Shear Modulation Force Microscopy Study of Near Surface Glass Transition Temperatures

S. Ge, Y. Pu, W. Zhang, M. Rafailovich, and J. Sokolov

Department of Materials Science and Engineering, State University of New York, Stony Brook, New York 11794-2275

C. Buenviaje, R. Buckmaster, and R. M. Overney

Department of Chemical Engineering, University of Washington, Seattle, Washington 98195-1750

(Received 1 March 2000)

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 ($t > 17$ nm), strength of substrate interactions, or even presence of substrate.

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 atomic 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 μm 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 naphththalene (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 ΔX 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]
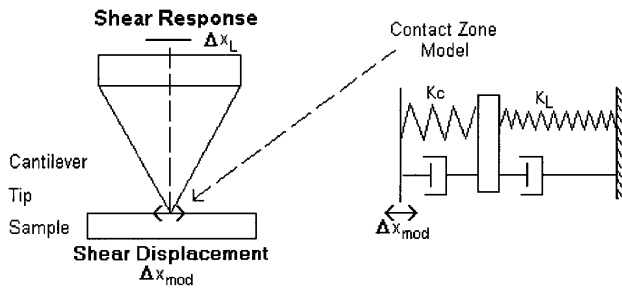
FIG. 1. Schematic of the SMFM method.

$$h = \left[D \, \frac{L}{R^{1/2}} \right]^{2/3}, \qquad D = \frac{3}{4} \frac{1 - \nu^2}{E}, \qquad (1)$$

where D is the so-called "plane stress modulus," L is the load applied to the tip, ν 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 $E_{Si} = 130$ 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_{drag}, on a sphere moving at velocity v in a fluid of viscosity, η: $F_{drag} = 6\pi\eta R v$. If we assume that $F_{drag} \approx$ the applied load L, then, for $L = 25$ nN, $R = 20$ nm, $\eta = 6.5 \times 10^9$ 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 6.5 Mg at 380 °K, 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 Δx 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, Δx is the same for PS and Si. For $T > T_g$ the increase in Δx 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 tem-
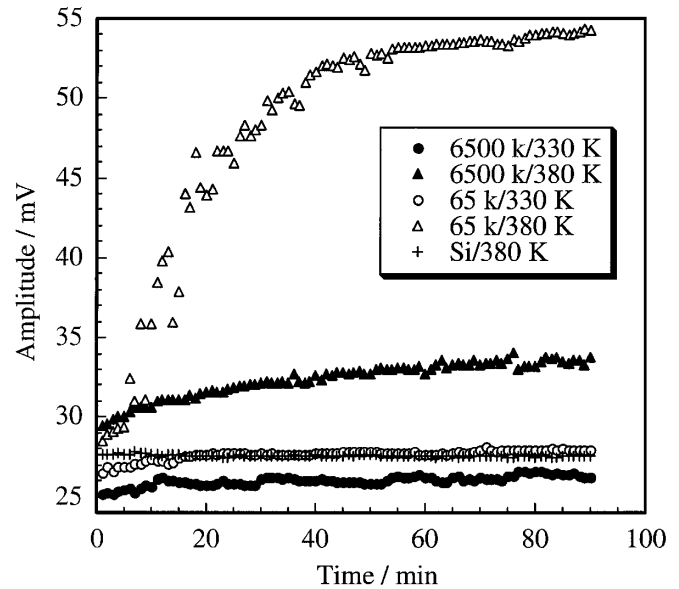
FIG. 2. Δx vs time curves for PS of Mw = 6.5 Mg and 65 kg thick film at different temperatures 330 and 380 K.

peratures, 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 ($P = L/R^2$, 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,

2341

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 Δx 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
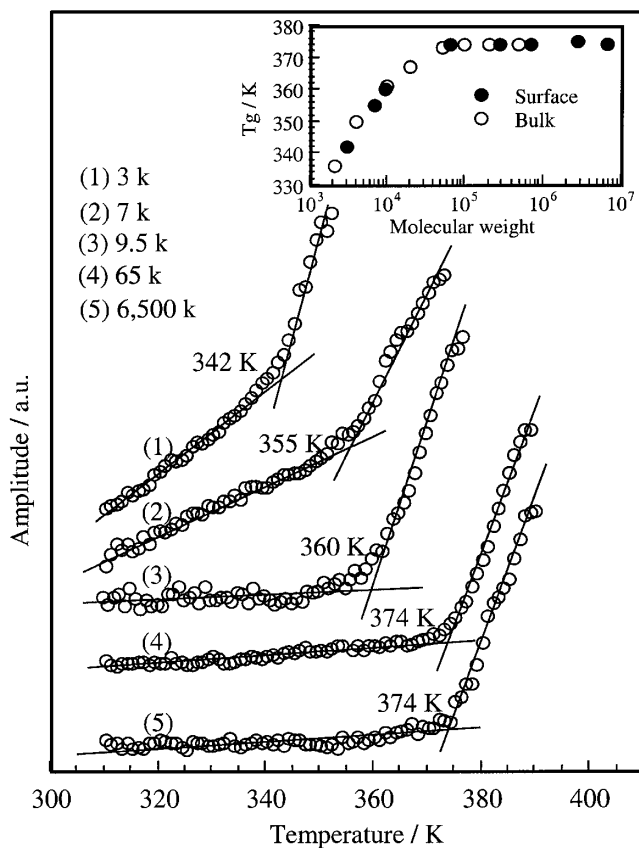

FIG. 3. Δx vs temperature curves for PS films 200–300 nm thick of Mw ranging from 3 to 6500 kg. Inset: T_g vs Mw, ●: this experiment, ○: bulk measurement of Ref. [23].

reported. Our results are in agreement with the simulations of Baschnagel and Binder [24] which show that the glass transition in confinement is a collective effect characteristic of the whole film and does not differ from layer to layer in a uniform medium. Furthermore, their simulations confirm earlier measurements [25] that the enhancement of chain ends at the surface is not large and hence no free volume anomalies are expected.

In order to probe the dependence of T_g on film thickness we applied the SMFM method to PS films ranging in thickness from 17 to 500 nm. Samples were prepared as described above on native oxide covered Si substrates using PS molecular weights ranging from 65 kg to 6.5 Mg. We expected to see the largest effects for the films where the degree of confinement was the highest. Confinement of the polymer chains occurs when the total film thickness, t, is less than the Gaussian dimension of the polymer chains in the melt, or $t < 2R_g$ where R_g is the radius of gyration. For example, for PS of Mw = 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 Δx 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 μm 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 $t \sim 30$ nm even though $t < R_g$ for the higher molecular weights. (3) A slight increase in T_g, no larger than $5° \pm 2°$, occurs for the thinnest films, $t \sim 20$ nm, that could be studied on Si. This increase is independent of Mw. 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
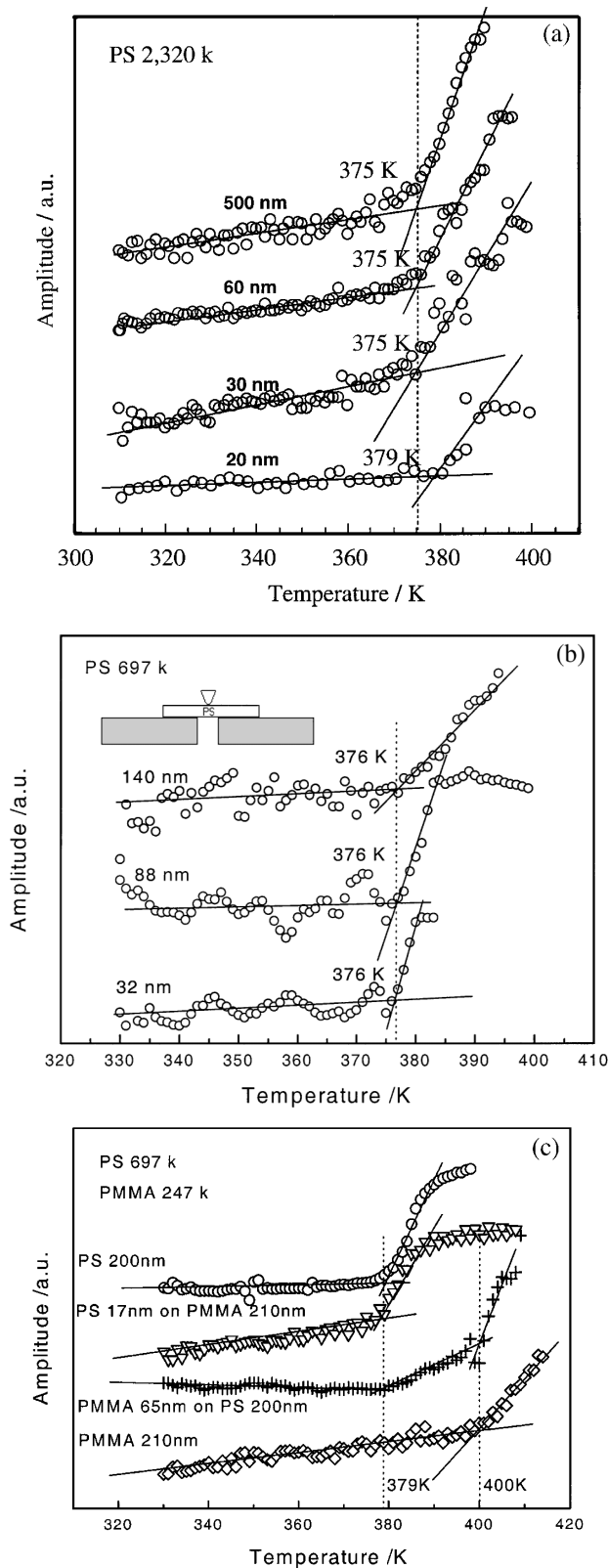
FIG. 4. Δx vs temperature curves for PS films of different thicknesses (a) spun cast on Si, (b) freestanding, and (c) PS/PMMA/Si and PMMA/PS/Si.

Δx 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 Δx modulation is no longer described by the above models given in Eq. (1).

[1] J. F. van der Veen, Surf. Sci. **1**, 433 (1999), and references therein.
[2] E. K. Lin, W-L. Wu, and S. K. Satija, Macromolecules **30**, 7224 (1997).
[3] G. Beaucage et al., J. Polym. Sci. B, Polym. Phys. **31**, 319 (1993).
[4] J. L. Keddie, R. A. L. Jones, and R. A. Cory, Europhys. Lett. **27**, 59 (1994).
[5] W. E. Wallace, J. H. VanZanten, and W. Wu, Phys. Rev. E **52**, 3329 (1995).
[6] L. Xie et al., Phys. Rev. Lett. **74**, 4947 (1995).
[7] G. B. DeMaggio et al., Phys. Rev. Lett. **78**, 1524 (1997).
[8] C. W. Frank et al., Science **77**, 2002 (1996).
[9] J. A. Forrest et al., Phys. Rev. Lett. **77**, 2002 (1996).
[10] K. Tanaka et al., Macromolecules **29**, 3040 (1996).
[11] T. Kajiyama, K. Tanaka, and A. Takahara, Macromolecules **30**, 289 (1997); Polymer **39**, 4665 (1998).
[12] O. Prucker et al., Macromol. Chem. Phys. **199**, 1435 (1998).
[13] R. C. Bretz, Y.-C. Lee, F. W. Wise, and W. Sachse, Bull. Am. Phys. Soc. **43**, 696 (1998).
[14] R. H. Schmidt, G. Haugstad, and W. L. Gladfelter, Langmuir **15**, 317 (1999).
[15] D. H. Gracias et al., Chem. Phys. **245**, 277 (1999).
[16] R. M. Overney, C. Buenviaje, R. Luginbuhl, and F. Dinelli, J. Therm. Anal. Calorim. **59**, 205 (2000).
[17] K. L. Johnson, Contact Mechanics (Cambridge University Press, Cambridge, England, 1985).
[18] K. L. Johnson, K. Kendall, and A. D. Roberts, Proc. R. Soc. London A **324**, 201 (1971).
[19] J. A. Ogilvy, J. Phys. D **26**, 2123 (1993).
[20] D. J. Acheson, Elementary Fluid Dynamics (Oxford University Press, Oxford, 1990), p. 226.
[21] D. J. Plazek and V. M. O'Rourke, J. Polym. Sci. A-2 **9**, 209 (1971).
[22] G. C. Berry and T. G. Fox, Adv. Polym. Sci. **5**, 261 (1968).
[23] A. Rudin and D. Burgin, Polymer **16**, 291 (1975).
[24] J. Baschnagel and K. Binder, Macromolecules **28**, 6808 (1995).
[25] W. Zhao et al., Macromolecules **26**, 561 (1993).
[26] B. Frank et al., Macromolecules **29**, 6531 (1996).
[27] X. Zheng et al., Phys. Rev. Lett. **79**, 241 (1997).
[28] H. W. Hu and S. Granick, Science **258**, 1339 (1992).