Reduced Glass Transition Temperatures in Thin Polymer Films: Surface Effect or Artifact?

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We have examined the direct effect of manipulating the number of free surfaces on the measured glass transition temperature T_g of thin polystyrene films. Thin films in the range $35\ \mathrm{nm} < h < 114\ \mathrm{nm}$ with molecular weights of 592 kg/mol and 1144 kg/mol were studied. Ellipsometry was used to determine the temperature dependence of the thickness and refractive index of freestanding films. By noting the change in slope in each of these quantities, a T_g value can be assigned in quantitative agreement with previously reported results. For thin freestanding films this value is reduced from that of the bulk. The exact same films are then transferred to a Si substrate and the T_g of the resulting supported film was determined. The T_g values of the now supported films are the same as the bulk value and the same as previous reports of similar supported films. These experiments unambiguously show that free interfaces are the dominant cause of the T_g reductions for the film thicknesses studied.

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A general theory of glass formation remains elusive even as glassy materials find widespread use in emerging areas such as nanotechnology. The persistent idea of a length scale associated with the glass transition suggests a possibility for anomalous behavior for samples approaching that size (~ 1–10 nm). This possibility contributes to a significant and continuing interest in the properties of nanoscale glassy materials [1,2].

While in principle systems of interest can encompass a broad range of materials, including molecular and even metallic glasses, most of the existing studies have focused on thin polymer films [2–19], though there have been some studies on different confinement geometries [20,21]. The main reason for this emphasis is that thin polymer films are easy to prepare, characterize, and measure. Ease of measurement is true even in the melt state due to the metastability provided by the use of long chains. The metastability allows the study of unstable thin liquid films as long as the measurement can be performed on a time frame shorter than that of the flow of the polymer chains.

Keddie, Jones, and Cory [3] first demonstrated that thin polystyrene (PS) films with $h \lesssim 40$ nm have measured glass transition temperatures T_g that are reduced below the bulk value. Since this seminal study, the past two decades have witnessed a surge of T_g measurements with largely similar conclusions. The original suggestion that the reductions in T_g are strongly related to the presence of the free surface has been supported by the much larger T_g reductions measured in freestanding films (a thin membrane with twice the free surface area-to-volume ratio compared to a supported film). This relation was strengthened considerably by the observation of a quantitative mapping between supported films of thickness h and freestanding films of thickness $2h$ [4].

Despite the consensus amongst many measurements, a key fundamental question has persisted in the literature regarding the contribution of sample preparation to the measured T_g values. Spin-cast polymer films are affected by solvent presence, chain configurations far from equilibrium, and potentially large stresses. Not only can these effects provide possible alternative explanations to lower measured T_g values in thin films [14,15] but may also be very difficult to remove within conventional annealing times and temperatures [22,23].

It has become increasingly evident that it is necessary to provide a distinction between reductions in T_g that can be removed by sufficient annealing and those that are an intrinsic property of the sample geometry and dimensions. Some simulations have been interpreted as consistent with reductions in the glass transition for thin films (see, for example, [11]); by design such studies are free of artifacts resulting from sample preparation. Experimentally, an important and potentially straightforward example of an intrinsic effect is one caused by the free surface. Studies comparing the measured T_g values in capped (no free surface) and supported (one free surface) PS films demonstrated that T_g reductions could be modified by manipulating the number of free surfaces from zero to one without requiring any additional annealing [10]. The strength of the conclusions that can be drawn by that work are diminished because the magnitude of T_g reductions are quite small. As we will show here, a much stronger conclusion would result from a study involving freestanding films. This sample geometry provides an ability to change the number of free surfaces from two to one, and in doing so the apparent T_g value changes by many 10s of degrees. A further advantage of changing a freestanding film to a supported one is that any observed difference between the two does not depend on how the film was prepared. This approach alleviates concerns raised about the validity of glass transition reductions [14,15]. Simply put, if a sample with two free surfaces exhibits a large reduction in the glass transition, and that reduction disappears when one of those free surfaces is covered, then the intrinsic effect of interfaces must dominate sample preparation artifacts.

Polymer film thicknesses ranging from 35 to 114 nm were prepared by spin-casting polystyrene (Polymer Source, Canada) from filtered toluene (Optima, Fisher Scientific, USA) solutions onto freshly cleaved mica substrates. Two different monodisperse molecular weights of PS were used with $M_w = 592$ kg/mol and 1144 kg/mol, which will be referred to as PS(592) and PS(1144) (the polydispersity index for both was 1.09). The PS films were preannealed on mica for 24 hours at 130 °C in vacuum ($\sim 10^{-5}$ mbar provided by a turbo molecular pump). Subsequently, films were floated onto a purified water surface (18.2 MΩ cm, Cascada, Pall, USA) and picked up by a stainless steel washer [24]. Sample preparation was performed in a laminar flow bench to reduce dust. Small wrinkles appearing in the freestanding film after transfer from the water surface are removed by annealing the films for several minutes on a heating stage (Linkam, UK) near the bulk glass transition temperature of PS. Once the wrinkles have been entirely removed, samples are cooled to room temperature at a rate of 1 °C/ min. After measurements were performed on the freestanding films with ellipsometry, the samples were transferred to Si substrates with a native oxide layer present (University Wafer, US). The Si substrates were cleaned prior to transfer by rinsing in purified water, methanol, and toluene.

Ellipsometry probes changes in the polarization state of light interacting with a sample [25]. The glass transition temperature was determined using a high precision homebuilt nulling ellipsometer, which measures the angle of two polarizers, called the polarizer P and the analyzer A [12]. P and A can be related to the film thickness h and the index of refraction n assuming some model for the sample properties and using the fundamental equations of ellipsometry [25]. By measuring the ellipsometric angles as a function of temperature and relating these to $h(T)$ and $n(T)$, T_g can then be obtained as the point that separates the glassy and melt expansion of the film [3,6,12,16].

Films supported on a Si substrate were measured in the reflection mode of the ellipsometer, whereas freestanding films were studied in transmission mode [6,16]. For the measurements reported a heater cell was constructed that can be used in both configurations to ensure that supported and freestanding films are measured in identical sample environments. Fixed angles of incidence of either 45° or 58° were chosen. The typical instrumental precision for P and A measurements was ±0.0002°.

The values for P and A were recorded as a function of the sample temperature T upon heating or cooling with a typical rate of 1 °C/ min (some experiments were also performed at slower ramping rates for testing reproducibility of measurements). The freestanding films were modeled assuming a homogeneous, nonabsorbing dielectric medium of thickness h and index of refraction n between two air interfaces. The h and n are free parameters in the model. The film thickness and the index of refraction of supported polymer films were modeled as a homogenous film (as in the freestanding case) supported on a Si substrate with a native oxide layer. The thickness of the native Si oxide layer and the dielectric parameters of the Si and its oxide were obtained with independent ellipsometry measurements and kept constant. The precision of these measurements is much better than the absolute accuracy, which can be affected by instrumental factors [25] as well as uncertainty in the angle of incidence.

Figure 1(a) illustrates a typical measurement of $P(T)$ and $A(T)$ obtained upon cooling of a freestanding PS film (raw data, no smoothing). The corresponding values of the film thickness $h(T)$ and of the index of refraction $n(T)$ are

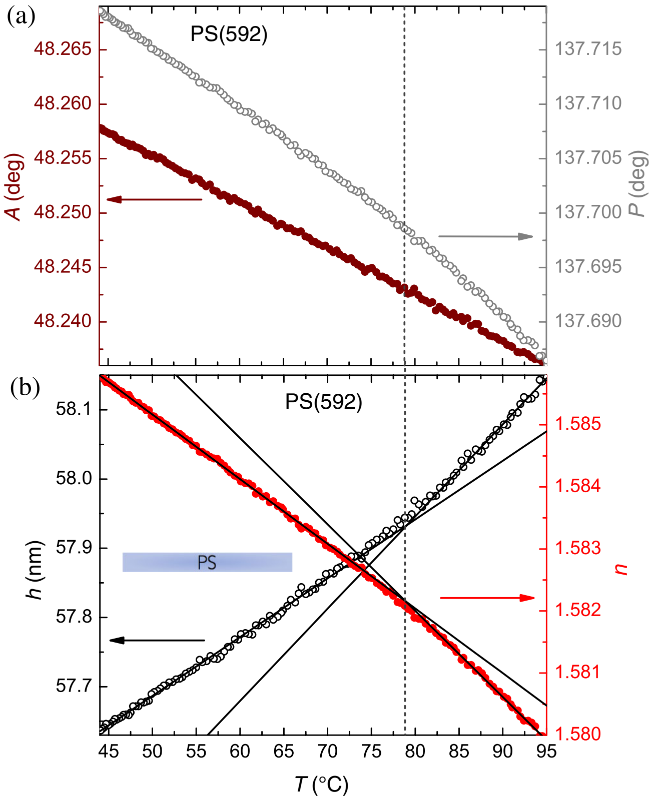

FIG. 1 (color online). Freestanding film: (a) the ellipsometric angles, P and A, and (b) the film thickness h and index of refraction n of a thin freestanding PS(592) film as a function of the sample temperature T. Straight lines represent best fits to the data.

shown in Fig. 1(b). With increasing temperature the polymer film thickness increases and the index of refraction decreases due to thermal expansion. Two linear regimes for each of the curves for h and n can be identified in Fig. 1(b), with an intersection of these lines at ~78 °C. These linear regions have different slopes corresponding to the different thermal expansion coefficients in the glass and melt state. The same transition is easily observed in the raw data for $P(T)$. At this angle of incidence, $A(T)$ is less sensitive due to the complex nonlinear relationship with $h(T)$ and $n(T)$ [25]. This PS(592) film with $h = 58$ nm has a T_g that is reduced from that of the bulk value of ~98 °C. Similar experiments were performed on a range of different film thicknesses for both molecular weights used here. During such measurements it was typically the case that upon heating from room temperature for the first time the data was often less reliable. Reproducible T_g values were obtained in subsequent heating and cooling cycles [6].

After the measurements of T_g were performed on freestanding films, the same films were transferred to Si wafers. The stainless steel washer with the film was placed on top of the Si substrate so that contact was made between the film and substrate. The washer could then be removed leaving the formerly freestanding film on the substrate for subsequent ellipsometry measurement. In Fig. 2 is shown a T_g measurement of *the same* PS(592) film that was studied as a freestanding film in Fig. 1. We note that the measured glass transition temperature T_g of the transferred (supported) film is now in agreement with that of the bulk $T_g \sim 98$ °C.

When comparing Fig. 1 and Fig. 2 the glass transition shifts by about 20 °C simply by covering one of the free surfaces and changing the free surface area-to-volume ratio by a factor of 2. In particular we stress that no long-time high-temperature annealing and no further treatment is required to induce this striking change in the measured T_g value. Interestingly, the freshly supported films show greater curvature in $h(T)$ through the first heating run at temperatures well below T_g. However, upon approaching T_g, linearity in $h(T)$ and $n(T)$ is recovered and reliable T_g values could be obtained even upon the first ramp to $T \sim 120$ °C. Subsequent cooling and repeated measurement cycles all show reproducible data of the quality shown in Fig. 2. The history of the freestanding state, and the associated reduced glass transition, is erased by manipulating the free interface and the heating required in preparation for the first cooling experiment.

We note that the contrast in the slope of the glass and melt region for the freestanding and supported cases is different. Directly comparing such contrasts has to be done with care due to the different boundary conditions of a supported and freestanding film. For example, a supported film can only expand in the film-normal direction, while expansion in a freestanding film can occur in all directions. Notwithstanding this caveat, for the freestanding film in Fig. 1 we measure a contrast of 1.57 while the transferred film has a contrast of 2.23 when supported (see Fig. 2). This trend is observed in all cases and we find that the reduced glass transitions of films with two free interfaces are characterized by a slope-melt contrast of 1.4 ± 0.3 and for the supported films the contrast is 2.8 ± 0.4. The low contrast in the reduced transitions in freestanding films could signify that this transition is not the only (or even main) structural relaxation of the polymer films, an observation that is consistent with those made by Pye and Roth [16]. We further note that the width of the bulklike glass transitions observed for the transferred films is consistent with previous measurements [5–7].

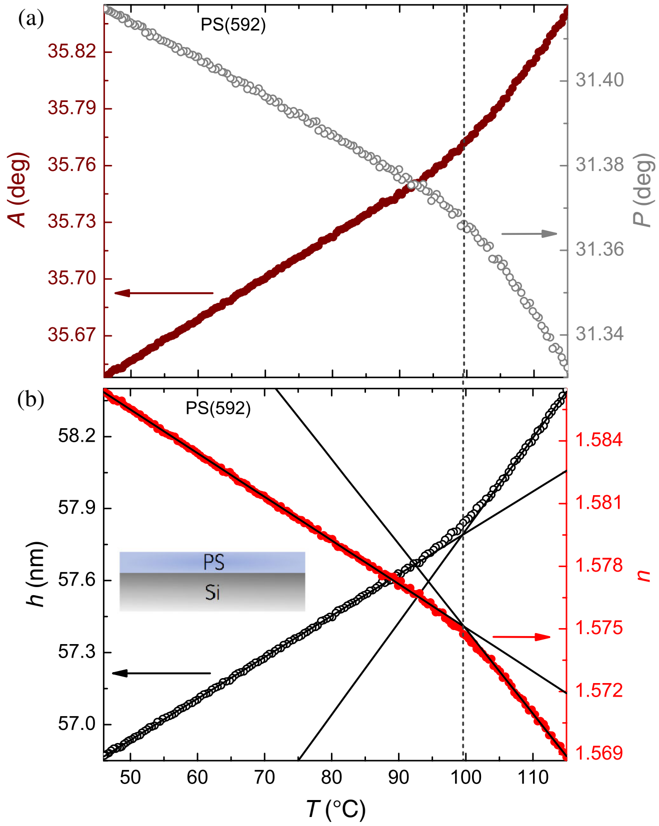

FIG. 2 (color online). Supported film: (a) the ellipsometric angles, P and A, and (b) the film thickness h and index of refraction n as a function of the sample temperature T for the same PS(592) film shown in Fig. 1 after transfer to a Si substrate. Straight lines represent best fits to the data.

The results of all T_g measurements before (freestanding) and after transfer (supported) to the Si substrates are summarized in Fig. 3. For the freestanding films of PS(592) and PS(1144), a linear reduction of the glass transition temperature T_g is found with decreasing film thickness. The values obtained are in excellent agreement with the molecular weight dependence for freestanding films reported in earlier studies [5,6] (note that the dashed lines shown in Fig. 3 are not fits to the data, but obtained from the equations given in [6]). After transferring the freestanding PS films to the Si substrate, all glass transition temperatures

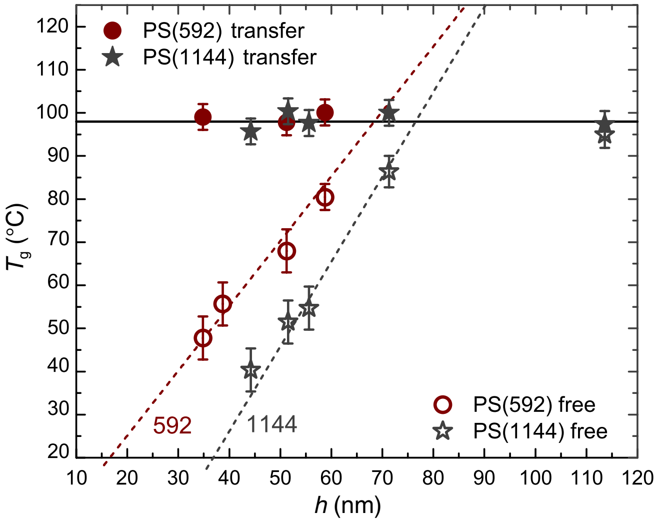

FIG. 3 (color online). Glass transition temperature T_g as a function of the film thickness h. Dashed lines represent the molecular weight dependence of T_g for the high-M_w regime as reported in [6] [see Eqs. (3) and (4) and associated parameters given in [6]]. The solid horizontal line corresponds to the bulk value of the glass transition as measured previously (for example, see [5–7]).

for film thicknesses between 35 nm and 71 nm shift to higher values. The results for this film thickness range are in excellent agreement with previous supported film measurements and are consistent with the bulk T_g (see solid line in Fig. 3 and [5–7]). The control measurement at $h = 114$ nm indicates that glass transition temperatures prior to and after transfer are identical within experimental error and are consistent with the bulk value of T_g.

There has been much discussion about nonequilibrium metastable states in thin films and the possibility that these might account for the reductions in the glass transition. For example, it has been found that the sample preparation can affect relaxation mechanisms and instabilities inducing flow [22,23]. Clearly if the large length scale molecular motion associated with flow is affected, then the glass transition may also be. More directly related to the glass transition studies presented here, it has been suggested that the T_g reductions observed are simply a result of artifacts induced by an inadequate duration of, or inappropriate atmosphere during, annealing [14,15]. Unfortunately those claims have not been substantiated with accompanying measurements showing that it is possible to observe reductions in the glass transition with the sample treatments used by others.

The claim that the sample preparation artifacts are the cause of reductions in the glass transition for films of PS has been disputed by researchers [12,17]. Much controversy still remains as does the fundamental question "Are the reductions in the glass transition dominated by an intrinsic physical effect or an artifact of sample preparation?" Here we have provided a simple experiment to probe whether or not we can manipulate the sample independent of extra annealing and cause large changes in the measured T_g. We find that the simple transfer of a freestanding film to a substrate, thereby reducing the free surface-to-volume ratio by a factor of two, can cause a 50 °C shift in T_g. Since this change in T_g is the same as the reduction in thin supported films (i.e., transferring to a solid surface restored bulk T_g for these film thicknesses rather than giving rise to a sample that still had a reduced T_g value), these experiments unambiguously show that free interfaces are the dominant cause of the T_g reductions observed here. The experiments presented in this Letter, combined with the previous results of Ref. [10] represent a complete quantification of the effect of zero, one, or two free surfaces on measured T_g values and rule out a dominant contribution due to sample preparation.

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