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SANS STUDY OF POLYMER CHAINS IN CONFINED SPACE

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ABSTRACT

The lateral and vertical components of the radius of gyration for a single block copolymer chain in the lamellar microdomain space formed by a mixture of diblock copolymers and homopolymers were investigated by means of small-angle neutron scattering (SANS), and the microdomain structures by small-angle X-ray scattering (SAXS). We used the homopolymers whose molecular weights are much smaller than that of the corresponding chains of the block copolymers so that the homopolymers are uniformly solubilized in the corresponding microdomains. The SANS result suggests that the block copolymer chains in the microdomain space are more compressed in the direction parallel to the interface and more stretched in the direction perpendicular to the interface than the corresponding unperturbed polymer chains with the same molecular weight. With increasing the volume fraction of the homopolymers the thickness of the lamellar microdomains increases. The block copolymer chains were found to undergo an isochoric affine deformation on addition of the homopolymers or with the change of the thickness of the lamellar microdomains.

INTRODUCTION

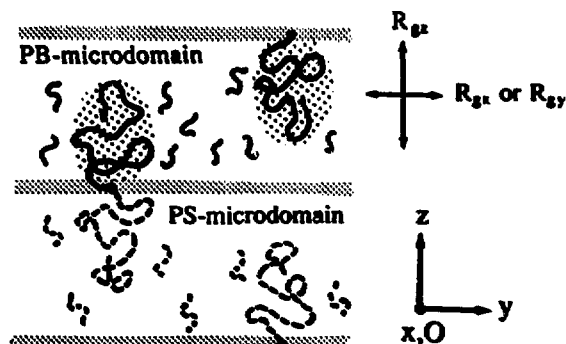
Block copolymers comprising immiscible polymer pairs undergo microphase separation. Although various microdomain morphologies are possible, the size of the microdomain is limited to the dimension of the block chains due to the connectivity by a covalent bond between the two polymers. The conformation of the single block chain in such a confined space is an important problem to understand the physics of microphase separation. Small-angle neutron scattering (SANS) is a useful technique to investigate this problem. We previously investigated the single chain conformation of block copolymers in the lamellar microdomains formed only by the block copolymers^{1),2)}. The results are summarized in Table 1 as well as the results by Hadziioannou et al.³⁾. The results show that the component of radius of gyration of the block chains parallel to the lamellar interface, $R_{gx,m}$ (measured value of R_{gx} as designated in Fig. 1 although it

is an illustration for the case of the block copolymer/homopolymer mixture) is about 70% of that of the unperturbed chain, $R_{gx,0}$, with the same molecular weight. On the other hand, the component of radius of gyration of the block chains perpendicular to the lamellar interface, $R_{gz,m}$ (measured value of R_{gz}), is about 110% of that of the corresponding unperturbed chain. In consequence, the net radius of gyration of the block chains in lamellar microdomain space, $R_{g,m}$, is about 90% of that of the corresponding unperturbed chain, $R_{g,0}$. Thus the block polymer chains in the lamellar microdomain space is laterally squeezed and longitudinally extended with respect to the interface.

Table 1. Radius of Gyration of Block Chains in Lamellar Domain Space

Sample Code	block chain	$M_{n,block} \times 10^{-4}$	$R_{gx,m}$ (Å)	$R_{gz,m}$ (Å)	$R_{gx,0}$ (Å)	$R_{gx,m} / R_{gx,0}$	$R_{g,m}$ (Å)	$R_{g,0}$ (Å)	Ref.
SDI-12	DPS	11.07	33.6		50.4	0.67			3)
SDI-7	DPS	6.89	30.8		39.8	0.77			3)
DSI	DPS	4.05	22	36	30.5	0.72	48	52	1)
B-7	DPB	3.34	32		44.3	0.72			2)

Figure 1 Schematic representation of block copolymer chains in a lamellar microdomain space. R_{gx} and R_{gz} denote the component of radius of gyration of the block-chain molecule in the direction parallel and perpendicular to the interface, respectively. The same notations were used for the homopolymer chains in the microdomain space.



In mixtures of poly(styrene-*b*-isoprene) diblock copolymer (SI) and polystyrene homopolymers (HS) and/or polyisoprene homopolymers (HI) with their molecular weights much smaller than the corresponding block chains, the homopolymers are solubilized in the corresponding microdomains of the block copolymer, and a microdomain structure with a long-range spatial order is formed up to a very high homopolymer concentration^(4),5). When both HS and HI are added to SI along the isopleth line, the same morphology can be maintained and only the average spacing of the microdomains (domain spacing) increases with increasing volume fraction of the homopolymers. The experimental evidence that the long-range spatial order is still maintained even after the domain spacing of the mixture exceeds twice of that of the pure block copolymer suggests that the polystyrene (PS) (polyisoprene (PI)) block chains emanating from the opposing interfaces have sufficiently extensive overlapping in the PS (PI) domains and that HS (HI) is more or less uniformly solubilized in the PS (PI) microdomains. The HS (HI) chains do not essentially screen the intermolecular interactions between the PS (PI) block chains. If the HS (HI) chains are localized in the center of the PS (PI) domains and screen the intermolecular interactions of the PS (PI) block chains, the amount of HS (HI) solubilized in the PS (PI) domains is expected

to vary one by one. Under this condition, the long-range order of the uniformly thick lamellae cannot be attained. The overlap of the block chains and the uniform solubilization of the homopolymers imply that the block chains in such a mixture are stretched more in the direction perpendicular to the interface than those in the pure block copolymer system. Therefore, the single chain conformation of block copolymers in such a system is very interesting. The purpose of this study is to evaluate the lateral and vertical components of radius of gyration, R_{gx} ($=R_{gy}$) and R_{gz} , respectively, for a single block copolymer chain in the lamellar microdomain space⁶), as schematically shown in Fig. 1.

EXPERIMENTAL

Table 2 summarizes the characteristics of the polymer samples used for the study of block-chain conformation as a function of the amount of the solubilized homopolymers. Three kinds of mixtures, BC1 to BC3, shown in Table 3 were prepared for the study of the block chain conformation.

Table 2. Characteristics of Sample Polymers Used in the Study on Block Chain Conformation in Lamellar Microdomain Space.

Sample Code	Polymer*	M_n $\times 10^{-4}$	Weight Fraction of PS	M_w/M_n
TOKI-12	HPS-HPB block	9.99	0.52	1.03
B-7	HPS-DPB block	8.49	0.56	1.02
H-11	HPB homo	0.69	0.00	1.10
H-12	HPS homo	0.44	1.00	1.06

* HPS: protonated polystyrene, HPB: protonated polybutadiene, DPB: deuterated polybutadiene

Table 3. Composition of Mixtures for the Study on Block Chain Conformation in Lamellar Microdomain Space.

Sample Code	TOKI-12 (wt%)	B-7 (wt%)	H-11 (wt%)	H-12 (wt%)	ϕ_b^*
BC1	80.7	19.3	0.0	0.0	1.00
BC2	29.9	20.1	26.6	23.4	0.50
BC3	0.0	15.0	42.5	42.5	0.15

* ϕ_b : volume fraction of block copolymer in a mixture.

In this study, the "contrast matching" technique^{2),7)} was utilized so that the scattering arising from the microdomain structures ("domain scattering") can be made insignificant and only the scattering from the isolated deuterated-polybutadiene (DPB) block chains ("molecular scattering") can be observed. The scattering length of a protonated styrene monomer unit for neutrons is between those of a protonated and a deuterated-butadiene monomer unit, and the contrast matching can be achieved when the volume fraction of DPB in the polybutadiene (PB) microdomain is 16.5% according to the calculation. The volume fraction of DPB for all the mixtures in Table 3 is 16.2% which is very close to the calculated value. The volume fraction of block copolymers in the mixtures, ϕ_b , is 1.00 for BC1, 0.50 for BC2 and 0.15 for BC3. The films of the mixtures for both studies were prepared by casting from 10 wt% solutions in toluene at 30 °C. As expected from the fact that the volume fractions of polystyrene (PS) component in all these

mixtures are close to 0.5, those cast films were found to have the microdomain structure of alternating lamellae with the preferential orientation of their interfaces parallel to the film surfaces from small-angle X-ray scattering (SAXS) analyses.

SAXS measurements give information about the microdomain structures, e.g., morphology, domain spacing, orientation of the microdomains, etc. The corrected SAXS profiles were obtained by the method as described elsewhere¹⁾. SANS measurements of the films were done with the SANS instrument equipped with a two-dimensional detector at the NIST research reactor³⁾. SAXS and SANS measurements were done with two different geometries; incident X-ray or neutron beam normal to the film surface (THROUGH) and parallel to the film surface (EDGE)²⁾. Due to the preferential orientation of the lamellar microdomains with respect to the film surface, the EDGE scattering patterns are anisotropic while the THROUGH patterns are isotropic. The dimension of the DPB block chains in the direction parallel to the interface can be obtained from the THROUGH data and both of those in the directions parallel and perpendicular to the interface can be obtained from the EDGE data.

RESULTS AND DISCUSSION

The SAXS EDGE profiles of the three films listed in Table 3 are shown in Fig. 2. All the profiles show higher-order maxima at the peak positions which are integer multiples of that of the first-order peak, suggesting the existence of the alternating lamellar microdomains with a long-range spatial order. Even BC3 in which ϕ_b is only 0.15 shows a highly regular structure. Average domain spacing evaluated from the first-order peak increased from 440 Å ($\phi_b = 1.00$) to 630 Å ($\phi_b = 0.5$) and 1100 Å ($\phi_b = 0.15$) by adding the homopolymers.

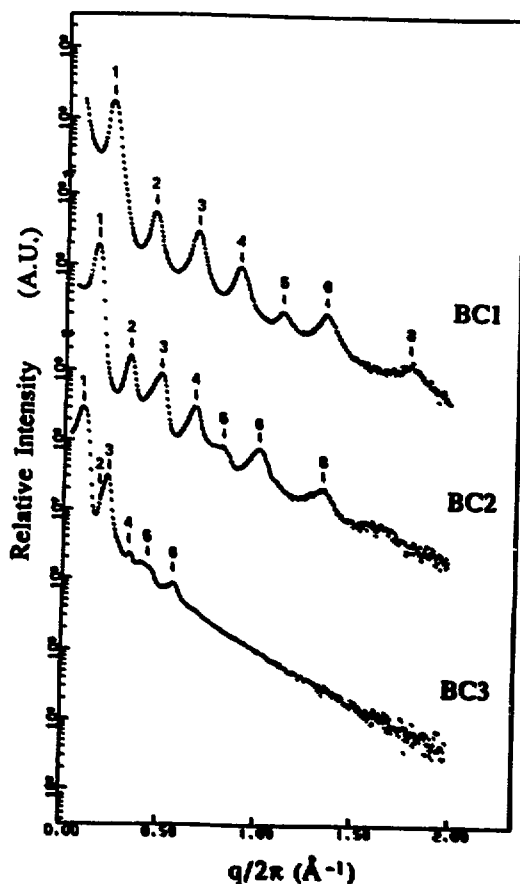


Figure 2 SAXS intensity distribution curves obtained for the cast films of the polymer mixtures listed in Table 3 with the incident beam parallel to the film surface and scanning direction normal to the film surface (EDGE).
 $q = (4\pi/\lambda) \sin \theta$ (2θ : scattering angle)

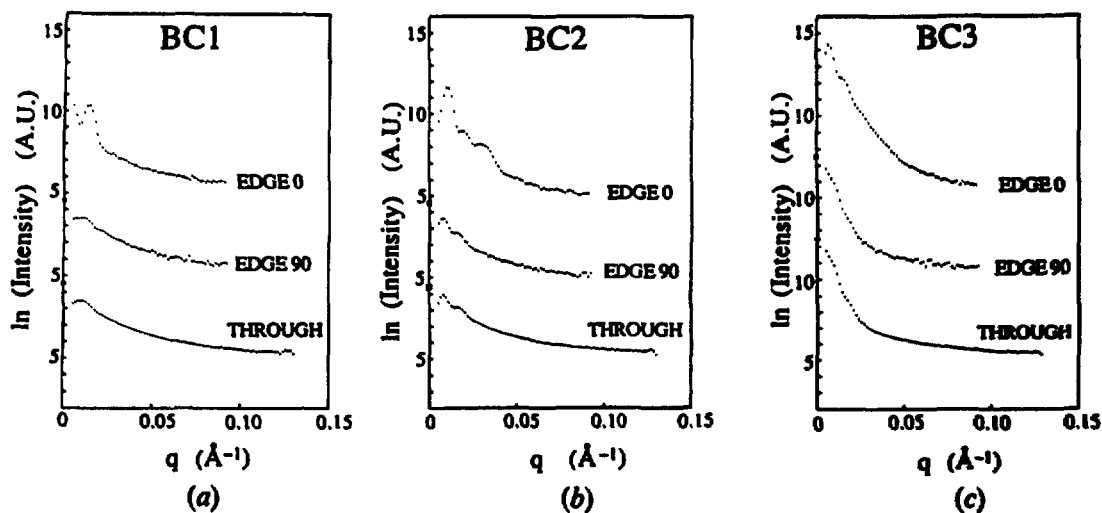


Figure 3 SANS profiles obtained for the cast films of (a) BC1, (b) BC2 and (c) BC3 (incoherent scattering not corrected).

Fig. 3 shows the SANS profiles from the films before the correction for the incoherent scattering. EDGE 0 in the figure denotes the scattering intensity distribution in the direction perpendicular to the film surface and EDGE 90 parallel to the film surface for the EDGE data. The EDGE 0 profiles of the three films show the scattering maxima caused by the long-range order of the lamellar domains, indicating the contrast matching was not perfect. Although the peak intensity of BC1 due to the microdomains is very effectively suppressed to less than 1/100 of that measured for pure TOKI-12 film by using the contrast matching technique, the matching was still imperfect and insufficient for the evaluation of R_{g2} . The reason for the imperfect matching was discussed elsewhere²⁾, on the basis of insufficient overlapping of the deuterated species within the PB microdomains. The insufficient overlapping causes concentration fluctuations of the DPB block chains in the PB domains. The concentration fluctuations give rise to the "molecular scattering" as predicted by the RPA⁹⁾ which, in turn, is responsible for the imperfect matching as it causes an excess scattering. Note that the fluctuations are not averaged out to zero in the scattering process except at $q = 0$ and hence cause the excess scattering or the imperfect matching at $q \neq 0$. Note also that this "molecular scattering" is different from that caused by the two-phase domain structure (the "domain scattering"). The domain scattering itself should be cancelled by the contrast matching.

However, our previous interpretation²⁾ is still insufficient and misleading in that the imperfect matching or the excess scattering occurs even in the case in which the labeled polymer coils have a sufficient overlapping. Even in this case there are thermal concentration fluctuations of the labeled chains in the PB domains in the length scale shorter than the radius of gyration of the PB coils. They cause the excess scattering and the imperfect matching. In our previous paper²⁾ the maximum in the EDGE 0 profile of BC1 in Fig. 3 was denoted as that caused by the "domain scattering". More rigorously this maximum should be described as that interference of the "molecular scattering" but not the "domain scattering" arising from the PB domains arranged in the one-dimensional paracrystal lattice¹⁰⁾.

Therefore, only the lateral dimension of the block chains, R_{gx} , was evaluated by analyzing the THROUGH and EDGE 90 data obtained for the cast films for which the domain scattering intensity is not significant. The Guinier plots for these mixtures showed reasonably linear regions, from the slopes of which the experimental value of the one-dimensional component of radius of gyration of the DPB block chains in the direction parallel to the lamellar interface, $R_{gx,m}$ ($=R_{gy,m}$), was obtained and the results are listed in Table 4. It should be noted that $R_{gx,m}$ decreases with increasing the volume fraction of the homopolymers.

Table 4. Comparison of Lamellar Spacing and Radius of Gyration of Block Chains in Lamellar Microdomain Space.

Sample Code	SAXS		SANS (cast film)		SANS (powder)		
	Domain Spacing	R_1	$R_{gx,m}$	R_2	$R_{g,m}$	$R_{gz,m}$	R_3
	D (Å)		(Å)		(Å)	(Å)	
BC1	440	1.0	32	1.0	65	47	1.0
BC2	630	1.4	28	1.4	71	59	1.3
BC3	1,100	2.5	20	2.5	130	130	2.8

$R_{gx,u} = 44.3 \text{ \AA}$ for the corresponding unperturbed chain.

$R_1 = D/D_{BC1}$; $R_2 = (R_{gx,m}/R_{gx,m,BC1})^{-2}$; $R_3 = R_{gz,m}/R_{gz,m,BC1}$

Evaluation of the component of radius of gyration of DPB block chains in the direction perpendicular to the lamellar interface, $R_{gz,m}$, was carried out on the basis of the following principle. If the lateral dimension of the lamellae is much larger than their thickness, as found in our experimental conditions, the perturbation of the molecular scattering due to the interference from the periodic domain structure in the one-dimensional lattice occurs only in the direction of Oz axis, the scattering in any other directions being essentially free from the perturbation and reflecting the true molecular scattering (see Fig. 1). Therefore, the perturbation is significantly reduced by randomizing the orientation of the lamellar microdomains and by detecting the scattering in a given direction. In this condition the molecular scattering becomes dominant to allow the analysis of the average radius of the overall labelled chains $R_{g,m}$ by the Guinier plot.

$$R_{g,m}^2 = 2R_{gx,m}^2 + R_{gz,m}^2 \quad (1)$$

The $R_{gz,m}$ can be determined from the separately determined values of $R_{g,m}$ and $R_{gx,m}$.

SANS profiles were obtained with the powdered specimens for each of the three mixtures which were made by pulverizing the cast films of BC1 to BC3 at liquid nitrogen temperature. The perturbation was significantly reduced by randomizing the orientation of the lamellar microdomains as seen in Fig. 4. Fig. 4 shows the SANS profiles of the powdered specimens of BC1 to BC3. The scattering peaks observed in the EDGE 0 profiles of the cast film in Fig. 3 are remarkably suppressed in those of the powdered specimens in Fig. 4. Thus, the molecular scattering is dominant in the profiles of the powdered specimens to allow the analysis by Guinier plots. Radius of gyration of the DPB coils ($R_{g,m}$) obtained for the powdered specimens was 65 Å for $\phi_b = 1.00$, 71 Å for $\phi_b = 0.50$ and 130 Å for $\phi_b = 0.15$. $R_{gz,m}$ was calculated from these experimental values of $R_{g,m}$ and previously obtained $R_{gx,m}$ using equation (1), and the results are listed in Table 4.

As listed in Table 4, the ratio, R_1 , of the average domain spacing for the mixture containing a given amount of homopolymers to that for the mixture containing no homopolymers, i.e. $\phi_b = 1.00$, D/D_{BC1} , the ratio, R_2 , of the inverse square of the component of radius of gyration parallel to the interface for the mixture with a given ϕ_b to that for the mixture with $\phi_b = 1.00$, $(R_{gz,m})^{-2}/(R_{gz,m,BC1})^{-2}$, and the ratio, R_3 , of the component of radius of gyration perpendicular to the interface for the mixture with a given ϕ_b to that of the mixture with $\phi_b = 1.00$, $R_{gz,m}/R_{gz,m,BC1}$ are the same within the experimental error. This implies that the block chains with the laterally squeezed conformation undergo an isochoric affine deformation on addition of the homopolymers, the expansion of lamellar thickness giving the linear extension of the block chains perpendicular to the interface, and the corresponding contraction of the chains parallel to the interface.

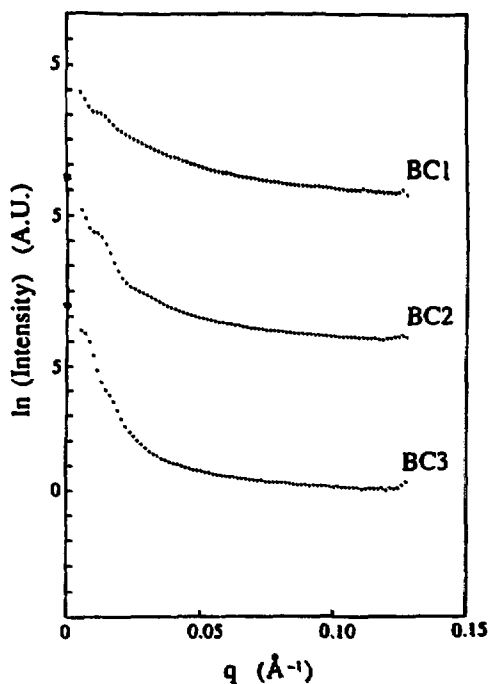


Figure 4 SANS profiles obtained for the powdered specimens of (a) BC1, (b) BC2 and (c) BC3 (incoherent scattering not corrected).

REFERENCES

- 1) H. Hasegawa, H. Tanaka and T. Hashimoto, *Macromolecules*, **20**, 2120 (1987).
- 2) H. Hasegawa, T. Hashimoto, H. kawai, T. P. Lodge, E. J. Amis, C. J. Glinka and C. C. Han, *Macromolecules*, **18**, 67 (1985).
- 3) G. Hadziioannou, C. Picot, A. Skoulios, M.-L. Ionescu, A. Mathis, R. Duplessix, Y. Gallot and J.-P. Lingelser, *Macromolecules*, **15**, 263 (1982).
- 4) T. Hashimoto, H. Tanaka and H. Hasegawa, *Macromolecules*, **23**, 4378 (1990).
- 5) H. Tanaka, H. Hasegawa and T. Hashimoto, *Macromolecules*, **24**, 240 (1991).
- 6) H. Hasegawa, H. Tanaka, T. Hashimoto and C. C. Han, *J. Appl. Cryst.*, **24**, 672 (1991).
- 7) F.S. Bates, C.V. Berney, R.E. Cohen and G.D. Wignall, *Polymer*, **24**, 519 (1983).
- 8) C. J. Glinka, J. M. Rowe and J. G. LaRock, *J. Appl. Cryst.*, **19**, 427 (1986).
- 9) P.G. deGennes, *Scaling Concepts in Polymer Physics*, New York, Cornell Univ. Press (1979).
- 10) T. Hashimoto, K. Nagatoshi, A. Todo, H. Hasegawa and H. Kawai, *Macromolecules*, **7**, 364 (1974).