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Character of the glass transition in thin supported polymer films

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We have used ellipsometry to study the thermal expansivity of thin polystyrene films on silicon substrates with thicknesses of 10–200 nm. We find well-defined glass transitions, and detailed analysis of the expansivities shows that for thinner films the transition width is broadened, while the strength of the transition, defined by the difference between the expansivities in the liquid and glassy state, is reduced; the expansivity in the glassy state is higher than in the bulk. These phenomena are consistent with the idea that a layer of roughly constant thickness, of order 10 nm, near the surface of the film has liquidlike thermal properties at all experimental temperatures.

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I. INTRODUCTION

The origins of the glass transition, despite its ubiquity in technology and everyday life, still remain mysterious. Recently, substantial interest has been generated by the discovery that large shifts in the glass transition temperature can be observed in small systems, such as thin films, either supported on substrates [1–5] or freely standing [6], or glass-forming liquids confined in nanoscopic pores [7,8]. These experiments are conceptually attractive because finite size effects on the glass transition may yield clues about the existence of a diverging length scale, which some theories postulate may underly glass transition phenomena [9,10], and which are difficult to probe in any other way. On the other hand, in practical systems pure finite size effects are inextricably linked to surface and interface effects. The free surface of a supported film may be intrinsically more mobile than the bulk [11] while, on the other hand, strong interactions with a solid substrate may lead to a layer of the molecules of the glass-forming liquid being effectively immobilized [12,13]. The potential importance of the substrate is revealed most clearly by experiments on poly(methyl methacrylate), which show an increase in T_g on a substrate with which the polymer segments may strongly interact [14], but a decrease on a more weakly interacting substrate [2]. The importance of the free surface is suggested by the experiments of Forrest *et al.* on freely standing polystyrene films [6], which revealed substantially larger depressions in T_g than for supported films.

Thus, while the existence of large shifts in glass transition temperature in small systems is not in doubt, it is not clear if this represents a uniform shift in the glass transition temperature throughout the system, or if this is a manifestation of spatially nonuniform mobility which results in some parts of the system falling out of thermal equilibrium before others. To shed more light on this problem, we have examined the character of the glass transition for supported polystyrene films in more detail. We find that in addition to the quantitative changes in the glass transition temperature, the character of the transition also changes in a systematic way, with the width of the transition increasing and the strength of the transition decreasing as the films become thinner. We suggest an interpretation for these findings in terms of a liquid-like layer, presumably at the surface of the film, of roughly constant thickness, which does not take part in the transition at all.

Thin polystyrene films on silicon substrates are by far the most widely studied example of a spatially confined glass-forming liquid. Since the initial discovery by Keddie *et al.* [1] that in films less than 40 nm in thickness depressions of the glass transition temperature of polystyrene are of order tens of degrees, a number of other experiments, using a variety of techniques, have yielded results in quantitative agreement [3–5]. In Fig. 1, we show a comparison of all previous results from the literature [16]. These show that there is a considerable degree of experimental consensus; different experimental techniques (e.g., ellipsometry, x-ray reflectivity, and local thermal analysis), different experimental conditions (e.g., in vacuum and in air), different surface treatments, and different polymer molecular weights all yield very comparable results, with only one set of data [15] in claimed disagreement.

The experimental glass transition manifests itself as a discontinuity in second derivative thermodynamic quantities, such as the thermal expansivity or the heat capacity, as the sample is heated or cooled at a controlled rate. The experimentally determined glass transition temperature T_g depends on the rate of heating or cooling, because it marks the temperature at which a relaxation time of the system becomes comparable to the experimental time scale. In our experiments, we follow the thickness of a thin polystyrene film as a function of temperature. In previous work, such data has been analyzed by drawing two straight line segments through the data points and defining the glass transition temperature as the intersection of the lines. This procedure becomes in-

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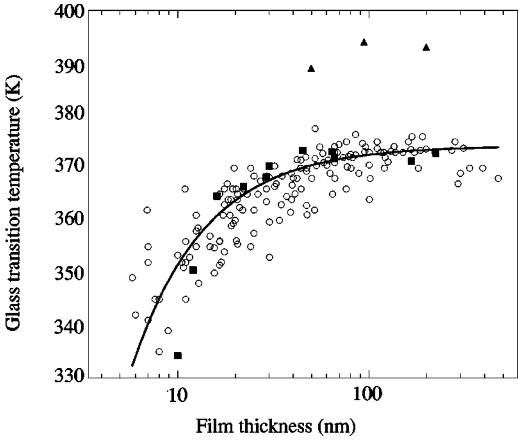

FIG. 1. Previously measured values of the glass transition temperature of polystyrene supported on silicon. Circles are from Refs. [1,3–5,26–28], filled triangles are from [15], while filled squares show the midpoints of the transition determined in this work. The solid line is the empirical fitting function $T_g(h) = T_g(\infty)[1 - (A/h)^{\delta}]$, where the bulk glass transition temperature $T_g(\infty) = 374$ K, the characteristic length $A = 8.3$ nm, and the exponent $\delta = 1.1$.

creasingly difficult for very thin films because, as we shall see, the difference in slopes in the thickness/temperature curves above and below the glass transition temperature becomes rather small. This difficulty is exacerbated when the number of data points is limited. The ellipsometry technique allows us to acquire data points almost continuously, and therefore to derive and plot the expansivity as a function of temperature through the glass transition. Rather than characterizing the transition by only a single number, T_g, we also determine the strength of the transition (i.e., the difference in expansivities between the liquid and glassy states) and its width.

II. EXPERIMENT

Samples were prepared by spin coating polystyrene [$M_w = 2.75 \times 10^5$, $M_w/M_n = 1.04$: PS275K; 1.95×10^6, $M_w/M_n = 1.04$: PS1950K, both from Polymer Laboratories (UK)] directly onto silicon wafers at 2000 rpm from the toluene solution with polymer concentrations of 0.3–3.0 % w/w. The silicon (111) wafers were first immersed in $NH_4OH(3.0\%)/H_2O_2(4.3\%)$ aqueous solution at 75 °C for 10 min to remove organic impurities. After rinsing and drying, the wafers were immersed in a solution of buffered HF at room temperature for 1 min. Subsequently, films were annealed at 150 °C for 24 h (PS275K), and 170 °C for 24 h (PS1950K) in vacuum to remove the residual solvent and to get equilibrated, then quenched to room temperature.

The film thickness as a function of temperature was obtained by ellipsometry. The details of the spectroscopic ellipsometer (Jobin-Yvon Uvisel) are given in other papers [1,2]. The essence of this method is that a small change in the film thickness, δh, is proportional to a change in the ellipsometric angle, $\delta\Psi$ or $\delta\Delta$. The ellipsometric angle is a function of $h \times n$, with h being the film thickness, and n being its refractive index. Although both h and n are functions of temperature, the resulting change in ellipsometric angles can be approximated by a simple linear function of h. We verified this relationship experimentally for samples with a thickness of 10–200 nm by acquiring full spectroscopic scans between 1.5 and 4.5 eV at every 10 °C from 150 °C to 30 °C after keeping samples at 150 °C for 1 h on the hot stage. The thickness and the refractive index at each temperature are uniquely determined by fitting the spectroscopic data to the classical model of the dielectric dispersion. An example of the result for the 64-nm film at $\lambda = 3.0$ eV is shown in Fig. 2. This confirms that after taking the temperature dependence of the refractive index into account, we can conclude that the ellipsometric angle is proportional to the film thickness throughout the temperature range of 30–150 °C.

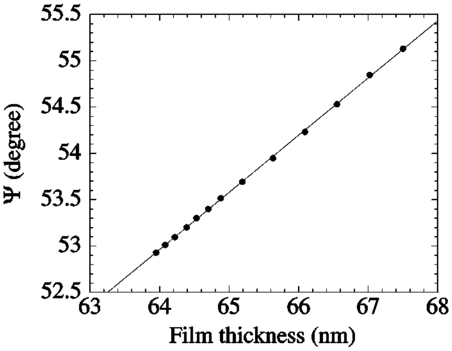

FIG. 2. An example of the linear relationship between the film thickness and the ellipsometric angle for 64-nm film; $\lambda = 3.0$ eV. The thicknesses and the refractive indices are calculated by fitting the full spectroscopic data, acquired at every 10 °C from 150 °C to 30 °C, to the classical model of the dielectric dispersion.

Using this relationship, we measured the film thickness continuously upon cooling by monitoring the ellipsometric angle at a single wavelength. Usually a few seconds of signal integration time is sufficient to obtain enough quality of a pair of Ψ and Δ so that we can monitor the film thickness almost continuously upon heating or cooling at the rate comparable to the conventional measurement of T_g. We chose 2.5 sec for the signal integration time and 2 °C/min for the cooling rate, corresponding to data acquisition intervals of 0.08 °C.

For a cooling scan from the liquid state, we first annealed the sample again on the hot stage at 150 °C for 1 h to erase any thermal history. This procedure is also effective in removing any influence by water molecules adsorbed onto the film surface, which affect the values of Ψ and Δ. We confirmed that there is no effect of water adsorption within the experimental time scale of this study, about 1 h. After confirming that Ψ and Δ were stable with time, the cooling scan was initiated.

We also checked that repeated heating to 150 °C in air did not lead to significant changes in the observed thermal behavior by carrying out the above procedure repeatedly on the same sample. We observed no significant difference in temperature-Ψ curves up to the fifth scan for all samples. Thus we concluded that films were free from significant ther-

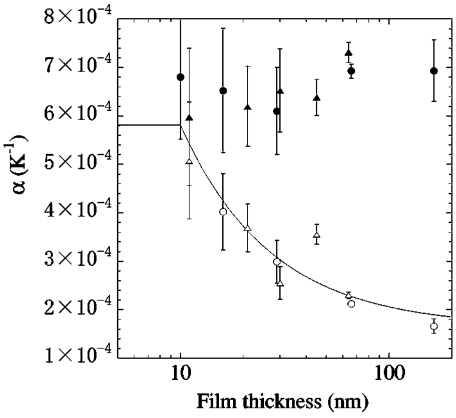

FIG. 3. Expansivity of ultrathin polystyrene films supported on silicon, measured at liquid state and at 40 °C by ellipsometry. ●, α_{Liq} for PS275K; ▲, α_{Liq} for PS1950K; ○, $\alpha(40\,°\mathrm{C})$ for PS275K; △, $\alpha(40\,°\mathrm{C})$ for PS1950K. Solid line represents the theoretical expansivity at 40 °C calculated from Eq. (2) with $h_{Liq}(40\,°\mathrm{C}) = 10$ nm.

mally induced damage within the temperature range employed in this study.

III. RESULTS AND DISCUSSION

Scans of Ψ as a function of temperature for 15-nm films, obtained by cooling at 2 °C/min from 150 °C to 30 °C were very similar to previously published data (but with better a signal-to-noise ratio due to instrumental improvements) [1]. Our data show a distinct kink separating two regions of roughly constant expansivity; this kink marks the experimental glass transition. By fitting straight line segments to the data above and below the glass transition one can obtain a value for T_g. Unfortunately, this method of determining T_g is relatively imprecise because the temperature-thickness curve below T_g has a slight curvature. Thus the obtained value of T_g is sensitive to the temperature range below T_g over which the curve is fitted. However, our data are of sufficient quality to allow numerical differentiation and to obtain a curve of expansivity versus temperature. We calculate $\alpha(T)$ by

$$\alpha(T)=\frac{h\left(T+\frac{\Delta T}{2}\right)-h\left(T-\frac{\Delta T}{2}\right)}{h_0\Delta T}, \tag{1}$$

with h_0 being the thickness at reference temperature, which we set to 30 °C, and ΔT being set to 4.2 °C. From the thickness-temperature curves obtained for a variety of film thicknesses of the two molecular weight films, we show the values of expansivity, α_{Liq}, deduced for the polymer melt state as a function of thickness. Here we define α_{Liq} as the average value of α over the temperature range of 113–120 °C. Values of α_{Liq} are shown as a function of thickness in Fig. 3. They fall within the range 5.8–7.2 $\times 10^{-4}/K$, consistent with the literature values 5.1–6.5 $\times 10^{-4}/K$ [17] and, within error, independent of film thickness. The scatter in α_{Liq} originates from the experimental error in determination of thicknesses at 30 °C and 150 °C, from which we calculated α_{Liq}. We can cancel out this experimental error by using the ratio $\alpha(T)/\alpha_{Liq}$. Since $\alpha(T)/\alpha_{Liq}$ is enough information on the character of glass transition as long as α_{Liq} is independent of the film thickness, we will conduct our discussion using $\alpha(T)/\alpha_{Liq}$ rather than $\alpha(T)$ itself.

Shown in Figs. 4(a)–4(e) are the changes in the ratio $\alpha(T)/\alpha_{Liq}$ upon cooling at 2 °C/min from 150 °C for PS275K with thicknesses of 10 nm, 16 nm, 29 nm, 66 nm, and 164 nm. For films with thicknesses of 66 nm and 164 nm, there is a steplike change in $\alpha(T)/\alpha_{Liq}$, characteristic of a glass transition. We will denote the temperatures of the onset and of the endpoint as T_+ and T_-, respectively. T_+ and T_- for the 66-nm and 164-nm film are independent of thickness and are approximately 105 °C and 90 °C, respectively. These temperatures are consistent with those obtained for bulk polystyrene at comparable cooling rates [18]. Although the data are somewhat noisy, the steplike change in $\alpha(T)/\alpha_{Liq}$ for the 29-nm and 16-nm films is still clear. However, T_- seems to be lower than those of 164- and 66-nm films, while T_+ is almost the same as those of the thicker films. Thus for thinner films the glass transition broadens to lower temperatures. For the 10-nm film, $\alpha(T)/\alpha_{Liq}$ seems to continue to decrease even at 30 °C; thus T_- cannot be determined from these experiments. Nonetheless, T_+ is the same as or slightly higher than those of thicker samples. Similar behavior was observed for higher molecular weight sample (PS1950K).

In Fig. 5 we show the values of T_+ and T_- obtained from the fits to the above data using three straight lines for the two molecular weights, PS275K and PS1950K. Both molecular weights behave in the same way; T_- decreases substantially for thinner films, while T_+ remains constant or slightly increases. The glass transition temperature T_g would typically be determined as the midpoint of the onset and endpoint temperatures, so these data are in agreement with the former results of Reiter [19,20], Keddie *et al.* [1,2], Forrest and coworkers [3,6], DeMaggio *et al.* [4], Fukao *et al.* [5,26], Russell [27], and Fryer *et al.* [28], indicating a decrease of T_g for thinner films. However, our more detailed analysis reveals that what takes place is not simply a decrease in T_g but a broadening of the transition in the direction of lower temperatures.

One possible explanation for a broadening of the transition is that the thin film is not uniform with respect to its mobility properties. As a consequence, different parts of the film fall out of thermal equilibrium at different temperatures. One can envisage, as proposed by DeMaggio *et al.* [4], three layers, each of which has a different thermal property. In this picture we would associate the decrease in T_- with a substantial layer with mobility increased over bulk values, presumably at the surface of the polymer. Similarly, a layer near the substrate, with mobility substantially less than bulk due to strong interactions between the polymer and the substrate, would lead to an increase in T_+. Interestingly, we do observe some evidence of such a rise, although it is much less pronounced than the decrease in T_-.

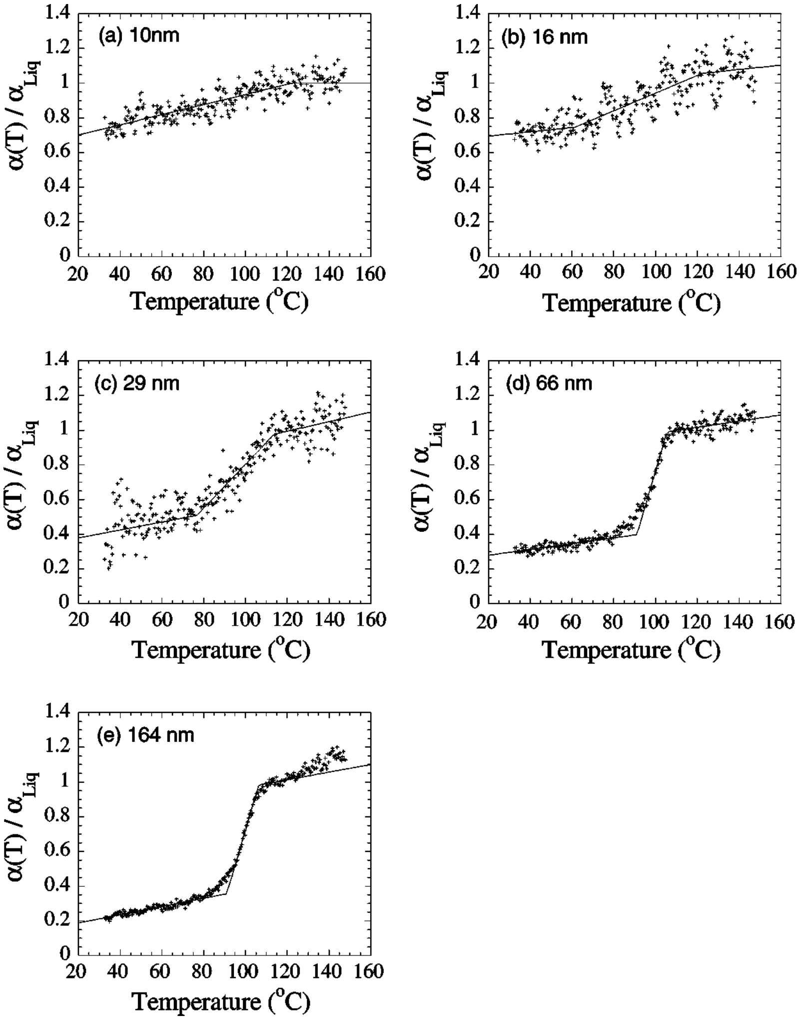

FIG. 4. Relative expansivity of thin polystyrene films, molecular weight 275 000, as a function of temperature, as measured by ellipsometry. The film thicknesses are (a) 10 nm, (b) 16 nm, (c) 29 nm, (d) 66 nm, and (e) 164 nm.

Additional evidence for this model is obtained if we study the changes in strength of the transition as the films become thinner. It is clear from Fig. 4 that the thinner the film, the larger the value of the expansivity below the glass transition temperature. This can be understood in terms of the layer model. Neglecting for the moment any effect of the substrate, we assume that the expansivity is simply the average of the value in the bulklike part of the film, with the value in the higher mobility surface layer weighted by the relative thickness of the surface layer. Thus

$$\alpha(T) = \frac{h_{Liq}(T)}{h}\alpha_{Liq}(T) + \left(1 - \frac{h_{Liq}(T)}{h}\right)\alpha_{glass}(T), \quad (2)$$

where h is the total film thickness $h_{Liq}(T)$ is the thickness of the surface liquidlike layer and $\alpha_{Liq}(T)$ and $\alpha_{glass}(T)$ are the expansivities in the liquid and glass states, respectively. We take these to be temperature dependent, as suggested by the nonzero gradients in Fig. 4. If we regard the behavior of the 164-nm film as being essentially bulklike, we can use the values of $\alpha_{Liq}(T)$ and $\alpha_{glass}(T)$ deduced from these curves to invert Eq. (2) and use it in conjunction with experimental expansivity-temperature data to deduce the thickness of the putative surface liquidlike layer $h_{Liq}(T)$.

The results of such an analysis are shown in Fig. 6. Within the limits of scatter, a consistent interpretation of these data can be made by assuming that at all experimental temperatures there is a layer of material around 10 nm in thickness which has an expansivity characteristic of the poly-

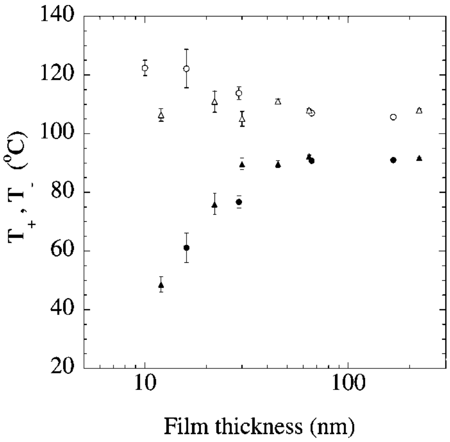

FIG. 5. Onset and endpoint temperatures, T_+ and T_-, for the glass transition in thin polystyrene films on silicon, as deduced from ellipsometric measurements of expansivity. ○, T_+(PS275K); △, T_+(PS1950K); ●, T_-(PS275K); ▲, T_-(PS1950K).

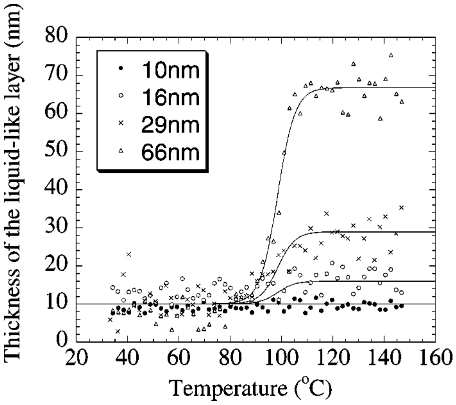

FIG. 6. Thickness of the portion of a thin, supported polystyrene film with liquidlike thermal expansion properties as a function of temperature. Solid lines are guides to the eye.

mer melt. Thus at low temperatures, the observed thermal properties of the film are weighted averages of a liquidlike surface layer and a glasslike bulk. Assuming $h_{Liq}(40\,°\mathrm{C}) = 10$ nm, we calculated $\alpha(40\,°\mathrm{C})$ from Eq. (2) as a function of thickness, and show the result as a solid line in Fig. 3, together with the observed values. This shows that the two-layer model with $h_{Liq}(40\,°\mathrm{C}) = 10$ nm works well throughout the thickness range examined.

Within the limits of the data there is no strong evidence that the thickness of the liquidlike layer depends either on temperature or on the total thickness of the film. The remainder of the film goes through a transition from liquidlike behavior to glasslike behavior at 98 °C. The dependence of this transition temperature on thickness, if any, is not resolvable in our data, while its width is around 20 °C.

The suggestion that the observed decrease in glass transition temperature in supported and freely standing films can be accounted for by a liquidlike surface layer has been previously made [1,4] on the basis of the observed shift in glass transition temperature. Forrest and Mattsson have argued that the existence of a liquidlike layer whose approximately constant thickness is in the range that we report here is to be expected on the basis of a cooperativity volume picture of the glass transition [21]. Another approach, due to de Gennes [22], explicitly identifies the cooperative mechanism by which the extra dynamical freedom associated with segments at the surface is transmitted to segments deeper in the film. This leads to a prediction for a depth-dependent glass transition temperature. Our more detailed analysis of the transition in thin films has allowed us to test these suggestions much more critically, and we believe that our results lend considerable credibility to the idea. However, a number of important questions remain. In particular, while the idea of a surface with liquidlike thermal properties implies that in some sense the mobility of the polymer is greater at the surface than in the bulk, as suggested by some computer simulations [11], it is not clear that the overall chain mobility at the surface is greater than in the bulk. Arguing against this are experiments studying the relaxation near the surface of oriented polystyrene chains, which show complete relaxation only above the bulk glass transition [23]. On the other hand, temperature-dependent lateral-force microscopy measurements suggest that segmental motion associated with frictional losses at the surface of polystyrene, rather than following the bulklike Williams-Landel-Ferry (WLF) kinetics [29] that lead to glass transition behavior, instead follow a simple Arrhenius temperature dependence. This implies that the glass transition of the surface region, if it exists, is at or below room temperature [24]. A macroscopic manifestation of this effect is found in the kinetics of adhesion between polymers at or below the bulk glass transition temperature, whose temperature dependence also does not follow bulklike WLF kinetics [25].

IV. CONCLUSIONS

Our experiments clearly show that the glass transition temperature in thin polystyrene films supported on silicon is not simply reduced but becomes broader and weaker. The broadening is more pronounced at low temperature, in the sense that while the onset temperature of the transition remains almost constant, the completion temperature is substantially reduced in thin films. The strength of the transition, in the sense of the difference between the expansivities on the glass and liquid sides of the transition, decreases with decreasing film thickness. A consistent interpretation of these results is possible by supposing that a layer with liquidlike thermal properties exists, presumably at the surface of the film, with a constant thickness of order 10 nm.

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