Size-Dependent Depression of the Glass Transition Temperature in Polymer Films

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Abstract. – The glass transition temperature of thin polystyrene films has been measured as a function of film thickness. It is found that the glass transition decreases in temperature as the thickness of the film is reduced. The effect is not strongly molecular-weight dependent, ruling out chain confinement as the major cause; instead we suggest that at the surface of the glassy film a liquidlike layer exists whose size diverges as the glass transition temperature is approached from below.

The nature of the glass transition is still imperfectly understood in bulk systems [1]. Even less is known about the effects of system size and surfaces on the transition, though there have been recent reports that the molecular mobility of polymers may increase as the system size is decreased [2,3]. In this paper we address this problem by making direct measurements of the apparent glass transition temperature in thin polymer films as a function of film thickness. In addition to having important technological implications, such experiments may well cast light onto the fundamental origins of the glass transition, just as the study of finite-size effects has improved the understanding of thermodynamic phase transitions [4,5].

The glass transition is not a thermodynamic phase transition, but it is marked by discontinuities in certain derivative thermodynamic quantities, such as the expansivity [6]. In our experiments we measure the glass transition temperature, T_g, for thin polymer films as a function of film thickness, by detecting with ellipsometry the discontinuity in expansivity as the films are heated at a constant rate [7]. We spin-cast narrow molecular-weight fractions of polystyrene from toluene solutions onto (111) single-crystal silicon wafers, which have previously been etched to remove the native oxide using hydrofluoric acid buffered with ammonium fluoride. This etching procedure produces a smooth, stable hydrogen-passivated

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surface [8] that is wetted by polystyrene [9]. To ensure that all our experiments are done on samples with equivalent and well-defined thermal histories, samples are first annealed in vacuum at 433 K (well above the bulk glass transition temperature) for 48 hours and then cooled in vacuum at a cooling rate of about 0.25 K/min. T_g measurements are performed in air on a Jobin-Yvon Uvisel spectroscopic ellipsometer equipped with a hot stage. We continuously monitor the ellipsometric angles (psi and delta) while the sample temperature is being raised from room temperature at a constant rate of 2 K per minute and record the ellipsometric angles in 2.25 s intervals. Prior to the T_g measurements, we conducted exploratory experiments to determine the angle of incidence and wavelength for which the ellipsometric angles are most sensitive to small thickness and refractive-index changes.

The thermal-expansion behaviour of the thin films is highly sensitive to thermal history, as might be expected for any glassy system. In contrast to previous work studying the temperature dependence of the thickness of thin polymer films [10], we are able to prepare samples of well-controlled thermal history and thereby obtain reliable T_g values. Figure 1 shows a typical result. The ellipsometric angle psi is essentially linear with thickness and refractive index over the small range sampled; thus the point at which the two straight-line segments intersect marks a discontinuity in both the thermal expansivity and the temperature coefficient of the refractive index, and this discontinuity defines the glass transition. (Since the refractive index is related to the density of the polymer, there is a change at the glass transition in the temperature dependence of both the thickness and the refractive index, assuming a constant mass.) We verified that this interpretation was correct by carrying out a more complete analysis for some samples in which the temperature was increased in roughly 5 °C increments and a wide spectroscopic scan taken at each temperature, thereby allowing an independent determination of the refractive index and thickness at each temperature. The results of one of these experiments are shown in fig. 2a). Although incremental measurements of thickness, such as these, can be used to determine T_g [7], scans like the one shown in fig. 1 are performed while heating continuously at a
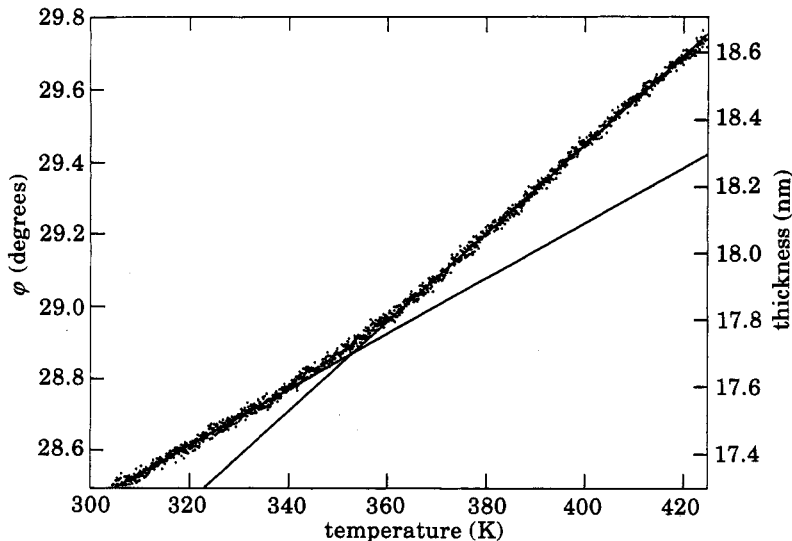

Fig. 1. – Typical data from an ellipsometric scan. This sample (MW = 2 900 000), initially 17.3 nm thick, shows a T_g of 353 K. Approximate film thickness is shown on the right axis. The scan was conducted with radiation having a wavelength of 387.5 nm and an angle of incidence of 80°.
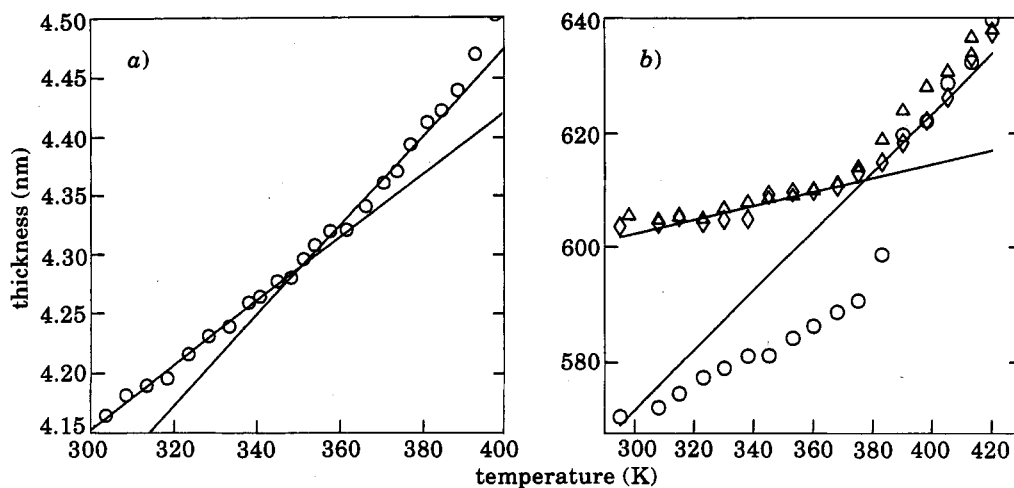
Fig. 2. – *a*) Film thickness measurements at approximately 5 K increments in temperature. Lines of best fit through the data indicate a T_g of 350.8 K for this sample (MW = 500 800) that had been equilibrated at 413 K prior to the experiment. *b*) Incremental thickness measurements for a sample (MW = 500 800) that was not equilibrated above the bulk T_g prior to the experiment. The circles are points obtained on first heating the sample; the triangles and diamonds are points obtained on cooling and re-heating, respectively. Upon re-heating, best-fit lines to the data indicate a T_g of 375 K.

constant rate and obtain many more data points; they are therefore less sensitive to errors in a single ellipsometric measurement.

Values of T_g and thermal expansivity were reproducible unless there was a change in thermal history between successive measurements, for example if the sample was cooled from the melt at a different rate. If there were such changes, we observed relaxation phenomena and shifts in T_g as predicted by the volume-temperature relationships for glasses. The value of T_g obtained on first heating an as-spun sample was not reproducible, as seen in fig. 2*b*). The figure shows that the large jump in thickness near the glass transition temperature of an as-spun sample was not observed upon re-hating. The conformation of the polymers in the as-spun sample differs significantly from the equilibrium conformation obtained from cooling at a controlled rate from the melt. In light of this observation, all of our T_g measurements were made on samples that had been annealed at temperatures above the bulk T_g (as already noted) in order to ensure reproducibility.

In fig. 3 we show the measured values of the glass transitions for three different molecular weights of polystyrene, each measured at about 15 different thicknesses, plotted against the film thickness. Thick films approach a constant bulk value which is close to that measured by other techniques. (For the molecular weights used, the small MW dependence of the bulk glass transition temperature is insignificant [11].) When the films are thinner than a few tens of nanometres, substantial reductions in T_g are apparent. Note that the dependence of this effect on molecular weight, if any, is weak; in particular it is much weaker than the dependence of radius of gyration on molecular weight.

We have fitted the data to the function

$$T_g(d) = T_g(\infty) \left[1 - \left(\frac{A}{d} \right)^{\delta} \right],$$

(1)

where d is the film thickness. We find for the best fit that the bulk glass transition temperature $T_g(\infty) = (373.8 \pm 0.7)$ K (comparable to previously reported values [11]), the characteristic length $A = (3.2 \pm 0.6)$ nm and the exponent $\delta = 1.8 \pm 0.2$. The characteristic length is not molecular-weight dependent, and thus cannot be associated with, for example, the overall chain dimensions of the polymer. This rules out a mechanism suggested by Reiter [2] to account for enhanced chain mobility in thin films, based on the idea that, as chains are constrained below their unperturbed size, they become less entangled. Another mechanism that has been suggested is that locked-in strain due to the different expansion coefficients of polymer and substrate may lead to lowering of the T_g. However, Beaucage *et al.* [7] have estimated such residual strains and found them to be small, even in the limiting case assuming no slip between polymer and substrate. As T_g depressions of a similar order of magnitude have been observed in small-molecule liquids imbibed in porous media [12, 13], we suggest that one should seek an explanation for this phenomenon which is not of specifically polymeric origin.

No such general theory for the effect on the glass transition of finite size, or of the presence of a surface, has yet been presented. However, a number of theories of the glass transition stress the importance of cooperativity of motion near the glass transition temperature [14-17]. This notion of cooperativity implies the existence of some length ξ which increases as the temperature decreases, implying that larger and larger regions have to move cooperatively to permit any motion at all. The existence of such a diverging length scale would be expected to lead naturally to finite-size effects, and indeed very recently there is some evidence for such effects from computer simulation of a 2-dimensional glass [3].

Molecular-dynamics simulations of a polymer melt near a wall [18] have found that the solid-melt interface is extremely narrow. The simulations indicate that mobility is affected only in chains within the interface that extends about two chain segments from the wall. This suggests that the T_g of polystyrene should not be substantially affected by the silicon substrate in our experiments. The presence of a free surface, on the other hand, is more
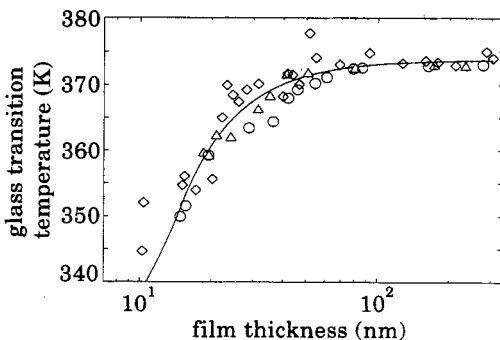

Fig. 3.   Fig. 4.

Fig. 3. – The glass transition temperature T_g as a function of film thickness for polystyrene of three molecular weights. The solid line is a best fit to the data (excepting the two thinnest films) using eq. (1), with $T_g(\infty) = 373.8$ K, $A = 3.2$ nm, and $\delta = 1.8$. $\triangle$ MW = 120 000, $\bigcirc$ MW = 500 800, $\diamond$ MW = 2 900 000.
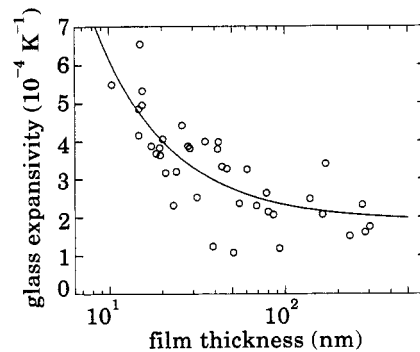
Fig. 4. – The coefficient of linear expansivity below the glass transition (for all three molecular weights) as a function of the film thickness d, as determined from data of the type shown in fig. 1. The solid line is a fit to eq. (3), with the melt expansivity fixed at $\alpha_{melt} = 7.2 \cdot 10^{-4}$ K^{-1}. Best-fit values of the average length $\bar{\xi}$ and the bulk value of the expansivity in the glass α_{glass}^{∞} are $\bar{\xi} = (8.0 \pm 0.8)$ nm and $\alpha_{glass}^{\infty} = 1.9 \cdot 10^{-4} (\pm 2 \cdot 10^{-5})$ K^{-1}.

likely to have an effect. The relaxation of constraints to motion at such a surface might be expected to result in a region of enhanced mobility; this suggestion is supported by recent computer simulations [19]. Thus, if we interpret the length scale ξ as characterising a near-surface mobile layer, and if it diverged at the bulk glass transition temperature as

$$\xi = A \left(1 - \frac{T}{T_g(\infty)} \right)^{-\nu'}, \tag{2}$$

we would recover an expression for the thickness dependence of the glass transition temperature of the form of eq. (1), with the exponent $\delta = 1/\nu'$. Thus, our data would imply a value of $\nu' = 0.56 \pm 0.06$. An additional testable implication of this picture is that for thin films below the glass transition temperature the meltlike layer will make a contribution to the expansivity which will become proportionally greater for thinner films. In fig. 4 we plot the expansivity below the glass transition as a function of film thickness. For thick films this tends towards a constant value; however, as the films become thinner the ratio rises towards the value of the expansivity in the melt, which we find to be $7.2 \cdot 10^{-4} (\pm 2 \cdot 10^{-4}) \, \mathrm{K}^{-1}$, which is within the range of other reported values of 5.5–$6.5 \cdot 10^{-4}$ [6,7,11]. Assuming that the contributions of the liquidlike layer and the rest of the films are simply additive, we might expect the expansivity α to be given by the expression

$$\alpha = \frac{\bar{\xi}}{d} (\alpha_{\mathrm{melt}} - \alpha_{\mathrm{glass}}^{\infty}) + \alpha_{\mathrm{glass}}^{\infty}, \tag{3}$$

where $\bar{\xi}$ is the average size of the liquidlike layer over the temperature range in which the glass expansivity is measured. The solid line is a best fit to the equation where the expansivity in the melt is fixed at the measured value. The value of the expansivity of the glass in bulk $\alpha_{\mathrm{glass}}^{\infty}$ is $1.9 \cdot 10^{-4} (\pm 2 \cdot 10^{-5}) \, \mathrm{K}^{-1}$, similar to other reported values [6,7,11]. The best-fit value of $\bar{\xi}$ is $(8.0 \pm 0.8) \, \mathrm{nm}$; using eq. (2) we would estimate $\bar{\xi} = (13 \pm 3) \, \mathrm{nm}$, in fair agreement.

The observed size dependence of T_g explains a number of observations and may lead to a better understanding of a number of important phenomena. It has already been observed that thin polymer films may dewet their substrates below T_g [2]; during fracture of polymers below the bulk T_g there is substantial evidence for chain disentanglement in craze fibrils and active zones. Furthermore, if the picture of a near-surface region with mobility greater than in the bulk is correct, this will have implications for mechanisms of sintering of polymer colloids and for the autoadhesion of glassy polymers. This kind of observation may also help to throw light onto the nature of the glass transition by probing diverging length scales characterising co-operative motion.

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