Macromolecules
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Molecular Motion in Free-Standing Thin Films of Poly(methyl methacrylate), Poly(4-*tert*-butylstyrene), Poly(α-methylstyrene), and Poly(2-vinylpyridine)

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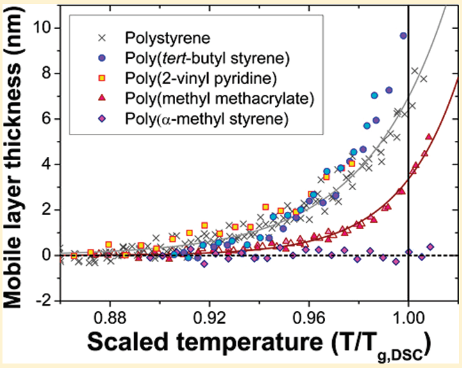
ABSTRACT: A photobleaching technique has been used to measure the reorientation of dilute fluorescent probes in free-standing polymer films from 7 nm to 20 μm thick. Similar to our previous report on free-standing polystyrene films, two subsets of probes with distinct dynamics were observed in free-standing poly(methyl methacrylate) films. The more mobile subset of probes is consistently interpreted in terms of a surface layer, and the thickness of the mobile surface layer is shown to increase with temperature. Poly(methyl methacrylate) has a mobile surface layer thickness of 4 nm at the bulk T_g. Similar measurements on free-standing poly(2-vinylpyridine) and poly(4-*tert*-butylstyrene) films indicate mobile surface layer thicknesses from 7 to 10 nm at their bulk T_g values, similar to the 7 nm value previously reported for polystyrene. In contrast to the other four polymers, free-standing poly(α-methylstyrene) films show no evidence of a mobile surface layer. We interpret these results in terms of contributions from a bulk correlation length and specific surface effects.



INTRODUCTION

The glass transition behavior of thin polymer films has drawn considerable attention in the past two decades. Part of the motivation for work on thin polymer films is the growing demand for miniaturization of polymer systems in various applications. Such applications have a large fraction of polymer segments near interfaces, and any interfacial effects on polymer dynamics could significantly affect adhesion, mechanical properties, and the transport of small molecules.

Many different methods have been developed to probe the glass transition temperature T_g of polymer thin films. It is widely reported that the value of T_g deviates from that of the bulk as films become thinner[1−8] although even this statement is controversial.[9−16] For supported films down to 10 nm, T_g can apparently increase or decrease by up to 20 K, depending upon the interaction of the polymer with the substrate and details of film preparation. Even larger T_g shifts have been reported for free-standing films, which are particularly interesting systems for investigating the influence of sample dimensions on the glass transition because polymer−substrate interactions are not relevant. For free-standing polystyrene films with high molecular weight, it has been reported that T_g can be reduced by 70 K even for films that are 50 nm thick.[7,8]

For bulk polymers, T_g is arguably the single most important material parameter. Segmental relaxation times are on the order of 100 s at T_g, and for a typical polymer melt, a 3−4 K shift in temperature near T_g corresponds to an order of magnitude change in relaxation times. Because of this, different polymer glasses have similar mechanical properties when temperature is scaled relative to T_g. If these same relationships hold in thin films, segmental relaxation times in thin films should be as much as 10^{10} times faster than in bulk polymers based upon a 70 K reduction in T_g. On the other hand, if the relationship between T_g and segmental dynamics is significantly different in thin films than in bulk polymers, then the utility of T_g as a material parameter is much diminished. In this case, more direct measurements of polymer dynamics would be required to understand thin film properties relevant for applications.

In a previous study, we used a photobleaching method to measure the reorientation of dilute probe molecules in free-standing polystyrene films as thin as 14 nm.[17] It was demonstrated that these probes are good reporters of segmental dynamics in bulk polystyrene. Under conditions where T_g for a free-standing film is reported to be lowered by ∼70 K, we observed that half of the probes in the film exhibit bulklike dynamics. Furthermore, the observed probe dynamics are independent of molecular weight from 160 to 7900 kg/mol, in sharp contrast to the T_g measurements reported for similar films.[7,8] These molecular reorientation measurements indicate the existence of a fast subset of probes at temperatures as low as 30 K below the bulk T_g. The fast subset was attributed to a mobile surface layer whose thickness grows exponentially with temperature and reaches 7 nm at bulk T_g. These findings are consistent with the view that modified dynamics in thin films result from an interfacial effect rather than from a confinement effect. Because these dynamics measurements are difficult to reconcile with T_g

Received: June 4, 2011
Revised: July 18, 2011
Published: August 04, 2011

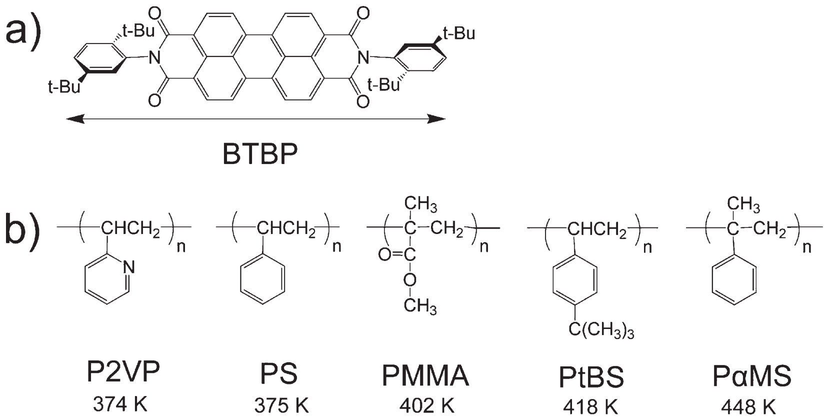


Figure 1. (a) Chemical structure of the fluorescent probe used in this study: BTBP (*N,N′*-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylenedicarboximide). The double-headed arrow indicates the direction of the absorption and emission transition dipole moments. (b) Chemical structures of polymers compared in this study: poly(2-vinylpyridine) (P2VP), polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(4-*tert*-butylstyrene) (PtBS), poly(α-methylstyrene) (PαMS). The temperatures below the names are bulk T_g values measured by DSC.

measurements, they raise the possibility that T_g values for thin free-standing films may not be reliable indicators of segmental dynamics.

Here we extend our previous study of probe reorientation to free-standing films of poly(2-vinylpyridine), poly(methyl methacrylate), poly(4-*tert*-butylstyrene), and poly(α-methylstyrene). Dilute fluorescent probes (≤10 ppm) were dispersed in the polymer films, and the reorientation of the probe molecules was probed by a photobleaching technique. Anisotropy decay measurements were performed during temperature ramping on free-standing films with thicknesses between 7 nm and 20 μm.

We find that probe reorientation in free-standing films of poly(2-vinylpyridine), poly(methyl methacrylate), and poly(4-*tert*-butylstyrene) is qualitatively similar to that previously reported for polystyrene. Two subsets of probes with distinct dynamics were observed in free-standing poly(methyl methacrylate) films. The more mobile subset of probes is assigned to a surface layer, and the thickness of the mobile surface layer is shown to increase with temperature. This analysis indicates that poly(methyl methacrylate) has a mobile surface layer thickness of 4 nm at the bulk T_g. Measurements on free-standing poly(2-vinylpyridine) and poly(4-*tert*-butylstyrene) films indicate mobile surface layer thicknesses of 7–10 nm at their bulk T_g values, similar to the 7 nm value previously reported for polystyrene. In contrast to the other four polymers, free-standing poly(α-methylstyrene) films show no evidence of a mobile surface layer. We interpret the results for these five polymers in terms of contributions from a bulk correlation length and specific surface effects. An extensive comparison is made to previous measurements of T_g and molecular mobility in thin films.

EXPERIMENTAL SECTION

Materials. The polymers used in this study are poly(2-vinylpyridine) (P2VP, M_n = 277 kg/mol, M_w/M_n = 1.09), poly(methyl methacrylate) (PMMA, M_n = 106 kg/mol, M_w/M_n = 1.08), and poly(α-methylstyrene) (PαMS, M_n = 160 kg/mol, M_w/M_n = 1.04). Data from these three polymers will be compared to previously reported results[17] for polystyrene (PS, M_n = 160 kg/mol, M_w/M_n = 1.05; M_n = 984 kg/mol, M_w/M_n = 1.03; M_n= 7370 kg/mol, M_w/M_n = 1.22) and to a new analysis of previously published results[18] for poly(4-*tert*-butylstyrene) (PtBS, M_n = 369 kg/mol, M_w/M_n = 1.05). The structures of all five polymers are shown in Figure 1b. T_g values measured by DSC on bulk samples of these polymers are indicated below each polymer structure. DSC measurements were performed with a TA Instruments Q2000 DSC using heating and cooling rates of 10 K/min. At least three scans were performed, and $T_{g,DSC}$ was determined as the onset of averaged heating scans after the first run. All polymers were obtained from Polymer Source, Inc., and used without any further purification.

The fluorescent probe used in this study is BTBP (*N,N′*-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylenedicarboximide); its structure is shown in Figure 1a. The double-headed arrow indicates the direction of the absorption and emission transition dipole moments. BTBP has high thermal and photostability and a high extinction coefficient (~5×10^4 L mol^{-1} cm^{-1}). When BTBP is dispersed in these polymers, the most pronounced absorption transition (0–0) occurs near 530 nm. The probe concentration used in this study was ~10^{-6} M for thicker films (>20 nm). For thinner films (<20 nm), concentrations up to 10^{-5} M were used.

Sample Preparation. Samples were prepared by either solvent-casting or spin-coating depending on the thickness. For samples thicknesses between 3 and 20 μm, the polymer was dissolved in 10^{-7} M dye solution (7–10 wt % polymer by mass) and solvent-cast onto a silicon wafer or microscope slide. Toluene was used as a solvent for poly(methyl methacrylate) and poly(α-methylstyrene), and either THF or DMF was used for poly(2-vinylpyridine). For samples thinner than 150 nm, a solution of 0.1–1.5 wt % polymer by mass was prepared and spin-coated onto freshly cleaved mica at 4000 rpm. For poly(2-vinylpyridine), either a glass substrate or a KBr pellet was used for spin-coating. Before floating the sample off onto water, all samples were annealed in a home-built vacuum oven (0.1 Torr) at T_g + 20 K for 12 h to remove solvent and then cooled at 1 K/min to room temperature. Annealing temperature and time did not change the anisotropy decay curve in subsequent experiments as long as the sample was annealed above T_g + 5 K for few hours. The free-standing geometry was achieved by floating the sample onto water and transferring onto a copper TEM grid (Pacific Grid Tech) with diameter of 3 mm and 97 μm square holes. After transfer, the sample was reannealed under vacuum at T_g + 20 K for thicker films (>50 nm) or near T_g for thinner films (<50 nm) to ensure the attachment of polymer to the grid and to remove residual water from the surface of the films.

Samples on the copper grid were placed in a cryostat dewar (Oxford Microstat N) using a home-built sample holder; a detailed description can be found elsewhere.[18] The sample holder is made from copper to ensure good thermal contact with the temperature controller. The cryostat dewar operated under vacuum, and an additional window was attached to the sample holder inside the dewar to prevent any temperature error due to radiative heat transfer. As described previously,[18] the temperature of a free-standing sample in this apparatus is known to within 1 K.

The film thickness was determined by an axial (z) scan of the confocal microscope for thick films (>3 μm) and ellipsometry for thin films (<150 nm). The resolution of the axial scan of the confocal microscope is ∼1.5 μm. For thin films, an Auto EL ellipsometer (Rudolph) with three wavelengths (632.8, 546.1, and 405 nm) was used for the sample thickness measurements. The polymer sample was spin-coated onto a substrate (∼10 mm square) and sectored using a razor blade. Small pieces (∼2 mm square) were floated off the spin-coated film and transferred to both TEM grids and silicon wafers. Film thicknesses measured on silicon wafers were assumed to be applicable to the free-standing samples on the TEM grid.

Temperature-Ramping Anisotropy Measurement. In order to study the reorientation of fluorescent probes in these polymer films, a photobleaching technique was used in conjunction with a confocal microscope. A trace amount of probe (10^{-5} M or less) dispersed in a polymer film was photobleached using linearly polarized light at least 40 K below $T_{g,DSC}$. The intense linearly polarized light selectively photobleaches probe molecules with transition dipole moments aligned with the polarization of the bleaching beam, thus preparing an anisotropic distribution of unbleached probes. The subsequent reorientation of the unbleached probes was monitored using less intense circularly polarized light while temperature ramping. A detailed description of the experimental apparatus and the data analysis can be found elsewhere.[18] Once an anisotropy is created by photobleaching, it does not decay until the host polymer allows the probes to reorient. In measurements on thick polymer films, the anisotropy does not decay until $T_{g,DSC}$ is approached.[17,18]

As is well-known for isothermal fluorescence anisotropy measurements, the anisotropy is a measure of the distribution of transition dipole moments, and it decays as a result of the reorientation of fluorescent probes.[19−22] The anisotropy $r(t)$ is proportional to the orientation autocorrelation function $CF(t)$ that describes the average reorientation of the transition dipole $\hat{\mu}$ between time 0 and t: $r(t) = r(0)CF(t) = r(0)\langle P_2[\hat{\mu}(0)\cdot\hat{\mu}(t)]\rangle$. Here, P_2 is the second Legendre polynomial. Isothermal anisotropy measurements have successfully been used to describe the segmental dynamics of bulk polymers in many studies.[19−22] The temperature dependence of the probe rotational correlation time strongly correlates with the α relaxation process of the host polymer.[19−23]

As we have shown elsewhere,[17,18] the segmental dynamics of polymers can also be probed by the reorientation of fluorescent molecules while temperature ramping. In temperature-ramping anisotropy measurements, the fluorescence intensities from bleached and unbleached regions are monitored alternately. The anisotropy is calculated as follows: $r(T) = (\Delta I_{\parallel}(T) - \Delta I_{\perp}(T))/(\Delta I_{\parallel}(T) + 2\Delta I_{\perp}(T))$. Here, $\Delta I_{\parallel}(T)$ and $\Delta I_{\perp}(T)$ are fluorescence intensity differences between unbleached and bleached regions for parallel and perpendicular polarizations, respectively, which are calculated by following equations: $\Delta I_{\parallel}(T) = I_{\parallel}^{ub}(T) - I_{\parallel}^{b}(T)$ and $\Delta I_{\perp}(T) = I_{\perp}^{ub}(T) - I_{\perp}{}^{b}(T)$. The analysis scheme utilized here eliminates the influence of temperature-dependent fluorescence intensities. The magnitude of the initial value of the anisotropy $r(i)$ depends on the bleach depth, probe molecule, polymer, and film thickness. For BTBP in thick polymer films, $r(i)$ is around 0.3 if the bleach depth is less than 30%. In this study, for ease of comparison, $r(T)$ was normalized by the initial anisotropy $r(i)$. Here, $r(i)$ is calculated by averaging $r(T)$ values for the initial 10 K range in the beginning of the experiment.

Photobleaching was performed in an oxygen-rich atmosphere (1 bar of O_2) with intense linearly polarized light. The oxygen-rich atmosphere facilitates permanent photobleaching which enables us to directly connect the anisotropy decay to probe reorientation.[18] About 30 min after photobleaching, the sample was evacuated to a pressure of 10^{-6} bar. The vacuum environment is desirable while probing the fluorescence since it enhances photostability of the probe. There is no detectable decay of anisotropy prior to the initiation of the temperature ramp.

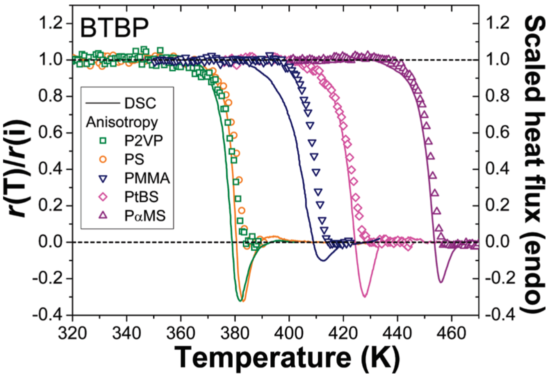


Figure 2. Temperature-ramping anisotropy measurements (points) of BTBP reorientation in five bulk polymers. The solid curves indicates DSC data for bulk samples of each polymer acquired while heating at 10 K/min and analyzed as described in the text. For these polymers, dye reorientation is closely tied to the glass transition. For the optical measurements, the sample thicknesses were 3−20 μm and the ramping rate was 2 K/min.

RESULTS

Bulk Polymers. Temperature-ramping anisotropy measurements on BTBP in thick films of poly(methyl methacrylate) (PMMA) and poly(α-methylstyrene) (PαMS) were performed with a ramping rate of 2 K/min. In Figure 2, these anisotropy data are compared with previously reported results[18] for bulk films poly(2-vinylpyridine) (P2VP), polystyrene (PS), and poly(4-*tert*-butylstyrene) (PtBS). All these samples were thick enough (3−20 μm) to ensure bulk response.

Figure 2 also shows DSC data obtained while heating bulk samples of these polymers at 10 K/min. At least three DSC scans were performed for each polymer, and the averaged heating scans after the first run are presented in the figure. The averaged scans were analyzed using a three-point baseline correction to flatten the slopes of the heat flux in the glassy and supercooled liquid regimes; the heat flux of the supercooled liquid was adjusted to 0 while that of the glass was normalized to unity.

For each bulk polymer sample shown in Figure 2, the anisotropy is constant at low temperature and drops to zero near T_g. Qualitatively, this indicates that the probe molecules cannot reorient on the experimental time scale deep in the glass; probe reorientation is observed only as T_g is approached and segmental dynamics occur on the time scale of hundreds of seconds. All the anisotropy decays are comparable in shape, and the transition temperature range is around 20 K. The temperature shifts between the anisotropy curves are comparable to the glass transition temperature shifts for these polymers. This result is consistent with previous work in which fluorescent probe reorientation has been used to study the segmental dynamics of bulk polymers.[18−22]

For four of the polymers in Figure 2, the anisotropy decay and the corresponding DSC curve have very similar shapes. Only the poly(methyl methacrylate) data show some difference in this regard. There are no rigorous arguments why the anisotropy and DSC experiments should precisely match each other.

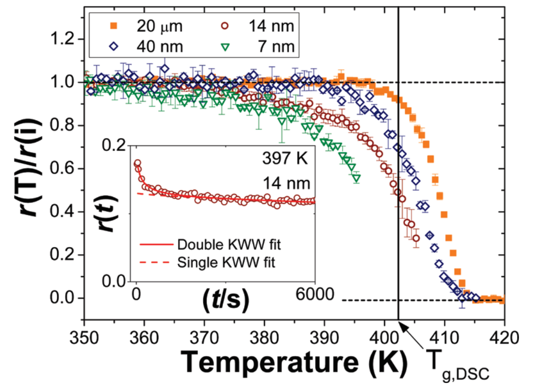


Figure 3. Temperature-ramping anisotropy measurements for BTBP in free-standing PMMA films of different thicknesses. For thinner films, the anisotropy decay initiates at lower temperature and the shape of the decay broadens. The vertical line indicates the glass transition temperature of bulk poly(methyl methacrylate) measured by DSC. The inset shows an isothermal anisotropy measurement at 397 K on a 14 nm film. The isothermal data are well-described by an additive function of two stretched exponentials (double KWW function).

Nonetheless, it is reasonable to say that the rotational correlation time of BTBP in these bulk polymer matrices is closely correlated with the segmental dynamics that are indirectly detected in the DSC experiment.

Free-standing Poly(methyl methacrylate) Films. In Figure 3, temperature-ramping anisotropy measurements on free-standing poly(methyl methacrylate) films are presented. For all measurements, BTBP was used as the probe and the ramping rate was 2 K/min. The samples shown have thicknesses ranging from 20 μm to 7 nm. For thinner films, the anisotropy decay systematically initiates at lower temperature and the shape of the decay broadens. The entire decay curves are not shown for the 7 and 14 nm films because holes formed if the scans were continued to temperatures higher than the range shown.

The data presented in Figure 3 are qualitatively consistent with results presented recently for free-standing polystyrene films.[17] In that work, the cause of the broadened decay in the temperature-ramping anisotropy measurement was determined to be a subset of probe molecules with fast dynamics. The inset to Figure 3 shows an isothermal anisotropy measurement on a 14 nm poly(methyl methacrylate) film at 397 K. The solid and dotted lines indicate fits to single- and double-stretched exponential [Kohlrausch−Williams−Watts (KWW)] functions, respectively. The data in the inset support the hypothesis of coexisting fast and slow populations of probe molecules in poly(methyl methacrylate), as we discuss below.

Free-Standing Poly(2-vinylpyridine) and Poly(α-methylstyrene) Films. Figure 4 shows temperature-ramping anisotropy measurements for BTBP in free-standing poly(2-vinylpyridine) and poly(α-methylstyrene) films. The temperature-dependent anisotropy is plotted as a function of scaled temperature for ease of comparison. For the case of poly(2-vinylpyridine), the 24 nm film shows a lower temperature decay in the anisotropy as compared to the bulk. These results are qualitatively similar to the behavior of free-standing films of poly(methyl methacrylate) and polystyrene.

Figure 4 also shows temperature-ramping anisotropy decay data for free-standing poly(α-methylstyrene) films. In contrast to the other four polymers that we have studied with BTBP, the

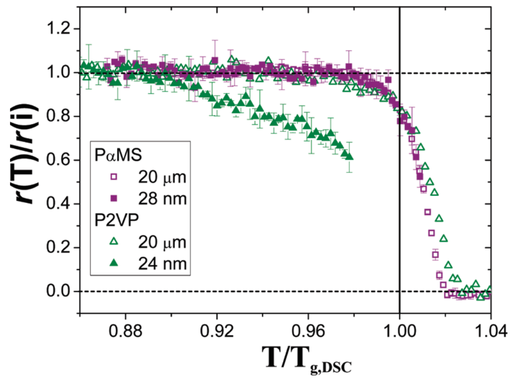


Figure 4. Temperature-ramping anisotropy measurements for BTBP in free-standing PαMS and P2VP films. The temperature was scaled by the bulk $T_{g,DSC}$ for each polymer. The 24 nm free-standing poly(2-vinylpyridine) film shows a broadened anisotropy decay while data from the 28 nm poly(α-methylstyrene) film agree with the corresponding bulk data.

anisotropy data for the 28 nm film are identical (within error) to the bulk data for poly(α-methylstyrene). Additional data collected on a 17 nm film (not shown) had more noise than the 28 nm film but are also consistent with the bulk anisotropy decay.

DISCUSSION

Two Populations of Probe Molecules. The inset to Figure 3 shows an isothermal anisotropy decay for the probe BTBP in a 14 nm free-standing film of poly(methyl methacrylate). This data are consistent with the existence of two populations of probe molecules, with one subset reorienting with a time scale of ∼200 s while the other subset reorients on a time scale exceeding 10 000 s.

For BTBP in polystyrene thin films,[17] a much more extensive set of measurements supports the existence of two probe molecule populations; isothermal anisotropy measurements showed that the slow decay process matched the dynamics of a bulk sample (both τ and β parameters in the KWW fit) at multiple temperatures. On the basis of this and other evidence, we interpreted the polystyrene results in terms of a slow bulklike population of probes at the center of the thin films and a much faster population of probes near the free surfaces. The inset to Figure 3 and other evidence presented below supports the application of this view to the poly(methyl methacrylate) data as well. While we did not perform isothermal anisotropy measurements on thin films of poly(4-*tert*-butylstyrene), poly(α-methylstyrene), or poly(2-vinylpyridine), we will also utilize this physical picture to analyze the temperature-ramping anisotropy decays for these three polymers.

Thickness of the Mobile Surface Layer. The large difference between the mobility of the fast and slow subsets of probe molecules allows us to quantify the relative populations of these subsets using the temperature-ramping anisotropy experiment. As demonstrated in the study of free-standing polystyrene films,[17] the rotational relaxation times of these two populations differ by ∼2 orders of magnitude at T_g and by ∼4 orders of magnitude at lower temperatures. The anisotropy decay seen at lower temperatures for thin films is directly related to the fraction of the probe molecules with fast dynamics (for a temperature ramp of 2 K/min, "fast dynamics" means probes with rotational correlation times less than ∼100 s).[17] If we assume that probe molecules are homogeneously distributed in the film, we can calculate the fraction of the film with fast dynamics. If we further assume that regions of fast dynamics are located adjacent to the free surfaces, we can calculate the thickness of the mobile surface layer $d(T)$:

$$d(T) = \frac{D}{2}\left[1 - \frac{\left\{\dfrac{r(T)}{r(i)}\right\}_{\mathrm{tf}}}{\left\{\dfrac{r(T)}{r(i)}\right\}_{\mathrm{bf}}}\right] \qquad (1)$$

Here D is the total thickness of the thin film and the subscripts tf and bf stand for thin film and bulk film, respectively. The mobile layer thickness can only be calculated in the temperature range before the bulk anisotropy decays to zero.

Figure 5 shows three independent calculations of the mobile layer thickness as a function of temperature for free-standing poly(methyl methacrylate) films. Equation 1 was used for the calculations. The fact that experiments on films of three different thicknesses (shown as triangles with different shades of red) yield very similar results strongly supports the interpretation of the data in terms of a mobile surface layer. The mobile surface layer thickness grows exponentially with temperature and reaches 4 nm at $T_{\mathrm{g,DSC}}$. These results are consistent with the view that probe mobility in thin free-standing films is completely controlled by the proximity of the probe to a free surface. We know of no other explanation of the temperature-ramping anisotropy data that is equally simple and comprehensive.

Figure 5 also shows results for free-standing polystyrene films.[17] For polystyrene, good agreement is observed among the mobile layer thicknesses calculated from temperature-ramping anisotropy data for several film thicknesses, three molecular weights, and three different dyes. In Figure 5, to allow an easy comparison among different polymers, we have normalized the temperature axis to the T_g value measured by DSC for the bulk polymers (see Figure 1).

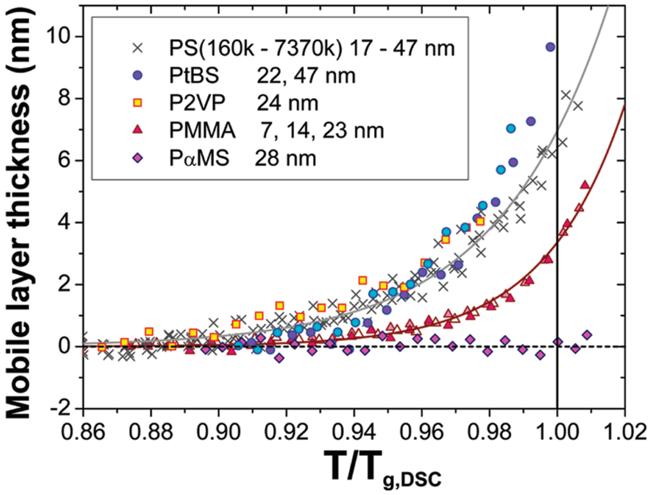


Figure 5. Temperature dependence of mobile layer thickness plotted versus scaled temperature for five polymers. All thicknesses were calculated from anisotropy decay data for free-standing films. Identical information about the mobile layer thickness is obtained from multiple film thicknesses for poly(methyl methacrylate), poly(*tert*-butylstyrene), and polystyrene. The curves are fits to exponential growth functions that serve as guides to the eye. Temperature has been normalized to T_g of the bulk polymers as determined by DSC.

Without further justification, we analyzed free-standing film anisotropy data in terms of a mobile surface layer for poly(2-vinylpyridine) and poly(α-methylstyrene) (data presented here) and for poly(4-*tert*-butylstyrene) (data from ref 18). These results are also plotted in Figure 5 as a function of scaled temperature and compared with data for the other polymers. As can be anticipated from Figure 4, poly(α-methylstyrene) shows no indication of a mobile surface layer even when temperature is increased above $T_{\mathrm{g,DSC}}$. The data fluctuate within ±0.5 nm of the zero line and can be regarded as an estimate of the error for this analysis. The mobile layer thickness for poly(4-*tert*-butylstyrene) is slightly larger than for polystyrene, and the mobile layer thickness for poly(2-vinylpyridine) is similar to these values. We note the excellent agreement between the mobile layer thickness determined from poly(4-*tert*-butylstyrene) films of two different thicknesses. For all the polymers except poly(α-methylstyrene), the mobile surface layer begins to be detectable between $0.88T_g$ to $0.92T_g$ or close to T_0 of the Vogel−Tammann−Fulcher (VTF) equation.

Dependence of Mobile Layer Thickness on Chemical Structure. The only feature in Figure 5 that depends upon the polymer identity is the thickness of the mobile surface layer at T_g. This thickness is 0 nm for poly(α-methylstyrene), 4 nm for poly(methyl methacrylate), 7 nm for polystyrene, and roughly 10 nm for poly(4-*tert*-butylstyrene) and poly(2-vinylpyridine). We first note that there is no correlation between the fragility of the polymer melts[24] and these length scales. There have been several attempts to connect the length scale where the properties of thin films deviate from the bulk to other polymer length scales.[2,25,26] The Kuhn length, which is related to chain stiffness, could be one possible candidate. The Kuhn length for all these polymers is between 1.5 and 2.0 nm, so this does not provide a simple explanation of the mobile layer thicknesses at T_g. A *dynamic* length scale, such as the length scale of cooperatively rearranging regions (CRR) or that of spatially heterogeneous dynamics, is likely to be more relevant.[26] The length scale of CRRs for poly(methyl methacrylate) has been reported about half of that of polystyrene ($\xi_{\mathrm{PMMA}} = 1.7$ nm, $\xi_{\mathrm{PS}} = 3.5$ nm)[27−29] which collapses the data in Figure 5 if the mobile surface layer thickness is scaled to the CRR length scale. The CRR length scale for poly(4-*tert*-butylstyrene) and poly(2-vinylpyridine) is expected to be in the range of 3−4 nm, and this would be consistent with the scaling suggested. However, the CRR length scale of poly(α-methylstyrene) would need to be less than 1 nm to fit into this pattern; no data are available on this point, but this result seems unlikely. Others have previously noted that the CRR length scale does not have a simple connection with T_g shifts observed for supported thin films of various polymers.[2,28]

We offer a rationalization of mobile surface layer thicknesses in these five polymers by drawing upon recent MD computer simulations of polymers and mixed Lennard-Jones spheres. As summarized in a recent review,[30] many simulations report that relaxation times change continuously as an interface is approached, whether the polymer is adjacent to a vacuum or a hard wall.[26,31−33] Relaxation times at an interface depend upon how the interface constrains local rearrangements, and near-interface relaxation can be faster or slower than in the bulk. For a given interface, as the temperature is lowered, the difference between surface and bulk relaxation times has been observed to become larger (up to a factor of 100) and the surface influence persists further into the bulk material. For a system of mixed Lennard-Jones spheres, Scheidler et al.[26] showed that various length scales characterizing the surface effect are 1−4 times larger than a bulk length scale characterizing the alpha relaxation. Collectively, these simulations indicate that interfacial dynamics are influenced by specific interface effects but limited in length scale to a few times the bulk correlation length for the alpha relaxation.[34]

All of the mobile layer thicknesses that we report at T_g are 10 nm or less and are at most a few times larger than the expected length scale for cooperative motion in the bulk polymer at T_g. In this sense, our results are consistent with the simulations. While we have interpreted our data in terms of a "two-layer" model, our results are also consistent with a continuous distribution in relaxation times as a function of distance from the free surface. We interpret the difference between polystyrene and poly(α-methylstyrene) thin films not in terms of the length scale of the surface perturbation but rather its amplitude. The apparent absence of a mobile surface layer for poly(α-methylstyrene) might be due to a specific packing effect at the free surface rather than an unusually small bulk correlation length. Our experiments provide no insight into the nature of surface packing in these systems, but it is conceivable that atomistic simulations might provide access to this.

We wish to make some qualitative comments about the temperature dependence of the mobile layer thickness in our experiments. In our experiments, the mobile probes are those that reorient on the time scale of ∼100 s or less. Since all relaxation processes are expected to slow with decreasing temperature, we expect that the fraction of mobile probes relative to this fixed time scale cannot increase. Otherwise, molecules in some position in the film would be reorientating faster at low temperature than at high temperature. Computer simulations are in qualitative agreement with this view (e.g., see Figure 1b of ref 26); while the fraction of a film that is substantially more mobile than the bulk *increases* with decreasing temperature, the fraction of the film with dynamics faster than some arbitrary time scale *decreases* with decreasing temperature. Some previous experiments on thin polymer films have been interpreted in terms of a surface length scale that increases with decreasing temperature.[8,35]

Comparison to T_g Measurements on Free-Standing Polymer Films. The glass transition of free-standing polymer films has been studied by ellipsometry, BLS, and X-ray reflectivity for polystyrene[3,7,8,36] and poly(methyl methacrylate).[37,38] These techniques directly measure density or volume changes with temperature and T_g is defined by a change in the temperature dependence. Free-standing polystyrene films are the best characterized system and show roughly a 70 K reduction in T_g as film thickness approaches 20 nm for molecular weight between 120 and 380 kg/mol.[8] Remarkably, the reduction in T_g becomes substantially more pronounced for even higher molecular weight polymers. For example, T_g is reduced by 80 K for a 60 nm film of 6680 kg/mol polystyrene chains.[7] In these studies, the T_g transition is relatively sharp, and no indication of any transition at the bulk T_g was reported. T_g reductions for poly(methyl methacrylate) films are smaller in comparison to polystyrene films, showing roughly a 30 K reduction for 20 nm films with molecular weight of a few hundred kg/mol.[37,38] Some elements of these T_g results for free-standing polystyrene films, including the molecular weight dependence, have been verified by indirect measurements of density or volume change with temperature. Examples include fluorescence intensity measurements[39,40] and confocal Raman spectroscopy[41] on free-standing polystyrene films.

If one assumes that T_g in a free-standing polymer film indicates the temperature where segmental relaxation occurs on the 100 s time scale, it is difficult to reconcile the T_g measurements described above with the results reported here and in ref 17. Our polystyrene results[17] indicate that a substantial fraction (about 1/2) of the probes in a 30 nm film exhibit bulklike dynamics, independent of molecular weight in the range 160−7400 kg/mol. In contrast, the T_g reduction reported[3,7,8,36,39−41] for such films varies from 20 K to at least 70 K in this molecular weight range, and those experiments give no indication that any portion of the film exhibits bulk dynamics.

The contrast between probe reorientation and T_g measurements is similar, if not as striking, for the case of free-standing poly(methyl methacylate) films. The probe reorientation experiment indicates that most of a 30 nm film exhibits bulklike dynamics while ellipsometry measurements[37,38] indicate a T_g reduction of 30 K for a sample with similar thickness and molecular weight. Another method of comparing probe reorientation with reported T_g shifts for free-standing polystyrene films is given in the Supporting Information to ref 17; any straightforward method of assessing temperature shifts in the probe reorientation data gives smaller shifts than the T_g measurements, and of course, such a comparison cannot reconcile the different molecular weight dependences of the two measurements.

How can the previously reported T_g measurements be reconciled with the probe reorientation measurements described here? We offer a short list of possibilities: (1) *The probes are too large.* We remind the reader that the reorientation of these probes tracks the temperature dependence of segmental dynamics in the bulk (see Figure 2, Figure 1S of ref 17, and Figure 8 of ref 18). We showed previously that two different dispersed probes (ranging in size from 1.3 to 2.3 nm) and a chain-tethered probe give identical results for the thickness of the mobile surface layer as a function of temperature for free-standing polystyrene films.[17] These results argue that the probes are reliable reporters. Given their size, it is likely that these probes will be fairly insensitive to changes in the fast side of the distribution of relaxation times associated with the glass transition; the possibility that this portion of the distribution is changing with film thickness has been discussed.[42] (2) *The probes are not uniformly dispersed.* It is possible that the probe concentration is systematically enhanced or reduced near the surface of the film relative to the interior. The consistency of results for the two dispersed probes and the tethered probe argues against this because the same partitioning would be required for all three systems. Even if some partitioning occurs, the probe reorientation results would still indicate that a substantial portion of a 30 nm free-standing polystyrene film exhibits bulklike dynamics, independent of molecular weight, in apparent contradiction with the T_g measurements. (3) *T_g measurements are mainly sensitive to surface dynamics.* We raise this possibility to emphasize that some of the probes reorient very rapidly far below T_g. Our experiment does not have adequate time resolution to accurately determine the temperature where a "surface T_g" might be observed. (4) *T_g is not a measure of segmental mobility in free-standing films.* While the correlation between T_g and segmental mobility is very well established in bulk polymers, it is possible that the inference that the segmental relaxation time is ∼100 s at T_g is not correct in thin free-standing films. In this case, the value of T_g would not be nearly as useful as it is in bulk polymers because inferences about dynamics and mechanical response would be suspect.

For poly(2-vinylpyridine), poly(*tert*-butylstyrene), and poly(α-methylstyrene) films, there are no reports of T_g measurements on free-standing films for comparison with our probe reorientation measurements. T_g measurements have been reported for supported thin films of these polymers. In particular, ellipsometric measurements of T_g reductions for supported poly(α-methylstyrene) films have been interpreted in terms of a mobile surface layer;[25] this conclusion seems inconsistent with our result for free-standing poly(α-methylstyrene) films shown in Figures 4 and 5. Probe reorientation studies in supported polymer films are the subject of future paper.[43]

Comparison to Previous Measurements of Molecular Mobility in Thin Films. In contrast to work in which T_g is measured by a change in the temperature dependence of a static property, there are only few studies where dynamics in free-standing polymer films are directly observed. One is the nanobubble inflation technique which measures the absolute creep compliance of a free-standing polymer film.[44,45] An effective T_g has been extracted from the creep compliance data. Although the effective T_g decreases with decreasing film thickness, the amount of reduction is significantly smaller than that reported by ellipsometry. For a 36 nm free-standing polystyrene film, the nanobubble experiment reports that the effective T_g drops by about 25 K,[45] while more than a 60 K drop would be expected from the ellipsometric T_g measurements for the same molecular weight (994 kg/mol).[8] At present, there are no studies of molecular weight dependence using this nanobubble inflation method. We do not know how to quantitatively compare the probe reorientation method (which reports the dynamics of two subpopulations of probes) to the single effective T_g extracted with the nanobubble method.

Another important study of dynamics in free-standing polymer films has been performed with dielectric relaxation using interdigitated comb electrodes.[46] With this method, the film is suspended between the electrodes and thus has two free surfaces. In one report, a polar probe was added to polystyrene (0.5% concentration), and the molecular weight dependence of the dielectric relaxation was tested for three different molecular weights (932, 1200, and 3000 kg/mol). Reference 46 reports probe dynamics consistent with the large T_g shifts measured by BLS and ellipsometry, including a substantial molecular weight dependence. However, in a later report with this technique,[47] where different thickness films were studied for 932 kg/mol polystyrene, the measured dynamics showed a significantly different thickness behavior as compared to ellipsometery and BLS data. The reported dynamics deviate strongly from the dynamics of the bulk polymer even for 120 and 225 nm films. Given that these dielectric measurements and our optical measurements both report probe reorientation in free-standing polystyrene films, it is striking that the results are so incompatible. While the dielectric relaxation method has many advantages and can be used to monitor dynamics in the absence of probes, we wish to emphasize two features of our probe reorientation measurements. We directly measure the ensemble average of a single particle correlation function, i.e., the orientation autocorrelation function of the probe. Thus, the connection between the polarized fluorescence intensity that is observed and probe reorientation is very direct. In contrast, the electric polarization monitored in dielectric relaxation is a collective observable that responds to the displacement of every charge in the system; the reorientation of a dipolar probe is not the only contribution to the observed signal. In addition, the probe concentration in our work is about 500 times lower than that reported in ref 46.

The terminal dynamics of polystyrene chains in free-standing films has been probed by hole formation and growth.[48,49] In spite of a large reduction in T_g as reported by BLS and ellipsometry, free-standing films as thin as 50 nm showed similar hole formation and growth behavior in comparison to bulk samples. These results seem easily compatible with the probe reorientation measurements that we report here and elsewhere.[17] Our measurements indicate that the central 36 nm region of a 50 nm polystyrene film exhibits bulklike dynamics at the bulk T_g. Since hole formation requires rearrangement of this interior section of the film, it is reasonable that films of this thickness should respond similarly to much thicker films.

A number of recent studies have reported on the dynamics of molecular motion at the free surface of a thick supported polymer film.[50−54] While this is a different geometry than the experiments reported here, comparisons with this type of experiment seem likely to be relevant since our results have been consistently interpreted in terms of two noninteracting free surfaces. Nanoparticle embedding experiments on polystyrene show a two-step process with a fast partial embedding followed by much slower further embedding.[51] If we identify the initial embedding with fast dynamics near the surface and the later embedding as bulk dynamics, these experiments are quite consistent with our results.[17] Near T_g, 20 nm particles quickly embed to a depth of about 5 nm; at $T_g - 30$ K, about 2 nm of embedding is observed.[51] In these experiments, the initial embedding at 366 K is roughly 2 orders of magnitude faster than the onset of further embedding. The thickness of the surface layer, the temperature dependence of this layer thickness, and the relative relaxation times for surface and bulk processes are all similar to the results that we report based upon probe reorientation measurements. For example, at 365 K, we report that near surface dynamics in polystyrene are 3 orders of magnitude faster than bulk dynamics.[17]

Finally, we make a comparison with dynamics at the surface of a low molecular weight glass-former, trisnaphthylbenzene. Given the absence of any molecular weight dependence in our probe reorientation data from free-standing polymer films, it seems plausible that polymeric and low molecular weight glass-formers might show similar patterns in dynamics near free surfaces. On the basis of neutron reflectivity experiments, it has been reported that a mobile surface layer is present on glasses of trisnaphthylbenzene, with the layer thickness decreasing from 9 nm at T_g to ∼1 nm at $T_g - 50$ K.[55] At $T_g - 50$ K, the mobile surface layer was estimated to be similar in mobility to the bulk material at T_g. These numbers are comparable to the length scales shown in Figure 5 and the time scales (for polystyrene) discussed in ref 17.

■ CONCLUDING REMARKS

Photobleaching measurements have been performed on dilute probes in free-standing polymer films with thicknesses between 7 nm and 20 μm. Results for polystyrene, poly(methyl methacrylate), poly(4-*tert*-butylstyrene), and poly(2-vinylpyridine) are qualitatively similar. Two subpopulations of dye molecules are present in thin films, and the fast subpopulation can be consistently associated with a mobile surface layer. The thickness of the mobile surface layer increases smoothly from roughly zero at $0.9T_g$ to 3−10 nm at the bulk T_g. The slow subpopulation of probe molecules exhibits bulklike dynamics.

Free-standing thin films of poly(α-methylstyrene) of 28 nm, in contrast, show bulklike dynamics within the resolution of our experiment. We interpret these results in light of recent computer simulations which indicate that surface effects penetrate into the bulk for a distance of the order of the characteristic length scale for the alpha relaxation process. The difference between near-surface and bulk dynamics is expected to be system specific. Thus, we speculatively interpret our results on free-standing poly(α-methylstyrene) films to indicate a packing arrangement at the free surface that causes only a small difference between near-surface and bulk dynamics.

The direct measurements of probe reorientation presented here are difficult to reconcile with T_g measurements on free-standing polymer films that rely on changes in the temperature dependence of the density or other static properties. Our results indicate that while dynamics are faster within ∼10 nm of a free surface near the bulk T_g, portions of the polymer sample that are more distant from the surface exhibit bulklike dynamics. Thus, for 30−50 nm films, it is difficult to understand why T_g measurements based upon volume changes do not report that a portion of the sample has the bulk T_g. We suggest the possibility that such T_g measurements do not provide accurate information about segmental dynamics in free-standing films.

In comparison to other work on free-standing films, these new results seem consistent with hole growth measurements and plausibly compatible with nanobubble inflation results. Our results also fit with free surface measurements of nanoparticle indentation and mobility measurements at the free surface of a low molecular weight organic glass. On the other hand, we do not understand the difference between our results and dielectric relaxation measurements of probes in free-standing polystyrene films.

It is possible that these probe molecules are not accurate reporters of segmental dynamics in thin films even though probe reorientation times in bulk polymers are directly proportional to segmental relaxation times. However, it is implausible to us that probes with dimensions of 1.2−2.3 nm show no change from bulk dynamics in the center of a 30 nm free-standing film while the dynamics of the segments that surround the probes are enhanced by many orders of magnitude. Even if this were to be the case, the probe reorientation measurements would still be providing an accurate view of how molecules in the size range of 1−2 nm move near free polymer surfaces, and for some applications, this would be more relevant than T_g or information about how the polymer segments themselves rearrange.

■ ACKNOWLEDGMENT

This work was supported by the National Science Foundation (NSF-DMR 1104770 and 0907301). We thank Kurt Binder and Connie Roth for useful discussions.

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