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SANS and SAXS Studies on Molecular Conformation of a Block Polymer in Microdomain Space. 2. Contrast Matching Technique[†]

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ABSTRACT: We critically tested the contrast matching technique in the small-angle neutron scattering from block polymers to study the molecular conformation of a block polymer chain in microdomain space. It was found that the blending of deuteriated and undeuteriated block polymers with a composition to produce zero contrast ("contrast matching") does not always result in true contrast matching even in the case of the two block polymers mixed at a molecular level in the microdomain space. The true matching is expected to occur only in the case when the deuteriated block polymers overlap each other in the domain space to produce uniform segmental density of their own at the given composition, giving rise to the zero contrast between each microdomain. However, even in the event of incomplete contrast matching, the suppression of the domain scattering by 2 orders of magnitude was attained, which enabled us to measure the component of the radius of gyration of the block polymer chain parallel to the interface with much better accuracy than the previous work without the contrast matching. The component was again found to be 70% of the component for the unperturbed chain.

I. Introduction

In a previous paper[1] we reported an analysis of the molecular conformation of a block polymer chain in a microphase-separated domain space by small-angle neutron scattering (SANS) with a deuterium labeling technique;[1-7] i.e., A polymer chains of an AB diblock polymer were labeled with deuterium, and the labeled block polymer was mixed with an unlabeled AB diblock polymer having the same degree of polymerization and the same composition in order to study the molecular conformation of an A block chain in the A domain space. Assuming (i) identical degree of polymerization for labeled and unlabeled block polymers, (ii) homogeneous mixing of labeled and unlabeled block polymer chains in the microdomain space, and (iii) no volume change on the mixing of the two block polymers, the SANS intensity from the mixture is given by

$$I(q) = \phi_D(1-\phi_D)(a_H - a_D)^2\phi_A P(q) + [a_H(1-\phi_D)/V_A + a_D\phi_D/V_A - a_B/V_B]^2 S(q) + I_{in} \quad (1)$$

where ϕ_D is the volume fraction of the deuterium-labeled polymer chain in the A microdomain, a_H and a_D are the scattering length of the protonated and deuteriated A monomer unit, respectively, $P(q)$ is the molecular scattering function of the A block chains, $S(q)$ is the scattering function from the microdomain structure, ϕ_A is the volume fraction of the A microdomain, and I_{in} is the net incoherent intensity. Thus the coherent intensity from the mixture is given by simple addition of the *domain scattering* and the *molecular scattering* from which the radius of gyration of the block polymer chain is obtained.

The conformation analysis of a block polymer chain in domain space is an interesting problem from the viewpoint of statistical mechanics of *confined chains*, i.e., random walk chains confined in a certain domain space with one end at the interface, while satisfying the uniform space-filling requirement with their segments. The chain in the domain space was found to be expanded along the direction perpendicular to the interface, and its dimension along this direction was found to control the domain size.[8-13] All

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the theories of the microdomain of the block polymer[8,9,12–14] assume no *lateral perturbations*; i.e., the block polymer chains in the domain space are unperturbed in the lateral direction. The hypothesis should be critically tested, and the SANS technique is the most powerful technique for this purpose.

In the previous study[1] the solvent-cast films of the polystyrene–polyisoprene diblock polymers (polystyrene chain being labeled) had a lamellar morphology. The lamellar microdomains were aligned extremely well with their interfaces parallel to the film surfaces. Therefore, it was possible to measure separately the components of radius of gyration of the block polymer chain parallel and perpendicular to the lamellar interface. The relationship between the perfectly aligned lamellar microdomains and the corresponding SANS patterns was schematically illustrated in Figure 8 of ref 1. When the neutron beam is irradiated perpendicular to the lamellar interfaces ("through radiation"), only the molecular scattering from deuterated polystyrene block chains causes the coherent scattering. On the other hand, when the neutron beam is irradiated parallel to the lamellar interfaces ("edge radiation"), along the direction normal to the lamellar interfaces, i.e., for the observations at $\Phi = 90°$ (Φ is the azimuthal angle defined in Figure 8 of ref 1), the sharp diffraction spots by the lamellar microdomain structure (domain scattering) superimpose on the molecular scattering. When the observations were made under the edge radiation and along the direction parallel to the interface, i.e., for the observations at $\Phi = 0°$, the coherent scattering arises only from the molecular scattering. In the solvent-cast films a small fraction of lamellar microdomains are misaligned, and some of them have their interfaces perpendicular to the film surfaces. Therefore the domain scattering from the misaligned lamellae superposed on the molecular scattering even for the through radiation. The intensity of the domain scattering from the misaligned lamellae was on the same order of the magnitude as that of the molecular scattering.[1]

In order to extract the molecular scattering, the domain scattering as evaluated by the scattering from pure block polymer films had to be subtracted from the net coherent scattering from the mixture of deuteriated and undeuteriated block polymers. In the subtraction, information on the degree of lamellar orientation simultaneously determined by small-angle X-ray scattering (SAXS) on the same specimens as those used for SANS was utilized. Thus the component of the radius of gyration of the block polymer chains parallel to the lamellar interfaces was obtained from the SANS intensity distribution under the through radiation as well as the intensity distribution along the direction parallel to the film surface under edge radiation. However, deuterium labeling of polystyrene block chains enhances the domain scattering from the polystyrene–polyisoprene lamellae as can be predicted from the coefficient of $S(q)$ in eq 1. Because even the undeuteriated polystyrene has a larger scattering cross section for neutrons than polyisoprene, blending the deuteriated polystyrene–undeuteriated polyisoprene block polymer further enhances the contrast of the polystyrene domains relative to the polyisoprene domains. Consequently the intensity of the domain scattering observed along the direction normal to the film surface in the SANS under edge radiation was 2 orders of magnitude larger than that of the molecular scattering. Thus the accuracy of the value of the component of the radius of gyration of the block polymer chain perpendicular to the lamellar interface obtained by the subtraction of the domain scattering was very poor.[1] In order to suppress the strong domain scattering and to obtain the intensity of the molecular scattering with good accuracy, the contrast-matching technique was employed in this study.

The contrast-matching technique was first employed to the SANS study of the chain conformation in a microdomain space of block polymers by Bates et al.[7] They used mixtures of polystyrene–polybutadiene block polymers (SB series) and polystyrene–perdeuteriated polybutadiene block polymers (SB_d series). Since the scattering length per unit volume of polystyrene for neutrons is larger than that of polybutadiene but smaller than that of perdeuteriated polybutadiene, the average scattering length per unit volume of polybutadiene microdomain in a mixture of SB and SB_d can be adjusted to match that of the polystyrene microphase by choosing an appropriate mixing ratio, if a uniform mixing of undeuterated and perdeuteriated polybutadiene block chains in the microdomains is assumed. This assumption is reasonable according to our previous study[15] which proved uniform mixing of undeuterated and perdeuteriated polystyrene block chains in the microdomain space. In the case of such contrast matching, the contrast factor C of the domain scattering which is given by

$$C = [a_H(1 - \phi_D)/V_A + a_D\phi_D/V_A - a_B/V_B]^2 \qquad (2)$$

becomes zero and only the molecular scattering can be observed as the coherent scattering from the mixtures. Bates et al.[7] successfully cancelled out the scattering from spherical microdomains of polybutadiene by mixing 16% SB_d with SB. They found that the overall radius of gyration of the labeled block polymer chains at the equilibrium condition is equal to that of corresponding homopolymers, at least for the case where the two block polymers SB_d and SB are similar in terms of total molecular weight and fraction of polystyrene component, and concluded that the block polymer chain in the domain space is unperturbed. Although they obtained the overall radius of gyration of the block polymer chains, the evaluation of the components of the radius of gyration parallel and perpendicular to the interface was not performed because the average orientation of the block chains in spherical microdomains was random. Since the distribution of the segments for a block chain in the domain space is generally asymmetric, their experimental observation does not necessarily lead to their conclusions that the block polymer chain in domain space is unperturbed. If the chain expansion normal to the interface is counterbalanced by the chain contraction parallel to the interface, the overall radius of gyration of the block chain can be equal to that for the unperturbed chain. However, this does not mean at all that the block chain is physically unperturbed.

We used a mixture of an unlabeled polystyrene–polybutadiene block polymer and a polystyrene–perdeuteriated polybutadiene block polymer following the example of Bates et al.[7] In contrast to their work, we employed a lamellar morphology with a very high macroscopic orientation to obtain the components of the radius of gyration parallel and perpendicular to the interface and to estimate the *asymmetry in the spatial segmental distribution.* But we found that there was a fundamental problem in the contrast-matching technique (section III-2). If the concentration of the deuteriated polybutadiene block chains is not sufficiently large at the contrast-matching composition, in some cases the deuteriated segments cannot be distributed homogeneously in the microdomain space (incomplete contrast matching). This happens when the radius of gyration of the deuteriated polymer chains is limited and the deuteriated chains do not sufficiently

Table I
Sample Characterization

sample code	type of polymer	total mol wt (M_n) × 10^{-4}	M_w/M_n	HPS fraction wt %	HPS fraction mol %	HPS fraction vol %
TOKI-12	HPS-HPB	9.99	1.02	51.2	35.3	47.0
B-7	HPS-DPB	8.49	1.02	56.2	40.0	54.6
H-7	HPB	10.9[a]	1.34	0	0	0
H-9	DPB	4.94	1.07	0	0	0

[a] This molecular weight was measured by GPC (polystyrene equivalent). The others were measured by osmometry.

overlap each other. The inhomogeneity of the concentration of the deuteriated segments in the directions both parallel and perpendicular to the lamellar interfaces causes the domain scattering. Consequently, the component of the radius of gyration of the block polymer chain perpendicular to the lamellar interface could not be obtained even with the contrast-matching technique for our particular case. On the other hand, the domain scattering in the through radiation was suppressed by 2 order of magnitude with this contrast-matching technique. Therefore, the component of the radius of gyration of the block polymer chains parallel to the lamellar interface could be determined with much better accuracy than in our previous work[1] done by the subtraction technique (section III-2). Possible sources of the incomplete contrast matching will be discussed in section III-3.

II. Experimental Section

Deuteriated 1,3-butadiene monomer (D_6, 98%) was purchased from Cambridge Isotope Laboratory.[16] In addition to an ordinary amount of moisture this monomer contained a large amount of unknown impurities which violently react with n-butyllithium to form two kinds of precipitates. One is white and the other is black. Therefore, after drying the monomer with calcium hydride and degassing, these impurities had to be removed by reacting with a large quantity of n-butyllithium. One to seven milliliters of 2.4 N n-butyllithium solution in n-hexane was poured from an ampule into a vacuum vessel for the purification reaction and the n-hexane was removed by distillation before mixing the deuteriated butadiene monomer with the n-butyllithium. The purification process was repeated 7 times. After that the precipitates did not further form and the n-butyllithium remained reactive. A total of 7.3 mmol of n-butyllithium was used to purify 45 mL of the deuteriated butadiene monomer. Twenty milliliters of the monomer remained after the purification. A polystyrene–deuteriated polybutadiene block polymer (B-7) was synthesized by anionic polymerization at 30 °C under high vacuum with sec-butyllithium as the initiator and benzene as the solvent. Styrene monomer and the deuteriated butadiene monomer were sequentially added to the mixture of the solvent and the initiator. The unlabeled polystyrene–polybutadiene block polymer (TOKI-12) of matching composition and matching degree of polymerization with B-7 was synthesized by a large-scale anionic polymerization under argon atmosphere in a 100-L flask, and 2.2 kg of polymer was yielded. Otherwise the polymerization conditions of TOKI-12 were the same as those of B-7. The details are reported elsewhere.[17] An undeuteriated and a deuteriated polybutadiene homopolymer (H-7 and H-9, respectively) were also prepared by anionic polymerization with the same conditions as B-7 in order to determine the Kuhn statistical segment length for bulk polybutadiene with this particular microstructure.

The number-averaged molecular weights determined by high-speed membrane osmometry were 9.99 × 10^4 (M_w/M_n = 1.02 by GPC) for TOKI-12, 8.49 × 10^4 (M_w/M_n = 1.02) for B-7, and 4.94 × 10^4 (M_w/M_n = 1.07) for H-9. The number-averaged molecular weight (polystyrene equivalent) of H-7 assessed by GPC was 1.09 × 10^5 (M_w/M_n = 1.34). The compositions of the block polymers were obtained from the ratios of the molecular weights of the polystyrene precursors and the block polymers. The weight fractions of the polystyrene components were 0.512 for TOKI-12 and 0.562 for B-7. These numbers are listed in Table I.

Table II
TOKI-12/B-7 Blend Composition

sample	blending ratio, wt % TOKI-12	blending ratio, wt % B-7	X^a
1	81.5	18.5	0.155
2	80.7	19.3	0.162
3	79.9	20.1	0.169

[a] Mole fraction of deuteriated species in monomeric units in polybutadiene microdomains. At the contrast matching composition X is 0.165.

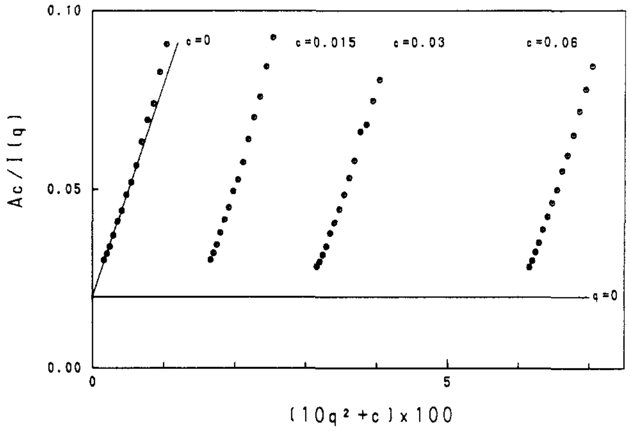

Figure 1. Zimm plot for small-angle neutron scattering of H-7/H-9 (protonated and deuteriated polybutadiene blends).

The films used for the SANS measurements were prepared by casting 10% solutions of these polymers and polymer mixtures in toluene. In addition to the films of pure TOKI-12 and pure B-7, the films of TOKI-12/B-7 mixtures were prepared in several compositions which were all in the vicinity of the contrast-matching composition but slightly different from each other. The purpose of this is to obtain specimens truly close to the contrast-matching composition. Because there might be an experimental error in the determination of the copolymer compositions, the calculated contrast-matching composition may not be necessarily equal to the true contrast-matching composition. SANS intensity profiles of all the mixture films were examined first with short exposure time, and three of the mixtures closest to the contrast matching composition (TOKI-12/B-7 blends no. 1, 2, and 3) were chosen. SANS measurements were done for the films of these three mixtures (listed in Table II) and the two pure block polymer films.

SANS measurements were performed by using the NBS small-angle neutron scattering instrument[18,19] with a two-dimensional position-sensitive detector (65 × 65 cm^2; 5-mm electronic resolution). The experimental conditions are the same as those previously reported[1] except for the collimation. A 12-aperture focusing configuration was used for the block polymer measurement and a four-aperture iris configuration was used for homopolymer measurement. An wavelength of 6.0 Å was used for all the measurements.

III. Results and Discussion

1. Determination of Statistical Segment Length for Polybutadiene. Kuhn statistical segment length (b) of polybutadiene in bulk was evaluated from the SANS data of H-7 (undeuteriated polybutadiene)/H-9 (deuteriated polybutadiene) blends. SANS intensity data were obtained for the blends with 1.5, 3.0, and 6.0 wt % H-9 in H-7. A Zimm plot is shown in Figure 1. The radius of gyration evaluated from the slope of the straight line obtained by extraporating to zero concentration of H-9 (c = 0) was 94.4 Å and, therefore, the Kuhn statistical segment length was 7.55 Å.[20] This value was used to calculate the component of the radius of gyration ($R_{gx,0}$) of the unperturbed deuteriated polybutadiene chain corresponding to the deu-

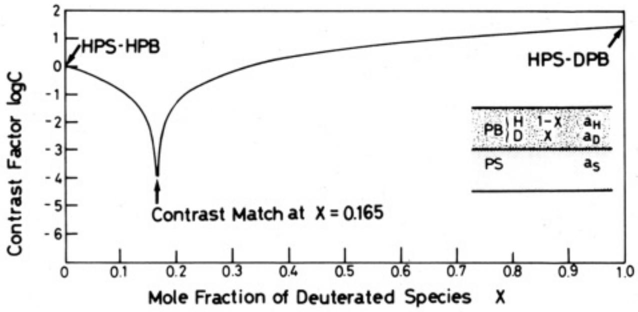

Figure 2. Dependence of calculated neutron contrast factor (C) on mole fraction (X) of deuteriated butadiene segments in microdomain space for the mixture of an unlabeled polystyrene–polybutadiene block polymer and a polystyrene–deuteriated (98% D) polybutadiene block polymer.

teriated polybutadiene block chain in B-7 ($R_{gx,0}$ = 44.3 Å).

It should be noted that the isotope effects on the measurements of the single-chain conformation have been reported to be very significant in several systems (e.g., segregation effects of the labeled chain during crystallization,[24] a change of the cloud-point curve by deuteriation of one of the components in polymer blends,[25] UCST behavior in isotope blends,[26,27] and so on). In case of protonated polystyrene–polyisoprene block polymer/deuteriated polystyrene–polyisoprene block polymer blends, homogeneous mixing of deuteriated and protonated segments in microdomain space was proved.[1,15] It was also shown that the interaction parameter between protonated and deuteriated polystyrenes was so small that phase separation of the blends of these isotopically labeled polymers did not occur under common experimental conditions,[28] although there is a controversy on this subject.[29] In contrast, the possibility of the phase separation between H-7 and H-9 should be carefully examined, since Bates et al.[26,27] reported that blends of protonated 1,4-polybutadiene ($M_n = 2.5 \times 10^5$) and perdeuteriated 1,4-polybutadiene ($M_n = 2.1 \times 10^5$) had a UCST phase diagram and were phase separated at room temperature due to isotope effects. However, Bates et al.[26,27] also reported that no phase separation was observed for the blends of protonated 1,4-polybutadiene ($M_n = 4.9 \times 10^4$) and perdeuteriated 1,4-polybutadiene ($M_n = 2.5 \times 10^5$) at room temperature. Therefore, the phase separation due to isotope effect can be ruled out for H-7/H-9 blends, because their molecular weights are small enough to form miscible blends at room temperature. In addition, the concentrations of H-9 used for the SANS measurements were very low (≤6.0%), which also makes phase separation less probable. In fact, the radius of gyration of H-9 determined from the SANS analysis was reasonable for a single chain of $M_n = 4.94 \times 10^4$. If H-9 chains had segregated, the radius of gyration would have been much larger.

2. Analysis on Contrast Matching and Conformational Studies. Contrast factor C for the mixtures of B-7 and TOKI-12 was calculated by using eq 2 and log C was plotted against the mole fraction (X) of the deuteriated species in the monomeric unit in Figure 2. X is essentially the same as the volume fraction ϕ_D, assuming no difference between the molar volumes of deuteriated and undeuteriated monomeric units. The values of the scattering length per monomeric unit used in the calculation were 6.537×10^{-12} cm for deuteriated (98% D) polybutadiene (a_D), 0.416×10^{-12} cm for protonated polybutadiene (a_H), and 2.328×10^{-12} cm for protonated polystyrene (a_S) based on the reported coherent scattering lengths[30] for the D atom (0.667×10^{-12} cm), the H atom (-0.374×10^{-12} cm), and the C atom (0.665×10^{-12} cm). The densities of protonated polystyrene and protonated polybutadiene used in the calculation were 1.052[31] and 0.89[22], respectively. According to the results in Figure 2, the contrast match should occur at $X = 0.165$ where contrast factor C becomes zero. The calculated result also suggests that the intensity of the domain scattering of the mixture becomes less than $^{1}/_{1000}$ of that of the pure unlabeled block polymer (TOKI-12) when $0.160 < X < 0.171$. The domain scattering from such a mixture is considered to be negligibly small compared with the molecular scattering. According to Table II, TOKI-12/B-7 blends no. 2 and 3 are in this composition range (X = 0.162 and 0.169, respectively), and the contrast-matching composition is located between these two.

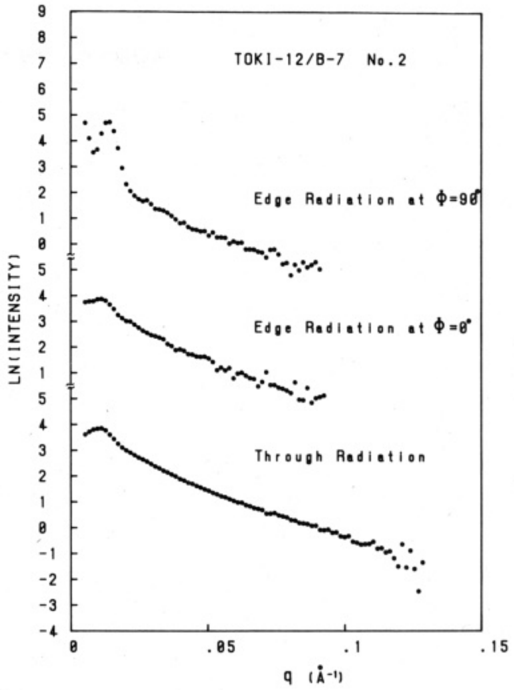

Figure 3. Small-angle neutron scattering profiles (net coherent scattering) from TOKI-12/B-7 blend no. 2 for edge radiation at Φ = 90° and Φ = 0° and through radiation.

Figure 3 shows the SANS profiles from TOKI-12/B-7 blend no. 2, the mixture closest to the contrast-matching composition. This mixture gave the SANS profiles least affected by the domain scattering, suggesting that the determination of the copolymer composition was accurate. Two-dimensional intensity data were either circular averaged or sector averaged to obtain the scattering intensity distribution curves. For the edge radiation the neutron counts were averaged in sectors of ±5° width in two azimuthal angle directions, Φ = 90° denoting the direction normal to the film surface (or lamellar interface) and Φ = 0° denoting the direction parallel to the film surface. For the through radiation the neutron counts were circular averaged. According to the calculation of the contrast factor, the strong domain scattering should not be observed. However, the profile for the edge radiation at Φ = 90° shows a sharp peak caused by the strong domain scattering. Weak peaks of domain scattering are also observed in the profiles for the edge radiation at Φ = 0° and the through radiation. These observations suggests that the contrast matching could not be achieved as expected from the composition analysis based upon eq 2. Although the intensity is shown in relative scale in Figure 3, the intensities of different profiles can be compared to each other. It should be noted that the peak intensity for the edge radiation at Φ = 90° is considerably higher than that for the edge radiation at Φ = 0° and that for the through

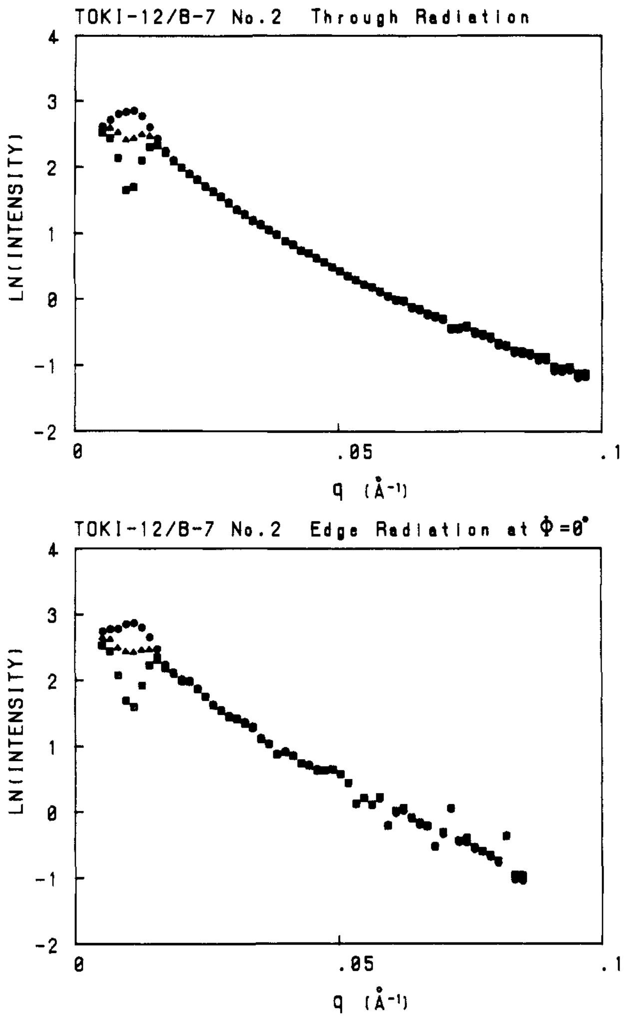

Figure 4. Small-angle neutron scattering profiles of TOKI-12/B-7 blend no. 2 for (top) through radiation and (bottom) edge radiation at Φ = 0°. Net coherent scattering (circles) and scattering after subtraction of domain scattering by eq 3 (triangles) and eq 4 (squares).

radiation. The profiles and the peak intensities of the latter two seem to be the same. In order to obtain the molecular scattering function $P(q)$ from such data, it is necessary to subtract the domain scattering intensity from the net coherent scattering intensity as performed in our previous work with HSI/DSI (unlabeled polystyrene–polyisoprene block polymer/deuteriated polystyrene–undeuteriated polyisoprene block polymer) system.[1] In contrast with the HSI/DSI system there is no theoretical basis for subtraction in the case of TOKI-12/B-7 blends because no significant domain scattering should appear in principle for the blend with the contrast-matching composition. Nevertheless, we tried the subtraction of domain scattering from the net coherent scattering. The subtraction was empirically performed by two methods using either of the following equations:

$$P(q) \sim I_S(q) = I_{net}(q) - KI_{TOKI\text{-}12}(q) \qquad (3)$$

$$P(q) \sim I_S(q) = I_{net}(q) - K[\phi_{TOKI\text{-}12}I_{TOKI\text{-}12}(q) + \phi_{B\text{-}7}I_{B\text{-}7}(q)] \qquad (4)$$

where $I_S(q)$ is the intensity related to molecular scattering, $I_{net}(q)$ is the net coherent scattering intensity. $I_{TOKI\text{-}12}(q)$ and $I_{B\text{-}7}(q)$ are the coherent scattering from the polymer films of TOKI-12 and B-7, respectively, and correspond to the domain scattering intensity. $\phi_{TOKI\text{-}12}$ and $\phi_{B\text{-}7}$ are the volume fraction of TOKI-12 and B-7 in the blend, and K is a constant which is used as an adjustable parameter.

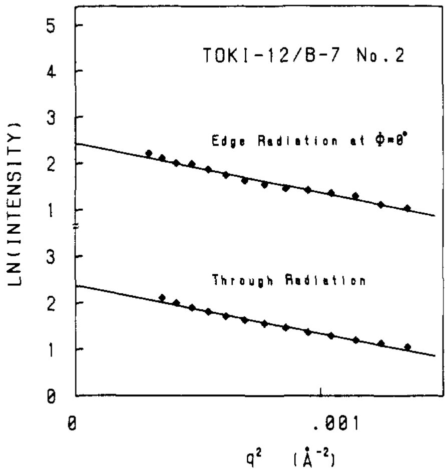

Figure 5. Guinier plot for TOKI-12/B-7 blend no. 2 for edge radiation at Φ = 0° and through radiation.

Equation 3 assumes no change of domain structure in TOKI-12, B-7, and the blend, while eq 4 takes care of the minor correction for the slight difference of the domain structure between TOKI-12 and B-7. The results are shown in Figure 4 for the through radiation and the edge radiation at Φ = 0° of TOKI-12/B-7 blend no. 2. The data points marked by circles, triangles, and squares designate, respectively, the net coherent scattering intensity, the intensity corrected by using eq 3, and that by using eq 4. Regardless of the subtraction methods, the subtraction of the domain scattering does not change the scattering intensity at all q's except for the small q region where the first-order peak of the domain scattering exists, even when the K value is overestimated, i.e., the scattering curve shows a dent at the q region where there used to be the peak. This suggests that the domain scattering intensity under the through radiation and the edge radiation at Φ = 0° for the blend with the contrast matching composition is negligibly small compared with the molecular scattering intensity except for the small q region near the first-order peak. Thus the radius of gyration of the block polymer chain can be analyzed with very good accuracy from the net coherent scattering curves for the through radiation and the edge radiation at Φ = 0° by using portions of the scattering profiles unaffected by the subtraction methods, i.e., if the data near the first-order peak of the domain scattering are omitted.

The Guinier approximation[32] is the only way to analyze the molecular scattering from the oriented block chains with no spherically symmetric segmental distribution.[33] The relation between the scattered intensity distribution at Φ = 0° and the corresponding component of the radius of gyration of the block chain R_{gx} is given by

$$P(q) \sim \exp(-q^2R_{gx}^2) \qquad (5)$$

Figure 5 shows the Guinier plots for the edge radiation at Φ = 0° and the through radiation of TOKI-12/B-7 blend no. 2. The data points are plotted for the Guinier region ($qR_{gx} \leq 1.3$).[34] The data points at the peak region were omitted. Both data fall on straight lines with the same slope except for the first two points on the small q side which deviate upward from the straight line. These two points are considered to be affected by the tail of the domain scattering due to the misaligned lamellae and were omitted from the least-square fit. The value of $R_{gx,m}$, the component of radius of gyration parallel to the lamellar interface, evaluated from the slope was 32 Å. The ratio $R_{gx,m}/R_{gx,0}$ is 0.72. This result coincides very well with the previous results by us[1] and by Hadziioannou et al.[6] for the

Table III
Radius of Gyration of Block Polymer Chains in the Lamellar Domain Space

sample	(M_n) block × 10^{-4}	$R_{gx,m}$, Å	$R_{gx,0}$, Å	$R_{gx,m}/R_{gx,0}$	$R_{gz,m}$, Å	$R_{g,m}$, Å	$R_{g,0}$, Å	ref
B-7[a]	3.34	32	44.3	0.72				this work
DSI[b]	4.05	22	30.5[c]	0.72	36	48	52	1
SDI-7[b]	6.89	30.8	39.8[c]	0.77				6
SDI-12[b]	11.07	33.6	50.4[c]	0.67				6

[a] Deuterated polybutadiene chains of HPS–DPB block polymer. [b] Deuteriated polystyrene chains of DPS–HPI block polymer. [c] Calculated by using 6.8 Å for the Kuhn statistical segment length for unperturbed perdeuteriated polystyrene chains.

conformation of the deuterium-labeled polystyrene chain in the domain space as compared in Table III. Thus the following result was also confirmed for polybutadiene block chains: compared with the unperturbed homopolymer chains with the same molecular weight, block chains in the domain space take a squeezed conformation in the direction parallel to the interface, therefore the interpenetration of the neighboring block chains is considerably decreased from the case that one would expect for the unperturbed chain.[1] *The chains are contracted in the lateral direction* in the microdomain space. It should be added that even if the literature value[27] of the Kuhn statistical segment length of polybutadiene (b = 6.9 Å) is used to calculate $R_{gx,0}$, it does not change this conclusion at all ($R_{gx,m}/R_{gx,0}$ = 0.79 for b = 6.9 Å).

3. Conditions To Attain True Contrast Matching in Block Polymers. Next to be considered is why the contrast-matching technique could not eliminate domain scattering. There are two possible reasons for the incomplete contrast matching: (i) incomplete overlap of the segments of deuteriated block chains at the matched composition in spite of uniform mixing of deuteriated and undeuteriated polybutadiene block chains and (ii) segregation between the deuteriated and undeuteriated block chains within the microdomain space due to the isotope effect.

First, the former case is examined. Uniformity of the distribution of the deuterium-labeled segments in the plane along the lamellar interface is examined below. The average interfacial area per block chain, S, is given by the following equation:

$$S = 2\bar{v}\bar{M}/DN_A \qquad (6)$$

Here N_A is Avogadro's number, $\bar{v}$ is the average specific volume, $\bar{M}$ is the total number-averaged molecular weight, and D is the lamellar spacing of the block polymer. The values of $\bar{v}$, $\bar{M}$, and D obtained for TOKI-12/B-7 blend no. 2 were, respectively, 1.027×10^{24} Å^3/g, 9.74×10^4, and 438 Å, and these numbers were used in the calculation below. Then the average interfacial area per single block chain (S) is 759 Å^2 ($S^{1/2}$ = 27.5 Å). Therefore, for the blend with the contrast-matching composition (16.5 mol %D) the interfacial area occupied by a single deuteriated block chain is 4600 Å^2 (759 Å^2/0.165). In other words, this is the minimum area that has to be occupied by the segments of one deuteriated block chain in order to achieve overlaps of the deuteriated segments and hence to achieve uniform distribution of the deuteriated butadiene segments in the plane along the lamellar interface. This value heavily depends on the blend composition. It should be noted that the uniform distribution of the segments requires a substantial overlap and hence a wide area has to be covered with a single deuteriated chain. However, the cross-sectional area of a single deuteriated block chain estimated from the component of radius of gyration parallel to the interface ($R_{gx,m}$ = 32 Å) is only 3200 Å^2 ($\pi(R_{gx,m})^2$). This is only 70% of the area that should be covered by at least one deuteriated block chain for the distribution of the deuteriated segments without interstices. This situation is schematically illustrated in Figure 6. Figure 6 emphasizes the contrast mismatch in the lateral direction. However, the mismatch occurs also in the longitudinal direction, i.e., along the Z direction.

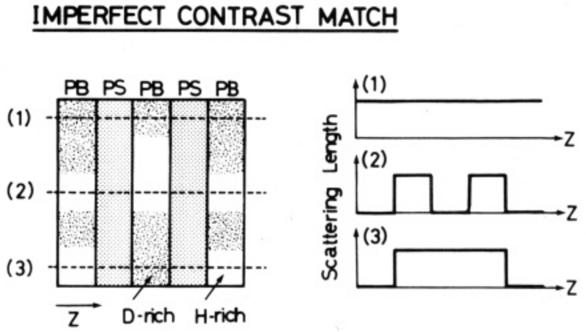

Figure 6. Schematic representation of imperfectly contrast-matched lamellar microdomains (left) and profiles of neutron scattering length along paths 1, 2, and 3 (right).

When the concentration of the deuteriated polybutadiene chains at the contrast-matching composition is not large enough, the fluctuation of the segmental density distribution of deuteriated segments in the polybutadiene microdomain becomes significant as shown in Figure 6. In other words, insufficient addition of deuteriated species creates deuterium-rich regions and hydrogen-rich region which becomes a new scattering source. For example, neutron scattering length along paths 1, 2, and 3 in Figure 6 gives different profiles as shown in the right side of the figure. Let us consider the scattering in the Z direction designated in Figure 6 when the neutron beam is irradiated from the normal to the paper.

The region like path 1, if it existed alone, does not cause any scattering due to the periodical microdomain structure since the contrast between PS and PB domains is matched. On the other hand, the regions like paths 2 and 3, if they existed alone, cause scattering due to the domain structure. Two effects are expected from this imperfectly contrast-matched structure. One effect is that the domain scattering observed will be much weaker than that of the pure block polymer systems because the contrast matching is attained in most of the sample. The other effect is that coexistence of the regions like path, 2 and 3 gives the same effect as the increase of the domain size distribution resulting in increase of Hosemann's g factor,[11,35] so that the higher order scattering maxima vanish. These two effects were examined below.

Figure 7 shows the net coherent scattering curves under the edge radiation at Φ = 90° for the three blends (Figure 7a, top) and the two pure block polymers (Figure 7b, bottom). These profiles correspond to the scattering intensity distribution in the Z direction in Figure 6. The scattering profiles of the TOKI-12/B-7 blends in Figure 7a all exhibit a single scattering maximum and no higher order peaks, while in the profiles of the pure block polymers, TOKI-12 and B-7 in Figure 7, bottom, at least the third-order peaks can be recognized. This result supports the model considered above.

Table IV
Comparison of SANS Peak Intensity and Peak Width of the First-Order Maximum for the Edge Radiation at $\Phi = 90°$

sample	peak intensity[a] I, au	ratio $I/I_{\mathrm{TOKI\text{-}12}}$	contrast factor[b] C	fwhm, Å^{-1}
B-7	2739245	7.23	26.09	0.0058
TOKI-12	378755	1.00	1.026	0.0058
TOKI-12/B-7 blend no. 1	57232	0.151	0.00412	0.0060
TOKI-12/B-7 blend no. 2	29755	0.0786	0.000456	0.0061
TOKI-12/B-7 blend no. 3	32709	0.0864	0.000461	0.0062

[a] Net coherent scattering intensity measured at $q = 0.0143$ Å^{-1} (the first-order peak position). [b] Calculated by eq 2.

The intensity measured at the first-order peak position ($q = 0.0143$ Å^{-1}) for the five curves in Figure 7 and the corresponding full width at half-maximum (fwhm) are listed in Table IV. According to the calculation of the contrast factor C, the domain scattering intensity from the blends is expected to become ca. $^{1}/_{1000}$ of that of pure TOKI-12. However, the peak intensity of the blends is only ca. $^{1}/_{10}$ of that of pure TOKI-12. Although the peak intensity is the sum of the domain scattering intensity and the molecular scattering intensity, the latter is considered to be much lower than the former. Therefore, it can be concluded that significantly high domain scattering intensity was observed for the blends with near contrast-matching composition but this domain scattering intensity is much lower than that of the pure block polymers. The peak widths at the first-order maximum are a little larger for the blends than the pure block polymers, suggesting the optical effect resulted from adding the deuterium-labeled chain, i.e., increase of the disordering in the periodicity of the scattering length. These results also support the model discussed above.

The possibility of segregation between the deuteriated and undeuteriated polybutadiene block chains can be also considered because of the incomplete contrast matching. Berney et al.[36] reexamined the SANS data obtained for the $\mathrm{SB_{d1}/SB_1}$ mixture by Bates et al.[7] and attributed the excess scattering to the clustering of the deuteriated chains. In our case this possibility can be ruled out. The most convincing experimental evidence which supports no clustering of the deuteriated polybutadiene chain is that $R_{\mathrm{gx,m}}$ of the deuteriated polybutadiene block chain from Guinier plot (32 Å) was much smaller than $R_{\mathrm{gx,0}}$ expected for the corresponding unperturbed chain (44.3 Å). If there had been any segregation of the deuteriated chains, $R_{\mathrm{gx,m}}$ should have been much larger than $R_{\mathrm{gx,0}}$. In addition, the molecular weights of the deuteriated and undeuteriated polybutadiene block chains are small enough ($<4.9 \times 10^4$) to form missible blends of any composition at room temperature according to the results of homopolymer blends reported by Bates et al.[26,27] Moreover, the low concentration of the deuteriated polymer (16.5%) makes the segregation less probable. Thus the incomplete overlap of the deuteriated block chains is considered to be the reason for the incomplete contrast matching.

The domain scattering that appeared in scattering profiles of the blends for the through radiation and the edge radiation at $\Phi = 0°$ is due to the misaligned lamellae, the volume fraction of which is very small from the beginning. Therefore, this domain scattering is weak even without contrast matching. The contrast-matching technique further reduces the domain scattering intensity from the misaligned lamellae to become negligible compared with the molecular scattering. Therefore, by using the contrast-matching technique molecular scattering can be evaluated much more accurately than by the subtraction technique,[1] which leads us to believe definitely the lateral contraction of the chain conformation in the domain space.

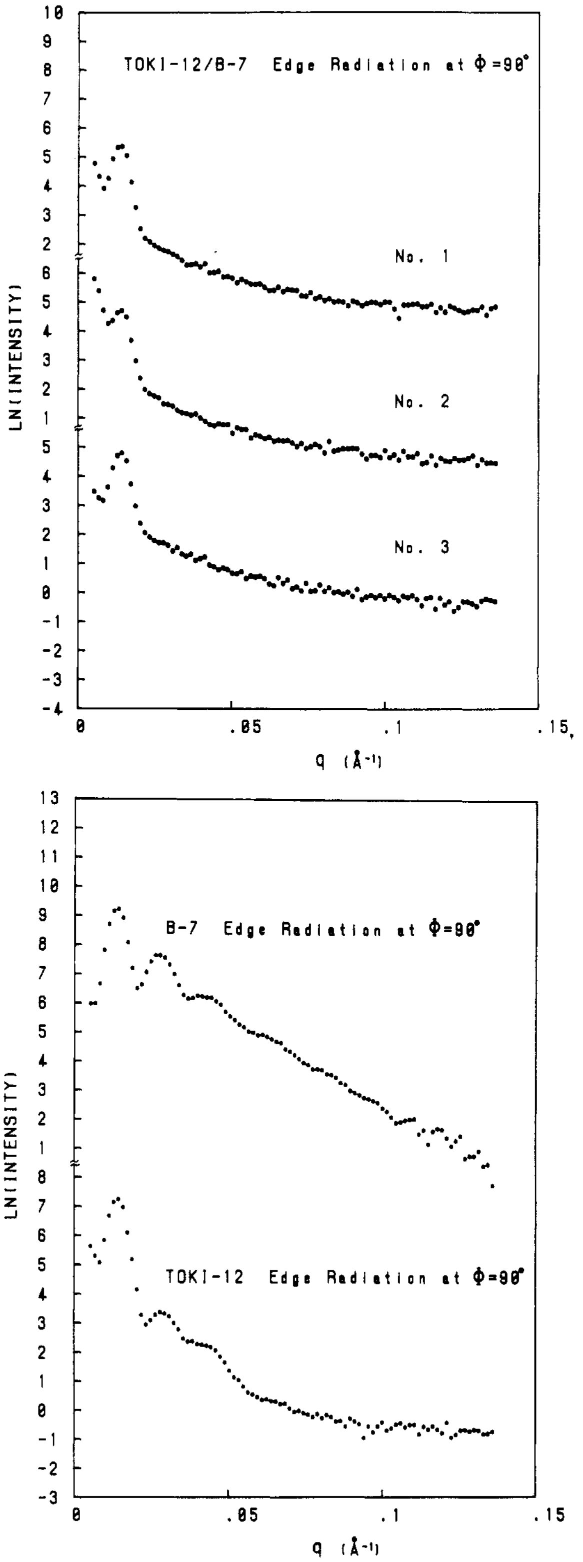

Figure 7. Small-angle neutron scattering profiles (top) from TOKI-12/B-7 blends no. 1, 2, and 3 and (bottom) from pure block polymers B-7 and TOKI-12 for edge radiation at $\Phi = 90°$.

IV. Conclusions

The SANS contrast-matching technique by blending polystyrene–polybutadiene block polymer and polystyrene–perdeuteriated polybutadiene block polymer did not work well as expected. The domain scattering could not be completely eliminated. This is because the concentration of the deuterated block polymer chain at the contrast-matching composition is too low and there is not enough overlapping of the deuterated chains which is necessary to produce the homogeneous distribution of the deuterated segments in the domain space and zero contrast between polystyrene and polybutadiene microdomains. Consequently, the component of the radius of gyration of the block polymer chains perpendicular to the lamellar interface ($R_{gz,m}$) could not be obtained.

However, the contrast-matching technique is effective for obtaining the component of the radius of gyration of block chains parallel to the lamellar interface ($R_{gx,m}$) with better accuracy than the subtraction technique. $R_{gx,m}$ for deuterated polybutadiene block chains thus obtained is 70% of $R_{gx,0}$ calculated for the corresponding unperturbed homopolymer chain. This result coincides with the previous result obtained for deuterated polystyrene chains.[1,6]

To achieve contrast matching successfully, it is necessary to increase the concentration of the deuterated block chains. For this purpose it is necessary to use partially deuterated monomer instead of fully deuterated monomer.

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Registry No. (1,3-Butadiene)(styrene) (block copolymer), 106107-54-4; (styrene)(perdeuterated 1,3-butadiene) (block copolymer), 108549-00-4; neutron, 12586-31-1.

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(20) To calculate the Kuhn statistical segment length (b) of the deuterated polybutadiene z-average degree of polymerization ($N_z = 939$; $N_z = \sum c_i N_i^2 / \sum c_i N_i$) determined from the M_n by osmometry and the GPC data was used.[21] It is well-known that b depends on the microstructures of polybutadienes which depend on the polymerization conditions. The reported values of b determined from solution experiments vary from 6.14 Å (95% cis, 4% 1,2) to 7.58 ± 0.36 Å (71% trans, 25% 1,2).[22] The value we obtained ($b = 7.55$ Å) is larger than that employed by Bates et al.[7,27] ($b = 6.9$ Å) but still within the range of reported b values. As far as we know, $b = 7.55$ Å is the first value obtained for bulk polybutadiene by using SANS. Fernandez et al.[23] measured R_g of polybutadiene in bulk by SANS but it was for the sample with fairly broad molecular weight distribution ($M_w/M_n = 1.23$) and just for one concentration (16% deuterated polybutadiene).

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(33) There may be two alternative methods to evaluate R_g of a polymer chain from the scattering function: nonlinear fit of the Debye-type function and the Zimm plot. Both of these methods are not applicable to our case (highly oriented asymmetrical non-Gaussian chain), because the Debye function assumes the Gaussian chain and Zimm-type analysis is not well established for oriented systems.

(34) It should be noted that the limiting value 1.3 was determined for a sphere (see Figure 38 of ref 32) but may be applicable to the projection of a single block chain on the x–y plane (a plane parallel to the interface) because the projection is considered to be circularly symmetric although the chain itself is stretched and nonspherically symmetric. The slope of the Guinier plots were obtained from the data points in the range of $qR_{gx} < 1.17$ by least-squares fit.

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