

Probe Diffusion in Thin PS Free-Standing Films

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ABSTRACT: Dynamic secondary ion mass spectrometry was performed to determine the dynamics of thin free-standing polystyrene films by investigating probe diffusion in a high molecular weight polymer matrix. It is found that the temperature dependence of the diffusion of small molecular probes can be described by the WLF equation above bulk T_g , whereas a weaker dependence is found below T_g for PS films with total thickness as thin as 69 nm. The results of probe diffusion as a function of film thicknesses show no change of T_g for the free-standing films with thickness ranging from 33 to 200 nm.

I. Introduction

The properties of thin polymer films can be significantly different from the bulk. Deviations from the bulk viscoelastic properties,¹ phase behavior,² mobility,^{3–7} and glass transition temperatures^{8–17} have been observed. Comparison with theory^{18–22} has been difficult since the results reported have often been contradictory. This is partly due to the fact that many experiments were measuring properties sensitive to polymer/substrate interactions, which depend strongly on experimental details and often required long-ranged center-of-mass motion in order to be observed.

To eliminate complications associated with the underlying substrate, free-standing films were examined.^{12,17} Using Brillouin light scattering and ellipsometry techniques, Dutcher et al.¹² measured the glass transition temperature, T_g , of thin PS free-standing films as a function of film thickness. They found that T_g decreases linearly with decreasing film thickness. In contrast, using shear modulation force microscopy,¹⁷ we directly measured T_g in free-standing films by observing the changes in the surface modulus and found no deviation of the T_g from the bulk value in the same thickness range as in ref 12.

Diffusion of small fluorescent molecules in a polymer matrix^{7,23,24} has been widely used for the study of macromolecular motion in polymers. The results have sometimes been controversial as well due to the fact that the chromophores are chemically different from the matrix, and hence, at elevated temperatures, they may react with functional groups of the polymer or segregate to the surface in an unknown manner. To explain the change in T_g with decreasing film thickness, many studies have invoked a multilayer model with each of the layers exhibiting different T_g .^{3,10,11,23} If the chromophore segregates or interacts with one particular layer that has a different T_g from the rest of the film, the fluorescence determination of T_g will be primarily based on the measured dynamics of that layer and not be representative of the entire polymer film.

In this paper, we probe T_g by measuring the diffusion of small molecular probes in a higher molecular weight polymer matrix as a function of temperature and film thickness. The concentration profiles of the probes are measured by DSIMS. Probe segregation can be greatly minimized by choosing deuterium-labeled oligomers with the same chemical composition as the matrix. Since the diffusion of small molecular probes provides information on segmental motion throughout the whole free-standing film, the data can then be compared more directly to previous experimental results.^{7,12}

II. Experimental Section

Monodisperse ($M_n/M_w < 1.04$) deuterated polystyrene oligomers (dPS) of $M_w = 4.3K$ and 10 K purchased from Polymer Laboratories Ltd., and small molecular compounds 1,3-bis(1-pyrenyl)propane (BPP) and 1,8-dibromopyrene (diBrPy) were used as probes in this study. Hydrogenated polystyrene (hPS) (Polymer Laboratories Ltd., $M_w = 6500K$, $M_n/M_w = 1.02$) was used as the polymer matrix.

Free-standing bilayer films, as shown in Figure 1, were made by spin-casting the hPS layer from a toluene solution onto a glass slide. A second layer composed of a blend of matrix and a small fraction of probe molecules was spun-cast on a glass slide and floated on top of the first hPS matrix layer (Figure 1a). The thickness of the layer with probe molecules was always fixed at 20 nm, while the total thickness of the free-standing film was controlled by varying the thickness of the matrix layer. The composition of the bilayer films is tabulated in Table 1. The bilayer film was then floated from distilled water onto the surface of a polished silicon wafer having a hole 8 mm in diameter which had been produced using an ultrasonic cutter (Figure 1b). The film was then placed in a high-vacuum oven and annealed at different temperatures and times in a vacuum of 10^{-7} Torr. After annealing, the free-standing portion of the film was transferred onto a silicon wafer by pushing a Teflon rod through the hole as shown in Figure 1c.

The concentration profiles of H^+ , D^+ , C^+ , O^+ , Si^+ , CH^+ , CD^+ , and Br^+ were measured with DSIMS as a function of distance from the top surface. A thin (~ 35 nm) sacrificial polystyrene layer is floated onto the polymer surface prior to DSIMS experiment to avoid artifacts due to an initial transient

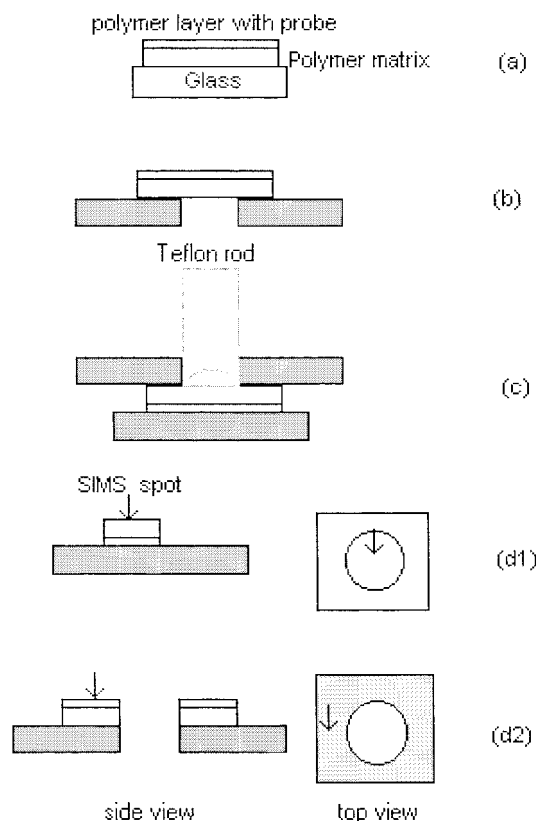


Figure 1. Schematic of the process for making free-standing films and transferring them onto substrates for DSIMS measurements. (a) A bilayer film is first floated onto a glass slide. (b) The bilayer is then floated onto a silicon substrate with a 4 mm hole where it is annealed. (c) After annealing the free-standing portion is transferred by pressing with a Teflon rod onto a Si wafer for DSIMS analysis. (d) Two sample geometries for the DSIMS analysis and location of the DSIMS sputtering beam: (1) transferred portion of the free-standing film; (2) supported section of the film, adjacent to the hole in the Si wafer.

Table 1. Composition of the Bilayer Samples

tracer layer	matrix
DPS($M_w = 4.3K$, 10%) + hPS($M_w = 6500K$, 90%)	HPS ($M_w = 6500K$)
DPS($M_w = 10K$, 10%) + hPS($M_w = 6500K$, 90%)	HPS ($M_w = 6500K$)
BPP(10%) + dPS(260K, 90%)	DPS ($M_w = 260K$)
dibrPy(1%) + hPS(1000K, 99%)	HPS(1000K)

sputtering rate and contamination. In this study, DSIMS was performed using an Atomika 3000-30 ion microprobe with a 2 keV/20 nA Ar^+ beam rastering over a 1.0 mm square region at 30° off-normal incidence. Data were collected from the free-standing and adjacent supported area of the film as shown in Figure 1 (d1, d2). This allowed us to directly compare the diffusion of the probes in free-standing and supported polymer films that were annealed under identical conditions for one sample.

To properly measure small molecule diffusion in ultrathin free-standing polymer films with DSIMS, one has to be careful in choosing the proper annealing condition. First of all, probe diffusion must be slow enough that the annealing time can be long enough for the temperature of the oven to reach equilibrium (approximately 10 min in our case). We were able to achieve this by using relatively large probes (PS oligomer) and annealing temperatures close to T_g . Any minor shift in T_g due to film thickness is expected to manifest itself at those annealing temperature. On the other hand, the diffusion of the probe has to be sufficiently fast such that we can resolve the concentration profile within the resolution of DSIMS and

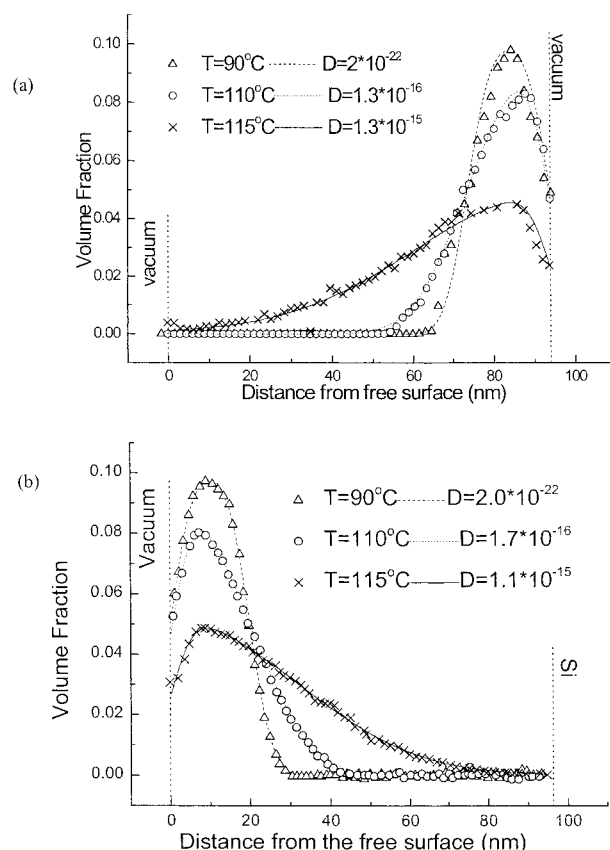


Figure 2. DSIMS profiles for dPS 10K/hPS 6500K matrix samples annealed for 60 min at different temperatures. The total film thickness in each case is 94 nm. The unit for the diffusion coefficient is cm^2/s . (a) Free-standing section of the film. (b) Supported section of film. Note the different location of the vacuum interface in the two figures reflects the transfer procedure shown in Figure 1.

complete the annealing before the free-standing films break up. The probes used in this experiment were chosen such that the diffusion coefficients would satisfy the above-mentioned conditions. After annealing, the surface of all films was examined by optical microscopy, and all the samples where multiple holes had formed were discarded.

In the data analysis procedure, the D^- trace was used to obtain the concentration profiles of the deuterated probes. Even though the H^- trace has high intensity, there can also be contamination from other sources, and hence this trace is not reliable. Instead, the background subtracted CH^- trace is used to profile the hydrogenated polymer. The background, assumed to be mostly from ^{13}C , can be determined from the isotopic abundance or 0.011 of the ^{12}C intensity profile. Whenever deuterated probes were present, the profiles were checked for internal consistency by requiring that the normalized concentration profiles obtained from $CD^- + CH^- = 1.0$.

III. Results and Discussion

Figure 2a shows the concentration profiles obtained for a set of free-standing bilayer samples, with $M_w = 10K$ oligomer as probe. The total thickness, which was marked by the vacuum interface, in this case was 93.4 nm. The samples were annealed for 60 min at 90, 110, and 115 °C. The initial volume fraction ϕ of the deuterium-labeled species was 0.1 in the probe layer, and therefore the volume fraction profiles could be described as tracer diffusion. The concentration profile for monodisperse chains diffusing in a semiinfinite

matrix can be described by the solution to Fick's second law;

$$\phi(x) = \frac{1}{2} \left[\operatorname{erf} \left(\frac{h-x}{w} \right) + \operatorname{erf} \left(\frac{h+x}{w} \right) \right] \quad (1)$$

Here x is the distance from the interface, h is the initial thickness of the tracer film as measured by ellipsometry, w is the characteristic diffusion distance $2(Dt)^{1/2}$, and D is the tracer diffusion coefficient, assumed to be constant. The data for both the free-standing and supported part of the film are plotted in parts a and b of Figure 2, respectively. The symbols correspond to data obtained after annealing at different temperature, and the lines are fits to eq 1 with the tracer diffusion coefficient shown. From the figure we can see that, for $T = 90^\circ\text{C}$, $D \leq 2.0 \times 10^{-22} \text{ cm}^2/\text{s}$, or almost no diffusion within the resolution of SIMS is observed to occur on both free-standing and supported films. This indicates that the probe indeed senses the T_g of the matrix, since the annealing temperature is above the T_g of the oligomer probe, which is 361 K. The change in the T_g of the matrix due to the addition of the probe is rather small based on a simple linear interpolation or $T_g^M = 0.1 \times 361 \text{ K} + 0.9 \times 378 \text{ K} = 376 \text{ K} = 103^\circ\text{C}$. A significant amount of diffusion occurred just above T_g . The diffusion coefficients are nearly identical within experimental error in the supported and free-standing films. The value of D , for $T > T_g$, is in agreement with the WLF prediction for PS probe of $M_w = 10\text{K}$. Hence, neither the substrate nor the confinement of the free-standing film has noticeable effect on the diffusion of the probe.

To directly compare our results with previous diffusion measurements using fluorescence spectroscopy, we studied the concentration profiles of the fluorescence molecules, BPP, and a similar small molecule, diBrPy, in the same PS matrix using DSIMS. The data for 96 nm free-standing bilayer films composed of a 20 nm 1% DiBrPy in a matrix of 1000K hPS layer flated onto a 76 nm 1000K hPS matrix layer and annealed at various temperatures are shown in Figure 3a. From the figure we can see that, for $T \leq 100^\circ\text{C}$, the diffusion profiles are Fickian, and no segregation of the brominated probe is observed. For $T > 100^\circ\text{C}$, the brominated probe is seen to segregate preferentially to the vacuum interface, and hence the concentration profiles can only be approximated by a Fickian relation. To determine whether the segregation is an equilibrium phenomenon or somehow related to the bilayer structure, in Figure 3b we show the normalized Br^- concentration profile of a 110 nm thick blend film composed of 10% BPP in 90% 1000 hPS spun-cast directly on the Si substrate and annealed for 4 h at 140°C . Here the segregation of the probe to both Si and vacuum interfaces is immediately apparent. Hence in this paper, we only use the fits to the profiles for short annealing times and low annealing temperatures, as shown in Figure 3a.

Comparing Figures 2 and 3, we find that the diffusion coefficient of diBrPy can be several orders of magnitude faster than that of the PS probe with $M_w = 10\text{K}$; e.g., at 90°C diBrPy diffuses faster than the PS oligomer by 3 orders of magnitude. The diffusion of fluorescent probes in PS and PMMA matrices below T_g has been ascribed by several authors^{25,26} to large displacements related with strain release or physical aging of the matrix. The length scale of the motion involved in these mechanisms has been reported to be on the order of 10

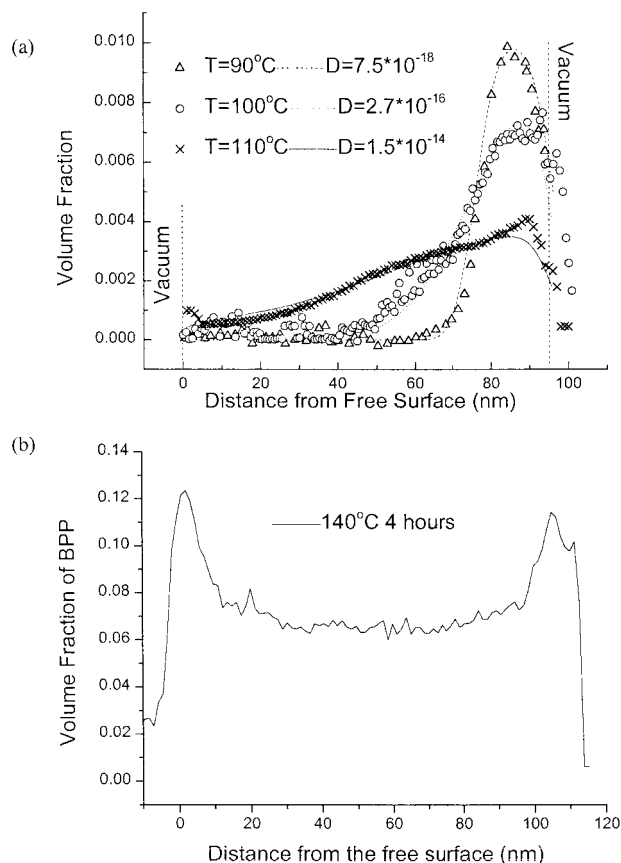


Figure 3. (a) Volume fraction of Br^- ions plotted as a function of distance from the vacuum interface for free-standing films composed of 1% diBrPy/1000K hPS/1000K hHPS bilayer films with total thickness = 96 nm. (b) Volume fraction of BPP in a 10% BPP/1000K PS blend film, 110 nm thick, spun-cast directly onto a Si wafer and annealed at 140°C for 4 h.

nm or larger and hence would also impact the diffusion of the larger oligomer probes. The absence of diffusion in both 4.3K and 10K probes indicates that the mobility may be specific to the molecular compounds (BPP and diBrPy). Since these compounds are much smaller than the oligomers, they can sense short-range fluctuations, which are known to occur below T_g .

In Figure 4, we plot the fitted values of D , for the 96 nm films, for both the small molecular compounds (diBrPy and BPP) and PS oligomers, as a function of annealing temperature. The data for both free-standing and supported films are shown for the 10K PS oligomer. It is well established^{24,27} that the temperature dependence of the diffusion of small molecule probes in rubbery polymers above their glass transition temperature can be described by a modified Williams–Landel–Ferry (WLF)²⁸ equation:

$$\log D(T) = \log D(T_g) + \frac{\xi C_{1g}(T - T_g)}{C_{2g} + (T - T_g)} \quad (2)$$

where C_{1g} and C_{2g} are the WLF parameters of the polymer matrix, which are independent of the probe. $D(T_g)$ is the diffusion coefficient of the probe at temperature $T = T_g$ of the matrix, and ξ is a parameter that characterizes the volume ratio of the probe jumping unit to that of the polymer matrix jumping unit.²⁴ In Figure 4, the solid line is the plot of the WLF equation, where we use parameters $C_{1g} = 15$ and $C_{2g} = 90\text{K}$ for the PS matrix.²⁷ We assume $\xi = 1$ since the size of the dPS

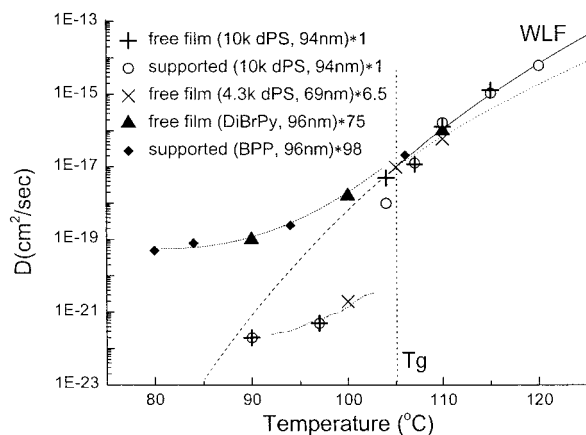


Figure 4. Diffusion coefficients of probes as a function of annealing temperature. $T > T_g$, solid line is the WLF fit and the dotted line is the modified WLF for $\xi = 0.8$; $T < T_g$, dashed line is the WLF extrapolation and short dashed line and the dash dot line are given as guides for the eye. The y axis for BPP and DiBrPy and 4.3K oligomer was scaled as shown in the legend.

oligomer is large enough that its translational diffusion is completely coupled with the polymer matrix α -relaxation processes.⁷ The dotted line is the modified WLF relation for the small molecular probes using a value of $\xi = 0.8$ from ref 24. From the figure we can see that, for $T > T_g$, the data from both oligomers and small molecular compounds are well fitted by eq 2. This confirms our assumption that the mechanism of diffusion of the oligomer is the same as that previously established for small molecules, where diffusion occurs through coupling of the Brownian motion of the probe to segmental motion of the matrix. The dashed line is the WLF extrapolation from which we see that $T_g = 105$ °C, a bulklike value for both free-standing and supported films, independent of the type of probe used in the measurement. The temperature dependence of the diffusion coefficients for $T < T_g$ is also qualitatively similarly for the oligomers and small molecular compounds in that a much weaker temperature dependence is observed, as has been previously reported.

There is general agreement in the literature that T_g is bulklike for films thicker than 90 nm. We also measured $D(T)$ for a free-standing film, 69 nm thick, where a reduced $T_g = 40$ °C has been reported.¹² Since thinner films are more susceptible to breaking up, we chose a $M_w = 4.3K$ dPS oligomer to shorten the annealing time. The data are included in Figure 4. From the figure we can see that the temperature dependence of D in the thinner film is similar to that in the 94 nm thick film. The fit with WLF relation yields a T_g of 105 °C, again bulklike.

The dependence of T_g in free-standing films was explored further by measuring the diffusion coefficient at a fixed temperature and varying the film thickness. The measured diffusion coefficient, D , value was used to calculate the T_g of the film based on the WLF relation. The DSIMS concentration profiles of the dPS 4.3K PS oligomer in free-standing films of thickness 41–200 nm are superimposed in Figure 5. The vacuum interface for each film is marked by a dotted line. The continuous lines are fits to the Fickian relation, and the values of D are tabulated in Table 2. To show the sensitivity of the concentration profiles to the value of tracer diffusion coefficient, we calculate the profiles predicted if T_g in the WLF relation were reduced by 10 °C. These profiles

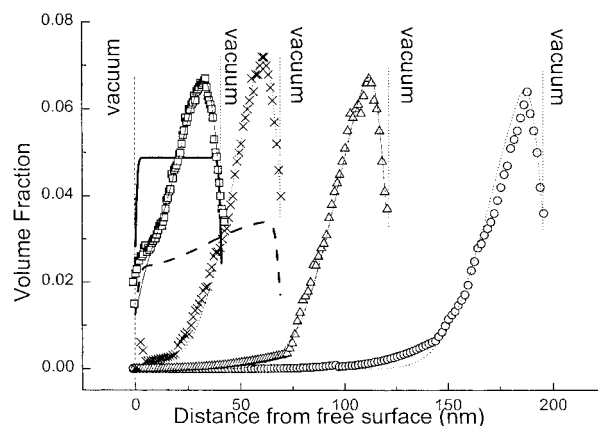


Figure 5. DSIMS profiles for free-standing film with different thickness. Probe: 4.3K dPS/6500K PS matrix after annealing at 110 °C for 30 min. The thick solid and dash line represent the diffusion profiles calculated assuming a downward shift in T_g by 10 °C for film thickness 41 and 69 nm, respectively.

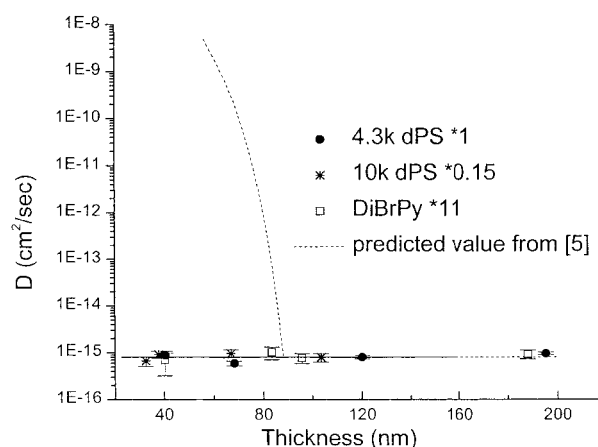


Figure 6. Average diffusion coefficients for diBrPy and dPS oligomers (M_w : 10K and 4.3K) diffusing into a high molecular weight (M_w : 6500K) matrix as a function of the thickness of the free-standing film. The values for dPS with $M_w = 10K$ and diBrPy have been rescaled as shown in the legend.

Table 2. Simulation Results for Figure 5

thickness (nm)	41	69	120	200
$D (\times 10^{-16} \text{ cm}^2/\text{s})$	8.5	6.0	8.0	9.5

are plotted in Figure 5 for the 41 and 69 nm thick films as solid and dashed lines, respectively, where can see that the diffusion profile is very sensitive to the shift in T_g . A similar set of diffusion profiles are also obtained for the PS $M_w = 10K$ oligomer.

The diffusion coefficients of the PS oligomers ($M_w = 4.3K$ and $10K$ dPS) into hPS ($M_w = 6500K$) matrix are averaged over three samples and plotted as a function of the total film thickness in Figure 6. Note that the values of D for dPS with $M_w = 10K$ and diBrPy were shifted vertically so that the data obtained from all probes could be plotted on the same scale. The calculated bulk diffusion coefficient from eq 1 at 110 °C is marked as a solid line. This value is confirmed by the diffusion of the probe on a supported thick film. The predicted values using T_g s from ref 12 and assuming a WLF shift are marked by thick solid and dashed lines. From the figure, we can see that the diffusion coefficients for all of the free-standing films are the same within the experimental error regardless of the film thickness. Hence, no deviation from the bulk T_g on the length scale sensed by the oligomer probes was detected.

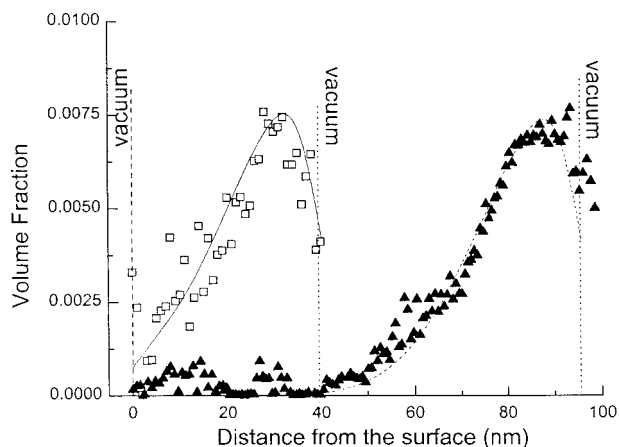


Figure 7. Diffusion profiles of diBrPy for free-standing films with total thickness 40 and 96 nm after annealing at 100 °C for 1 h.

To compare with the results performed on the smaller length scales probed by the fluorescent probes, a similar set of data was obtained on the free-standing films containing 1% diBrPy probes. The DSIMS profiles of the Br concentration for films 40 and 190 nm thick after annealing at $T = 100$ °C for 1 h are shown in Figure 7. The normalized diffusion coefficients for this set of data and two intermediate thicknesses are also superimposed in Figure 6. From the figure, we can conclude that, for all length scale probes studied, no change in T_g is observed for free-standing films with thickness greater than 33 nm.

Thus, it is determined that the glass transition temperature of the free-standing films ranging from 33 to 200 nm does not change. This is in good agreement with the shear modulation force microscopy results.¹⁷ These results are also consistent with probe diffusion⁷ in PiBMA and P₂VP on supported thin films with comparable or larger thicknesses than this study.

IV. Conclusion

In conclusion, we have probed the segmental mobility in free-standing and supported PS films using both small fluorescent molecules and PS oligomers as probes. The concentration profiles of both types of probes were measured in the high molecular weight matrix as a function of temperature and film thickness using DSIMS. The diffusion coefficients as a function of temperature followed the WLF relationship for the matrix. The extrapolated value of T_g , 105 °C, is the same as the bulk value. The results were identical for free-standing and supported films and did not depend on the type of probe used or the film thickness in the range 33–200 nm.

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