

Neutron Reflectivity Study of Surface and Interfacial Structure in Polymer Thin Films

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Neutron reflectivity was applied for the analysis of surface and interfacial structures of polymer thin films. It was revealed that the fluoroalkylsilyl end groups of polystyrene were preferentially partitioned to the surface, whereas the hydrophilic carboxylate end groups were migrated into the internal bulk region. Also, it was revealed that the surface concentration of chain ends was strongly dependent on the environment. In the case of miscible blends, NR revealed the surface enrichment of lower surface free energy components. Dynamics at the (polymer/polymer) interface was also studied by NR on the basis of time evolution of interfacial thickness in polymer bilayers at a temperature below its bulk glass transition temperature.

Key words: Neutron reflectivity, polymer thin film, interfacial structure, molecular motion

1. INTRODUCTION

Surface and interface structures of polymer thin films play an important role in various technological applications such as friction control, wettability control, adhesion, biocompatibility, etc. Nevertheless, precise analyses of the surface structure, particularly, the compositional distribution along the thickness direction and the buried interface have not been systematically studied yet. Neutron reflectivity (NR) is one of promising and potential methods to characterize the structural change along the thickness direction,[1] since a part of polymer or one of the components can be labeled by deuterium. The purpose of this paper is to summarize how to analyze surface and interface structures by NR.

2. EXPERIMENTAL

NR measurements were performed using the multilayer interferometer for neutrons (C3-1-2-2, MINE) at the Institute for Solid State Physics, the University of Tokyo[2] and ARISA (Advanced Reflectometer for Interface and Surface Analysis) at KENS pulsed spallation neutron source.[3]

MINE has a θ vs. 2θ scattering geometry with the incident neutrons with the wavelength of 1.26 nm and a resolution of 5.1%.

On the other hand, ARISA has a vertical scattering-plane geometry and uses white neutrons with a broad band wavelength, λ , so that it can cover wide range of neutron momentum transfer, $q_z (=4\pi/\lambda)\sin\theta$, in the vertical direction at one incident angle, θ .

The reflectivity was calculated on the basis of the scattering length density profile along the depth direction by using Spreadsheet Environmental

Reflectivity Fitting.[4]

3. RESULTS AND DISCUSSION

3.1 Chain End Distribution near the Surface in Polymer Film[5]

Manifestation of surface functions for polymeric materials is closely related to its surface aggregation structure and thermal molecular motion. Chain end distribution is one of a key factor to control the surface structure. Also, their distribution might be dependent on the environment. By labeling end group by deuterium, the chain end distribution near the surface under hydrophobic and hydrophilic atmosphere can be analyzed studied by neutron reflectivity.

The polymer used in this study was symmetric (tridecafluoro-1,1,2,2-tetrahydro-octyl)dimethylsilyl-terminated poly(styrene- d_8 -block-styrene- d_8 -block-styrene- d_8) triblock copolymer [R_f -P(dSt-St-dSt)- R_f] synthesized via living anionic polymerization. The number average molecular weight (M_n), the molecular weight dispersity (M_w/M_n), PS weight fraction, and functionality was 25.7k, 1.09, 0.74, and 2.02, respectively. The two R_f -P(dSt-St-dSt)- R_f films were coated from a toluene solution onto silicon wafers with native oxide layer by a spin-coated method, and then annealed at 423 K for 24 hrs under vacuum in order to remove any sample preparation history. One of the films was further annealed under water vapor atmosphere at 373 K. At that time, the relative humidity was 100%. NR measurements were made with MINE.

Figure 1 shows the scattering vector, q , dependence of neutron reflectivity for the R_f -P(dSt-St-dSt)- R_f films annealed under vacuum and water vapor. The solid

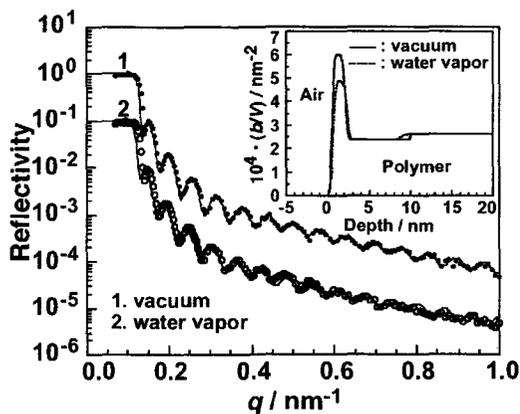


Fig.1 The scattering vector, q , dependence of reflectivity for the R_f -P(dSt-St-dSt)- R_f films. The inset shows the model scattering length density, (b/V) , profiles along the direction perpendicular to the film surface.

curves denote the best-fitted reflectivity calculated on the basis of model scattering length density, (b/V) , profile along the direction normal to the surface shown in the inset. The (b/V) values for dPS and PS were postulated to be 6.46×10^{-4} and $1.41 \times 10^{-4} \text{ nm}^{-2}$, respectively. Since both (b/V) values at the surface were higher than that of its interior region, it seems reasonable to consider that fluoroalkylsilyl end groups are preferentially partitioned to the surface. Also, the surface concentration of chain ends is strongly dependent on the environment such as vacuum and water vapor.

3.2 Interfacial Composition in Blend Films of Polystyrene and Poly(vinyl methyl ether) [6]

Surface segregation in miscible polymer blends composed of deuterated polystyrene (dPS) and polystyrene (hPS) with hydrophilic and hydrophobic chain end groups was examined by ARISA reflectometer.

hPSs used in this study were carboxy-acid-terminated polystyrene (α,ω -hPS(COOH)₂) and fluoroalkylsilyl-terminated one (α,ω -hPS(R_f)₂). Figure 2 shows NR curves for the ($\text{dPS}/\alpha,\omega$ -hPS(COOH)₂) and ($\text{dPS}/\alpha,\omega$ -hPS(R_f)₂) blend films annealed at 393 K for 36 h. The inset illustrates the (b/V) profiles along the normal to the surface to obtain the best-fit calculated reflectivity. From the inset, it is clear that in the case of the ($\text{dPS}/\alpha,\omega$ -hPS(COOH)₂) blend film, the surface dPS fraction was higher than the bulk one. On the other hand, in the case of the ($\text{dPS}/\alpha,\omega$ -hPS(R_f)₂) blend film, the α,ω -hPS(R_f)₂ was preferentially segregated at the surface. These results make it clear that chain end chemistry is an important factor for the surface segregation in miscible polymer blend films.

Surface and interfacial chemical compositions in miscible blends of monodisperse dPS and poly(vinyl methyl ether) (PVME) were studied as well. In the case of symmetric blends in terms of degree of polymerization, N , PVME and dPS were preferentially

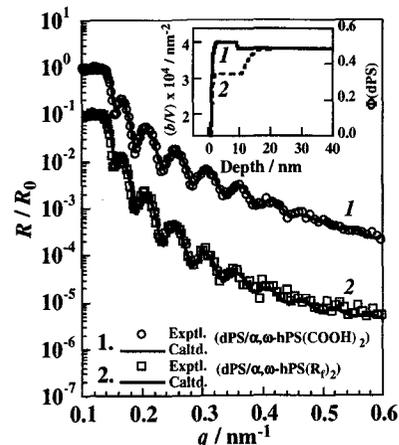


Fig.2 Neutron reflectivity curves for ($\text{dPS}/\alpha,\omega$ -hPS(COOH)₂) and ($\text{dPS}/\alpha,\omega$ -hPS(R_f)₂) blend films annealed at 393 K for 36 h. The inset is scattering length density, (b/V) profiles along the normal to the surface.

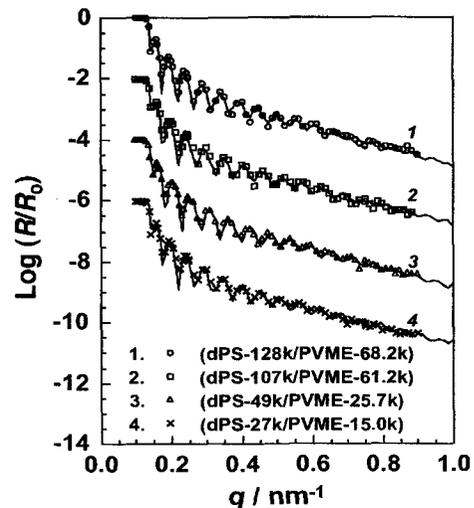


Fig.3 NR profiles for symmetric dPS/PVME blend films with different M_n pairs. Experimental data sets are shown by symbols. Solid curves depict the best-fit ones calculated from model scattering length density profiles, which are shown in Figure 4.

segregated at the film surface and the interface with a silicon wafer, respectively, to minimize free energy of the system. The concentration profile near the surface obtained by experiments was consistent with a mean-field prediction.

Figure 3 shows the q dependence of neutron reflectivity for the dPS/PVME blend films. Each film thickness was fixed to be about 110 nm. The solid curves denote the best-fit calculated reflectivity to the experimental data based on the model (b/V) profiles, as shown in the inset of Figure 3. Since the calculated curves are in good agreement with the experimental data, it can be claimed that the model (b/V) profiles well reflect to the compositional changes in the blend films

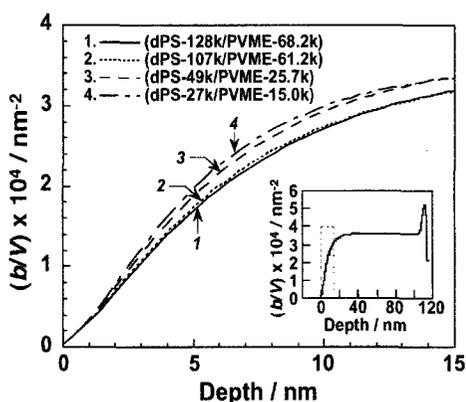


Fig.4 Enlarged scattering length density profiles near the surface region for symmetric dPS/PVME blend films. The inset figure shows the whole profile of dPS-128k/PVME-68.2k blend film as a typical example.

along normal to the surface. For PVME, the (b/V) value of $3.40 \times 10^{-5} \text{ nm}^{-2}$ was used. The PVME fraction exponentially decayed with increasing depth in the surface region and eventually reached the bulk value, whereas dPS was enriched at the polymer/substrate interface. This result can be simply explained in terms of minimization of free energy at the both of surface and interface.

3.3 Time Evolution of Interfacial Thickness in Polymer Bilayers below Its Bulk Glass Transition Temperature [7]

Surface mobility in polystyrene (hPS) films was studied by neutron reflectivity (NR) using (hPS/deuterated PS) bilayer films. When the bilayer was annealed at a temperature above bulk glass transition temperature, T_g^b , the interfacial thickening was well expressed by Fickian diffusion. On the other hand, at a temperature above surface glass transition temperature, T_g^s , and below T_g^b , the interface monotonically thickened with the time at first, and then, turned to be independent. This means that chains went across the “mobile” interface and then reached the “dead” bulk region in which the diffusivity should be frozen.

Bilayers composed of hPS and dPS with the number-average molecular weight, M_n , of 190k were used. NR measurements were made with MINE. Figure 5 shows the NR curves for the bilayer film annealed at 365 K for various times. The solid lines denote the best-fit calculated reflectivity to the experimental one based on model (b/V) profiles normal to the surface shown in Figure 6. Since the calculated curves are in good agreement with the experimental data, it can be claimed that the model (b/V) profiles correspond well to the composition profiles in the bilayer film along the direction perpendicular to the surface. When the annealing time increased, the bilayer interface broadened out, resulting in gradual loss of the sharpness for higher order fringes on the reflectivity curves. The interfacial thickness monotonically increased with the annealing, and then,

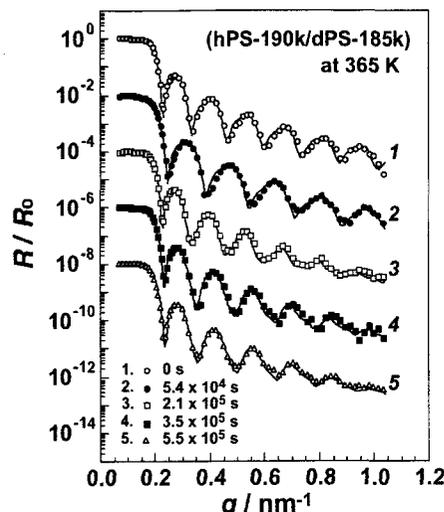


Fig.5 NR curves of the as-prepared (hPS-190k/dPS-185k) bilayer and annealed ones at 365 K for various times.

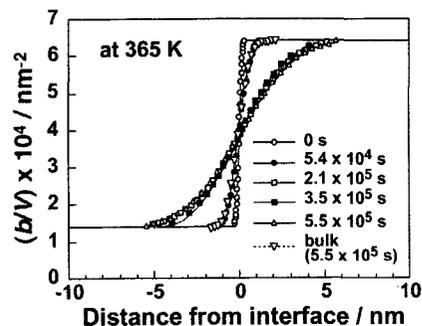


Fig. 6 Scattering length density profiles at the as-prepared (hPS-190k/dPS-185k) interface and annealed ones at 365 K for various times.

reached a constant value of 4.7 nm at 5.5×10^5 s. Using the bulk diffusion coefficient being under the same condition, temperature and M_n , after 5.5×10^5 s, the interfacial broadening was predicted by open reverse triangles in Figure 6. This exhibits visibly how the surface layer is mobile in comparison with the bulk.

4. CONCLUSIONS

NR technique has successfully applied to examine surface and interfacial structure on nanometer scale. Especially, buried structure at interfaces could be clearly seen by the technique. This may not be the case for usual spectroscopy.

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