

Free Surfaces Cause Reductions in the Glass Transition Temperature of Thin Polystyrene Films

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(Received 6 February 2003; revised manuscript received 14 October 2003; published 3 December 2003)

The effect of free surfaces on the glass transition temperature (T_g) of thin polystyrene films was studied. Measurements were performed on films ($8 \text{ nm} < h < 290 \text{ nm}$) with one free surface and on films capped with a 5 nm thick metal layer (no free surfaces). Potential problems with evaporative deposition were eliminated by studying samples made of two supported films placed with their free surfaces in contact and annealed. Uncapped films displayed reduced T_g values for $h \lesssim 40 \text{ nm}$ while all “properly” capped films exhibited a T_g value the same as that of the bulk polymer ($370 \pm 1 \text{ K}$). When the free surface was restored, the measured T_g values the same as those of uncapped films of the same thickness. These results show that free surfaces are crucial for observing T_g reductions in thin polymer films and address the role of the sample preparation history.

DOI: 10.1103/PhysRevLett.91.235701

PACS numbers: 64.70.Pf, 68.60.-p, 68.35.-p

A proper physical description of the glass transition remains a key outstanding problem in condensed matter physics [1]. One recurring theme is the idea of a correlation length for the dynamics in glass forming materials which increases in size as the temperature is lowered [2]. Simulations of bulk glass forming materials (both polymeric and nonpolymeric) have provided evidence for a dynamical correlation length even above the mode coupling critical temperature T_c [3]. The study of confined glass forming systems may be one of the only ways to directly prove the existence (or lack thereof) of such a dynamical correlation length $\xi(T)$. A prominent example of anomalous dynamics in confined systems is found in recent studies of the glass transition temperature T_g of thin polymer films. Such studies are of tremendous current interest [4–7], and it has recently become possible to make a detailed discussion for the case of atactic polystyrene (PS) [6,7]. Many researchers have investigated the properties of thin films of PS [6,8]. For PS films supported on substrates, the T_g value is reduced below the bulk value for films thinner than 40 nm and exhibits only a weak sensitivity to the substrate material. Freestanding PS films display much larger T_g reductions than supported films of similar thickness. For $M_w \lesssim 350\,000$, the measured T_g values of freestanding films of thickness h are quantitatively similar to those measured for supported films of thickness $h/2$ [9]. This relation was first noticed in the application of layer models to describe the T_g values in freestanding films [9] and provides strong evidence that the volume fraction of the near surface layer is important in determining the thin film T_g value. Direct measurements of the free surface properties have thus far proven inconclusive [10,11]. A direct way to ascertain the effects that free surfaces have upon the T_g value is to

modify the surface and study the resulting effect on T_g . Measured T_g values for SiO_x coated PS films were determined to be essentially the same as those for supported films with one free surface [12]. This surprising result was confirmed in dielectric studies of Al coated PS which also showed T_g behavior the same as that of supported films [13]. The comparison between these results and the suggestion from the T_g values measured in freestanding films results in an apparent and striking inconsistency. If the free surface is important in causing reduced T_g values in thin films, then eliminating the free surface *must* have an influence on the measured T_g values. The fact that this does not seem to be the case has proven to be a major obstacle in understanding the basic physics behind thin film glass transitions. In this Letter, we motivate the idea that simply evaporating a coating on top of the free surface may not remove memory of its existence. We then describe a simple alternative method for producing samples with no free surface that does not involve evaporating metals onto polymer surfaces. Such samples show bulk T_g values for all film thicknesses studied. Chemically removing the layer is shown to restore the reduced T_g values, while the chemical process is shown not to affect the T_g value of simple uncapped supported films. The results provide compelling evidence that the free surface is the dominating factor in determining the T_g reductions in thin polymer films. At the same time, the results rigorously address any questions regarding the suggested influence of the spincasting procedure on measured T_g values of thin polymer films.

Polystyrene ($M_w = 601,200$, $M_w/M_n = 1.07$, polymer source) films of thicknesses $8 \text{ nm} \leq h \leq 290 \text{ nm}$ were spincast onto Si(100) substrates. The PS films were annealed under vacuum at 403 K [$T_g(\text{bulk}) = 369 \pm 1 \text{ K}$]

for 8 h, allowed to cool to room temperature, and then placed on a Linkam hotstage and mounted to the ellipsometer. The films were then heated to 403 K, allowed to thermally equilibrate, and then cooled to 313 K at 1 K min^{-1} . Ellipsometric measurements of the glass transition temperature (T_g) were performed using an Exacta 2000 nulling ellipsometer (Waterloo Digital Electronics) with a laser wavelength of 633 nm and an incident angle of $60.0 \pm 0.1^\circ$. The ellipsometric angles P and A were recorded during cooling. For many sample configurations (as in the present study), inversion of the ellipsometric data is not necessary and plots of P and/or A vs temperature can be used to determine the T_g of the polymer films [6]. The data can then be analyzed by using two straight line constructions or by calculating the numerical derivatives dA/dT and dP/dT [14]. Both techniques give similar values for T_g (see inset of Fig. 1). Ellipsometry has been used extensively in the literature to measure T_g values [6,14] that agree with data obtained from dielectric relaxation measurements [15,16]. In all data sets in the present study, the T_g values obtained with the P and A data agreed within the quoted uncertainty. Measurements of the T_g were also performed on PS films that had been coated with a 5 nm thick, thermally evaporated layer of aluminium (Al) and on PS films coated with a 5 nm thick evaporated gold (Au) layer. These samples had been annealed under vacuum at 403 K for 8 h and allowed to cool to room temperature before the metal layer was evaporated on to the PS films. The thermal evaporation of the metal capping layers was performed at an ambient pressure of 8×10^{-6} torr. Low evaporation rates (0.5 nm s^{-1} for Au and 3 nm s^{-1} for Al) were used so that the thickness of the metal capping layers could be reliably reproduced. The thickness of 5 nm was chosen so that the

PS films were capped with a continuous metal layer, but also so that sufficient optical transmission through the capping layer could be achieved to perform the ellipsometric T_g measurements. Confirmation that the evaporated layers were continuous was provided by atomic force microscope images of the samples taken both before and after the T_g measurements. During the evaporation procedure, a 40 awg thermocouple was suspended in the evacuated evaporation chamber. The maximum temperature of the thermocouple samples during the evaporation was 350 K.

Effects due to the evaporation procedure were isolated from those intrinsic to covering the free surface by using a novel sample configuration. These samples comprised of two films of similar thickness that had been placed with their free surfaces in contact and annealed. The first film (of thickness $h/2$) was spin coated directly onto a Si substrate. A second film of thickness $h/2$ was spin coated from the same PS solution onto a single crystal sodium chloride (NaCl) optical window (Alfa Aesar) that had been coated with a 5 nm thick thermally evaporated Al layer (using the evaporation rate above for Al). The PS film supported on the Al coated NaCl was then turned upside down and placed on top of the PS film supported on the Si substrate. A drop of deionized water (Milli-Q) was placed in contact with one edge of the NaCl substrate. This was done to partially dissolve the optical window. The water preferentially wetted the NaCl/Al interface and caused the PS film with thin Al layer to debond from the NaCl window. The two PS films were pulled into intimate contact by surface forces. The resulting $2(h/2)$ films of thickness h were rinsed thoroughly with deionized water to remove any residual NaCl and then annealed under vacuum at 403 K for 8 h. This procedure produced samples of high quality that had essentially the same appearance as a spincast film of the same total thickness. The T_g values of these samples was then determined. This was done for $2(h/2)$ films in the thickness range 7 to 270 nm. The effects of completely removing the Al capping layer from the $2(h/2)$ films were also considered. This was done by immersing the films in a 1M NaOH solution for 5 min. This concentration and immersion time were sufficient to completely remove a 500 nm thick evaporated Al layer from a Si substrate. After the NaOH treatment the samples were rinsed with deionized water and the T_g values measured again.

The thickness dependence of the T_g of thin supported films of PS with one free surface is shown in Fig. 1. This figure also shows data for the PS films that were evaporatively coated with metal layers. The uncapped films show depressions in T_g as the film thickness is decreased below 40 nm with a maximum measured T_g depression of 15 K for an 8 nm thick film. The Au capped films are shown to have a bulk T_g of $370 \pm 1 \text{ K}$, and this value persists for all film thicknesses $\geq 8 \text{ nm}$. Coating the PS films with an evaporated Au layer in this way is

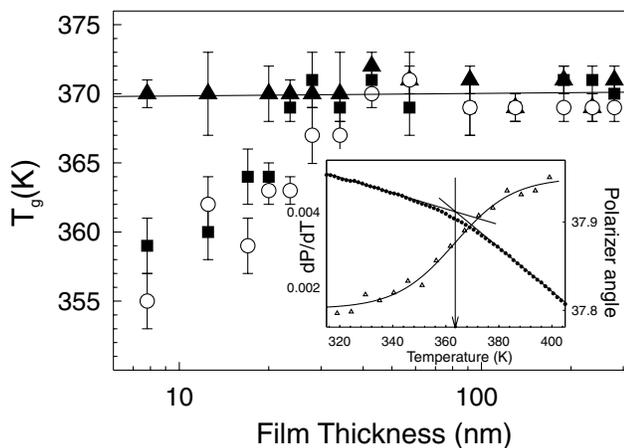


FIG. 1. Glass transition temperature (T_g) in PS films for simple supported films (O), PS films coated with a 5 nm evaporative Au layer (▲), and PS films that have been coated (evaporatively) with a 5 nm layer of Al (■). The inset shows raw ellipsometric data (●) as well as the temperature derivative (Δ) for an uncapped film of thickness 12.5 nm.

expected to remove the effects of the free polymer surface and to give rise to bulklike behavior even for the thinnest films studied. The PS films with evaporated Al coatings have T_g values essentially the same as those of uncapped films. This has also been observed by Fukao *et al.* [13]. The differences between the thickness dependence of the T_g values of PS films with different evaporated metal coatings is unexpected and warrants further discussion.

As mentioned above, capping the PS films with a metal layer is expected to suppress the film thickness dependence of the T_g . This is clearly not the case for the Al capped films. One reason for this could arise from differences in the interfacial properties of the two metal-polymer interfaces studied. Studies [17,18] have shown that the structure of metal-polymer interfaces depends upon the choice of metal used during thermal evaporation. In systems where the metal-polymer interaction is relatively weak (such as gold/polyimides and gold/polycarbonates), the width of the polymer-metal interface is much broader (typically tens of nanometers) than the interface between more reactive metals such as Al and the same polymers [17,18]. Strunskus *et al.* have suggested [18] that, as a result of the evaporation procedure, the metal capping layer and polymer film are not in perfect contact and that the mismatch in expansion coefficients of the polymer and metal capping layer can give rise to mechanical failure during the heating provided by evaporation. In the case of Al capped films [17], this could cause the bilayer to partially delaminate. Such a mechanism provides a *possible* explanation for why the measured T_g in the Al capped PS films are similar to those measured for uncapped films. The broader interfaces for Au capped PS films [19] are expected to be more resistant to this mode of failure. However, regardless of whether or not the above mechanism occurs and is responsible for the differences in the measured T_g in the present study, it highlights some of the frequently discussed difficulties associated with the use of evaporated coatings to cover the free surface. More importantly, it suggests that such a process is not ideally suited to quantify the effect that free surfaces have upon the T_g of thin polymer films. To circumvent this difficulty, we consider Al capped films that have been prepared in such a way as to remove (as much as possible) the effects of the free surface. This is done by preparing a series of $2(h/2)$ films as described above. Annealing the $2(h/2)$ films should cause the interface between the two films to broaden and after annealing give rise to bulk properties at the center of the resulting composite films. The annealing temperature and times used in these experiments have been shown to result in a broadening of the initially sharp interface between two PS films of similar molecular weights of between 5 and 8 nm [20–22]. This method of sample preparation also ensures that the top surface of the $2(h/2)$ samples has been in intimate contact with the capping layer during the

spin coating process and removes any density defect at this top interface.

Figure 2 shows the thickness dependent T_g data for the $2(h/2)$ films. This plot shows that the $2(h/2)$ films have a bulk T_g value of 370 ± 1 K and that there are no significant changes in the measured T_g as the film thickness is decreased, for films as thin as 7 nm. The results show convincingly that it is possible to suppress the film thickness dependence of the T_g in Al capped films by preparing the samples in such a way that they do not have any free surfaces. This lends strong support to the idea that the existence of a free surface is crucial to the existence of reduced T_g values in thin PS films. To illustrate that the NaCl is not responsible for suppressing the thickness dependence of the T_g , measurements were performed on uncapped PS films that had been immersed in saturated NaCl solutions for 4 h. For all the film thickness studied, the measured T_g values were the same as those measured for the uncapped PS films of the same thickness. To determine whether or not removing the capping layer (and restoring the free surface) restores the reduced T_g values that are characteristic of uncapped PS films, the Al layer was chemically removed from the $2(h/2)$ films using the technique described above. The circles in Fig. 2 are the measured T_g values of the *same* $2(h/2)$ films used for the measurements represented by the diamonds *after* the Al coating has been removed. In order to separately quantify the effects of the NaOH solution and show that it is the reintroduction of the free surface that is most important, a number of uncapped PS films over the entire range of thickness were immersed in 1M NaOH and the resulting T_g measured. This test confirmed that immersing samples in a NaOH solution has no effect on the T_g of uncapped films. The measurements shown in Figs. 1 and 2 demonstrate that covering the free surface suppresses T_g reductions and subsequently removing the

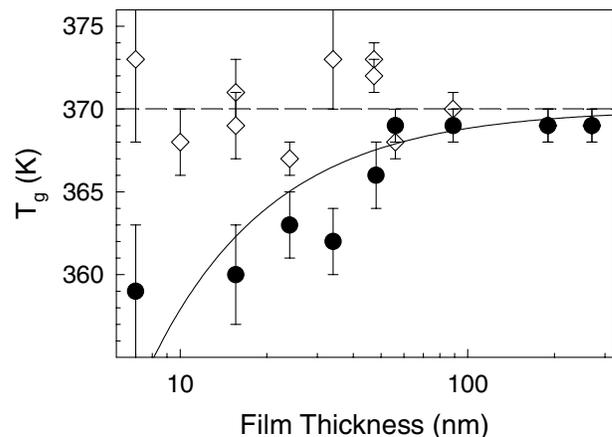


FIG. 2. T_g values for the $2(h/2)$ films (see text) before (\diamond) and after (\bullet) removal of the Al capping layer. The solid line describes the thickness dependence of the T_g in thin PS films obtained for the uncapped PS films in Fig. 1.

coating restores the T_g reductions. This series of measurements provides compelling evidence that it is the existence of free surfaces that results in T_g reductions in thin PS films. It is important to note that these measurements of the glass transition are indirect measures of the dynamics on fairly long time scales (cooling rate ~ 0.02 K/s). Such effects do not imply that the dynamics at other time scales will necessarily be similarly affected in thin films. In fact thin films of *i*-poly(methyl methacrylate) show lower T_g values but no anomalous dynamics on shorter time scales [15,16]. A lack of film thickness dependence of fast dynamics in PS has also been recently reported by Efremov *et al.* [23]. Those studies use calorimetric measurements at cooling rates $\sim 10^3$ K/s to reveal no film thickness dependence of the high frequency calorimetric glass transition for films as thin as 3 nm. The difference between the present studies, and those of Ref. [23] should be viewed as an example of the complicated dependence of confinement effects on the time scales probed by the experiments rather than as a contradiction between the two studies.

The data for the $2(h/2)$ films can also be used to address some of the issues concerning the origin of T_g reductions. Thin polymer films have a tortuous sample preparation history and are not in equilibrium. Vitrification upon solvent removal followed by continuing solvent evaporation results in significant in-plane stress as well as a lower density than bulk samples. Even though the samples are vigorously annealed, it is not clear that such annealing is sufficient. The observed T_g reductions could therefore arise as a result of this preparation history. Such concerns are addressed by the measurements on the $2(h/2)$ films. In making the $2(h/2)$ films, the intermediate stage involves two samples of thickness $h/2$. It is clear from Fig. 2 that, for $h < 40$ nm, each of the $h/2$ films (measurably shown in Fig. 2) has a reduced T_g value. If this reduced T_g value were due to sample formation history, then the formation and subsequent annealing of the $2(h/2)$ composite sample would not remove the preparation history any more than annealing the single $h/2$ sample. The fact that $2(h/2)$ samples do not exhibit T_g reductions provides a strong argument against the specific process of spincasting the film out of a solvent as a cause for the observed T_g reductions.

In summary, we have considered the effects of thin metal capping layers upon the glass transition temperature of thin spincast polystyrene (PS) films supported on Si substrates and show that the results obtained depend upon the choice of evaporated metal. Measurements performed on samples that are prepared by placing two films with their free surfaces in contact and annealing them reveal bulk T_g values for all film thicknesses studied.

Subsequent removal of the Al capping layer restores the T_g reductions that are characteristic of simple uncapped films. These experiments provide clear evidence that the free surface is important in determining the T_g in thin PS films and, by preparing the samples in this way, it is possible to remove the effects of the free surface and recover bulklike behavior.

We gratefully acknowledge the Natural Sciences and Engineering Research Council (NSERC) of Canada, and the province of Ontario (PREA program) for financial support of this work.

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