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Quantifying glass transition behavior in ultrathin free-standing polymer films

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We have used Brillouin light scattering to make a detailed study of the behavior of the glass transition temperature T_g in ultrathin, free-standing polystyrene films. The glass transitions were experimentally identified as near discontinuities in the thermal expansion. The effects of film thickness, molecular weight, and thermal history on the measured T_g values have been investigated. While the size of the glass transition effects was comparable for all molecular weights, a complicated M_n dependence suggested a separation of the results into two regimes, each dominated by a different length scale: a low M_n regime controlled by a length scale intrinsic to the glass transition and a high M_n region, where polymer chain confinement induced effects take over.

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I. INTRODUCTION

The fundamental physics behind the glass transition remains unresolved. The idea of cooperative motion, introduced by Adam and Gibbs [1], suggests that there is an intrinsic length scale for cooperative dynamics, $\xi_{coop}(T)$, which increases as the temperature is lowered in the vicinity of T_g. Since the introduction of this idea, many different theoretical developments have been formulated around the concept of cooperative dynamics [2–4]. A direct connection between cooperative motion and Vogel-Fulcher dependence of transport properties has been established by Edwards and Vilgis [5]. Recent computer simulations have further emphasized the importance of cooperativity in explaining the dynamics of glass-forming materials at temperatures approaching T_g [6–10]. It is interesting to note that qualitatively similar behavior of strongly correlated particle movements has been found near the mode coupling critical temperature T_c [4] for systems as diverse as binary Lennard-Jones mixtures [8–10], a melt of short unentangled polymeric chains [6], and a metallic glass former (see reference in [6]). This indicates that finite size effects due to a length scale inherent to the glass transition should not be strongly affected by chain connectivity. In addition to confirming the existence of stringlike cooperative regions, with a length scale that increases as the temperature is lowered, these simulations have also revealed a second length scale—that of dynamic heterogeneity, ξ_{het}. For times shorter than the structural (α) relaxation time the systems were found to be composed of dynamically distinct regions of highly correlated motion. A detailed analysis of the simulation results revealed that cooperative movements were associated only with high mobility clusters, an observation which suggests that ξ_{het} may be considered as an upper limit for ξ_{coop} [11]. It has furthermore been noted that both ξ_{het} and ξ_{coop} increase as the temperature is lowered [9,12]. Despite the correlations between the two length scales, the exact relation between the two remains unclear.

One way to experimentally investigate the existence of an intrinsic length scale is to study the glass transition dynamics, or the glass transition temperature, in samples confined to dimensions approaching this length scale. A number of experimental studies have concentrated on this issue of *finite size effects* on the glass transition. A large fraction of these studies have been performed on glass-forming liquids confined to nanoporous glass, and a range of different techniques have been employed including calorimetric [13–15] as well as dielectric spectroscopy [16,17]. Reduced T_g values and enhanced dynamics for strongly confined systems have been reported. These effects have often been attributed to a length scale of cooperative motion. One complication of the studies of porous glasses is that the interactions with the interior of the pore can strongly affect the dynamics [16], and for this reason most studies involve pretreatment of the pores [13,16]. For polymeric glass formers, the influence of a characteristic length scale for glass transition dynamics has been inferred from relaxation studies of polymers in solution [18], from analysis of calorimetric or dielectric data by the use of fluctuation models [19,20], or from the relaxational behavior of naturally confined semicrystalline polymers [21,22]. As a result of these types of measurements a length scale of cooperative dynamics near the bulk T_g has been reported to be of the order of a few tens of Ångström for a large range of both polymeric and nonpolymeric glass formers. Additionally, a number of experiments on glass-forming materials have provided evidence for strongly heterogeneous dynamics at temperatures approaching T_g [23]. In particular,

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multidimensional NMR experiments have been used to directly measure the length scale of dynamic heterogeneities in poly(vinyl acetate) near its T_g, revealing a value of ~ 30 Å.

In summary, experiments have suggested that the length scale of heterogeneous dynamics, $\xi_{het}(T)$, is similar to that of cooperative motion, $\xi_{coop}(T)$, although the exact relation between them is not yet clear. It is worth pointing out that in general the existence of a particular length scale, as inferred from the analysis of experimental data, is by itself not enough to determine its origin. In addition, most of the experimental studies are not able to probe the characteristic length scale over an appreciable range of temperatures. An attractive alternative sample choice for studies of finite size effects in glass formers is that of thin polymer films. In these samples the confining dimension, the film thickness, can be continuously adjusted over many orders of magnitude, and samples can easily be prepared on a variety of substrates, even those the polymer melt itself does not wet. The interaction between the polymer and the substrate is further readily quantified by the use of contact angle measurements. The versatility in accessible polymer-substrate combinations as well as the possibility of studying free-standing films (which lack the specific interfacial interactions present in any supported system) allow for detailed studies of the various interactions and their respective effects on the glass transition.

The first direct measurements of anomalies in the T_g values of thin polymer films supported on solid substrates were performed by Keddie *et al.* [24] using ellipsometry. The samples for these studies were thin films of polystyrene (PS) on hydrogen passivated Si. For film thicknesses below ~ 400 Å the measured T_g values were found to be reduced below the bulk value, with the T_g reduction increasing as the film thickness was lowered. Since these initial studies a number of experiments, using several different techniques, have confirmed these observations [25–29]. The reductions in T_g observed in supported polymer films show no clear dependence on molecular weight for M_n values from $\sim 30\times 10^3$ to $\sim 2900\times 10^3$, although a very weak molecular weight dependence cannot be ruled out due to the scatter in the data. In addition to the T_g value itself, interesting behavior has been observed in the contrast of the glass transition, i.e., the ratio between the thermal expansivity (or quantities related to it) in the melt and the glass. This contrast, which is instrumental in identifying the glass transition, was measured to be a monotonically decreasing function of the film thickness [24,27,30]. These studies differ, however, regarding which expansivity (that of the melt or the glass) is film thickness dependent. X-ray reflectivity [30] and positron annihilation lifetime spectroscopy [27] data show the expansivity of the PS glass to be independent of thickness. On the other hand, ellipsometry measurements [24] suggest that the melt expansivity is instead independent of film thickness.

The large surface area to volume ratio of a thin film sample means that effects due to both the release of steric constraints at the free surface and specific interactions at the polymer-substrate interface may affect the segmental dynamics and hence the T_g value. Evidence for the effect of strongly attractive interfacial interactions on the glass transition was revealed in studies of poly(methylmethacrylate) (PMMA) [31] and poly(2-vinyl pyridine) (P2VP) [32] films. When supported on substrates for which a substantial polymer-substrate attraction is expected, both polymers showed T_g values that *increased* with decreasing film thickness. Grohens *et al.* [33] have further investigated the dependence of T_g in films of PMMA of varying tacticity and found a direct correlation between the density of polymer-substrate interactions and the effect on the T_g value.

A way to eliminate the difficulties associated with sensitivity to the polymer substrate interaction is simply to remove the substrate and study films in a free-standing configuration. Such measurements have been performed [34] and revealed much larger reductions in T_g with film thickness than those observed for supported films. The T_g reductions were also observed for larger film thicknesses (~ 700 Å) than in the supported case. Subsequent studies, involving an additional molecular weight [26], revealed a substantial M_n dependence in the T_g value for free-standing films. For the two M_n values investigated, reductions of T_g were observed at length scales of the order of the end-to-end distance R_{EE} for the polymer. This M_n dependence demonstrates that *chain confinement* may be an important contributing effect to T_g reductions in films of high M_n polymers. While interesting in its own right, the strong dependence on molecular weight suggests that the large T_g reductions observed for free-standing polymer films may be restricted to polymeric materials; a fact that limits the usefulness of these studies in investigating the more general problem of intrinsic length scales for glass transition dynamics. If such length scales were the determining factor of the T_g reductions observed in those free-standing films, then an M_n dependence would not be expected. In addition, it is difficult to conceive of finite size effects due to an intrinsic length scale for glass transition dynamics having a significant effect at such large values of the film thickness.

In looking for finite size effects the glass transition temperature may not be the ideal quantity to study, since it is affected by both the preparation and thermal histories of the sample as well as the mode of measurement. In light of this, a number of complementary investigations of related physical quantities have been performed in order to broaden the understanding of anomalous behavior in the structure and dynamics of thin polymer films. Neutron reflectivity [35] as well as Brillouin light scattering [36] techniques have been applied to provide evidence that the mass density in thin films of glassy polystyrene (both supported and free standing) is the same as in the bulk to within $\sim 0.5\%$. For the case of free-standing films, where the T_g reductions are large, such constraints on density anomalies rule out a simple relation between the observed T_g reductions and a reduced mass density. Structural relaxation due to segmental mobility has been observed in free-standing films of polystyrene with T_g values reduced by ~ 70 K using photon correlation spectroscopy [37]. In addition to providing quantitative agreement between measurements of T_g [26] and measurements of relaxation dynamics, the studies also showed that the shape of the relaxation function in thin free-standing films with reduced T_g values was the same as that of the bulk material within the experimental certainty.

Despite what is now a large body of experimental results [38], there have been only a few attempts [39,40] to provide a theoretical picture for the T_g reductions in thin films. A number of simulation studies have been performed using Monte Carlo or molecular dynamics techniques to investigate glass-forming systems in confined geometries. These simulations reveal that both structural and dynamical properties of polymers can be affected by the confinement [41,42]. The studies generally show enhanced segmental motion and meltlike dynamical properties near the free surface, extending some distance into the film. This is consistent with the experimental finding of reduced glass transitions in ultrathin films. Monte Carlo simulations of a dense polymer melt confined between hard walls [43] have further provided evidence for a relaxation function shifted to shorter times (faster dynamics), but with the same shape as that of the bulk. The faster dynamics, which might be used to suggest a lower T_g value, occurs for film thicknesses that are of the order of several R_g, where R_g is the radius of gyration of the polymer chain. While many of the above studies show evidence for anomalous dynamics in a surface region $\sim R_g$, the size of the simulation molecules is not generally varied and computational constraints mean that most simulations of this type involve molecules of similar sizes. It is thus not clear if the length scales observed in simulations of polymer melts and glasses are directly related to the size of the molecules or are instead due to an intrinsic effect on a similar length scale. In addition, most experiments use polymer lengths above the entanglement threshold, while simulations normally are restricted to much shorter chains. Interestingly, simulations on free-standing films of both polymeric and nonpolymeric materials [44–46] have shown very similar dynamical behavior. This observation suggests the existence of effects with some degree of universality.

The fact that additional studies have so far been unable to provide an explanation for the observed T_g reductions in thin polymer films suggests the need to return to more detailed T_g measurements. In particular, a number of questions that were raised by the previous studies on free-standing films remain outstanding. Foremost among the issues regarding T_g in free-standing films are the details and origins of the molecular weight dependence of the measured T_g values. In addition, a detailed examination of the effects of sample thermal history is necessary to investigate the role of potential nonequilibrium effects in the observed behavior.

In this paper, we report on the behavior of the glass transition with regards to changes in both the film thickness and the polymer molecular weight. We also discuss the inferred behavior of the thermal expansion in the glassy and rubbery states and show that free-standing films behave substantially differently from supported ones. By making measurements of T_g upon cooling samples that have been equilibrated above the bulk glass transition temperature and comparing those measurements to samples without such treatment, we rigorously address concerns about the sensitivity of the measured T_g values to the sample preparation history. The resulting insensitivity of the T_g values to the preparation and thermal histories demonstrates beyond doubt the validity of glass transition measurements in free-standing polymer films. In addition, we measure the sensitivity of the thermal expansivities of the glassy and rubbery states to the thermal history of the film sample. Most significantly, the detail of the study provides insight leading to a qualitative description of the physical causes for the observed behavior. The data provide evidence for two different physical effects which occur on similar length scales. The analysis of the data suggests that for molecules with $M_n \geqslant 514\times 10^3$ the relevant length scale for the T_g reductions is the size of the constituent molecules and the system is dominated by effects due to *polymer chain confinement*. Conversely, for $M_n \leqslant 347\times 10^3$ the relevant length scale is one intrinsic to glass transition dynamics and the T_g reductions are dominated by *finite size effects*. A model quantifying the effects of a characteristic length scale for glass transition dynamics is discussed. This model, together with the present measurements, provides insight into the length scale of glass transition dynamics near and below the bulk T_g value.

TABLE I. Polymers used in the experiment. (All polymers were purchased from Polymer Source Inc).

M_n	M_w/M_n
115 900	1.04
196 700	1.05
347 000	1.06
513 600	1.12
691 000	1.11
1 227 900	1.13

II. EXPERIMENT

The films used in this study were prepared from dilute solutions of monodisperse polystyrene in toluene. The films were spin cast onto clean glass slides, annealed above the bulk glass transition temperature for 14 h, and then slowly cooled at ~ 0.5 K/min to room temperature. Once cooled, the films were transferred onto a specially designed film holder using a standard water transfer technique [26]. In this process, films from the same glass slides were transferred to Si wafers for thickness determination by ellipsometry. By varying the concentration of the polymer solution, films with varying thickness were produced from six different molecular weight polystyrenes (see Table I) ranging from 116×10^3 to 1228×10^3. The lowest value of M_n represents a practical lower limit to T_g measurements of free-standing films using the techniques described below.

The thin free-standing films were measured using Brillouin light scattering (BLS). This technique measures light scattered from thermally excited phonons in the material. Since the light is scattered from propagating phonons, it is Doppler shifted from the incident frequency with a frequency shift that depends on the phonon velocity. In polymeric materials this frequency shift is typically of several GHz, corresponding to sound velocities of ~ 2000–3000 m/s. The phonon velocities are given by the square root of the ratio of the elastic constants to the mass density. This makes the BLS technique very sensitive to changes in the mass density, not only through the direct dependence, but also through a strong dependence of the elastic constants on mass density [47]. In conclusion, the BLS technique is an indirect but highly sensitive probe of the mass density and hence is very well suited for measurements of quantities that couple to the density, such as the glass transition temperature. An additional advantage of using BLS to study the glass transition in free-standing films is that it is relatively insensitive (compared to ellipsometric techniques) to surface roughness or even more extreme sample flaws such as wrinkles or small holes in the film.

For the specific case of a BLS experiment on a thin film sample, light scattered from a series of film-guided acoustic modes is measured. The film-guided modes are dispersive with mode velocities varying as the product $Q_{||}h$, where $Q_{||}$ is the phonon wave vector component in the plane of the film, and h is the thickness of the film. For very thin free-standing films there are only two modes that may be conveniently studied as the remaining modes diverge to large velocity values for very small thicknesses [36]. The lowest velocity mode, denoted A_0, approaches zero as $Q_{||}h \rightarrow 0$. For the thinnest films in this study the A_0 peak is not usually resolved from the central elastic peak, limiting its suitability for T_g studies. The second lowest velocity mode, denoted S_0, has a velocity that is a very weak function of $Q_{||}h$, approaching a constant value as $Q_{||}h \rightarrow 0$. This means that the relative error ($\Delta f/f$) in a BLS experiment is independent of the film thickness. This should be contrasted with other techniques applied to measure T_g in thin films, which have a relative error that is *continuously increasing* as the film thickness decreases. This relative insensitivity to changes in $Q_{||}$ and h, together with its nonvanishing velocity and high sensitivity to changes in the mechanical properties of the film, makes measurements of the S_0 mode velocity ideal for the study of small changes in the mass density of thin free-standing polymer films.

As the sample temperature is changed the density varies according to the appropriate thermal expansion. This results in changes in the phonon mode velocities and hence in the measured frequency shifts. At temperatures below T_g the variation in the phonon velocity with temperature is determined by the thermal expansivity in the glass and above T_g it is determined by the expansivity in the melt. Because the thermal expansivity exhibits a near discontinuity at T_g, a sharp and very well defined kink is observed at the glass transition. This kink can be used to identify the transition. The BLS measurements probe the density of the sample and thus the resulting T_g value is in a low frequency limit. Relaxations at the measured frequency (~GHz) are observed only at much higher temperatures [48].

The BLS studies were performed in air using the backscattering geometry with the sample in an optical furnace, in which the temperature is controlled to within ± 0.10 K. The temperature was measured using a fine gauge thermocouple junction in close proximity to the film. Each spectrum was acquired at constant sample temperature and the heating rate between consecutive measurements was 0.5 K/min. Single longitudinal mode laser light with a wavelength of $\lambda = 5145$ Å was focused onto the film at an angle of incidence of $\theta_i = 45°$. The direction of the light reflected from the film was monitored to ensure that the value of θ_i, and thus also $Q_{||} = (4\pi/\lambda)\sin(\theta_i)$, remained constant throughout the measurements. The scattered light was collected and collimated by the focusing lens and then input to a $3\times(1+1)$ pass Sandercock tandem Fabry-Pérot interferometer. A vertical slit was placed in the path of the collimated light to reduce line broadening due to the nonzero light collection aperture [49]. To determine the value of T_g for a free-standing film, a series of BLS spectra were collected at fixed temperatures in steps of typically 4–5 K. In a normal run 5–15 spectra were acquired for temperatures below T_g, and 4–10 spectra above T_g. Each spectrum was acquired for a time of ~5–45 min. The recorded S_0 modes were fitted to an instrumental response function using a nonlinear least-squares routine. The reason for the fewer data points above T_g, particularly for the thicker films, is the eventual formation of holes in the films at these temperatures. The frequency versus temperature graph shows two linear regions. Where the two linear regions intersect we define our experimental glass transition temperature. We estimate that we can determine the value of T_g to within ± 3 K.

III. RESULTS AND DISCUSSION

A. Measuring the glass transition

Figure 1 shows a series of BLS runs on free-standing PS films with an M_n value of 347×10^3. In all cases a T_g value can be clearly identified as a well defined kink in the temperature dependence of the BLS frequency shift. An important observation, which is readily apparent from the data shown in the figure, is that for the thinner films the T_g values, as determined by the intersection between the two linear regions of frequency shift versus temperature, are reduced below the measured bulk value of 370 ± 3 K. The measured T_g values follow a continuously decreasing function as the film thickness is lowered, reaching a value of only 312 ±3 K for a film with thickness of 216 Å. Film thicknesses of this order represent a lower practical limit to the measurements of glass transitions in free-standing films, as much thinner films are too fragile for standard room temperature sample preparation.

Recent measurements of dielectric relaxation in thin films of PS between aluminum electrodes have shown that as the film thickness is decreased there is a significant broadening of the relaxation peak [28,29]. This relaxation behavior suggests that these samples may exhibit a broadening of the kinetic glass transition. A broadening has also been reported in recent ellipsometric studies of supported polymer films [50]. In this case the broadening, which was observed as an extended region where the temperature dependence of the thermal expansivity changed from a value typical of the glass to one typical of the rubber, was found to increase as the film thickness was reduced. The resulting decreased T_g was suggested to be solely a result of this broadening. As seen from the data in Fig. 1, broadening to this extent is not observed in the glass transitions of the free-standing films. While it is apparent from Fig. 1 that there are always sufficient data to reliably obtain a T_g value, sample degradation often results in the inability to obtain enough data at temperatures above the measured T_g value to make strong statements about broadening of the transition.

A more rigorous test of glass transition broadening in free-standing films is provided by the data in Fig. 2. The plot shows results from a 466 Å thick film of $M_n = 691\times10^3$ polymer. For this film it was possible to obtain data over a temperature region extending more than 50 K above the measured T_g, up to temperatures just above the bulk glass transition. While the large region of temperatures studied is not typical of all samples, the lack of observed broadening is.

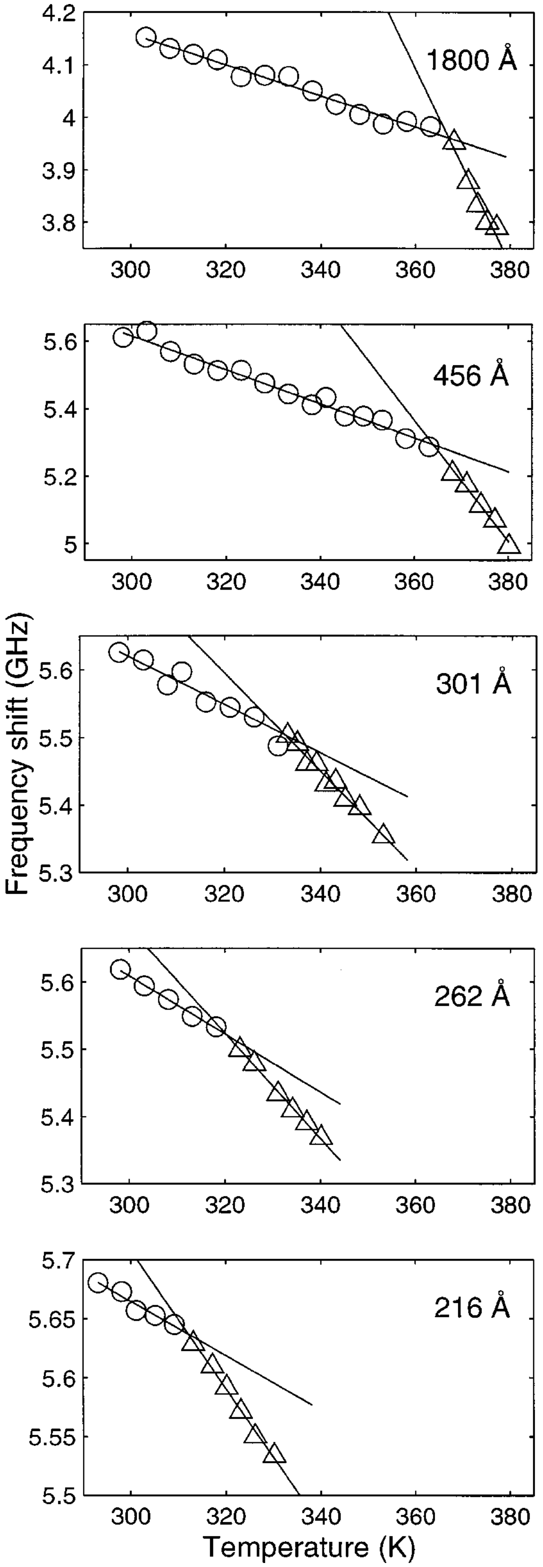

FIG. 1. BLS measurements of the S_0 phonon as a function of temperature for five free-standing polystyrene films ($M_n = 347\times10^3$) as a function of sample temperature. Linear fits to the data used to determine the T_g values of the films are also shown. The thicknesses of the film samples are indicated in the figure.

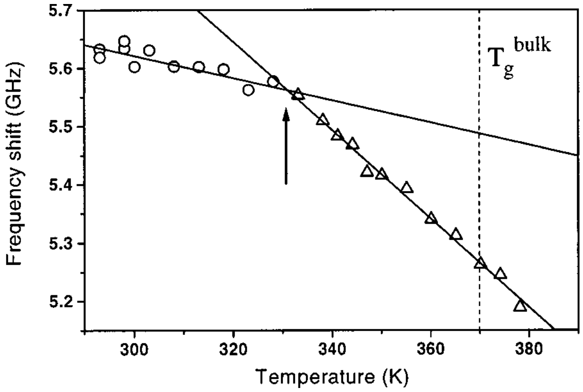

FIG. 2. BLS measurements of the S_0 phonon as a function of temperature for a free-standing polystyrene film with thickness 466 Åand $M_n = 691\times10^3$. The measured T_g value is indicated by an arrow. The bulk T_g, as observed for thicker films, is marked in the figure by the vertical dashed line.

It is evident from the data shown in Fig. 2 that there is no evidence for broadening of the transition; the slope of the melt region can be seen to be the same both just above, as well as 40 K above, the measured T_g. This is most clearly and easily illustrated by doing independent least-squares fits to the data for the six data points nearest to the measured T_g value (i.e., the range from 328 to 348 K) and the six data points at the highest temperatures (i.e., from 353 to 378 K). This analysis reveals that the slope in the lower temperature region is $-(8.3\pm0.5)\times10^{-3}$ GHz/K, and that in the higher temperature region is $-(8.2\pm0.5)\times10^{-3}$ GHz/K. These two values of the slope are practically the same even though the centers of the two temperature regions are 30 K apart. Although our measurements cannot totally exclude the possibility of an increased broadening for thin films, the analysis rules out any broadening more than ~5 K, and instead reveals very sharp glass transitions.

Finally, we stress the importance of noting that this observation should not be taken as contradicting the observations for supported films, but rather as an indication of some of the qualitative differences that exist between T_g studies in free-standing films and similar studies in supported films.

B. Thickness and M_n dependence

The data of Fig. 1 are for a single M_n value. Since it has been shown that the T_g value in a free-standing polymer film can exhibit a substantial M_n dependence, one of the major goals of this work is to quantify that M_n dependence. We have placed particular emphasis on measurements of smaller M_n polymers, which are less likely to suffer from nonequilibrium effects. Figure 3 shows measured T_g values as a function of film thickness for seven different values of M_n (the average end-to-end distances R_{EE} are also shown as arrows in the upper part of the graph), and includes the data for the two M_n values studied in Refs. [26,34]. Where there is overlap in the data between the two studies (such as measurements of the $M_n = 691\times10^3$ polymer) the agreement between the present data and the values reported in those references is excellent. For all M_n values in the study the behavior may be qualitatively characterized by the existence of a film thickness value below which the measured T_g val-

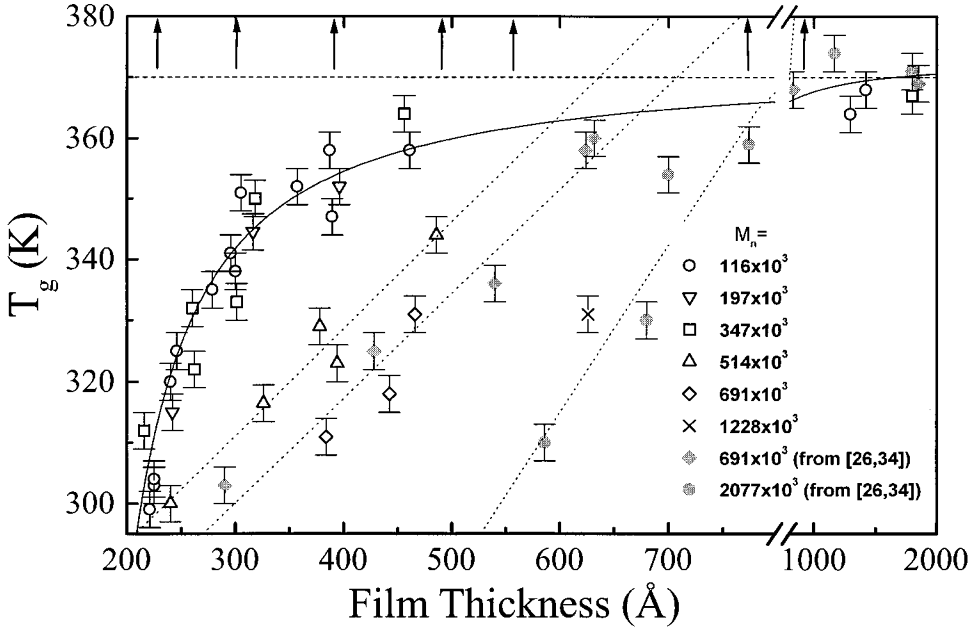

FIG. 3. T_g values recorded by BLS measurements of seven different molecular weights (see Table I) plotted versus film thickness. The unfilled symbols indicate data from this work, while the filled symbols are data included from Refs. [26,34]. End-to-end distances of the unperturbed polymer molecules are indicated with arrows in the upper part of the graph. The horizontal dotted line marks the location of the bulk T_g. Linear fits of the $M_n=514\times10^3$, $M_n=691\times10^3$, and $M_n=2077\times10^3$ data are displayed with dotted lines. The solid line going through the data of the three lowest molecular weights is a fit to the model discussed in the text. Typical error bars of the T_g determination are included, while the estimated accuracy of the film thickness determination is $\sim\pm10$ Å, which is roughly indicated by the size of the data symbols.

ues are less than in the bulk. The most significant observation about the data in Fig. 3, however, concerns the very interesting and complicated M_n dependence of the measured T_g values. From the figure it is evident that the relatively strong variation of T_g with M_n at constant film thickness, which is seen for samples with $M_n\geqslant514\times10^3$, is either much weaker or vanishes altogether for polymers of $M_n\leqslant347\times10^3$. In addition, the transition from the low M_n to the high M_n behavior is relatively sharp with no data sets showing *intermediate* behavior. Concentrating on the higher M_n data initially, we note that for M_n values of 514×10^3 or greater, a threshold thickness is easily defined because of the linear nature of the T_g versus h data (discussed in more detail below). Figure 3 shows that for M_n values ranging from 514×10^3 to 2077×10^3 this threshold thickness shows a considerable M_n dependence, which is monotonic in that lower M_n values always lead to lower values of the threshold thickness. To further quantify the behavior seen in Fig. 3 we consider fits of the data for M_n values of 514×10^3, 691×10^3, and 2077×10^3, respectively, for which there are enough data points to warrant such fitting, to the linear function introduced in Ref. [26]:

$$T_g(h)=\begin{cases} T_g^{bulk}\left[1-\left(\dfrac{h_0-h}{\zeta}\right)\right], & h<h_0,\\[2ex] T_g^{bulk}, & h\geqslant h_0. \end{cases} \qquad (1)$$

In this function the parameter h_0 is the threshold film thickness for T_g reductions. As we consider M_n values from 514×10^3 to 691×10^3 to 2077×10^3 the ratio h_0/R_{EE} varies from 1.1 to 1.2 to 0.8, where R_{EE} is the average end-to-end distance of the polymer molecules. The fact that these h_0/R_{EE} values are *all* $\simeq1$ provides strong evidence that the T_g reductions for these M_n values are due to confinement of the polymer molecules as was originally suggested in Ref. [26]. For the $M_n=514\times10^3$ and $M_n=691\times10^3$ polymers we can see that the linear function depicted by Eq. (1) provides an excellent description of the data for films with $T_g<T_g(\text{bulk})$, though we do not necessarily expect that this line can be extrapolated to the bulk T_g value. Fits to other functional forms, such as Eq. (2) (given below), which has been used to describe the T_g reductions in supported polymer films [24], are notably less accurate. While the approximate coincidence of the h_0/R_{EE} values provide evidence of the importance of chain confinement effects, it is not possible to continue this idea and collapse the data by plotting the measured T_g values as a function of the reduced variable h/R_{EE}. The reason for this is that the length scale associated with the slope of the linear fits, ζ, has a much weaker dependence on R_{EE} than that of h_0. A detailed study of the high M_n regime has recently been performed [51], and a more complicated scaling than that suggested above was found to exist for those data [52].

The behavior of the film thickness dependent T_g values for polymer films with $M_n\leqslant347\times10^3$ is intriguing. For these low molecular weights the film thickness dependence of the T_g value is quantitatively the same within the scatter of the data for films of polymers with R_{EE} values differing by a factor of 1.7 or 170 Å. This should be contrasted with the $M_n=514\times10^3$ data and the $M_n=691\times10^3$ data, where a very substantial difference (up to ~30 K for films with the same value of h) in the film thickness dependence of the T_g

value is observed for R_{EE} values differing by only a factor of 1.1 (or only 80 Å). This comparison shows that if an M_n dependence exists at all, it is much weaker for polymers with $M_n < 347\times10^3$ than that observed for polymers with $M_n > 514\times10^3$.

In addition to the abrupt and qualitative change in the M_n dependence of the T_g values, the T_g data for the three lowest values of M_n display a film thickness dependence that is clearly quite different from that which is found in the high M_n region. This is obvious from the data in Fig. 3, where the T_g versus h data display substantial curvature. This qualitative change in film thickness dependence is reflected in the very different fitting functions that can be applied to describe the data. The linear function that is so successful at describing the data for the higher molecular weight polymers provides a poor fit to the low M_n data. A better fit can be obtained, for instance, by using the functional form introduced by Keddie *et al.* [24] to describe T_g data for supported films,

$$T_g(h) = T_g^{bulk}\left[1 - \left(\frac{\alpha}{h}\right)^{\delta}\right]. \tag{2}$$

For the supported PS films of Ref. [24], the best fit to this equation was obtained for $\alpha = 32\pm6$ Å and $\delta = 1.8\pm0.2$. Applying this same equation to the T_g values for the low M_n free-standing films (with T_g^{bulk} fixed to our measured value of 370 K, and $\delta = 1.8$ to allow direct comparisons of the length scales between free-standing and supported films), we find $\alpha = 78\pm1$ Å. While it is noteworthy that samples with two free surfaces are described by a characteristic length that is approximately twice that found for samples with only one free surface, a detailed discussion of fitting is not warranted without the context of a physical model.

The results presented above show that the behavior of the low M_n free-standing films, except for the actual magnitude of the effect, is more similar to that of supported polymer films than that of free-standing films of higher M_n. The lack of molecular weight dependence as well as the nonlinear dependence of T_g on film thickness are characteristics observed in T_g values of low M_n free-standing films and supported polymer films, but not in those of free-standing films of higher M_n values. This striking similarity between the behavior of the low M_n films and supported films extends far enough that to a good approximation the T_g value for a free-standing film of thickness h is the same as that of a supported polymer film with thickness $h/2$ [53]. With this in mind we can address the question of whether or not the behavior we have attributed to low M_n polymers persists for arbitrarily small polymer molecules, or whether there also exists some lower bound of M_n beyond which the behavior is different. The quantitative relation described above between the T_g reductions in free-standing and supported films allows us to make comparisons with the supported film data of Refs. [28,29]. This comparison allows us to suggest that the behavior exhibited for the low M_n free-standing films might be expected to persist down to M_n values of at least 30×10^3, if such measurements were possible. The effect of supporting a polystyrene film is hence both to reduce the magnitude of the T_g reductions compared with the free-standing case and to cause an almost complete loss of chain confinement induced effects. The qualitatively different film thickness dependence in the two M_n regions is strongly suggestive of two distinct physical effects causing reductions in the T_g value. A more detailed discussion of such effects will be given in Sec. IV.

C. Film stability

An observation that might provide insight into what models can best describe the dynamics in these systems concerns the stability of the thin free-standing films. It has been noted before that very thin films, with measured T_g values far below the bulk value, appear to be stable to temperatures much above their experimental glass transitions [34]. An excellent example of this is given in Fig. 2, where data were acquired up to 50 K above the measured T_g. We can compare this to the behavior of films with $h \sim 1000$ Å for which it is only possible to measure to temperatures $\simeq 20$ K above the T_g value ($\sim T_g^{bulk}$) before they burst. In fact, regardless of the measured T_g value of a particular film, the films appear stable to temperatures *near* the bulk T_g value. In order to understand the stability of films, we first consider the possible mechanisms of film bursting. One such is the spinodal mechanism proposed by Vrij [54], where the films are unstable due to the attractive van der Waals interaction between the two free surfaces. From this mechanism, we can estimate a characteristic film lifetime $\tau \propto h_0^5 \eta$ where h_0 is the initial film thickness and η is the viscosity. Let us consider, as an example, two films of the $M_n = 691\times10^3$ polymer having h values of 500 Å and 600 Å, respectively. Both films are held at a temperature of $\simeq 355$ K and if we adapt the temperature dependence of the viscosity for bulk PS [55], we obtain an estimate of the characteristic time for film bursting for the two films differing by more than four orders of magnitude (mostly due to the differences in T_g values of the two films). Even though we have not quantitatively measured the film stability, we can easily rule out such a difference simply on the basis that measurements such as those shown in Fig. 2 are possible. An alternative mechanism for the eventual destruction of the films is that of nucleation and subsequent growth of holes. Studies on free-standing PS films have recently revealed that hole growth above T_g for films with thicknesses $\simeq 1000$ Å ($T_g \sim T_g^{bulk}$) is significantly faster when the film thickness is decreased [56].

These two arguments both lead to the conclusion that films should become much less stable (relative to their measured glass transition) as their thickness is decreased. This is in contrast to what is observed experimentally. The additional observation that all films, regardless of their apparent glass transition, rapidly form holes at temperatures near (but in some cases less than) the bulk T_g leads us to suggest that the film is stabilized by some part having dynamic properties characteristic of a material with a T_g value near that of the bulk polymer. This does not necessarily mean that there is a part of the film that remains glassy through an extended temperature region, but only that there exists, even when the film is above its measured glass transition, a fraction of the film with a substantially higher viscosity (or slower dynamics). While in no way rigorous, this suggestion serves as motivation to consider layer models to describe the phenomena observed for free-standing polymer films.

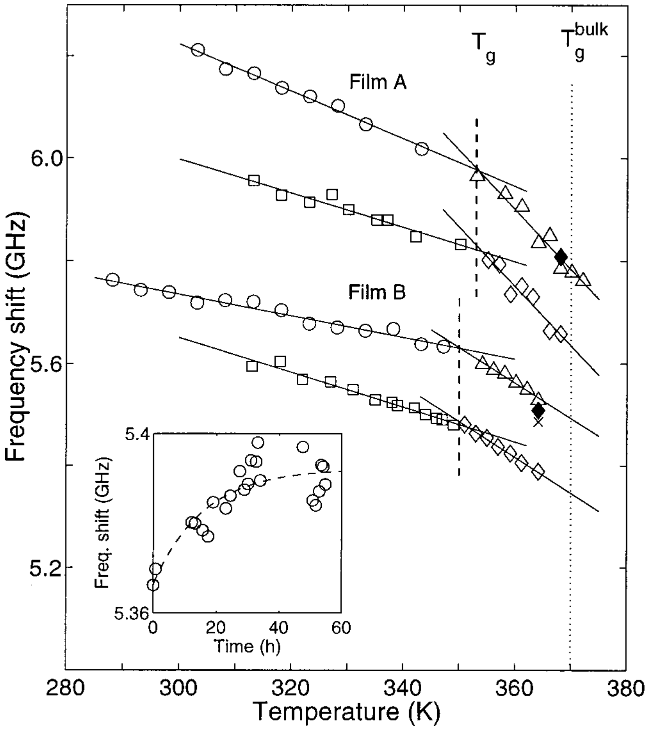

FIG. 4. BLS measurements of the S_0 phonon as a function of temperature for two different film samples, film A and film B, both of $M_n = 347\times10^3$ and with a film thickness of ~320 Å. The circles indicate the glassy and the triangles the rubbery regions in the heating cycle, while the squares mark the glassy and the diamonds the rubbery regions in the corresponding cooling cycle. For clarity, the heating and cooling runs are displaced vertically; however, the filled diamonds indicate where the first data point on the cooling scan is situated on a scale relative to that of the corresponding heating run. The two samples were subjected to the annealing procedures described in the text. The vertical dashed lines mark the location of the T_g values as measured in the two heating runs. The inset shows the relaxational behavior (discussed in the text in detail) for film B.

D. Effect of sample history

The complicated sample preparation that is necessary for all thin film studies, and especially those involving free-standing films, brings up the importance of path dependence for the glass transition. In addition to the thermal history of the sample, polymer films may be further affected by stresses induced during solvent evaporation and annealing on a solid substrate. An example illustrating the importance of the formation path on the properties of bulk glasses is the recent study by Colucci *et al.* [57] of the glass transition in samples of polycarbonate under both isobaric and isochoric cooling conditions. These studies revealed that, while the isobaric and isochoric rubber states were similar, there were large differences in the resulting glasses produced upon cooling. Based on the importance of the history dependence of the properties of glasses, in general, a very valid criticism may be presented against any measurement of T_g that is conducted upon heating a sample (especially samples with such complicated thermal histories as ultrathin polymer films) from the glassy state. While this fact results in most measurements of T_g in bulk materials being made upon cooling from the equilibrium melt, the delicate nature of the thin free-standing samples makes a similar treatment more difficult. Previous studies have provided some evidence against sample preparation details as a dominant factor in the observed T_g reductions [26], but the most convincing answer to criticism concerning the effect of sample preparation history is to equilibrate the samples above the bulk glass transition, and then perform measurements upon cooling from the equilibrium melt. While the fragility of free-standing film samples does not allow such treatment for all samples, we have performed some measurements aimed at directly addressing this concern.

The thermal path dependence for free-standing films with $M_n = 347\times10^3$ and a thickness of $h \simeq 320$ Å has been studied in detail. The lower M_n samples were chosen despite the more pronounced sample fragility because results from these samples may have the most relevance for general statements about finite size effects inherent to the glass transition. Two separate films, prepared under identical conditions, were investigated and the T_g values were initially measured upon heating from the glass. Both the experimental runs are shown in Fig. 4, where the circles indicate the glassy and the triangles the rubbery regions in the heating experiments, while the squares mark the glassy and the diamonds the rubbery regions in the corresponding cooling experiments. For clarity, the heating and cooling runs are displaced vertically in the figure. However, the filled diamonds indicate where the first data point on the cooling scan is situated on a scale relative to that of the corresponding heating run.

The two samples were subjected to the following annealing procedures: After a completed heating run the first sample (the upper data set, denoted film A, in Fig. 4) was further heated to 370 K for 1 h. The temperature was then raised 2 K to 372 K where it was kept for another hour. At both annealing temperatures, measurements were performed and gave values consistent with the melt slope obtained below bulk T_g. After this annealing procedure the film was slowly cooled at 0.5 K/min to 368 K and subsequently a full

TABLE II. Comparison between results obtained upon heating and cooling for two different film samples.

	T_g (K)	Glass slope (MHz/K)	Melt slope (MHz/K)
		Film A	
Heating	353.4±3	−4.64±0.20	−11.55±1.02
Cooling	354.0±3	−3.31±0.31	−11.49±1.48
		Film B	
Heating	350.3±3	−2.10±0.12	−6.91±0.53
Cooling	351.6±3	−3.40±0.17	−7.01±0.21

T_g run was performed upon cooling. Individually fitting the two data sets for film A gave the results shown in Table II. A number of interesting observations can be made from these data. We note that the slopes in the melt region are the same within 0.5%, while those in the glass show some variation. This behavior might be expected as above the measured T_g value the sample should be in equilibrium and we expect the properties to be independent of history. The slightly different slopes in the glassy region are most likely a result of different thermal stresses which are frozen into the film. Some stresses will be relieved (perhaps by the formation of small cracks in the film) and these will differ from sample to sample. Despite the difference in glassy slopes between the heating and cooling curves, the fact that the glassy slopes are much less than those of the melt results in the two measured T_g values being the same within the experimental uncertainty.

The second sample (the lower data set, denoted film B, in Fig. 4) was subjected to the following thermal treatment: it was first subjected to a normal heating run, subsequently heated to 372 K for 15 min, heated briefly (~ 100 s) to 379 K, and then slowly cooled at 0.5 K/min to 364 K, where it was allowed to remain for 54 h in order to equilibrate. During the heating run, close to the bulk T_g, this film sample exhibited a frequency shift changing with time. This was most likely due to the onset of film degradation, whereupon hole formation can lead to an overall thickening of the film, resulting in a smaller measured frequency shift [36]. The pronounced fragility of this sample made a long annealing time above bulk T_g impossible. Upon returning to a temperature of 364 K after annealing above the T_g of the bulk, the frequency shift was lower than on the corresponding initial heating scan (see the × symbol) and the shift in frequency was seen to change with time. To investigate this effect more quantitatively, the measured phonon velocity was monitored during the total annealing period of 54 h, and it was found that after ~ 10–20 h the measured frequency shift, and hence the underlying mechanical properties, had reached an equilibrium value. The inset in Fig. 4 shows the time dependence of this relaxation process. It is interesting to note that the time scale of the relaxation behavior shown in the inset is comparable to that observed in relaxation experiments performed on bulk polystyrene a few degrees below the glass transition [58,59]. This suggests that the small, but significant, relaxation effect observed may result from some fraction of the film possessing bulklike dynamical properties, a suggestion that quantifies the similar statement based on observations of film stability. Finally, it is important to notice the very small difference between the last unfilled triangle data point, being recorded before equilibrating, and the filled diamond data point, denoting the frequency shift after the full 54 h annealing period. Even though the effect is clearly discernible, it is still a small effect that is noticeable only because of the high sensitivity of the technique. The results for the slopes obtained upon fitting the data for film B are found in Table II. As for film A, the slopes of the two melt regions in the heating and cooling cycles are the same within the uncertainty of the fitting. In contrast, there are significant differences in the slopes of the glassy regions between the heating and cooling cycles. Again, note that the two measured T_g values overlap within the experimental accuracy. Thus the observed sample-to-sample variation in the properties of the PS glass cause at most only ~ 3 K variation in the measured T_g value. In summary, these studies have shown directly that the properties of the polymer glass are path dependent, but those of the melt, and the actual value of the glass transition temperature, are reproducible and not significantly dependent on the thermal history. Perhaps most importantly, the measured T_g values are the same within the quoted precision despite the slight variations in the expansivity of the glassy state.

E. Contrast of the transition

A further observation from the data in Fig. 1 concerns the slopes of the straight line segments of the data which are used to determine the T_g value. As found in previous studies [36] the slope of the frequency shift versus temperature plot in the glassy region did not show any particular trend with film thickness, while the slope of the rubbery region was found to exhibit a significant film thickness dependence. The most remarkable consequence of this fact is that the *contrast* of the transition, which we define as being the ratio of the slope in the rubbery region to the slope in the glassy region, is also a function of the film thickness. The main significance of this is that a sufficient contrast in the expansivity values is required in order to identify the glass transition. For a contrast value of unity there is no discontinuity in the thermal expansion and it becomes impossible to measure a T_g value. Lower values of the contrast necessarily lead to higher uncertainty in the resulting T_g value. As mentioned previously, in supported polymer films the contrast has been observed [24,27] to decrease monotonically as the film thickness, and hence the T_g value, is lowered. In some cases the contrast becomes so small that identification of the transition is not possible [30,38]. For supported films, this behavior of the contrast results in the lowest T_g values having the greatest uncertainty. In free-standing films the behavior is quite different, as can be seen from the data in Fig. 1. As the film thickness is reduced from 301 Å to 262 Å, the contrast decreases (to a minimum value of typically ~ 1.7). Further de-

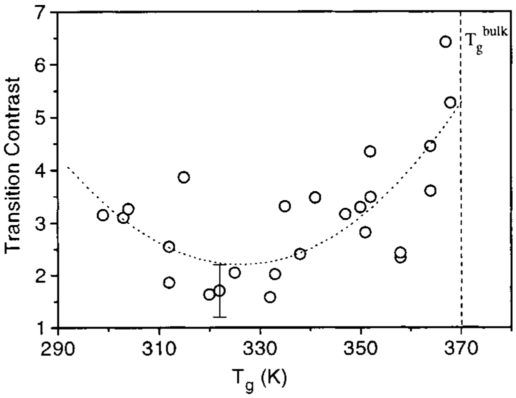

FIG. 5. The transition contrast (ratio of the frequency vs temperature slope in the melt to that in the glass) for the low M_n data, i.e., $M_n = 116 \times 10^3$, 198×10^3, and 347×10^3. The vertical dashed line indicates the location of the bulk T_g value. An error bar is included as an indication of the accuracy of the experimental method. The dashed line should be considered as a guide to the eye and is a fit of the data to a second order polynomial.

creases of the film thickness normally lead to an increase in the contrast above the minimum value, making measurements of very thin films, with very large reductions in the T_g value, relatively simple. Figure 5 shows the measured values of contrast for the polymer films with $M_n \leqslant 347\times 10^3$ as a function of the T_g value. This figure reveals exactly the behavior suggested by the data in Fig. 1. The contrast values are given as a function of T_g simply because the T_g is such a strong function of h that plotting contrast as a function of film thickness might possibly obscure the behavior. We note also that we observe a non-negligible sample-to-sample variation in both the melt and glass slopes, though the effect is much more pronounced in the glassy region. The result of this is that simply plotting the slope of the melt region as a function of T_g does not show the behavior shown in Fig. 5 as clearly. By studying the contrast instead, we are able to normalize this variation to reveal the trends shown in Fig. 5.

While it is not possible on the basis of these data alone to say that the contrast always exhibits a minimum value for *intermediate* values of film thickness, it is certainly true that the contrast is not a simple monotonically decreasing function of the T_g value (or, equivalently, film thickness). Finally, we note that in any technique (such as ellipsometry or reflectivity) where the measured quantity is directly related to the film thickness, the increasing relative error in the slopes as the film thickness decreases results in a high uncertainty in the contrast for ultrathin films, which might make identification of the effects shown in Fig. 5 impossible. While the scatter in the actual values of the slopes does not allow us to make rigorous statements about the film thickness dependence of the glass and melt slopes, the interesting behavior of the contrasts of the glass transition shows that BLS measurements are a powerful way to probe the properties of ultrathin free-standing films.

IV. POSSIBLE ORIGINS OF T_g REDUCTIONS

We have already remarked that the data in Fig. 3 suggest the presence of two different mechanisms that cause reductions of the T_g value in thin free-standing films. In light of this, it is necessary to consider what physical effects might give rise to the observed results. For polymers with $M_n \geqslant 514\times 10^3$, the relation between the observed film thickness dependence of the T_g reductions and the polymer size suggests that the important length scale is that of the macromolecule itself. This leads to the suggestion that, for these values of M_n, the dominant effect comes from *polymer chain confinement*. In contrast, the apparent lack of M_n dependence exhibited for polymers with $M_n \leqslant 347\times 10^3$ together with the qualitatively different dependence of T_g on film thickness suggest a *finite size* effect, caused by a length scale intrinsic to glass transition dynamics itself. In the following, these two mechanisms will be further discussed.

A. Chain confinement effects

It was first suggested by Reiter [60], on the basis of observed dewetting of PS films from glass, that the polymer chain dynamics in films with thickness less than the unperturbed molecular size might be different from that in thicker films. Similar suggestions have also been made based on experiments of whole-chain diffusion in polymer films [61,62] or measurements of the mechanical response of confined low molecular weight polymers [63]. Most experimental studies have investigated the motion of whole polymer chains, and it is important to note that, in a polymer film, such dynamics might be strongly influenced by effects such as pinning of segments to the substrate or enhanced density fluctuations [64]. It is hence not necessarily straightforward to relate changes in diffusion with changes in glass transition behavior [38]. Additionally, it has been proposed that chain structure could be significantly affected in ultrathin films [65] and hence that the observed T_g reductions might be due to conformationally mediated changes in dynamics [39]. In support of such suggestions, computer simulations have indicated altered dynamics correlated to structural changes in confined polymers [41]. In fact, in the direct vicinity of a hard wall (or free surface) the random walk path of the polymer chain is subject to reflecting boundary conditions, and based on this a slight layering of the polymer chains near an interface is expected [66]. Recently, small angle neutron scattering experiments have been performed on polystyrene thin and ultrathin films on a passivated Si substrate to investigate to what extent these predicted effects occur in real physical systems, and thus to what extent they may be applied to explain the changes in dynamics observed for polymer films. These measurements did not, however, detect any significant change in chain size or conformation in the plane parallel to the film even for strongly confined films, where $h/R_g^{bulk}\sim 1$ [67,68]. One of the most striking contrasts between the glass transition behavior in thin free-standing films compared with that of supported films is the difference in the molecular weight dependence. While the T_g values of free-standing PS films with $M_n \geqslant 514\times 10^3$ display a strong dependence on M_n (see Fig. 3), supported films show no discernible M_n dependence for $30\times 10^3 < M_n < 2100\times 10^3$ [38]. This experimental fact strongly suggests that the effect causing M_n dependent T_g reductions in free-standing films requires the existence of two free surfaces. In addition, the fact that the threshold thickness for T_g reductions $h_0 \sim R_{EE}$ suggests that the effect is related to confinement of the polymer chain. One possible mechanism that satisfies these properties has recently been proposed by de Gennes [69]. The approach introduces a polymer relaxation mode (referred to as sliding motion) that is highly ineffective in the bulk but becomes more efficient for thin films and that eventually for thin enough films will dominate over the normal bulk dynamics. The extra mobility provided by the suggested relaxation route originates from chain segments having loops or bridges in contact with the *soft* interfaces, where the activation barrier for mobility is much lower. A scaling argument, based around the competition between the suggested mechanism and the relaxational behavior characteristic of the bulk, was found to exhibit an M_n dependence similar to that observed both in this work and in studies extending to larger values of M_n [51,52]. This approach might provide an explanation for at least some of the qualitative aspects of the high M_n data for free-standing films. We note that the relevance of this sliding motion may be tested by the investigation of different polymer systems and/or polymer structures. The proposed mechanism should be very sensitive to the polymer chain architecture, and the study of statistically branched polymers in thin films (where sliding should be suppressed) or of ring polymers in the bulk might shed further light on the significance of this relaxation mode for structural relaxation. Despite this recent progress, the strong molecular weight dependent effects on the glass transition temperature observed for thin free-standing polymer films still remain to be quantitatively explained. Certainly, more experimental work is needed in order both to characterize the phenomenology and to form a basis for further theoretical work.

B. Finite size effects

For the low M_n free standing films, as well as all measurements on supported films, the lack of M_n dependence suggests that the observed T_g reductions are not influenced by the polymeric nature of the sample molecules. This indicates that finite size effects due to a length scale intrinsic to the glass transition might be used to describe the observed T_g values for these systems. In order to describe our low M_n data, we have recently incorporated the fundamental idea of such a length scale into a layer model [53,70]. To our knowledge this is the first occasion on which T_g data from thin polymer films have been analyzed in a context compatible with explanations proposed to explain a lower T_g and faster dynamics in other glass-forming materials. The success of the approach has suggested that observations from such distinctly different samples can be explained with the same underlying physical cause. A notable aspect of the approach is that in fitting our model to experimental data we may learn about the temperature dependent characteristic length for glass transition dynamics over an extended temperature range. In constructing the model, we consider a free-standing polymer film to contain a region of enhanced segmental mobility near its free surfaces, with the remainder of the film having bulklike dynamics. In this picture the film is regarded as dynamically inhomogeneous. This dynamical inhomogeneity is simply *modeled* by dividing the film into three layers, each having average dynamical properties as indicated by its respective T_g value. The dynamics of the two regions near the free surfaces are modeled by a surface layer with a different (lower) glass transition temperature than the bulk. The remainder of the film, in turn, is modeled as having dynamics characterized by the T_g value of the bulk material. This simple construction is supported by comparisons with simulation work, where both an enhanced mobility at the free surface as well as a dynamically bulklike central part have been observed [44,46]. The size of a surface region of lower T_g should be closely related to the length scale characterizing the distance over which dynamics in bulk glass-forming systems are correlated [at least for film thicknesses $h > 2\xi(T)$], and should be determined by the length scale of either cooperativity or dynamic heterogeneity. We prefer, however, to simply state that the surface region is determined by a characteristic length scale for the dynamics, without specifying its origin. A schematic drawing of the model is shown in Fig. 6, where the temperature dependent characteristic length scale is denoted $\xi(T)$.

Since the construction of our model is meant to reflect inhomogeneous dynamics in the thin films rather than real physical layers with different T_g values, we need to consider whether one would expect to observe either several glass transitions (as in Ref. [71]) or a distinct broadening of the observed transitions. The existence of a single glass transition in a sample with strongly inhomogeneneous dynamics is suggested by comparisons with simulations of confined glass formers. In a number of such studies it has been found that, despite strongly inhomogeneous dynamics, the kinetic freezing of the sample occurred in all parts of the film simultaneously [42,46,72]. The same conclusion was reached for the case of a confined binary Lennard-Jones liquid [72], a free-standing metallic glass film [46], and a confined polymer melt [42]. In all cases, the dynamic glass transition was observed to be a *collective* effect, taking place in all parts of the film simultaneously and seemingly unaffected by the strong variation in segmental dynamics. These simulation results as well as our own experimental observations of sharp glass transitions support the use of a single average T_g. With this in mind, we construct an arithmetic average $\langle T_g \rangle$ as simply

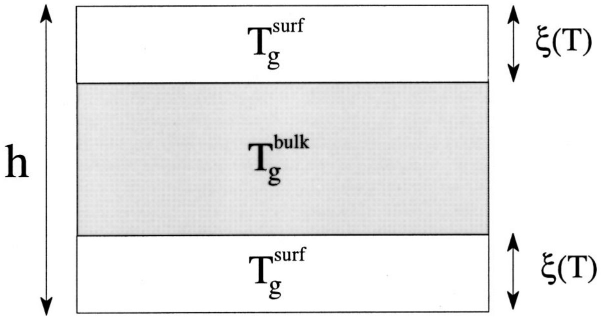

FIG. 6. Sketch showing the model described in the text. The two surface regions are modeled by $T_g = T_g^{surf}$, while the remainder of the film is modeled by $T_g = T_g^{bulk}$. The film thickness is denoted, h, and the temperature dependent length scale characteristic of the dynamics near a free surface, $\xi(T)$, defines the size of the two surface layers.

$$\langle T_g \rangle = T_g^{bulk} + \frac{2\xi(\langle T_g \rangle)}{h}(T_g^{surf} - T_g^{bulk}). \tag{3}$$

Following the treatment of Donth [73] we write the temperature dependence of the characteristic length $\xi(T)$ as a power law expansion about a characteristic temperature T^*. A natural choice for T^* is either T_g^{bulk}, since our data are limited to temperatures below this value, or alternatively T_{ons}, the so called cooperativity onset temperature. The latter is the temperature below which the dynamics should be influenced by cooperative motion and which coincides with several anomalous behaviors encountered in supercooled liquids [74]. For polystyrene T_{ons} has been reported to be ~465 K [75]). $\xi(T)$ is consequently given by

$$\xi(T) = \xi(T^*) + \alpha(T^* - T)^{\gamma}. \tag{4}$$

In fitting the model to our data [53], we have found that the exact choice of T^* used in Eq. (4) is not important, and a reasonable parametrization of $\xi(T)$, which generates a successful fit to the data, gives similar results for the actual *values* of $\xi(T)$. The value of T_g^{surf} was found to be similarly robust and insensitive to the parametrization of $\xi(T)$. In the following, we will restrict our attention to the case where $T^* = T_g^{bulk}$. We note that the case of a temperature independent surface layer leads simply to $\Delta T_g \propto 1/h$, and that this function is not able to provide a reasonable fit to the present data. One reason for the success of simpler layer models [27] to describe effects in supported films is that the T_g reductions in these systems are generally much smaller, and as a result the length scale for the dynamics changes little over the temperature range studied.

The fitting function [Eq. (3)], derived from a reasonable physical model, has four free parameters (the value of T_g^{bulk} has been fixed at 372 K). While this is more than the two parameters in the empirical relation given by Eq. (2), the values of $\xi(T_g^{bulk})$ and T_g^{surf} resulting from any fit must be physically reasonable, and three of the four parameter values can be compared with results from other studies. The fitting procedure is made slightly more complicated by the fact that Eq. (3) is transcendental in $\langle T_g \rangle$, and hence we solve for h as a function of $\langle T_g \rangle$ and perform the fitting with h as the dependent variable. We have also performed the fitting with T_g as the dependent variable. This procedure gave essentially the same results, and hence in the following we use the results where h was taken as the dependent variable.

We should note that in the first instance it is not possible to perform a fully unconstrained fit, as the fit is relatively insensitive to a simultaneous variation of T_g^{surf} and $\xi(T_g)$. Since the fit is primarily determined by the lowest measured T_g values [and thus the largest values of $\xi(T)$], we can set $\xi(T_g^{bulk})$ to some low value (~ 1 Å) in order to find T_g^{surf}. This leads to a value of $T_g^{surf} = 305 \pm 5$ K. We note that if we use the alternative parametrization, with the power law expansion around T_{ons} [53], there is no similar complication as $\xi(T_{ons})$ and T_{ons} are approximately known and can be fixed. This procedure leads to the same value of $T_g^{surf} = 305 \pm 5$ K.

Fixing $\xi(T_g^{surf})$ to 305 K and fitting the rest of the parameters [including $\xi(T_g)$] produces a best fit to Eq. (3) for the fit parameters $\xi(T_g^{bulk}) = 22 \pm 3$ Å, $\gamma = 0.90 \pm 0.05$, and $\alpha = 2.1 \pm 0.1$. The fit generated by the model with these parameters is shown as the solid line in Figs. 3 and 7. The value of $\xi(T_g^{bulk}) = 22 \pm 3$ Å is in good agreement with the range 25–35 Å predicted by Kahle *et al.* [75] from fitting differential scanning calorimetry data of bulk PS to a fluctuation model. It is also in agreement with the 20 Å surface region suggested by DeMaggio *et al.* [27] to model T_g reductions in thin supported PS films.

Some recent experimental work has been addressed to directly measure the surface glass transition temperature or relaxation properties of the surface. Jean *et al.* have used positron annihilation techniques to find a significant surface effect on the dynamics of PS [76]. These studies suggested that the ~ 50 Å region near the free surface had a T_g value of 317 K, in reasonable agreement with our obtained value of 305 K. It should be mentioned, however, that the application of positron annihilation techniques is not uncontroversial and contradictory results exist [77]. In a recent friction force microscopy study of the surface dynamics of several polymers (including polystyrene) [78], convincing evidence was obtained for surface glass transitions reduced by tens of degrees. However, as pointed out by the authors, the difficulty involved in obtaining exact knowledge of the actual depth probed by the technique makes it difficult to give a quantitative measure of the surface region and its associated effective glass transition value.

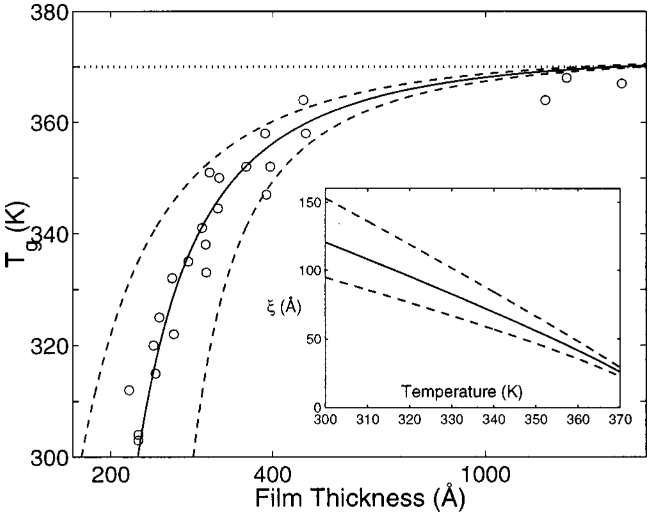

FIG. 7. The low M_n data as a function of film thickness. The solid line is a fit to the model described in the text and the two dashed lines indicate the upper and lower bounds as determined by the errors in the parameters. The dotted line marks the T_g value of the bulk material. The inset shows the characteristic length scale $\xi(T)$, as obtained from fitting the model described in the text to the low M_n data. The dashed lines indicate the upper and lower bounds of $\xi(T)$.

The most significant aspect of the data analysis, based on the model described above, is the predicted behavior of $\xi(T)$, describing the growth of the characteristic length scale at temperatures in a significant range below the bulk T_g value. Figure 7 quantifies the $\xi(T)$ explicitly by showing the range of $\xi(T)$ predicted within the uncertainties of the fitting procedure. There are a number of notable aspects of the $\xi(T)$ behavior shown in Fig. 7. Very few experimental studies claim to give access to the temperature variation of an inferred length scale of cooperative dynamics. In bulk systems for $T > T_g$, however, the temperature dependence of the cooperativity length, deduced from fluctuation arguments, has been reported as $\xi \propto (T_{ons} - T)^{2/3}$ [73]. The analysis of data presented in this work suggests that the growth of $\xi(T)$ might be a stronger function of temperature below T_g^{bulk} than it is above. Despite the growth of $\xi(T)$ below T_g^{bulk}, Fig. 7 clearly shows that, as T approaches the Vogel-Fulcher temperature T_0, $\xi(T)$ remains finite. This is an obvious corollary of measuring T_g values less than T_0. While we have argued that the $\xi(T)$ shown in Fig. 7 represents the behavior of a characteristic length scale for the dynamics in the free-standing film samples, it is not necessarily obvious that the same length scale will describe the dynamics in bulk samples of the same material. The lower activation barrier for segmental motion near the free surface could be simply thought of as a source of excess *free volume*. Hence, the temperature dependence of a length scale characterizing a surface region might be different from that of the corresponding bulk material. It is important to find theory, simulations, or other experiments to help determine to what extent the results presented in Fig. 7 can be applied to describe the length scale of the dynamics of bulk glass-forming materials.

V. SUMMARY AND CONCLUSIONS

We have performed a detailed study of the glass transition behavior in ultrathin free-standing polystyrene films. While the size of the effects was comparable for all molecular weights, a complicated M_n dependence suggested the separation of the results into two regimes each dominated by a different length scale: a low M_n regime controlled by a length scale intrinsic to the glass transition and a high M_n region, where polymer chain confinement induced effects dominate. The magnitude of the observed T_g reductions, the ease of identifying the glass transition, and the lack of specific interfacial interactions make this type of study ideal for investigations of finite size effects on the glass transition. A model of the dynamics was introduced to describe the low M_n data. This model makes predictions for the length scale of dynamics for an extended temperature range below the bulk glass transition temperature.

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