Reductions of the glass transition temperature in thin polymer films: Probing the length scale of cooperative dynamics

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We report measurements of the glass transition temperature, T_g, in free standing polymer films in a low M_n limit where chain confinement effects are not observed. The measured T_g values are *accurately* described by a layer model incorporating a mobile surface layer with a size determined by the length scale of cooperative dynamics. The analysis leads to a surface T_g value and length scale of cooperative motion near bulk T_g which quantitatively agree with independently determined values. The model and parameters provide a framework within which *all* previous measurements of T_g values in thin supported films may be understood and provides values for the length scale of cooperative motion over an extended range of temperatures below the bulk T_g value.

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Despite much theoretical and experimental effort [1], the nature of the glass transition remains an unsolved problem. Theoretical attempts to describe the glass transition range from thermodynamic approaches [2] to purely kinetic ones [3]. Adam and Gibbs [4] introduced the notion that dynamical behavior near the glass transition temperature was a result of cooperative motion. Edwards and Vilgis [5] demonstrated explicitly the importance of cooperative motion by deriving a dynamical theory of the glass transition where cooperative motion alone was enough to result in Vogel-Fulcher dynamics. Central to most descriptions of cooperative motion is the existence of a length scale $\xi(T)$ over which the dynamics are cooperative; the size of this region increasing as the temperature is lowered. The lack of an adequate theoretical description of the cooperativity length and its temperature dependence has led to substantial experimental efforts to first prove the existence of such a length scale and further to determine its magnitude.

The experimental determination of a length scale for cooperative motion presents a difficult challenge [6]. Calorimetric measurements analyzed in terms of a fluctuation model allow a characteristic length for cooperative motion at T_g, $\xi(T_g)$ of a few tens of Å to be estimated [7]. A more direct approach has been to study the glass transition behavior in glass forming systems confined to spatial dimensions comparable to the cooperativity length. The motivation for such studies is that as the temperature is lowered to the point where the $\xi(T)$ reaches the sample dimensions, anomalies in the T_g value and related dynamics should be observed. In samples confined to nanoporous glass where the pore surfaces have been specifically treated both reductions in the T_g value [8] and faster segmental dynamics [9] have been reported. These studies provide only an estimate of the actual value of $\xi(T_g)$ and more importantly are influenced strongly by the pore surface chemistry [10]. There are other ways to introduce spatial confinement, and the incorporation of samples into thin films is one approach which is particularly

suited for the study of polymeric glass formers. Keddie *et al.* [11] measured T_g values of supported polystyrene (PS) films which were reduced below T_g^{bulk} for films with thickness $h < 400$ Å. Since these initial investigations a number of different groups have reported measurements of anomalous T_g values and dynamics in thin polymer films [12–15]. A key issue in these thin film studies is the effect of the interaction between the polymer and the substrate. Different strengths of this interaction have been shown to lead to qualitatively different behavior in the thickness dependence of the T_g value [16]. The influence of the substrate may be avoided by measuring the T_g of free standing polymer films. Such measurements have been performed and have revealed larger T_g reductions than similar supported films [12,17,18] as well as a strong M_n dependence, which suggests that polymer chain confinement defines the length scale for these T_g reductions [12,19]. Despite the promise of thin film experiments, they have as yet failed to provide further insight into the length scale of cooperative motion near T_g.

In this Rapid Communication we report measurements of the glass transition temperatures of thin free standing polymer films in a low M_n limit where chain confinement effects are not observed. The symmetry of the system and the lack of specific substrate interaction makes such studies ideal for investigating finite size effects. We develop a simple layer model for the glass transition behavior with a size determined by the temperature dependent length scale for cooperative dynamics. In spite of its simplicity, the model is found to provide an excellent *quantitative* description of the data, and the fitting procedure provides us with a T_g value of the polymer surface region, T_g^{surf} and the temperature dependent $\xi(T)$ near and *below* the bulk value of T_g. Both the T_g^{surf} and the $\xi(T_g^{bulk})$ values determined from the analysis agree with independent estimates. The model is found to accurately describe previous data of supported films and in general provides a framework within which *all* previously measured T_g values in thin supported films can be under-
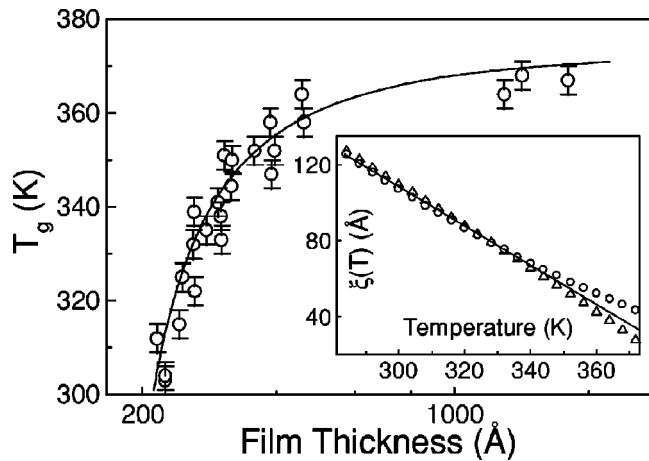
FIG. 1. T_g vs film thickness for low M_n ($\leqslant 347k$) PS. The solid line is the fit to the data using the model described in the text. Inset: Size of the surface region of enhanced mobility as determined by the fits of the data to the model. The circles are the values of $\xi_1(T)$ and the triangles are $\xi_2(T)$. The straight line is a best fit line used to fit the supported film data.

stood. This surprising universality suggests that the model parameters accurately correspond to the real physical properties of the near surface region in thin polystyrene films. Even more significant is the ability of the analysis to provide a length scale for cooperative motion at temperatures below the bulk T_g value.

The samples used in these studies were prepared from monodisperse polystyrenes with M_n values ranging from $116k$ to $347k$. The detailed preparation of the free standing films is similar to previous studies [12]. The T_g values were determined using Brillouin light scattering [12,18]. This technique, which involves measurement of the frequency shift of light scattered from film guided acoustic phonons, has previously been shown to be an effective technique for determining the glass transition temperature T_g of thin free standing polymer films [12].

A detailed investigation of the M_n dependence of the T_g versus film thickness will be published separately [18] and here we state only that for M_n values less than $\sim 350k$, the T_g values display no M_n dependence which could be determined within the experimental uncertainty of ± 3 K. Figure 1 shows the T_g values for free standing PS films with M_n values of 116, 200, and $347k$ and film thicknesses ranging from 210 to 2000 Å . The behavior of the T_g values for the low M_n samples clearly differs from the behavior observed for greater M_n values [12] and, except in magnitude, is more similar to the supported film data [11]. This *lack of M_n* dependence suggests that the T_g reductions may be a result of the characteristic length for glass transition dynamics, and below we motivate and develop a model based on this idea which we use to explain our results as well as previous results of other groups.

To describe our results, we incorporate the ideas of a length scale for cooperative dynamics into a simple layer model. We consider the film to have a region near the free surface with enhanced mobility due to the release of steric constraints in a manner similar to that observed in simulations [20] of glassy free standing films. This mobile surface region will exhibit an enhanced rate of conformational tran-

sitions which will extend into the bulk of the film, decaying with some characteristic length. For simplicity we *model* this as a surface layer with $T_g^{surf} < T_g^{bulk}$. Since a surface layer with constant thickness results in a T_g value which varies as $1/h$ (a behavior contrary to that observed for either free standing or supported films), temperature dependence of the surface layer size is a necessary ingredient in constructing a model to accurately describe T_g data. A reasonable physically based estimate for the size of a surface region with different dynamical properties is the length scale of dynamic heterogenieties in bulk glass forming materials, and such a length can be considered as an upper limit for the cooperativity size [21]. More quantitative justification for this hypothesis will be obtained by comparison of the length values we obtain through our analysis to values of $\xi(T_g)$ estimated through methods *not* involving observations of finite size effects [7]. We stress that while our model requires only the *existence* of a temperature dependent length scale describing the surface layer *without specifying* its origin, the same is true for most studies of finite size effects related to cooperative dynamics [9]. It is worth qualifying that only experiments with relatively large T_g reductions need to invoke a temperature dependent layer model, and this observation explains the moderate success of other approaches [14]. We further note that a surface region of anomalous dynamics whose size increases as the temperature is lowered is also observed in simulations [22]. The remaining step in the development of a useful model is to parametrize the temperature dependence of the size of the surface region. The cooperativity length increases to larger sizes at smaller values of temperature and, since it is unlikely that there is only a single parametrization leading to the correct temperature dependence, we consider two physically realistic possibilities. Donth [7] has suggested that the cooperativity volume $V_c \propto \xi^3$ has a temperature dependence of the form $V_c \propto (T_{ons} - T)^2$, where T_{ons} is the onset temperature for cooperative motion. For PS T_{ons} is estimated to be 463 ± 15 K [7]. A reasonable parametrization for the size of the surface region is $\xi_1(T) = r_0 + \alpha(T_{ons} - T)^\gamma$, where r_0 is the average distance between monomer units. We do not fix the value of γ as the behavior in the temperature region relevant for the present experiments may not be the same as that above the bulk T_g value. An alternative approach is to write $\xi_2(T) = \xi(T_g) + \alpha(T_g^{bulk} - T)^\gamma$, where $\xi(T_g)$ is the size of the cooperativity length at the glass transition temperature.

The model system is constructed of a surface layer with $T_g = T_g^{surf}$ and size $\xi(T)$ and the remainder of the film with a T_g value the same as the bulk value. We emphasize that the different T_g values of the layers reflect the inhomogeneous dynamics, and we do not necessarily expect the sample to exhibit two distinct T_g's. A single T_g in a film displaying similarly strong dynamic heterogeneities is also observed in simulations [22]. With this in mind we write the following simple expression relating the *average T_g* value, $\langle T_g \rangle$ of the free standing films to the film thickness as

$$\langle T_g \rangle = T_g^{bulk} + \frac{2\xi(\langle T_g \rangle)(T_g^{surf} - T_g^{bulk})}{h}. \tag{1}$$

We note that for film thicknesses $h < 2\xi(T_g)$ this relation is no longer expected to be valid as points throughout the film are influenced by both free surfaces; an effect not accounted for in our model. Since both of our parametrizations may overdetermine the fit, we reiterate that we are really only

interested in finding $\xi(T)$ and not necessarily the exact parameters. In order to minimize the number of free parameters we fix T_g^{bulk} and r_0 to their accepted values of 373 K and 6 Å . If we use $\xi(T) = \xi_1(T)$ we find $T_{ons} = 485 \pm 6$ K, $T_g^{surf} = 300 \pm 7$ K, $\gamma = 2.00 \pm 0.1$, and $\alpha = 2.95 \pm 0.3 \times 10^{-3}$. If we instead employ our alternative expression $\xi_2(T)$ we find $T_g^{surf} = 305 \pm 21$ K, $\xi(T_g) = 26 \pm 21$ Å, $\gamma = 0.95 \pm 0.15$, and $\alpha = 1.4 \pm 0.7$. The film thickness dependent T_g values from these different fits are essentially indistinguishable, and the solid line in Fig. 1 shows the best fit line. From the figure, it is evident that behavior exhibited by the model agrees very well with the measured T_g values for the free standing films.

Since it is only the actual size of the near surface layer $\xi(T)$ which is important, we compare $\xi_1(T)$ and $\xi_2(T)$ in the inset of Fig. 1. This comparison shows that both fits give essentially the same values for $\xi(T)$ although with different parametrizations. Differences between $\xi_1(T)$ and $\xi_2(T)$ are evident only for $T \sim T_g$ where they have little effect on the calculated average T_g value. The model determines the T_g only through the values of T_g^{surf} and $\xi(T)$, and since both of these physical quantities are found to be robust and independent of the details of the fitting procedure, we can be confident that the final values represent physically meaningful quantities. This confidence allows us to make a number of observations about the $\xi(T)$ determined from the fit to our data. First, by inspection we see our model gives a $\xi(T_g^{bulk})$ of 25–50 Å, a value in excellent agreement with the cooperativity length range of 25–35 Å for PS estimated by Donth [7]. This agreement demonstrates that the size of the surface region is approximately equal to other estimates of the cooperativity length, justifying the link tentatively suggested above. The data also shows that $\xi(T)$ may be very well approximated by a linear function of temperature for $T < T_g$. Finally, we note that, to our knowledge, there are no other measurements or predictions for the cooperativity length at temperatures below the bulk T_g value and so the values presented here are uniquely able to test any new theories of the growth of the cooperativity length in this temperature region. While the finite values of $\xi(T)$ below the Vogel-Fulcher temperature $T_0 \sim 323$ K might seem surprising, even thermodynamic theories of the glass transition can be shown to lead to finite viscosities below T_0 [23]. The value of $T_g^{surf} = 305 \pm 21$ K provided by fitting the model to the free standing film data is in excellent agreement with the positron annihilation measurements of Jean et $al.$ [24] who reported a T_g^{surf} of 317 K for the 50 Å region nearest the free surface of a supported PS film.

The success of this model to describe the T_g data for free standing films with physical quantities in agreement with those determined using other methods is compelling evidence for the validity of the underlying physical ideas. If the predicted values for $\xi(T)$ and T_g^{surf} correctly characterize the near surface properties of polystyrene films, it should be possible to *directly* export them and obtain quantitative agreement with other data for the same glass forming system. To do this we consider the results of Keddie et $al.$ [11] for supported PS films as this is the most extensive collection of such data for a single system. The most straightforward application of our ideas to the case of a supported film involve
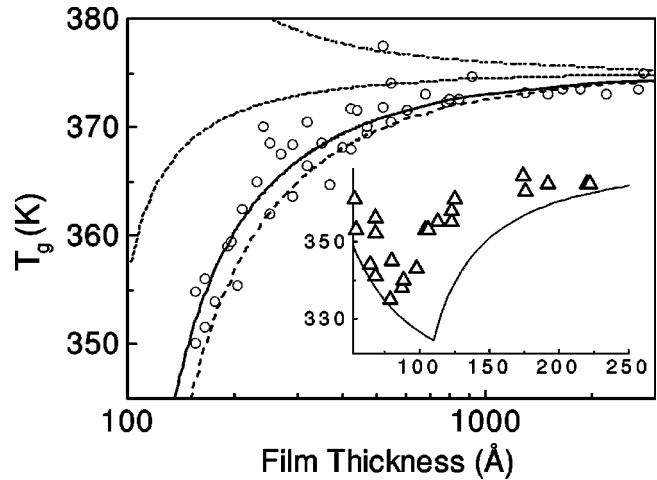

FIG. 2. Application of the model to the T_g values of polymer films supported by substrates. The circular data points are the data of Keddie et $al.$ [11] for PS on Si-H, and the triangle points in the inset are the results of Keddie and Jones for PS-COOH grafted onto Si-SiO$_x$. The lowest dashed curve is the application of the model assuming no effect due to the substrate, the solid line is the best fit with parameters of the substrate region given in the text, and the other dashed curves have $\lambda = 27$ Å , but with $T_g^{sub} = 441$ K (lower dashed curve) and 491 K (upper dashed curve).

ignoring any interaction between the polymer and the substrate. Such a treatment simply results in a direct mapping between supported films of thickness $h/2$ and free standing films with a thickness h. This procedure (using $T_g^{bulk} = 375$ K for agreement at large h) is shown as the lowest dashed line in Fig. 2, and provides a remarkably good description of the data. This treatment validates beyond doubt the conclusions of Keddie et $al.$ that the T_g reductions in their supported film samples were caused by the effect of the free surface, and the substrate had little effect. While surprisingly accurate, the T_g values resulting from this direct mapping are still slightly lower than those measured for supported films. To get more accurate agreement with the data we consider the interaction between the polymer and substrate. This interaction will generally result in a region near the substrate with reduced mobility, and we model this as a region of thickness λ with a slightly higher glass transition temperature T_g^{sub} [13]. Since the region near the substrate will be affected directly by a combination of chain packing constraints and short range attraction between the substrate and monomer units, its size will be determined by the persistence length of the polymer. For PS the temperature dependence of this region will be negligible ($\sim 10\%$) compared to that of the $\xi(T)$ values for 330 K$<$T$<$373 K, and we use a constant value of λ. We can then use the $\xi(T)$ and T_g^{surf} obtained above to describe the near surface layer of supported films. This results in a two parameter fit with parameters representing the size and mobility of the near substrate region. Applying this layer model to Keddie's data results in the best fit solid line shown in Fig. 2. The best fit parameters correspond to a $\lambda = 27 \pm 13$ Å region near the substrate with a T_g value of 391 ± 9 K. We explore the effect of different polymer-substrate interaction by varying the T_g value of the layer near the substrate, with a fixed layer size of $\lambda = 27$ Å . The results of this procedure are shown as the dashed lines in Fig. 2 and show that de-

pending on the strength of the polymer-substrate interaction the model can be used to describe T_g values of supported films which decrease, exhibit very little dependence, or even increase with decreasing h.

In our discussion so far, we have described the film thickness dependent T_g values for cases where some part of the film has bulk relaxation properties. We may also address what happens for film thicknesses less than this for the case of supported films where such an attempt is more straightforward. As the temperature is lowered the fact that the value of λ is essentially constant, means that the size of the mobile surface region can increase *only* to the point where $h = \xi(T) + \lambda$, and for lower temperatures or film thicknesses the size of the surface region is not determined by the cooperativity length and we must use $\xi(T) = h - \lambda$. This suggestion leads to the behavior shown by the solid curve in the inset of Fig. 2, where for thickness below some critical value the T_g value actually increases again. While surprising this behavior is exactly what has been observed by Keddie and Jones [25] and this data is shown by the triangles in the inset. Unfortunately many of the samples in the ultrathin film studies involved grafting the PS to the substrate, and we do not expect the interaction between the polymer and substrate in this case to be the same as that for the other data shown in Fig. 2. The result is that while T_g values are comparable for the thin and ultrathin films of PS, they are not entirely coin-

cident. This rules out a direct comparison between our model predictions and these data for the ultrathin films, but the qualitative agreement is outstanding.

In conclusion, we have presented T_g values for free standing film samples which are in a low M_n limit where effects due to polymer chain confinement are not observed. We present a simple layer model of the films that combines the idea of release of steric constraints at the free surface with the length scale for cooperative motion. This model is found to provide an accurate description of the data over a large range of temperatures for very reasonable physical parameters. The model is further applied to previous data of the T_g values of supported polymer films and is found to accurately describe that data as well. The model predicts length scales for cooperative motion below the bulk T_g value, and the simplicity and apparent universality of the model suggests that these values may be used to test theories of cooperative motion in glass forming materials.

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