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PAPER

Molecular mobility in supported thin films of polystyrene, poly(methyl methacrylate), and poly(2-vinyl pyridine) probed by dye reorientation

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Temperature-ramping anisotropy measurements were used to probe the molecular mobility of fluorescent probes in polystyrene, poly(methyl methacrylate), and poly(2-vinyl pyridine) films supported upon silicon wafers with native oxide coatings. All polymer films showed evidence of high mobility at the free surface. The fraction of a film with high mobility was characterized as a mobile surface layer thickness, which increased with temperature. The mobile surface layer thickness for supported films of polystyrene and poly(methyl methacrylate) reasonably matched that previously deduced from freestanding films of these polymers; for poly(methyl methacrylate), enhanced mobility extends about 4 nm into the film from the free surface at T_g . For supported polystyrene and poly(methyl methacrylate) films, the results are consistent with no decrease in mobility near the solid substrate but do not eliminate this possibility. On the other hand, the mobility of supported poly(2-vinyl pyridine) thin films provides some evidence for slower-than-bulk relaxation near the solid substrate.

Introduction

In the last 20 years, there has been tremendous interest in the properties of nanometre thick polymer films, and in particular, in the glass transition temperature T_g as a function of film thickness.^{1–8} Such films are not only important technologically but also hold promise for revealing fundamental features of the behavior of polymer chains near surfaces and interfaces. T_g for thin films has been widely determined by measuring a static property (such as volume or enthalpy) as function of temperature; a break in the temperature dependence is interpreted as T_g . In contrast to direct measurements of molecular mobility, such approaches have been described as “pseudo-thermodynamic” methods.¹ For the best-studied system, polystyrene supported by silicon with a native oxide coating, pseudo-thermodynamic measurements (mainly ellipsometry) from many labs show roughly comparable behavior, with T_g being 10–30 K lower than bulk polystyrene for a 10 nm film.^{1,2,4–6,9} Others have argued that thoroughly annealed samples of this type show no T_g change.^{10–12} For other polymers, T_g increases upon decreasing film thickness have been reported.^{13–17} For example, for poly(2-vinyl pyridine) on silicon with a native oxide, a 40 K increase of T_g was reported for a 10 nm film.^{14,18,19} For bulk polymers, a 10 K change in T_g is typically associated with a 1000-fold change in molecular

mobility and thus the reported T_g changes have the potential to significantly modify polymer properties.

The T_g changes observed in thin polymer films have usually been interpreted in terms of changes in dynamics near the interfaces. If a T_g decrease is observed for thin films, it is generally interpreted in terms of fast dynamics near the free surface^{4,5} while T_g increases have been associated with slower than bulk dynamics near the substrate. For sufficiently thin films, the interfacial material will constitute a significant fraction of the polymer present. Many methods have been utilized in an attempt to directly measure dynamics at the free surface. Several papers have reported that roughened or patterned surfaces of polymer glasses smooth to some extent below T_g , consistent with the idea of fast surface dynamics.^{20,21} The sub- T_g relaxation of orientation of the rubbed surface of a polymer glass also supports this view.²² Nanoparticles can embed rapidly into polymer glass surfaces below T_g , and if the particles are removed, the nanoholes also fill rapidly below T_g .^{23–26} A local dielectric relaxation experiment has presented evidence that the top surface of a poly(vinyl acetate) film has faster dynamics than the bulk.²⁷ “Local T_g ” measurements performed by monitoring the temperature-dependent emission properties of chromophores in layered polymer films have been reported to indicate very fast surface dynamics that penetrates more than 10 nm into a thick film.^{28,29} In addition, many computer simulations have shown evidence of fast dynamics at free surfaces.^{30–34} Other experiments have been interpreted to indicate that dynamics are not faster at the free surface than in the bulk material.^{10–12}

We recently developed an optical method for studying molecular mobility in thin polymer films.³⁵ A low concentration

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of a fluorescent probe molecule (~ 10 ppm) is dissolved in the polymer of interest and a temperature-ramping anisotropy measurement based upon photobleaching is used to monitor the reorientation of the probe. For bulk polymers, it is known that the probe is an accurate reporter of segmental dynamics. This method provides a very direct measure of molecular motion. In addition, mobility near the interface and in the bulk can be quantitatively compared. As has been noted elsewhere,¹ this is not the case for many of the surface-selective methods described above.

Temperature-ramping anisotropy experiments on freestanding films of several polymers indicate two subsets of probe molecules, one with bulk-like dynamics and the other with considerably higher mobility.^{36,37} The high mobility subset can be consistently interpreted as a mobile surface layer whose thickness increases as T_g is approached from below. The mobile layer thickness for polystyrene is about 7 nm at T_g , and is independent of total film thickness (between 14 and 47 nm), molecular weight, and identity of the probe. These results, particularly the molecular weight independence, are not consistent with the results of pseudo-thermodynamic measurements^{2,38,39} of T_g in freestanding polymer films. This comparison highlights the importance of direct measurements of dynamics in thin polymer films.

Here we utilize temperature-ramping anisotropy measurements to investigate supported films of polystyrene, poly(methyl methacrylate), and poly(2-vinyl pyridine), studying films as thin as 8 nm on silicon with a native oxide coating. Supported films are more relevant technologically than freestanding films but the presence of a solid substrate adds significant complexity to thin film dynamics. Experiments on supported films provide an important test of the interpretation of the results already obtained on freestanding films. A weakness of the temperature-ramping anisotropy method as utilized to date is that the position of the probes in the film is not controlled; the perturbation of the dynamics introduced by the substrate allows an important check on the interpretation of the freestanding film studies.

We find that supported films of polystyrene, poly(methyl methacrylate), and poly(2-vinyl pyridine) all show evidence of enhanced mobility at the free surface. The mobile surface layer thickness for supported films of polystyrene and poly(methyl methacrylate) reasonably match those previously deduced from freestanding films of these polymers. For polystyrene, surface mobility extends about 7 nm into the film from the free surface at T_g . For poly(methyl methacrylate), we deduce a 4 nm length scale for surface mobility at T_g . For supported polystyrene and poly(methyl methacrylate) films, our results show no evidence of diminished mobility near the solid substrate although our experiments do not exclude this possibility. On the other hand, the mobility of supported poly(2-vinyl pyridine) thin films provides some evidence for slower-than-bulk relaxation near the solid substrate.

Experimental section

Materials

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 the inset of Fig. 1. BTBP has high thermal and

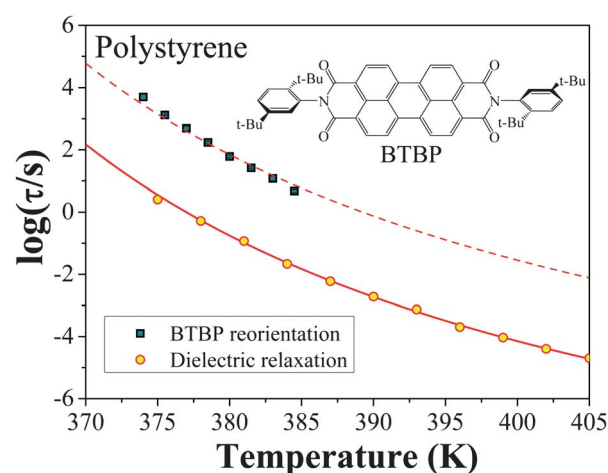


Fig. 1 Reorientation times for BTBP (squares) in bulk polystyrene at temperatures just above T_g . The circles are dielectric relaxation measurements and the solid line is a fit to the Vogel-Tammann-Fulcher (VTF) equation. The dashed line shows that the temperature dependence of the dielectric measurement matches reasonably with that of BTBP reorientation. Inset: Structure of BTBP.

photo stability, and high solubility in hydrophobic polymers. For these experiments, the concentration of fluorescent molecules in the polymer films was typically on the order of 10^{-6} M. For films less than 20 nm, a concentration on the order of 10^{-5} M was used to increase the fluorescence signal.

The polymers used in this study are poly(2-vinyl pyridine) (P2VP, $M_n = 277$ kg mol $^{-1}$, $M_w/M_n = 1.09$), polystyrene (PS, $M_n = 160$ kg mol $^{-1}$, $M_w/M_n = 1.05$), and poly(methyl methacrylate) (PMMA, $M_n = 106$ kg mol $^{-1}$, $M_w/M_n = 1.08$); their structures are shown as insets in Fig. 2, 4, and 6. Differential scanning calorimetry (DSC) measurements were used to obtain T_g for the bulk polymers. Measurements were performed with a TA Instruments Q2000 DSC with heating and cooling rates of 10 K min $^{-1}$. At least three scans were performed and T_g was

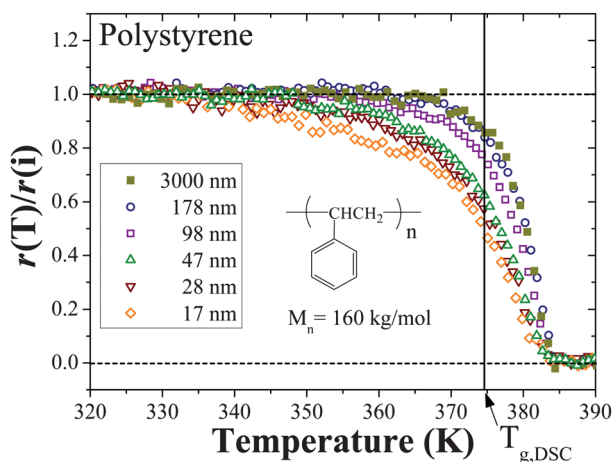


Fig. 2 Temperature-ramping anisotropy measurements for BTBP in supported polystyrene films of different film thicknesses. The vertical line indicates the glass transition temperature of bulk polystyrene measured by DSC ($T_{g,DSC} = 374.6$ K). Inset shows the chemical structure and molecular weight of polystyrene.

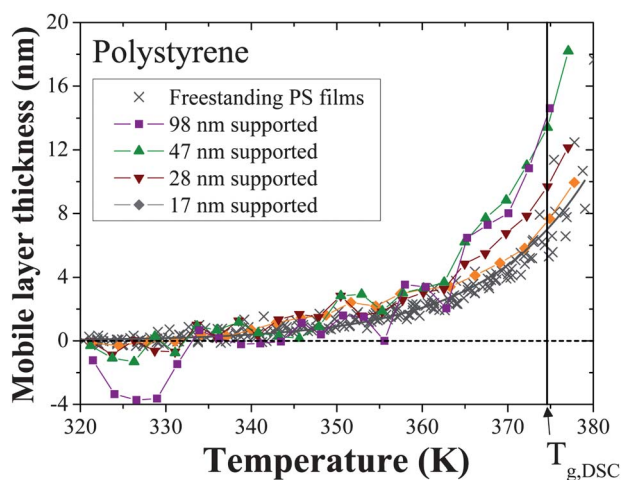


Fig. 3 The temperature dependence of the mobile layer thickness for supported polystyrene films (colored symbols). The cross symbols are mobile surface layer thicknesses deduced for freestanding polystyrene films in ref. 36; the grey curve is a fit of the freestanding data to an exponential growth function. The surface mobile layer thicknesses deduced from supported films agree reasonably well with those obtained from freestanding films, especially below $T_{g,DSC} - 10$ K.

determined as the onset temperature of averaged heating scans after the first run. All polymers were obtained from Polymer Source Inc. and used without further purification.

Sample preparation

Thin films (<150 nm) were prepared by spin coating onto silicon wafers. For samples with thickness of 3 to 20 μm , solvent casting was utilized. The native oxide layer on the silicon wafer was approximately 2 nm as measured by ellipsometry. For films of polystyrene and poly(methyl methacrylate), toluene was used as a solvent and either THF or DMF was used for poly(2-vinyl pyridine). Before solvent-casting or spin-coating, the silicon wafers were cut into 5×5 mm pieces in order to fit into the sample holder. The silicon wafer pieces were cleaned using 3 : 1 mixture of H_2SO_4 and H_2O_2 solution followed by several DI water and ethanol rinses. All the samples were annealed in a vacuum oven (0.1 torr) at $T_{g,DSC} + 20$ K for at least 12 h to remove solvent. The samples were then cooled at 1 K min^{-1} to room temperature. The annealing temperature and time did not have any influence on our measurements for annealing temperatures between $T_{g,DSC} + 5$ K and $T_{g,DSC} + 25$ K and annealing times between 3 to 36 h.

For samples thicker than 3 μm , the film thicknesses were determined by the z scan of the confocal microscope (resolution: $\sim 1.5 \mu\text{m}$). For samples thinner than 150 nm, the film thicknesses were measured by ellipsometry, either utilizing an Auto EL ellipsometer (Rudolph) with three wavelengths (632.8, 546.1, and 405 nm) or a Woollam M-2000 spectroscopic ellipsometer.

Temperature-ramping anisotropy measurements

Temperature-ramping fluorescence anisotropy measurements were performed in a cryostat dewar (Oxford Microstat N) using a homebuilt sample holder designed to maximize temperature

accuracy.³⁵ The cryostat dewar operates under vacuum (10^{-3} torr). The sample temperature was within 1 K of the set temperature for all measurement conditions.³⁵ A confocal microscope is utilized to excite probe molecules and to collect fluorescence from a small volume of the sample ($1 \mu\text{m}^2$ in the sample plane and up to $1.5 \mu\text{m}$ thick). For films less than $1.5 \mu\text{m}$ thick, the entire film thickness is uniformly sampled. For thicker films, fluorescence is collected from a $1.5 \mu\text{m}$ slice in the interior of the film.

The temperature-ramping fluorescence anisotropy technique has been described elsewhere.^{35,36} In brief, an isotropic set of chromophores is illuminated by intense linearly polarized light that selectively photobleaches molecules with transition dipoles aligned with the polarization of the bleaching beam. As a result, an anisotropy in the distribution of transition dipoles of unbleached probes is created in the sample. The reorientation of the unbleached probes is monitored through the polarized fluorescence generated by less intense circularly polarized light. As the probes reorient, the fluorescence becomes less polarized. In the temperature-ramping experiment, the sample is photobleached at low temperature where molecular orientation is frozen. The polarized fluorescence is then monitored while the sample temperature is ramped (at 2 K min^{-1} for the experiments reported here). Once the anisotropy is created by photobleaching, it does not diminish until the host polymer allows the probes to rotate. It is well established that the reorientation of dilute probes in a polymer matrix correlates with the segmental dynamics of the host polymer.^{35,36,40–43}

The anisotropy created by photobleaching is a direct measure of the distribution of transition dipole moments and its decay describes probe reorientation. The anisotropy $\bar{r}(t)$ describes the average (single particle) reorientation of the transition dipole $\hat{\mu}$ between the time 0 and t : $\bar{r}(t) = \bar{r}(0) \langle P_2[\hat{\mu}(0) \cdot \hat{\mu}(t)] \rangle$. Here P_2 is the second Legendre polynomial. In the temperature-ramping anisotropy experiment, the time is a fixed function of temperature and so we measure $r(T)$. In this study, for ease of comparison, $r(T)$ is normalized by $r(i)$. Here, $r(i)$ is calculated by averaging the $r(T)$ values for the initial 10 K range in the beginning of the experiment where the anisotropy is constant.

Results and discussion

Relationship between probe reorientation and segmental dynamics

Fig. 1 shows the temperature dependence of rotational correlation times for BTBP in a bulk polystyrene film (3 μm). These results were obtained from isothermal anisotropy decay measurements.^{42,44,45} Also shown are the results of dielectric relaxation measurements on neat polystyrene (same source material). The solid curve is a fit of the dielectric relaxation data to the Vogel-Tammann-Fulcher (VTF) equation: $\log(\tau) = \log(\tau_0) + B/(T - T_0)$. The parameter values are $\log(\tau_0) = -12.83$, $B = 617.6 \text{ K}$, and $T_0 = 328.8 \text{ K}$, and these are similar to what has been previously reported for dielectric relaxation measurements on polystyrene.^{46–48} The dotted line that runs through the BTBP reorientation data is the VTF fit for the dielectric data with a constant vertical shift.

The good agreement between the probe reorientation data and the temperature dependence of the dielectric data establishes that, at least for bulk polystyrene, BTBP is a good reporter of the segmental dynamics of polystyrene. This result is consistent with results for BTBP reorientation in poly(methyl methacrylate) and poly(2-vinyl pyridine),³⁶ and more generally with previously reported probe reorientation studies involving various polymer systems.^{40–43,49–51}

Supported polystyrene thin films

Fig. 2 shows temperature-ramping anisotropy measurements for BTBP in supported polystyrene films with thicknesses between 17 nm and 3000 nm. As the films become thinner, the anisotropy decay initiates at lower temperature, indicating that at least a fraction of probe molecules reorient more rapidly in thin films. However, thinner films also show a broader anisotropy decay and the effect of film thickness clearly cannot be represented by a simple temperature shift.^{36,37}

The data shown in Fig. 2 is qualitatively similar to temperature-ramping anisotropy measurements on freestanding polystyrene films.^{35–37} One difference is the extent to which the anisotropy decay curves are broadened. For a given film thickness (in the regime below 100 nm), the anisotropy decay curves for supported films are generally more similar to the bulk data than are the curves for freestanding films. A second difference is that the anisotropy curves for supported films in Fig. 2 decay fully to zero. The corresponding anisotropy measurements for freestanding films were stopped near the bulk T_g because holes formed in the films if the experiments were continued to higher temperature. Dewetting of the supported films of polystyrene was not observed during these anisotropy measurements. This is consistent with expectations from the literature based upon molecular weight, time, and temperature.⁵²

Given the qualitative similarity between temperature-ramping anisotropy experiments on freestanding and supported polystyrene films, we wish to explore if the quantitative scheme used to understand the freestanding film results might also work for supported films. For freestanding films, two subsets of probe molecules with distinct dynamics were shown to exist (see Fig. 2 in ref. 36). The slow subset showed bulk-like dynamics while the fast subset reoriented up to 10^4 times faster. This result was interpreted to indicate that the fast subset of probes was located near the free surface. Within this scenario, temperature-ramping anisotropy measurements were used to evaluate the fraction of the sample showing fast dynamics and this was expressed as a mobile layer thickness at the free surfaces of the film:

$$d_{\text{freestanding}}(T) = \frac{D}{2} \cdot \left[1 - \frac{\left\{ \frac{r(T)}{r(i)} \right\}_{\text{tf}}}{\left\{ \frac{r(T)}{r(i)} \right\}_{\text{bf}}} \right] \quad (1)$$

Here D is the total film thickness and the subscripts tf and bf stand for thin film and bulk film respectively. For freestanding polystyrene films, the same mobile layer thickness is obtained for a given temperature independent of total film thickness (in the range 17–47 nm), ramping rate, molecular weight, and probe identity. To understand the supported film data in Fig. 2, we use a similar approach to that used for freestanding films. Instead of eqn (1), we use eqn (2) to analyze the data:

$$d_{\text{supported}}(T) = D \cdot \left[1 - \frac{\left\{ \frac{r(T)}{r(i)} \right\}_{\text{tf}}}{\left\{ \frac{r(T)}{r(i)} \right\}_{\text{bf}}} \right] \quad (2)$$

The only difference is the factor of 2 in eqn (1) that stems from the number of free surfaces. Eqn (2) should be valid if surface mobility is an interfacial effect, if the film is thick enough that the influence of the interfaces is additive, and if the dynamics of probes are not significantly altered near the solid substrate. The scan rate used in these temperature-ramping experiments (2 K min^{-1}) separates the fast (surface) process from the slow (bulk) process, as shown explicitly for freestanding films in ref. 36. Fig. 3 shows the thickness of the mobile surface layer for supported polystyrene films as calculated from eqn (2). Results for 17, 28, 47, and 98 nm films are presented as colored symbols. For comparison, the grey crosses show results obtained previously³⁶ (from eqn (1)) for 17–47 nm freestanding polystyrene films with molecular weights between 160 and 7370 kg mol^{-1} ; the grey line through these results is a fit to an exponential function.

In Fig. 3, the thickness of the mobile surface layer as a function of temperature for 17 and 28 nm supported films agree reasonably with each other and with the thickness deduced from freestanding polystyrene films. The simplest interpretation of this result is that the probe dynamics in supported polystyrene films are bulk-like except for a surface layer of higher mobility that grows to a thickness of $\sim 7 \text{ nm}$ at $T_{g,\text{DSC}}$. The thickness of the mobile layer deduced for the 47 and 98 nm supported films is in good agreement with the results for the thinner supported films and the freestanding films below $T_{g,\text{DSC}} - 10 \text{ K}$, but clearly larger than these values at higher temperatures. As films become thicker, the error associated with the mobile layer thickness calculation becomes larger and this may play a role. Alternately, thicker supported films may have a thicker region of high mobility at the free surface. This would be consistent with the picture of Torkelson and coworkers, based on pseudo-thermodynamic measurements of T_g in individual layers of supported films.²⁸ Regardless, the temperature-dependent mobile layer thickness deduced for freestanding polystyrene films provides

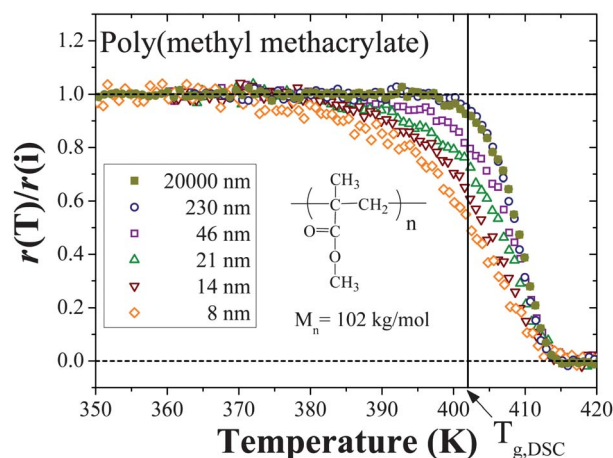


Fig. 4 Temperature-ramping anisotropy measurements for BTBP in supported poly(methyl methacrylate) films of different film thicknesses. The vertical line is the glass transition temperature of bulk poly(methyl methacrylate) measured by DSC ($T_{g,\text{DSC}} = 402 \text{ K}$). The chemical structure and the molecular weight of the polymer is shown in inset.

a quite reasonable approximate description of the data for supported films.

Supported poly(methyl methacrylate) thin films

Fig. 4 shows temperature-ramping anisotropy measurements performed on supported BTBP/poly(methyl methacrylate) films on the native oxide layer of a silicon wafer. The thicknesses of the poly(methyl methacrylate) films varied from 8 nm to 20000 nm. These results are qualitatively similar to those shown for supported polystyrene films in Fig. 2. In detail, deviations from the bulk behavior are less pronounced for poly(methyl methacrylate) films than for polystyrene films of the same thickness.

Fig. 5 shows the temperature dependence of the mobile surface layer thickness calculated from the data on four supported poly(methyl methacrylate) films between 8 and 46 nm, using eqn (2). The grey asterisk symbols and grey line represent previously reported mobile surface layer thicknesses deduced from three freestanding poly(methyl methacrylate) films with thicknesses between 7 and 23 nm.³⁷ The layer thicknesses calculated from the supported poly(methyl methacrylate) film data agree quite well with the thicknesses calculated from experiments on freestanding films, especially considering that there are no fitting parameters involved in this comparison.

Supported poly(2-vinyl pyridine) thin films

Fig. 6 shows temperature-ramping anisotropy measurements for supported poly(2-vinyl pyridine) films on silicon wafers with native oxide. Films from 18 nm to 150 nm are compared with a 20000 nm bulk film. Consistent with the results on supported polystyrene and poly(methyl methacrylate) films, the anisotropy decay initiates at lower temperatures for thinner films. Bulk behavior is recovered when the film thickness reaches 150 nm. In contrast to polystyrene and poly(methyl methacrylate), for supported poly(2-vinyl pyridine) films the slope of the anisotropy decay does not continuously decrease upon increasing temperature up to $T_{g,DSC}$.

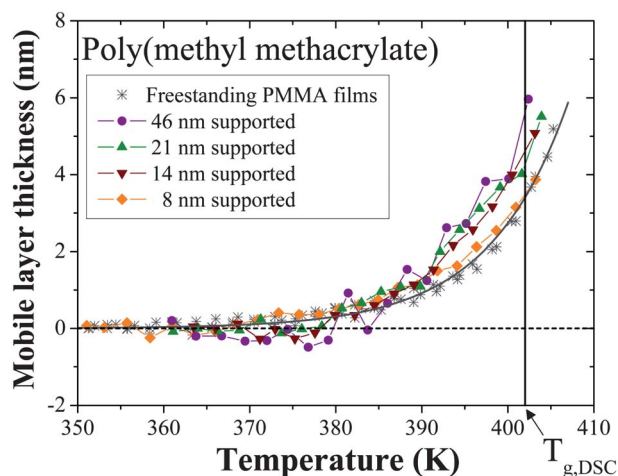


Fig. 5 The temperature dependence of the mobile layer thickness for supported poly(methyl methacrylate) films (color symbols). The asterisk symbols for freestanding films with a fit (grey curve), from ref. 37, are shown for comparison. The mobile surface layer thicknesses deduced for supported films agree well with those obtained from freestanding films.

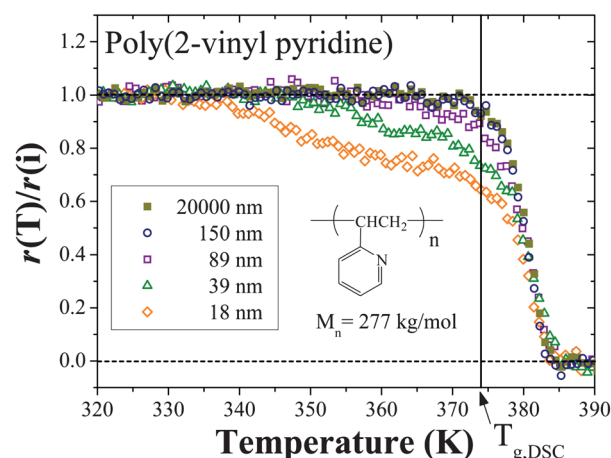


Fig. 6 Temperature-ramping anisotropy measurements for BTBP in supported poly(2-vinyl pyridine) films of different film thicknesses. The vertical line indicates the glass transition temperature of bulk poly(2-vinyl pyridine) measured by DSC ($T_{g,DSC} = 374$ K). Inset shows the chemical structure and molecular weight of poly(2-vinyl pyridine). Supported thin films show an early decay which can be interpreted as a mobile layer effect and also some evidence of a delayed decay which may be caused by strong polymer-substrate interactions.

In Fig. 7, the mobile layer thickness of supported poly(2-vinyl pyridine) films is analyzed with the same procedure used for supported polystyrene and poly(methyl methacrylate) films. The grey plus symbols are previously reported results for a 24 nm freestanding poly(2-vinyl pyridine) film along with a curve fitted to these points; the dashed line is an extrapolation of this solid line. Below 365 K, the mobile layer thicknesses deduced from the three supported films (18–39 nm) are similar to each other and reasonably follow the thickness values obtained from the freestanding film. We interpret this to mean that supported poly(2-vinyl pyridine) films have a mobile surface layer that is very similar to the mobile surface layers present in freestanding films.

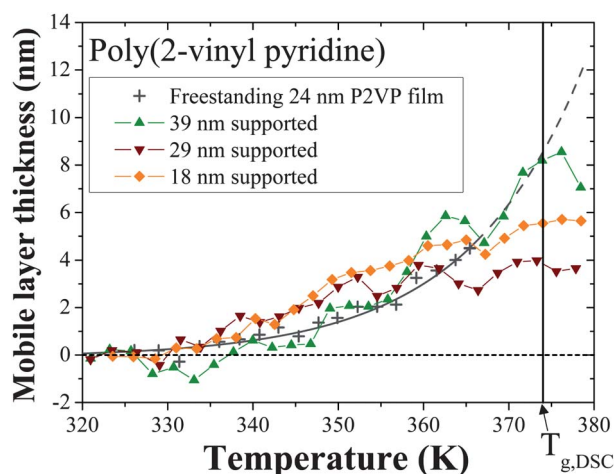


Fig. 7 The temperature dependence of mobile layer thickness for supported poly(2-vinyl pyridine) films. The cross symbols are thicknesses calculated from a 24 nm freestanding film, with a fit to this data shown in grey. The deviation of the supported film data from the trend of the freestanding film data may be due to strong polymer-substrate interactions.

Above 365 K, the three curves calculated from the freestanding films are less similar and lie below the thicknesses obtained for the freestanding films. As we discuss below, this behavior may indicate the presence of a slow subset of probes, likely located near the solid substrate.

Low mobility near the solid substrate?

T_g measurements of supported polymer films are often performed with pseudo-thermodynamic methods such as ellipsometry that measure a static property (such as film thickness) as a function of temperature. In analogy to dilatometry measurements on bulk polymers, a break in the temperature dependence of the static property is interpreted as the glass transition temperature T_g . For supported polystyrene films, T_g is reported to be lower than the bulk T_g . This has been interpreted as the influence of enhanced mobility at the free surface and little or no change in mobility at the solid surface. For supported poly(methyl methacrylate) films, T_g for supported films can increase or decrease depending upon the substrate utilized. An increase in T_g is generally interpreted to indicate that a strong attraction between the polymer and substrate slows dynamics near that interface more than the mobility is increased near the free surface. Direct experiments on low molecular weight glassformers support the view that dynamics can slow substantially near a substrate.⁵³ Our temperature-ramping anisotropy experiments for supported polystyrene and poly(methyl methacrylate) films are consistent with bulk-like mobility near the solid substrate as opposed to diminished mobility. If a population of probes were reorienting slower than the bulk response, a part of the anisotropy decay for thin supported films would occur at higher temperatures than the bulk anisotropy decay. A careful inspection of Fig. 2 and 4 reveals no evidence for such behavior. For polystyrene, our conclusion is consistent with the interpretation of pseudo-thermodynamic T_g measurements showing decreases in T_g for films supported by silicon with a native oxide coating.^{2,4,28} On the other hand, about a 5 K increase in T_g was reported for 15 nm films of poly(methyl methacrylate) on the native oxide layer of a silicon wafer.⁵ From these observations, the existence of regions with reduced mobility near the polymer-substrate interface was inferred, yet no evidence for slower-than-bulk probes is apparent in our experiments on poly(methyl methacrylate).

The temperature-ramping anisotropy measurements for films of poly(2-vinyl pyridine) are not satisfactorily interpreted by our simple model that considers only enhanced mobility. While both freestanding and supported film data below 365 K are reasonably described by our model, as the temperature is increased, clear discrepancies are seen in Fig. 7. A careful inspection of Fig. 6 gives some indication that the thin film anisotropy decay can be slower than the bulk curve, consistent with the existence of a slower-than-bulk subset of probes. Furthermore, for the two thinnest supported films, the calculated mobile layer thickness in Fig. 7 is lower than the expected behavior based upon freestanding films, consistent with the idea that a less-mobile-than-bulk population near the substrate is partially offsetting the influence of the higher mobility probes at the free surface. This interpretation would be broadly consistent with the substantial increase in T_g reported for poly(2-vinyl pyridine) supported by silicon with a native oxide coating.^{14,18,19} We note that slower-

than-bulk probes will only be apparent in the temperature-ramping anisotropy experiment within a few K of the bulk T_g . That is, probes that are slower-than-bulk at $T_g - 15$ K will not influence the experiment if their dynamics become similar to bulk probes by T_g .

Recent work has shown that annealing protocols can have an important impact on the T_g observed for supported thin films.^{12,54} Ref. 54 shows that more aggressive annealing of polystyrene on silicon with a native oxide coating gives rise to an increased adsorption of polymer chains. These authors report that annealing at 423 K is required to fully anneal thin polystyrene films with molecular weight similar to those used here. In contrast, we chose to anneal our supported polystyrene samples at 395 K in order to match the annealing conditions that we used to prepare freestanding films, thus allowing a direct comparison between the two film geometries. More aggressive annealing makes it difficult or impossible to prepare freestanding films because the annealed films cannot be floated off of mica. It is possible that temperature-ramping anisotropy experiments on supported films that have been more aggressively annealed would provide evidence of a slower-than-bulk subset. Such a result might be expected based upon dielectric evidence of a “dead-zone” in aggressively annealed supported polystyrene films.^{55,56}

It is also possible that a strongly adsorbed polymer layer on a substrate might exclude the probe molecules for thermodynamic reasons. In that case, the temperature-ramping anisotropy experiment might not show any evidence of a subpopulation with delayed relaxation relative to the bulk sample. Thus, the results presented here for polystyrene and poly(methyl methacrylate) could also be consistent with slower-than-bulk regions of polymer segments near the silicon substrate if the probe molecules were excluded from these regions. If we assume that mobility at the free surface of a supported and freestanding film is identical, Fig. 3 and 5 allow us to estimate that such a dead zone could be as thick as 2 nm for poly(methyl methacrylate) and as thick as 5 nm for polystyrene. This hypothesis could be tested with temperature-ramping anisotropy measurements by covalently attaching probe molecules to the polymer and possibly stacking labeled and unlabeled polymer layers as done in ref. 28 or by directly attaching the probes to the surface as in ref. 57.

Comparison to T_g measurements of supported films

There is no simple relationship between our probe reorientation measurements and the T_g values determined by pseudo-thermodynamic methods such as ellipsometry. For supported polystyrene films, the results presented here are similar to ellipsometry measurements. For example, the temperature at which the anisotropy decays to 0.7 of its initial value (Fig. 2) correlates well with the T_g values measured by Kawana and Jones.⁵⁸ Furthermore, the breadth of the transition detected by ellipsometry also corresponds reasonably to the starting and ending temperatures of the anisotropy decay.^{58,59} In addition, these pseudo-thermodynamic measurements are often interpreted in terms of a liquid-like layer at the free surface whose thickness is comparable to the results in Fig. 3.⁴ On the other hand, for supported poly(methyl methacrylate) films, the anisotropy curves shift to lower temperatures with decreasing film thickness while T_g is reported to increase.⁵

There are a number of important considerations when comparing these probe reorientation measurements with pseudo-thermodynamic determinations of T_g : 1) Our measurements directly sense molecular motion in contrast to methods such as ellipsometry. The strong correlation between dynamics and pseudo-thermodynamic measurements of T_g in bulk systems has not been demonstrated to be valid in thin films. Our probe reorientation measurements in freestanding polystyrene films, which are independent of molecular weight, cannot be reconciled with the strong molecular weight dependence of T_g observed with pseudo-thermodynamic methods.^{36,37} 2) As discussed above, freely dispersed probes might be thermodynamically excluded by an adsorbed polymer layer. 3) The segmental relaxation process of polymers has a broad distribution associated with it and it may be that pseudo-thermodynamic methods are biased toward the fast side of this distribution.⁵⁹ Probe reorientation, on the other hand, would be expected to probe the slow side of this distribution.

Layered films and a technique based upon the temperature-dependence of fluorescence emission (not the anisotropy decay) have been used to characterize the distribution of local T_g values in supported polystyrene films.²⁸ It is thought that this method senses changes in the local thermal expansion coefficient upon heating. Ref. 28 reports that both the top and bottom 12 nm sections of a 24 nm supported polystyrene film have T_g values 11 K lower than the bulk polymer. The temperature-ramping anisotropy curves shown in Fig. 2 for 17 nm and 28 nm films do not have the same shape as the bulk curve and thus a simple temperature shift of ~ 11 K is not consistent with our data; however, 11 K is a reasonable value for the average temperature shift of our 28 nm data. In contrast to ref. 28, we interpret our data to indicate that the top half of a 24 nm film has faster dynamics than the bottom half. Isothermal anisotropy decay experiments on supported 24 nm films at $T_{g,DSC}$ could test these views. Based upon the analysis presented here, we expect a slow subpopulation with bulk-like dynamics to account for approximately 70% of the anisotropy decay under these conditions. Such experiments have been performed on freestanding polystyrene and poly(methyl methacrylate) films, and they show a coexistence of probe populations with bulk-like mobility and with significantly enhanced mobility.^{36,37}

Comparison with previous measurements of mobility at surfaces

A number of recent studies have reported on the time scale of molecular motion at the free surface of thick supported polymer films.^{23,24,26} When nanoparticles are placed on polystyrene, they show a two-step embedding process, with a fast partial process followed by much slower further embedding.^{24,26} These experiments are quite consistent with the results presented here if we identify the initial embedding with fast dynamics near the surface and the later embedding as bulk dynamics. For example, near T_g , 20 nm particles quickly embed to a depth of about 5 nm in polystyrene; at $T_g - 30$ K, about 2 nm of embedding is observed.²⁴ These values are comparable to those shown in Fig. 3. It also appears that the ratio of surface to bulk mobility is similar in the anisotropy decay measurements^{36,37} and the nanoparticle embedding experiments.^{24,26}

Some recent dielectric relaxation and nanocalorimetry experiments have concluded that there is not a mobile surface layer for supported polystyrene films above $T_g + 7$ K.¹² Our results are consistent with this conclusion as we only observed enhanced mobility up to $\sim T_g$. Furthermore, in ref. 36, we showed that the mobility of the surface region appears to converge with the bulk mobility near $T_g + 5$ K. A similar conclusion regarding the convergence of the bulk and surface processes for polystyrene near T_g has been reached by others.^{23,26,60}

A recent optical experiment examined the reorientation of single probe molecules tethered to polystyrene chains in supported films.⁶¹ The authors report higher mobility in thinner films as judged by the onset temperatures for small angle jumps. These experiments are in qualitative agreement with the results reported here but cannot be compared quantitatively without information on larger scale reorientation.

Finally we make a comparison with dynamics at the surface of trisnaphthylbenzene, a low molecular weight glassformer. It has been reported on the basis of neutron reflectivity experiments 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.⁶² At $T_g - 50$ K, the 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 Fig. 3, 5, and 7, and the time scales (for polystyrene) discussed in ref. 36.

Concluding remarks

Temperature-ramping anisotropy measurements have been used to measure the rotational mobility of a fluorescent probe molecule (BTBP) dispersed in supported films of polystyrene, poly(methyl methacrylate), and poly(2-vinyl pyridine). For all three systems, we observe that as films become thinner, the anisotropy decay becomes broader and initiates at a lower temperature. This indicates that while probe reorientation in these films is on average faster than the bulk, the results cannot be described as a simple " T_g shift" relative to thick films.

A strength of the temperature-ramping anisotropy measurement is that it provides a very direct measurement of molecular mobility, in contrast to pseudo-thermodynamic measurements of T_g . The polarized fluorescence, measured against a dark background, is directly related to the ensemble-average single particle orientation autocorrelation function.

We interpret these results for supported films in light of previous work on freestanding polymer films. Temperature-ramping anisotropy measurements on freestanding films indicate the presence of a mobile surface layer whose thickness increases with temperature but does not depend upon total film thickness, molecular weight, or probe identity. To compare mobility in supported and freestanding films of these three polymers, we calculate the mobile layer thickness for supported films on the assumption that dynamics are bulk-like except near the free surface. Remarkably, the mobile layer thicknesses that result from this treatment of the supported film data are in quite good agreement with the mobile layer thicknesses calculated from the freestanding film data. The agreement is nearly quantitative for temperatures at least 10 K below T_g of the bulk polymer. No data fitting or adjustable parameters are involved in this comparison.

These experiments indicate that the mobile layer thickness at the bulk T_g is in the range of 4–7 nm for these polymers.

A weakness of the anisotropy method is that the mobility of the probe molecules, not the polymer segments, is directly observed. For bulk polymers, the reorientation of BTBP is an accurate reporter of segmental mobility, and we assume that this is also the case in thin films. Supporting this view is the observation that, for freestanding films of polystyrene, multiple probe molecules provide the same value of the mobile layer thickness as a function of temperature.³⁶ A second weakness of the method is that the location of a specific subset of probes, for example the mobile ones, is inferred rather than known or controlled. While the identification of the mobile probes with the free surface is strongly supported by the experiments, the potential presence of a slower-than-bulk subset at the substrate complicates the interpretation of the anisotropy data, as in the case of poly(2-vinyl pyridine) films. Similar experiments in which the probes are covalently attached to polymers located at specific positions relative to the substrate and surface, along the lines of ref. 28, could eliminate these problems and make this approach more powerful.

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