Long-Range Effects on Polymer Diffusion Induced by a Bounding Interface

X. Zheng, M. H. Rafailovich, and J. Sokolov
Department of Materials Science and Engineering, State University of New York at Stony Brook,
Stony Brook, New York 11794-2275

Y. Strzhemechny and S. A. Schwarz
Physics Department, Queens College of The City University of New York, Flushing, New York 11376

B. B. Sauer
E. I. DuPont de Nemours & Company, Inc., Experimental Station, Wilmington, Delaware 19880

M. Rubinstein
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599

(Received 31 March 1997)

We have measured the diffusion of deuterated polystyrene of molecular weight 90×10^3 in various matrices of hydrogenated polystyrene as a function of distance from an attractive interface, oxide-covered silicon. Surprisingly long-range effects are observed. Diffusion rates an order of magnitude slower than bulk persist up to $10R_g$ (radius of gyration) from the interface of either the diffusant or matrix polymers. The slowdown is independent of matrix molecular weight over a broad range. However, mixing of polymers within the matrix strongly influences the rates of diffusion. [S0031-9007(97)03536-9]

PACS numbers: 61.41.+e, 66.10.Cb

Kinetics and thermodynamic properties of fluids near interfaces and in confined geometries can be substantially different from their bulk counterparts. Recent studies have focused on the behavior of mechanical properties [1], glass transitions [2–7], diffusion in thin films [8–10] and colloidal particles [11], and phase separation [12–14]. Central issues in all these cases are the following: By what mechanism and over what distance is the influence of the bounding interfaces propagated? In this Letter, we report the results of an investigation of polymer melt diffusion near an attractive interface. Using a direct profiling technique, secondary ion mass spectrometry (SIMS), we are able to measure diffusion rates of deuterium-labeled polymers as a function of distance of the diffusant from the interface. The main result is the direct observation of very long range effects on the polymer dynamics, with diffusion rates showing *order of magnitude* reductions relative to the bulk even at distances up to *10 times* the radius of gyration, R_g, of either the labeled tracer polymers or the matrix polymers.

Previously we have shown [9] that for polymers in direct contact with an attractive interface-hydrogenated polystyrene (hPS) near native oxide covered silicon—the diffusion coefficient D for escape from the wall is on the order of 100 times slower than bulk diffusion and has a different molecular weight dependence, $D_{\text{near-surface}} \propto (M_W)^{-3/2}$ compared to $(M_W)^{-2}$ in the bulk. We interpreted these results in terms of a reptation picture where monomer-surface contacts ($\sim N^{1/2}$ per chain, where N is the number of monomers) restrict the chain mobility and modify the frictional force per chain from the bulk behavior, $F_{\text{friction}} \propto N$ to one where $F_{\text{friction,surface}} \propto N^{1/2}$. This model suggests that once chains have diffused more than R_g the influence of the surface should be greatly reduced. However, closer examination of the depth profiles shown in Ref. [9] shows that the concentration profiles are well fit by the reduced diffusion coefficients even though they extend for distances far greater than R_g. These observations were confirmed by subsequent time dependence experiments on PS films of molecular weight, 90×10^3, which showed that the mean diffusion coefficient increased only by a factor of 2, from 1.85×10^{-16} to 4.15×10^{-16} cm^2/sec after annealing at 153 °C for 40 min and 24 h, respectively. For the longer anneal, typical polymers diffused ~1000 Å. Since $D_{\text{bulk}} \approx 4 \times 10^{-14}$ cm^2/s at 153 °C [15] and $R_g(90 \times 10^3$ hPS$) = 78$ Å, it became clear that the surface was inducing a long-range effect. Similar results were obtained with 200×10^3 hPS. A possible explanation for this behavior could be a model where polymers moving randomly will return to the wall, get stuck for a long time, and escape again. If the residence time is sufficiently long, set diffusion would be slowed down for long times. The dynamics for such a “multiple hit and stick” model have been worked out by Bychuk and O’Shaughnessy [16]. In between surface “hits,” the polymers are postulated to diffuse at the bulk rate.

In order to test this theory, we prepared multilayer samples (Fig. 1) where a labeled layer of deuterated polystyrene (dPS) was placed in a matrix of hPS at varying distances X_W from the interface. If the above model is applicable, the diffusion rates for short times, before the dPS has reached the wall, should be bulklike.

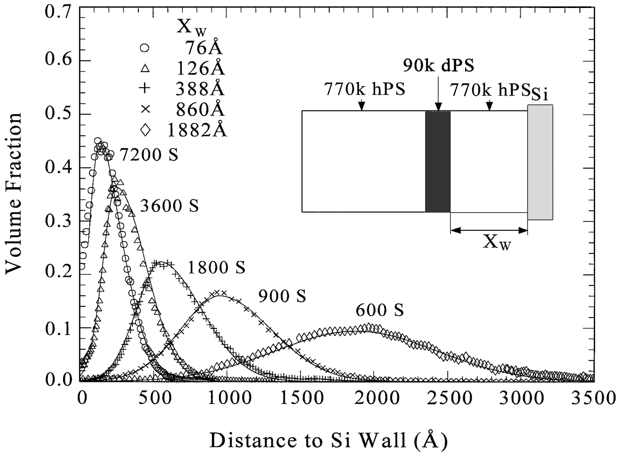

FIG. 1. Profiles of dPS volume fraction vs distance for samples annealed at 153 °C for times from 600 to 7200 s. Curves through the data are diffusion calculations to fit the slopes on either side of each peak with a single average diffusion constant. The inset shows the sample geometry.

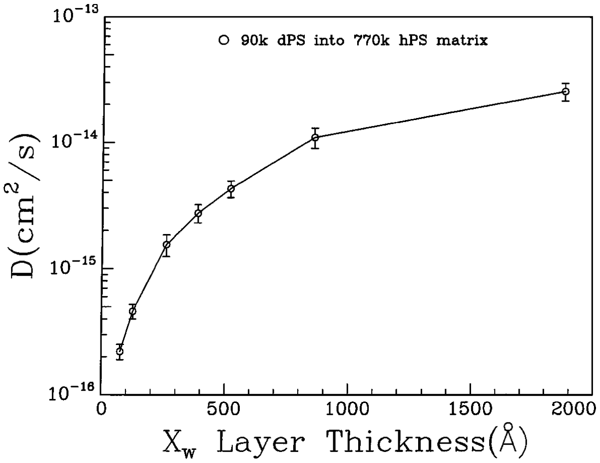

FIG. 2. The average diffusion constants, fitted to the tails of the profiles of Fig. 1, as a function of X_W.

Dynamic SIMS experiments, using a rastered Ar^+ ion beam of energy 2 keV to sputter through the samples at a rate of approximately 400 Å/h, were run to obtain volume fraction versus distance profiles of the diffusing species. The setup is described in Ref. [17]. Samples were vacuum annealed at 153 °C for times ranging from 10 min to 2 h. Three surface preparations of the Si substrates were used: (1) native oxide covered (used as received from the supplier, Semiconductor Processing Co., after confirming with x-ray reflectivity on selected samples that the surfaces had 10–15 Å thick oxide layers and were free of adsorbed organic layers), (2) covered with oxide grown with a modified Shiraki technique [18], and (3) hydrogen passivated surface [18]. Atomic force microscopy was used to verify that the films did not dewet the substrates or roughen following annealing. Reproducible results were obtained, the three surfaces exhibiting the same diffusion behavior within experimental errors. We note that partial oxidation of the hydrogen passivated surfaces might explain their similarity to the oxide surfaces. The majority of samples reported in this study used native oxide covered Si. The SIMS profiles, for 90×10^3 dPS in a matrix of 770×10^3 hPS ($R_g = 235$ Å), are shown in Fig. 1, and the corresponding average diffusion coefficients are plotted in Fig. 2. The profiles are asymmetric, the diffusion rates on the side nearest the SiO interface being considerably smaller than those on the vacuum side. The solid lines in Fig. 1 are calculated diffusion profiles [19] fitting the SiO side and vacuum side slopes to different diffusion constants. The D's in the figure are for the vacuum side and therefore represent an average over distance from the SiO ranging typically from X_W to $X_W + (400 \pm 200$ Å). The results indicate the dynamics are dramatically slowed out to $X_W > 1000$ Å, more than $10R_g$ of the 90×10^3 dPS ($R_g = 78$ Å). As can be seen in Fig. 1, dPS polymers have not reached the interface and, therefore, no *direct* contacts with the wall are necessary to effect a slowdown. We have also checked in several experiments with initial dPS volume fractions of 20% that our measured D's are close to the tracer limit. These experiments gave D's within 10%–20% of the values in Table I.

Long-range forces between the diffusing polymers and the substrate, such as van der Waals forces, are not expected to be significant here due to the large distances from the interface. Excluding a direct effect of the interface, we can assume that the matrix polymers mediate the polymer-surface interaction. We performed two types of experiments to probe this effect: (1) Variation of the matrix molecular weight, with X_W of the initial dPS labeled layer fixed, to test the influence of matrix polymer size, and (2) split layers, where X_W is again fixed but the layer of total thickness X_W is divided into two sublayers of thicknesses X, Y with $X + Y = X_W$ (see Fig. 4). The X and Y layers are deposited separately onto the silicon, the first, X, being spun cast from a toluene solution, the second, Y, floated from distilled water on top of X using a layer spun on a glass slide. The purpose of these experiments is to modify the degree of mixing, or entanglements, within the layer intervening between the interface and the layer at X_W. Polymers in the X layer are slowed due to direct contacts with the interface, and we ask to what degree may subsequent layers not in direct contact be slowed down when the X and Y layers are *not* initially entangled.

In the first set of experiments we prepared samples with a 90×10^3 dPS layer 130 Å thick set at $X_W \cong 520$ Å and varied the molecular weight of the hPS matrix from 9×10^3 to 8×10^6. Samples were annealed at 153 °C for times varying from 15 min to 1 h. Less extensive sets of data were obtained for $X_W = 388$ and 810 Å (at $T = 135$ °C, these samples were bilayers, the outer hPS layer not being present). The corresponding diffusion constants (representing an average, since the profiles are asymmetric) are plotted in Fig. 3. The data show an approximately constant D for a large intermediate range of matrix molecular weights, from 27×10^3 to 1×10^6, and

TABLE I. Average diffusion constants from Fig. 1 and "effective" T_g's as a function of X_W for 90×10^3 dPS at $T = 153\,^\circ\mathrm{C}$.

X_w (Å)	76	126	260	388	521	860	1882
D (10^{-16} cm^2/s)	2.2	4.6	15.5	27.5	43.0	110.0	255.0
T_g^{eff} (°C)	125.5	122.6	117.5	114.8	112.6	107.5	102.6

an increase in D for both low and high matrix M_W. The low M_W region is qualitatively consistent with observed bulk trends [20], where the onset of the constraint release mechanism [21] and lowered glass transition, T_g, lead to increasing D with decreasing molecular weight. However, these effects are much reduced near the interface. For example [19], constraint release alone would account for D (90×10^3 into 27×10^3 matrix) to be more than 10 times greater than D (90×10^3 into 770×10^3 matrix), in contrast to the far weaker dependence shown near the interface. The upturn in D for high matrix $M_W (\geq 1 \times 10^6)$ is quite different from bulk tracer diffusion, which reaches an asymptotic value for matrix M_W's greater than about 200×10^3 in the case of 90×10^3 PS tracer [20], and runs counter to the expectation that larger matrix polymers will propagate the surface effect out to greater distances. However, for these matrices, the width of the matrix polymers, $\sim 2R_g$, is becoming larger than X_W so that the increased diffusion rates of the 90×10^3 may reflect the tendency of the matrix chains near the wall to swell back to bulk dimensions.

The split layer experiments were done using X_W fixed at 388 Å with 90×10^3 dPS diffusing into hPS matrices of three different molecular weights: 27×10^3, 90×10^3, and 770×10^3, having bulk R_g of 44, 80, and 235 Å, respectively. The first part of the split layer, of thickness X ranging from 30 Å to the full X_W, was annealed in vacuum for 1 h at 153 °C to relax the polymer configurations induced by the spinning process. Subsequent layers of thicknesses (388 Å $-$ X) of hPS, 130 Å of 90×10^3 dPS, and approximately 2300 Å of hPS were floated on top and annealed for 30 min at 153 °C. The results (Fig. 4) indicate that the diffusion at distance X_W increases significantly, nearly approaching bulk values, for small X. For larger X, the D's rapidly decrease to an asymptotic value independent of matrix molecular weight (for the matrix M_W ranging from 27 to 770×10^3). The span of X over which D decreases and levels off correlates well with the R_g of the matrix polymers (see Fig. 4). As a further check, a sample was prepared with $X = 38$ Å (annealed for 1 h at 153 °C), $Y = 350$ Å, and the composite $X + Y$ layer was annealed for 10 h at 153 °C to restore equilibrium entanglements within the entire layer. The 90×10^3 dPS layer and bulk layer were then prepared and annealed as above. The diffusion constant obtained was equal to that for a single deposited 388 Å layer, within experimental error; i.e., all memory of the original structure was removed.

These last experiments emphasize the importance of mixing in the layer separating the wall from the diffusing layer at X_W. For short times, the layers having $X < R_g$ present a fairly impenetrable gel-like coating of the surface which is unentangled with the outer layers. The contact interactions across this interface between these chemically identical layers are much weaker than between PS and the silicon substrate, leading to more rapid diffusion in the outer layers. This is similar to our previous observation [9] that covering the silicon with an ultrathin layer of polyvinyl pyridine (PVP) (immiscible with PS) also led to a large increase in the rate of near-surface diffusion.

To conclude, we return to the question of how a bounding wall influences particle dynamics within the fluid.

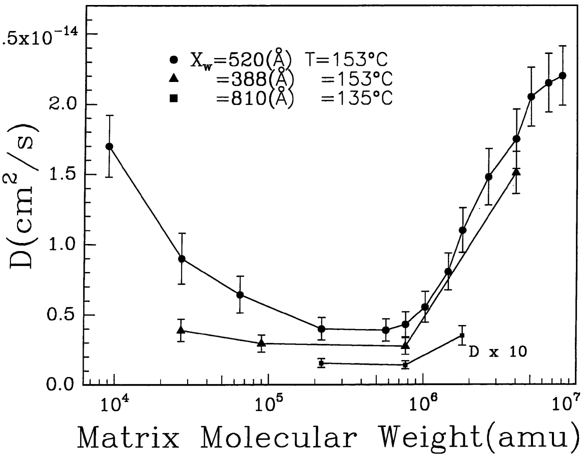

FIG. 3. The average diffusion constants of 90×10^3 dPS at 153 °C as a function of hPS matrix molecular weight for various X_W thicknesses. Sample geometry as in Fig. 1.

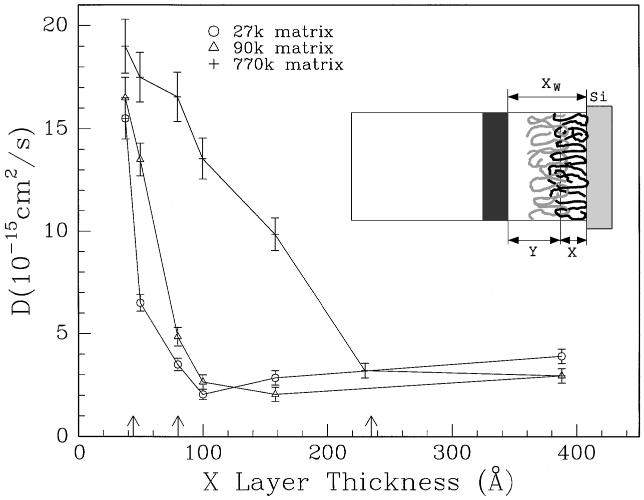

FIG. 4. Results of split layer experiments for $X_W = 388$ Å showing the diffusion coefficient of 90×10^3 dPS at 153° for various X layer thicknesses. Inset shows sample geometry. Arrows indicate $R_g$values for the 27×10^3, 90×10^3, and 770×10^3 hPS matrix polymers.

If we examine the expression for the diffusion constant of entangled polymers in the reptation picture, we may consider the possible factors which could change near an interface. The reptation model expression [22] is $D = (k_B T N_e / 3N^2 f_0)$, where k_B is Boltzmann's constant, $T =$ temperature, $N_e =$ number of monomers between entanglements, $N =$ number of monomers per chain, and f_0 is a monomeric friction coefficient. Polymer conformations enter through N_e and certainly might be different close to the wall. Bruinsma [23] has considered a two-fluid model of polymer transport near an interface consisting of a near-immobile group of chains having direct contacts, and a more mobile group of chains reptating through the network of the first group. The model of Ref. [23] may be applicable here, with a series of interlocking loops—at the interface causing N_e to be far smaller than the bulk value—providing a mechanism to propagate the influence of the surface. The other factor which may be modified, if the above reptation expression is valid, is the friction coefficient f_0. Though f_0 is believed to be due primarily to local molecular interactions, it depends on temperature and rapidly increases as the glass transition temperature T_g is approached. If the T_g of the PS films *is increased,* as reported by Wallace *et al.* [3], we would expect the dynamics to be slowed even above T_g, since the value $(T - T_g)$ is thereby reduced. The temperature dependence of D in bulk PS has been found [15] to be of the Williams-Landel-Ferry (WLF) form: $\log(D/T) = A - B/(T - T_0)$, where A, B are numerical constants and T_0 is a reference temperature. This WLF form may be fitted to the data of Fig. 2 assuming only T_0 changes (with the corresponding T_g changing by an equal amount). The resulting "effective" T_g's are listed in Table I. Some recent measurements of T_g in thin PS films indicate shifts of this order for T_g but disagree on whether T_g increases or decreases. It has been suggested that T_g is increased near strongly attractive walls and decreased near the free surface. At the moment, there is no consensus among experimental groups. Even if the actual T_g is different than the bulk values, the question arises as to why a local phenomenon, where the motional behavior on a scale of a few tens of monomers is believed to be relevant, should be changed at large distances from the wall. Baschnagel and Binder [7] have identified perturbations of polymer structure extending greater than R_g from Monte Carlo simulations in thin films, and Thompson *et al.* [5] performed molecular dynamics simulations which exhibit wall-induced glass transitions with shifts from the bulk depending on the magnitude of the wall-monomer interaction. A large length scale may enter through a divergent characteristic length identified with the approach of the glass transition. It may also be that the films *do not* have a T_g shift, but that the dynamics are "solidlike" or "glasslike" due to the effects of contacts with the wall. Possibly, the mechanism is long-range dynamic correlations of chains mediated by the incompressible melt, giving the friction coefficient a nonlocal character which is influenced by the boundary condition on monomers at the extended two-dimensional boundary (i.e., the "stickiness" of the wall). Clearly, more experimental and theoretical work needs to be done.

We thank H.L. Frisch, B. O'Shaughnessy, and M. Turner for useful discussions, and O. Bahr and T. Petersen for experimental support. Support from the NSF (DMR-9316157 and MRSEC, DMR-9632525) and the DOE (DE-FG02-93ER45481) is gratefully acknowledged.

[1] J.V. Alsten and S. Granick, Macromolecules **23**, 4856 (1990); H.-W. Hu and S. Granick, Science **258**, 1339 (1992).
[2] J.L. Keddie, R.A.L. Jones, and R.A. Cory, Faraday Discuss **98**, 219 (1994); Europhys. Lett. **27**, 59 (1994).
[3] W.E. Wallace, J.H. van Zanten, and W.L. Wu, Phys. Rev. E **52**, R3329 (1995).
[4] J.A. Forrest *et al.*, Phys. Rev. Lett. **77**, 2002 (1996).
[5] P.A. Thompson, G.S. Grest, and M.O. Robbins, Phys. Rev. Lett. **68**, 3448 (1992).
[6] A.K. Chakraborty and P.M. Adriani, Macromolecules **25**, 2470 (1992).
[7] J. Baschnagel and K. Binder, Macromolecules **28**, 6808 (1995); P. Ray and K. Binder, Europhys. Lett. **27**, 53 (1994).
[8] J.G. van Alsten, B.B. Sauer, and D.J. Walsh, Macromolecules **25**, 4046 (1992).
[9] X. Zheng *et al.*, Phys. Rev. Lett. **74**, 407 (1995).
[10] B. Frank, A.P. Gast, T.P. Russell, H.R. Brown, and C. Hawker, Macromolecules **29**, 6531 (1996); B.B. Sauer and D.J. Walsh, Macromolecules **27**, 432 (1994).
[11] C. Cheung *et al.*, Phys. Rev. Lett. **76**, 2531 (1996); X. Qiu *et al.*, Phys. Rev. Lett. **65**, 516 (1990).
[12] R.A.L. Jones *et al.*, Phys. Rev. Lett. **66**, 1326 (1991).
[13] G. Brown and A. Chakrabarty, Phys. Rev. A **46**, 4829 (1992).
[14] G. Krausch *et al.*, Phys. Rev. Lett. **71**, 3669 (1993).
[15] P.F. Green and E.J. Kramer, J. Mater. Res. **1**, 202 (1986).
[16] O.V. Bychuk and B. O'Shaugnessy, Langmuir **10**, 3260 (1994); Phys. Rev. Lett. **74**, 1795 (1995).
[17] S.A. Schwarz *et al.*, Mol. Phys. **76**, 937 (1992).
[18] G.S. Higashi *et al.*, Appl. Phys. Lett. **56**, 656 (1990).
[19] J. Crank, *The Mathematics of Diffusion* (Oxford University Press, Oxford, 1975), 2nd ed.
[20] P.F. Green and E.J. Kramer, Macromolecules **19**, 1108 (1986).
[21] W.W. Graessley, Adv. Polym. Sci. **47**, 67 (1982); J. Klein, J. Polym. Prepr. **22**, 105 (1979).
[22] P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
[23] R. Bruinsma, Macromolecules **23**, 276 (1990).