Communications to the Editor

Real-Time Measurement of Polymer Diffusion Coefficients Using Neutron Reflection

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Preliminary results are presented in which the interdiffusion coefficient for hydrogenated and deuterated polystyrene has been measured at 115 °C in situ and in real time using neutron reflectivity (NR). The interfacial width shows a $t^{1/4}$ time dependence in the initial stages of diffusion which changes to $t^{1/2}$ at longer annealing times, from which a diffusion coefficient $D = (1.7 \pm 0.2) \times 10^{-17}$ cm^2 s^{-1} is obtained. Similar in situ real-time NR methods have been used to measure the ingress of oligomeric styrene into high-molecular-weight polystyrene at 65 °C. A highly asymmetric interfacial profile is seen which is qualitatively in agreement with theory.

The early stages of interdiffusion at polymer interfaces has been studied by a number of techniques.[1−6] Neutron reflectivity (NR) has been shown to be ideally suited to these problems,[7−10] allowing the accurate determination of not only the width of the interface but also the interfacial profile between the interdiffusing polymers. The normal way of studying the diffusion process is to use an "anneal−quench" procedure where the sample is heated for a given time above the glass-transition temperatures (T_g's) of the polymers and then rapidly quenched to room temperature, after which a full reflection profile is collected. This procedure is repeated for each successive annealing time. Classical Fickian diffusion[11] has been shown to apply only at annealing times greater than the reptation time, τ_r. Detailed NR studies of interdiffusion between polymers with similar molecular weights have shown that for times below τ_r different power law time dependencies exist for the interfacial width.[7] In these cases, the interfacial profile can be described by symmetric functions, either error or hyperbolic tangent functions. When the polymer molecular weights are dissimilar, the interfacial shape becomes highly asymmetric[8,12,13] with a discontinuous interfacial profile that has components relating to the different diffusion rates of the two species. Although the anneal−quench procedure has proved very successful for amorphous polymer systems where the T_g of both polymers are well above room temperature, it is not applicable for the study of systems where the T_g for one or both polymers is close to or less than room temperature or if small-molecule ingress into a polymer layer is to be studied. Since the interface remains mobile at room temperature, an extremely rapid quench to below room temperature must be made where the diffusing species are immobilized for the length scale of the NR measurement. Difficulties may arise if either the quench is not rapid enough or the interface is disturbed by the quench process, which it undoubtedly will be when heating the sample for the next annealing.

Another approach, which has only recently become possible with the advent of higher flux NR instruments, is in situ real-time reflectivity measurements. Such measurements have been attempted in the past using point-by-point $\theta-2\theta$ fixed-wavelength NR measurements by taking a partial reflectivity curve of a limited number of points.[14,15] In this work, data were only collected over a limited Q space with a large step size in θ. Data collection in this case was rapid (10−15 min for each reflectivity partial profile), but the technique is limited due to the difficulties presented by fitting models to a severely limited data set. By contrast to these point-by-point θ-2θ fixed-wavelength methods, NR profiles collected using a pulsed white beam neutron source give a full reflectivity profile for a fixed incident angle. Data collection times are then limited by the time required to gain adequate statistics. Since the neutron pulse is limited to a specific wavelength and therefore momentum transfer range, Q [$=(4\pi/\lambda)\sin\theta$, where θ is angle of incidence], a complete reflectivity profile over an extended Q range is normally obtained by splicing together data collected from two or more angles. Measurement of a complete reflectivity profile of a sample with an instrumental resolution of approximately 5% (d/dθ) using either CRISP or SURF reflectometers at the ISIS Facility, Rutherford Appleton Laboratory, would typically take 1−2 h, consisting of data taken at three angles with a wavelength window of 0.5−6.5 Å. This is clearly not applicable for the study of systems where the interface changes within the time of the measurements. However, at each incident angle, a full reflectivity profile is obtained, and we have therefore been able to collect NR profiles in 6 min with statistics that are adequate enough to extract interfacial widths and profiles from the data despite the restricted Q range.

We present here our preliminary data that demonstrate the effectiveness of this approach in measurements of systems where the anneal−quench approach is not possible. The polymers used were deuterated polystyrene (dPS$_1$ with $M_w = 40$k, PD = 1.02, and $T_g =$ 84 °C and dPS$_2$ with $M_w = 101$k, PD = 1.02, and $T_g =$ 103 °C), hydrogenated polystyrene (hPS with $M_w = 49$k, PD = 1.03, $T_g = 104$ °C) and oligo-styrene (OSt with $M_w = 1.11$k, PD = 1.1, and $T_g = 27$ °C). Two systems were used for these real-time diffusion NR measurements. The initial measurements were conducted using

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samples of high-molecular-weight polystyrene (hPS−dPS$_1$) to establish the viability of real-time experiments. Subsequently we have extended our investigations to examine the diffusion of oligomeric-styrene into high-molecular-weight polymer (OSt−dPS$_2$).

The technique used to measure the two different systems were slightly different although both were measured in situ and in real time. The SURF reflectometer used for these measurements has been described elsewhere.[16] Standard fitting procedures[17]were used to analyze the NR data although with the limited Q range of the profiles severe constraints on the fittable parameters were imposed, on the basis of the initial full reflectivity profile measured. For the hPS−dPS$_1$ system, a bilayer sample was prepared in the normal way by separately spin casting the individual layers. The bilayer was built up by floating the dPS$_1$ layer onto the surface of water and picking it up onto the hPS-coated silicon substrate. The samples were dried in a vacuum oven at 42 °C for several days before a full three-angle reflectivity profile was measured at RT. The normal sample holder was replaced by a thermostatically heatable brass plate preheated to 115 °C. The sample was placed on the heated plate and rapidly aligned using a laser, and data collection was started as soon as possible afterward. Reflectivity profiles were collected every 6 min starting at a fixed incident angle of 0.8° giving a window in Q of approximately 0.027−0.1 Å^{-1} when accepting neutrons in the wavelength range 2−6.7 Å. The angle was chosen to place the Q window in the region of most interest along the reflectivity curve, where the interference fringes were expected to be seen to dampen. The angle was incrementally decreased in steps of 0.1° as the dampening fringes progressed to lower Q values as the polymers interdiffuse (see Figure 1) moving the minimum Q at 0.5° to 0.0164 Å^{-1}. After almost 4 h annealing, the sample was removed from the heater and rapidly quenched to room temperature, before measuring a full three-angle reflection profile.

The interfacial widths were determined from the reflectivity data by fitting the profiles with a standard two-layer model and assuming a simple Debye−Waller Gaussian interfacial profile between the dPS$_1$ and the hPS. Fits to the data from the as-made sample gave thicknesses of the deuterated and hydrogenous PS layers of 107.8 and 61.0 nm, respectively, with an interfacial width, w, of 2.73 nm. The interfacial profile is seen to be symmetric, as may be expected for a system where the polymers are of approximately equal molecular weight. The interfacial width as a function of time obtained from fits to the reflectivity profiles is shown in Figure 2 on a log−log plot. The size of the interfacial widths for long annealing times has been confirmed using DSIMS.[18] The solid lines in Figure 2 are calculated assuming the relationship $w \propto t^{\beta}$, taking the theoretical values for $\beta = {}^1/_4$ or ${}^1/_2$ for short and long times, respectively. The agreement between the theory with the measured data is very close. Where the time dependence of w changes to $t^{1/2}$, classical Fickian diffusion applies, in which case the solution to the diffusion equation gives $w = (4Dt)^{1/2}$.[7,11] Fitting the interfacial width−time data over the regime 5200 < t(s) < 11 200 using this equation gives a diffusion coefficient $D = (1.7 \pm 0.2) \times 10^{-17}$ cm^2 s^{-1}. Given this value of D, the reptation time for these polymers can be calculated using the formula $\tau_r = Nb^2/3\pi^2 D$,[7] where b is the segment length (=0.67 nm), and N is the degree of polymerization. This gives τ_r(dPS$_1$) = 3223 ± 363 s and τ_r(hPS) = 4333 ± 489 s.

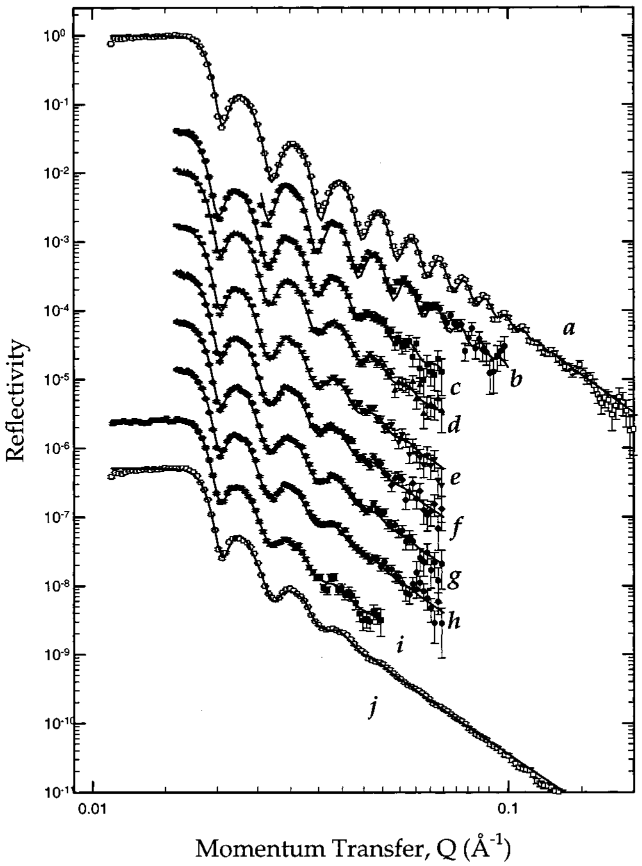

Figure 1. Plot of a selection of reflectivity, R, versus momentum transfer, Q, profiles for the hPS−dPS$_1$ bilayer measured in real time (solid symbols) at 115 °C and at room temperature (open squares) before and after annealing (*a* and *j*, respectively). The real-time reflectivity profiles were measured at a fixed angle with 6 min count times and individually scaled for clarity. The mean time for the profiles plotted are 5 (*b*), 32 (*c*), 63 (*d*), 93 (*e*), 124 (*f*), 155 (*g*), 186 (*h*), and 212 (*i*) minutes. The solid lines are fits to data assuming a model as described in the text.

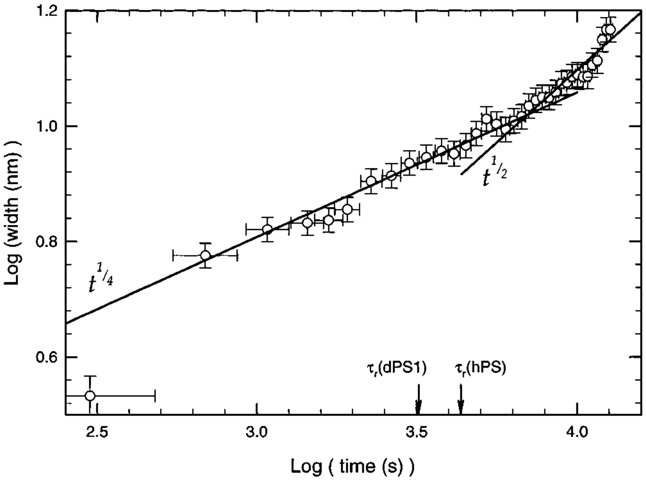

Figure 2. Log−log plot of interfacial width, w, versus annealing time, t, obtained from fits to reflectivity data for the hPS−dPS$_1$ bilayer, as shown in Figure 1. The lines through the data are calculated assuming a $t^{1/4}$ time dependence for t < 7000 s and a $t^{1/2}$ dependence for t > 6000 s giving a diffusion coefficient, $D = 1.7 \times 10^{-17}$ cm^{-2} s^{-1}, as explained in the text. The positions of the reptation times for the two polymers based on this value of D are indicated on the time axis.

The value of the diffusion coefficient for hPS−dPS interdiffusion has been obtained by a number of workers using varying molecular weights and annealing temperatures, giving $D = 2.44 \times 10^{-17}$ (M_w = 660k and 752k, T = 140 °C),[5] 5.45×10^{-18} (M_w = 233k, T = 120 °C),[9] 5.6×10^{-16} (M_w = 111k and 93k, T = 125 °C),[19] and 9.14×10^{-18} cm^2 s^{-1} (M_w = 641k and 649k, T = 133 °C).[20]

To directly compare these literature values to the value of D obtained in this work, it is necessary to reduce the data for temperature and molecular weight differences. Although thermodynamic slowing down (TSD) often causes changes to the diffusion coefficient due to the isotope effects,[21,22] calculations indicate that the TSD effect is expected to be negligible (less than a few percent) in this system due the low-molecular-weight polymers used. The William−Landel−Ferry (WLF) equation, although widely used to normalize data to a specific reference temperature,[7] is not believed to be applicable to these data measured at 115 °C. This temperature is close to the T_g's of the polymers and therefore in the regime where application of the WLF equation is not valid.[23] Molecular weight scaling according to the relationship $D \approx M^{-2}$,[24] would give D scaled to M_w = 233k at 120 °C of approximately 7×10^{-19} cm^2 s^{-1}. This compares with a value of 5.45×10^{-18} cm^2 s^{-1} obtained by Karim and co-workers;[9] considering the slowing associated with the lower annealing temperature, the value of D obtained in the current work is not unreasonable. A further check on the value of D can be made by using the equation derived by Doi and Edwards relating the diffusion coefficient to the monomeric frictional coefficients, ζ, so that $D = k_B T d_T^2/3N^2\zeta b^2$,[24] where d_T is the tube diameter of a reptating polymer (d_T = 5.7 nm).[7] Taking a value of ζ(115 °C) = 0.199 dyne s cm^{-1}, obtained by extrapolating between values given in the literature for T = 100 and 125 °C,[25] gives a value for $D = 2.81 \times 10^{-17}$ cm^2 s^{-1} which is remarkably close to the value obtained in the current study. On the basis of the experimental value of the diffusion coefficient, the calculated Rouse time, τ_R, for these polymers ($\tau_R = d_T^2/9\pi^2 D$)[7,12] is 215 ± 23 s. The expected change in time dependence at low times from $t^{1/4}$ to $t^{1/8}$ therefore will not be observed in these experiments due to the time resolution of the reflectivity measurements.

Reflectivity measurements of the dPS$_2$−OSt system were carried out using a specially developed cell.[26] This consisted of an inverted silicon substrate held rigidly with the dPS$_2$ spin-coated surface facing downward. The initial thickness of the dPS$_2$ layer from fits to the NR data was 95 nm. A brass trough containing the OSt was held several centimeters below the Si while the Si−dPS$_2$ interface was aligned using the neutron beam. Both the silicon and brass trough are thermostatically controlled to within ± 0.5 °C. Once the substrate had been aligned at the required measurement temperature of 65 °C, the brass trough was raised remotely to bring the OSt into contact with the dPS$_2$ surface and data collection started. Since the neutrons are transmitted through the Si substrate, the data were corrected for the transmission of the silicon. As with the bilayer sample of hPS−dPS$_1$ described above, reflectivity profiles were collected every 6 min over a limited reciprocal space window in Q, which is determined by the angle of incidence. The angle was incrementally decreased from 0.8 to 0.5° over the course of the experiment, thus progressively moving the window to lower Q ranges. A representative set of NR data is shown in Figure 3, together with the fits to the data plotted as the solid lines. Fits to the data using a bilayer model with a single interfacial profile were unsuccessful, and ab initio methods[17,27] were applied. These methods showed that the interface could be modeled as a number of layers that gave a highly asymmetric interfacial profile. This indicated that the profile could be described by two error functions each defined by a width, w, which are discontinuous about the interface center, x_0. Details of the fitting procedure are given elsewhere.[26] These asymmetric interfacial profiles show that the width w on the dPS$_2$ side of the interface is much larger and more extended than that on the OSt layer side, creating a profile with a diffuse tail and an otherwise sharp interface. This interfacial profile confirms that the oligomer diffusion into the polymer is much faster than the polymer diffusion in the opposite direction, as may be expected.[8,12,13] The time-dependent behavior of the error function widths used to describe the scattering length density profile are shown in Figure 4. The width, w_1, on the dPS$_2$ layer side of the interface appears to form instantaneously in the time resolution of the reflectivity measurements and then gradually increases with time. The error function width, w_2, which describes the dPS$_2$ diffusion into the oligomer, is initially much smaller but also shows an increase with time. As may be expected, the position of the interface, x_0, also decreases, indicating that the interface is moving further into the dPS$_2$ layer.

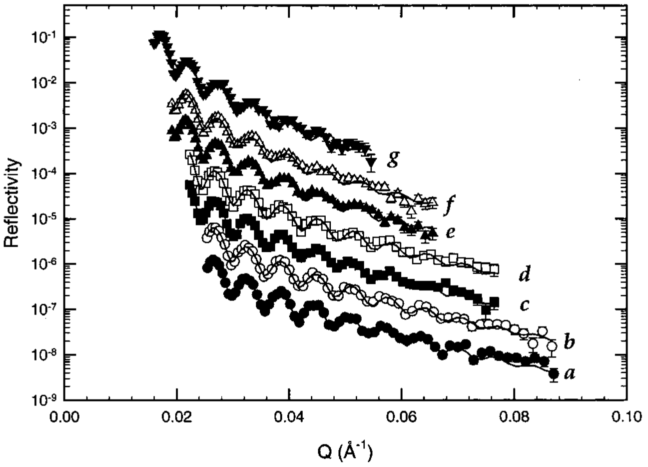

Figure 3. Selection of the reflectivity profiles of the OSt−dPS$_2$ system measured in situ in real time at 65 °C, each offset on the reflectivity axis for clarity. Each reflectivity profile was measured for 6 min at a fixed angle for mean annealing times, t, equal to 3 (*a*), 27 (*b*), 47 (*c*), 65 (*d*), 101 (*e*), 123 (f), and 135 (g) min.

The total width of the interface at longer times for such asymmetric systems is expected to show a $t^{1/2}$ dependence[12] that is related to the small-molecule diffusion coefficient by $w = (D_s t)^{1/2}$. In this case, the oligomer is the smallest molecule, so taking $w = w_1 + w_2$ gives a value of D_s for the OSt in this system at 65 °C of 8 (±1) × 10^{-17} cm^{2}s^{-1}. This time-dependence relationship holds when time is larger than the small-molecule reptation time, $\tau_r(S)$, and the polymer chains behave like a transient network swollen by the oligomer chains. This value of the diffusion coefficient would give $\tau_r(S)$ equal to 20 s. Under these circumstances, it is not expected to see the change to different time dependent behavior at $t < \tau_r(S)$, as predicted by theory.[12]

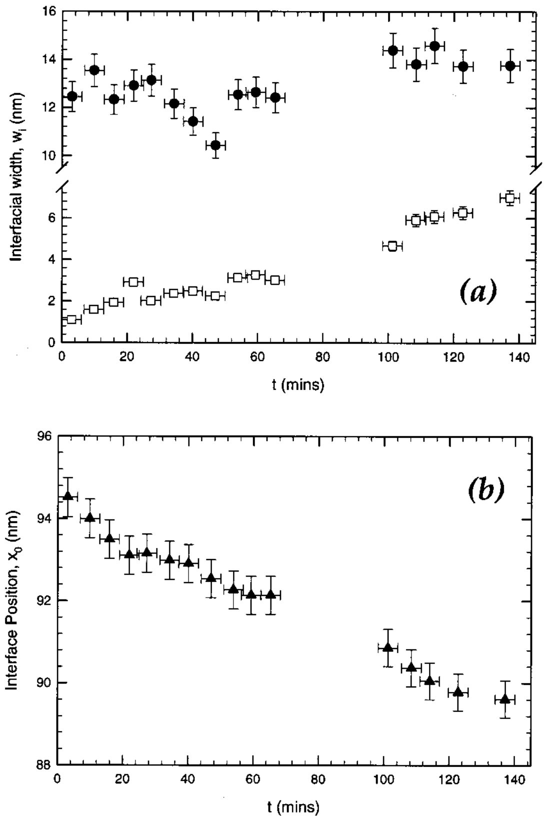

Figure 4. Plots of interfacial width (a) and interface position (b) as a function of annealing time, *t*, obtained from the discontinuous error functional form of the interfacial profile model used to fit a selection of the reflectivity data obtained for the OSt−dPS$_2$ system shown in Figure 3.

We have demonstrated that by careful NR measurements it has been possible to measure the interdiffusion of high-molecular-weight polymers (polystyrene and deuterated polystyrene) in situ in real time. As may be expected, the interfacial width was shown to vary linearly with $t^{1/2}$ for times greater than τ_r. The value of the diffusion coefficient obtained from this linear dependence is in agreement with those found in the literature and demonstrates the viability of these real-time NR measurements. Using this technique, we have also investigated the ingress of oligomeric styrene into high-molecular-weight deuterated polystyrene. The results obtained were in agreement with those expected from theory, and the interfacial profile was shown to be discontinuous and highly asymmetric. The reflectivity data has been fitted using a discontinuous interfacial profile using two error functions. Further evaluation of the data is ongoing, and further experiments to reduce the data collection times for each reflectivity profile down to below 1 min are currently being undertaken.

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