

Mobility of Polymer Chains Confined at a Free Surface

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Dynamic secondary ion mass spectrometry was used to investigate the chain mobility of polystyrene (MW ranging from 4.3 to 957 kg/mol) at the free surface. The data show that the diffusion coefficient was reduced relative to the bulk value within a distance, $d \leq 4R_g$, from the surface and scaled as $1/N^{2.5}$ at fixed d . These results are in excellent agreement with self-consistent field calculations of the surface segmental distribution and provide the first direct confirmation of various theoretical models that predict asymmetric segmental fluctuation which arises from surface induced orientation of polymer chains.

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Understanding the dynamics of polymer chains at a free surface is critical to many applications, including welding, adhesion, and lubrication [1]. While at first glance it would seem that the free surface presents none of the complications that are observed in studies of polymers adsorbed at solid surfaces [2–6], studies on polymer dynamics at a free surface have yielded contradictory results. For example, several groups [2,7,8] have claimed large reductions of the glass transition, T_g , in the near surface region, and other groups [9,10] found no evidence of reduced T_g at the free surface. While the glass transition is assumed to be controlled by local segmental motion, the rheological properties of a polymer surface are controlled by the long-range center of mass motion of the polymer chains. Hence, in order to form a comprehensive picture of the rheological properties at the surface of a polymer melt, one must understand the interrelation between the local segmental fluctuations and the structure of the entire chain.

In this Letter, we report a comprehensive set of experiments to determine the long-range center of mass dynamics of polymer chains normal to the free surface of a melt, and we correlate these results to a theoretical model that predicts the equilibrium chain conformations in the near surface region. In particular, in this paper we directly probe the interrelationship between structure and dynamics. We use dynamic secondary ion mass spectrometry (DSIMS) to systematically investigate the center of mass diffusion of the polymers with different molecular weight as a function of distance from the vacuum interface. We then use mean field theory to calculate the chain conformation at the free surface and compare with the experimental measurements of the chain dynamics.

In order to directly compare the diffusion coefficients at the free surface with those in the bulk, it was crucial that the probes which sense the diffusion at the two locations be annealed under identical conditions. We therefore prepared multilayer samples of monodisperse (polydispersity index < 1.1) polystyrene (hPS) and its deuterated analogue, dPS, as shown in the inset of Fig. 1.

A 200 nm layer of matrix hPS was first spun cast onto native oxide covered silicon from toluene solution. A second layer, 25 nm thick, composed of 20% monodisperse dPS and 80% matrix hPS, was spun cast onto a glass slide and floated on top of the first layer. A third layer, composed of matrix hPS, 200 nm thick, was floated on top of the second layer. Finally, the sample was covered by a fourth layer of the same composition and thickness as the second layer. The samples were annealed in vacuum of 10^{-6} Torr, and the concentration profiles were measured with DSIMS with a depth resolution of 8 nm. The details of this method are described in Ref. [3].

Figure 1 shows the concentration profiles for a multilayer sample, where the matrix is hPS (MW = 600k) and the top and middle layer are 27 nm thick and contain 20% dPS (MW = 250k). The sample was annealed at 150 °C for 2 h. From the figure, we can see that the middle layer is more diffuse than the free surface layer. Since the two tracer layers are sufficiently far apart, they were both fit

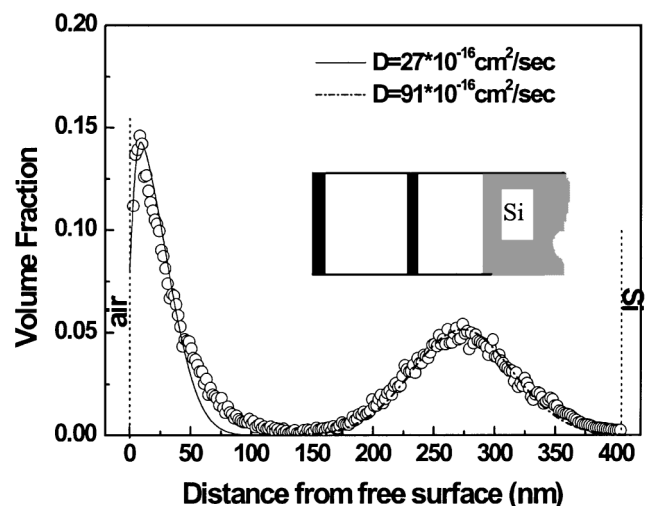


FIG. 1. DSIMS concentration profiles of the dPS volume fraction as a function of distance from the free surface for a four-layer sample. Inset: Sample geometry.

separately to the Fickian relationship, with a constant tracer diffusion coefficient D for diffusion into a semi-infinite and an infinite medium for the top layer and the middle layer, respectively. The value $D = 91 \times 10^{-16} \text{ cm}^2/\text{s}$, obtained from the best fit of the middle layer, is in agreement with the “bulk” values previously reported by several groups [11–13] and therefore will be defined as D_{bulk} . The diffusion coefficient obtained from the layer at the top surface, $D_{\text{surf}} = 27 \times 10^{-16} \text{ cm}^2/\text{s}$, is approximately 3 times slower than the bulk value.

A systematic study of the molecular weight dependence of the surface effect was done by varying the molecular weight of the tracer polymer, ranging from 4.3k to 957k, using the same sample geometry as shown in the inset of Fig. 1. In each case, the layers containing dPS were kept at a constant initial thickness of approximately 25 nm. The temperature/time of the anneal was adjusted so as to limit the broadening of the top dPS layer to approximately 45 nm. The molecular weight of the matrix was chosen such that it is close to the molecular weight of the tracer chains. Figure 2 is a log-log plot of the diffusion coefficients, scaled to 150 °C using the standard parameters for PS [14], vs the tracer molecular weight. To eliminate possible isotopic segregation effects [15] at the free surface, four-layer samples were also prepared with hydrogenated PS (MW = 90k and 957k) as the tracer probe and dPS (MW = 250k and 860k) as the matrix (solid symbols in Fig. 2). From the figure, we can see that, for both hPS and dPS tracer probes, the diffusion coefficients measured at the surface and bulk fall on two distinct lines. The slope, m , for the middle layer is $m = -2.0$, as expected from the reptation theory for a chain in the bulk [1]. The slope at the free surface, on the other hand, is $m = -2.5$.

Several groups have reported a decrease in the self-diffusion coefficients for PS films near a solid substrate [3,5]. Zheng *et al.* [3] measured the molecular weight scal-

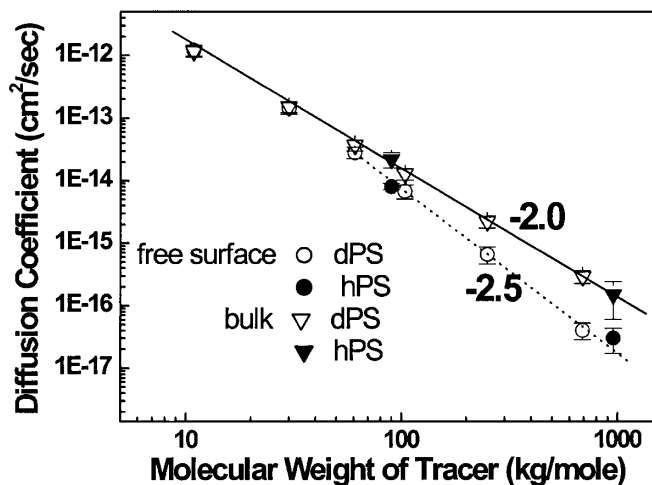


FIG. 2. Diffusion coefficient as a function of tracer molecular weight. Note the different slopes for the chains located near the surface and in the bulk regions.

ing and found $m = -3/2$, which they explained in terms of a modified reptation model where an additional interfacial friction coefficient, much larger than the bulk value f , was included to account for the enthalpic interactions of the monomers in direct contact with the surface. In our case, the large surface tension [16] of the polymer ($\gamma = 33 \text{ dyn/cm}$) maintains an atomically flat air/polymer interface ($\sim 0.6 \text{ nm}$) [1,6]. Consequently, the free surface can be approximated as a hard but neutral wall where the monomers would have a somewhat reduced friction coefficient or $f_0 \leq f$. From Ref. [3], we find that the modified reptation model would predict a scaling where only values of $m \leq 2$ are allowed. Hence, a purely enthalpic argument cannot explain our results.

The simulation results of Binder [17], Bitsanis [18], and others [19,20] have shown that a neutral wall induces an orientation in all chains which have at least one segment in contact with the wall. These simulations predict two observable consequences: (1) The segmental motion of the chains is anisotropic; i.e., the motion perpendicular and parallel to the free surface is respectively slower or faster than the bulk. (2) Since the induced orientation requires segmental surface contact, it persists only within a distance, d , of $\sim(2-3)R_g$ from the surface, where R_g is the chain radius of gyration.

We therefore propose the following explanation for our results. Since the center of mass diffusion consists of a coordinated set of motions by the polymer segments, the more segments a chain has at the surface the more anisotropic would be its diffusion into the bulk. However, in order to test this hypothesis we have to determine precisely how many segments a chain has near the surface as a function of its position from the surface. In molecular dynamics and Monte Carlo simulations, such calculations often yield large errors in their estimate because of the small system sizes that are necessitated by computational limitations. Hence, in order for us to test our hypothesis, we applied the self-consistent field (SCF) theory and devised a method whereby we could identify the average number of monomers *on a given chain* that are present at the free surface [21,22].

In the calculation, which is a one-dimensional equilibrium lattice method, we consider two types of chains. The matrix is represented as a homopolymer with a chain length of $N = 100$ lattice units. We then examine the effect of introducing a small number of tracer chains (also of chain length $N = 100$) into the matrix. The tracer chains are constrained such that one end of the chain is fixed at a particular distance, d/R_g , away from the hard, neutral surface. Since the location of our end point is fixed only in the direction perpendicular to the interface, we assume translation invariance in the other two directions; i.e., we average over all possible locations of the end point in the plane parallel to the interface. We then examine the equilibrium concentration profiles of the tracer chains as a function of d/R_g . From the concentration profile we can extract the number of segments that are present at the surface layer

as a function of the pinning distance of the end point. To check that we were probing the statistics of a single chain, we also calculated the probability distribution of the end to end distance of the chain, when it was located far away from the hard wall and confirmed that it obeyed Gaussian statistics for a single chain.

In Fig. 3, we plot the probability that a segment on the chain (which has one end pinned at a distance d away from the surface) is located at the free surface as a function of d/R_g . Notice that there is a large linear portion of the curve and the function drops off rapidly once we exceed $(2-3)R_g$, in agreement with previous studies. As per our hypothesis, if we assume that the center of mass motion of the polymer chain is controlled by the number of segments that are present near the surface, we can then expect that the tracer diffusion coefficient of the whole chain in the direction normal to the surface will be decreased relative to the bulk. The amount by which it is decreased, given by the ratio $D_{\text{surf}}/D_{\text{bulk}}$, will be directly proportional to the number of chain segments at the surface, which we can see from Fig. 3 scales as d/R_g . An observable verification of this hypothesis would then be a scaling of the diffusion coefficient with R_g rather than the molecular weight.

In order to test this hypothesis, we replotted the data shown in Fig. 2 to reflect this scale. In Fig. 4, we plot $D_{\text{surf}}/D_{\text{bulk}}$ vs d/R_g , where d is the initial thickness of the tracer layer. For this set of data corresponding to Figs. 2 and 4, d was constant and the molecular weight of the tracer chains was varied. The data was fitted by two straight lines where the intersection point was arbitrarily defined as the crossover thickness, $d_{\text{crossover}}$, to bulk behavior. From the figure, we can see that the effect is largest for the higher molecular weight polymers. For

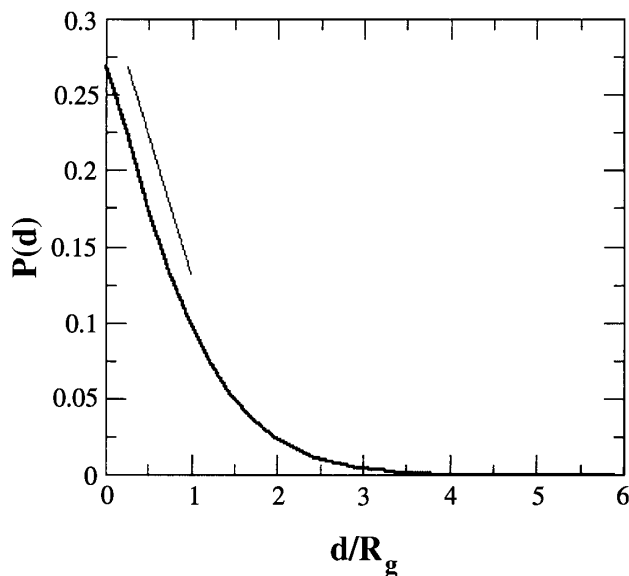


FIG. 3. SCF calculation of the probability that a segment on a chain that has one end pinned at a distance d from the surface is located at the surface. The straight line is a guide to show the linear region for the surface segment distribution.

$d \geq 4R_g$, the surface diffusion coefficient is bulklike, or the ratio $D_{\text{surf}}/D_{\text{bulk}} \sim 1$. This scaling implies that, for a given molecular weight, D_{surf} is no longer a constant, but depends on the diffusing distance or time; i.e., at large distance/time, the surface and bulk diffusion coefficients must be equal. Close examination of Fig. 1 shows that, for large distances from the surface, the observed diffusion is somewhat faster, and the fitted curve and, hence, the profile cannot be fit by a single value of D_{surf} . In the inset of Fig. 4, we plot $D_{\text{surf}}/D_{\text{bulk}}$ as a function of annealing time for a sample of MW = 104k. From the figure, we can see that, for the diffusion times used in this study, $t \leq 3$ h, only a slight increase in $D_{\text{surf}}/D_{\text{bulk}}$ with time occurs. For longer times, the ratio seems to increase rapidly such that bulklike diffusion is observed for $t > 7$ h.

In order to probe the assumption that the chains gradually recover the bulk dimension away from the surface, we measured the diffusion coefficient into the same matrix (hPS MW = 900k) for a set of samples as a function of d , the initial layer containing the tracer probe. For this set, we kept the diffusing time fixed at $t = 1$ h and the molecular weight of dPS at 250k ($R_g = 13$ nm) and 690k ($R_g = 22$ nm) respectively. The ratio, $D_{\text{surf}}/D_{\text{bulk}}$, obtained from fits to the data are plotted as a function of d/R_g in Fig. 5. The dashed lines superimposed on this set of data are the same as those obtained from the fits to the points shown in Fig. 4. From the figure, we can see that the same scaling is observed when we vary d as when we varied R_g . This is further confirmed by the fact that the two curves for MW = 250k and 690k overlap, as expected. From the results, we can conclude that a distance of approximately $4R_g$ is required for the surface induced orientation to decay and for the polymer chains to recover bulklike conformation and dynamics. We note that this effect persists longer than what the theory predicts, but we believe this is a result of an underestimation of the excluded volume effect in the mean field theory which could

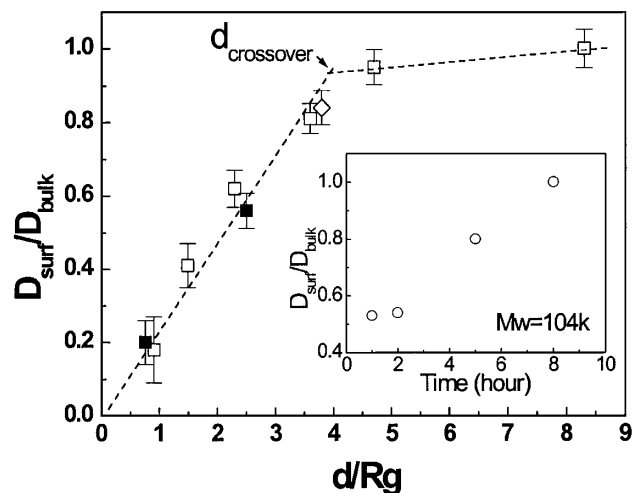


FIG. 4. The ratio of the tracer diffusion coefficient in the surface and in the bulk, $D_{\text{surf}}/D_{\text{bulk}}$, as a function of scaling factor d/R_g . Inset is the time dependence of the ratio of $D_{\text{surf}}/D_{\text{bulk}}$.

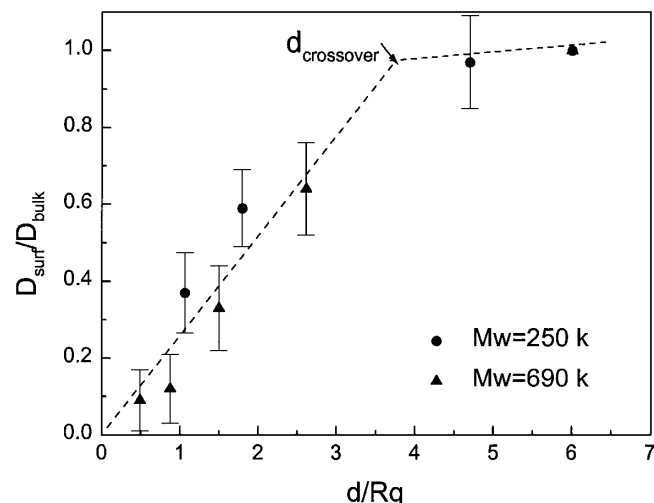


FIG. 5. The ratio of the tracer diffusion coefficient in the surface and in the bulk, $D_{\text{surf}}/D_{\text{bulk}}$, as a function of scaling factor d/R_g . Here, R_g is fixed while d is allowed to vary.

extend the linear portion in Fig. 3. These results are also in good agreement with the distance predicted by Bitsanis [18], Binder [17], and Kumar [19].

We can then use the linear approximation for the number of surface segments shown in Fig. 3 for $d < 3R_g$ to understand the molecular weight scaling shown in Fig. 2. From the slope to the dashed line in Figs. 4 and 5, we find that $D_{\text{surf}} = 0.27 \times D_{\text{bulk}}(d/R_g)$. In an entangled melt of Gaussian chains, $R_g \propto aN^{1/2}$ and $D_{\text{bulk}} \propto N^{-2}$ [14]. Hence, at a fixed distance from the free surface or constant value of d , we obtain $D_{\text{surf}} \propto 1/N^{2.5}$, in excellent agreement with the scaling shown in Fig. 2.

For the data used to obtain the molecular weight scaling, the molecular weight of the matrix was taken to match that of the probe. In the reptation model, the matrix determines the tube diameter and contributes to the dynamics through the tube renewal fluctuation time. The presence of the free surface orients the matrix chains as well for a distance $d < 4R_g$ of the matrix. Hence, when the molecular weight of the matrix is larger than that of the probe, the diffusion occurs through a network or oriented chains.

In order to determine the effect of the matrix orientation on D_{surf} , a set of samples were prepared where the same tracer chains (MW = 61 K) were allowed to diffuse for a fixed d into a matrix of MW = 90k and Mw = 6.5M. For the first case, d/R_g for the matrix is comparable to that of the tracer polymer and the value for the ratio, $D_{\text{surf}}/D_{\text{bulk}}$ lies, as expected, on the curve shown in Fig. 4. In the second case, d/R_g for the matrix is only 0.4 and, hence, the matrix is highly oriented. The value of $D_{\text{surf}}/D_{\text{bulk}}$ is plotted as a diamond in Fig. 4. From the figure, we can see that $D_{\text{surf}}/D_{\text{bulk}}$ as obtained for the matched molecular weight matrix. Hence, the orientation induced by the free surface in the matrix does not affect the dynamics of the probe. The matrix contributes to the probe dynamics

indirectly, by forming the reptation tube which contains the reptation of the probe. The relatively small degree of orientation induced by the surface should not affect the entanglement length of the melt. The asymmetric segmental motion of the oriented matrix can affect the tube renewal dynamics. But since tube renewal contributes to tracer the diffusion coefficients as $D \propto 1/M_p^2 + 1/M_m^3$, we are not sensitive to it when the matrix molecular weight is much larger than that of the probe.

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- [22] We repeated the calculation by increasing the chain lengths to 200 lattice units. Our results indicate that, by scaling the x axis by d/R_g and the y axis by R_g , the data for the two chain lengths collapse on the same curve. The scaling of the y axis is necessary since the longer chain length will always have more monomers present at the surface.