

Neutron Reflectivity Measurements of Molecular Weight Effects on Polymer Mobility near the Polymer/Solid Interface

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ABSTRACT

Neutron reflectometry is used to measure the rate of interdiffusion between bilayer samples of deuterated and hydrogenated poly(methyl methacrylate) (PMMA) films with the polymer-polymer interface near the native oxide surface of a silicon wafer. In this work, the effects of a favorable substrate interaction and the molecular weight of each polymer layer are determined. Both the film thickness and the molecular weight of the lower d-PMMA layer are kept constant with a thickness of approximately one radii of gyration (R_g) of the polymer and the molecular weight of the upper hydrogenated layer is varied. Earlier experiments show that the mobility of the polymer chains within R_g of the substrate is much lower than that of the bulk, suggesting that the mobility of surface-pinned polymers controls the interdiffusion rate. In this study, we find that the rate of interdiffusion is strongly dependent upon the molecular weight of the top layer.

INTRODUCTION

A fundamental understanding of polymer mobility near the polymer-solid interface is important in many different applications including adhesion, electronics packaging, coatings, and composites. Although the length scale of the interaction between a polymer segment and a solid substrate is short, the effect of the substrate may influence the mobility of polymer chains at length scales much greater than the local level one. Changes in mobility have a strong influence on many physical properties of polymers near interfaces [1-4]. Recent experiments have investigated changes in mobility near solid substrates using a variety of techniques [5-10]. The available data show that the chain mobility is dramatically reduced near surfaces with attractive polymer-solid interaction energies. Neutron reflectivity measurement show that the effective range of the substrate on the short time interdiffusion is approximately (3 to 4) times the radius of gyration, R_g , for polymers of several molecular weights [9,10]. Longer length scale measurements suggest that the diffusion of polymer chains can be affected at distances up to 20 R_g away from the substrate [8]. At distances less than one R_g of the polymer, the chains are effectively pinned to the surface [7,9,10]. It is not clear if the short range mobility of the interfacial polymer chains is limited only by the strong interaction with the substrate or if the relative mobility of the bulk, unpinned, matrix polymer layer also plays a role.

To address this question, neutron reflectometry is used to determine polymer mobility near the solid substrate over distances comparable to R_g . Samples are prepared with a deuterated polymer layer of constant molecular weight [12] and thickness less than R_g is placed on an attractive surface and several hydrogenous overlayers with varying molecular mass. The rate of interdiffusion between layers is determined and compared with predictions from a scaling theory [7].

EXPERIMENT

Deuterated poly(methyl methacrylate) (d-PMMA) and a series of hydrogenated PMMA (h-PMMA) polymers with varying molecular masses were used in this study. The d-PMMA polymer has a molecular mass of 135000 g/mol and a polydispersity index of 1.10. The h-PMMA polymers have molecular masses of 28900 g/mol, 69000 g/mol, 143000 g/mol, 364900 g/mol, and 660000 g/mol, with polydispersity indices less than 1.05. The d-PMMA films are spin-coated from toluene solutions onto the silicon wafers with its native oxide surface. The d-PMMA layers are annealed at 150 °C for at least 14 h to completely remove the solvent. The h-PMMA layers are spin-coated from toluene solutions onto glass slides and floated from ultrapure water onto the d-PMMA layers and dried under vacuum for at least 14 h at 25 °C. The thicknesses of the d-PMMA layers are (120 ± 3) Å as measured by x-ray reflectivity. The thicknesses of the h-PMMA layers are all greater than 950 Å. The bilayer samples are annealed at 150 °C for varying times under vacuum in a large slotted aluminum block. After each annealing step, the samples are quenched to room temperature on a cool aluminum block (within 30 s) to halt interdiffusion and to measure the neutron reflectivity.

The neutron reflectivity measurements are performed at the NG7 reflectometer at the NIST Center for Neutron Research. A monochromatic neutron beam ($\lambda=4.768$ Å) was sent through the silicon wafer with a transmission of approximately 0.90. The specular reflectivity was measured at different incident angles, θ , and is presented as a function of q where $q=(4\pi/\lambda)\sin\theta$. The reflectivity data are fit with model real space profiles using the recursive multilayer method [11]. Additional experimental details are available elsewhere [9,10].

RESULTS AND DISCUSSION

Figure 1 shows a series of neutron reflectivity data as a function of annealing time at 150 °C for a d-PMMA/h-PMMA bilayer sample with molecular masses of (135000 / 364900, respectively). The reflectivity profile of the as-cast film has several well-defined fringes indicating a sharp interface between the polymer layers. As the annealing time increases, the fringes dampen because of the interfacial broadening as the polymer layers interdiffuse. Higher frequency oscillations present in both the as-cast and annealed samples are due to the overall thickness of the bilayer structure.

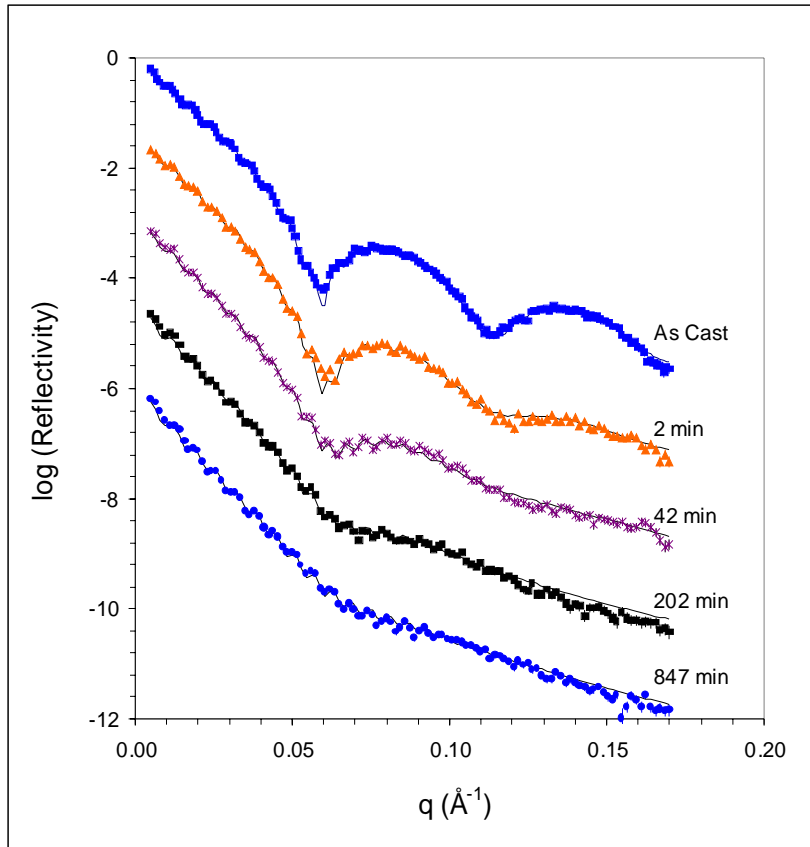


Figure 1. Neutron reflectivity data for a bilayer sample of *d*-PMMA ($M_w=135000$) and *h*-PMMA ($M_w=364900$) after different annealing times at 150 °C. The symbols are the experimental data and the solid lines are best fits to the data. The curves are offset for clarity.

The rate at which the polymer-polymer interface broadens provides a measure of the polymer mobility. The interfacial width, σ , is determined from the second moment of the derivative of the fitted real space profile (not shown here). The broadening is corrected for the initial interfacial width, σ_0 , through the equation, $\Delta\sigma = (\sigma^2 - \sigma_0^2)^{1/2}$. Figure 2 summarizes the interfacial broadening as a function of the square root of the annealing time for all of the molecular masses studied. We define an effective diffusion coefficient, D_{eff} , with linear fits to the data to parameterize the rate of interdiffusion or the mobility of the polymer chains. From Figure 2, it is clear that there are large changes in the rate of interdiffusion with overlayer molecular mass. In general, a larger *h*-PMMA molecular mass results in a slower rate of interdiffusion. It should be noted that small differences in the rate of interdiffusion are observed between *h*-PMMA molecular masses of (28900 and 69000) and (364900 and 660000). Differences in the interdiffusion rate for these molecular masses may not be distinguishable in these experiments. The data show that the mobility of the *h*-PMMA layer strongly affects the rate of interdiffusion for a given *d*-PMMA film thickness. Although the *d*-PMMA layer is effectively attached to the substrate, the rate at which the *d*-PMMA layer detaches from the attractive substrate remains strongly dependent upon the mobility of the *h*-PMMA layer.

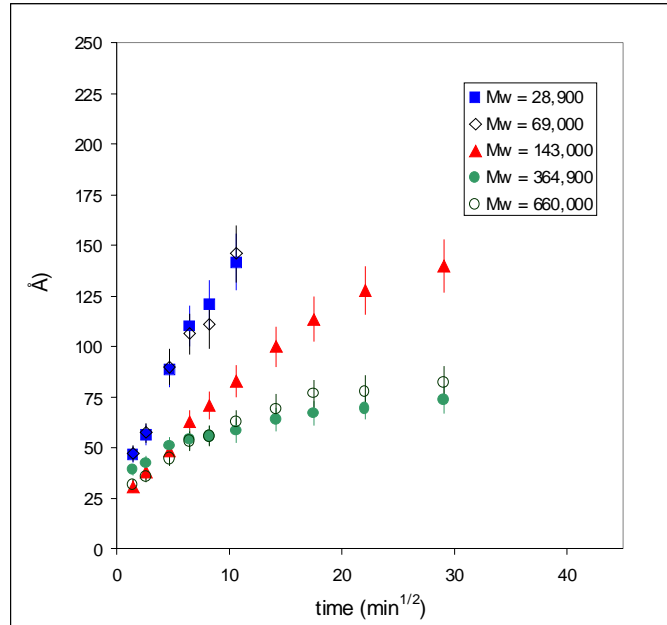


Figure 2. The interfacial width between the d-PMMA and h-PMMA layers plotted versus the square root of the annealing time at 150 °C. Linear fits to the data provide a measure of the effective polymer diffusion coefficient. Higher molecular mass h-PMMA overlayers result in a slower rate of interdiffusion.

Zheng et al. used a generalization of the reptation model to describe the mobility of polymer chains near an attractive surface [7]. In this scaling model, the chain diffusion is postulated to be hindered by approximately $N^{1/2}$ contacts of the polymer with the surface (where N is the number of segments in the chain). Because of the chain contact assumption, this model is applicable to experiments where the polymer chain remains within a R_g of the attractive surface. In these reflectivity experiments and unlike the DSIMS measurements, the polymer chains do not diffuse much more than R_g from the surface and the data should provide a test of the scaling predictions. In Figure 3, the effective diffusion coefficient is shown as a function of the h-PMMA molecular mass on a log-log plot and the data show that the interdiffusion rate decreases strongly with molecular mass. For reference, the effective diffusion coefficient for the 135000 / 143000 d-PMMA / h-PMMA molecular mass pair far from the polymer-substrate interface is $0.25 \times 10^{-16} \text{ cm}^2/\text{s}$ [9]. The solid line in Figure 3 is the $D \sim N^{-3/2}$ scaling prediction suggested by Zheng et al. [7] of the molecular mass dependence of the diffusion coefficient. Within the experimental error, the scaling law is consistent with both the neutron reflectivity data presented here as well as DSIMS measurements of the interdiffusion of d-PS /h-PS bilayers reported elsewhere [7]. Although the scaling law appears consistent with the neutron reflectivity data, there are several issues that need to be addressed before a full understanding of the polymer mobility is available. For example, the lowest molecular weight h-PMMA is near the entanglement molecular weight where the reptation assumptions are not met.

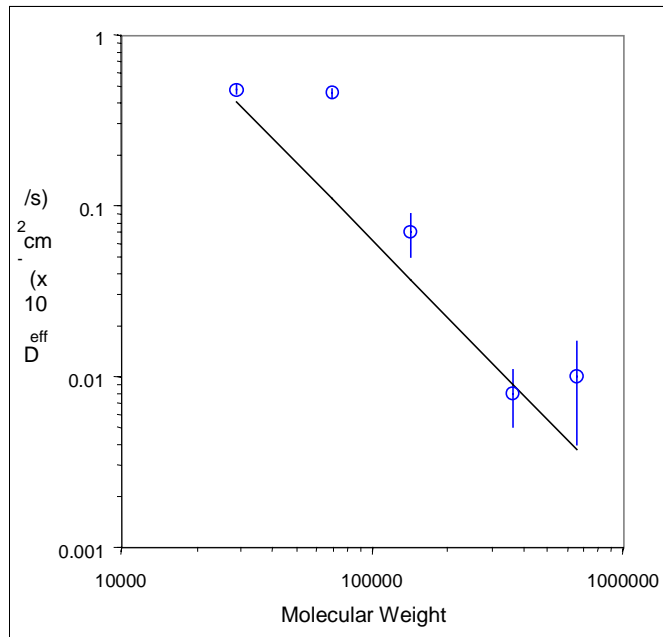


Figure 3. The effective diffusion coefficient is plotted as a function of the h-PMMA overlayer molecular mass. The solid line represents the prediction of the scaling law of the diffusion coefficient on molecular mass from reference [7] of $D \sim M_w^{-3/2}$.

SUMMARY

Neutron reflectometry is used to study the interdiffusion between d-PMMA / h-PMMA bilayers on silicon wafers over distances comparable to the size of the polymer ($< 150 \text{ \AA}$). The interaction energy between the native oxide of silicon and the PMMA segments is highly attractive. The effect of the molecular mass of the h-PMMA layer on polymer chain mobility is studied with respect to d-PMMA layers with a constant thickness (120 \AA) and molecular mass (135000). It is observed that the rate of interdiffusion is significantly greater for the lower molecular mass h-PMMA, even when the d-PMMA layer is effectively bound to the substrate [9,10]. These results suggest that the mobility of the overlayer plays an important role in determining the rate at which the d-PMMA layer desorbs from the substrate. In addition, the neutron reflectivity data are consistent with scaling predictions by Zheng et al. [7] using a modification of the reptation model. However, a rigorous analysis of the validity of this scaling argument remains to be performed.

In the future, more detailed analysis for the rate of d-PMMA segment desorption as a function of annealing time and h-PMMA molecular mass is needed. Analysis of the surface concentration of d-PMMA is also needed to better understand the mechanisms of polymer mobility near the polymer-solid interface. In addition, experiments are underway to measure the interdiffusion rate between mismatched molecular masses of PMMA far from the polymer-solid interface to determine the degree to which the d-PMMA mobility at the surface in these experiments is decreased.

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10. Lin, E. K., Kolb, R., Wu, W. L., and S. K. Satija, *Macromolecules*, **32**, 3753 (1999).
11. Ankner, J. F. and C. J. Majkrzak in *Neutron Optical Devices* (SPIE Proceedings 1738; Bellingham, WA, 1992) p. 260.
12. According to ISO 31-8, the term “molecular weight” has been replaced by “relative molecular mass,” symbol M_r . Thus, if this nomenclature and notation were to be followed in this publication, one would write $M_{r,n}$ instead of the historically conventional M_n for the number average molecular weight, with similar changes for M_w , M_z , and M_v , and it would be called the “number average relative molecular mass.” The conventional notation, rather than the ISO notation, has been employed for this publication.
13. The data throughout the manuscript and in the figures are presented along with the standard uncertainty (\pm) involved in the measurement.