Effect of Free Surfaces on the Glass Transition Temperature of Thin Polymer Films

J. A. Forrest, * K. Dalnoki-Veress, J. R. Stevens, and J. R. Dutcher*

Department of Physics and Guelph-Waterloo Program for Graduate Work in Physics, University of Guelph, Guelph, Ontario, Canada N1G 2W1

(Received 9 April 1996)

We report the first measurements of the glass transition temperature T_g for thin freely standing polystyrene (PS) films. We have used Brillouin light scattering to measure T_g for freely standing films of different thicknesses. We find that T_g decreases linearly with film thickness h for $h \leq 700$ Å, with a reduction of 70 K for a film with $h = 290$ Å. These measurements characterize unambiguously the effects of the free surface on T_g of thin polymer films. Results are compared to similar results for supported PS films [Keddie *et al.*, Europhys. Lett. **27**, 59 (1994)], and we find that their measured values are influenced strongly by the substrate. [S0031-9007(96)01093-9]

PACS numbers: 64.70.Pf, 68.60.Bs, 78.35.+c

From organic liquids to metals to polymers, almost any substance can be transformed into a glassy state. One of the fundamental parameters describing a glass is the glass transition temperature T_g. For temperatures greater than T_g, the material is a viscous liquid. As the liquid is cooled below this temperature, the material forms an amorphous solid. Despite the technological significance of glass forming materials, the glass transition itself is poorly understood. In particular, it is not clear whether the glass transition is a thermodynamic transition [1] or a purely kinetic phenomenon [2]. Adam and Gibbs [3] introduced the concept of cooperative rearrangement in an attempt to unify these two views of the glass transition by demonstrating that such cooperativity, coupled with a thermodynamic glass transition, resulted naturally in system dynamics such as those described by the WLF equation [4] for temperatures near T_g. Donth [5] has estimated the size of such cooperatively rearranging regions (CRR) to be of the order of 10 Å for a number of glass forming materials. The introduction of such a length scale suggests that studying samples with dimensions comparable to the CRR may lead to the observation of finite size effects.

An attractive choice for studies of finite size effects on the glass transition is the use of polymer molecules. For polymers the molecule can be characterized by the end-to-end distance $R_{EE} \sim 2R_g$, where R_g is the radius of gyration of the molecule. R_{EE} is typically much larger than the size of the CRR, and R_{EE} can be adjusted by changing the molecular weight M_w of the molecules. Polymer molecules can be confined by preparing samples in a thin film geometry. The relevant length scale is the film thickness h which can be adjusted to be comparable to, much larger than or smaller than R_{EE} so that the effects of chain confinement can be investigated. Glassy polymer films can be cast onto any substrate, even those that the polymer melt itself does not wet.

The first direct measurements of the glass transition temperature in thin polymer films were performed recently by Keddie, Jones, and Cory [6]. For polystyrene (PS) films on hydrogen-passivated Si(111), the measured T_g values were lower than the bulk value $T_g(\mathrm{bulk})$ for films with thicknesses $h \leq 400$ Å. Because the changes in T_g occur for film thickness values that are much larger than the size of the CRR, the T_g reduction is not related directly to cooperative rearrangement. Data were collected for films made with polymers of $\overline{M}_w = 120\,000$ to $2\,900\,000$ (R_{EE} from 230 to 1120 Å) The results were collectively described by a single empirical relation of the form

$$T_g(h) = T_g(\mathrm{bulk})\left[1 - \left(\frac{\alpha}{h}\right)^{\delta}\right], \qquad (1)$$

where $T_g(h)$ is the measured glass transition temperature for a film of thickness h. The best fit parameters describing their data were $\alpha = 32$ Å and $\delta = 1.8$. Because there is little difference between the results for $\overline{M}_w$ values that differ by a factor of 25, chain confinement can be ruled out as the cause of the T_g reductions. The reduction in T_g values was suggested to be a result of the existence of a "liquidlike" layer near the free surface of the film. This two-film model was used to describe the supported films, with the liquidlike surface layer thickness increasing in size as the temperature was increased. The authors did not expect that the presence of the Si substrate substantially affected the measured T_g values [6].

Subsequent ellipsometry measurements of T_g for PMMA films [7] revealed the strong influence of the substrate on the glass transition temperature for thin polymer films. With decreasing film thickness the T_g values were observed to increase for PMMA films on Si(111) with the native oxide layer, and to decrease for PMMA films on Au. It was speculated that the observed behavior for PMMA films on Si(111) was due to hydrogen bonding between the polymer and the SiO_x surface.

In neutron and x-ray reflectivity studies [8,9] of supported polymer films it has been observed that T_g values increase with decreasing film thickness, as in the PMMA

 0031-9007/96/77(10)/2002(4)$10.00

films on SiO_x [6]. For the case of PS on hydrogen-terminated Si(111) surfaces [8], this was in contrast to the ellipsometry measurements [6]. The authors rationalize this apparent contradiction with the suggestion that, contrary to their own studies, the substrates in Ref. [6] actually had a SiO_x layer. Increases in the measured glass transition temperature were especially large for systems for which there was a strong attraction between the polymer and substrate [9]. As in Ref. [6], each sample was modeled as a two-film system but with a layer of decreased mobility near the substrate and a melt layer above. Such modeling emphasizes the effect of the substrate in contrast to Ref. [6] which emphasized the effect of the free surface. Positron annihilation lifetime spectroscopy [10] has been used to selectively probe the glass transition of a PS film near the polymer-vacuum interface. These studies showed a surface T_g value which was the same as the accepted bulk value, providing evidence against the existence of a meltlike surface region.

Molecular dynamics simulations of a freely standing glassy polymer film have been performed by Mansfield and Theodorou [11]. Their simulations show that the effect of the free surface is to decrease the density and to enhance the mobility of the polymer chain near the polymer-vacuum interface. The length scale for both of these effects was larger than R_g. These findings are consistent with the prediction of Keddie *et al.* for PS on Si(111), i.e., that the presence of the free surface lowers the glass transition temperature. Monte Carlo simulations of static [12] and dynamic [13] properties of a confined polymer melt by Baschnagel and Binder have shown that the presence of confining (but not attracting) walls results in an increase in the density and a decrease in the mobility near the polymer-wall interface. The length scale for these effects was also larger than R_g.

The results of these simulations, along with the experimental results, suggest that the effect of the free surface is to lower the T_g value, while that of the substrate is to increase the T_g value. What is actually observed in the case of supported films depends on which of these effects dominates for the particular polymer-substrate combination used. Because of this inherent asymmetry, which is further complicated by sensitivity to substrate preparation, it seems unlikely that T_g data for supported films can be used to understand the effects of either interface on its own.

An obvious way of avoiding the difficulties with interpreting data affected by both free and confining surfaces is to eliminate the substrate entirely and measure the glass transition of symmetric freely standing films. We have shown recently that Brillouin light scattering (BLS) can be used to measure the glass transition of thin, freely standing polymer films [14]. We have also shown that the T_g values obtained from BLS measurements of bulk polymers are the same as those measured using differential scanning calorimetry (DSC) [14]. In BLS studies of bulk polymers, one measures the velocity v_L of the bulk longitudinal phonon, where $v_L = (c_{11}/\rho)^{1/2}$, c_{11} is the longitudinal elastic constant, and ρ is the density. Since c_{11} is a strong function of ρ, as the sample temperature is changed, the temperature dependence of v_L exhibits an abrupt change in slope at the temperature at which the thermal expansivity is discontinuous, i.e., the glass transition temperature T_g. For thin films, BLS probes the elastic properties through observation of film-guided acoustic phonons. The guided acoustic modes are referred to as Lamb modes [15] for freely standing films. These modes are dispersive, with the mode velocity varying as a function of $Q_\parallel h$ (where $Q_\parallel$ is the scattering vector, and h is the film thickness). For thin films ($Q_\parallel h \leq 1$), all but the two lowest order modes diverge to large velocities. The lowest velocity mode is denoted A_0 and has particle displacements that are primarily transverse. The velocity of this mode approaches 0 as $Q_\parallel h \rightarrow 0$, and thus is not suitable for studies on very thin films. The second lowest velocity mode is denoted S_0, and the velocity of this mode approaches a constant value in the low $Q_\parallel h$ limit. The particle displacements for the S_0 mode are primarily longitudinal which makes it ideal for comparison to BLS studies of bulk longitudinal phonons [16]. The application of BLS to measure T_g for freely standing films has been described in detail in Ref. [14]. This Letter describes a BLS study of freely standing films in which we have obtained the first unambiguous observation of the effect of free surfaces on the glass transition temperature in thin polymer films.

Thin freely standing films of PS were prepared using a spin-coating technique. Solutions of PS ($\overline{M}_w = 760\,000$, $\overline{M}_w/\overline{M}_n = 1.10$, $R_{EE} = 570$ Å) [17] in toluene were spin coated onto glass slides at 4000 rpm. The resulting films were vacuum annealed at 385 K for 12–16 h, and then cooled to room temperature at 1 K/min. This procedure resulted in films with a well-defined and reproducible thermal history. After cooling, the films were cut and then floated onto distilled water. A small piece of the floating film was picked up onto a sample holder containing a 3 mm diameter hole, resulting in a freely standing film which was then dried in air at 320 K to remove any residual water. Other sections of the same floating film were transferred to a Si(001) wafer for ellipsometry measurements of the film thickness.

BLS measurements were performed with the sample in an optical furnace. BLS spectra were acquired using a $3 \times (1 + 1)$ tandem Fabry-Pérot interferometer using 50–100 mW of laser power ($\lambda = 5145$ Å) incident on the sample. A slit was placed in the scattered light beam to limit the line broadening caused by the nonzero light collection angle [18]. The frequency of the S_0 mode was measured as the sample temperature was raised from room temperature through T_g. The maximum heating rate between spectra was 1 K/min, and, during the acquisition of each spectrum, the sample temperature is held constant to within ± 0.25 K.

The S_0 mode frequency was measured as a function of temperature for seven freely standing films, ranging in thickness from $h = 290$ to 1840 Å. Figure 1 shows the frequency versus temperature data for three films of different thicknesses. The data for each film can be represented very well by fitting straight lines of different slopes to the low temperature (glass) and high temperature (melt) regimes. As for bulk BLS measurements [16], the temperature corresponding to the intersection of the lines defining the low temperature and high temperature regimes is identified as T_g. In Fig. 1, the T_g values for each film are indicated by vertical arrows. For the seven freely standing films, the slopes of plots of the phonon frequency versus temperature $(df/dT)_{\text{glass}}$ in the glass regime ($T < T_g$) ranged from -2.9×10^{-3} to -4.8×10^{-3} GHz/K. This corresponds to a typical frequency change of only 0.03 GHz for a change in sample temperature of 6 K between BLS spectra. This frequency change corresponds to only 0.3% of the free spectral range of the Fabry-Pérot interferometer, and its measurement is at the limits of the frequency resolution of the BLS spectrometer. The slopes of plots of frequency versus temperature in the melt regime ($T > T_g$) were larger than those in the glass regime, ranging from -3.48×10^{-2} to -7.12×10^{-3} GHz/K. The glass transition temperature can be determined accurately only if there is sufficient contrast between the slopes for the melt and glass regimes. For the seven films used in this study, the ratio of slopes for the melt and glass regimes $[(df/dT)_{\text{melt}}/(df/dT)_{\text{glass}}]$ ranged from 1.8 to 10. These relatively large values of the ratio of the slopes allow us to determine the glass transition to within ± 2 K. We note that the transition between the glass and melt regimes occurs over a narrow range in temperature for all of the films, including those with the smallest film thicknesses. This implies that, for each film, the film undergoes the glass transition at a single temperature.

Although the slope of the glassy regions in the lower two plots in Fig. 1 are almost identical, the magnitude of the slope in the melt region for the $h = 640$ Å film is clearly larger than that of the $h = 420$ Å film. By calculating the dependence of c_{11} on density from experimental data [14], the slopes of the lines in Fig. 1 can be related to the thermal expansivity. Figure 1 illustrates that, as the film thickness is decreased, the glass expansivity remains relatively constant while that of the melt region decreases.

The linewidth of the S_0 mode was measured for all spectra, and no increases were observed for $T > T_g$. In the particular case of the $h = 420$ Å film, measurements were performed up to $T = T_g + 40$ K. Linewidths of 0.5 GHz were measured for all temperatures, and were only slightly larger than the 0.4 GHz instrumental linewidth.

The measured T_g values are shown in Fig. 2 as a function of film thickness h. The film thickness values were determined using room temperature ellipsometry

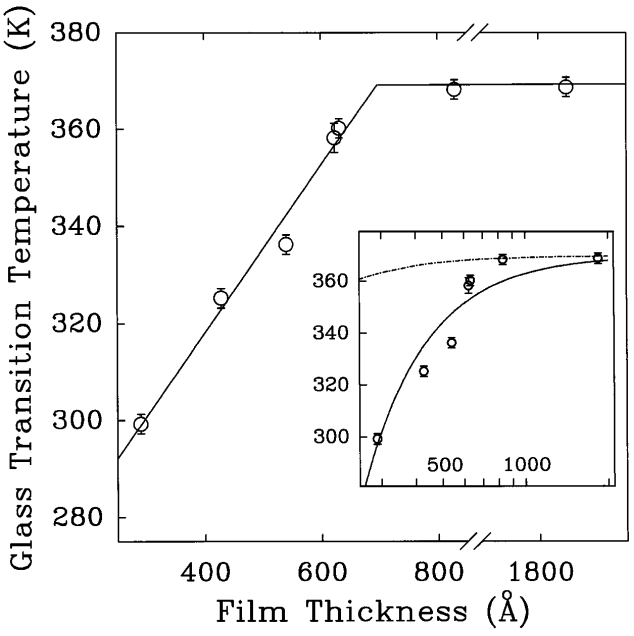

FIG. 1. Frequency of the S_0 mode as a function of temperature for three freely standing PS films. The film thicknesses are, from top to bottom, 1840, 620, and 420 Å. The assigned glass transition temperatures, as indicated by the vertical arrows, are 369, 360, and 325 K.

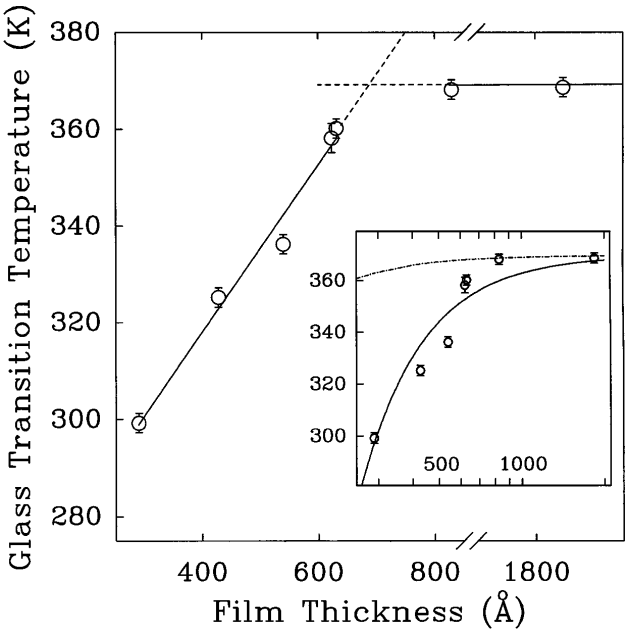

FIG. 2. Measured glass transition temperature T_g as a function of film thickness h for freely standing PS films. The solid (and dashed) lines are a fit of the data by Eq. (2) in the text. In the inset, which has a logarithmic thickness axis, the data for freely standing films is shown (symbols), together with the data of Ref. [6] (dashed line), and a fit of our data by Eq. (1) described in the text (solid line).

measurements. The most striking feature of this data is the large reduction in T_g for very small film thicknesses. In particular, for the smallest film thickness measured ($h = 290$ Å), the glass transition occurs at a temperature just slightly above room temperature ($T_g = 299$ K). For the largest film thickness values, $h = 820$ and 1840 Å, the measured T_g values were equal (within ± 1 K) to that measured using BLS and DSC for bulk samples of the same polymer with the same thermal history. For $h \leq 620$ Å, the measured T_g values decrease monotonically with h, and are described very well by a linear function of h:

$$T_g(h) = \begin{cases} T_g(\text{bulk})\left(1 - \frac{(h_0 - h)}{\zeta}\right), & h < h_0, \\ T_g(\text{bulk}), & h \geq h_0. \end{cases} \quad (2)$$

The best fit parameter values to Eq. (2) are $h_0 = 691 \pm 20$ Å and $\zeta = 2130 \pm 170$ Å, with $T_g(\text{bulk}) = 369$ K. The measurement uncertainty of T_g (± 2 K) in the present experiments is insufficient to quantify the T_g values for films with thicknesses in the range $640 < h < 820$ Å, and the dashed portion of the lines in Fig. 2 reflects this uncertainty. The inset in Fig. 2 shows our data together with two curves. The upper curve is a schematic representation of Keddie, Jones, and Cory data [6] for supported PS films. Comparison of the upper curve to our data shows that, for a given film thickness, the reductions in T_g are much larger for freely standing PS films than for supported PS films. The lower curve in the inset to Fig. 2 corresponds to the best fit of Eq. (1) to our data; we found that this fit depended strongly on the lowest T_g data point included in the fitting procedure. This indicates that Eq. (1) is not an appropriate functional form to describe our data. The χ^2 value obtained from a least squares fit of our data to the linear function of h given in Eq. (2) is a factor of 2.8 smaller than that obtained by fitting our data to Eq. (1).

Although Eq. (2) is purely empirical, it is intriguing that the film thickness h_0 corresponding to the intersection of the two linear regions is only slightly greater than the end-to-end distance R_{EE} of the polymer molecules used in these experiments. Such large length scales are consistent with the simulation results [11–13] which suggest that surface effects occur on a length scale which is larger than R_g. BLS measurements on freely standing films of higher molecular weight PS are in progress to determine if the effects are M_w dependent.

At present, there is no theory to describe the effects of free surfaces on the observed glass transition. While a decreased density has been observed in experiments on thin supported films [19], as well as in simulations of thin freely standing films [11], it is not possible to predict the magnitude of changes in the glass transition due to the presence of the free surface. Mayes [20] has used a simple scaling argument to predict that the enrichment of chain ends near a polymer surface results in a surface T_g which is reduced from the bulk value. This argument cannot explain the film thickness dependence of T_g observed in the present and previous work [6,7]. The fact that the best fit to the present data is obtained for a linear relation between T_g and h suggests that a simple theoretical picture is possible. The fact that there are no theoretical or simulation results to predict the very pronounced free surface effects on the glass transition described in this Letter is an indication that more theoretical work is required.

We thank Waterloo Digital Electronics for the use of their ellipsometer. Also, we acknowledge helpful discussions with Dr. B. G. Nickel, Dr. G. B. McKenna, Dr. J. H. van Zanten, Dr. E. A. DiMarzio, and Dr. J. Baschnagel. The financial support of the Natural Sciences and Engineering Research Council (NSERC) of Canada is gratefully acknowledged.

*To whom correspondence should be addressed.

[1] J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys. **28**, 373 (1958).
[2] W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).
[3] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).
[4] See, for example, J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1990), p. 280.
[5] E. Donth, J. Non-Cryst. Solids **53**, 325 (1982).
[6] J. L. Keddie, R. A. L. Jones, and R. A. Cory, Europhys. Lett. **27**, 59 (1994).
[7] J. L. Keddie, R. A. L. Jones, and R. A Cory, Faraday Discuss. **98**, 219 (1994).
[8] W. E. Wallace, J. H. van Zanten, and W. Wu, Phys. Rev. E **52**, R3329 (1995).
[9] J. H. van Zanten, W. E. Wallace, and W. Wu, Phys. Rev. E **53**, R2053 (1996).
[10] L. Xie, G. B. DeMaggio, W. E. Frieze, J. DeVries, D. W. Gidley, H. A. Hristov, and A. F. Yee, Phys. Rev. Lett. **74**, 4947 (1995).
[11] K. F. Mansfield and D. N. Theodorou, Macromolecules **24**, 6283 (1991).
[12] J. Baschnagel and K. Binder, Macromolecules **28**, 6808 (1995).
[13] J. Baschnagel and K. Binder (to be published).
[14] J. A. Forrest, K. Dalnoki-Veress, J. R. Dutcher, and J. R. Stevens, Mater. Res. Soc. Symp. Proc. **407**, 131 (1996).
[15] G. W. Farnell and E. L. Adler, in *Physical Acoustics, Principles and Methods*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1972), Vol. 9, Chap. 2.
[16] R. W. Coakely, R. S. Mitchell, J. R. Stevens, and J. L. Hunt, J. Appl. Phys. **47**, 4271 (1976).
[17] Polymer samples were obtained from Polymer Source Inc.
[18] C. Gigault and J. R. Dutcher (to be published).
[19] G. Reiter, Europhys. Lett. **23**, 579 (1993).
[20] A. M. Mayes, Macromolecules **27**, 3114 (1994).

Effect of Free Surfaces on the Glass Transition Temperature of Thin Polymer Films [Phys. Rev. Lett. 77, 2002 (1996)]

J. A. Forrest, K. Dalnoki-Veress, J. R. Stevens, and J. R. Dutcher

[S0031-9007(96)01632-8]

An incorrect figure was printed as Fig. 1 in this article. Below is the proper figure.

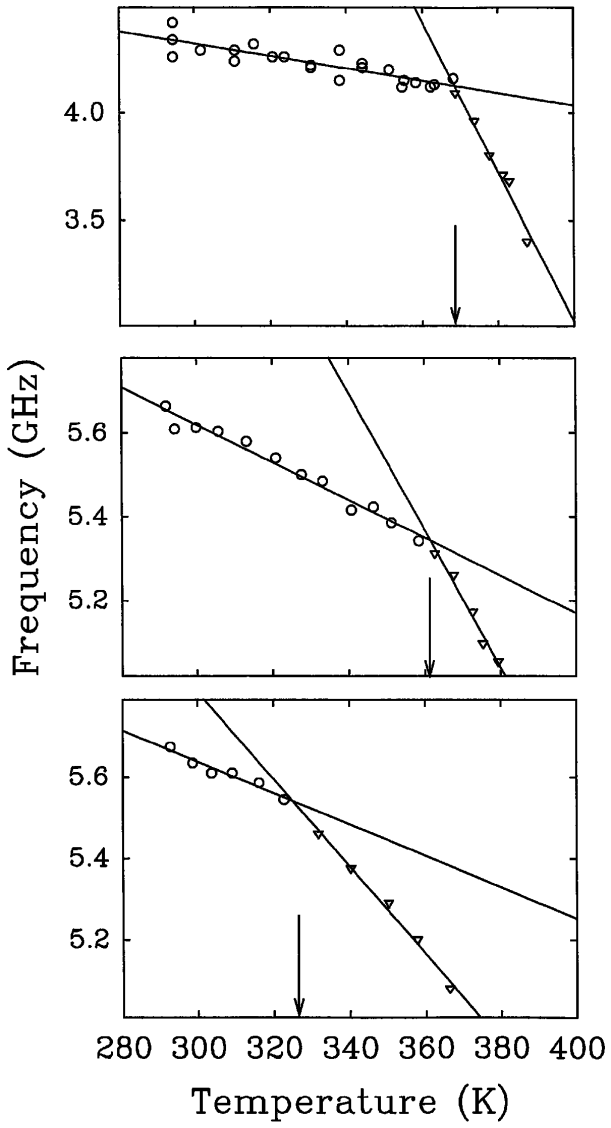

FIG. 1. Frequency of the S_0 mode as a function of temperature for three freely standing PS films. The film thicknesses are, from top to bottom, 1840, 620, and 420 Å. The assigned glass transition temperatures, as indicated by the vertical arrows, are 369, 360, and 325 K.

 0031-9007/96/77(19)/4108(1)$10.00