Probing Slow Dynamics in Supported Thin Polymer Films

Zahra Fakhraai and James A. Forrest*

*Department of Physics and Guelph-Waterloo Physics Institute, University of Waterloo, 200 University Avenue W.,
Waterloo, Ontario, Canada N2L 3G1*
(Received 3 September 2004; published 7 July 2005)

We have used variable cooling rate ellipsometric measurements to probe the slow dynamics in thin supported polystyrene films. For the slowest cooling rates (~ 1 K/min) the measured T_g values are reduced below the bulk value with the measured T_g of 341 K for a 6 nm film. As the cooling rate is increased the T_g reductions become smaller until at cooling rates >90 K/min there is only slight evidence for a film-thickness-dependent T_g value. By relating the cooling rate to a relaxation time, we show that the relaxation dynamics of the thin films appears to become Arrhenius with an activation energy that decreases with decreasing film thickness. We discuss this in terms of a possible connection to a length scale for cooperative motion. Finally, the results can be used to resolve a number of outstanding contradictory reports in the literature.

PACS numbers: 64.70.Pf, 61.41.+e, 68.60.Bs

The nature of the glass transition remains an unsolved problem despite decades of study. Many different theoretical approaches have been applied to glass formation, but as yet none have been able to provide a description to encompass the known behavior. For this reason the glass transition is often noted to be the ''deepest and most interesting unsolved problem in solid-state theory'' [1]. One persisting theme in the literature is the existence of a characteristic length scale for the dynamics in glass forming materials [2–4]. This length scale has been studied in computer simulations at temperatures much above the calorimetric glass transition, and some experimental evidence for such a length scale has been presented [3]. The glass transition in highly confined geometries is among the most promising approaches to learn about the existence of a temperature dependent length scale in glass forming materials [5–7].

One particular sample configuration that has attracted a great deal of attention is that of thin polymer films. For such samples the dynamics are often inferred through measurements of the glass transition temperature T_g. This is a convenient, though obviously indirect measure of the dynamics in the sample. Since the original report by Keddie, Jones, and Cory [8] of the T_g value of thin films of polystyrene (PS) being reduced below the bulk value for films with thickness $h < 40$ nm, many researchers have performed similar studies, mainly using what can be termed as dilatometric techniques [9–11]. There is a growing consensus that for the particular case of PS, the T_g value decreases below the bulk value for sufficiently thin films. In addition there is growing evidence that the free surface plays a key role in these effects [12,13]. Despite this significant agreement between many groups, there are outstanding contradictory reports. Foremost among these reports is the recent observation that T_g values measured using nanocalorimetric techniques do not display a film-thickness-dependent T_g value. This conclusion seems to apply equally well to T_g values measured directly at cool-

ing rates of 1000 K/s [14] to those inferring the T_g through the fictive temperature T_f at rates of 2 K/s [15]. The qualitative difference between the dilatometric and calorimetric measured T_g values is striking and indicates an unsettling lack of understanding of the glass transition in nanoconfined geometries. In turn, the resolution of such a paradox is sure to add significantly to our understanding of dynamics in highly confined geometries and to the glass transition in general. A more serious concern is the fact that despite many measurements of T_g there are almost no measurements of dynamics for supported polymer films: the sample configuration for most of the T_g data. Since it has recently been demonstrated that the glass transition can be strongly affected by the presence or absence of the free surface [12,13] it is not clear that previous dielectric and thermal expansion spectroscopy studies of PS films have sufficient relevance to the systems they are being compared to [16]. The only dielectric relaxation studies on films with a free surface have used isotactic poly(methyl methacrylate) (*i*-PMMA) [17]. In this Letter we present the results of ellipsometric measurements of the T_g value of thin PS films supported by Pt coated SiN substrates at cooling rates ranging from 1 to 130 K/min. Such studies allow the use of T_g measurements as a measure of the dynamics in supported polymer films over 2 orders of magnitude. For the 1 K/min studies we observe large reductions in the measured T_g value of thin films. As the cooling rate is increased, the film thickness dependence of the T_g value becomes less pronounced until at a rate of 130 K/min there are only slight indications of any dependence of the T_g on the film thickness. The particularly striking aspect of the results is the very narrow range of cooling rate that results in reduced T_g values. The findings show that only the very slow dynamics are affected by nanoconfinement and that the effects persist for a relatively short time window of 2 orders of magnitude in relaxation time. The significance of this work is threefold. Most importantly, it

provides a quantification of the dynamics in thin supported films; second, it leads to a reasonable resolution of existing contradictory reports. Finally, it may lead to significant advances in our understanding of the glass transition.

PS films were produced by spin coating solutions of PS ($M_w = 641$ K, $M_w/M_n = 1.11$, Polymer Source Inc.) in toluene. The substrates used were the same ones employed for the nanocalorimetry studies of [14], Pt(50 nm)/Ti/SiN(50 nm)/Si, in order to be able to address the possibility of a strong substrate sensitivity being a cause for the aforementioned discrepancy. The samples were annealed under dry N_2 at a temperature of 393 K for 15 h and cooled to room temperature at <1 K$/$min. The samples were placed on the block of a Linkham temperature controlled stage. The T_g values were measured using an EXACTA 2000 fast nulling ellipsometer. The sampling time of the ellipsometer could be set to values as low as 0.3 s and still have sufficient resolution in the measured ellipsometric angles (P, A) for reliable T_g determination. We believe that such measurements are at the limit of those feasible with ellipsometry. For ellipsometric measurements, the sample is heated to 403–423 K, and then cooled to 293 K at rates of 1, 3, 6, 10, 20, 30, 40, 50, 70, 90, and 130 K$/$min. The heating rate is 130 K$/$min for all measurements. Since the thermal properties are dominated by the substrate, we can make quantitative comparisons between thin films and thick films. Since the analyzer angle (A) of the Pt coated substrates changes linearly in the high and low temperature ranges (and the polarizer angle changes very little), unlike some other polymer-substrate combinations (such as *i*-PMMA on Al) [17], the ellipsometric data do not need to be numerically inverted to determine T_g. The ellipsometric data are analyzed by taking the numerical derivative of the A data, and the T_g is defined as the midpoint of the high (T_+) and low (T_-) temperature limits. Figure 1 shows an example of raw

data, as well as how the data are used to determine T_g for a 6 nm film measured at a cooling rate of 30 K$/$min. Although the contrast between the low temperature range and the high temperature range is very small in very thin films, the technique allows us to determine the T_g with an accuracy of ± 2 K.

Measured T_g values as a function of film thickness are shown in Fig. 2 for cooling rates of 1 or 3 K$/$min, 50 K$/$min, and 130 K$/$min. The most striking aspect of these data is that the film thickness dependence of the T_g values depends strongly on the cooling rate. The 1 K$/$min data show a strong T_g dependence to the film thickness. As the cooling rate is increased the thickness dependence of the T_g values decreases, so that at the cooling rate of 130 K$/$min the film thickness dependence of the T_g values are only slightly more than the experimental error. More quantitatively, the largest T_g reductions occurs for the 6 nm film and is 32 K below that of the 90 nm film for 1 K$/$min and is only 10 K below that of the 90 nm film for 130 K$/$min. The fact that the 1 K$/$min and 3 K$/$min data do exhibit large T_g reductions allows us to rule out the substrate as a cause of the discrepancies between previous T_g studies and those of Ref. [14]. By making comparisons between thin films and a thick film (rather than bulk PS) we can eliminate any possible effects due to different temperature gradients at different cooling rates.

Other studies of T_g in thin films have suggested that for the case of supported PS films (though not for freestanding films [11]) the apparent T_g reductions are due to a broadening of the transition [18]. This observation also holds true in the present work, and, in particular, the diminishing of T_g reductions at high cooling rates is a reflection of a narrowing of the transition as compared to lower cooling rates. In our experiments, we observe that the difference
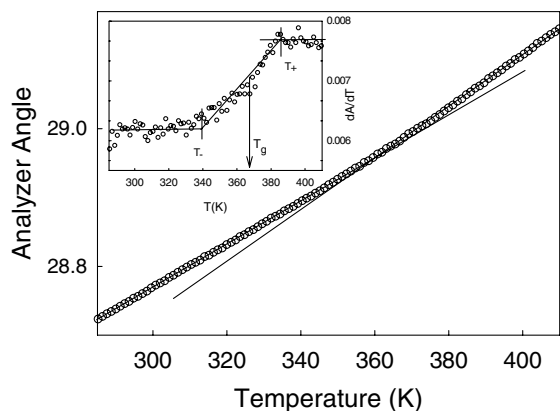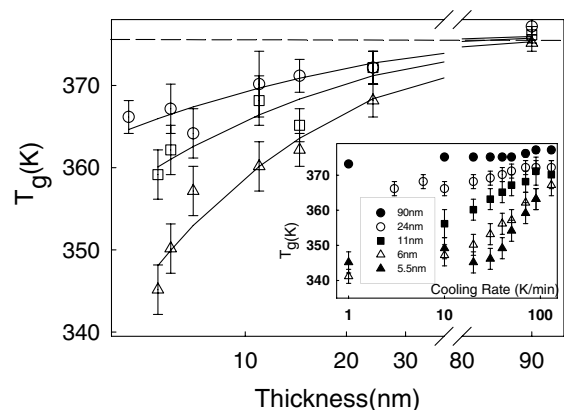

FIG. 1. The analyzer data and their temperature derivative (inset) for a 6 nm PS film as a function of temperature. The T_g is defined as the midpoint of T_+ and T_- values. The cooling rate is 30 K$/$min.

FIG. 2. Measured T_g values as a function of film thickness at 1 or 3 K$/$min ($\triangle$), 50 K$/$min ($\square$) and 130 K$/$min ($\bigcirc$) cooling rates. The T_g values of 90 nm film are used as an indication of bulk T_g values. The solid lines are to guide the eye. The inset shows T_g as a function of cooling rate for 90 nm ($\bullet$), 24 nm ($\bigcirc$), 11 nm ($\blacksquare$), 6 nm ($\triangle$), and 5.5 nm ($\blacktriangle$) films.

between T_+ and T_- (which defines the width of the transition) remains almost independent of film thickness at a cooling rate of 130 K/min, while the difference is increasing as the thickness is decreasing in the cooling rates of 1 or 3 K/min. It is interesting to note that the value of T_+ is also decreasing, but T_- decreases more rapidly, so that the width of transition increases in thinner films.

The T_g values for all cooling rates and films of thickness 5.5, 6, 11, 24, and 90 nm are shown in the inset of Fig. 2. We can see that the T_g of 5.5 and 6 nm film show the strongest cooling rate dependence. As we increase the thickness the T_g value depends less strongly on the temperature, so that the T_g of 90 nm film displays a cooling rate dependence one would expect from a bulk material. The cooling rates used to measure a T_g value can be considered as an inverse of some relaxation time probed by that experiment. The data for the 90 nm film can be used as a measure of the dynamics of ''bulk'' PS over the range of relaxation times of 7 to 1000 s, using the relation that a cooling rate of 10 K/min corresponds to a relaxation time of 100 s [16,19]. As expected there is only a slight rate dependence due to the fact that the relaxation time is such a strongly varying function of temperature.

In order to make a sensible comparison between the T_g values presented in the present work, and other studies of relaxation time (τ) in confined systems, it is useful to cast it in the form as a plot of $-\log(\tau)$ versus $1/T$ [6,7,20]. Figure 3 shows such a plot where the relaxation time is written in terms of the experimental cooling rate. The results cast in this form are quite remarkable and are
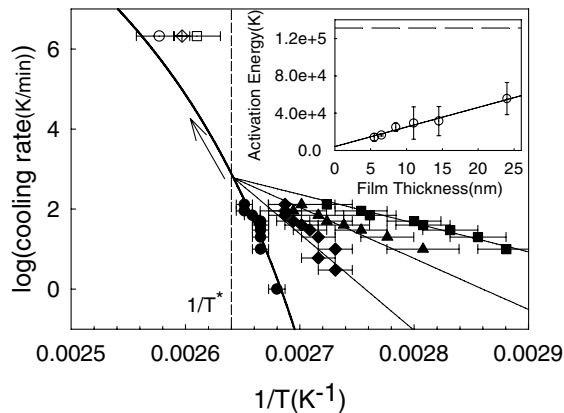

FIG. 3. The log(cooling rate) vs $1/T$ for 90 (●), 24 (◆), 11 (▲), and 6 nm (■) films. The curved line is the bulk Vogel-Fulcher-Tamman (VFT) curve for PS and other lines are Arrhenius fit, passing through a single incidence point on the VFT curve. The data points at high cooling rates are the data from Ref. [14] for three different film thicknesses. The dashed line indicates T^* above which no confinement effect is seen. The inset shows the plot of activation energy vs film thickness and the linear fit to the data. The dashed line indicates the slope of the VFT curve at the incidence point which corresponds to a film thickness of 61 nm.

similar to effects reported in dielectric studies of liquids in pore glass [20], polymethylphenylsiloxane (PMPS) intercalated into galleys of silicates [7], and i-PMMA confined between Al surfaces [6]. Before commenting specifically on the results, it is worth reiterating that these measurements correspond to relaxation in supported PS films (with no capping layer) and as such are unique in their comparison to a broad and extensive literature on the T_g value of such samples. The thick solid curved line is obtained using the parameters of the Vogel-Fulcher-Tamman (VFT) equation

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \qquad (1)$$

obtained by fitting relaxation time data for bulk polystyrene [19] in the same temperature range as the present experiments ($B = 1169$ K, $T_0 = 342.8$ K). Since the molecular weight used in the current study is between the two high molecular weight polymers used in Ref. [19], the parameter values of those fits are averaged to obtain the curve in Fig. 3. We employ the relation between the cooling rate and the relaxation time as that obtained for bulk PS [19] (10 K/min ~100 s). It is encouraging to note that although these values are derived from bulk measurements and do not come from a fit to our data (which we do not believe to be meaningful given the small range of cooling rates), they agree with our data within the experimental error. This comparison demonstrates that the 90 nm film behaves like a bulk polystyrene sample. The most prominent feature of the data for thin films is the strong deviation from the bulk (and thick film) VFT-like behavior. For all of the thin film data, the relaxation times exhibit Arrhenius behavior (rather than VFT), with a film-thickness-dependent activation energy. Equally remarkable is that if we fit the data to a simple Arrhenius form and then extrapolate each line to where it intercepts the bulk VFT line, we find that all films intersect at essentially the same temperature of $T = 378.5 \pm 1.4$ K. This corresponds to a cooling rate between 158 and 2068 K/min. For any cooling rates above this critical value, all films will have a T_g the same as the bulk polymer. It is interesting to note that this temperature is very similar to the value of where the surface of PS films seems to show viscoelastic properties that differ from the bulk [21]. This provides a further link between T_g reductions in thin films and surface properties of the polymer.

The slope of each of the straight line fits provides an activation energy E_a. The inset shows how these E_a values vary with the film thickness, if we fit each curve so that it passes through the intersection point shown in the graph. The decreasing value of E_a with film thickness is certainly indicative of a smaller total barrier for relaxation. The fact that this effect occurs only for fairly thin films can be discussed in terms of the idea of a length scale for the dynamics in glass forming materials. In the bulk material,

as the temperature is lowered, more segments have to be involved in any rearrangement, and the apparent activation energy increases. As the film thickness is decreased, once the length scale for cooperative dynamics approaches the film thickness, all rearrangements can be affected by the different constraints at the free surface. Once this condition is reached, the process would be a simple activated process with an activation energy that depended on film thickness. The onset of such a confinement effect could occur only when the value of E_a is tangent to the bulk VFT behavior. This limit is given by the dashed line on the figure inset and the intercept of the E_a versus h plot with this value occurs at a film thickness of 61 ± 6 nm. It is remarkable that this is so similar to the *maximum* value of h where T_g reductions are first observed in supported PS films [11]. It is also interesting to consider the limit of $h \rightarrow 0$. That corresponds to the case where all segments are at the free surface. Such a system would be expect to be Arrhenius with a value of E_a similar to the high temperature limit of the bulk VFT (i.e., $E_a \sim B$). If we do that extrapolation we find $E_a = 4180 \pm 2099$ K. This is the same order of magnitude as that for the high temperature limit of the bulk value $B = 1169$ K. Aside from the possible connection to an intrinsic length scale for the dynamics, the data and analysis above can be used as a stringent test of *any* theories used to describe the glass transition in thin films.

An interesting consequence of the data presented above is the resolution of the contradiction between the body of literature measuring T_g reductions for thin PS films and those studies reporting no change in T_g or even increases in T_g for thin films. Figure 3 shows the existence of a very well defined region (simplified to a single point $1/T^*$, (rate)*, the dashed line in Fig. 3) that serves as a boundary for anomalous dynamics. We have explicitly shown that experiments probing relaxation times shorter than those corresponding to (rate)* show bulk behavior, and it also follows that measurements at temperatures higher than $T^* \simeq 378$ K must similarly fail to reveal anomalies. This is a fascinating suggestion. For instance, in the calorimetric measurement of Ref. [14], even in the measurements of the fictive temperature, the smallest cooling rate was 2 K/s (120 K/ min) [15]. This is very close to the largest cooling rate used in the present experiment, and the results from the two studies are similar. These cooling rates can be compared with an oscillatory technique employing a frequency of $\simeq 0.6$ Hz. Indeed, it seems that almost all reports in the literature that contradict reports of anomalous T_g values are taken in the region beyond $1/T^*$, (rate)*, and thus are entirely consistent with the behavior shown in Fig. 3.

We have demonstrated that the reduced T_g values often reported in thin PS films display a striking cooling rate dependence, which is qualitatively different from that of the bulk polymer. This effect is so pronounced that for cooling rates only as high as a few K/s, we would not expect to see any film-thickness-dependent reductions in

T_g. The cooling rates are related to relaxation times, and when plotted in this way, we see that thin films display a clear Arrhenius behavior. The film-thickness-dependent activation energies can be used to suggest an onset of confinement effects of 61 ± 6 nm, in excellent agreement with experiment. A possible explanation of the effect is given in terms of a temperature dependent correlation length for the dynamics in glass forming materials. Finally, the results provide a natural explanation for most of the remaining apparently contradictory experiments in the literature.

---

*Corresponding author.
Electonic address: jforrest@uwaterloo.ca

[1] P. W. Anderson, Science **267**, 1609 (1995).
[2] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).
[3] *International Workshop on Dynamics in Confinement*, edited by B. Frick, R. Zorn, and H. Buttner [J. Phys. IV (France) 10 (2000)].
[4] G. B. McKenna, Eur. Phys. J. E **12**, 191 (2003).
[5] K. Jackson and G. B. McKenna, J. Non-Cryst. Solids **131**, 221 (1991).
[6] L. Hartmann, J. Gorbatschow, J. Hauwede, and F. Kremer, Eur. Phys. J. E **8**, 145 (2002).
[7] S. H. Anastasiadis, K. Karatasos, G. Vlachos, E. Manias, and E. P. Giannelis, Phys. Rev. Lett. **84**, 915 (2000).
[8] J. L. Keddie, R. A. L. Jones, and R. A. Cory, Europhys. Lett. **27**, 59 (1994).
[9] Special issue on ''Properties of thin polymer films,'' edited by G. Reiter and J. A. Forrest [Eur. Phys. J. E **8** (2002)].
[10] J. A. Forrest, Eur. Phys. J. E **8**, 261 (2002).
[11] J. A. Forrest and K. Dalnoki-Veress, in Adv. Colloid Interface Sci. **94**, Nos. 1–3, 167 (2001).
[12] J. S. Sharp and J. A. Forrest, Phys. Rev. Lett. **91**, 235701 (2003).
[13] C. J. Ellison and J. M. Torkelson, Nat. Mater. **2**, 695 (2003).
[14] M. Y. Efremov *et al.*, Phys. Rev. Lett. **91**, 085703 (2003).
[15] M. Yu. Efremov, E. A. Olsen, M. Zhang, Z. Zhang, and L. H. Allen, Macromolecules **37**, 4607 (2004).
[16] K. Fukao and Y. Miyamoto, Phys. Rev. E **64**, 011803 (2001).
[17] J. S. Sharp and J. A. Forrest, Phys. Rev. E **67**, 031805 (2003).
[18] S. Kawana and R. A. L. Jones, Phys. Rev. E **63**, 021501 (2001).
[19] C. M. Roland and R. Casalini, J. Chem. Phys. **119**, 1838 (2003).
[20] M. Arndt, R. Stannarius, H. Groutheus, E. Hempel, and F. Kremer, Phys. Rev. Lett. **79**, 2077 (1997).
[21] J. S. Sharp, J. H. Teichroeb, and J. A. Forrest, Eur. Phys. J. E **15**, 473 (2004).