Reduced Polymer Mobility near the Polymer/Solid Interface as Measured by Neutron Reflectivity

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ABSTRACT: Neutron reflectometry is used to measure polymer mobility over distances less than 200 Å as a function of distance from an attractive solid surface and molecular size. Effective diffusion coefficients, D_{eff}, are determined from the rates of interdiffusion between supported bilayers of deuterated and hydrogenated poly(methyl methacrylate) (PMMA). The thickness of the d-PMMA layer is varied from less than the radius of gyration, R_g, of the bulk polymer to $11R_g$ for three molecular weight pairs of polymers. D_{eff} dramatically decreases in samples with d-PMMA layers less than $3R_g$ thick and approaches bulk interdiffusion rates from layers greater than $5R_g$ thick.

1. Introduction

The understanding of the mobility of polymer chains near surfaces and interfaces impacts many technological areas such as electronics packaging, coatings, adhesion, and composite materials where the properties of polymer thin films and polymers at interfaces are critical. Bulk property values are often not applicable in these areas because the interfacial properties and behavior can be very different from those of the bulk polymer. For example, in polymer thin films, the glass transition temperature, T_g, changes depending upon the film thickness and the interaction energy between the polymer and the substrate (or lack of a substrate).[1−5] Dewetting kinetics,[6,7] rheological properties,[8] and phase separation kinetics[9] have also been observed to change in thin polymer films. Despite these experimental observations of physical phenomena that suggest changes in polymer mobility near surfaces and interfaces, a clear understanding of the effects from the polymer/surface interactions and chain confinement is not yet available.

Several experimental techniques have been used to study the interfacial properties of polymer melts. Van Alsten et al. used neutron reflectometry to study the reduced center of mass mobility of deuterated poly-(methyl methacrylate) (PMMA) monolayers into a melt.[10] Zheng et al. used dynamic secondary ion mass spectrometry (DSIMS) to study tracer diffusion of polystyrene (PS) into polymeric matrices of varying molecular weights from different surfaces.[11] More recent studies of diffusion from an initial layer sandwiched between polymer matrices and located at varying distances from the silicon substrate show diffusion coefficients an order of magnitude smaller than bulk values even at distances greater than 10 radii of gyration of the bulk polymer, R_g, from the surface.[12] Frank et al. studied the lateral mobility of polymers in thin films using a fluorescence technique and observed that the polymer diffusion coefficient was smaller than bulk values for films up to $25R_g$ thick.[13] Hall and Torkelson used small molecule probe diffusion to monitor the segmental mobility of polymers in thin supported films

and found that the polymer/substrate interaction energy did not affect segmental mobility at distances greater than 400 Å.[14] Neutron reflectometry has been used to measure the initial stages of interdiffusion between PMMA bilayers near an attractive substrate (the native oxide of silicon). These results suggested that the substrate affected the polymer mobility up to $\approx 3R_g$ from the surface.[15] These experimental results show that the strength of the polymer/substrate interaction energy has a large effect on the polymer chain mobility, but are not consistent with respect to the length scale of the influence of the substrate on polymer mobility. The interaction energy between the surface and the polymer segments is short-ranged (a few angstroms) so the longer-ranged effects on the mobility arise from the connectivity of the molecules.

In this paper, neutron reflectivity measurements probing the mobility of polymer chains with different molecular sizes over distances comparable to the size of the unperturbed polymer chain (≈ 100 Å) near an attractive substrate are reported. The mobility is determined from measurements of the rate of interdiffusion between two chemically similar polymer layers where the thickness of the lower layer is varied. The molecular size dependence of the range where the substrate affects the mobility is studied by using several closely matched molecular weight pairs of deuterated and hydrogenated polymers. Neutron reflectometry provides a precise and nondestructive technique to measure the concentration profile between the two layers because of the large contrast to neutrons between the hydrogenated and deuterated species. Since the measurements for each molecular weight pair are over very short diffusion distances, these experiments focus on the mobility of polymers directly at a polymer/polymer interface placed at different distances from the substrate. Information about how the movement of these chains is affected either directly by the substrate or indirectly by the chain conformations next to the surface is obtained. The polymer mobility is found to dramatically decrease at distances less than $3R_g$ from the surface for each molecular weight pair. The decrease in the chain mobility is attributed to the initial chain conformation or the adsorbed chain structure of polymer chains near the polymer/substrate interface.

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2. Experimental Section

A series of bilayer samples on polished silicon wafers was prepared from each of three matching molecular weight, M_w,[16] pairs of deuterated poly(methyl methacrylate) (d-PMMA) and hydrogenated PMMA, 38 000/33 250, 135 000/143 000, and 260 000/262 000, with R_g's of 49, 93, and 129 Å, respectively. Each polymer has a polydispersity (M_w/M_n) of 1.1 or less and is approximately 57% syndiotactic, 37% atactic, and 6% isotactic. The silicon wafers (75 mm in diameter; 5 mm thick) were first placed into a buffered etch solution to remove the native oxide layer. They were then placed into a UV/ozone cleaner to remove organic contaminants and to reform the oxide surface. The thicknesses of the oxide layers are typically between 15 and 25 Å thick and have roughnesses of 5−7 Å as measured by X-ray reflectivity. Layers of d-PMMA with thicknesses, h, ranging from 35 to 670 Å were spin cast from o-xylene solutions with polymer mass fractions between 0.4% and 2.0%, and annealed for at least 14 h at 150 °C under vacuum. The h-PMMA overlayers were spin cast onto glass slides and then floated from 18 MΩ·cm water onto the deuterated layers and extensively dried under vacuum. Before each neutron reflectivity measurement, the bilayer samples were annealed in a slotted aluminum block under vacuum at 150 °C for varying times. They were then quenched to room temperature, below T_g, on a cool aluminum block (within 30 s) to halt the interdiffusion process.

The specular neutron reflectivity measurements were performed at the National Institute of Standards and Technology Center for Neutron Research (NCNR) NG-7 reflectometer. The wavelength, λ, of the neutrons was 4.768 Å with $\Delta\lambda/\lambda = 0.2$. The neutron beam was passed through the silicon wafer with a transmission of 0.90 relative to the beam intensity through air. The reflectivity (ratio of the reflected intensity to the incident beam intensity) was measured at grazing incident angles less than 3°. The reflectivity is plotted as a function of the momentum transfer normal to the surface, $q = (4\pi/\lambda) \sin \theta$, where θ is the incident angle. The reflectivity is sensitive to the neutron scattering length density profile perpendicular to the sample surface. The physical quantity used in the determination of the concentration profile is the elastic coherent-scattering per unit volume, Q_c^2. Q_c^2 is related to the neutron scattering length, b, through $Q_c^2 = 16\pi nb$ where n is the number density of the scattering nuclei. The Q_c^2 values for d-PMMA, h-PMMA, and silicon are 3.50×10^{-4}, 5.15×10^{-5}, and 1.06×10^{-4} Å^{-2}, respectively. The concentration profiles are determined by generating model profiles and fitting the calculated reflectivity to the reflectivity data through the recursive multilayer method.[17] Details about the neutron reflectivity technique are available elsewhere.[18]

Figure 1a shows a typical set of reflectivity data after different annealing times from the (260 000/262 000) molecular weight pair with a lower film thickness (d-PMMA) of 124 Å and an upper film thickness (h-PMMA) of 1420 Å.[19] The symbols are the experimental data, and the solid lines are the corresponding best fits to the data from model density profiles. The initially prepared bilayer sample has a reflectivity profile with several distinct interference fringes with a spacing determined by the thickness of the deuterated lower film. Oscillations with a narrower periodicity are also present in the data and arise from the overall thickness of the sample. As the sample is annealed, the fringes at higher q values dampen out, showing that the interface between the two layers broadens with time. Figure 1b shows the volume fraction profiles of the deuterated component from the best fits to the data. In general, the error function is used to fit interfacial profiles, including those between the silicon/d-PMMA and h-PMMA/air interfaces. For the d-PMMA/h-PMMA interface, the error function adequately fits the data for interfaces <30 Å wide. For larger interfacial widths, a more complicated interfacial function is used. In this work, a combination of four different layers is used to create profiles having a steeper gradient at the center of the d-PMMA/h-PMMA interface. The fits are performed under the constraint that the mass of each component is conserved to within 5%. The modified interfacial
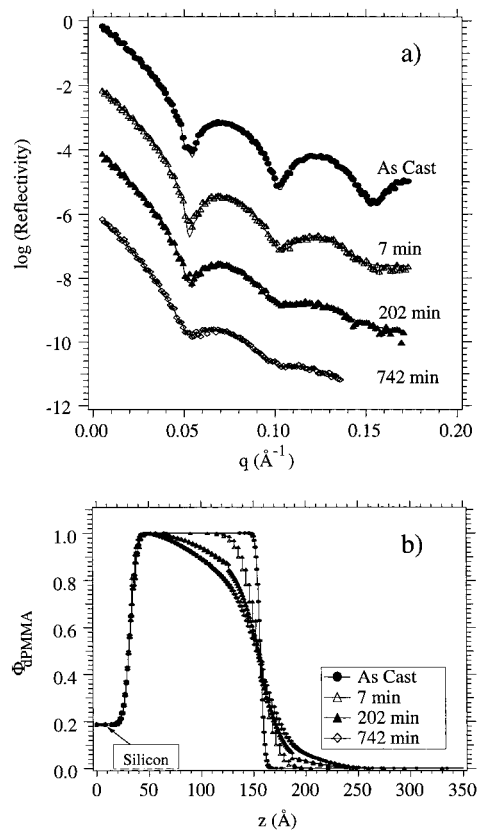

Figure 1. (a) Neutron reflectivity data from different annealing times for the bilayer sample with a lower layer (d-PMMA, $M_w = 260\,000$) 124 Å thick and an overlayer (h-PMMA; $M_w = 262\,000$) 1420 Å thick. The solid lines represent the best fits to the experimental data. The data sets are offset for clarity. (b) Fitted volume fraction of d-PMMA, $\Phi_{d-\text{PMMA}}$, as a function of distance from the silicon interface.

profiles reduce χ^2 (from the χ^2 statistical test) by at least a factor of 2 relative to that from the error function profiles.[15] The steeper gradient in the interfacial profile has also been observed in bulk interdiffusion studies and have been correlated with the reptative motion of polymer chains.[20−23] The slight asymmetry in the real space profiles arises from the fitting procedure used here. Although the modified profiles fit the data better than a simple error function, the results discussed below are nearly quantitatively identical with those from fits with the error function.

3. Results and Discussion

To facilitate comparisons between different sets of reflectivity data, the d-PMMA/h-PMMA interfacial width is parameterized by numerically calculating the second moment of the derivative of the fitted real space profile of the interface. The initial interfacial width between the layers is quadratically subtracted out through $\Delta\sigma = (\sigma^2 - \sigma_0^2)^{1/2}$ where σ is the interfacial width determined from the reflectivity data and σ_0 is the interfacial width of the as prepared sample. In Figure 2, $\Delta\sigma$ is plotted as a function of the square root of time for the (260 000/262 000) molecular weight pair for bilayer samples with varying d-PMMA thicknesses. For polymer interdiffusion free from substrate effects, the rate at which the interface broadens has been shown to be consistent with the presence of several scaling regions corresponding to those described by reptation theory.[24] The scaling behavior of the samples with the largest d-PMMA layers for all three molecular weight pairs are consistent with these observations. Deviations from
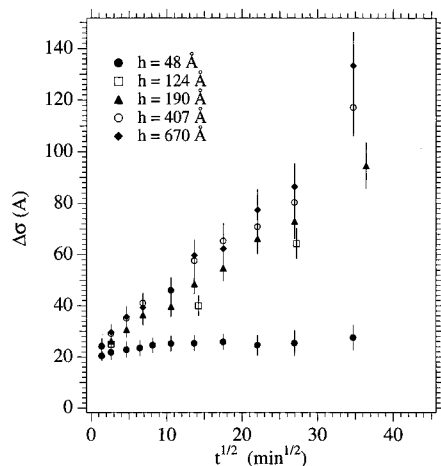
Figure 2. Interfacial width for the 260 000/262 000 molecular weight pair with varying lower *d*-PMMA thicknesses plotted as a function of the square root of time. The effective diffusion coefficient, D_{eff}, is determined from the slope of a linear fit to the data from each bilayer sample.

Figure 3. Effective diffusion coefficient, D_{eff}, is plotted as a function of the lower layer (*d*-PMMA) thickness, *h*, for each molecular weight pair (38 000/33 250, 135 000/143 000, and 260 000/262 000). Several of the error bars are within the size of the symbols.

these power laws for the thinnest *d*-PMMA films are discussed in more detail in an earlier publication.[15]

From Figure 2, the rate at which the interface broadens decreases dramatically as the *d*-PMMA layer thickness decreases. For bilayers with a *d*-PMMA thickness greater than 200 Å, the values of $\Delta\sigma$ are very similar for interdiffusion times less than 30 min. Interdiffusion over this time scale is not perturbed by the presence of the substrate. Differences in $\Delta\sigma$ are greater at longer interdiffusion times because the diffusing polymer chains are sufficiently close to the substrate to have their mobility affected. The interdiffusion distances in Figure 2 are short enough, less than 150 Å, such that hydrogenated segments in the bilayers with larger *d*-PMMA layers do not come into direct contact with the surface. Over these short interdiffusion distances, decreases in the rate of interdiffusion at the *d*-PMMA/*h*-PMMA interfaces located greater than R_g from the surface must arise from surface effects propagated by chain connectivity through an adsorbed chain structure.

Markedly different behavior is observed for the thinnest *d*-PMMA layer, *h* = 48 Å. For the thinnest *d*-PMMA layers, the interfacial width remains nearly constant with time. For these thicknesses, nearly all of the deuterated polymer chains have multiple contacts with the surface. Any broadening of the *d*-PMMA/*h*-PMMA interface is limited by the segment/segment displacement kinetics and the rate at which the hydrogenated chains can penetrate the *d*-PMMA layer. Some error is introduced in $\Delta\sigma$ for the thinnest layers because of a truncation in the shape of the concentration profile derivative due to the substrate surface. However, the very high fraction of *d*-PMMA at the surface (greater than 0.85 by volume at the longest annealing times) further shows that the interfacial polymer is strongly attached to the substrate. Effects from significant decreases in the interdiffusion rate from thin polymer layers have also been observed by Ruths and Granick in the rate dependent adhesion between very thin polybutadiene layers in the surface forces apparatus.[25]

In analogy to small molecule diffusion, the data for each bilayer sample in Figure 2 are linearly fit and the slope of the fitted line is used to determine an effective diffusion coefficient, D_{eff}. D_{eff} is not strictly the self-
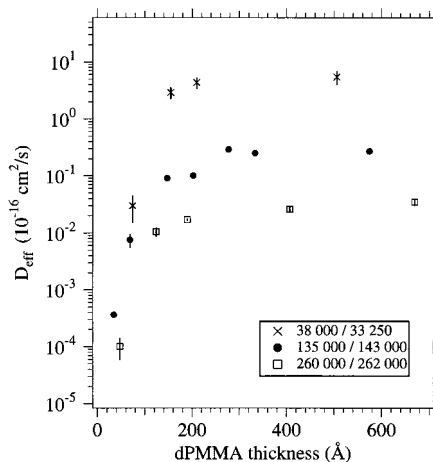
diffusion coefficient of the polymer chain because of the short interdiffusion distances, but it is an effective monomer diffusion coefficient over a given diffusion time range. However, the values of D_{eff} of each molecular weight pair from the thickest *d*-PMMA films after diffusion times greater than 200 min are consistent with tracer diffusion coefficients from similar PMMA samples as determined from other experimental measurements.[23,26] The values for $\Delta\sigma$ from the linear fits at zero time do not intercept at the value for σ_0, but at approximately 20−25 Å for each sample. This rapid broadening of the interface after annealing times of 2 min or less has also been observed in previous interdiffusion studies and has been attributed to either thermal capillary waves or Rouse modes within the expected size of the reptation tube.[15,20−23]

Figure 3 shows a semilog plot of the D_{eff} values as a function of the *d*-PMMA layer thickness. For each molecular weight pair, D_{eff} asymptotically approaches relatively constant values as the *d*-PMMA layer thickness increases. The asymptotic values of D_{eff} are approximately 5.4×10^{-16}, 0.29×10^{-16}, and 0.035×10^{-16} cm²/s for the 38 000/33 250, 135 000/143 000, and 260 000/262 000 molecular weight pairs, respectively. The asymptotic values for D_{eff} are consistent, within the error from three data points, with the expected scaling of $D \sim M_w^{-2}$.[24,27] As the *d*-PMMA thickness decreases, D_{eff} decreases by nearly 2 orders of magnitude for each molecular weight pair. At the smallest *d*-PMMA film thicknesses, all of the deuterated polymers have multiple segments in contact with the substrate. The interaction energy between PMMA and the silicon oxide surface is very attractive, so the energy needed to fully detach an entire chain from the surface is very high.[15] One may expect that this should reduce any molecular weight effects because the Boltzmann probability factor for the detachment of an entire chain is very small for each of these molecular weights. In addition, the local segment replacement kinetics at the substrate surface should not depend on molecular weight. However, D_{eff} is consistently larger for the lower molecular weight pair at any given *d*-PMMA layer thickness, even in the thinnest films. The shorter chains do have fewer contacts per chain than the longer polymers so perhaps a shorter time is needed to effectively release a surface bound chain into the bulk matrix. The increase in the
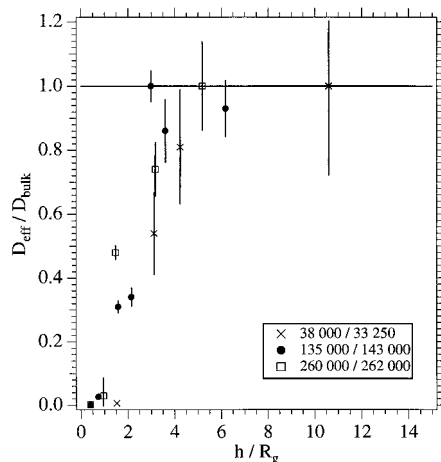
Figure 4. Effective diffusion coefficient, D_{eff}, normalized by the maximum value as determined by neutron reflectivity, as a function of the lower layer (*d*-PMMA) thickness, *h*, normalized by the bulk radius of gyration, R_g, of the constituent *d*-PMMA polymer chain.

rate of desorption may also result from the higher mobility of the lower molecular weight *h*-PMMA polymers. The chain desorption process is complicated because it depends intimately on the configurations of the chains near the interface and the configurations of the *d*-PMMA chains initially confined into ultrathin layers.

To examine the molecular size dependence of the surface effect on the mobility of polymer chains, D_{eff} is rescaled by D_{eff} from the thickest *d*-PMMA layers (bulklike) and the *d*-PMMA thickness is rescaled by R_g of the bulk constituent polymer. The results are shown in Figure 4. The data in Figure 4 generally collapse onto a single curve with a transition point at approximately $2-3$ R_g for each molecular weight pair. No substantial decreases in D_{eff} for film thicknesses greater than $5R_g$ are observed. The length scale for the transition is clearly larger than R_g, indicating that the surface effect on the polymer chain mobility is mediated by the polymer chain structure closer to the substrate. This suggests that entanglements between polymer chains not in contact with the substrate and the less mobile loops and tails of the adsorbed *d*-PMMA can affect the mobility of chains at distances greater than the extent of the adsorbed layer structure ($\approx R_g$), but less than $5R_g$ from the surface. The size of the molecule is important with respect to the thickness of the lower polymer film because of the dependence of the size of the adsorbed layer structure on the chain length.

The results in Figure 4 are not consistent with the results from diffusion measurements using a different polymer and longer length scale techniques. The DSIMS measurements of the diffusion in polystyrene (PS) trilayer samples[12] showed that the diffusion coefficient is reduced by an order of magnitude from bulk values from polymers up to $10R_g$ from the surface. Significant perturbations in the polymer chain mobility more than $300-400$ Å from the surface are not observed in this study. The differences in the studies may lie in the length scales of the measurement techniques. The DSIMS data are from measurements of the concentration profile after the molecules diffuse over several hundred angstroms, whereas these experiments probe the polymer mobility over a length scale (≈ 100 Å) that emphasizes the effect of the initial chain conformations.

Because of the longer length scale of the DSIMS measurements, the diffusion coefficients determined in the DSIMS experiments involve convolutions of the entire range of effective mobilities measured in that study. The reduced diffusion coefficients at larger distances from the surface may be strongly weighted by the population of polymer chains that remain strongly attached to the surface and have a lower mobility because the entire profile is used to determine the diffusion coefficient. On the shorter length scales of the neutron reflectivity measurements, the surface does not appear to perturb the mobility of chains at the *d*-PMMA/*h*-PMMA interface for large enough *d*-PMMA layers thicknesses. The neutron reflectivity results also involve a convolution of mobilities, but does so over a much smaller length scale. The results here are consistent with small molecule probe diffusion experiments of Hall and Torkelson.[14] They also determined that the influence of the substrate on molecular mobility does not appear at distances greater than 400 Å for poly(isobutyl methacrylate) near a fused quartz substrate. Their technique also probes the mobility locally rather than from longer ranged effects as in the DSIMS experiments. However, they do observe decreases in polystyrene diffusion coefficients with decreasing film thickness and suggest that the differences are not due to the interaction energy between the polymer and the substrate but are due to details in the molecular packing structure. More work is clearly needed to better understand the influence of a solid substrate on polymer chain structure and mobility. An important variable is the specific interaction energy between the polymer and the substrate and has not been experimentally addressed for polymers less than 400 Å from the polymer/solid interface. Experiments on samples with variable polymer/surface interaction energies are currently under way in order to clarify this issue.

4. Summary and Conclusion

The mobility of polymer chains near an attractive solid substrate was determined from neutron reflectivity measurements of the interdiffusion of PMMA bilayers. The concentration profile between *d*-PMMA and *h*-PMMA layers is measured as a function of annealing time at 150 °C. The thickness of the *d*-PMMA layer is varied from 35 to 600 Å to elucidate the effect of the solid substrate on the interdiffusion dynamics. Effective diffusion coefficients, D_{eff} are determined from the rate at which the interface broadens. Three different molecular weight pairs of *h*-PMMA and *d*-PMMA were used to determine the molecular size dependence of the length scale at which the substrate affects polymer mobility. The sensitivity of the neutron reflectivity technique allows for measurements of interfacial broadening over distances comparable to R_g (less than 200 Å) so that the direct and indirect influences of the solid substrate on the polymer motion at a polymer-polymer interface can be elucidated.

At distances greater than $5R_g$ from the interface, no substantial decreases in D_{eff} are observed and appear to be free from any effects from the solid substrate. The measured values of D_{eff} were normalized by the limiting values of D_{eff} at large distances from the substrate and the distance from the substrate was normalized by the R_g for the bulk polymer. The normalized curves of polymer mobility versus distance from the substrate was found to dramatically decrease within $3R_g$ of the surface

for all three different molecular sizes. This shows that the distance at which the substrate affects polymer mobility is dependent upon the molecular size of the polymer. At the shortest distances, the polymer chains have multiple contacts with the surface and are effectively adsorbed to the substrate. The absolute mobility of the smallest molecular weight polymers remains larger than those of the larger molecular weight polymers even at distances very near the solid substrate where molecular weight effects are expected to be reduced. At intermediate distances, the polymer mobility is affected by the substrate indirectly through the extent of the adsorbed layer.

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