

Comparison between Interfacial Structures of a Block Copolymer and Two-Component Homopolymers by Neutron Reflectivity Measurement

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Polystyrene/poly(2-vinylpyridine) (PS/P2VP) homopolymer interface and the microphase-separated interface of a PS-P2VP diblock copolymer with alternating lamellar structure were investigated by neutron reflectivity measurements. The interfacial thicknesses evaluated for PS/P2VP and PS-P2VP are apparently larger than the predictions of a mean-field theory. These discrepancies between experimental and theoretical results were interpreted as the contributions of thermally-induced capillary waves on the polymer interface.

KEYWORDS: interfacial structure, homopolymer interface, block copolymer interface, neutron reflectivity measurement, capillary wave

§1. Introduction

It has been well accepted that neutron reflectivity (NR) measurement is a powerful technique for studying the polymer interface and surface because of its high spatial resolution. So far, interfaces between various pairs of immiscible polymers have been studied by the NR technique. Above all, a pair of polystyrene (PS) and polymethylmethacrylate (PMMA) with a low Flory-Huggins interaction parameter χ ($=0.041$)¹ at 298 K has been intensively studied, and its precise NR results have greatly contributed to the development of the theory of polymer interfaces.^{2–6} Anastasiadis *et al.*²) reported that the interfacial thickness between PS and PMMA homopolymers is identical to that of a PS-PMMA diblock copolymer with lamellar microphase-separated structure. However, the apparent interfacial thicknesses evaluated for homopolymer and diblock copolymer were much larger than those predicted by a mean-field theory. This discrepancy between experimental and theoretical results was quantitatively interpreted as the contribution of thermally-induced capillary waves on the polymer interface.³) The interfacial properties, such as interfacial thickness, capillary wave, etc., strongly depend on the magnitude of χ parameter. Thus, it is significant for a further understanding of polymer interfaces to study the interfacial structure of another polymer pair with a different χ parameter.

For this study a pair of PS and poly(2-vinylpyridine) (P2VP) was chosen because this pair has a much higher χ parameter ($=0.11$ at 298 K) than the PS and PMMA pair, and they have ideally almost the same statistical segment lengths. A bilayer film of PS and P2VP homopolymers was prepared by making use of the spin-

coating technique for the reflectivity measurement on the homopolymer interface. In this study, the interfacial structures of a PS/P2VP bilayer film and a PS-P2VP diblock copolymer with lamellar microphase-separated structure were investigated by NR measurement.

§2. Experimental Section

Samples used are a poly(styrene- d_8) (dPS) with molecular weight, M , of 130×10^3 , a poly(2-vinylpyridine) (P2VP) with $M=370 \times 10^3$ and a diblock copolymer (dPS-P2VP) having $M=88 \times 10^3$ and the volume fraction of dPS block chain of 0.50. They were all synthesized by an anionic polymerization method. A thin film specimen of block copolymer was prepared by spin-coating from p-dioxane solution onto a polished silicon wafer. On the other hand, a bilayer film of homopolymer was prepared by spin-coating a dPS film from toluene solution onto the P2VP film spin-coated on a silicon wafer. They were sufficiently annealed at the temperature above T_g before the reflectivity measurement.

Neutron reflectivity measurements were performed on LTAS⁷) of the Japan Atomic Energy Research Institute, PORE⁸) of the High Energy Accelerator Research Organization, Japan and CRISP⁹) of ISIS Facility, Rutherford Appleton Laboratory, UK. The monochromated neutrons with a constant wavelength, λ , of 0.63 nm were used on LTAS, while white neutrons with a wide λ band were used on the others. X-ray reflectivity measurements were performed on the RUH450 diffractometer of ultra-high intensity x-ray diffraction laboratory at Nagoya University, Japan for determining the total thicknesses of the film specimens. Specular reflection, in which the incident angle, θ , of neutron or x-ray to the film surface is equal to the reflected angle, was observed as a function of

momentum transfer, $q_z (=4\pi\sin\theta/\lambda)$, of radiation along the direction perpendicular to the film surface. The data analysis for specular reflectivity was performed by using a recursion algorithm of Parratt¹⁰⁾ and an optical matrix method.¹¹⁾

§3. Results and Discussion

Figure 1 shows x-ray and neutron specular reflectivity profiles for a dPS/P2VP bilayer film as a function of momentum transfer, q_z , of radiation along the direction perpendicular to the film surface. Both profiles show total reflection at low q_z region. It is also noted that the x-ray profile has two critical q_z values for total reflection. The x-ray profile exhibits a number of fringes with a high frequency reflecting total film thickness, since the difference in electron density between the film and silicon wafer is much larger than that between dPS and P2VP. The total film thickness was evaluated to be about 83 nm from the frequency of fringes. On the other hand, the neutron profile also shows several fringes, but the frequency of the fringes is low because it reflects the thickness of an upper dPS layer with higher coherent scattering length density, b/v . Thus, the neutron profile is insensitive to the thickness of a lower P2VP layer, i.e., total film thickness, so that a fitting procedure for the neutron data was performed using 83 nm as the total film thickness which was estimated from the x-ray data. The solid line on the neutron experimental data is the best-calculated reflectivity profile from a b/v profile shown in the inset, where the origin of abscissa, z , corresponds to the air surface of the film. From the b/v profile it is apparent that the upper layer is dPS with $b/v=6.2\times 10^{-4}$ nm⁻² and the lower layer is P2VP with $b/v=1.9\times 10^{-4}$ nm⁻² as designed. The thickness of the upper dPS layer was evaluated to be about 30 nm. The interfacial thickness, t_I , defined as $(d\phi_i(z)/dz)^{-1}$ at $\phi_i=0.5$, where $\phi_i(z)$ is an interfacial profile of the i -component and an error function was assumed in this study, was evaluated to be 4.4 nm.

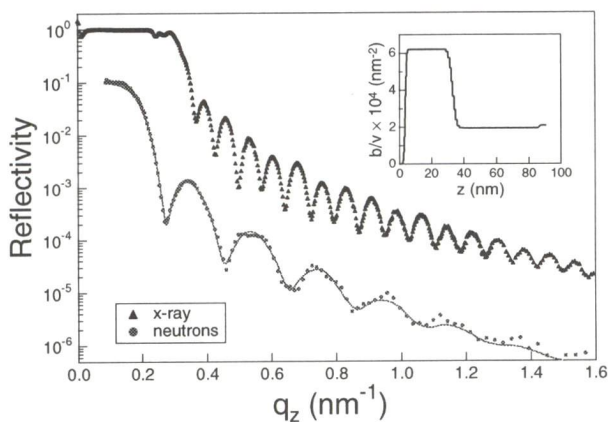


Fig.1. X-ray and neutron specular reflectivity profiles for a dPS/P2VP bilayer film as a function of q_z . The solid line on neutron data is the best-calculated reflectivity from a b/v profile shown in the inset.

profiles for a dPS-P2VP diblock copolymer with lamellar microphase-separated structure. The total film thickness of dPS-P2VP was evaluated to be 113 nm from the frequency of fringes in the x-ray profile. The neutron profile shows several Bragg peaks superimposed on the fringes with a high frequency. The existence of Bragg peaks at high order implies that the lamellar structure is preferentially oriented along the direction parallel to the film surface. The solid line is the calculated reflectivity from a b/v profile, shown in the inset, along the film depth direction. It was found that dPS lamellae with $b/v=6.2\times 10^{-4}$ nm⁻² and P2VP lamellae with $b/v=1.9\times 10^{-4}$ nm⁻² are alternatively stacked with the repeating period of about 43 nm. A dPS lamella appears at the air surface of the film due to its lower surface energy than P2VP, while a P2VP lamella does at the silicon surface due to its higher affinity for the oxide layer covering the silicon surface. The value of t_I for the lamellar interface of dPS-P2VP was evaluated to be about 3.3 nm.

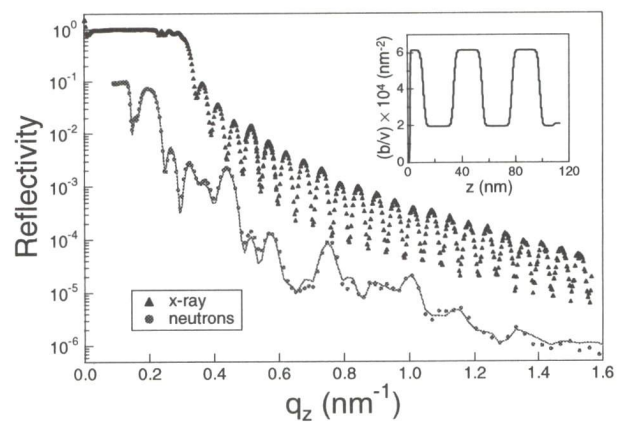


Fig.2. X-ray and neutron specular reflectivity profiles for a dPS-P2VP diblock copolymer film. The solid line through the neutron data is the best-calculated reflectivity from a b/v profile shown in the inset.

Table I. Comparison between experimental and theoretical interfacial thicknesses.

Sample	χ^a	χN^b	$t_{I,EX}^c$ (nm)	$t_{I,HE}$ (nm)	$t_{I,CO}$ (nm)	$t_{I,FL}$ (nm)
dPS/P2VP	0.11	-	4.4 (0.6)	1.7	-	4.4
dPS-P2VP	0.11	89	3.3 (0.3)	1.7	2.1	3.1

a) The χ value (at 298 K) was estimated from its temperature-dependence determined by SANS for a dPS-P2VP with low molecular weight.

b) N is the degree of polymerization of the block copolymer.

c) The number in parentheses is an error in determining interfacial thickness.

The evaluated t_I values are summarized in Table I. In the theory of Helfand *et al.*,^{12,13)} the block copolymer interface in the strong segregation limit is approximated to be the same as the interface between homopolymers having infinite molecular weights, and their interfacial thicknesses are given by

$$t_{I,HE} = 2a/(6\chi)^{1/2} \quad (3.1)$$

Figure 2 shows x-ray and neutron specular reflectivity

where a is the statistical segment length. The value of $t_{I,HE}$ is estimated to be 1.7 nm from Eq. (3.1) by using 0.68 nm^{14,15)} and 0.11 (at 298 K) for a and χ , respectively. This value is apparently smaller than the $t_{I,EX}$ values for dPS/P2VP and dPS-P2VP. Thus, according to the approach of Shull *et al.*,³⁾ $t_{I,HE}$ for the homopolymer interface was corrected for interfacial fluctuation, which is not considered in the theory of Helfand *et al.* Finite molecular weight effects¹⁶⁾ were not considered here since dPS and P2VP used in this study have sufficiently high molecular weights. The magnitude, $\Delta t_{I,FL}$, of interfacial fluctuation due to a capillary wave is given by³⁾

$$(\Delta t_{I,FL})^2 = (k_B T / 2\pi\gamma) \ln(\lambda_{max}/\lambda_{min}) \quad (3.2)$$

where k_B is the Boltzmann constant, T is absolute temperature, γ is the interfacial tension, and λ_{max} and λ_{min} are the upper and lower wavelength limits of fluctuations, respectively. The value of γ was estimated from the equation¹³⁾

$$\gamma = a\rho k_B T (\chi/6)^{1/2} \quad (3.3)$$

where ρ is the number density of polymer. The $\Delta t_{I,FL}$ value for the homopolymer interface was estimated to be 1.6 nm by using the neutron coherence length, 20 μm ,⁶⁾ and $t_{I,HE}$, 1.7 nm, for λ_{max} and λ_{min} , respectively. Actually, the neutron coherence length does not have a distinct value, so that one of the representative values was used in this study since $\Delta t_{I,FL}$ is not so sensitive to λ_{max} value. The interfacial thickness, $t_{I,FL}$, corrected for the fluctuation is evaluated to be 4.4 nm according to

$$(t_{I,FL})^2 = (t_{I,HE})^2 + 2\pi(\Delta t_{I,FL})^2 \quad (3.4)$$

and it is in good agreement with $t_{I,EX}$ for the dPS/P2VP homopolymer interface.

On the other hand, $t_{I,HE}$ for the block copolymer was corrected for the connectivity of the block chain by using the mean-field calculation results of Shull.¹⁷⁾ However, the interfacial thickness, $t_{I,CO}$, corrected for the connectivity is still considerably lower than the experimental value as shown in Table I. The $\Delta t_{I,FL}$ for the block copolymer was estimated to be 0.9 nm from eq. (3.2) by using the lamellar domain spacing, 43 nm, and $t_{I,HE}$, 1.7

nm, for λ_{max} and λ_{min} , respectively. The interfacial fluctuation is suppressed by the size of microdomains, so that the apparent fluctuation effects on the block copolymer interface could be smaller than those on the homopolymer interface. The value, 3.1 nm, of $t_{I,FL}$ corrected for the connectivity and fluctuation agrees well with $t_{I,EX}$ for dPS-P2VP within experimental errors.

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