homopolymer in the S phase and pure ordinary block copolymer, *i.e.*, SP-15, respectively. Strictly speaking, we should use the data of the blends from ordinary homopolymer and ordinary block copolymer for the denominator in eq 2; however, the data of pure block copolymer was used in this study because the difference in domain spacings between blends and SP-15 is not so large. Since the first-order peaks at the low q values (0.006 $Å^{-1}$) may be affected by the primary beam, the second-order peaks, which are representing the characteristics of the present samples, were used to evaluate the magnitude of the contrast. Moreover, the intensities at 0° and 90° were obtained by averaging the data in the sectors of ±5° around 0° and 90°. As shown in Figure 5, all the data are far above the calculated curve, and R increase with increasing x. Furthermore, the data of DHL are lower than those of ELB. This implies that the homopolymer is located in the middle of lamella, but it is concentrated less than the ends of the block polymer.

Assuming that the styrene homopolymers are dissolved in a S domain but are completely isolated in the middle of the domain so that the chain conformation of block polymers and the distance between neighboring junction points are not changed from that of pure diblock copolymer, the increment of domain thickness of an S lamella should be $D_0x/2(1-x)$, while that of a P lamella is constant. Consequently, we have the following equation for the lamellar domain spacing, D, as a function of x.

$$D = D_0(2-x)/2(1-x) \qquad (3)$$

where D_0 is the domain spacing of pure block copolymer. The solid line in Figure 4 denotes the theoretical curve calculated from eq 3 by using the experimental value of SP-15 for D_0.

On the other hand, assuming that styrene homopolymers are uniformly mixed in the S domain so that the S domain is extended uniformly but the P domain is contracted as the result of increase of distances between junction points so as to keep the segment density constant, we have

$$D_S = D_0/2(1-x)^{1/3} \qquad (4)$$

$$D_P = D_0(1-x)^{2/3}/2 \tag{5}$$

$$D = D_S + D_P = D_0(2-x)/2(1-x)^{1/3} \tag{6}$$

where D_S and D_P denote the domain thicknesses of S and P lamellae. The dotted line in the figure expresses the theoretical curve calculated from eq 6. Comparing the data points with the calculated curves, we found that the observed domain spacings increase with increasing x and that they are closer to the solid line than the dotted line, though they are always between the two curves.

In summary, from the diffraction profiles in SANS and the dependence of domain spacing on the volume fraction of the styrene homopolymer dissolved in a polystyrene domain, we conclude that the styrene homopolymers are mostly isolated in the middle of the polystyrene domain, though they are concentrated less than the ends of the block polymers.

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.

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