

Studies on Microphase-Separated Structures of Block Copolymers by Neutron Reflectivity Measurement

Naoya TORIKAI, Ichiro NODA, *Yushu MATSUSHITA, †Alamgir KARIM,
‡Sushil K. SATIJA, †Charles C. HAN and ‡Toru EBISAWA

*Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku,
Nagoya 464-01, Japan*

**Neutron Scattering Laboratory, The Institute for Solid State Physics, The University of Tokyo,
Tokai, Naka-gun, Ibaraki 319-11, Japan*

†National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

‡Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka 590-04, Japan

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Segmental distributions of block copolymer chains in lamellar microphase-separated structure and those of homopolymers in block copolymer/homopolymer blends also with lamellar structures were studied by neutron reflectivity measurements. It was revealed that polystyrene and poly(2-vinylpyridine) lamellae were alternately stacked within the thin films of pure block copolymers spin-coated on silicon wafers, and they were preferentially oriented along the direction parallel to film surface. Polystyrene lamella appeared at air surfaces of the films, while poly(2-vinylpyridine) lamella did on silicon surfaces. Segment distribution at lamellar interface was well described by an error function, and the width of the lamellar interface, defined by a full-width half-maximum value of interfacial profile, was estimated to be about 4.5 nm. Segments of block chains adjacent to the chemical junction points connecting different block chains were strongly localized near the lamellar interfaces, while those on the free ends of block chains were distributed all over the lamellar microdomains with their distribution maxima at the centers of lamellae. On the other hand, it was clarified that homopolymers dissolved in the corresponding lamellar microdomains of block copolymers were also distributed throughout the microdomains with their concentration maxima at the centers of the lamellae.

KEYWORDS: Block Copolymer, Microphase-Separated Structure, Segment Distribution,
Neutron Reflectivity

1. Introduction

It has been well-established that diblock copolymers composed of two incompatible component polymers form various morphologies of microphase-separated structures: spherical, cylindrical, ordered-bicontinuous, and alternating lamellar structures, in bulk, according to their own compositions.¹⁻³⁾ Alternating lamellar structure has been studied most at the molecular level because of the simplest geometry among microphase-separated structures. The sizes of their repeating structural units have been known to be proportional to about 2/3 power of the molecular weights of diblock copolymers by both experimental and theoretical studies.⁴⁻⁷⁾ It was clarified by small-angle neutron scattering (SANS) that the dimensions of block chains in lamellar microdomains are extended along the direction perpendicular to lamellar interface, while they are shrunk along the direction parallel to the interface in order to keep their volumes unchanged.^{8,9)}

On the other hand, diblock copolymer/homopolymer blends exhibit more complicated phase diagrams, where macrophase separation of copolymer-rich and homopolymer-rich phases coexists with microphase separation.¹⁰⁾ Their phase diagrams depend not only on the volume fractions of homopolymers, Φ_H , in the blends but also on the molecular weights of homopolymers, M_H . When the molecular weights of blended homopolymers are much lower than that of the corresponding block chain, the block/homo blends exhibit microphase-separated structures except for in extremely high Φ_H .

However, it was found that homopolymers dissolved in the corresponding lamellar microdomains tend to be localized at the centers of the lamellae with increasing their molecular weights.¹¹⁻¹⁴⁾ Further, it turned out that chain dimensions of homopolymers in lamellar microdomains are almost the same as those of unperturbed chains with the same molecular weights, while the dimensions of block chains are almost the same as those of the pure block copolymers irrespective of Φ_H and M_H of the blended homopolymers, at least along the direction parallel to lamellar interface.¹⁵⁻¹⁷⁾

Neutron reflectivity (NR) measurements are particularly useful for studies on interfaces and surfaces because they have high resolution along the depth direction of film specimens. It is difficult to obtain information on interfaces between polymers by small-angle x-ray scattering (SAXS) and SANS with the same accuracy as NR measurement. Recently, homopolymer / homopolymer interfaces and lamellar interfaces have been investigated by NR measurement.^{18,19)} The segmental distributions at the lamellar interfaces of styrene-methylmethacrylate diblock copolymers were well described by hyperbolic tangent function, and the effective thicknesses of the interfaces were estimated to be about 5.0 nm, which were consistent with those of homopolymer / homopolymer interfaces.

In this study, segmental distributions of block copolymer chains in lamellar microdomains and those of homopolymers in diblock copolymer/homopolymer blends with lamellar structures were investigated by NR

measurements to understand microphase-separated structures at the molecular level.

2. Experimental Section

Three types of samples were used in this study: (1) a styrene- d_8 -2-vinylpyridine (DP) diblock copolymer, (2) a center-labeled styrene- h_8 -styrene- d_8 -2-vinylpyridine (SDP) and an end-labeled styrene- d_8 -styrene- h_8 -2-vinylpyridine (DSP) block copolymers, and (3) a blend of a styrene- h_8 -2-vinylpyridine (SP) diblock copolymer and the constituent homopolymers, poly(styrene- d_8) (TUN) and poly(2-vinylpyridine) (VPK). All the polymers were synthesized by an anionic polymerization method. Molecular characteristics of all the polymers are listed in Table I. As for the sample of type (3), both the constituent homopolymers, TUN and VPK, with almost equal molecular weights, were added to SP diblock copolymer at the volume fraction of each component homopolymer in the corresponding lamellar microdomain, Φ_H , of 0.33. It was confirmed by SAXS that all the samples exhibit lamellar structures in thick film specimens, about 0.2 mm in thickness, prepared by solvent-casting.

Table I. Molecular Characteristics of Polymers

Type	Sample Code	$M_n \times 10^{-3}$ ^a	Φ_s ^b
(1)	DP-77	92-75	0.50
(2)	SDP-5	30-17-42	0.51
	DSP-2	17-37-45	0.57
(3)	SP-34	53-66	0.51
	TUN-02	48	--
	VPK-18	57	--

^a M_n is number-averaged molecular weight determined by membrane osmometry. Bold-faced figures stand for molecular weight of deuterium-labeled part, poly(styrene- d_8), in sample. ^b Φ_s is volume fraction of styrene block chain determined by elemental analysis.

One-side polished silicon wafers were immersed into a strong acid bath, a mixture of hydrogen peroxide (30%) and conc. sulfuric acid at the ratio of 3:7, to remove impurities on the silicon surfaces, and then were thoroughly rinsed with deionized water and dried by blowing an inert gas. After this cleaning procedure, the silicon wafers were immediately used for preparation of film specimens.

Thin films for NR measurement were spin-coated on the cleaned silicon wafers from about 2 wt% of polymer solutions in toluene or p-dioxane at rotation speed of 2.0 or 2.5×10^3 rpm, and then were annealed at 150 °C in vacuum for at least 3 days. Thicknesses of all the films thus prepared were determined to be in between 100 nm and 250 nm by x-ray reflectivity measurements.

NR measurements were performed on three different reflectometers: BT-7 and NG-7 reflectometers at NIST, and C3-1-2 reflectometer at JAERI. Performance of each reflectometer has been described in detail elsewhere.²⁰⁻²² In this study specular reflections, where the incident angle of neutrons irradiated to film surface, θ_{in} , and the reflected angle, θ_{out} , are equal, were observed as a function of momentum transfer of neutrons in air, q_0 , perpendicular to

film surface given by $q_0 = (4\pi/\lambda)\sin\theta$, where λ is the wavelength of neutrons.

Specular reflectivities were calculated from model scattering length density, b/v , profiles along z direction perpendicular to film surface using Parratt's recursion algorithm.²³ This algorithm is applicable to multi-layered system with distinct interfaces, of which b/v profile changes stepwisely. In reality film/air, film/Si interfaces, and microdomain interfaces have finite thicknesses, where b/v profiles change gradually. Such interfaces were approximately regarded as groups of very thin layers with distinct interfaces, so that their b/v profiles were described by step functions instead of continuous functions. Also, it was assumed that phase-separated structures formed are equilibrated by annealing procedure and that same structural units are repeated in thin films. Scattering length densities, b/v , of pure components relevant to this study are listed in Table II.

Table II. Coherent Scattering Length Densities, b/v , of Pure Components.

Component	$b/v \times 10^4$ (nm ⁻²)
Poly(styrene- h_8)	1.41
Poly(styrene- d_8)	6.47
Poly(2-vinylpyridine)	1.95
SiO ₂	3.48
Si	2.09

3. Results and Discussion

In Figure 1 reflectivity profile of DP-77 as a function of q_0 is shown. The measured reflectivity profile, represented by open circles, exhibits Bragg's peaks with high-order, indicating that phase-separated structure is highly ordered along the direction perpendicular to the film surface. The solid line is the best calculated reflectivity from scattering length density, b/v , profile along z direction as shown in inset, where $z = 0$ corresponds to the air surface of the film. From the b/v profile, it was found that polystyrene (D) lamellae with b/v value of 6.2×10^{-4} nm⁻² and poly(2-vinylpyridine) (P) lamellae with $b/v = 1.9 \times 10^{-4}$ nm⁻² are alternately stacked through the film, and that they are highly oriented parallel to the film surface. Its lamellar domain spacing evaluated, 69 nm, is consistent with that evaluated from SAXS measurement for the thick film specimen prepared by solvent-casting. Further, the ratio of the thickness of polystyrene lamella to the lamellar domain spacing well agrees with the volume fraction of styrene block chain, Φ_S , determined by elemental analysis. At air surface of the film, D lamella whose thickness is half of the corresponding lamella inside the film appeared because of its lower surface energy as compared with P, while on silicon surface P lamella whose thickness is half of the corresponding lamella appeared because of its affinity with silicon oxide, SiO₂, covering silicon surface. A SiO₂ layer with thickness of about 1.5 nm was observed as a sharp peak on the right of the b/v profile. The b/v profile at the interface between D and P lamellae was well described by an error function,

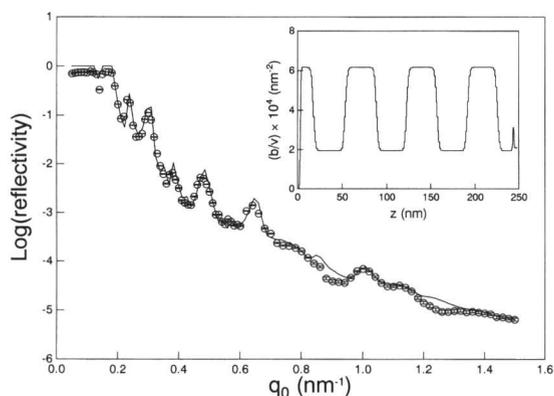


Fig. 1. Reflectivity profile of DP-77 as a function of q_0 . Open circles denote the measured reflectivity profile, while the solid line does the best calculated one from scattering length density, b/v , profile along z direction as shown in inset.

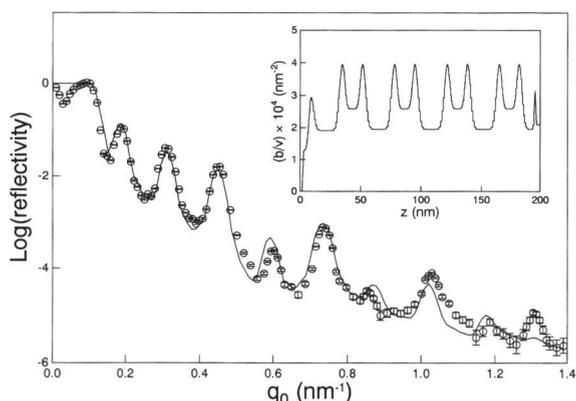


Fig. 2. Reflectivity and the best b/v profiles of a center-labeled block copolymer, SDP-5.

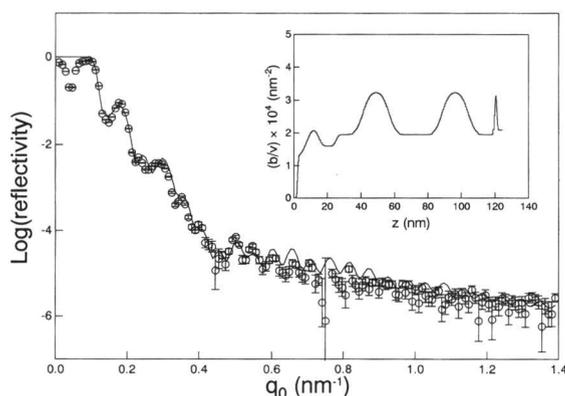


Fig. 3. Reflectivity and the best b/v profiles of an end-labeled block copolymer, DSP-2.

and the interfacial width, defined by a full-width half-maximum value of interfacial profile, was estimated to be about 4.5 nm.

In Figures 2 and 3 reflectivity profiles of two kinds of partially-labeled block copolymers, SDP-5 and DSP-2, respectively, are shown. SDP-5 exhibits strong Bragg's peaks with very high-order in its reflectivity profile, while DSP-2 exhibits weaker peaks than SDP-5. This implies that styrene- d_8 (D) segments of SDP-5 are more strongly localized in lamellar structure, which is ordered along the direction perpendicular to the film surface, than those of DSP-2. In the reflectivity profile of DSP-2 oscillation with high frequency, which is related to total film thickness, was observed in the q_0 region above 0.5 nm^{-1} . In the inset of each figure, b/v profile for the best-fit calculated reflectivity profile is shown. It was assumed that the widths of interfaces between polystyrene and poly(2-vinylpyridine) lamellae for partially-labeled block copolymers are the same as that of DP-77, i.e., about 4.5 nm. In both cases SiO_2 layers with thicknesses of about 1.5 nm were also observed on the surface of Si wafer. Both block copolymers formed lamellar structures oriented parallel to the film surfaces, although air surfaces of their films were considerably rough. The lamellar domain spacings of SDP-5 and DSP-2, evaluated to be 43 and 47 nm, respectively, are consistent with those evaluated from SAXS for their thick films prepared by solvent-casting. Further, the ratios of lamellar thickness for both block copolymers well agree with their own Φ_S values. SDP-5 exhibited sharp twin peaks with each peak position near lamellar interface, while DSP-2 exhibited broad peaks at the centers of polystyrene lamellae. The peak b/v values of SDP-5, $4.0 \times 10^{-4} \text{ nm}^{-2}$, were higher than those of DSP-2, $3.3 \times 10^{-4} \text{ nm}^{-2}$; nevertheless two polymers have almost equal D contents. However, it should be noted that they were still lower than b/v value of pure poly(styrene- d_8), $6.5 \times 10^{-4} \text{ nm}^{-2}$.

Partially-labeled block copolymers, SDP-5 and DSP-2, are composed of three components: S, D, and P segments, and their lamellar microdomains are oriented parallel to the film surfaces. Therefore, the b/v profiles in their thin films, as shown in the insets of Figures 2 and 3, are written as the following

$$b/v(z) = \sum_i (b/v)_i \phi_i(z), \quad (i=S, D \text{ and } P) \quad (1a)$$

$$\sum_i \phi_i(z) = 1 \quad (1b)$$

where $(b/v)_i$ and $\phi_i(z)$ are b/v value and volume fraction of pure i component, respectively. $\phi_i(z)$'s in each component lamella were derived from the above equations assuming that $\phi_P = 0$ in polystyrene lamellae, while $\phi_S + \phi_D = 0$ in poly(2-vinylpyridine) lamellae. At the lamellar interfaces both segment distributions of styrene (S+D) and 2-vinylpyridine (P) were described by error functions with full-width half-maximum values of 4.5 nm. The results for SDP-5 and DSP-2 are shown in Figures 4 and 5, respectively. Solid and broken lines in the figures

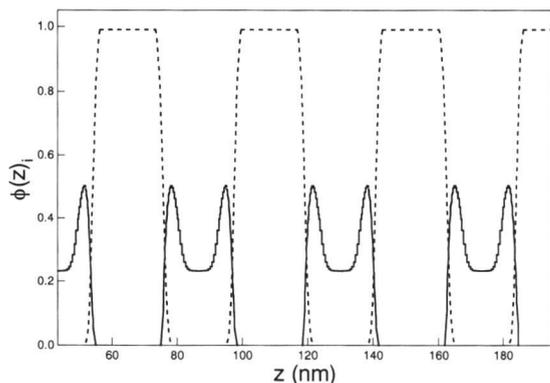


Fig. 4. Volume fraction profiles, $\phi_i(z)$, of styrene- d_8 (D) and 2-vinylpyridine (P) segments along z direction for SDP-5. The solid line represents $\phi_D(z)$, while the broken line $\phi_P(z)$.

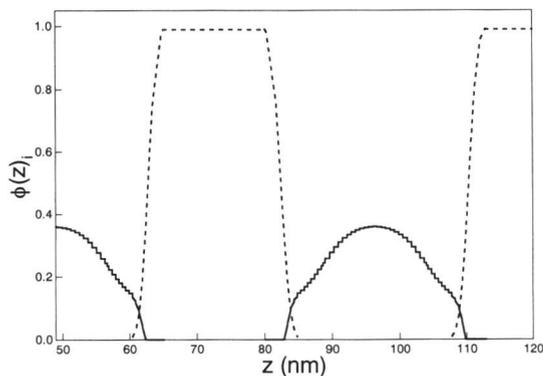


Fig. 5. $\phi_D(z)$ and $\phi_P(z)$ profiles for DSP-2.

represent the volume fraction profiles, $\phi_i(z)$, of D and P segments, respectively. From the $\phi_D(z)$ profile, shown in Figure 4, it was found that the segments adjacent to the chemical junction points between two different block chains are strongly localized near lamellar interfaces, since those chemical junction points are constrained at the lamellar interfaces. On the other hand, Figure 5 indicates that the segments at the free ends of block chains are distributed throughout polystyrene lamellae with their distribution maxima at the centers of lamellae. These broad maxima in the $\phi_D(z)$ profile result from overlap of block chains emitted from opposite lamellar interfaces as schematically shown in Figure 6, where end-distributions of both block chains should be symmetrical to the center of lamellar microdomain.

Figure 7 shows reflectivity profile of a diblock copolymer/homopolymer blend, SP-34/TUN-02/VPK-18,

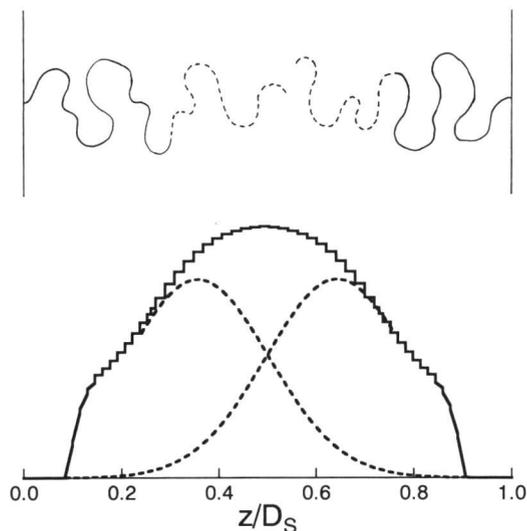


Fig. 6. A schematic sketch of end-labeled block chains emitted from opposite lamellar interfaces, where labeled parts are represented by broken lines. In the lower figure broken lines denote the distributions of two block chains, while the solid line does the sum of them. The magnitude of z is normalized using thickness of polystyrene lamella, d_S .

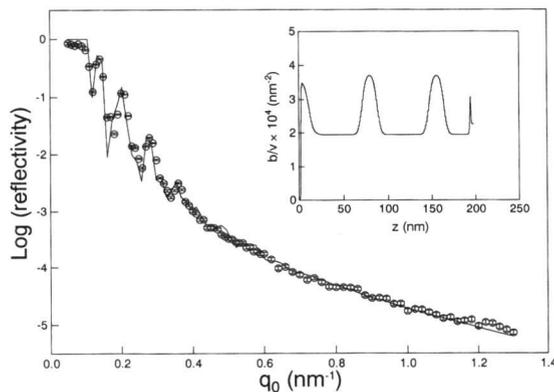


Fig. 7. Reflectivity and the best b/v profiles of a diblock copolymer/homopolymer blend, SP-34/TUN-02/VPK-18, at the volume fraction of each homopolymer, Φ_H , of 0.33. The molecular weight ratio of homopolymer to the corresponding block chain is 0.83.

at the volume fraction of each homopolymer, Φ_H , of 0.33. The best b/v profile, shown in inset, indicates maxima at the centers of polystyrene lamellae with their peak b/v values of $3.7 \times 10^{-4} \text{ nm}^{-2}$, which are much lower than that of pure D segment, $6.5 \times 10^{-4} \text{ nm}^{-2}$. However, attention should be paid to the fact that the heights of the peaks of homopolymers dissolved in lamellar microdomains are higher than those of block polymers on chain ends.

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