polymer papers

Neutron reflection investigation of the interface between an immiscible polymer pair

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Neutron critical reflection experiments are reported for the interface between polystyrene and poly(methyl methacrylate). It is shown that, contrary to predictions in the literature, the interfacial mixing is not greater than 20 ± 5 Å.

(Keywords: polymer blends; diffusion; neutron critical reflection; interfaces; thin films)

INTRODUCTION

The structure and composition profile of the interface between two polymeric species is of interest currently for a number of reasons. On the one hand, the degree of interfacial mixing between components in a binary mixture has profound significance for the mechanical properties of the resulting material[1,2]. On the other hand, observation of the degree of interfacial mixing at a model interface achieved at chosen temperatures as a function of time provides information about the interdiffusion coefficient of the polymer pair[3–5]. The interdiffusion coefficient depends on both a thermodynamic term involving the Gibbs free energy of mixing and a mobility or transport term, which will itself be determined by the intradiffusion coefficients of the component polymers. There has, moreover, been a recent lively discussion about the theories which predict the appropriate dependence of the mobility term on these intradiffusion coefficients[6–8].

Various techniques have been developed for investigating the composition profile of the model interface[9–12]. In each case the interface is set up between two polymer layers, which may be the pure components or two mixtures of different concentration. The sample is annealed for a given length of time at temperatures above the glass transition temperature of either component and then quenched. In one type of experiment a section is cut through the profile and infra-red spectroscopy[9] or X-ray microanalysis[10] used to scan the composition profile. In other experiments the interface is observed in a bulk sample using scattering of ion beams—both forward recoil scattering (FReS)[13] and Rutherford back-scattering (RBS)[14] have been applied. One of the properties shared by these techniques is a resolution limited to some tens of nanometres. For investigating the short-range detail of the interface they leave something to be desired, although they have been proved very successful in the study of long-range variation in composition[10–12].

It has become evident that the newly developed technique of neutron total reflection is capable of providing information about surfaces on a scale much smaller than is available from these other techniques. The parallel between neutron and optical wave properties, especially with regard to reflection at surfaces, has been extensively studied since the early experiments in 1946 because of its practical importance in such applications as neutron guides[15] or storage of cold neutrons[16,17]. In neutron total reflection experiments information is obtained about the neutron refractive index profile normal to the reflection surface. This refractive index depends on the neutron scattering length density. The neutron scattering length is a nuclear property which varies not only with atomic number but also with isotope. The experiments thus provide a sensitive probe of the chemical composition profile normal to the surface. Together with the use of isotopic substitution, such measurements allow a wide range of interfacial problems to be investigated.

In recent years spectrometers applying reflectometry have been set up both on reactor sources[18,19] and on the recently developed pulsed neutron sources[20,21]. The technique is similar in its resolution to X-ray critical reflection[22] but, because of the large penetration of neutrons, use of these latter is particularly advantageous in the study of solid–solid or solid–liquid interfaces as compared to solid–air interfaces (i.e. surfaces). Early studies included measurements on thin metal films[23,24], 'black' soap films[25] and organic multilayers[26]. More

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recently a wider range of experimental studies have been undertaken and include measurements on adsorbed fatty acid[27] and surfactant[28,29] monolayers, solid multilayers[30], ferromagnetic thin films[31] and polymer–solvent systems[32–34].

Applications to solid polymer systems are more recent[35,36] and to date have been concerned only with the use of intradiffusion probed by examining mixing at an interface between a protonated and deuterated pair of the same polymer, i.e. deuterated polystyrene into hydrogenous polystyrene[35,36] or of perdeuterated polyimide into hydrogenous polyimide[36]. These experiments address the question of the self-diffusion of a polymer within a matrix of its own kind, but not the thermodynamics of polymer–polymer miscibility.

We report here preliminary results from the first series of experiments investigating interfaces between different polymer species. The results highlight the great sensitivity of the technique to the detailed structure of the interface. In this paper we consider the case of an immiscible mixture, polystyrene (PS) with poly(methyl methacrylate) (PMMA)[37,38]

Singh[37] demonstrated the domain microheterogeneity of a PS–PMMA mixture using ultrasonic measurements. These authors also summarize other data supporting the incompatibility including electron micrographs which show two phase structures characteristic of two pure homopolymer phases. The samples used in this work were cast from co-solution in toluene. Some molecular mixing was achieved by other authors when they freeze-dried a co-solution in naphthalene[39]. Helfand and Sapse[39] calculated an interfacial tension and an interfacial thickness for PMMA–PS based on solubility parameters and a mean-field approximation. The interfacial thickness predicted was 160 Å, but the surface tension was very much lower than experimentally determined. Using an empirical relationship between surface tension and interfacial thickness given by Wu[40] a value of 50 Å would be predicted from the measured surface tension. Unreported electron micrographs seem to indicate a much lower value. The suggested interfacial thicknesses are ideally suited to the neutron critical reflection technique and we report here data giving the first measurement of the interface for this mixture. In another paper we report preliminary measurements of the interface in an acknowledged miscible blend.

NEUTRON CRITICAL REFLECTION

The theory of the technique has been described in detail elsewhere. Here we will only outline the principles of the measurement with the aim of relating the experimental observations to parameters arising from surface or interfacial structure.

The phenomenon of total reflection of the neutrons at an interface or surface can be dealt with using the formalism for optical reflection and refraction.

Neutron refractive indices for non-absorbing materials can be expressed as:

$$n = 1 - \lambda^2 Nb/2\pi \qquad (1)$$

where Nb is the neutron scattering length density of the material. Values of n are typically very close to but less than unity, $(1-n)$ being of the order 10^{-6}. As n is approximately equal to unity, for air, total external reflection takes place. From Snell's law we can write an approximate form for the critical glancing angle θ_c as:

$$\theta_c/\lambda = (Nb/\pi)^{1/2} \qquad (2)$$

Reflection of neutrons of a given wavelength from a bulk interface is unity for glancing angles less than θ_c and drops off sharply for larger angles. The shape of the reflectivity curve for $\theta > \theta_c$ is given by Fresnel's law:

$$R = \left| \frac{\sin\theta - (n^2 - \cos^2\theta)^{1/2}}{\sin\theta + (n^2 - \cos^2\theta)^{1/2}} \right|^2 \qquad (3)$$

A typical experimental reflectivity curve is seen in *Figure 1*. Instead of varying θ, the experiment was performed at fixed angle and scanning λ (see equations (2) and (3)). In either method what is in effect measured is the neutron specular reflectivity as a function of the wavevector transfer κ perpendicular to the reflectivity surface:

$$\kappa = (4\pi \sin\theta)/\lambda \qquad (4)$$

where θ is the reflection angle and λ is the neutron wavelength.

Neutrons are specularly reflected in the same way as light polarized perpendicular to the plane of reflection[41]. Hence the standard and well established methods used to calculate optical reflectivities are applicable. The most general is the multilayer optical matrix method[42]. However, there are alternative ways of looking at the interface. It has been shown quite generally[43] that deviations from Fresnel's law for reflection at an interface can be expressed approximately as the Fourier transform of the derivative of the refractive index normal to the scattering surface. Alternatively, Thomas and coworkers[44] have shown that the kinematic approximation for reflectivity can give good insight into the nature of scattering from interfaces in appropriate ranges of κ. In general, for the air–polymer interface, therefore[44], the critical angle (or position of the Fresnel edge as it is sometimes called) is a function of the scattering length density of the medium while the shape of the reflectivity profile is determined by the composition or density of the material near the surface.

For a thin film resting on a substrate, interference will occur between waves reflected at the two surfaces. The reflectivity profile is thus modulated by interference

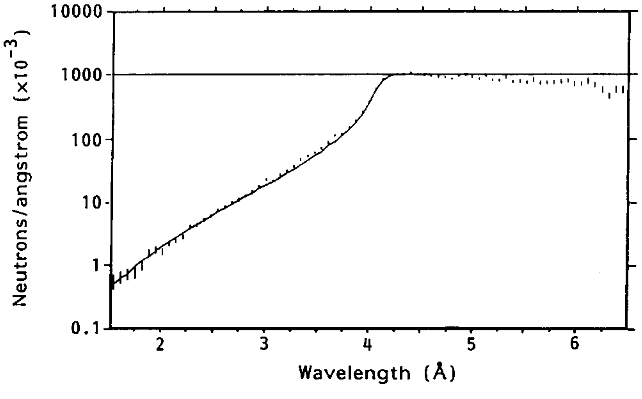

Figure 1 Reflectivity profile of a polystyrene film 8000 Å thick, on top of an optical flat. The error bars represent the experimental points and the full curve is the simulated profile for which the parameters listed in *Table 1* have been used

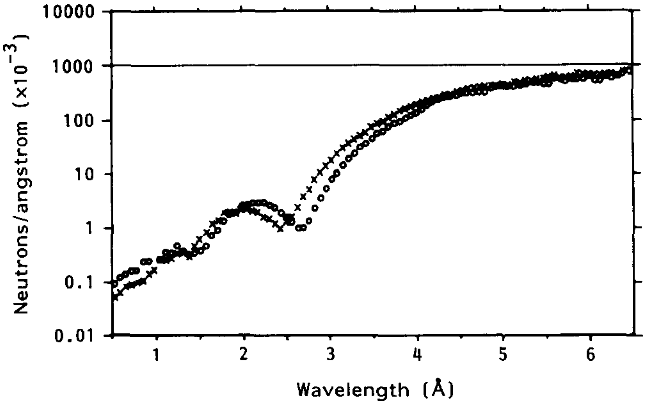

Figure 2 Reflectivity profiles of a bilayer of deuterated poly(methyl methacrylate) (d-PMMA) and hydrogenous polystyrene (h-PS) on top of an optical flat: (○) before annealing; (×) after annealing. The sample was annealed for 6 h at 120°C followed by storing at room temperature for 18 weeks

fringes whose period is determined by the film thickness. An experimental example is shown in *Figure 2*. The profile is now a function of the refractive index of the film and of its substrate, as well as the film thickness and any interfacial composition or density profile.

For the specific case of a single thin film between two bulk media, the reflectivity can be written explicitly as:

$$R=\frac{r_{12}^2+r_{23}^2+2r_{12}r_{23}\cos(2\beta)}{1+r_{12}^2+r_{23}^2+2r_{12}r_{23}\cos(2\beta)} \qquad (5)$$

where

$$\beta=(2\pi/\lambda)n_2 d\sin\theta_2 \qquad (5a)$$

and r_{12} and r_{23} are the Fresnel coefficients of the air–film and film–substrate interfaces such that:

$$r_{ij}=\frac{n_i\sin\theta_i-n_j\sin\theta_j}{n_i\sin\theta_i+n_j\sin\theta_j} \qquad (5b)$$

The subscripts 1, 2 and 3 refer to the air, film and substrate phases, respectively.

EXPERIMENTAL PROCEDURE

The polymers used in this work were hydrogenous polystyrene ($M_w=220000$, $M_w/M_n=2.073$) and deuterated poly(methyl methacrylate) ($M_w=19200$, $M_w/M_n=2.04$).

Three samples were produced. The first consisted of a film of hydrogenous polystyrene (h–PS) on an optical flat and it was prepared by spinning a 10% solution of the polymer in xylene directly onto the substrate.

The other two samples were diffusion couples formed by a thin (hundreds of angstroms) layer of deuterated poly(methyl methacrylate) (d-PMMA) on top of a thick (thousands of angstroms) layer of hydrogenous polystyrene. Both films were supported on an optical flat. The bottom layer was prepared as above, then the optical flat coated with the h-PS was used as the substrate for spin casting of a 1% solution of d-PMMA in 2-methoxyethylene.

This procedure secures a quick and total evaporation of the solvent, and also high-quality samples with reproducible characteristics can be obtained.

The neutron critical reflection measurements were carried out at the CRISP reflectometer at the ISIS pulsed neutron source, Rutherford Appleton Laboratory. The instrument is described in detail elsewhere[21]. A broad wavelength band is collimated onto the sample at the angle of incidence θ_i. The scattered neutrons are detected at the reflection angle $\theta_r=\theta_i$ and analysed in terms of their time-of-flight over a measured sample–detector distance. In this way the reflectivity is accumulated over a wide range of κ simultaneously.

DATA CORRECTION AND FITTING PROCEDURES

The raw time-of-flight data have been reduced using standard procedures to take account of the incident spectral shape and detector efficiency: the corrected data are then represented as reflectivity (in absolute units) as a function of incident neutron wavelength.

The corrected data have been analysed using programs based on equations (5) and (5a). The non-ideal natures of the surfaces and interfaces have to be taken into account. Any long-range surface waviness will smooth interference features identically to the resolution $\Delta\theta$, and can be considered as an additional component to the instrumental resolution. Roughness and concentration gradients are, over the wavevector transfer range studied, essentially indistinguishable. Their effect is to cause the reflectivity to fall faster than for the ideal case, and modulate the interference structure.

The case of an interface between two bulk media is accounted for by the addition of a Debye–Waller like factor[45]:

$$R'=R\exp(-q_0q_1\langle z^2\rangle) \qquad (6)$$

where R is the ideal reflectivity, $q_0=2k\sin\theta_0$, $q_1=2k\sin\theta_1$, θ_0 and θ_1 are the glancing angles of incidence and refraction respectively, $k=2\pi/\lambda$, the neutron wavevector and $\langle z^2\rangle$ is the mean-squared roughness.

For thin films a similar Gaussian factor is applied to each Fresnel coefficient, such that[46]:

$$r_{ij}=\frac{(n_i\sin\theta_i-n_j\sin\theta_j)}{(n_i\sin\theta_i+n_j\sin\theta_j)}\exp(-0.5q_iq_j\langle z^2\rangle) \qquad (7)$$

RESULTS AND DISCUSSION

The reflectivity profile for the film of h-PS on an optical flat is shown in *Figure 1* where the error bars represent the experimental reflected intensity as a function of κ. The full curve is the calculated reflectivity profile for which the parameters in *Table 1* have been used.

We can make several observations about the h-PS data. The position of the critical edge is, of course, dominated by the optical flat. However, the reflectivity, at shorter wavelength is sensitive to the h-PS layer and although insensitive to the thickness provides a good estimate of the scattering length density of the layer. Assuming a density $\rho=1.04$ g cm^{-3} the scattering length density obtained for the h-PS is in good agreement with tabulated scattering lengths[18]. The value of $\Delta\theta$ obtained is close to the instrumental resolution, and so indicates a well defined polymer film. The 'roughness' parameters z_1 and z_2 for the two interfaces are identical and so reflect the optical flat substrate quality. The value is in good agreement with measurements on other optical flats[47].

Figure 2 represents the experimental reflectivity profile for a d-PMMA/h-PS sample as made and after annealing

Table 1 Parameters used in the simulations, where Nb is scattering length density, d is thickness, z_1 is the air–top layer roughness, z_2 is the top layer–bottom layer roughness and $\Delta\theta$ is the long-range waviness of the sample. The subindexes b and t refer to the bottom and top layer respectively. In the case of the PS sample on the optical flat (*Figure 1*), the subindex b refers to the glass substrate

Figure	Nb_b (10^5 Å^{-2})	Nb_t (10^5 Å^{-2})	d_t (Å)	z_1 (Å)	z_2 (Å)	$\Delta\theta$ (%)
1	0.355	0.14	8000	20	20	4
3a	0.14	0.70	203	20	20	8
3b	0.14	0.75	183	20	20	14

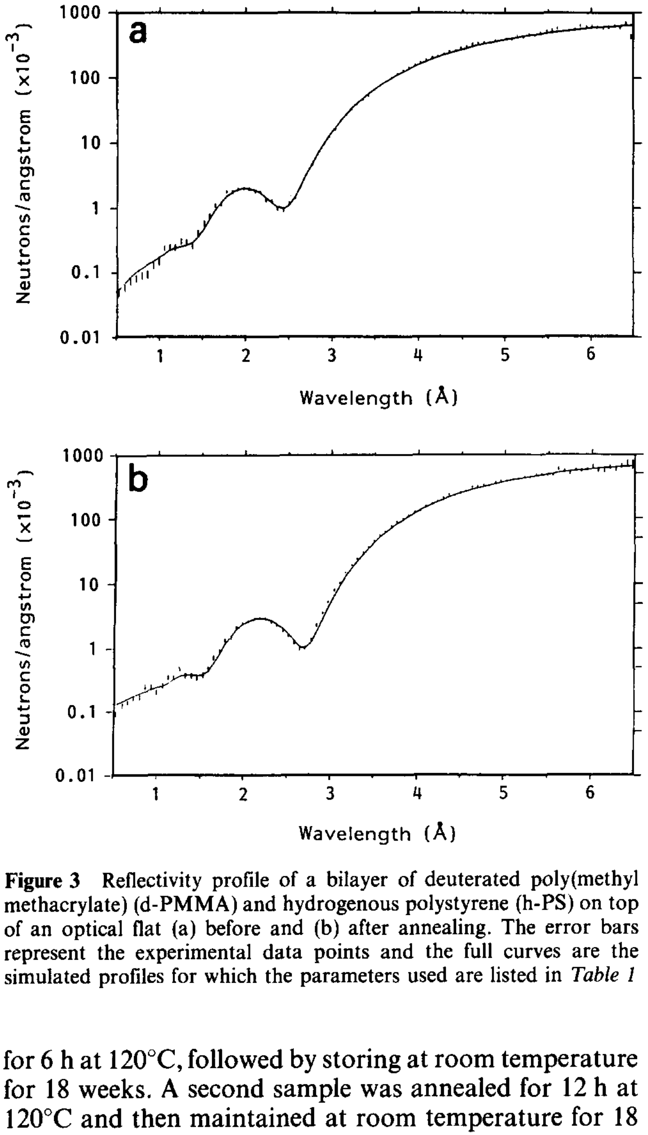

Figure 3 Reflectivity profile of a bilayer of deuterated poly(methyl methacrylate) (d-PMMA) and hydrogenous polystyrene (h-PS) on top of an optical flat (a) before and (b) after annealing. The error bars represent the experimental data points and the full curves are the simulated profiles for which the parameters used are listed in *Table 1*

for 6 h at 120°C, followed by storing at room temperature for 18 weeks. A second sample was annealed for 12 h at 120°C and then maintained at room temperature for 18 weeks. The reproducibility between these two samples was extremely good so that the profiles and fitting parameters were identical both before and after annealing. From now on we will only refer to one of the samples. *Figures 3a* and *3b* represent the experimental and fitted profiles analysed in *Figure 2*.

The d-PMMA films are of sufficient thickness that the glass substrate no longer contributes to the reflectivity: the modelling and analysis can therefore be effectively done by considering only the h-PS and d-PMMA layers.

The observed profiles can be well matched to calculated reflectivities. The parameters used are summarized in *Table 1*. In addition to these parameters it has been necessary to include a wavelength-dependent background:

$$\mathrm{bgd} = 2.3 \times 10^{-4}\lambda \tag{8}$$

to account for the incoherent scattering for the h-PS.

The reproducibility between samples is good, and the high quality of the data suggests well defined films. We observe that $\Delta\theta$ has now increased beyond the instrumental resolution, indicating that the addition of the d-PMMA layer has made the air interface more wavy; this further increases with annealing.

The interfacial roughnesses z_1 and z_2 are identical to the h-PS data and again reflect the substrate roughness, and are not attributable to significant interdiffusion at the interface.

Several conclusions can be drawn from a comparison of the results obtained before and after annealing the sample. The top film gets thinner with annealing while its scattering length density either remains constant or increases slightly. The long-range waviness is higher after annealing but the roughnesses air/d-PMMA and d-PMMA/h-PS do not change. This result indicates that although the surface of the top film becomes more wavy with annealing, the polymer–polymer interface is sharp and does not alter. We can conclude therefore that if diffusion at the polymer–polymer interface has occurred it is on a scale smaller than our sensitivity, and the simulations indicate no increase of the interfacial thickness after annealing beyond the initial 20 Å. This is the limiting value of the interface in contrast to the larger values predicted in the literature and mentioned above[39,40].

The fitting procedure is very sensitive to the values of the parameters chosen and it is unlikely that an alternative set of parameters could be found to produce the same quality of fit. To explore this point we undertook an exhaustive search for a possible interfacial profile which could fit the data as well as the sharp interfaces used so far:

(1) We analysed the profiles obtained assuming an increasing Gaussian roughness between the films and a slight thinning of the top layer to compensate for this effect.

(2) We then invoked an exponential density gradient in the interface. We considered two cases: (a) An exponential function increasing from the top film to the bottom film; in order to compensate for this effect in the fitting of the profile we assumed a thinner top layer. (b) An exponential function increasing from the bottom film to the top film, and a thicker top layer in order to compensate for this effect.

From these results we can conclude that the existence of an interface broader than the initial 20 Å cannot explain the observed reflectivity profiles and so the upper limit for the interdiffusion of the d-PMMA/h-PS blend at 120°C for these molecular-weight values is much smaller than 20 ± 5 Å.

The question arises whether the annealing times used are long enough for the samples to come to equilibrium, i.e. whether the polymers have had enough time to diffuse across the interface and produce an interface of equilibrium width. In order to discuss this point, a value for the mutual diffusion coefficient is required.

The mutual diffusion coefficient D is given by the following equation[6–8,48]:

$$D = 2(\chi_s - \chi)\phi_1\phi_2 D_T \tag{9}$$

where ϕ_i is the volume fraction of component i, $\phi_1\phi_2 D_T$ is an Onsager transport coefficient and χ_s is the interaction parameter at the spinodal:

$$\chi_s = 0.5(\phi_1^{-1}N_1^{-1} + \phi_2^{-1}N_2^{-1}) \tag{10}$$

where N_i is the degree of polymerization of component i.

At present there are two theoretical approaches predicting rather different expressions for D_T. The 'slow theory' was developed separately by Brochard *et al.*[6] and by Binder[48], who express D_T as:

$$D_T^{-1} = \phi_1(D_2^* N_2)^{-1} + \phi_2(D_1^* N_1)^{-1} \tag{11}$$

where D_i^* is the self-diffusion coefficient of component i.

The 'fast theory' was proposed, also separately, by Kramer *et al.*[7] and by Sillescu[8], who predict the expression:

$$D_T = \phi_1 D_2^* N_2 + \phi_2 D_1^* N_1 \tag{12}$$

In order to calculate a value of D_T, it is necessary to know the values of the self-diffusion coefficients for both polymers. At the moment these values are not available but we can approximate $D^*(\text{PS at } 120°\text{C}) \simeq 9.57 \times 10^{-18}\ \text{cm}^2\ \text{s}^{-1}$ by scaling in temperature the results obtained by Composto *et al.*[4] and $D^*(\text{PMMA at } 120°\text{C}) \simeq 5.4 \times 10^{-16}\ \text{cm}^2\ \text{s}^{-1}$ by scaling the results obtained by Jud *et al.*[49] to the low molecular weight of the d-PMMA. With these values we calculate $D_T(\text{PS/PMMA at } 120°\text{C}) = 5.81 \times 10^{-14}\ \text{cm}^2\ \text{s}^{-1}$ according to the fast theory and $D_T(\text{PS/PMMA at } 120°\text{C}) = 3.34 \times 10^{-14}\ \text{cm}^2\ \text{s}^{-1}$ following the slow theory.

If we assume that the polymer–polymer interface has got the conventional error function form, the width of the interface is given by[50]:

$$\Delta x = 2(4Dt)^{1/2} \tag{13}$$

The limiting value for the width of the interface after annealing for 12 h is 25 Å, so from equation (13) we obtain the result that under these circumstances $D(\text{PS/PMMA at } 120°\text{C}) < 3.62 \times 10^{-21}\ \text{cm}^2\ \text{s}^{-1}$.

Since the limiting mutual diffusion coefficient for the pair PS/PMMA is four orders of magnitude smaller than the self-diffusion coefficients of the homopolymers, it becomes clear that the polymer–polymer interaction does not favour mixing.

By substituting the values of D, D_T, θ_1, θ_2 and χ_s in equation (9) we obtain the result that for both the fast and the slow theories, the interaction parameter $\chi = 6.1 \times 10^{-3}$ and this is a limiting value. If χ were lower than 6.1×10^{-3}, then an observable interface would have been obtained even at very short annealing times. As an example, if $\chi = 4 \times 10^{-3}$ we would have obtained an interface 50 Å thick after 22 min annealing, according to the fast theory, and after 43 min annealing, according to the slow theory. If χ were higher than 6×10^{-3} then we would obtain the result that the mutual diffusion coefficient is negative and consequently we would be inside the spinodal regime where the previous diffusion equations are not applicable.

All these calculations have been done assuming that the values of the self-diffusion coefficients for PS and PMMA are correct. However, it becomes clear that for the diffusion coefficient to have any effect in equation (9), the ratio D/D_T should be of the order of 10^{-3}. Since $D/D_T \simeq 10^{-7}$, even if the self-diffusion coefficients were four orders of magnitude lower, our discussion would still be valid.

Although no significant change to the interface could be detected before or after annealing, subtle changes in the film thicknesses and densities were revealed by the neutron reflection experiments. Increase in scattering length density and reduced thickness of the d-PMMA layer after annealing could be attributed to a change from a rather loosely packed structure arising from the fast removal of solvent in the spinning technique. On the other hand, the density required before annealing is $1.278\ \text{g cm}^{-3}$ and after annealing is $1.369\ \text{g cm}^{-3}$. The former value is only slightly smaller than that of bulk PMMA corrected for the 8% increase in monomer mass. Evidence from polystyrene measurements is that the density change on deuteration can be accounted for by this correction with an accuracy of 99.9%[51]. This leaves us with the result that in its annealed state the thin film of d-PMMA is adopting a 5.7% denser structure than the normal bulk. Russell *et al.*[36] report a similar densification of their upper layer although they did not comment on this observation. From these results it is clear that some quite extensive density changes take place with annealing, although the cause or causes of these variations are as yet obscure. The problem is complicated mainly for two reasons: On one hand, the phenomenon of interdiffusion in polymer blends is subject to controversy and it is far from being satisfactorily explained. On the other hand, the structure and consequently the thermodynamics of thin polymer films could be somewhat different from those of the bulk. From the results obtained so far it is already evident that neutron critical reflection is a unique technique for the detailed study of interfaces and we believe that a careful analysis of suitable experiments will lead to the solution of multiple problems in the field of polymers.

CONCLUSIONS

Neutron critical reflection is a suitable technique for the study of interfaces in polymer–polymer systems with a spatial resolution as good as 5 Å. It provides detailed information about the chemical composition and structure profile normal to the reflection surfaces, which makes it a unique probe for the study of the interfacial region.

The h-PS/d-PMMA system is immiscible at 120°C since it presents a sharp interface. Contrary to predictions in the literature, the interfacial mixing is not greater than 20 ± 5 Å. Unpublished electron micrographs seem to agree with our results.

With annealing, the d-PMMA layer gets thinner, denser and more wavy although the short-range roughness does not change. Before annealing, the density of the d-PMMA is the same as that of the bulk ($\rho = 1.278\ \text{g cm}^{-3}$); with annealing, the density increases to $\rho = 1.369\ \text{g cm}^{-3}$. At present we cannot explain the reason for this change.

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