Polymer Dynamics at the Melt/Solid Interface: Experimental Evidence of Reduced Center of Mass Mobility

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Despite great advances, many questions regarding the influence of a solid surface on a polymer melt remain unanswered. To date, there has been no experimental information on the perturbation of the chain center of mass mobility by a contacting solid surface. A number of polymer displacement studies have been conducted in dilute solution,[1,2] but these studies are probably not representative of dynamic equilibria at the melt/solid interface. We seek to determine the relevant time scales for molecular exchange at this interface and to determine the fundamental factors governing this process.

Due to experimental limitations, melt/solid interfaces have been probed primarily via computational models, with fruitful results. Madden[3] was the first to show that the presence of immobile surfaces induces a fair degree of organization in the first several segmental layers, and this work has spurred other theoretical studies on melt interfaces of various types.[4-6] Mansfield and Theodorou have extended the study of melt/solid structure to the perturbation in dynamics within the interfacial region,[7] including cases in which appreciable surface/segment interaction energies exist. In these studies of oligomers, the influence of surface adsorption sites was found to have a profound impact on the chain center of mass diffusivity, decreasing chain mobility from its bulk value by a factor of approximately 0.5.

Despite the obvious need, complementary experimental work has not been forthcoming, probably due to the difficulties of separating interface from bulk phenomena. To provide this necessary discrimination, we have applied the technique of neutron reflectivity, which combines the requisite ability to observe buried interfaces with extremely high spatial resolution (ca. 0.1 nm in the z direction) and the ability to prepare distinguishable but chemically similar species via deuteration. In our system, we preadsorb a single layer of deuterated poly(methyl methacrylate) (dPMMA) and then apply a second layer of hydrogenated PMMA (hPMMA) on top. The bilayer can then be annealed at various temperatures above T_g in order to initiate the molecular exchange of chains at the solid interface.

Silicon wafers were pretreated by soaking in an oxidizing Nochromix/H_2SO_4 bath. This treatment removes adventitious organic contaminants and leaves an oxidized silicon surface. The wafers were rinsed with several aliquots of distilled water, then dipped in a methanol bath, blown dry, and placed in a 150 °C vacuum oven for several hours. Monolayers of atactic dPMMA (M_w = 146 000, M_w/M_n = 1.04) were deposited onto the surfaces of the wafers in two ways. In two cases, the wafer was immersed in a 3 mg/mL solution of polymer in carbon tetrachloride overnight to adsorb a polymer layer and then removed from the bath followed by an exhaustive methylene chloride rinse. In a third case, the monolayer was deposited onto the wafer using Langmuir–Blodgett deposition. A thick layer (ca. 2000 Å) of atactic hPMMA (either M_w = 123 000, M_w/M_n = 1.25, or M_w = 330 000, M_w/M_n = 1.11) was subsequently spun coated from a xylene solution onto the deuterated monolayer. The adsorbed dPMMA layers and Langmuir–Blodgett dPMMA layers were characterized by spectroscopic ellipsometry before spin coating giving 18 ± 1 and 13 ± 1 Å, respectively.

Specular neutron reflectivity measurements were performed using the POSY-II spectrometer at Argonne National Laboratory and analyzed as described previously.[8] Over the neutron momentum transfer ($q = 2\pi \sin \theta/\lambda$) range we have studied, we cannot determine a unique profile for the adsorbed layer. We have modeled our system as two layers (polymer/polymer/silicon) and have found that the data are equally well fit by models in which the deuterated layer is either concentrated and thin or somewhat dilute and thicker, although there is a definite limit to this combination as the dPMMA concentration becomes too dilute (Figure 1). This ambiguity represents no difficulty for the purpose of this study, since we seek only information on the relative number density of adsorbed dPMMA. In this spirit, we shall henceforth, and somewhat arbitrarily, regard the adsorbed film as a layer 40–42 Å thick (approximately half the polymer radius of gyration) with a variable concentration of dPMMA, in contact with pure hPMMA. The composition of the surface layer is manifested by the magnitude of the reflectivity, which diminishes as the concentration of high "index" deuterated polymer decreases in the surface region. Typically, this measurement yields compositions with a precision of ~2% (Figure 2).

The three samples were run after oven annealing for various times at temperatures above the PMMA glass transition temperature of 106 °C. All three samples lost ~3–5% of the total initial thickness during annealing, which is typical of materials prepared in this fashion and is believed to be due to the removal of residual solvent.[9] At no time did any change in the dPMMA layer concentration occur during solvent removal at 100 °C < T < 145 °C. Sample A (146 000 dPMMA/123 000 hPMMA), in which the monolayer was deposited by Langmuir–Blodgett deposition, contained the lowest starting composition of deuterated polymer at the silicon surface at 24%. This sample was treated for a total of 35 min at a temperature of 115 °C, with no detectable loss of deuterated polymer from the solid surface region.

Sample B (146 000 dPMMA/330 000 hPMMA), which had a starting monolayer composition of 40% deuterated polymer, was annealed at a temperature of 140 °C. Reflectivity measurements were performed after annealing times of 0, 3, 8, 13, 17, and 21 min. Experimental data for this sample are presented as Figure 3 and also indicate no loss of deuterated material from the surface.

In sample C (146 000 dPMMA/123 000 hPMMA), the starting monolayer composition was 42% deuterated polymer. A temperature of 115 °C was applied for a total of 6 min without exchange of surface material, and the temperature was subsequently raised to 160 °C. Reflectivity data were taken after 2, 7, 17, and 23 min of annealing (Figure 4). This temperature was sufficient to activate the exchange of molecules, as the fraction of deuterated polymer on the surface diminished gradually from 40 to 0%. A summary of the monolayer composition versus time for all three runs is presented in Figure 5.

These findings show a remarkable difference in the time scales for center of mass diffusion between adsorbed polymer chains and those existing entirely in a melt. Sample B, for example, appeared completely static despite annealing 21 min at 34 °C above the polymer glass

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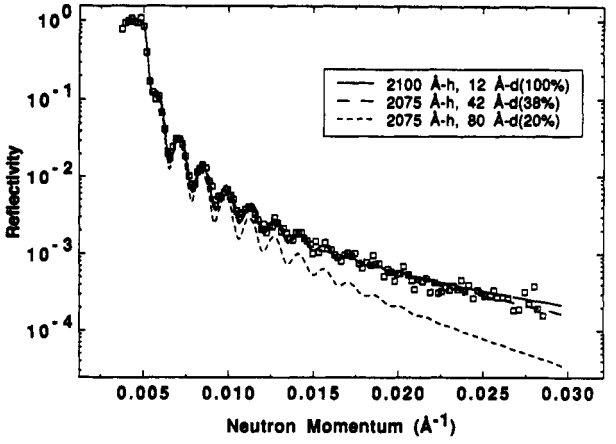

Figure 1. Modeling of the reflectivity data using three representations of the hPMMA/dPMMA/silicon sample. Within experimental error, the data may be equally well fit by models assuming a thin and concentrated or a thick and diluted deuterated layer at the polymer/silicon interface. Very dilute interfaces, as represented by the short dashed curve, do not provide acceptable representations.

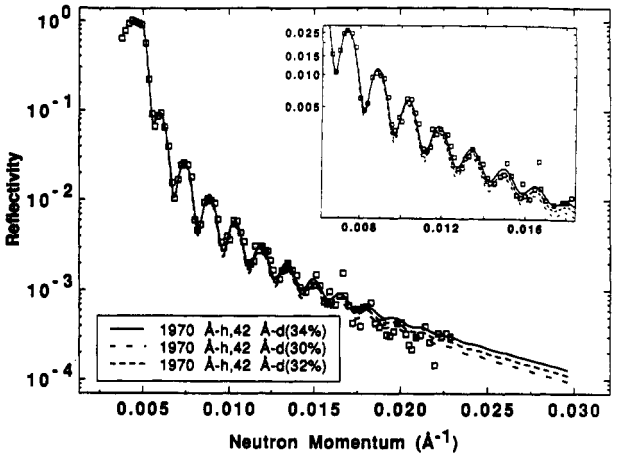

Figure 2. Uncertainty in measuring the monolayer composition. Reflectivity data are presented with models representing three different concentrations of deuterated polymer in the 42-Å interfacial layer. The inset is an expansion of the region where our data are most sensitive to differences in composition.

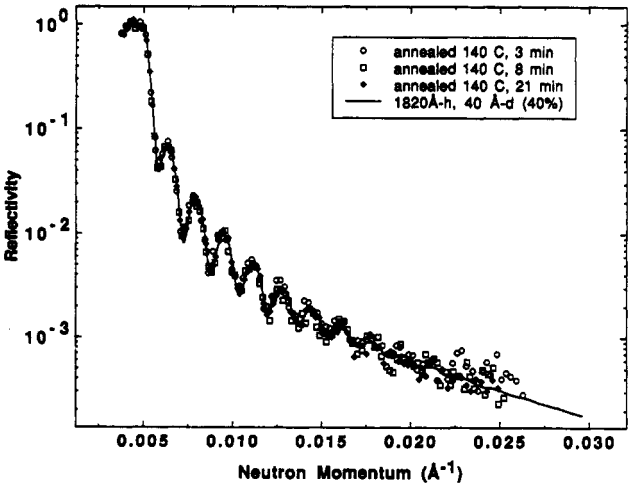

Figure 3. Reflectivity data for sample B after annealings at 140 °C. Despite treatment 34 °C above the T_g of the polymer, there is no detectable loss of material from the silicon surface.

transition temperature. Sample C shows that mobility can indeed be activated with sufficient thermal energy but that this mobility is still quite low at the temperatures we have studied so far. It is important to recognize that

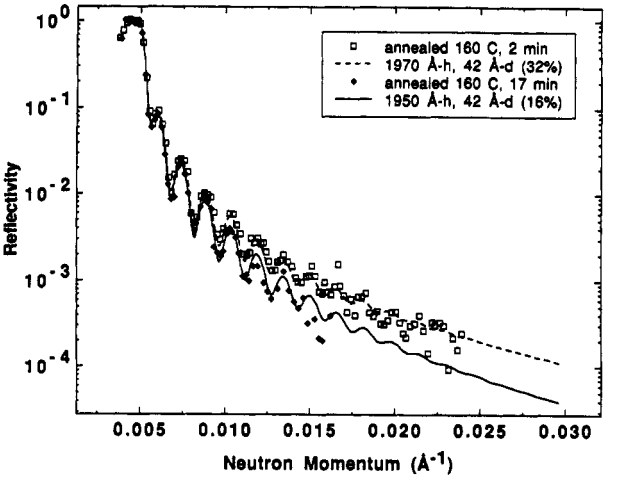

Figure 4. Reflectivity data for sample C after annealings at 160 °C. The decrease in the reflected intensity is manifest of the loss of deuterated polymer from the silicon surface.

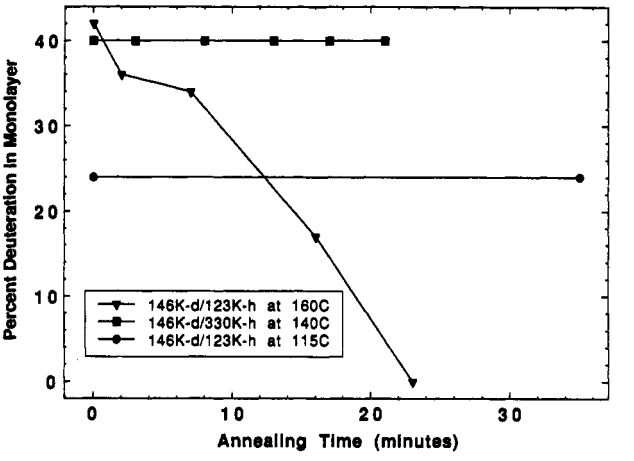

Figure 5. Composition versus time for three annealing temperatures. Only the sample annealed at 160 °C loses deuterated polymer from the silicon surface, and then only at a rate far below that characteristic of melt diffusion.

the dynamics in these cases are *not* dictated by transport within the bulk melt phase. Using diffusivities of 2.0 and 11×10^{-15} cm^2/s at 140 and 160 °C, respectively,[10] we can calculate that the center of mass of the deuterated chains should have moved 320 and 780 Å, respectively, into the bulk if the exchange process were diffusion controlled. For our modeling of the adsorbed dPMMA layer, diffusion ~100 Å away from the surface causes the deuterated species to be practically undetectable.

At present, we can only speculate on the mechanics of the slow exchange of material at the interface. It is well-established that macromolecules adsorb tenaciously to surfaces with high aggregate adsorption energies due to the large number of segmental contacts each chain makes with the surface. Because the adsorbed chains are mixed intimately with chains from the bulk melt, it would appear plausible that surface exchange on the *segmental* scale would be quite rapid but that the requisite simultaneous loss of every segmental contact point to activate large-scale center of mass motion might be somewhat improbable. In addition, the topology of the adsorbed layer itself may contribute, since a dense mesh of adsorbed loops might play the role of a network with an extremely large entanglement density.[11] This would also greatly impede the mobility of chains seeking escape from the boundary region.

These experiments have important ramifications throughout the field of polymer/solid interfaces. The

segregation of a high molecular weight polymer to the surface, for example, might be dictated by the rate at which the previous occupants of surface sites are removed. In addition, the reasonably long time scales involved (tens of minutes) suggest that such segregation phenomena may not be critical to many industrial processes. It is clear that a great deal more work will be required to understand the remarkably slow dynamics at the melt/solid interface.

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