Effect of atmosphere on reductions in the glass transition of thin polystyrene films

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Abstract. We have used nulling ellipsometry to measure the glass transition temperature, T_g, of thin films of polystyrene in ambient, dry nitrogen, and vacuum environments. For all environments, the measured T_g values decrease with decreasing film thickness in a way that is quantitatively similar to previously reported studies in ambient conditions. These results provide strong reinforcement of previous conclusions that such reduced T_g values are an intrinsic property of the confined material. Furthermore, the results are in contrast to recent reports which suggest that the T_g reductions measured by many researchers are the results of artifacts (*i.e.* degradation of the polymer due to annealing in ambient conditions, or moisture content).

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The value of the glass transition temperature, T_g, and in particular how it is affected by film thickness, type of polymer, and substrate has been a subject of significant discussion because of the importance of thin polymer films. Since the first observations of reduced glass transitions in thin films of polystyrene (PS) by Keddie and coworkers [1], there have been many other experimental results (using a variety of techniques) that have measured T_g values less than that of the bulk polymer [2–4]. Despite the considerable experimental evidence for lower T_g values in thin films of PS, there are contradictory reports that must be considered for a complete understanding. In particular, recent concerns have been raised about the possibility of polymer chain scission due to annealing in air [5], the effect of water adsorption [6], and disagreements with other measures of the glass transition, in particular dynamical dielectric and calorimetric measurements [7]. In this work we present a study of the T_g value in thin PS films measured with ellipsometry. We consider films held in ambient air, dry nitrogen, and vacuum, and find that the measurements under these conditions all agree quantitatively with each other, and with the range of previous reports of T_g reductions in thin PS films. These results lead to a strong reinforcement of previous conclusions regarding reduced T_g values in thin PS films.

Films of monodisperse (polydisperity index of 1.07) high molecular weight ($M_w = 734$ kg/mol) polystyrene (Polymer Source, Canada) were spincast out of toluene solutions onto cleaned silicon with the native oxide. The Si substrates were cleaned by successive rinsing with Milli-Q water, methanol, and toluene. Prior to the solvent rinses, some of the substrates were additionally cleaned with super-critical CO_2 (Snow Jet, Applied Surface Technologies) and UV-Ozone in order to remove surface contaminants and residual organics. These additional steps did not cause any appreciable difference in the T_g values measured for the films.

Multiple annealing methods were also used. Some samples were placed in a vacuum oven and annealed at 423 K for 1 hour, and slowly cooled in vacuum overnight (< 1 K/min). Films were removed from vacuum one at a time for ellipsometry measurement while the remainder of the films were returned to vacuum. In other cases samples were annealed *in situ* on the ellipsometer's heating stage in a nitrogen atmosphere or in vacuum at 423 K for 1 hour, and then cooled at 1 K/min. No observable dependence upon type of annealing was seen. Note that all vacuum, for both annealing and measurement, was provided by a turbo molecular pump (clean and oil-free vacuum) at less than $\sim 10^{-4}$ mbar at the sample. It is important to note that this annealing is at higher temperatures than most T_g confinement studies.

Ellipsometry is one of the most common techniques used to measure T_g in thin polymer films, and this tool has been described in depth [8]. In short, ellipsometry mea-

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sures the ellipticity induced in the polarization of light upon reflection from a sample. There are many variations of ellipsometry and here we utilize a home-built self-nulling ellipsometer operating at 632 nm. In this type of instrument two linear polarizers, denoted the polarizer and analyzer, are rotated to angles P and A, such that a null light intensity is observed at the detector. The ellipsometric angles, P and A, are related to the ellipticity of the light. For the simple geometry of an isotropic film on a substrate it is straightforward to calculate the index of refraction, n, and the film thickness, h, from P and A. The film thicknesses provided here are all obtained from ellipsometry and atomic force microscopy (AFM). Small changes in the thickness and index of refraction can be shown to be linearly related to the angles P and A. Since h and n vary with the change in density as a function of temperature, $P(T)$ and $A(T)$ exhibit a "kink" at T_{g}.

The samples were mounted within a sample stage which enables the control of the temperature and atmosphere (air, nitrogen, and vacuum). Ellipsometry measurements were carried out while the temperature was cycled many times, heating to ~ 403 K and cooling below the glass transition at 1 K/min. By collecting multiple runs, we could ensure that the measurement signal was not changing due to sample changes such as solvent removal, degradation, or appreciable surface roughening or dewetting. Furthermore, the thinnest sample investigated was analyzed by AFM and showed no measurable roughening after many temperature cycles in both vacuum and air. All measurements presented here were obtained upon cooling.

Analysis was performed by fitting to

$$y = w\frac{M-G}{2}\ln\left[\cosh\left(\frac{T-T_{\mathrm{g}}}{w}\right)\right] + (T-T_{\mathrm{g}})\frac{M+G}{2} + C, \tag{1}$$

where M and G are the slopes of quantities varying linearly with the density (i.e. P, A, h, and n) in the melt and glass region, T_{g} is at the position of the kink, w is the width of the transition region (fixed to 5 K), and C is the value of y at the kink [2]. Note that fitting to equation (1), is essentially the same as the derivative technique employed by Efremov and coworkers [6], since the starting point is the assumption of a sigmoidal profile for the thermal expansivity. A common alternative approach is to fit lines to the glassy and melt regions of the data, with the intersection providing T_{g}. In samples where both types of analysis could be performed the resulting T_{g} values agreed to within experimental uncertainty. In Figure 1 we show a typical plot of the analyzer angle A as a function of T. From such data T_{g} was obtained for films ranging in thickness from $h \sim 6$ nm to $h \sim 124$ nm in various atmospheres as shown in Figure 2. Values of the glass transition were fit to the empirical equation first proposed in [1]

$$T_{\mathrm{g}}(h) = T_{\mathrm{g,bulk}}\left[1 - \left(\frac{a}{h}\right)^{\delta}\right], \tag{2}$$

where $T_{\mathrm{g,bulk}}$ is the glass transition temperature in bulk samples. The best fit was obtained with the parameters $T_{\mathrm{g,bulk}} = 372 \pm 2$ K, $a = 1.86 \pm 0.24$ nm, and $\delta = 1.7 \pm 0.2$.
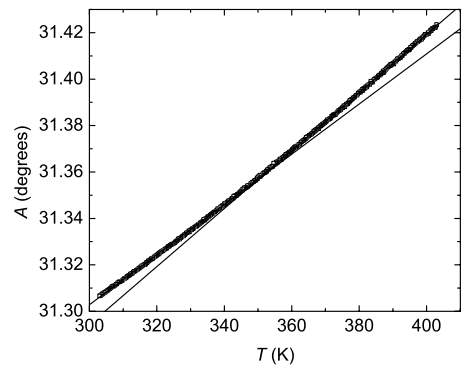

Fig. 1. Ellipsometer analyzer angle as a function of temperature for an 8.5 nm thick film upon cooling at 1 K/min from 403 K in air. The lines are fit to the data, resulting in a glass transition temperature of ~ 350 K.
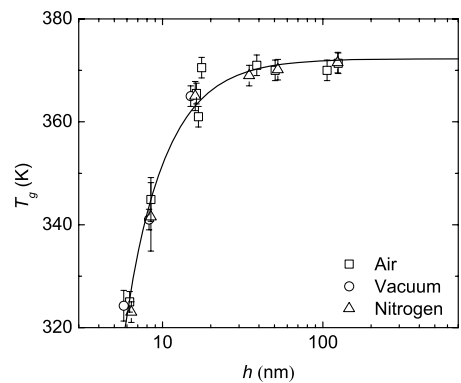

Fig. 2. The glass transition temperature *vs.* film thickness. Films have been annealed on silicon (with native oxide) substrates. Values were obtained upon cooling at 1 K/min in various atmospheres. The error bars represent the uncertainty in fits to equation (1) or intersection point of lines drawn as well as the variation over many repeated heating and cooling cycles. The solid line is the experimental fit to equation (2).

The data in Figure 2 can be compared with previous measurements of T_{g} values in thin PS films. Perhaps the most obvious comparison is with the previous compilations of such results [2–4] and the agreement in this case is excellent. We note that the parameters obtained from the fit to equation (2) are consistent with the data of a large number of research groups presented in Figure 1 of [2]. It is also important to compare to studies that have not led to the same conclusions as the majority of the studies. In the work by Serghei and co-workers there is an observation of enhanced mobility due to annealing in air [5]. The authors infer that a similar effect could be at least partially responsible for the observed T_{g} reductions. Clearly this inference is not supported by the data in Figure 2. Dilatometric measurements of the glass transition, such as those obtained with ellipsometry, are often compared directly to dynamical glass transition measurements. Measurements of the dynamical glass transition in PS at a frequency of 380 Hz show no reduction for films as thin as 12 nm [7]. While not noted in reference [7], a

very likely explanation for this apparent contradiction has already been presented in the literature [9]. Previous ellipsometric studies of T_g in PS films at different cooling rates have suggested that frequencies even smaller than 1 Hz may be required in dynamical measurements before one would expect to see such effects. The T_g values in Figure 2 do not show appreciable reductions until the film thickness is decreased to ~ 15 nm. The similarity between the results presented here and in reference [7] at a frequency of 380 Hz, makes it difficult to imagine that any contradiction exists. We note that there is a large spread in T_g values reported for PS on thin films, and especially on the onset of T_g reductions. Extension of the dynamical measurements to smaller film thickness, and 2 orders of magnitude lower frequency, would be required before a credible claim of contradiction could be made. Finally, we note that in the temperature cycling leading to the T_g values, we did not observe any effects attributable to water adsorption/desorption such as those discussed by Efremov and co-workers [6].

In conclusion, we have shown that reduced T_g values as measured in thin supported films of PS are the same whether the film is measured in ambient conditions, dry nitrogen, or vacuum. These results reinforce previous conclusions and suggest that such T_g reductions are an intrinsic property of the confined material rather than an experimental artifact. Comparisons to other experiments where conflicting conclusions were drawn regarding thin film T_g values were shown to not lead to any contradictions as long as reasonably direct comparisons are made.

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