After irradiation with a strong light, the heat-treated sample had a dark current five times higher than that before irradiation with the *n* value of 1.0. In contrast, the original sample showed only a slightly higher dark current after irradiation with the *n* value of 1.4. Since the dark current of the heat-treated film after irradiation was ohmic, the persistent conductivity in the heat-treated sample may be related to a phase-separation structure different from that reported by Abkowitz et al.[6] In the heat-treated sample, each carrier is in a different phase and has a longer lifetime than in a homogeneous system, because the recombination of carriers can occur only in the interfacial EDA complex layer. This situation could account for the persistent conductivity of the heat-treated sample.

Registry No. (I)(II) (copolymer), 114563-27-8; I (homopolymer), 71356-19-9; II (homopolymer), 82008-07-9.

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Specular Reflectivity of Neutrons by Thin Polymer Films

Introduction. The reflectivity of neutrons provides a novel means of investigating a wide range of surface and interfacial phenomena with a spatial resolution that is on the nanometer size scale. Neutron reflectivity is emerging as a technique that can quantitatively address segment density depth profiles by simple isotopic substitution of light hydrogen by deuterium. Only recently has the utility of this technique in polymer science been realized. For example, Jannink and co-workers[1,2] have used the reflection of neutrons to evaluate the concentration profile of polymer segments in solution near the air–solution interface. There have also been preliminary reports on block copolymer solutions[3] and immiscible polymer bilayers.[4,5] In the present paper, we report the application of specular neutron reflection to investigate the interdiffusion of two layers, composed of polymer molecules where one of the polymers is deuteriated and the other is protonated.

Two different samples were studied. The first sample was a bilayer composed of deuteriated polystyrene on the top of protonated polystyrene; the latter layer was deposited on an optical flat of fused silica. The object here was not only to measure the segment profile for the specimen as prepared but to observe its evolution following an annealing treatment. The second sample consisted of a deuteriated/protonated bilayer of polyimide on fused silica.

Neutron Reflectivity. Neutron reflectivity principles have been extensively treated in the literature.[6] It is sufficient here to recall a few concepts to clarify which quantities can be obtained for the problem at hand. The neutron reflectivity profile is solely a function of the component of the neutron momentum perpendicular to the film:

$$q_{z0} = (2\pi/\lambda)\sin\theta \tag{1}$$

where θ is the angle of incidence of the neutron beam with the surface and λ is the neutron wavelength. In a medium composed of nuclei with neutron scattering amplitudes[7] b in a volume[8] V,q_{z0} is modified such that

$$q_{zi} = (q_{z0}^2 - 4\pi b/V)^{1/2} \tag{2}$$

The component of the neutron momentum parallel to the surface is identical with that in vacuum. For this reason the reflectivity process can be described in terms of the one-dimensional motion of a particle in a potential. The problem of finding the potential from the reflecitivity is nothing but the well-known "inverse problem" in quantum mechanics. The reflectivity cannot be described in an explicit form except for a few analytical forms of the potential; the simplest of which is a histogram of layers of different thicknesses and different refractive indices to which the effective profile can be approximated. The reflectance at the boundary between the *i*th and (*i* + 1)th layers is

$$r_{i,i+1} = \frac{q_{z,i} - q_{z,i+1}}{q_{z,i} + q_{z,i+1}} \tag{3}$$

and the total reflectance of the system r_t is a suitable combination of the products of the reflectances at the single boundaries. In our case the system is vacuum/deuteriated polymer/hydrogenated polymer/silica; the reflectance takes the form[9]

$$r_t = [r_{01} + r_{12}\exp(2iq_{z1}d_1) + r_{23}\exp(2i(q_{z1}d_1 + q_{z2}d_2)) + r_{01}r_{12}r_{23}\exp(2iq_{z2}d_2)]/[1 + r_{01}r_{12}\exp(2iq_{z1}d_1) + r_{12}r_{23}\exp(2iq_{z2}d_2) + r_{01}r_{23}\exp(2i(q_{z1}d_1 + q_{z2}d_2))] \tag{4}$$

where d_i is the thickness of layer i.

Using tabulated values for b and V, we obtain (for a bilayer of polystyrene) $(b/V)_{PSD} = 6.1 \times 10^{10}$ cm^{-2}, $(b/V)_{PSH} = 1.4 \times 10^{10}$ cm^{-2}, and $(b/V)_{silica} = 3.48 \times 10^{10}$ cm^{-2}. The strongest reflectances occur at the front and back faces of the deuteriated layer. Hence, to a first approximation we can simply substitute the real system by a layer of deuteriated polystyrene over an infinitely thick layer of protonated polystyrene. For real values of q_{z1}, the reflectivity takes the simple form[10]

$$R = r_t^2 \simeq \frac{r_{01}^2 + r_{12}^2 + 2r_{01}r_{12}\cos(2q_{z1}d_1)}{1 + r_{01}^2r_{12}^2 + 2r_{01}r_{12}\cos(2q_{z1}d_1)} \tag{5}$$

Equation 5 gives basically an interference function in

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which the thickness of the deuteriated layer d is easily obtained from the q_{z0} values of the maxima and minima. The larger is the thickness d, the shorter is the period of the oscillations. Up to now we have considered sharp interfaces. The smearing of an interface into a layer of finite thickness with graded density has, in general, the effect of lowering the reflectivity from its ideal values. Whatever the sequence of layers, if all interfaces are sharp, the reflectivity, multiplied by q_{z0}^4, oscillates around a constant value at large q_{z0}. If there is disorder or roughness and the interface is rough over a mean-squared thickness $\langle z^2\rangle$ with a distribution that we assume to be Gaussian, then at the boundary between the ith and $(i + 1)$th layers the effective reflectance is modified from the ideal form by

$$(r_{i,i+1})_{\text{eff}} = (r_{i,i+1})_{\text{ideal}} \exp(-2q_iq_{i+1}\langle z^2\rangle) \tag{6}$$

This equation is rigorous for the surface only[11] but is valid numerically for the other interfaces if the interface thickness is significantly smaller than that of the adjacent layers. Although it is rather simple to reveal the presence of diffuse interfaces in the system, it is considerably more difficult to pinpoint which interface is diffuse even in simple cases, like that described by eq 5. In fact, for the totally symmetric case, where $r_2 = -r_1$, substitution into eq 5 and 6 shows that is impossible to distinguish between a diffuse front face and a diffuse back face of the deuteriated layer.

Once the data are analyzed on the basis of the single deuteriated layer, yielding a thickness d_1, the more complete model should be adopted, and the reflectance has the more complex form given by eq 6. In practice, however, the value of d_1 does not need to be readjusted if the total thickness of the polymer on the glass is much larger than that of the deuteriated polymer. This is because the next highest term in the reflectivity is $r_{01}r_{23} \cos(2(q_{z1}d_1 + q_{z2}d_2))$, whose rapid oscillations do not alter the deep minima associated with the deuteriated layer. Also, in the analysis, even the effective scattering amplitudes of the layers can be adjusted. However, the relative amplitudes are readily assessed from the relative heights of the interference patterns to which they are associated. The absolute magnitude depends on the precision in determining the glancing neutron angle θ.

In conclusion, the analysis of the data is done starting with a model that is reasonable to expect, as, for example, a deuteriated layer on a protonated layer. The model is then treated in such a way to obtain in a hierarchical manner the thickness of the deuteriated layer, the sharpness of its interfaces, the thickness of the protonated layer, and the relative scattering amplitudes of the two layers. Of course, this is not a many-parameters least-square fitting method: for this highly nonlinear transformation, a suitable and reliable least-square procedure has not yet been found. Instead, by the present "hierarchical" method, fairly complex profiles have been determined on metallic films, which were later confirmed by independent techniques such as Rutherford backscattering and X-ray fluorescence.[12]

Experimental Section. The first sample used in this study was prepared by solvent casting a protonated PS film ($M_w = 1 \times 10^7$; $M_w/M_n = 1.15$) from toluene onto a fused silica substrate. The thickness of this layer was ca. 1×10^3 Å with a diameter of 5 cm. The film was then annealed at 120 °C for 4 h to remove solvent and to minimize molecular orientation with respect to the substrate. A 350-Å-thick film of predeuteriated PS ($M_w = 2 \times 10^5$; $M_w/M_n = 1.05$) was prepared from a toluene solution onto a 5.0×7.5 cm^2 glass microscope slide. After evaporation of the solvent, the sides of the microscope slide were scored and the film was floated off onto a pool of water. The substrate with the protonated film was then used to pick up the deuteriated film, thus making a bilayered specimen. The bilayer on the substrate was evacuated at room temperature to remove residual water and air bubbles that may have been present between the films.

Table I
Reflectivity Profile Fitting Parameters

sample	as prepared	5 min at 140 °C
PSD thickness, Å	320 ± 5	185 ± 5
PSD $b/V \times 10^{-10}$ cm^{-2}	6.1 ± 0.1	6.6 ± 0.1
interface thickness, Å	60 ± 20	80 ± 20
PSH thickness, Å	1120.0 ± 200	1240.0 ± 50
PSH $b/V \times 10^{-10}$ cm^{-2}	1.9 ± 0.1	2.4 ± 0.1

Following the neutron reflectivity experiment at room temperature, the specimen was annealed for 5 min in an oven preheated to 140 °C. Due to the thickness of the substrate (ca. 1 cm) the effective temperature and time of annealing might have been slightly different from the nominal value. The substrate needed to be thick so that it could be polished flat and stay flat during the heat treatments as well as during the neutron reflection measurements.

In a second study a specimen was prepared consisting of a thin film of aromatic polyamic acid prepared from the condensation of pyromellitic dianhydride with oxydianiline. A film of the protonated polymer was spin coated onto a fused silica substrate from an N-methylpyrollidinone solution. The film was then heated to 400 °C for $^1/_2$ h to fully convert the polyamic acid to the corresponding polyimide. A second layer of perdeuteriated polyamic acid was spin coated on top of the existing protonated layer. This bilayered specimen was then heated to 400 °C for $^1/_2$ h to convert the perdeuteriated polyamic acid to the polyimide. Under these conditions the extent of interpenetration of the two layers, as measured by forward recoil spectrometry, had been found to be small and in fact at the limit of the instrumental resolution of the forward recoil spectrometry measurements.[13]

The neutron reflectivity measurements were performed at the Intense Pulsed Neutron Source at Argonne National Laboratory. The instrument, used primarily for polarized neutron reflection studies of magnetic layers, has been discussed in detail elsewhere.[14] Briefly, a collimated (0.01°) beam of cold neutrons impinged upon the surface of the bilayered sample at a glancing angle of a fraction of a degree. The transmitted and reflected beams were detected with a two-dimensional position-sensitive detector which was a microchannel plate with integral photocathode and resistive anode readout. A lithium glass scintillator placed before the fiber optic faceplate served to make the detector neutron sensitive. The full sensitive area of the detector was 25 mm and the angular range of acceptance could be changed by translation of the detector. Due to the pulsed nature of the neutron source, the measurements were taken in time-of-flight, utilizing a large spectrum of neutron wavelengths (4.0–12 Å) to cover an adequate range of q_{z0} (cf. eq 1). When an even larger region was needed, reflectivity measurements were taken at two different angles and then spliced together.

Results and Discussion. The reflectivity profiles of the PS bilayer before and after heating are shown in parts a and b of Figure 1, respectively. The fits, which are presented in the figures as solid lines, were obtained for the scattering length density depth profiles in real space described by the parameters in Table I. Comparison of the scattering length densities calculated for bulk PS and

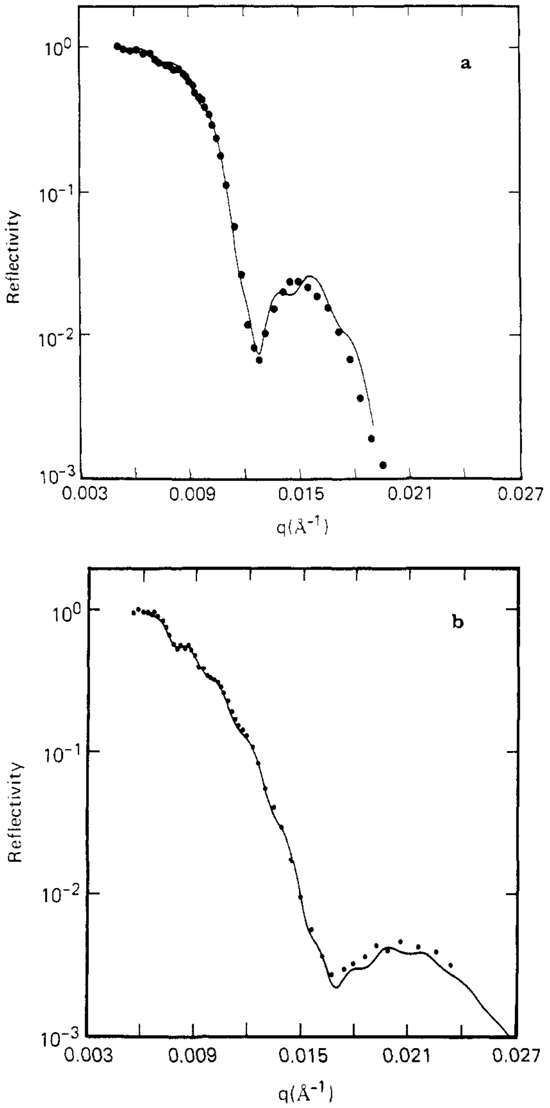

Figure 1. Reflectivity profiles of a bilayer of deuteriated and protonated polystyrene on a fused silica substrate. The molecular weights of the deuteriated and protonated polymer are 2×10^5 and 1×10^7, respectively. In (a) the reflectivity profile for the specimen as prepared is shown and in (b) is shown the reflectivity profile for the specimen after heating to 140 °C for 5 min. The solid lines are the calculated reflectivity profiles described by the sets of parameters in Table I.

those used in the calculations show close agreement for the as-prepared bilayer specimens. Thus, to within experimental errors the initial bilayered specimen is essentially a 320-Å layer of deuteriated PS on top of a 1120-Å layer of protonated PS with densities close to the bulk values. The apparent interface between the two layers has a thickness of 60 Å. Analysis of the reflectivity profile of the specimen that was annealed at 140 °C for 300 s shows that while the total thickness of the bilayered sample remained constant the thickness of the deuteriated layer has decreased by 120 Å.

The interface between the layers has not changed substantially during the course of the annealing. The slight overall increase in the scattering length density of the deuteriated layer might be due, in part, to an imperfect calibration of the glancing angle (cf. eq 1 and 2). The relative scattering amplitudes (to which the error limits in Table I refer) indicate that some of the deuteriated polymer has diffused into the "protonated" layer but, in contrast, there has been little or no diffusion of the protonated polymer into the "deuteriated" layer. In short, as a result of the heat treatment, the protonated layer has been swollen by the deuteriated polymer but a sharp interface between the layers has been maintained.

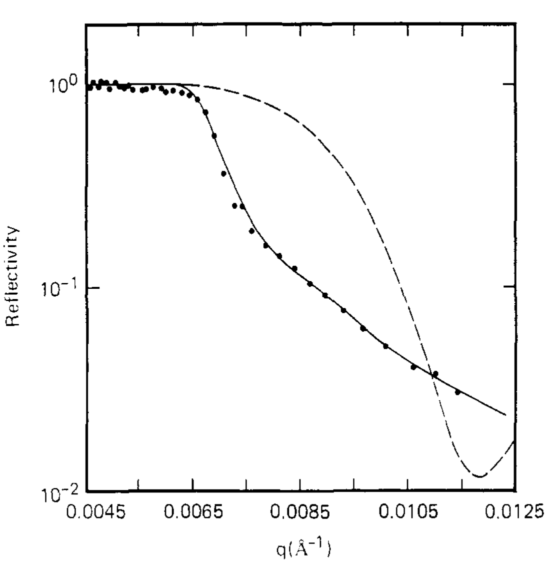

Figure 2. Reflectivity curve of an aromatic polyimide sample prepared by casting a protonated polyamic acid film onto a fused silica substrate, heating to 400 °C, and then casting a deuteriated polyamic acid film on top of this followed by heating to 400 °C. The final heating converted the amic acid to the corresponding polyimide and allowed interdiffusion to occur. The dashed line is calculated for a well-defined deuteriated layer of 70 Å on top of a 700-Å-thick protonated film. The solid line is obtained by incorporating a concentration gradient between the layers as described in the text.

The question arises whether these results are consistent with present knowledge of the polymers. The motion of the interface has been predicted and demonstrated[15,16] to occur when the two polymers have different molecular weights. In our case, the molecular weights of the polymers are drastically different, with the protonated polymer having a molecular weight that is 50 times greater than that of the deuteriated polymer. The evolution of the concentration profile resulting from the diffusion equation of Green et al.[15,16] shows that the diffusion is markedly asymmetric where the higher molecular weight component absorbs the lower molecular weight component. However, in this process,[15,16] the concentration gradient at the interface becomes progressively broader. This last point is contrary to our observations. The question then arises whether these experiments are truly in the time regime where ordinary diffusion would be expected. The molecular weight of the protonated layer is very large (1×10^7) so that the time allowed for the interdiffusion is short in comparison with the reptation time of the higher molecular weight component.[17-19] In these "short times" for a high molecular weight polymer in the presence of an effective solvent (a much lower molecular weight polymer) a concentration gap is predicted which is maintained even if the interface moves because of a swelling mechanism. This is the behavior that is seen in the present experiment.

For the polyimide sample, the experimental reflectivity cannot be described by a bilayered model with a sharp interface, otherwise the interference pattern would be much more evident (cf. the dashed curve in Figure 2). While the details of the structure cannot be defined unequivocally due to the limited range of q_{z0} studied and the statistics of the experimental data, the data could only be fit, as shown by the solid line in Figure 2, by taking a large region with a concentration gradient. The particular model chosen to fit the data was one where there was a gradient in the concentration of the deuteriated polyimide changing gradually from the fully deuteriated to the fully protonated polyimide over a thickness of 200 Å. Below this region is a layer of purely protonated polyimide approximately 500 Å thick on top of the glass substrate. Notice that it is impossible to decide from reflectivity measurements alone if the concentration gradient is due to roughness at the interface or diffusion. This is because the reflectivity is a function of the density averaged over a plane parallel to the surface and does not provide information on the length of the density–density fluctuations in the plane. These fluctuations cause neutron scattering over an angular region defined by their length. Thus for interdiffusion on the atomic scale the scattering is isotropic, while for fluctuation lengths of the order of a hundred angstroms distinct satellites appear adjacent to the reflected beam.[20–23] With our position-sensitive detector we were unable to detect scattered radiation for these polymeric samples, a scattering component that was well in evidence in some of the metallic samples used in the past.

The results of the two studies presented here show that neutron reflectivity provides a novel, nondestructive means of probing the thickness and the interdiffusion of polymer bilayers with a spatial resolution that is superior to other current techniques. Neutron reflection can be used for testing predictions made on the equilibrium profile of polymers in solutions and in melts. It can also explore the kinetics of polymer diffusion, and test in detail the validity of the present theoretical understanding, either by taking snapshots of the profiles at sufficiently low temperature after repeated annealing or eventually by monitoring in real time the evolution of choice systems.

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Registry No. PS, 9003-53-6; (pyromellitic dianhydride)(oxydianiline) (copolymer), 25038-81-7; (pyromellitic dianhydride)(oxydianiline) (SRU), 39421-28-8; neutron, 12586-31-1.

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