Reptation Dynamics of a Polymer Melt near an Attractive Solid Interface

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The tracer diffusion coefficients D^* of polystyrene (PS) chains near PS melt-solid interfaces have been measured by secondary ion mass spectrometry. The D^* for poly(2–vinylpyridine) (PVP) and oxide (SiO) covered silicon surfaces were smaller by, respectively, ~ 3 and $\sim 10^2$ than for diffusion near the vacuum interface. D^* scaled with degree of polymerization N as $N^{-\alpha}$, with $\alpha_{\mathrm{PVP}} = 1.7(1)$ and $\alpha_{\mathrm{SiO}} = 1.5(1)$. These results are in excellent agreement with reptation theory modified to account for increased friction due to surface-monomer contacts. The monomeric friction coefficients were found to be 98 ± 13 (PVP) and 5750 ± 450 (SiO) times greater than the bulk melt values.

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The interaction energy of a polymer film with a solid surface can strongly influence its rheological properties. The friction coefficient f for the monomers in contact with a strongly attracting surface can be much higher than the monomeric friction coefficient f_0 in the bulk and can change the polymer dynamics near the surface. This effect has been observed in a number of different experiments. For example, Manias *et al.* [1] show that the interaction with the wall can enhance layering in a polymer film subjected to shear flow. The appearance of slippage at the wall depends on the polymer-wall friction coefficient f, which is a function of the interaction strength. Tsagaropoulos and Eisenberg [2] have proposed a similar decrease in mobility for polystyrene homopolymers adsorbed to silica filler beads to explain the presence of two glass transitions in the composite system. The wetting properties of thin polymeric films can also depend on the monomer-surface friction coefficient. Bruinsma [3] has shown that as f increases a steplike region of thickness R_g (the polymer radius of gyration) forms on the periphery of a spreading polymer drop. The step is due to an immobile polymer network with chains stuck to the wall, and a mobile polymer liquid whose chains do not contact the wall but reptate through the porous layer [3]. Silberzan and Leger [4] and Novotny [5] measured the spreading rate of a polymer droplet on a surface and found that the measured diffusion constant was at least an order of magnitude smaller than that of the bulk. In the absence of shear, the wetting properties of thin polymer films have been shown to be determined by f, as well as the usual spreading parameter. Zhao *et al.* [6] also obtained reduced diffusion rates relative to the bulk and found that the temperature dependence of the diffusion constant was much steeper than in the bulk, implying that the diffusion process required a significant activation energy to remove the stuck chains from the surface.

Although the effects of an enhanced monomer friction coefficient at the surface have been demonstrated experimentally, a direct measurement of its magnitude has not yet been made. In the case of a spreading droplet [4], the motion of the step region was faster than the experimental time resolution. But even if the motion of the step region could be measured, it would still be difficult to extract the monomer-surface friction coefficient f, because of other factors controlling the spreading rate, such as the droplet height or the structure of the contact line.

In the present Letter we report on the implementation of a simple and straightforward procedure, first proposed by Van Alsten, Sauer, and Walsh [7], for measuring the monomer-surface friction coefficient f. The same frictional coefficient which affects the spreading of the drop also controls the diffusion of the chains away from the solid interface into the melt. This motion is independent of the spreading parameter (which has not been accurately measured for very thin polymer layers) because one starts with a uniform layer at the wall.

Films of monodisperse polystyrene (PS) were spin coated directly onto Si wafer from toluene solution. Three different surface preparations of the Si were used: (1) native oxide covered, (2) hydrogen passivated via HF etching [8], and (3) covered with a 21 Å thick layer of poly(2-vinylpyridine), referred to as SiO, SiH, and PVP. The diffusion results for SiO and SiH surfaces were equal within experimental errors, and the results quoted below are for SiO. PVP surfaces were prepared by spin casting monodisperse PVP ($M_w/M_n < 1.1$, $M_w = 150\,000$) from acetic acid onto the silicon, followed by annealing for 2 h at 153 °C to produce a thin layer strongly adhered to the native oxide surface [9] which is immiscible with PS. Films of monodisperse polystyrene were spin coated directly onto the Si wafers from toluene solution. Films of monodisperse deuterated polystyrene (DPS) were floated from water directly onto the PVP covered surface.

TABLE I. Experimental values of the tracer diffusion coefficients at 153 °C.

N_{hPS}	212	481	635	865	1923	2115	5528	6442
D_{bulk} (cm^2/s) × 10^{-15}	595	125	64.5	34.0	6.80	5.55	0.87	
D_{Si} (cm^2/s) × 10^{-17}	155	48.5	26.5	18.5	5.90	5.05	1.25	0.93
N_{dPS}				865	1808		5288	6856
D_{PVP} (cm^2/s) × 10^{-16}				94.0	24.5		4.25	2.85

The PS and DPS molecular weights listed in Table I were chosen to be greater than the entanglement molecular weight, $M_e = 18\,000$ g/mol, so that the diffusion mechanism could be compared to the normal reptation process in the bulk [10]. The PS or the DPS film thickness, 50 Å, was chosen such that it would be no larger than $2R_g$ for the shortest polymer chains, and hence most chains in the layer would initially have some contact points with the wall.

A layer of deuterated polystyrene ($M_w = 713\,000$) or hydrogenated polystyrene ($M_w = 770\,000$) 4000 Å thick was floated from water onto the hydrogenated PS/DPS layer. The PS layer was positioned near the wall to insure diffusion away from the substrate since previous work has shown that DPS preferentially segregates to the SiO surface [11]. No preferential segregation of either component to the PVP or SiH surfaces was observed. It is therefore possible to place the thin DPS layer near the PVP covered surface. Control samples to measure the bulk tracer diffusion coefficient were prepared by spinning the thick DPS layer onto the Si surface and floating the thin PS layer on top. The samples were then annealed in a vacuum of 10^{-4} Torr at 153 °C for various times, and the diffusion profiles were measured using dynamic secondary ion mass spectrometry (SIMS). The conditions required to obtain the experimental spatial resolution of 90 Å have been described previously [12].

Figure 1 shows the concentration profiles, as determined from the CH^- or D^- ion intensity, of a PS layer ($M_w = 90$ K) or DPS layer ($M_w = 104\,000$) annealed at 153 °C and allowed to diffuse away from SiH and SiO surfaces for 2 h and from the PVP and vacuum interfaces for 15 min. From the figure it can be seen that the diffusion is slower when the diffusant layer is present at the PVP interface than when it is present initially at the vacuum surface. Furthermore, the diffusion away from the SiO and SiH surfaces is even more hindered than that away from the PVP covered surface. Note that stripping the oxide layer has a minimal effect on the diffusion rate. Figure 2 shows the concentration profiles obtained for PS layers of different molecular weights allowed to diffuse away from the SiO interface for various times at 153 °C. For comparison, the initial unannealed layer for the $M_w = 575\,000$ sample is also shown. The solid lines are fits (convoluted by a Gaussian of FWHM = 90 Å) to the solution of the Fickian equation for a thin film of thickness h, diffusing into a semi-infinite medium given by

$$\phi(x) = 0.5\,\mathrm{erf}\left[(h - x)/\sqrt{4D^* t}\right] + 0.5\,\mathrm{erf}\left[(h + x)/\sqrt{4D^* t}\right], \tag{1}$$

where x is the distance away from the interface and D^* is the tracer diffusion coefficient. The values of diffusion coefficients for polystyrene of various molecular weights near the different interfaces are summarized in Table I. The tracer diffusion coefficients from layers adjacent to SiO and PVP are smaller by approximately a factor of 3 and 2 orders of magnitude, respectively, than those for the layer at the free surface, in agreement with the previous droplet spreading measurements [4,6]. The diffusion coefficients away from the free surface are comparable to the bulk tracer diffusion coefficients of PS previously reported by Kramer and co-workers [13–15]. The difference in the diffusion coefficients away from the SiH, SiO, and PVP covered surfaces is a reflection of the, respectively, strong and weak interaction strengths between the PS monomers and these surfaces.

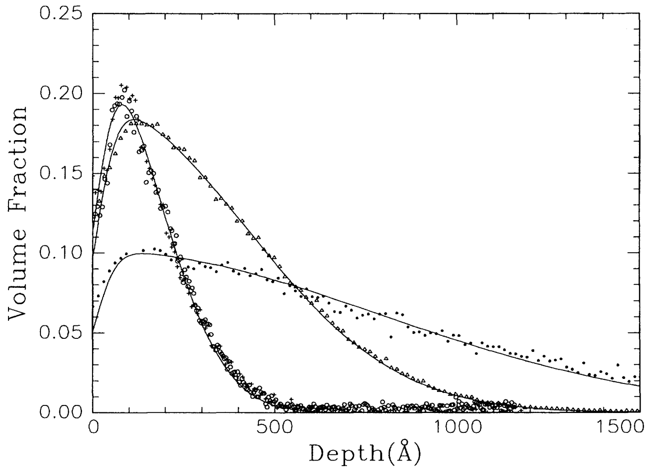

FIG. 1. Diffusion profiles obtained from the CH^- or D^- ion concentrations of a PS (M_w =90 000) or a DPS (M_w = 104 000) layer annealed at 153 °C and allowed to diffuse into a DPS (M_w =713 000) or a PS (M_w = 770 000) layer from Si (○) and SiO (+) interfaces for 2 h and from PVP (△) and vacuum (●) interfaces for 15 min. Solid lines are fits to Eq. (1)

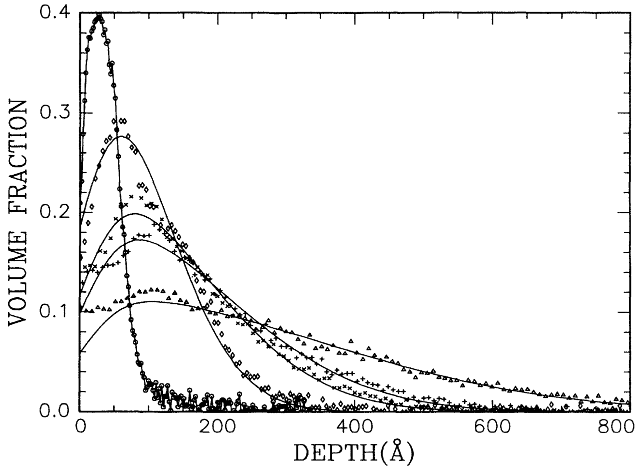

FIG 2. Concentration profiles of PS films, approximately 50 Å thick, of $M_w = 575\,000, 90\,000, 66\,000, 22\,000$ allowed to diffuse into a DPS ($M_w = 713\,000$) matrix at 153 °C for 10 h (◇), 2 h (×), 2 h (+), and 1 h (△), respectively. Solid lines are fits to Eq. (1). (○) are the spectra (divided by 2) of an unannealed PS ($M_w = 575\,000$) layer.

Figure 3 is a log-log plot of the diffusion coefficient away from the SiO, PVP, and free surfaces vs the PS molecular weight. From the figure we can see that the slope at the free surface is –2.0(1), as expected from reptation theory [13,16]. The slope at the strongly interacting surface, on the other hand, is –1.5(1), while at the weakly interacting surface it is intermediate with the value of –1.7(1).

These results can be explained by generalizing the reptation model to the motion of a chain at an attractive surface. Consider a melt of entangled chains, each consisting of N monomers in contact with a solid surface. A typical chain near the surface has $N^{1/2}$ monomers in contact with it. If there is a strong attraction between the polymer and the surface, the monomer-surface friction coefficient f is higher than the monomeric friction coefficient f_0 in the bulk. The total friction coefficient of all monomers belonging to a chain near the wall is

$$F = f_0 N + f N^{1/2}. \tag{2}$$

A polymer chain in a high molecular weight melt is confined by its neighbors to a tubelike region both in the bulk and near the surface [16]. The curvilinear motion along the tube (reptation) is unaffected by the topological constraints and the chain diffusion coefficient is [13–18]

$$D_c \simeq \frac{kT}{F}. \tag{3}$$

The length of the confining tube is $L \approx aN/N_e$, where $a \approx bN_e^{1/2}$ is the tube diameter, b is the monomer length, and N_e is the number of monomers between entanglements. The time it takes for the chain to diffuse out of the tube is

$$\tau_{\mathrm{rep}} = \frac{L^2}{2D_c} \simeq \frac{b^2 N^{5/2}}{2kTN_e}(f + f_0 N^{1/2}). \tag{4}$$

During this reptation time the chain moves a distance on the order of its size $R \approx bN^{1/2}$. Therefore the three-dimensional diffusion coefficient is

$$D_{\mathrm{surf}} \simeq \frac{R^2}{6\tau_{\mathrm{rep}}} = \frac{\alpha}{N^{3/2}(f + f_0 N^{1/2})}, \tag{5a}$$

where at 153 °C for PS with $N_e = 173$

$$\alpha \simeq \frac{kTN_e}{3} = 3.4 \times 10^{-12}\ \mathrm{erg}. \tag{5b}$$

The simple generalization of the reptation model shows that when a very strong attraction exists between the polymer and the surface, i.e., when the surface friction coefficient satisfies the condition $f \gg f_0 N^{1/2}$, the diffusion coefficient is given by

$$D_{\mathrm{surf}} = \frac{\alpha}{fN^{3/2}}, \tag{6}$$

which scales as the $-3/2$ power of the degree of polymerization, in excellent agreement with experiment. In the case of weak interactions, $f \ll f_0 N^{1/2}$, we recover the bulk diffusion coefficient as

$$D_{\mathrm{surf}} = \frac{\alpha}{f_0 N^2} \approx D_{\mathrm{bulk}}. \tag{7}$$

In order to test the validity of Eq. (5), the data at the vacuum surface were first fitted with Eq. (7), to obtain $f_0 = 1.2(1) \times 10^{-4}$ g/s. Substituting this value

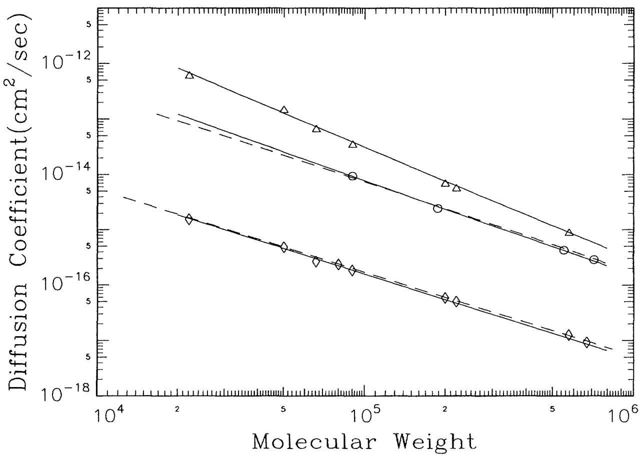

FIG. 3. Tracer diffusion coefficients measured from the vacuum (△), PVP (○), and SiO (◇) interfaces as a function of PS molecular wight. The solid lines are fits with corresponding slopes of –2.0(1), –1.7(1), and –1.5(1). The dashed line is a fit to Eq. (5)

into Eq. (5), we then fit the data at the SiO and PVP surfaces with f being the only free parameter. The results are plotted as dashed lines in Fig. 3. For the SiO surface we obtain $f = 0.69(5)$ g/s. Note that $f/f_0 = 5750 \pm 450 \gg N^{1/2}$, showing that the SiO is a strongly attractive surface and the dashed line [Eq. (5)] coincides with the limiting power law in Eq. (6) (solid line in figure). This confirms our assumption that the polymer dynamics near the strongly interacting surfaces are dominated by the monomers in direct contact with the surface. On the PVP covered surface the fitted value of the surface friction coefficient is much lower than for SiO, $f = 0.012(2)$ g/s. The ratio f/f_0 of the surface to bulk friction coefficients is 98 ± 13, which is comparable to $N^{1/2}$, indicating that the system is in the crossover region where both surface and bulk effects are important.

In conclusion, we have found that the diffusion coefficient of a chain in a melt near a strongly attractive interface scales as $N^{-3/2}$, in excellent agreement with reptation theory modified to account for the effect of the $N^{1/2}$ surface-monomer contacts. The measurement of the diffusion away from a planar interface was shown to be a convenient method to accurately determine surface friction coefficients. Even for the case of diffusion near a weakly interacting interface between two highly immiscible polymers, PS and PVP, where mostly Van der Waals interactions are present, significant departures from bulklike dynamics were observed.

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