MEMBRANE MEDIATED POLYMER INTERDIFFUSION

Understanding the interdiffusion of polymer chains at interfaces is critical to many applications such as coatings, adhesion, composite lamination and fracture strength development. Neutron reflectivity has proven to be a very powerful technique for studying polymer interdiffusion at polymer-polymer interfaces [1]. These studies have examined the role of temperature and molecular weight on interdiffusion between hydrogenated and deuterated polymer bilayers. More recently, the sensitivity of the neutron reflectivity technique has allowed the analysis of thickness dependent diffusion when the film thickness approaches the radius of gyration of the polymer.

The present study probes how the introduction of ultra-thin barrier layers between the interdiffusing polymers affects their dynamics. The study of interdiffusion through barrier membranes is of significant importance in many areas of material science, including metallurgy, biology and polymer science. As an example, consider a system where the barrier is in fact an oxidized layer brought about by degradation of one of the materials. This is an important aspect in materials science where the effects of oxide layers on the interdiffusion in metallic systems have received considerable attention [2]. For polymeric systems one can create an ultra-thin barrier membrane composed of a crosslinked polymer. The crosslinking makes the barrier insoluble in the surrounding polymers while still allowing the interdiffusion of polymers through the membrane. The geometry of a model system designed for this study is shown in Fig. 1. It is a trilayer system, containing two polystyrene (PS) layers separated by a membrane. One of the polymer layers (either the top or bottom layer) is hydrogenated while the other is deuterated. Molecular weights of both the hydrogenated and deuterated polymer layers were closely matched
(hPS: M_w = 40 kg · mol^{-1}; dPS: Mw = 39 kg · mol^{-1}).

The sample was prepared in three stages. First, a polymer layer was spin coated on a silicon substrate covered with a uniform oxide layer (~10Å). The barrier membrane itself consisted of a blend of isopentylcellulose cinnamate (IPCC) and PS (34 wt%). It was transferred on top of the bottom polymer layer by the Langmuir-Blodgett technique. The IPCC/PS layers can be transferred in increments of 10Å. Using a blend of IPCC and PS as a membrane material allows for the control of the membrane's porosity as the PS component is free to leave the

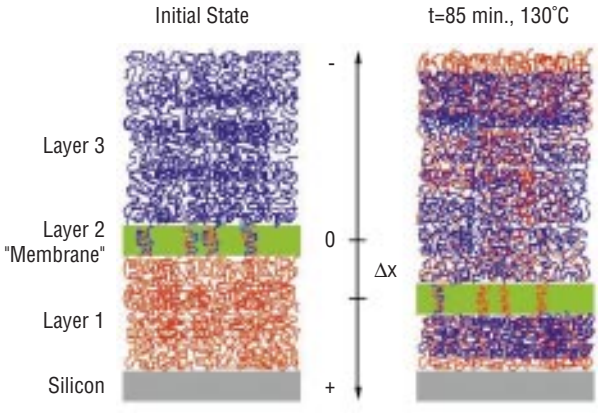

FIGURE 1. Schematic drawing of the sample geometry for Air//hPS/IPCC(34 wt% PS)/dPS//SiO_2/Si. Red (dPS) and blue (hPS) are used to distinguish between isotopically different polymer chains. The membrane (green) is displaced by Δx from its original position as hPS and dPS mix during annealing.

barrier layer during the experiment thereby creating holes and channels in the membrane's network which facilitate PS transport across the membrane. In the present case the IPCC (34 wt%PS) membrane is 60Å (6 layers) thick. After transfer the IPCC in the film was cross-linked for 15 min. by UV irradiation under a nitrogen atmosphere. The third and final PS layer was floated on top of the sample. The trilayer system was dried under vacuum at 70°C to remove residual solvents from the polymer. The thickness and roughness of the trilayer system was characterized at each stage by x-ray reflectivity.

A neutron reflectivity curve from the as prepared sample

Air // hPS/IPCC(34 wt% PS)/dPS // SiO_2/Si

is shown in Fig. 2. The orange curve is a fitted reflectivity profile based on the corresponding scattering length density (sld) profile shown in the inset (also orange). The position of the three films, dPS (~500 Å), IPCC(34 wt% PS) membrane (~60 Å), and hPS (~800 Å) can be accurately determined by neutron reflectivity. After annealing the sample at 130°C for 80 minutes, changes in the thicknesses and compositions of the PS layers as well as the location of the membrane can be obtained by fitting the reflectivity data (black). The inset shows the corresponding sld profile (also black) for the annealed sample revealing an excess of dPS at both the air and SiO_2 interfaces as has been observed in blank experiments with bilayers of dPS and hPS without the membrane. It takes about 10 times longer to achieve this final state with the

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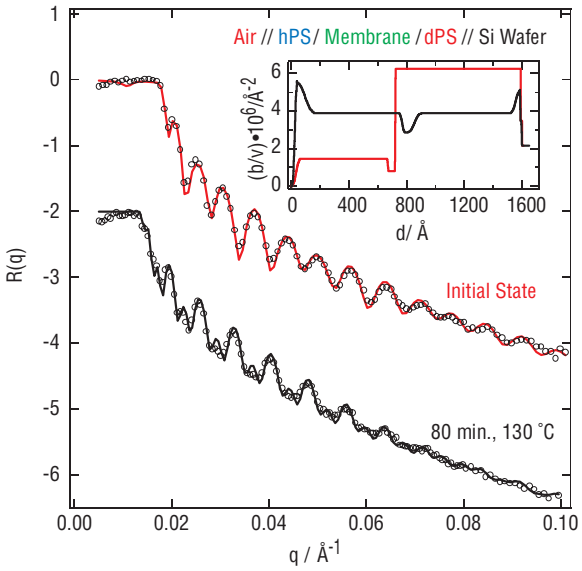

FIGURE 2. Neutron reflectivity data for initial and final state of the sample Air//hPS/IPCC(34wt% PS)/dPS//SiO_2/Si. The lines are the best fit to the data. The corresponding sld profiles are shown in the insert.

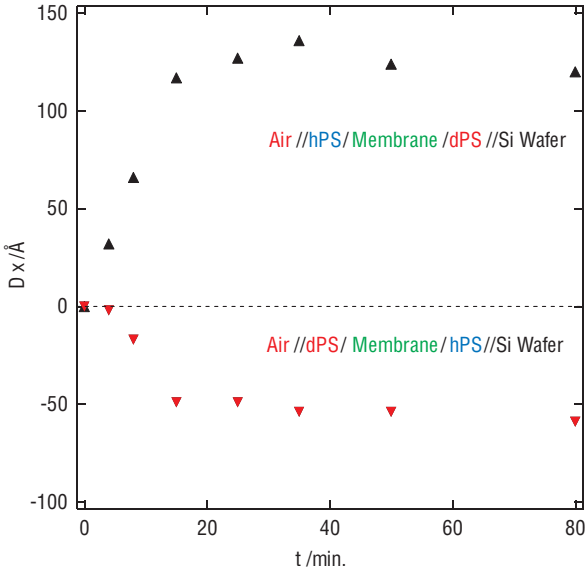

FIGURE 3. Displacement of the membrane relative to Si as a function of annealing time.

membrane present (80 min) than the corresponding time without a membrane (8 min).

More importantly, we see a movement of the membrane, Δx, relative to its initial position as measured from the Si interface. Neutron reflectivity measurements are very sensitive to the location of the membrane in this trilayer system and its position can be very accurately tracked as a function of annealing time which is shown for this sample in the upper half of Fig. 3. At later annealing times (80 min), the membrane has moved by ~120Å from its original position in the film relative to Si.

An interesting result is observed in a sample where the position of the dPS and hPS layers have been switched. The bottom panel of Fig. 3 shows the relative movement of the membrane in a sample

Air // dPS/IPCC(34 wt% PS)/hPS // SiO_2/Si

as a function of annealing time. It is obvious that the two different geometries result in a reversal of the travel direction of the membrane. In both cases, the membrane moves towards the dPS rich side of the membrane indicating a higher mobility of dPS through the membrane as compared to hPS.

In bilayer interdiffusion studies the influence of unmatched molecular weights has been investigated where the movement of the diffusion boundary has been tracked by observing the movement of gold marker particles (3). Those results show a movement of the interdiffusion boundary towards the direction of the lower molecular weight component. In the present study, the molecular weights of the hPS and the dPS were closely matched, therefore the observed movement of the membrane can be connected to slightly different interactions between the membrane's material (IPCC) and the two isotopically different polymers hPS and dPS leading to a higher permeability of dPS through the barrier.

This result opens up the possibility of a number of new experiments in this area. These include the effects on the mobility of polymers through membranes as a function of: 1) the molecular weight of the polymer, 2) the degree of crosslinking of the barrier layer, 3) the wt% of PS in the membrane (porosity), and 4) the thickness of the barrier. Besides providing valuable insight into the transport properties of ultra-thin membranes, this project serves as a stepping stone for designing future reflectivity experiments to probe transport properties in biological membranes.

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