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Tracer diffusion in thin polystyrene films

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Abstract

In order to determine how confinement of a polymer melt alters segmental scale mobility, we used fluorescence recovery after photobleaching (FRAP) to measure tracer diffusion coefficients, *D*, of a low molecular weight fluorescent probe in supported polystyrene (PS) thin films. The effect of film thickness was investigated for a polydisperse polymer over the range $\simeq 10^2$–10^4 Å at conditions above the bulk glass transition temperature, T_g. For relatively thick films (thicknesses $\simeq 1$ μm), the *D* agree with bulk values reported in the literature. As the film thickness decreases below $\simeq 10^3$ Å, the *D* increase significantly, by as much as two orders of magnitude. At the same time the temperature dependence of *D* becomes much weaker. Analysis by free volume theory shows the data are consistent with both the effective T_g and liquid state thermal expansion coefficient, α, decreasing with film thickness. This agrees qualitatively with a number of recent thermal property studies on thin PS films which suggest that changes in local packing near the free surface significantly enhance the average segmental scale mobility in sufficiently thin films. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer thin films; Tracer diffusion; Free volume theory

1. Introduction

The behavior of amorphous polymer films less than 1 μm thick has received great attention recently because their structure and properties are critical in a number of modern applications, including encapsulants and dielectrics for microelectronics, resists in photolithography, lubricants in information storage devices and alignment layers in flat panel displays [1]. As films become thinner, the effect of the interfaces eventually becomes noticeable, changing the film's average properties, including its glass transition (T_g), thermal expansivity (α), and dynamic properties. Although there has been considerable progress towards understanding flexible polymers at interfaces, experimental results on the properties of thin melt and glass-state films have only been obtained recently [2–14]. While a number of definite conclusions have been reached concerning the effects of film thickness, there remain significant inconsistencies and some confusion concerning interpretation (see, for example, the discussions in [8,14]).

Several groups have studied the thermal properties of ultrathin polystyrene (PS) films on substrates and as free standing films. The results show that both the free surface (polymer/air or polymer/vacuum interface) and the interaction between polymer and a substrate substantially affects the apparent thermal properties in sufficiently thin films [2–6]. For example, a free surface tends to decrease the apparent T_g. Evidently there exists a highly mobile layer near a free surface, which may result from a local suppression of density, disruption of segmental packing, or the aggregation of chain ends near the surface, and this can significantly influence the average thermal behavior of a thin film. The interface between the polymer and a neutral or weakly-interacting solid substrate has similar effects although much weaker tendencies are observed. Thin films on attractive solid substrates show apparent increases in T_g, presumably because polymer segments get 'pinned' on the attractive surface creating a slightly densified surface 'gel'. Although these features seem clear, discrepancies exist as to the range of influence of the interfaces, i.e. as to the range of film thicknesses where thermal property changes first become evident.

The experimental picture for dynamic properties of thin films is less clear. Reiter [9] studied dynamics of dewetting of ultrathin PS films on 'float' glass substrates, and concluded that polymer chain mobility *increases* in films with thickness less than the average coil size (R_g), based on detecting the onset of dewetting at temperatures much lower than the bulk T_g. More recent, direct measurements of chain self diffusion near attractive solid substrates in PS [10,11] and poly(methylmethacrylate) [13] melts show a

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very strong *decrease* in chain mobility near the solid surface, by as much as two orders of magnitude. These studies disagree on the range of the effect: The Stony Brook group found significant decreases in chain mobility at distances from the substrate more than an order of magnitude greater than R_g while the NIST group observed effects at distances no greater than a few R_g. The Stony Brook researchers also reported strong influences of the substrate surface chemistry and the preparation history of the film. Another recent work [12] studied chain self diffusion in thin PS melt films supported on silicon oxide. Here, both the free surface and substrate influence the chain mobility. The self diffusion coefficients decreased with film thickness, but very weakly compared to the Stony Brook and NIST studies, and the effects were only seen in films on the order of R_g in thickness. Yet another recent work focused on small tracer molecule diffusion in thin melt films of poly(isobutyl methacrylate) on quartz [14]. The small molecule tracer diffusivity was nearly *unaffected* by film thickness even for films approaching R_g in thickness.

These efforts establish clearly that attractive solid substrates retard chain mobility nearby, but the mechanisms are unclear. The effects of a free surface on chain mobility has not been isolated. The influences of the interfaces on segmental-scale mobility and longer-range topological constraints (entanglements) have not been sorted out. Clearly, further experimental efforts are needed to clarify the picture. We report here initial results of direct measurements of small molecule mobility in thin melt films. We use fluorescence recovery after photobleaching (FRAP) to study in-plane tracer diffusion of a small probe molecule in very thin films of PS melt supported on fused quartz plates. The effect of film thickness is the main interest.

The diffusion of a low molecular weight tracer is primarily influenced by small length scale packing in the melt, i.e. the local average density and backbone alignment. We expect our measurements probe the extent to which this feature changes because of the interfaces in a thin film. They are not sensitive to changes in longer length scale features, such as the topological constraints on chains. To our knowledge, only one prior investigation has focused on small probe molecule diffusion in thin melt films [14], and this study found no effect of film thickness. We find significantly *enhanced* small probe mobility in sufficiently thin films.

2. Materials and sample preparation

We chose a polydisperse polystyrene (PS) (Aldrich), with a weight-average molecular weight, M_w, of 280,000 g/mol and $M_w/M_n = 3.3$ (GPC), and rubrene (Aldrich) as the tracer molecule. For substrates, we used flat fused quartz plates (2 in. × 2 in. × 0.059 in., Heraeus Amersil 52615, polished SUPRASIL 3, flatness: 10 waves per inch at 633 nm). Before contacting the polymers with the quartz plates, the substrates were cleaned and rendered hydrophilic. First, the substrates were immersed in aqua regia (3:1 concentrated hydrochloric acid: concentrated nitric acid) for 6 h followed by rinse with a millipore filtered, de-ionized (18.2 MΩ) water. Then, the quartz plates were oxidized in a UV ozone plasma (Jelight Company, Inc., Model 342) for 2 h. This procedure effectively removes organic contaminants. The oxidation steps were followed by immersion in concentrated hydrochloric acid for 2 h, which hydroxylates the surface [15]. Contact angle measurements indicated that the protocol indeed removes the organic contaminants and forms a hydrophilic surface.

To prepare thin polymer films, PS was dissolved in toluene to prepare polymer solutions with concentrations between 1 and 10% (w/w). The rubrene dye was added to the polymer solutions to a nominal concentration of 10^{-4} M. The resulting dye/polymer solutions were filtered and spun onto clean quartz plates using a film spinner (Headway Research, EC101DT-R485). The resulting films were annealed in a vacuum oven at 150°C for 2 h to dry and relax residual stress. The film thicknesses were measured by ellipsometry (Rudolph Instruments, Inc., Model 444A12) at room temperature. Ellipsometry showed that for the range of thicknesses studied, the films were stable against dewetting for the duration of the experiments.

3. FRAP measurements

We used the FRAP technique discussed by Davourst et al. [16] employing lasers crossed on the sample to create an interference pattern. For our FRAP experiments, an argon–ion laser (Coherent Innova 70) equipped with an etalon assembly provides high- and low-power beams at $\lambda = 488$ nm for photobleaching and subsequent observation. Typically, the bleaching power was 170 mW while the bleaching time was varied from 100 ms to 3 s. The reading (observation) power was typically about 20 μW. The pattern was projected onto the sample plane so that in-plane diffusion is monitored. The grating spacing, d, which controls the diffusion distance, was varied from 1 to 15 μm by changing the intersection angle, 2θ. After photobleaching, lock-in detection is applied to enhance the signal-to-noise ratio, by oscillating the reading pattern over the photobleached pattern via a piezoelectrically driven mirror in the excitation train, and locking in at the oscillation frequency.

The thin film samples were first heated to 160°C in a thermostated sample cell, and then brought down to the experimental temperature to carry out FRAP measurements. FRAP recovery curves decay exponentially to zero, if the translational motion is diffusive. Curve fitting gives a characteristic time. Then the diffusion coefficient is determined by

$$D = \frac{1}{\tau q^2} \tag{1}$$

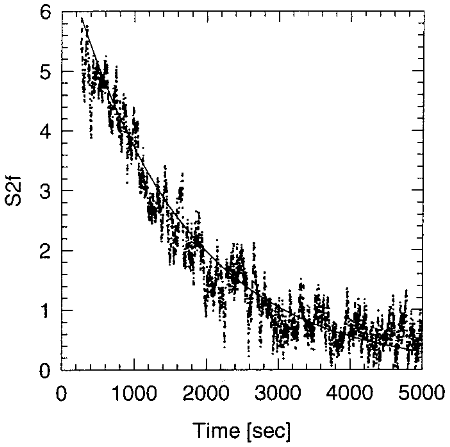

Fig. 1. FRAP recovery measurement for rubrene in a thin PS film (914 Å) at 125°C.

where $q = 2\pi/d = 4\pi \sin \theta/\lambda$. For a linear diffusion, the decay time constant τ should be proportional to the square of diffusion distance, d^2, with a slope = $1/(4\pi^2 D)$.

4. Results

Fig. 1 shows a typical example of FRAP recovery for rubrene in PS films formed by spinning a 1 wt% PS solution in toluene. The film thickness is 914 (± 12) Å. The fringe spacing d, which is the diffusion distance, was 13.2 μm, corresponding to $q = 4760\ \text{cm}^{-1}$. The bleaching intensity was 170 mW, and the bleaching time was 500 ms. The sample was measured at temperature 125°C with ±1°C error in temperature control. The measured signal decays exponentially with a characteristic time $\tau = 1582$ s, corresponding to diffusion coefficient of $2.79 \times 10^{-11}\ \text{cm}^2/\text{s}$ by Eq. (1).

Fig. 2 shows τ plotted against the square of diffusion distance for the 914 Å PS films at 125°C. A good linearity is observed, indicating recovery dominated by diffusion. The error bars in τ were calculated from the standard deviation in the decay time constants in a set of five single FRAP runs. A least-squares fit of the data gave the diffusion coefficients $D = (2.80 \pm 0.07) \times 10^{-11}\ \text{cm}^2/\text{s}$.

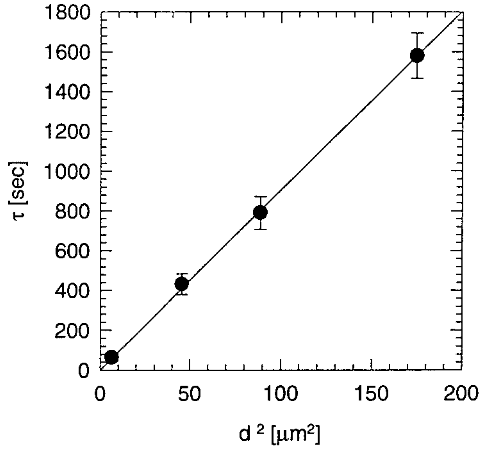

Fig. 2. Decay time constant versus the square of diffusion distance for rubrene diffusion in a thin PS film at 125°C.

Fig. 3 shows the log of the in-plane diffusion coefficients of rubrene dye in PS films, determined from slopes in plots like Fig. 2, as a function of inverse temperature. The results of thicker films (9240 Å) are in agreement with previous measurements in another laboratory [17], shown as the dashed line in Fig. 3, on the same system in bulk. Our results indicate that rubrene diffusion coefficients increase as the film thickness is reduced to $\simeq 10^3$ Å. The increase depends on temperature, and can be as much as two orders higher than in bulk PS melts. Said differently, decreasing the film thickness to $\simeq 10^3$ Å generally increases the tracer diffusion coefficients and drastically reduces its temperature dependence.

5. Discussion

The average radius of gyration of a bulk polymer coil, R_g, is about 150 Å for our samples. The characteristic size of rubrene dye, R_D, is in the range 5–10 Å. Now, the interfaces in thin films perturb the topological constraints a polymer chain feels within a few R_g of each surface. For a film of 900 Å ($\simeq 6\ R_g$), this perturbation would certainly affect the average chain mobility in the film noticeably, but, it would not likely have a strong effect on the average mobility of the rubrene dye, which is perhaps a few Kuhn lengths in size at most, and oblivious to changes in much longer length scale topological features. However, one also expects that the interfaces perturb local segmental packing in their immediate vicinity, i.e. the local density and backbone alignment, over relatively short length scales from the interface of perhaps a dozen Kuhn lengths at most [18,19]. These disturbances can influence the measured dye probe mobility and we believe this is the main mechanism responsible for our observations. In particular, near a free surface or a neutral or weakly interacting solid substrate, a local suppression of the melt density occurs, as well as in-plane segmental alignment. Both effects favor enhanced small-probe mobility in the plane of the film. One can also show that our results are consistent with previous observations of a suppression in the apparent T_g in thin films, as follows.

If the effect of film thickness on the average in-plane dye diffusion coefficients is through changes in the segmental packing and short length scale mobility near the interfaces, this should change other properties controlled by these features, such as thermal expansivity and glass transition. Small molecule diffusion in polymer systems has been successfully described by free volume theory [20] which rests on the idea that the diffusive motion of a small molecule through a medium is controlled by the amount of interstician space. This depends directly the medium's thermal expansion and transition characteristics. We

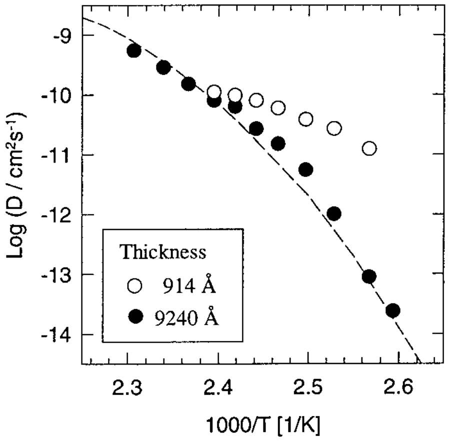

Fig. 3. log D versus 1/T for rubrene in PS films.

therefore used the free volume model, in form proposed by Vrentas and Duda (VD) [20], as a framework for analyzing our experimental results with the purpose of connecting to thermal property changes in thin layers.

From the VD model, the tracer diffusion coefficient D is

$$D = D_0 \exp\left(- \frac{\gamma \hat{V}^* \xi}{\hat{V}_{\mathrm{FH}}} \right) \tag{2}$$

where γ is a dimensionless overlap factor for free volume (between 0.5 and 1), $\hat{V}^*$ is the specific critical free volume of polymer required for a diffusive jump, ξ is the ratio of the critical molar volume of the tracer's jump unit to the critical molar volume of the polymer chain's jump unit, and $\hat{V}_{\mathrm{FH}}$ is the average specific free volume of polymer. For $T > T_g$, $\hat{V}_{\mathrm{FH}}$ can be expressed as

$$\hat{V}_{\mathrm{FH}} = K_{12}(K_{22} + T - T_g) \tag{3}$$

where K_{12} and K_{22} are free volume parameters for the polymer, simply related to the WLF constants, and T_g is the glass transition temperature. D_0 is a much weaker function of temperature than the exponential term and is treated here as a constant. If we define the parameters X and Y as $X = (K_{12})/\gamma$ and $Y = T_g - K_{22}$, then, Eq. (2) becomes

$$\ln D = \ln D_0 - \frac{\hat{V}^* \xi}{X(T - Y)}. \tag{4}$$

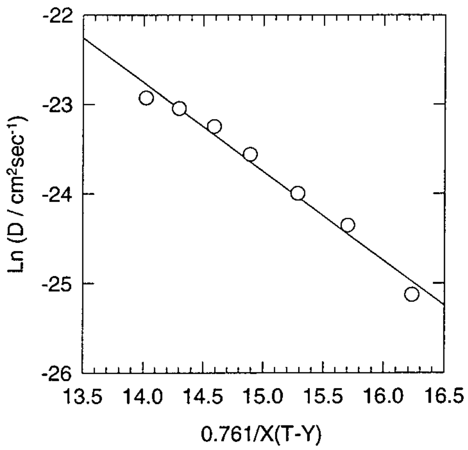

Fig. 4. Data analysis by free volume theory for diffusion in thin PS films.

The quantities $\hat{V}^*$, X and Y for polystyrene have been reported as $\hat{V}^* = 0.850\ \mathrm{cm}^3/\mathrm{g}$ [21], $X = 5.82 \times 10^{-4}\ \mathrm{cm}^3/\mathrm{g\ K}$ and $Y = 327$ K [22]. Putting these into Eq. (4), we obtain the second term on the right in Eq. (4) as $-(1461\xi)/(T - 327)$. If the data for "bulk" PS in Fig. 3 are re-plotted as $\ln D$ versus $1461/(T - 327)$, indeed a straight line results. From the intercept and slope, we find $\ln D_0 = -8.72$, corresponding to $D_0 = 1.63 \times 10^{-4}\ \mathrm{cm}^{-2}/\mathrm{s}$, and $\xi = 0.895$. It is relevant to ask if $\xi = 0.895$ for rubrene in PS is reasonable. VD [23] studied the variation of ξ for a series of small tracers in PS. For small, simple tracers, expected to jump as a single unit, ξ should increase linearly with the size of the penetrant. Indeed VD found that the parameter $(\gamma \hat{V}^*/K_{12})\xi\ (\sim \xi)$ increases linearly with the tracer's hard-core volume, V_0 (see Fig. 3, in [23]). For larger, more complex tracer molecules which diffuse by coordinated segmental jumps, the value of $(\gamma \hat{V}^*/K_{12})\xi$ falls below the line for simple tracers. For rubrene, $(\gamma \hat{V}^*/K_{12})\xi = 1310$ K and $V_0 \simeq 400\ \mathrm{cm}^3/\mathrm{mol}$ also falls below the correlation for simple tracers, in line with data for other 'complex' tracers in PS, which diffuse by segmental motion.

Once fixed by analysis of data on a thick, bulk-like film, the D_0 and ξ are fixed to fit the thin-film data by a non-linear regression, to determine the X and Y values for the thin PS films. The fit results, shown in Fig. 4 for a film 914 Å thick, give $X = 2.64 \times 10^{-4}\ \mathrm{cm}^3/\mathrm{g\ K}$ and $Y = 212$ K. In the thin PS film, both X and Y are reduced from the bulk values.

From the VD model, it can be shown

$$X = \frac{\hat{V}(T_g)[\alpha - (1 - f^G)\alpha_c]}{\gamma};\ Y = T_g - \frac{f^G}{\alpha - (1 - f^G)\alpha_c}$$

where $f^G = (\hat{V}_{\mathrm{FH}}(T_g))/(\hat{V}(T_g))$; $\hat{V}(T_g)$ and $\hat{V}_{\mathrm{FH}}(T_g)$ are the specific volume and specific free volume of the polymer at T_g, respectively, α is the thermal expansion coefficient of the liquid-state polymer and α_c is the thermal expansion coefficient for the polymer occupied volume. In a simple view of the free volume theory, where the occupied volume is temperature independent ($\alpha_c = 0$), X is proportional to the thermal expansion coefficient of liquid-state polymer α, and $Y = T_g - f^G/\alpha$. The observed changes of X and Y in thin films indicate that both of the thermal expansion and glass transition of the film are perturbed from bulk values by the interfaces present. The reduction of X can be interpreted as a decrease of α in the thin film. This implies that the second term in Y, f^G/α, becomes larger than the bulk value. Consequently the reduction of Y is consistent with a decrease of T_g.

6. Conclusion

The average mobility of a low molecular weight probe in thin melt films of polystyrene (PS) supported on quartz increases significantly as the film thickness is reduced to below about 10^3 Å. From a free volume analysis, this result is qualitatively consistent with suppression of the apparent T_g detected by ellipsometry for PS films on silicon [2], by positron annihilation for PS films on silicon [5], and by Brillouin light scattering for freely standing PS films and for PS films confined by one or two glass slides [4], although noticeable effects appear in our study in somewhat thicker films than in the studies just mentioned. Evidently the changes in segmental packing near the free surface and the substrate noticeably enhance the average short length scale mobility in 10^3 Å thick films. The difference between our results and those reported by Torkelson [14] may arise from differences in the polymer-substrate interaction; it is likely stronger in their system.

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