Shear Modulation Force Microscopy Study of Near Surface Glass Transition Temperatures

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We report results of glass transition \( T_g \) measurements for polymer thin films using atomic force microscopy (AFM). The AFM mode, shear modulation force microscopy (SMFM), involves measuring the temperature-dependent shear force on a tip modulated parallel to the sample surface. Using this method we have measured the surface \( T_g \) of thin (17–500 nm) polymer films and found that \( T_g \) is independent of film thickness \((t > 17 \text{ nm})\), strength of substrate interactions, or even presence of substrate.

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It is well known that in simple molecular systems the amplitude of the thermal vibrations of molecules and the thermal expansion coefficients at the surface are much larger than in the bulk. Usually, surface melting at temperatures lower than bulk is observed, though in rare cases the opposite is found [1]. The dynamics of polymer thin films at surfaces, where a new length scale, the polymer molecular size, is introduced, can show large deviations from bulk behavior. A basic question that remains to be answered is to what extent polymeric and simple molecular systems are similar in regards to confinement and surface effects. An important characteristic property is the glass transition temperature, which is the subject of this work.

The glass transition temperatures \((T_g)\) of polymer films ranging in thickness from 3 to 3000 nm have been determined using numerous types of experiments [2–15]. The results on what are nominally the same systems show large disagreements, and no consensus has yet emerged. In contrast to simple molecular systems, the complexity of polymer chains introduces various length scales that must be considered when interpreting dynamical properties. The length scales probed by the various methods previously used have been difficult to quantify and hence comparison of the results has been difficult and the theoretical interpretations confusing. A detailed review and comparison of the previous experiments is given elsewhere [16]. In this paper we show how it is possible to apply a new, highly sensitive force microscopy (AFM) mode, shear modulation force microscopy (SMFM), to measure \( T_g \) on a local scale and determine to what extent it is dependent on the surface interactions or the structure of the film. Samples were made using monodisperse polystyrenes (Mw/Mn < 1.1) of molecular weights (Mw) ranging from 3 kg to 6.5 Mg per mole which were dissolved in toluene and spun cast onto polished silicon wafers or glass substrates. Freestanding films were prepared by floating onto an electropolished stainless steel holder with a 10 \(\mu\)m pinhole. The supported and freestanding samples were annealed in a vacuum of \(10^{-4}\) Torr at 170 °C or 110 °C, respectively, for at least 4 h prior to performing the AFM experiments to anneal out residual orientational effects from the spinning procedure.

\( T_g \) measurements were made using either a TopoMetrix Explorer or a Digital Instruments Dimension 3000 located in sealed glove boxes which were purged with dry nitrogen. Samples were mounted on an MMR Technologies heating/cooling stage which was calibrated by determining the melting point of naphthalene (353.3 K) and indium (429.7 K) crystals.

There is a considerable number of variables which influence SFM based measurements of \( T_g \), such as tip shape, size and stiffness, surface chemistry, applied load, scan rates and amplitudes, tip modulation frequencies, and modulation direction (parallel or perpendicular to the surface). Fortunately, to measure \( T_g \) with the SMFM method we require only that some measured property reflects—in a relative way—the large change in viscoelastic behavior around \( T_g \). Hence the determination of a relative change in tip response as a function of temperature is a fairly straightforward and robust indicator of \( T_g \). The experimental setup of the SMFM method is pictured in Fig. 1. A sinusoidal drive signal with a frequency of 1400 Hz is applied to the X-piezo controlling the cantilever, inducing a small oscillatory motion of the tip parallel to the sample surface. We used a drive signal amplitude of 15 mV which corresponds to a nominal lateral tip deflection of 3 nm. A normal load force of 25 nN was applied to maintain tip contact with the sample, though no dependence on the normal force was observed up to approximately 75 nN. \( T_g \) was measured by slowly ramping (1.0 °C per min) the sample heating stage from room temperature to 20 °C above \( T_g \) while measuring the X-amplitude response of the photodiode detector, called \( \Delta X \) in this paper, at 1400 Hz with a lock-in amplifier.

Though a quantitative theory of the tip shear response is not yet available, we may make some rough estimates based on simple elastic and viscous models. The indentation of an elastic substrate by a hard spherical tip of radius \( R \), \( h \), is given in the Hertz model by [17]
where $D$ is the so-called “plane stress modulus,” $L$ is the load applied to the tip, $\nu$ is the Poisson ratio, and $E$ is the Young’s modulus of the polymer film. For $T < T_g$, $E = 3.4$ GPa, $\nu = 0.38$ for polystyrene (PS), and an applied load of 25 nN with tip radius 20 nm leads to a sample indentation depth $h$ of 1 nm, indicating minimal penetration and a small contact radius. Above $T_g$, at 110 °C, $E$ drops by more than 3 orders of magnitude and $h \sim 100$ nm. Despite the rapid increase in the X amplitude due to sample surface softening above $T_g$, the indentation of the tip is far smaller than predicted by (1). Inclusion of the work of adhesion between the tip and surface (as, for example, in the Johnson-Kendall-Roberts theory [18]) would even increase the calculated penetration. The proximity of the hard silicon substrate, which has a Young’s modulus of $E_{\text{Si}} = 130$ GPa, would reduce $h$ as the films became thinner since as the tip approaches the substrate it “feels” the hard substrate. However, numerical calculations of this effect [19] show that the expected modifications would be modest, less than 20%, for a 200 nm sample. We believe the main reason that the tip penetration is much lower than the Hertz calculation is the high polymer viscosity, which causes a sufficiently large damping force to prevent attainment of the deep indentations expected from elastic-only calculations. The rate of penetration, $v$, can be estimated from the Stokes relation [20] for the drag force, $F_{\text{drag}}$, on a sphere moving at velocity $v$ in a fluid of viscosity, $\eta$: $F_{\text{drag}} = 6\pi \eta R v$. If we assume that $F_{\text{drag}}$ is the applied load $L$, then, for $L = 25$ nN, $R = 20$ nm, $\eta = 6.5 \times 10^{10}$ kg m /s$^{-1}$, and $\eta \approx 10^{13}$ kg m /s$^{-1}$ corresponding to the bulk viscosity [21,22] of PS of Mw 65 kg and 65 Mg at 380 °C, respectively, $v$ is approximately 6 Å/min and $\sim 10^{-2}$ Å/min, respectively. The creep of the tip is shown in Fig. 2 where we plot $\Delta x$ as a function of time for Si, and PS of Mw = 6.5 Mg and 65 kg. From the figure we can see that, below $T_g$, $\Delta x$ is the same for PS and Si. For $T > T_g$ the increase in $\Delta x$ is relatively slow for both samples though it is noticeably faster for the Mw = 65 kg polymer, reflecting the differences in viscosity of the two materials. In either case, the tip does not penetrate to the Si substrate within the observed measurement time of 90 min. At higher temperatures, such as the 140–160 °C range used by Schmidt et al. [14], similar calculations indicate that the tip would rapidly reach the substrate as they observed. In our experiments, the data are limited to $T \leq T_g + 10$ °C and the time to take the data above $T_g$ was less than 20 min. Therefore the effect of creep on the amplitude vs T curves is not large but will influence the slope of the curves above $T_g$. Below $T_g$, the small tip penetration, the contact area and drag force remain low, resulting in a correspondingly small X-amplitude response. Above $T_g$, the polymer softening leads to increased penetration and lateral force, causing a large increase in X-amplitude response.

Before discussing our results further, we need to address the issue of the effect of the large pressure under the tip. Bulk samples of PS subject to hydrostatic pressure exhibit shifts in $T_g$ given by $dT_g/dP = 0.32$ °C/MPa. Two groups [14,15] have reported $T_g$ increases relative to bulk measured by AFM and believed to be due to high tip pressure. In order to test the effect of pressure, we performed experiments on the same sample using sample loads $L = 25, 50,$ and 75 nN. The corresponding average pressures immediately under the tip would be approximately $(P = L/R^2, \text{ with } R = 20$ nm) 19.9, 39.8, and 59.7 MPa. Bulk $T_g$ shifts under these hydrostatic pressures would be 6.2, 12.3, and 18.5 °C, easily detectable in our measurements. The results clearly indicate no observable shift in $T_g$ even under a load of 75 nN. As an explanation, we may note that the high pressure under the tip is localized within a region of the size of the radius $R$ of the tip, decreasing rapidly with distance from the tip. The average pressure within this region will be considerably less than calculated above. Outside this small region, strains will be nearly zero and as this material softens through the bulk (of the film) $T_g$, the X amplitude of the tip will increase,
as observed. It is as if the tip has an additional shell (of size \( R \)) of stiffer material surrounded by the unstressed “bulk.” The thin shell might have a higher average \( T_g \), but one would not expect any sharp transition in this region as the pressure is not uniform. This picture will break down when the film thickness is of the order of \( R \) on a hard and attractive substrate. Indeed, for such thin films on silicon, we do observe a modest increase of \( \approx 5 \) °C in \( T_g \) (see below).

Figure 3 shows the \( \Delta x \) vs temperature curves for 200–300 nm thick PS films of molecular weight ranging from 3 kg to 6.5 Mg. The plots are characterized by two linear regions. We identify the intersection of the two straight line fits to the data as the glass transition temperature. The precision of the \( T_g \) determined this way is about \( \pm 2 \) °C. The data and derived \( T_g \)'s are shown as solid circles while the results from bulk differential scanning calorimetry (DSC) [23] are superimposed as open circles in the inset. As may be seen from the figure, the \( T_g \) values measured agree well with the bulk values over this large range of molecular weight and transition temperatures. These results are in agreement with the majority of previous measurements that have reported bulk values for \( T_g \) for films thicker than 200 nm, the exception being Refs. [10,11], where lower \( T_g \)'s were measured. For example, for PS of \( M_w \) = 65 kg, 2.3 Mg, and 6.5 Mg for bulk \( R_g \)'s are 6.8, 41, and 68 nm, respectively. In Fig. 4 we show \( \Delta x \) as a function of temperature for a series of PS films ranging in thickness from 20 to 500 nm spun cast on native oxide Si [Fig. 4(a)] or freestanding film on a 10 \( \mu \)m hole [Fig. 4(b)]. From the figures the following is clear.

(1) The presence of the highly attractive Si interface which significantly shows diffusion rates [26,27] does not significantly perturb the value of \( T_g \). (2) The bulk value of \( T_g \) persists for films down to \( t \approx 30 \) nm even though \( t < 2R_g \) for the higher molecular weights. (3) A slight increase in \( T_g \), no larger than \( 5 \pm 2 \)°C, occurs for the thinnest films, \( t \approx 20 \) nm, that could be studied on Si. This increase is independent of \( M_w \). These results show that the \( T_g \) measured is indeed a local effect of the polymer and is uncorrelated to the large change in dynamical properties that have been previously reported for thin polymer films near solid surfaces [26–28]. Furthermore, the bulk value of \( T_g \) is unaltered even in freestanding films and hence is an intrinsic property of the polymer independent of substrate interactions in the range studied. Finally, the insensitivity to \( R_g \) or degree of confinement further confirms that the technique is mainly sensitive to local changes of sample response and not to the overall structure of the polymer chains. The slight increase in \( T_g \) observed for the 20 nm films is probably due to the increased proximity of the Si and the pinning of the polymers to the surface. PS films deposited on Si surfaces where the interactions have been screened by an octadecyltrichlorosilane (OTS) or polymethylmethacrylate (PMMA) layer do not show this shift even for films as thin as 17 nm [Fig. 4(c)].

The sensitive volume probed by this method is also illustrated in Fig. 4(c). From the figure we can see that when the tip is placed on the PMMA substrate we obtain the bulk \( T_g \) of PMMA, as determined by DSC for our sample. When a PS film is placed on top of the PMMA film we measure only the \( T_g \) of PS, even though the film is only 17 nm thick. The \( T_g \) of the substrate is not felt since the
\[ D_x \] amplitude saturates as the tip penetrates the PS layer. Conversely, if the PMMA is placed on top of the PS, then both \( T_g \)'s are sensed. This case is more complicated, since the upper layer is glassy, and the \( \Delta x \) modulation is no longer described by the above models given in Eq. (1).

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