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Neutron Reflectivity of Polymer-Plasticiser Diffusion

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SUMMARY: Neutron reflectivity (NR) has been widely exploited to look at polymer thin films and in many ways is an ideal technique for studying polymer interfaces and surfaces, providing high-resolution concentration - depth profiles across the film thickness. Most NR studies to date have concentrated on thin films of amorphous polymers which possess T_g values well above room temperature. These polymers are ideally suited to NR measurements, firstly because they form homogeneously flat films and, secondly, heat-quench cycles can be used to study time-dependent processes. This has been used to great effect in NR studies of the initial stages of polymer - polymer interdiffusion or the kinetics of surface segregated layers for instance. One of the biggest drawbacks to this approach is that in polymer systems where one or more of the components has a T_g close to or less than room temperature, the polymers can still move during the measurement time of an NR profile, which typically takes 1-2 h for a full profile. Therefore, in order to study such systems, we have developed an approach to NR measurements that allows us to investigate diffusion processes *in situ*. Our new approach allows us to take NR profiles in only 20 s. This paper describes the method of real-time NR measurements in detail and illustrates the capabilities of the technique with highlights from some of our recent work on the early stages of polymer-plasticiser interdiffusion.

Introduction

Neutron reflectivity has been widely used to study polymer - polymer interfaces,[1,2] including detailed investigation of interdiffusion.[3-7] To date most of these studies have utilised 'anneal-quench' procedures where the sample is heated for a given time above the T_g's of the polymers, rapidly quenched to room temperature and then a full reflectivity profile collected. This process is repeated for each successive annealing time, allowing a detailed picture of the change in interfacial composition as a function of time to be built up. Although this

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measurement procedure has proved to be highly successful for amorphous polymer systems, where the T_g's of both polymers are well above room temperature,[3-7] it is not applicable for the study of systems where the T_g of one or both of the polymers is close to or less than room temperature, or where small molecule ingress into a polymer layer is to be studied. The problem lies in the mobility of the interface at room temperature, which would then require a fast quench to a temperature below which the diffusing species is immobilised. Experimentally this creates a problem if either the quench is not rapid enough or the interface is disturbed by this thermal cycling processes, which undoubtedly occurs when the sample is heated for the next annealing stage.

An alternative approach and one we have been developing recently is *in-situ* real-time reflectivity measurements. We have shown that by utilising the white beam of a pulsed neutron source, it is possible to collect a limited reflectivity profile at a fixed angle within a few minutes or less. This very rapid measurement time compares to the 1-2 h which is typical for a full reflectivity profile over an extended momentum transfer range. To make these very rapid measurements, only one angle is used which gives a fixed range of momentum transfer values, Q (= $(4\pi/\lambda)\sin\theta$, where λ is the neutron wavelength and θ is the angle of incidence). The length of the measurement time per reflectivity profile is simply limited by the time required to gain adequate statistics. To measure diffusion processes, it is important to remember that for simple systems diffusion will initially appear as an apparent increase in interfacial width with increasing time. In a reflectivity profile this manifests itself as an increase in dampening of the high Q fringes which themselves are associated with one of the polymer layer thicknesses. An assumption which must therefore be made is that the rest of the low Q data is unaffected by this increase in interfacial width. This is true for simple systems but may become increasingly less reliable as time increases or for more complex systems. This therefore remains a limitation for the current technology and can only be alleviated by increased neutron flux and, at the same time, utilising a larger wavelength range which would allow a much larger Q window to be measured.

Nevertheless, we have shown the effectiveness of this technique for a number systems. Our approach was first demonstrated by studying the interdiffusion of normal polystyrene (PS) and deuterated PS (dPS) at 115 °C, *i.e.* above the T_g of both polymers, using the SURF reflectometer (ISIS Facility, Rutherford Appleton Laboratory).[8] This allowed us to determine a diffusion coefficient of $2\text{x}10^{-17}$ cm^2s^{-1}, entirely consistent with expectations compared to other techniques, validating the capability of these real-time NR measurements. We have also extended this method to study ingress of low-molecular-weight oligostyrene into high-molecular-weight dPS,[8] where asymmetric interfacial composition profiles were observed. More recently, we have also studied ingress of oligo(methyl methacrylate) and oligo(ethylene glycol) into high-molecular-weight deuterated poly(methyl methacrylate) (dPMMA).[9]

This paper describes the early results of studies of a series of phthalate plasticisers into high-molecular-weight dPMMA. Whereas our initial measurements for the PS-dPS system were about 6 min per reflectivity profile, we have reduced this to 20 s, thus opening up tremendous possibilities in many areas of diffusion studies.

Experimental

The characteristics of the dialkyl phthalate plasticisers used in this study are listed in Table 1.

Table 1: Dialkyl phthalate plasticisers characteristics, including bulk scattering length density value (ρ_s) used to fit the NR data.

Alkyl	**Name**	**Molar Mass (g/mol)**	**Density (g/cm^3)**	**$\rho_s \times 10^6$ (Å^{-2})**
C_9H_{19}	diisononyl phthalate (DINP)	418.6	0.97	0.54
$CH_2CH(C_2H_5)(CH_2)_3CH_3$	dioctyl phthalate (DOP)	390.5	0.98	0.62
$(CH_2)_3CH_3$	dibutyl phthalate (DBP)	278.4	1.04	1.06

Deuterated PMMAs of two molecular weights were used: M_w = 188 000 g/mol and 100 000 g/mol. Thin films of these PMMA films were spun-cast onto 70×50×5 mm polished silicon substrates from dilute toluene solutions with a concentration of 20 mg/ml. After spin casting the samples were dried at 55 °C for several days before use in the reflectivity experiments. Full NR profiles of the as-made dPMMA films were measured using three-angle measurements at room temperature. Real-time NR measurements at temperatures above room temperature were made using a specially constructed cell,[10] where the dPMMA-coated silicon is held inverted and facing a small trough containing the plasticiser. The silicon and plasticiser are held apart until the moment the reflectivity measurements are ready to start. Then the two are brought together remotely and the data collection started together with the clock at the moment the two touch each other.

Reflectivity measurements were initially taken at a fixed incident angle of 0.8° giving a fixed window in Q of approximately 0.027-0.08 Å^{-1}. This angle was chosen so as to place the

Q window in the region of most interest along an imagery full reflectivity profile, where the interference fringes are expected to be seen to dampen. The incident angle was incrementally decreased in steps of 0.2° as the most significant changes in the reflectivity profile progressed to lower Q values as the diffusion process occurs. The lowest incident angle used was 0.4° giving a Q range of approximately 0.013-0.05 Å^{-1}. At this lowest angle and a higher flux, measurement times of just 20 s were possible.

The preliminary analysis of these data has been performed using standard single-layer models assuming a simple Debye-Waller Gaussian interfacial profile[1] between the dPMMA and the plasticiser. As discussed below, use of a single-layer model is only adequate for an initial period of time, which depends on the plasticiser used. Although the analysis of the later-time NR profiles is still ongoing, it is clear that a much more complex composition profile through the dPMMA layer is evident than could be approximated by using a single-layer model.

Results and Discussion

The reflectivity profiles of the plasticiser diffusion into the dPMMA layers were measured at T = 70 °C for DINP and DOP studies and 32 °C for DBP. Clearly, for direct comparison, the same temperature for all the samples would have been ideal, but at the higher temperature the diffusional processes in the dPMMA/DBP system were so fast that all reflectivity interference fringes were lost within the first few minutes. Therefore, even at the fastest measurement times of 20 s per reflectivity profile, there are significant changes in the composition profile of the system, invalidating any data we can collect over this period. We therefore had to choose a lower temperature where the motion was slow enough so that there is not a noticeable change in reflectivity over the time scale of each individual measurement.

A series of selected reflectivity profiles for DINP and DOP systems are shown in Figs 1 and 2. The limited Q range windows for each incident angle are evident from these plots. As can be seen, the interference fringe spacing decreases with increasing time indicating that the layer thickness of the dPMMA, d, increases. The rate at which this happens for the two plasticisers is clearly different. A quantitative analysis of the initial stages of the ingress of the plasticiser into the dPMMA was achieved as described above by fitting each reflectivity curve using a single-layer model. As can be seen from Figs 1 and 2, even within the limits imposed by the statistics of the data associated with these very short collection times, this simple model adequately describes the data at very early stages, but becomes increasingly less accurate for later stages. The results of the fitting analysis for the DOP and DINP are shown in Fig. 3, where the time dependence of the change in dPMMA thickness, Δd, is plotted. Both plasticisers show a linear dependence of Δd as a function of time, suggesting that this early-stage diffusion process is Case II. Although Fickian behaviour showing a $t^{0.5}$ dependence is typical for solvent and gas diffusion into polymers,[11,12] this is normally only true for polymers above their T_g and is common for rubbers. For glassy amorphous polymers, Case II behaviour is often observed. In Case II sorption of fluids into polymers, there is expected to be an induction period where the fluid concentration at the film surface increases forming an asymmetric interfacial profile or front. Once this fluid front has developed, it then propagates into the film at constant speed with an equilibrium concentration of fluid.[12] We do not observe the development of the fluid front in our data which would manifest itself as an asymmetric interface with a long concentration tail into the bulk plasticiser. It is entirely possible that this does in fact happen but, without extended Q range data, we cannot say with any certainty whether this happens.

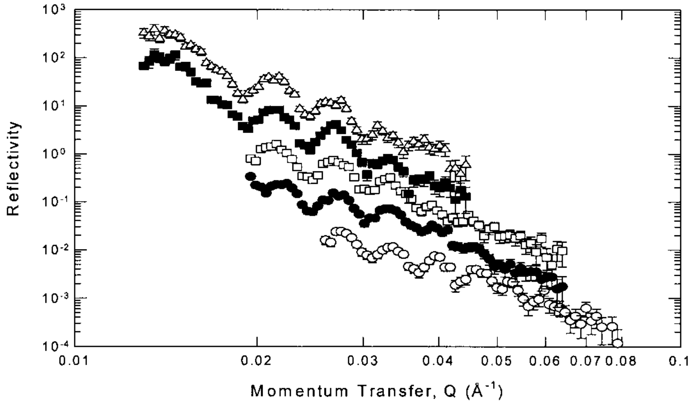

Figure 1: Reflectivity profiles of dPMMA/DOP measured in real time at 70 °C after 2.6 (○), 8.3 (●), 13.6 (□), 18.9 (■) and 22.8 (△) min. The plots have been scaled for clarity.

Circumstantial evidence to support the development of a fluid front during the initial stages of the sorption process can be seen from the DINP system where an induction period is observed. During this induction period over the initial 4 min, the value of the dPMMA thickness does not appear to change. Only after this period does the film thickness begin to increase linearly with time, as expected for Case II behaviour.

The differences in the rates of film thickness increase for DINP and DOP are evident from the linear fits to the data shown in Fig. 3. The DOP system shows a marked deviation from this linear behaviour after about 6 min, and this reflects the breakdown in the adequacy of the single-layer model to describe the data, which after about 10 min is not adequate to describe the DOP system data.

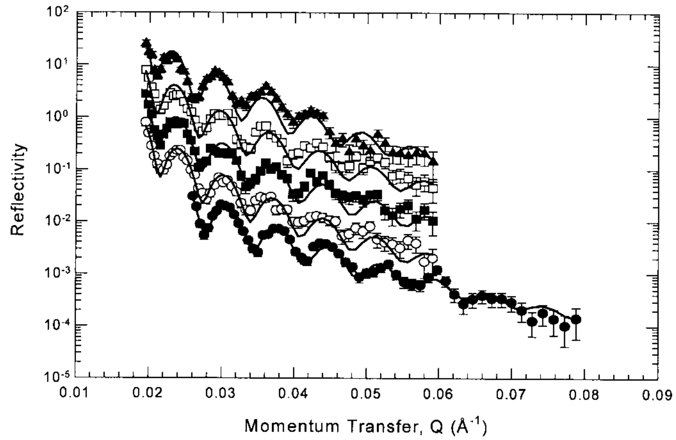

Figure 2: Reflectivity profiles of dPMMA/DINP measured in real time at 70 °C after 0.5 (●), 5.6 (○), 9.4 (■), 12.8 (□) and 26.0 (▲) min. The plots have been scaled for clarity.

On the basis of the gradient of the initial portion of the DOP system plot, *i.e.* the first 6 min and over the entire DINP range, rates of change of thickness, $\dot{s}$, $(=\Delta d/\Delta t)$ equal to $+(3.5\pm0.1)\times10^{-12}$ and $+(2.33\pm0.05)\times10^{-11}$ m/s for the DINP and DOP systems were obtained, respectively. The positive sign of $\dot{s}$ indicates that the dPMMA/plasticiser interface is moving towards the plasticiser and is indicative of the polymer swelling. The values of $\dot{s}$ are consistent with the change in molar masses of the plasticisers, where the smaller plasticiser is expected to penetrate into the layer fastest.

Single-layer fits to the DBP data do not adequately model the data, except for the single reflectivity profile taken in the first 30 s. In this case the initial dPMMA thickness of 87.4 nm has increased to 98.6 nm over that time period. As a first approximation, we can estimate the rate of change of the dPMMA layer, $\dot{s}$, using these values, to give a value of $+(7.5\pm0.5)\times10^{-9}$ m/s at 32 °C. There is still a significant difference in the measured values of $\dot{s}$, between the DINP and DOP and the very fast process observed for DBP, even with the latter measured at a reduced temperature compared to the other two systems. Unlike the DINP and DOP systems after the very early times, the dPMMA layer when exposed to DBP begins to decrease in thickness, as observed by an increase in the reflectivity interference fringe spacing. This suggests that this is no longer a swelling process caused by sorption of the plasticiser. Without further detailed analysis, it is difficult to determine whether this apparent decrease in the dPMMA layer thickness is a dissolution process or not.

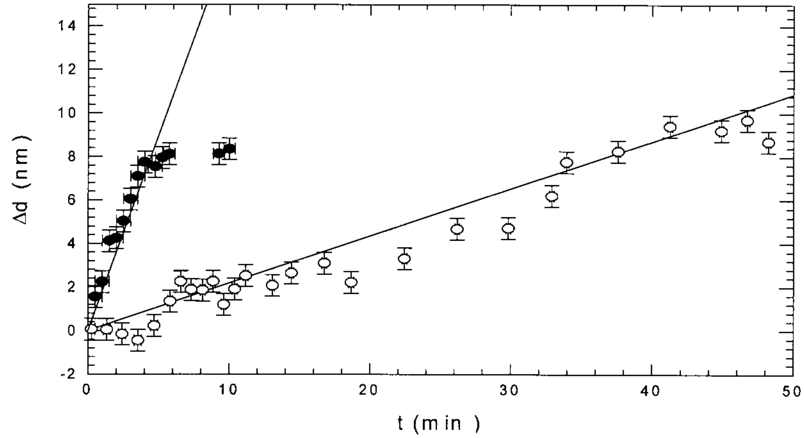

Figure 3: Plot of change in dPMMA layer thickness as a function of time for DINP (○) and DOP (●) systems.

As the plasticiser front moves into the dPMMA during the sorption process, an equilibrium concentration is expected to result. This can be calculated from the change in scattering length density of the dPMMA layer, which is directly related to the volume fraction of plasticiser sorbed into the polymer through the relationship, $\rho_s^T = (1-\phi_s)\rho_P + \phi_s\rho_s$, where ρ_S^T is the scattering length density obtained from the model fit, ϕ_s is the volume fraction of the plasticiser and ρ_i are the scattering length densities of the plasticiser (i = s) and dPMMA (i = P). Based on the fitting parameters for the DINP (after 50 min) and DOP systems (after 10 min), the values of ϕ_s are 0.02 ± 0.007 and 0.05 ± 0.01, respectively. The apparent large error on each of these values derives from the lack of extended Q range data, and again demonstrates the limitations that are incurred when using only restricted data sets. However, given that these data are only for very early times, it is unlikely that either of these values of ϕ_s represents the true value anticipated from the Case II model.

Similar analysis of the DBP system is not possible using the assumptions made for DINP and DOP. Indeed, the fits to the data do not support a simplistic single-layer model except for the initial reflectivity profile. Further work is required on this system and for the later stages for the other plasticisers, but initial work shows that a front does appear to move into the polymer, as expected for the Case II sorption process.

Conclusions

We have shown that real-time neutron reflectivity can be used to study plasticisier ingress into deuterated poly(methyl methacrylate). Three plasticisers have been studied, diisononyl phthalate, dioctyl phthalate and dibutyl phthalate, with measurements made in situ at 70 °C, except for the latter which was measured at 32 °C.

Single-layer fits to the restricted momentum transfer reflectivity data were only applicable for the early times of the sorption process for all the systems. Where a single-layer model could be used to fit the data, an increase in dPMMA layer thickness was observed for all three plasticiser systems. The DINP and DOP systems demonstrate a linear growth rate of the dPMMA layer thickness which is characteristic of Case II diffusion behaviour. As may be expected intuitively, the rate of plasticiser ingress into the polymer film, $\dot{s}$, is largest for DBP which is the smallest and more mobile plasticiser of the three studied. Similarly, $\dot{s}$ is smallest for DINP which is the largest and therefore least mobile plasticiser.

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