

Interfacial Width in Polymer Bilayer Films Prepared by Double-Spin-Coating and Flotation Methods

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ABSTRACT A spin-coating method with the aid of selective solvents has been used to construct multilayer structures for organic devices under the assumption that the solvents do not invade a preformed structure. To confirm the assumption, we examined the interfacial width (λ_i) of model polymer bilayers, composed of polystyrene and perdeuterated poly(methyl methacrylate), prepared by spin-coating and flotation methods. Neutron reflectivity measurements revealed that the λ_i value was larger for the spin-coating method than for the flotation method. These results cast doubt on the validity of the assumption. This knowledge should be kept in mind when this method is applied to construct multilayer structures.

KEYWORDS: interfacial width • bilayer • spin coating • flotation • neutron reflectivity

Organic devices, having the advantages of flexibility and light weight, have received a great deal of interest in the domains of academia and industry. This trend can be seen in recent progress in the development of organic “multilayer” devices such as organic field effect transistors (1), organic light-emitting diodes (2, 3), and organic thin solar cells (4, 5). These devices have been prepared by traditional vacuum deposition and vapor-deposition methods (6), which require expensive equipment, resulting in high fabrication costs. In addition, those vacuum techniques are unlikely to scale well to a large area fabrication. On the other hand, solution processes such as spin coating, dip coating, and inkjet printing can be easily applied for purposes in any laboratory with simple and inexpensive instruments. In addition, an intriguing advantage of solution processing is that a large area substrate can be coated, leading to higher throughput.

Spin coating from a polymer solution onto a substrate is probably the most popular and well-established solution processing method. To apply the method to the preparation of multilayers, one layer is supposed to directly coat another layer preformed using a selective solvent. Here, a selective solvent means one that can dissolve the polymer to be coated but does not dissolve polymers already present on the substrate. That is, the application of the method to multilayers assumes that the process does not affect preformed structures or lead to retention of the solvent.

We have previously studied the density profiles of a perdeuterated poly(methyl methacrylate) (dPMMA) film in various nonsolvents along the direction normal to the interface by specular neutron reflectivity (NR) (7). The original definition of “nonsolvent” is that the liquid cannot dissolve macroscopic amounts of a polymer. However, careful analysis of the interface for dPMMA with the nonsolvents revealed that the interfaces were much more diffuse than the pristine interface with air. Presumably, such a diffuse interface with the nonsolvents results from interfacial roughening and swelling of segments at the outermost region of the film (7). If this is always the case, the aforementioned assumption related to spin coating used to prepare multilayers may not hold. Because the functionality of the organic devices is strongly related to that of the interfacial structures between layers, it is of pivotal importance to know to what extent, if at all, the actual interface produced by spin coating differs from the ideal.

In this study, the interfacial widths (λ_i) for polymer bilayers, which are the simplest case of a multilayer, prepared by both spin-coating and flotation methods are precisely examined by NR measurements and compared with each other.

We here chose to study a mixture of the polymers polystyrene (hPS) and dPMMA because it has been extensively studied and is thus well understood (8–11). Mono-disperse hPS and dPMMA with number-average molecular weights of 54K and 49K, respectively, were purchased from Polymer Source Inc.; they are immiscible over the temperature range employed. As the bottom layer, films of dPMMA were spin-coated from a toluene solution onto silicon wafers with a native oxide layer. The films were dried under an ambient atmosphere at room temperature for more than 24 h and then annealed under vacuum at

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423 K for at least 24 h. This temperature was higher than the glass transition temperature of dPMMA. The film thicknesses, evaluated by ellipsometry, were ca. 50 nm. Then, the top layers of hPS were put onto them in two different ways: by spin coating or by flotation. In the former case, the second spin coating was made from a cyclohexane solution of hPS, namely, double spin coating. It is widely accepted that cyclohexane does not dissolve macroscopic amounts of dPMMA (12). In the latter case, a hPS film was spin-coated from a toluene solution onto a silicon wafer, and then the hPS film was scored with a blade and floated off onto the surface of purified water. Next, it was transferred onto the dPMMA film by attaching it from the air side, resulting in the bilayer interface. The thickness of the top hPS layers for both cases was approximately 55 nm. The bilayers so prepared were dried under vacuum at room temperature for more than 24 h to remove adsorbed water and residual solvent.

NR was applied to the hPS/dPMMA bilayer films, before and after annealing under vacuum at 413 K for 6 h, using a multilayer interferometer for neutrons (C3-1-2-2, MINE) (13) at the Institute for Solid State Physics, The University of Tokyo, Tokyo, Japan. The reflectivity was calculated on the basis of the scattering length density (b/V) profile along the depth direction using *Parratt32*, which is freeware from the Hahn-Meitner Institute (14). In the fitting, the b/V values for silicon, the native oxide layer, dPMMA, and hPS were taken as 2.21×10^{-4} , 4.18×10^{-4} , 6.62×10^{-4} , and $1.43 \times 10^{-7} \text{ nm}^{-2}$, respectively.

Panels a and b of Figure 1 show the scattering vector [$q = (4\pi/\lambda) \sin \theta$, where λ and θ are the wavelength and the incident angle of the neutrons, respectively] dependence of NR for the hPS/dPMMA bilayers before annealing. Panel b covers a restricted q range from 0.6 to 1.0 nm^{-1} for the double-spin-coated bilayer. Open circles and triangles denote the experimental data for the bilayers prepared by the flotation and double-spin-coating methods. For clarity, the data set for the double-spin-coated bilayer is offset by 2 decades. The different periodicities of the fringes as a function of q in the two samples are simply due to the sample thicknesses not being exactly the same. The interfacial profiles were estimated by fitting the reflectivity curve, calculated on the basis of a model b/V profile along the direction normal to the surface, to the NR data. The model is composed of air, hPS, dPMMA, and silicon substrates, as illustrated in panel c of Figure 1. The thicknesses of the top hPS layers mounted by the flotation and double-spin-coating methods were 60.9 and 54.7 nm, respectively. Also, the value for the bottom dPMMA layers was respectively 53.7 and 50.0 nm for the flotation and double-spin-coating samples. These values were in good accordance with those by ellipsometry. The air/hPS and dPMMA/substrate interfaces are simply expressed by Gaussian roughness (σ_1 and σ_2). Our main interest in the model is the interfacial width (λ_i) between the hPS and dPMMA layers modeled as a hyperbolic tangent function rather than an error function (15).

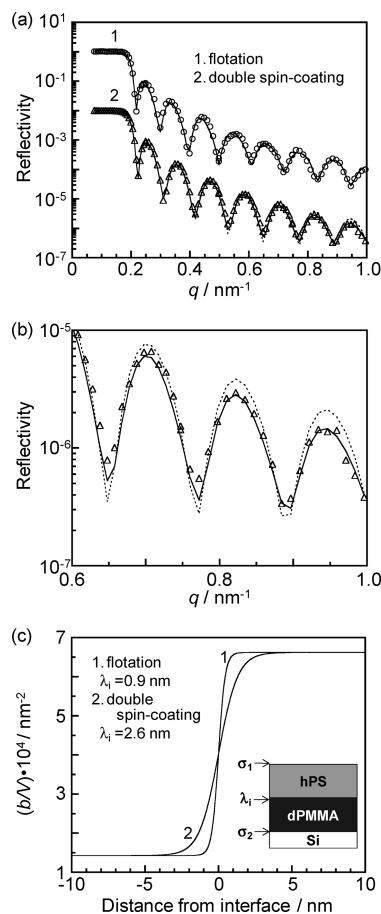


FIGURE 1. (a) NR data for as-prepared hPS/dPMMA bilayers made by flotation and double-spin-coating methods. Open circles and triangles depict experimental data, and solid lines are the reflectivity calculated on the basis of scattering length density profiles. For clarity, the data for the double-spin-coated bilayer are offset by 2 decades. (b) Data for the double-spin-coated bilayer in the q range from 0.6 to 1.0 nm^{-1} . The dotted line is the reflectivity calculated with a value of λ_i of 0.9 nm. (c) Model b/V profiles near the interface between hPS and dPMMA in the flotation and double-spin-coated bilayers. The schematic illustration in the panel denotes the model used for the analysis.

Thus, the b/V profile at the interface is given by

$$b/V = \frac{(b/V)_{\text{dPMMA}} - (b/V)_{\text{hPS}}}{2} \tanh\left(\frac{z}{\lambda_i/2}\right) + \frac{(b/V)_{\text{dPMMA}} + (b/V)_{\text{hPS}}}{2}$$

where $(b/V)_{\text{dPMMA}}$ and $(b/V)_{\text{hPS}}$ are the scattering length densities of dPMMA and hPS, respectively, and z is the distance from the interface. The solid curves in Figure 1a are the best fits to the experimental results. Panel c displays the interfacial region of the best model b/V profile; the λ_i values for the flotation and double-spin-coating bilayers were 0.9 and 2.6 nm, respectively.

To confirm whether the interface for the double-spin-coated bilayer is truly broader than that made by flotation, the reflectivity curve calculated with a value of λ_i of 0.9 nm, without changing other parameters, was superimposed onto the corresponding experimental result. Figure 1b clearly

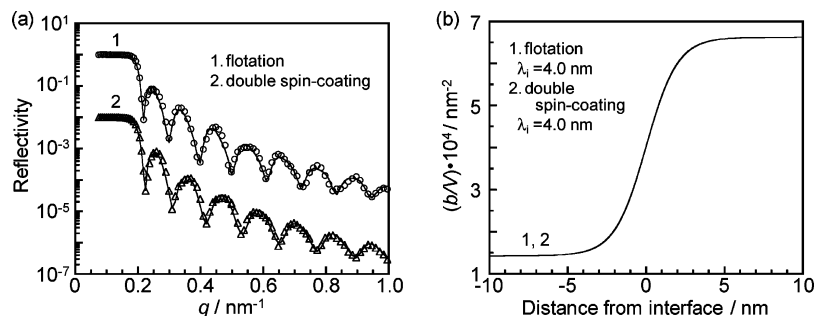


FIGURE 2. (a) NR data for the flotation and double-spin-coated hPS/dPMMA bilayers after annealing under vacuum at 413 K for 6 h. Open circles and triangles depict experimental data, and solid lines are the reflectivity calculated on the basis of scattering length density profiles. For clarity, the data for the double-spin-coated bilayer are offset by 2 decades. (b) Model b/V profiles near the interface between hPS and dPMMA in the flotation and double-spin-coated bilayers.

shows that, while the dotted calculated curve fits the experiment well in the low- q region, it fits poorly in the q region greater than 0.6 nm^{-1} . Taking into account that the data at a higher q region reflects the fine structure of the sample, the fitting result is quite reasonable. Thus, it appears that the interface between hPS and dPMMA in the as-prepared double-spin-coated bilayer is definitely broader than that produced by the flotation method, a fact that practitioners of multiple spin coating should keep in mind.

Panel a of Figure 2 shows the q dependence of reflectivity for the bilayers after annealing. Circles and triangles correspond to the flotation and double-spin-coating bilayers. The data for the double-spin-coating bilayer are again offset by 2 decades. The solid curves are the best-fit reflectivity calculated on the basis of the model b/V profiles shown in panel b. The λ_i values for the interface between hPS and dPMMA in the flotation and double-spin-coated bilayers were both 4.0 nm. Other groups have reported slightly larger values of λ_i between PS and PMMA, $5 \pm 1 \text{ nm}$ (8–11, 16).

We now turn to a discussion of the width of the interface between immiscible polymers in a quasi-equilibrium state. The miscibility of a polymer pair is generally judged on the basis of the value of $\chi_{\text{FH}}N$, where χ_{FH} and N are the Flory–Huggins parameter and degree of polymerization. Using the temperature dependence of the χ_{FH} parameter suggested by Russell (17), the χ_{FH} value for our system at 413 K is calculated to be 0.0369. Because the value of $\chi_{\text{FH}}N$ is 18.0 and is much larger than the critical value of 10.5 (18), it is clear that our system is in the strong segregation limit. Thus, the Helfand–Tagami theory can be used to estimate the interfacial width (λ_{HT}). According to them, λ_{HT} is given by $2b/(6\chi_{\text{FH}})^{1/2}$, where b is the Kuhn statistical segment length (15). The values of b are 0.68 nm for PS (19) and 0.74 nm for PMMA (20) at room temperature and 0.67 nm for PS and 0.65 nm for PMMA at our annealing temperature of 413 K (21). From these values, we obtained $\lambda_{\text{HT}} = 2.8 \text{ nm}$, a value that was much smaller than the one that we obtained experimentally. The most plausible explanation is that the experimental value of λ_i includes a contribution from thermally excited capillary waves.

Sferrazza et al. have proposed that the contributions to the interfacial width for thin bilayers of deuterated PS and PMMA, due to the intrinsic interface ($=\lambda_{\text{HT}}$) and due to

capillary wave broadening, are combined with Gaussian quadrature (11). Thus, λ_i can be written as follows:

$$\lambda_i^2 = \lambda_{\text{HT}}^2 + |\sqrt{2\pi}\sigma_{\text{cw}}|^2$$

where σ_{cw} is the capillary-wave contribution to the observed width given by

$$\sigma_{\text{cw}} = \left(\frac{k_{\text{B}}T}{4\pi\gamma} \ln \frac{[2\pi/(\lambda_{\text{HT}}/\sqrt{2\pi})]^2}{(2\pi/\lambda_{\text{coeh}})^2 + (2\pi/a_{\text{dis}})^2} \right)^{1/2}$$

where k_{B} and T are the Boltzmann constant and annealing temperature, respectively. The quantities γ and λ_{coeh} are the interfacial energy between PS and PMMA and the in-plane coherence length of the neutrons. With respect to these parameters, we adopted the same values as those described in their paper (11). The quantity a_{dis} is the dispersive capillary length given by

$$a_{\text{dis}} = \left(\frac{4\pi\gamma l^4}{A} \right)^{1/2}$$

where l is the thickness of the top hPS layer and A is the Hamaker constant for the dPMMA interacting with air across the hPS layer, estimated as $2 \times 10^{-20} \text{ J}$. We finally obtained a value of 4.1 nm for λ_i following this approach, a result almost completely consistent with our experimental results of 4.0 nm for the flotation and double-spin-coating methods. This result suggests that, as expected, the interface between polymers in the bilayers is unaffected by the method of preparation but conforms to the thermodynamic outcome if the sample has been sufficiently annealed to be in a quasi-equilibrium state.

In conclusion, we have used NR to investigate any differences in the interfacial width of the hPS/dPMMA bilayers prepared by two methods: double spin coating and flotation. In the case of as-prepared bilayers, the interfacial width was broader for the double-spin-coated sample than for the flotation sample. This implies that the solvent affects the preformed structure during the second spin coating, even when using a nonsolvent. Once the bilayers were annealed

at a temperature above the glass transition temperature, the discrepancy in the interfacial width for the two bilayers disappeared. A calculated value of the interfacial width for the quasi-equilibrium bilayers, including the contribution of capillary waves, was in good accordance with the experiment. The results of this study should be useful to researchers who frequently use double/multiple spin coating to construct multilayer structures.

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