

## Influence of an impenetrable interface on a polymer glass-transition temperature

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The thermal expansion of polystyrene thin films, supported on hydrogen-terminated silicon substrates, is measured by x-ray reflectivity. Films on the order of 400 Å and thinner show no glass transition up to at least 60 °C above the bulk glass-transition temperature, while a break in the thickness versus temperature curve, signaling the glass transition and the onset of bulk behavior, is observed for thicker films. This increase in the glass-transition temperature is in contrast to similar studies on the silicon native-oxide surface where a decrease in the glass-transition temperature is observed. This illustrates the importance of the character of the substrate surface in determining thin film behavior.

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The technological drive to place into service ever-thinner polymer films cast onto solid substrates has advanced beyond the current level of fundamental scientific understanding [1]. In applications such as adhesion, dielectric isolation, and lubrication, successful performance can depend critically on the details of thin film behavior [2]. In general, the constraints imposed by the thin film geometry perturb both thermodynamic and kinetic properties from their bulk values. This has been confirmed through a wide variety of studies, most notably from dewetting experiments [3–5].

Both theory [6] and computer simulation [7] suggest that the effects of the solid substrate, specifically on the polymer density, extend only several polymer repeat units (i.e., tens of angstroms) away from the interface. However, it is difficult to include the true long-range effects of chain connectivity in such calculations. Recent experiments show that chain connectivity extends the influence of the surface much farther into the bulk than a few segment lengths. A recent study by Hu and Granick [8] on confined poly(phenylmethylsiloxane) melts shows that the effect of the substrate on the polymer viscoelastic properties extends to five or six times the radius of gyration away from a solid wall. Several different studies have been made on the thermal expansion and glass-transition temperature ( $T_g$ ) of thin polymer films supported on silicon as a function of initial film thickness. It was found that films as thick as several hundred angstroms can have properties substantially different from the bulk [9–12]. Although these studies encompass several different polymers, careful consideration has not been made as to the role of the substrate surface on polymer thin film thermal expansion and glass-transition properties. It has been suspected that for thin films the role of the substrate surface may have a measurable effect. This work shows that effect to be quite large.

Measurements of film thickness as a function of increasing temperature for monodisperse polystyrene on hydrogen-terminated silicon surfaces were made using x-ray reflectivity. We report here observation of a thermal expansion coefficient indicative of the glassy material for temperatures at least 60 °C above the bulk  $T_g$ . That is, for these films the  $T_g$  appears to be greatly increased. This is in sharp contrast to an apparent 30 °C decrease seen in polystyrene thin films on the silicon native-oxide surface [10]. Furthermore, in the temperature range studied, the absence of the glass transition

extends to films as thick as 400 Å indicating that surface effects extend much farther into the films than theory has predicted [6,7].

The polystyrene thin films studied had initial thicknesses between 75 and 1988 Å. The silicon substrates were prepared by first removing any organic contaminants by ultraviolet light–ozone cleaning [13]. Then the native oxide was etched away in a solution of 1% hydrofluoric acid in distilled, deionized water. To form the passivated silicon monohydride surface, the substrates were submerged in a concentrated ammonium fluoride solution [14]. After a distilled, deionized water rinse, the polystyrene ( $M_w=233\,000$  g/mol;  $M_n/M_w=1.06$ ;  $R_g^{\text{bulk}}=135$  Å) was spin coated immediately onto the substrates from toluene solution. Thickness was varied by changing the concentration of polymer in solution from 0.2 to 3.0 wt % while keeping the spin speed constant at 2000 rpm. After spin coating, the samples were placed in the vacuum system of the reflectometer where they were annealed at 130–140 °C for 2 h at  $6.7 \times 10^{-3}$  Pa and cooled at 0.5 °C per minute to room temperature.

Figure 1 shows representative x-ray reflectivity curves, as

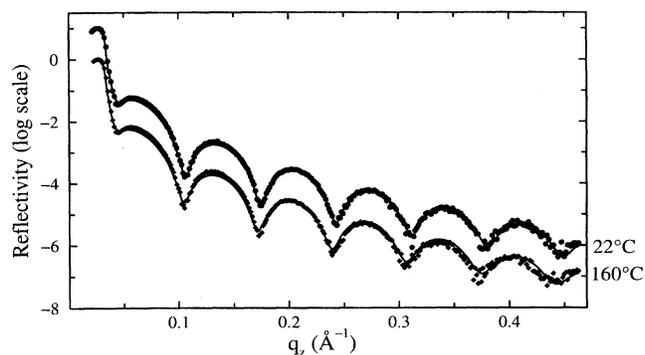


FIG. 1. Representative x-ray reflectivity curves for the 91 Å thick film. Notice that, as the temperature increases, the spacing between the minima becomes smaller indicating that the film is expanding normal to the silicon substrate. For 22 °C, the solid line fit corresponds to a thickness of 91.22 Å, while for 160 °C the fit corresponds to a thickness of 92.73 Å. (For clarity, the data for 22 °C are offset by one decade in intensity.)

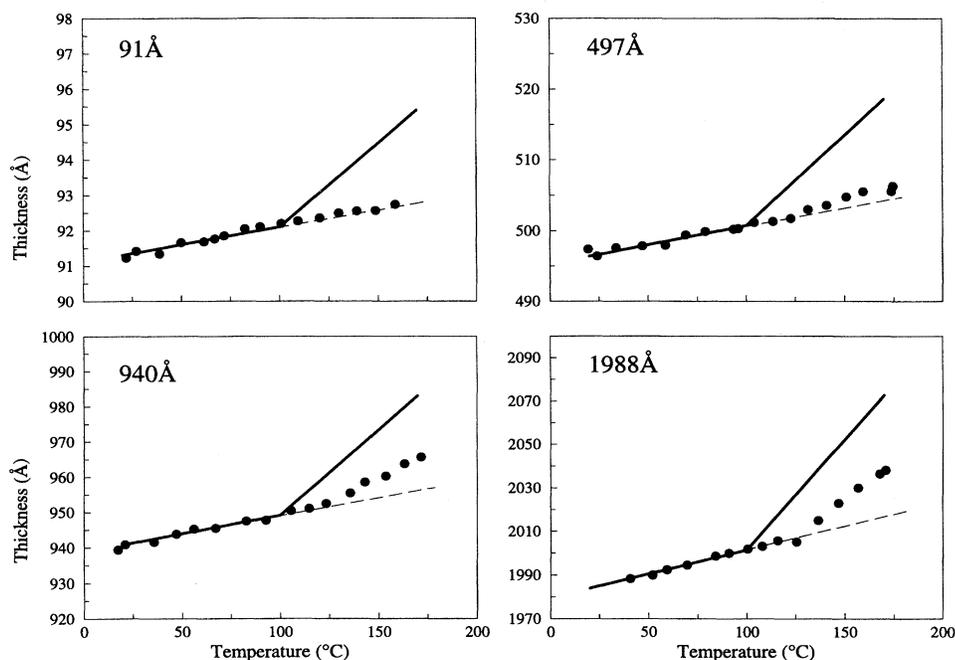


FIG. 2. Temperature versus thickness plots for four different initial film thicknesses. The solid lines correspond to predictions made solely from extrapolation from bulk behavior using Eq. (1). The break in the solid lines corresponds to the bulk glass-transition temperature of 100 °C. Uncertainty is expressed by the scatter in the data points.

well as fits to the data, for a film with an initial thickness of 91 Å taken at two temperatures. As the film expands normal to the silicon surface, the separation between the minima in the curve becomes smaller. This separation is the principal aspect that determines film thickness. Unlike ellipsometry, the film thickness determination is not convoluted with the film density through the index of refraction. Thus, x-ray reflectivity gives an unambiguous determination of thickness. The samples were heated in vacuum ( $1.3 \times 10^{-4}$  to  $6.7 \times 10^{-3}$  Pa). The temperature was increased incrementally, nominally in 10 °C steps. The samples were held for 45 min at each temperature before a reflectivity curve was measured. The time to measure a reflectivity curve was on the order of 30 min. For such a series of measurements, the effective heating rate was only a few degrees per hour.

Figure 2 shows the thermal expansion for four samples with different initial, room-temperature thicknesses. The solid lines in each figure represent the thermal expansion, as predicted from bulk properties assuming continuum linear elasticity, for a film laterally constrained along the substrate surface. For such a situation [15], the thermal expansion in the third dimension normal to the substrate,  $\alpha_N$ , is given by

$$\alpha_N = \frac{(1 + \nu)}{(1 - \nu)} \alpha_L, \quad (1)$$

where  $\nu$  represents Poisson's ratio and  $\alpha_L$  is the bulk linear coefficient of thermal expansion. For bulk polystyrene,  $T_g$  is equal to 100 °C. Below  $T_g$ ,  $\nu = 0.325$  and  $\alpha_L = 0.57 \times 10^{-4}/^\circ\text{C}$ , while above  $T_g$ ,  $\nu = 0.5$  and  $\alpha_L = 1.7 \times 10^{-4}/^\circ\text{C}$  [16]. These values give a predicted thermal expansion for a constrained film normal to its substrate of  $\alpha_N$

$= 1.1 \times 10^{-4}/^\circ\text{C}$  and  $\alpha_N = 5.1 \times 10^{-4}/^\circ\text{C}$ , above and below  $T_g$ , respectively. For comparison, the thermal expansion coefficient of the silicon substrate is two orders of magnitude smaller.

The 91 Å film, discussed previously, shows a thermal expansion indicative of the below- $T_g$  material for temperatures up to 160 °C. Thus, a film of this thickness shows below- $T_g$ , i.e., glassy, behavior up to a temperature well above the bulk  $T_g$  of 100 °C. The same results were observed for films of 190, 325, and 437 Å initial thicknesses (not shown); that is, glassy behavior up to at least 160 °C (near the temperature limit of the apparatus used). From this observation it is concluded that the glass transition in polystyrene films supported on hydrogen-terminated silicon surfaces for thickness less than about 400 Å is raised to a substantially higher temperature than found in the bulk. This is in contrast to polystyrene on the silicon native-oxide surface where a decrease in  $T_g$  of about 30 °C was observed [10].

At an initial film thickness of 497 Å there is a break in the thickness versus temperature curve at about 125 °C. Above this temperature the film expands more than projected by the glassy-state behavior, but not as much as expected for the melt state. Likewise, for initial thicknesses of 940 and 1988 Å the same break near 125 °C is seen but with the thermal expansion above this temperature more closely following the melt-state value as the initial thickness increases. This observation suggests that as the initial film thickness increases the bulk behavior is recovered, as expected. However, it might also be expected that the apparent  $T_g$  should move toward the bulk value of 100 °C for thicker films. This is difficult to determine from the results in Fig. 2 because of uncertainty in the thickness measurement and because the temperature in-

crement used, 10 °C, does not offer a sufficiently precise determination of the apparent  $T_g$ .

The thermal expansion for the films above the apparent  $T_g$  of 125 °C was fit using a simple two-layer model. The thermal expansion of the overall film was taken to be the sum of two terms: the thermal expansion of a glassy layer next to the solid substrate, whose thickness is  $A$ , and the thermal expansion of a melt layer comprising the remainder of the film.

$$\frac{1}{h} \frac{\delta h}{\delta T} = \alpha_N^{\text{glass}} \frac{A}{h} + \alpha_N^{\text{melt}} \left[ 1 - \frac{A}{h} \right]. \quad (2)$$

The coefficient of thermal expansion for the layer adjacent to the silicon substrate,  $\alpha_N^{\text{glass}}$ , is taken to be that of the film in its glassy state, i.e., below the apparent  $T_g$ . The coefficient of thermal expansion for the melt layer,  $\alpha_N^{\text{melt}}$ , as well as the thickness of the glassy layer,  $A$ , are fit to the data. The overall thickness of the film is measured experimentally, and given as  $h$ . When the above variables are fit to the measured thermal expansion above the apparent  $T_g$  (for samples that showed an apparent glass transition) it is found that  $A = 397 \text{ \AA}$  and  $\alpha_N^{\text{melt}} = 3.2 \times 10^{-4} / ^\circ\text{C}$ . The value of  $A$  recovers the approximate film thickness below which no glass transition was seen. (Recall that films thinner than this showed no break in the thickness versus temperature curve in the temperature range studied.) This reinforces the idea that this is the characteristic distance over which the substrate exerts its influence. The thermal expansion of the melt is about 60% of that predicted from Eq. (1). This may indicate that there is a gradient of thermal expansion coefficients extending through the glass/melt interface which cannot be adequately described by a two-layer model.

These results indicate that there is something fundamentally different in the region within about 400 Å of the solid surface. It has been suggested [17] that, due to chain-end segregation, the chains at the free surface possess a greater mobility, and therefore, a lower  $T_g$ , than the bulk of the material. This would lead to an overall decrease in the  $T_g$  of the thin film because many of the polymer chains would be in proximity to the free surface. Apparently this does not occur in films thinner than 400 Å, since the  $T_g$  appears to increase. In this case, the effect of the substrate appears to control the behavior of the polymer chains without regard to whether or not they are also at a free surface. This is also supported by the studies on thicker films where the data suggest that a 400 Å glassy layer was seen to

persist above the bulk  $T_g$ . Future experiments will concentrate on varying the polystyrene molecular weight to see if the range of the glassy layer depends on the radius of gyration ( $R_g$ ).

Why do two different surfaces give such dramatically different thin film glass-transition temperatures in polystyrene? We believe the answer must lie in the specific interaction between the polymer repeat unit and the substrate surface. For the hydrogen-terminated silicon surface it would appear as if the polymer were strongly attracted to the substrate. Strong adhesion would be expected to have an effect similar to that of cross-linking on bulk specimens where it inhibits the chains from attaining the entropy necessary to reach the melt state [18]. It has been shown for bulk polystyrene that the presence of a high degree of cross linking can raise the glass-transition temperature by 70 °C [19]. Chain connectivity could extend the influence of the polymer-substrate interaction out several hundred angstroms from the surface. In contrast, adhesion to the silicon native-oxide surface must be appreciably weaker. In this case the polymer thin film is not effectively pinned to the substrate. In the extreme case of weak interaction between the polymer and the substrate the polymer film might be expected to show a decrease in the glass-transition temperature.

The work reported here on the observed  $T_g$  increase contrasts with a previously published study on the same polymer-substrate combination. Keddie *et al.* [11] found a decrease in  $T_g$  for polystyrene films on hydrogen-terminated silicon surfaces when heated up to 150 °C in air. Work in our laboratory using x-ray reflectivity has shown a substantial increase in root mean square (rms) roughness of the polymer/silicon interface from 5 to 11 Å rms, when such samples are exposed to air at 150 °C for as little as 15 min. Auger electron spectroscopy studies [20] confirmed that this change in the character of the interface is due to oxidation of the silicon surface. For this reason, we believe that the work of Keddie *et al.* may be more indicative of the behavior of polystyrene on the silicon native-oxide surface. This would have the consequence of emphasizing how important control of the substrate surface is on determining polymer thin film behavior.

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