

SURFACE GLASS TRANSITION TEMPERATURE OF AMORPHOUS POLYSTYRENE MEASURED BY SFM

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Abstract

Surface glass transition temperature (T_g) behavior has been studied for amorphous polystyrene (PS) with implementation of a scanning force microscopy (SFM) force-distance mode. Narrow molecular weight distribution samples have covered the range of the molecular mass M_n from 3,900 to 1,340,000. We present measurements of the surface T_g , as a function of film thickness (h) and molecular mass. A hysteresis in retracting-contracting cycles in force-distance curves is observed above the T_g and is ascribed to the appearance of high viscoelasticity of the polymer surface. The surface T_g is depressed in comparison to the bulk values for low molecular mass fractions of PS ($M_n < 30,000$) and for spin-coated films with $h < 8R_g$ (radius of gyration of the polymer chain). Scaling law dependence of the surface T_g on the molecular weight (M_n^{-1}), and on the film thickness ($h^{-0.8}$) is revealed. Our analysis shows that an entanglement of polymer chains, rather than localization of chain ends at the surface, is responsible for the enhanced polymer chain mobility in a surface layer whose thickness is comparable with the polymer chain dimensions.

A key parameter for characterizing a polymer is the glass transition temperature T_g . This affects every aspect of its properties as an engineering material. The elastic modulus can decrease by as much as three orders of magnitude on heating through T_g . For polymers confined in nanoscale geometries (such as ultrathin films) T_g can differ by as much as 50 K from the bulk value.¹⁻⁴

Theoretical models and computer simulations suggest that polymer chain dynamics at a surface should be different from the bulk.^{5,6} Experimental observations confirm that the glass transition temperature is generally lower in thin films, and this effect has been modelled as a layer of increased polymer mobility near the surface.⁷ There are two basic approaches to a theoretical description of the polymer surface anomalies. The first considers a non-symmetrical polymer segment distribution within a characteristic layer near the surface, where labile entanglements are “non-compensated” from one side.⁸ This leads to different cooperative dynamics for the surface, which are characterised by a greater correlation length. An alternative approach considers the chain ends as the major factor responsible for the changes of the specific free volume, hence influencing polymer chain mobility near the surface.

In this paper we present our measurements of the surface glass transition temperature variation on a set of polystyrene (PS) fractions with a narrow molecular mass distribution by scanning force microscopy (SPM), using force-distance mode experiments. The T_g is measured as a function of the film thickness or polymer molecular mass, and is analysed in terms of possible mechanisms of chain mobility depending on the entanglement of polymer chains for a very thin layer of the polymer surface comparable with the polymer chain dimensions.

We have used SFM force-distance measurements to determine the dependence of T_{g0} on molecular mass M_n for a set of PS samples chosen to cover three orders of magnitude in M_n (3,900 to 1,340,000), obtained from Polymer Source, Inc. (Dorval, Quebec, Canada). Polydispersity index (the ratio of the weight-averaged molecular weight, M_w , to the number-averaged molecular weight, M_n) was below 1.15 for all the polymer fractions under study, and typically did not

exceed 1.05. PS samples were deposited by spin coating from a toluene solution on a glass or silicon substrate to form films whose thickness h was greater than the radius of gyration R_g of the molecules (1.7 to 31.8 nm for the PS set under investigation). Polymer films were annealed for at least 2 hours at 110° C before SFM experiments. Our previous study of amorphous polymer surface structure¹¹ revealed that such annealing was sufficient to achieve structural equilibrium. The film thickness was measured by SFM as a depth of the step produced by an artificial scratch on the polymer film.

A Park Scientific Instruments Autoprobe CP atomic force microscope operated in contact mode has been employed for these experiments. Si₃N₄ cantilevers with a spring constant of 0.26-0.40 N/m and a typical radius of curvature of the tip ~10 nm have been chosen for force distance measurements near the glass transition where the mechanical properties such as stiffness are expected to change from gigaPascal to several megaPascal range. Temperature scanning and temperature measurements were performed with a specially designed miniature heater calibrated with several standard materials (In, and In/Sn alloys) to give ±3 K precision of the sample surface temperature measurement in the range 40 to 160°C.

Typical force-distance curves are shown in Figure 1 at four different temperatures for thick ($h > 8R_g$) PS samples of $M_n = 347,000$ (347k). At 25°C, which is well below T_g , the retraction force-distance curve is indistinguishable from the approach curve; the same is true for the glass substrate. At successively higher temperatures the force-distance curves develop three related features: (i) the slope becomes less steep throughout the cycle, indicating a reduction in stiffness; (ii) the slope for retraction is steeper than for approach, creating hysteresis in the complete curve; (iii) there is pronounced adhesion (negative force) just before separation. All of these effects originate in the variation of the complex-valued viscoelastic modulus ($E^* = E' + iE''$) around the glass transition temperature.

Associated with the drop in the real parts (E') of the elastic stiffness tensor elements there is a peak in the imaginary parts (E''), corresponding to maximum viscoelastic loss. The strains at the edge of the contact

area can be very large¹³ and so when the contact area changes the strain rates can be large too. This leads to a diminished effective adhesion energy during approach and to higher adhesion energy during retraction, an effect that has long been known in the dynamic adhesion of rough surfaces to viscoelastic solids.¹⁴ The reduction in stiffness

(i) is dominated by the change in E' at T_{g0} , and the hysteresis (ii) and enhanced adhesion (iii) are dominated by the peak in E'' at T_{g0} .¹⁵

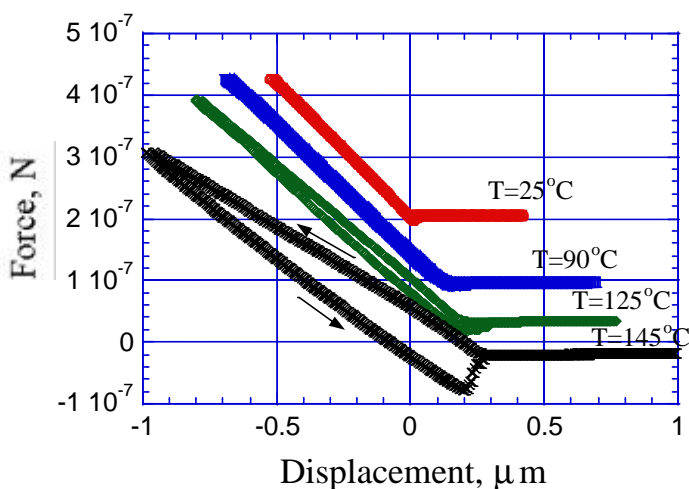


Figure 1. SFM force-distance curves obtained at different temperatures for a narrow molecular mass fraction of PS: $M_n = 347k$. Curves are displaced vertically for clarity. Hysteresis of the approach-retraction curve was observed for all PS samples above their glass transition temperatures, and was more pronounced for lower molecular mass PS samples. No hysteresis was detected in force-distance curves for the glass substrate, or for PS samples at $T < T_{g0}$.

In Figure 2 we show how the surface glass transition temperature T_{g0} can be independently determined from each of these three phenomena by implementation of linear regression analysis. Figure 3 presents the glass transition properties of a series of thin spin-coated films, $2R_g < h < 30R_g$ (and also $100R_g$) of $M_n = 115,900$ ($R_g = 9.3$ nm).

The T_g is observed to deviate significantly from bulk values for film thicknesses less than about $8R_g$. The dependence of T_g on the thickness h can be described by an empirical equation^{1,4}:

$$T_g = T_g^\infty [1 - (d/h)^d] \quad (1)$$

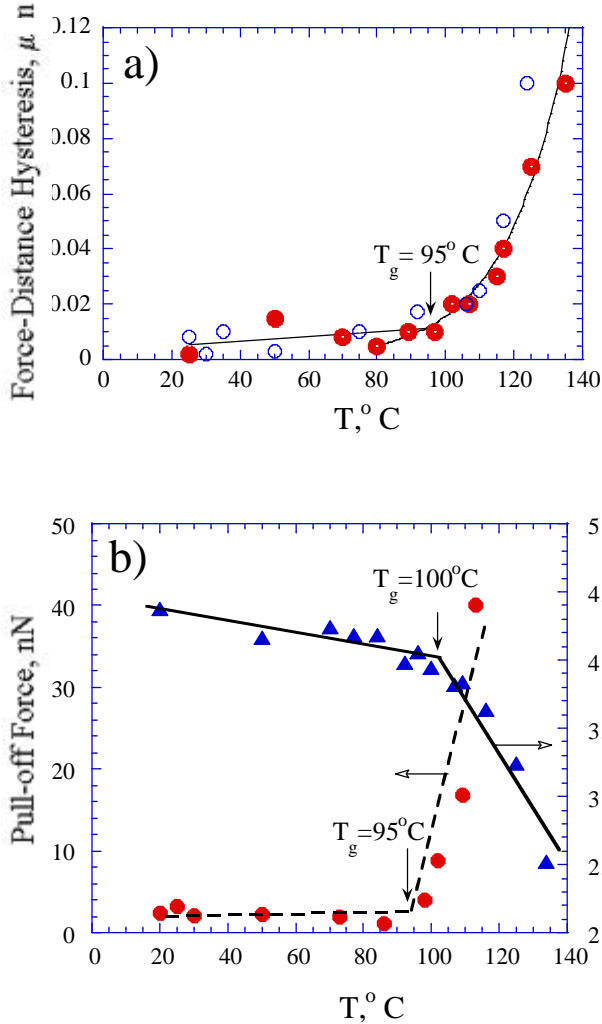


Figure 2. How to estimate the surface glass transition temperature T_{g0} from the nano-mechanical measurements from the variation with temperature for $M_n = 347k$ PS film: (a) approach-retraction hysteresis values measured during heating (solid circles) and cooling (open circles) of the sample in SFM force-distance experiments; (b) tip-surface contact stiffness (triangles) and pull-off force (circles) characteristics of the same sample. The best fit curves have been drawn following the procedure described in the text, and T_{g0} is determined from their intersection.

where d describes the strength of the film-surface interaction, and d represents the depth of the correlated near-interface polymer layer, correspondingly. The data are in a good agreement with previous experiments, with values of $d = 0.83$ and $d = 5.3$ nm.⁴ This confirms that we are indeed measuring changes in the intrinsic properties of the polymer layer, and not simply the geometrical effect of a stiff substrate on the tip-sample contact mechanics.

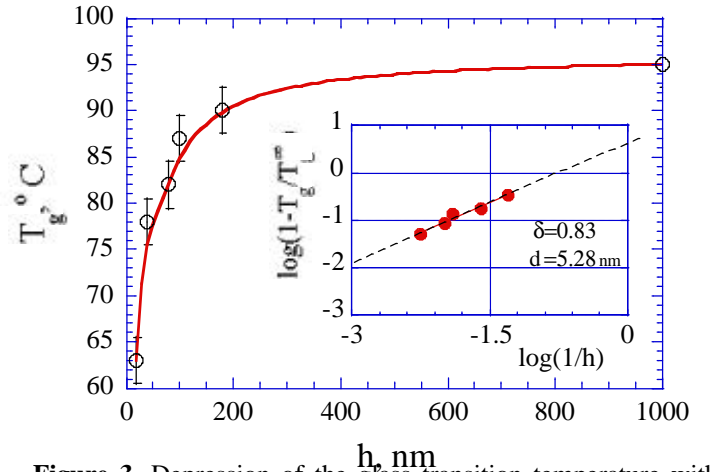


Figure 3. Depression of the glass transition temperature with a thickness of PS 116k spin-cast films on a glass substrate. The inset shows the best fit achieved with Eqn (1).

In order to elucidate the mechanism responsible for the surface depression of T_g , we measured T_g for a series of relatively thick ($> 8R_g$) PS films with molecular mass ranging from $M_n = 3.9k$ to $M_n = 1,340k$. The results are plotted in Figure 4, together with three best-fit candidate theoretical curves.

The localization of chain ends at a polymer surface can depress T_{g0} by locally increasing the free volume. To model this, an effective chain length is postulated that gives the molecular weight equivalent for the same fraction of chain ends as in the bulk.¹⁶ The reduction in T_{g0} then scales as $M_n^{-0.5}$ because of the Gaussian (random walk approximation) distribution of the chain segments in a polymer:

$$T_{g0} = T_g - C_1(a/D) M_n^{-0.5}, \quad (2)$$

where a is the chain segment length, D is the effective depth of the surface layer, and C_1 is a constant to be determined. The dotted curve in Fig. 4 is T_{g0} calculated from Eqn (2), with the surface glass transition temperature for infinite molecular mass T_g^∞ set at 100°C and the value of $C_1(a/D)$ chosen to fit the data point at $M_n = 3.9k$.

Alternatively, the Fox-Flory equation^{16,17} describes the increase in T_g with molecular weight due to the associated decrease of the free volume resulting from

the increase of the probability of entanglements and the smaller fraction of the chain ends in the system.

$$T_g = T_g^\infty - \frac{C}{M_n}. \quad (3)$$

This relationship is plotted as the dashed curve in Figure 4, using literature values for the infinity-molecular mass glass transition temperature $T_{g0}^\infty = 100^\circ\text{C}$, and the empirical parameter $C = 1.2 \times 10^{5.18}$. In this case the reduction in T_g from the infinite molecular mass bulk value is generally understood in terms of polymer chain entanglement behavior such as reptation mediated diffusion and non-Newton viscosity. These become significant below a characteristic molecular mass M_c (an average length of polymer chain segments between the entanglements) that depends on the polymer type: for PS previous bulk experiments suggest $M_c = 19,500$.¹⁹ In Figure 4 the first significant departure from T_g^∞ occurs for $M_n = 22\text{k}$, which is not too different.

As is apparent from Figure 4, neither of these theoretical models gives satisfactory fit to our data. A best fit to a function of the form: $T_{g0} = T_{g0}^\infty - C_0 M_n^m$ yielded the parameters $T_{g0}^\infty = 96.9 \pm 0.3$; $m = -1.06 \pm 0.05$ and $C_0 = (4.3 \pm 2.0) \times 10^5$. The value for m indicates that the T_{g0} depression should be accounted for in terms of entanglement of chains rather than in terms of localization of chain ends at the surface.

There have been plenty of other studies of this phenomenon that have come to different conclusions, including a number that use *lateral* vibration of an AFM tip. Some experiments²⁰ find no difference between surface T_{g0} and bulk T_g , or even $T_{g0} > T_g$. One very thorough investigation finds a depression in T_{g0} that varies as $M_n^{-0.6}$.²¹ The relaxation process associated with cooperative motion of relatively long chain segments will be different from small fragments of PS chains at the surface. It may be that the lateral measurements are more sensitive to the elastic deformation associated with Herzian indentation, and less affected by viscoelastic peeling, though that can also occur even with lateral vibration.²² It will be interesting to see what results emerge from quantitative scanning thermal expansion microscopy.²³

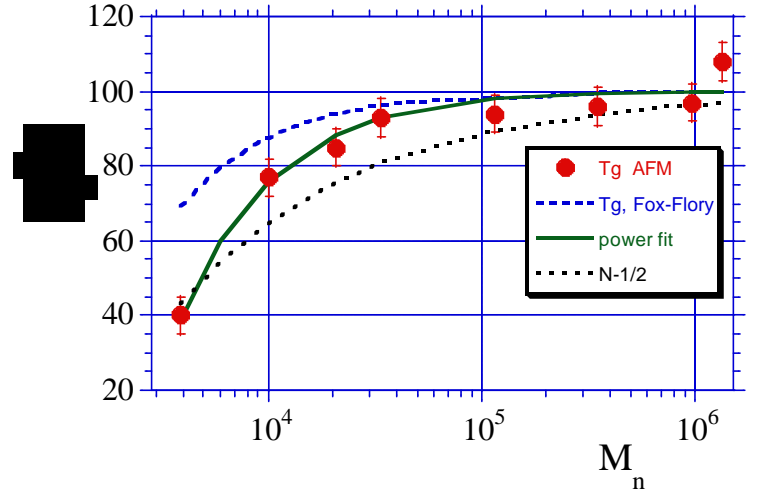


Figure 4. Surface glass transition temperature as a function of polymer molecular mass. The curves show different theoretical scaling law predictions (on a number of monomer segments per polymer chain, N): $N^{0.5}$ for the localisation of the chain ends on the surface (Eqn 2: dotted curve); N^1 bulk T_g curve calculated by application of Fox-Flory equation and bulk parameters (Eqn 3: dashed curve); and the best power fit of our data with parameters: $T_{g0}^\infty = 96.9 \pm 0.3$; $m = -1.06 \pm 0.05$ and $C = (4.3 \pm 2.0) \times 10^5$.

Our data give a very close fit to the Fox-Flory scaling relationship, but with a greater value of C than reported in the literature for the bulk material. The empirical coefficient C is inversely proportional to the difference between the thermal expansion coefficients above and below T_{g0} , $\Delta a = (a_m - a_g)$,^{16,17} which in turn depends on the average length of polymer chain segments between the entanglements.^{18,19} Computer simulations yield anisotropic thermal expansion in the vicinity of a surface, and indicate that segments situated close to the free surface are more mobile than those in the bulk.⁶ The associated anisotropy of chain mobility at the polymer surface gives a drop in Δa by a factor of 1.75. Since the loop is confined to a hemisphere, a further factor of 2 is introduced, giving a value of the C coefficient for the surface 3.5 times greater than the bulk. On this model we therefore predict $C_0 = 1.2 \times 10^5 \times 3.5 = 4.2 \times 10^5$, which is close to the value determined from our data.

In conclusion, a simple and reliable technique for the measurement of the surface glass transition (and other

stress relaxation phase transitions) based on analysis of SFM force distance curves has been suggested and successfully tested for a set of polystyrenes with the molecular mass ranging from 3.9 to 1,340 kiloDalton. The values of the surface glass transition for the samples with $M_n > 30,000$ have been found to be the same as the corresponding bulk values. However, low molecular mass polymers behave differently. Our experiments revealed a depression of the glass transition at the polymer surface. The magnitude of this depression increases with decreasing molecular weight. The molecular mass dependence of T_g correlates with structural and dynamical parameters of polymer chains: that are best accounted for in terms of a virtual network of labile entanglements.

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