

Relaxation dynamics in ultrathin polymer films

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We have used photon correlation spectroscopy and quartz crystal microbalance techniques to examine the relaxation dynamics of ultrathin ($h < 400$ Å) polystyrene films in both supported and freely standing geometries. These studies probe relaxation dynamics of polymer films in which the glass transition temperature (T_g) is reduced below the bulk value. Both the shape of the relaxation function and the dependence of relaxation time on temperature above the glass transition are remarkably similar to that of the bulk polymer, though the range of relaxation times is shifted according to the shift in T_g . The results indicate that the microscopic relaxation dynamics of thin films remain similar to that of the bulk polymer even, in the extreme case in which the T_g value is shifted more than 70 K below the bulk value. [S1063-651X(98)50508-9]

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The increasing number of applications for polymer thin films has spurred a surge of activity aimed at increasing our understanding of the properties of these materials. Polymers in a thin film configuration may have physical properties different from those of the bulk material due to interfacial interactions and effects of molecular confinement. Of particular interest are anomalies in the glass transition temperature T_g , which have been recently reported for thin polymer films. The T_g values have been measured for polymer films supported by substrates [1–5] as well as for freely standing films [4,6]. These experiments reveal that the T_g values decrease for decreasing film thickness unless there is a strongly attractive polymer-substrate interaction [2]. Films of polystyrene (PS) have been extensively studied on a number of different substrate materials encompassing both wetting [1,3,5] and nonwetting [4] systems. The measured T_g values show only weak substrate dependent behavior. While the strength of the polymer substrate interaction does not strongly influence the measured T_g for supported PS films, the simple presence of a substrate has been shown to alter dramatically the T_g value in recent studies involving freely standing films [4,6].

The glass transition temperature is intrinsically related to structural relaxation and thus in polymers to the segmental mobility. Structural relaxation dynamics of glass forming materials are generally well described by the stretched exponential function

$$\phi(t) = \phi_0 e^{-(t/\tau)^\beta}, \quad (1)$$

where the stretching parameter β describes the shape of the relaxation time distribution. The variation of the average relaxation time $\langle \tau \rangle = \int \phi(t) dt$ with temperature T generally obeys the empirical Vogel-Tammann-Fulcher (VTF) equation

$$\langle \tau \rangle = \tau_0 e^{B/(T-T_0)}, \quad (2)$$

where the parameter τ_0 is a microscopic relaxation time, B describes the fragility of the glass former, and T_0 for polymers is generally $T_0 \sim T_g - 50$ K. For bulk polymers the relaxation behavior is well characterized by Eqs. (1) and (2). In order to help elucidate the origin of the large T_g reductions observed for thin polymer films, a systematic study of the relaxation dynamics near T_g must be performed. Differences in the relaxation behavior between bulk and ultrathin film samples, such as changes in the β value, the VTF “ B ” parameter, or the $(T_g - T_0)$ value may indicate finite-size effects as the sample size approaches the cooperativity length in the glass forming system. If only negligible deviations from bulk relaxation behavior are observed then explanations not involving cooperativity must be favored.

Segmental mobility is a necessary precursor to polymer chain diffusion, and experiments have been performed to examine the chain diffusion in thin polymer films. Lateral diffusion studies of PS chains in thin films [7] showed a decrease in the lateral diffusion constant and hence lower mobility for films with a thickness $h \leq 1500$ Å, in contrast to the observations of a reduced T_g . Direct measurements of the relaxation dynamics in ultrathin films are required, especially in samples where the T_g is reduced below the bulk value. Such direct measurements have proven to be extremely difficult and have been reported only for the special case of isobutyl methacrylate copolymerized with chromophore probe molecules [8]. These studies revealed a broadening of the structural relaxation function for thin films (230 Å) compared to thick films (5200 Å). In a manner consistent with T_g studies in similar methacrylate films (PMMA) [2], no change in the average lifetime $\langle \tau \rangle$ near the bulk T_g was observed. These studies are not extendable to arbitrary polymer-substrate systems as they necessarily involve large ($\approx 36\%$) amounts of probe molecule copolymerized with the sample.

In this Rapid Communication, we report the measurement of the relaxation dynamics in both freely standing and supported polystyrene films where T_g is known to be reduced

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below the bulk value. The relaxation dynamics can be compared directly to both the T_g studies [1,3–6] and the polymer chain diffusion studies [7]. Using photon correlation spectroscopy we measure the segmental relaxation of freely standing PS films with a T_g reduction greater than 70 K. We employ a quartz crystal microbalance technique to measure the mechanical relaxation behavior in PS films supported by Au coated quartz substrates. The combination of techniques is applicable to a wide variety of polymer systems.

Polystyrene ($M_w = 767\,000$, $M_w/M_n = 1.11$) was spin coated from (0.2 μm) filtered solutions in toluene onto either gold coated AT cut quartz-crystal substrates (supported films), or cleaned glass slides (freely standing films). The spin coated films were annealed above the bulk T_g for ~ 12 h (then to 420 K for ~ 1 h for supported films), and subsequently cooled (0.5 K/min) to produce samples with a well-defined and reproducible thermal history. The supported films were of thicknesses as low as 115 \AA . Freely standing films were prepared, using a water-transfer technique [4], with thicknesses as low as 220 \AA .

Photon correlation spectroscopy (PCS), commonly used to investigate relaxation dynamics in bulk melts, has in this work been extended to the study of ultrathin freely standing films. In the PCS experiments 400 mW of spatially filtered laser light ($\lambda = 532$ nm) was focused onto the surface of the freely standing PS film at an angle of incidence of $\approx 45^\circ$. Temperature measurement was provided by a fine gauge thermocouple wire near the surface of the film, and the sample temperature was varied by changing the temperature of the experimental enclosure. Light scattered in the direction approximately normal to the film was selected by apertures and then detected. The pulses from the detector were input to an ALV 5000 fast autocorrelator that calculated the intensity autocorrelation function $g_2(t) = \langle I(0)I(t) \rangle / \langle I \rangle^2$. The measured relaxation strength [$0.001 < g_2(0) - 1 < 0.01$] indicates that only a very small fraction of the light reaching the detector was scattered from dynamical processes in the film. The low relaxation strengths indicate that we are in the limit of heterodyne detection, the local oscillator being the light scattered by static surface roughness. The measured correlation function is then proportional to the density-density autocorrelation function [$g_2(t) - 1 \propto \langle \delta\rho(0)\delta\rho(t) \rangle$]. The low count rate restricted the time domain in which the relaxation function could be reliably measured. Mechanical relaxation dynamics in supported polymer films were studied using [12] a quartz crystal microbalance (QCM) technique. In the QCM experiment, which is an ultrasonic technique that measures the shear response of the system at a frequency of 10 MHz, the data are comprised of the frequency f and per cycle energy loss D of the QCM crystal onto which a sample has been deposited. The temperature of the sample was ramped at 4 K/min to 425 K, while a computer calculated the f and D values.

Figure 1 shows the intensity autocorrelation functions obtained from a 220 ± 5 \AA thick freely standing PS film at temperatures ranging from $T = 291$ K to 302 K. Raw data are shown for three temperatures and best fit lines to Eq. (1) for all data sets. It can be seen that for $T > 297$ K the system completely relaxes within the time window of the experiment, whereas at $T = 291$ K only the initial part of some slow relaxation process is observed. The findings demonstrate that

the T_g for this film is < 297 K, i.e., more than 70 K below the bulk value of 370 K. We interpolate to estimate a T_g (approximately the temperature at which $\langle \tau \rangle \approx 200$ s) of 294 ± 3 K for this film. Extrapolation of previous results for freely standing films of the same M_w [6] suggests a T_g for this film of 287 ± 10 K, in agreement with the above estimate. The β parameters obtained for the temperatures at which the complete relaxation function was collected are all similar with an average value $\bar{\beta} = 0.39 \pm 0.08$. This value is identical within error to previous PCS measurements of bulk PS samples [9], showing that the relaxation functions in Fig. 1 are simply shifted by many orders of magnitude from that of bulk PS. The distribution of relaxation times, determined by the parameter β , is a strong indicator of the system dynamics at the molecular and intermolecular level [10]. The fact that the β value for the very thin films is indistinguishable from that of bulk PS suggests that the microscopic relaxation dynamics are not affected despite a T_g reduced from the bulk value by more than 70 K. While experimental restrictions have limited the temperature range of the present investigations, we have observed relaxation dynamics similar to those shown in Fig. 1 for at least four different films with $220 \text{\AA} < h < 250 \text{\AA}$.

Photon correlation spectroscopy is not ideal for studies of relaxation dynamics in supported polymer films. Absorption or scattering of light by the substrate introduces experimental difficulties [11] and, instead, a quartz crystal microbalance technique was employed. We found that for films with $h \geq 6000$ \AA , the nonzero shear viscosity of the melt film resulted in a directly measurable energy loss. The dashed curve in Fig. 2 shows the D versus T data for a thick (~ 3 μm) film. This demonstrates that at the frequency of oscillation (10 MHz), the onset of shear relaxation for the bulk PS sample is at $T \approx 390$ K, in agreement with other ultrasonic techniques [13]. For films with $h \leq 6000$ \AA , the addition of the polymer film did not introduce a detectable change in D , and the shift in frequency Δf was used to accurately determine the mass (and film thickness) of the polymer films.

In order to detect relaxation processes for thin ($h < 6000$ \AA) films, small (~ 1 μm) SiC particles were carefully introduced onto the film surface such that no particle aggregates were observed using optical microscopy. This procedure results in an increase in the dissipation of the particles-film-oscillator system due to the sliding friction of the particles on the film during oscillation [14]. This can be seen in Fig. 2 in which we show D versus T plots for a number of the SiC covered PS films. The formation of strong bonds between the polymer and particles would result in a decrease of the excess dissipation and thus the D value acts as a sensitive probe of the adhesion between the SiC particles and the polymer film. The behavior of the 5490 \AA thick film can be described as follows. As the temperature is raised to 390 K (the onset of shear relaxation in bulk PS) the segmental mobility of the polymer is high enough that adhesive bonds can be formed with the SiC particles. We expect this to result in a sharp decrease in the dissipation, which is indeed observed over a narrow temperature range. We associate the onset of relaxation with the small dissipation peak that is observed consistently at a temperature (T_{max}) just below the decrease in dissipation discussed above. This pro-

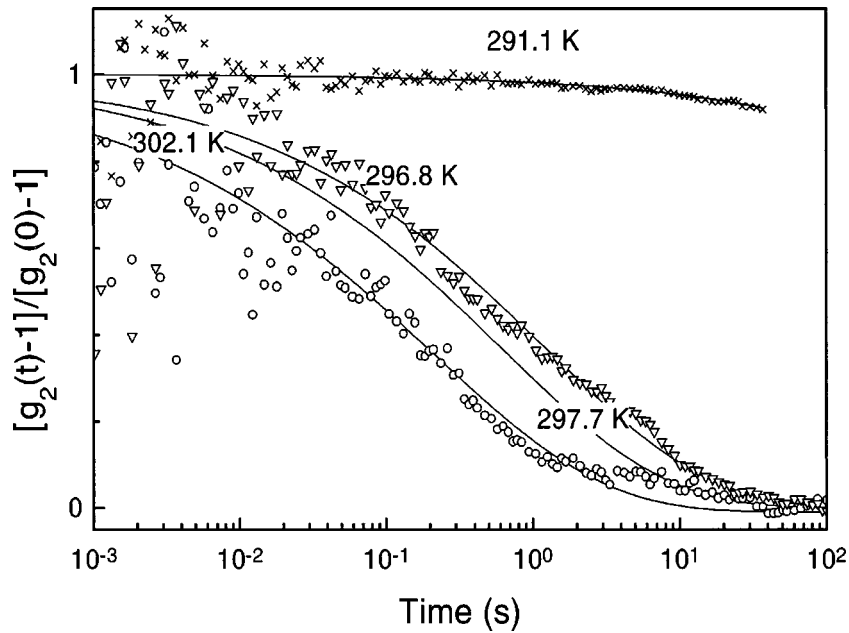


FIG. 1. Intensity autocorrelation functions for a 220 Å thick freely standing PS film. Experimental data are omitted from the 297.7 K curve for clarity, and fits to Eq. (1) are shown for all data sets. The best-fit parameters are $T=296.8$, $\tau=1.2$ s, and $\beta=0.39$; $T=297.7$, $\tau=0.62$ s, $\beta=0.39$, $T=302.1$, $\tau=0.20$ s, and $\beta=0.37$. Uncertainties in β values are ± 0.08 , and uncertainties in $\tau \pm 10\%$.

vides us with a reproducible signature of the relaxation dynamics, though it does not reveal the shape of the relaxation function. The reproducibility of the shape of the data allows us to define the onset of relaxation within ± 3 K. Since the features consistently observed in Fig. 2 are a result of structural relaxation processes in the polymer films, we can use the measurement involving a thick (5490 Å) sample (for which the relaxation signature is observed at 390 K) and Eq. (2) for bulk PS [13] (solid line in Fig. 3) to estimate a value of $\langle \tau \rangle \sim 2 \times 10^{-4}$ s, which can be identified as the ‘probe time’ of this technique. Upon cooling the sample, the particles remain bonded, and the observed dissipation does not

change significantly (shown in Fig. 2 for the 115 Å thick film). Repeated heating and cooling cycles do not restore the original dissipation. The qualitative behavior of the D versus T data is identical for all films studied. This demonstrates that the sensitivity of the technique is independent of film thickness for thicknesses as low as 115 Å. We have measured the T_{\max} for five films with $100 \text{ \AA} < h < 400 \text{ \AA}$, and the inset of Fig. 2 shows this temperature as a function of the film thickness. For films with thickness less than $h \approx 400 \text{ \AA}$ we note a shift in the T_{\max} value to lower temperature. Also included in this plot is the best-fit line calculated from the T_g data in Fig. 4 of Ref. [3] in which a system similar to that of

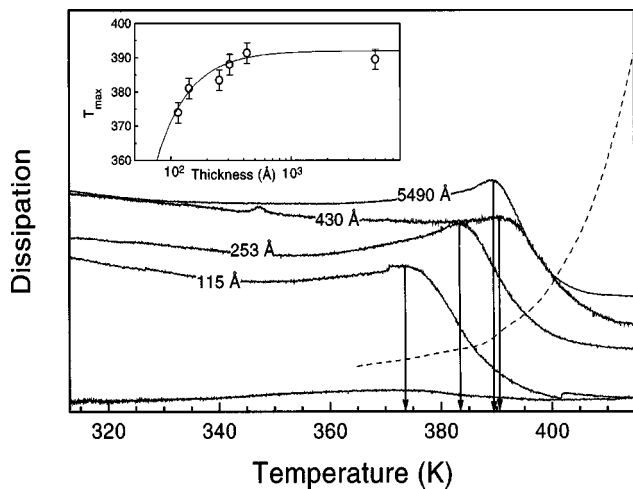


FIG. 2. Dissipation as a function of temperature for a thick (3 μm) PS film as well as a representative number of SiC covered PS films supported on Au coated quartz using the QCM technique. The arrows indicate the T_{\max} values. The inset shows the measured T_{\max} values as a function of film thickness. The curve in the inset is described in the text.

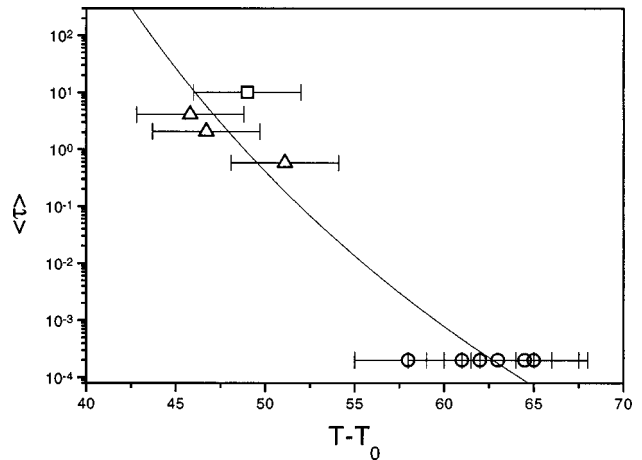


FIG. 3. VTF plot using data for both supported and freely standing films. The solid curve is calculated using VTF parameters for bulk PS [13]. The hollow triangles are calculated from the PCS data in Fig. 1, the single hollow square from a second freely standing film with similar thickness, and the hollow circles from the QCM data for supported films shown in Fig. 2. Uncertainties represent those of T_g (all data) and T_{\max} for the supported films.

PS on Au were considered. The solid curve was adjusted by the 20 K necessary for agreement between the respective bulk measurements. Once this shift is applied, the relaxation data are seen to exhibit a film thickness dependence very similar to that of the T_g value.

The similarity between the film thickness dependence of the T_{\max} value ($\tau \sim 10^{-4}$ s) and that of the T_g value ($\tau \sim 10^2$ s) suggests that the VTF relationship [Eq. (2)], besides a necessary shift in T_0 , is not strongly affected by the T_g reductions. In order to more fully explore this idea we combine both supported and freely standing samples and consider the hypothesis that the shift in the T_0 value for the thin-film samples is the same as that of the experimentally determined glass transition T_g (i.e., $T_g - T_g^{bulk} = T_0 - T_0^{bulk}$), realizing that deviations from this relation will become evident in our analysis. Using T_g values, which are determined by interpolation of PCS results (freely standing films) or from previous measurements [3], allows us to plot the measured $\langle \tau \rangle$ values as a function of $(T - T_0)$, as shown in Fig. 3. The solid line in the figure is the VTF relation found for bulk PS using ultrasonics techniques [13]. It is evident from Fig. 3 that in this time range there is no systematic deviation between the relaxation behavior of bulk PS and that in PS films with T_g reductions up to 75 K. With the exception of the 253 Å thick supported film, all relaxation data are, within experimental error, consistent with Eq. (2) and bulk values of B and $(T_g - T_0)$. We note that the reasonable alternative approach of adjusting T_0 by keeping the ratio T_g/T_0 constant [15] would result in deviations between the measured values and calculated curve greater than the error limits for all of the freely standing film data.

The results of the current experiments are consistent with previous measurements of the T_g value in thin polymer films [1,3–6]. We have shown conclusively that the reductions in T_g are concurrent with an increase in the segmental mobility, which is indicated by a shift in the entire relaxation function to shorter times. We have further demonstrated that the mi-

croscopic relaxation dynamics, in the form of the actual relaxation function and the relation between $\langle \tau \rangle$ and $(T - T_g)$, in thin polymer films are not strongly affected by T_g reductions in the sample. This suggests that the length scale that determines the T_g value is much larger than the cooperativity length scale for the dynamics of the glass forming polymer melt. The present results do not agree with chain diffusion studies of similar supported films [7]. This demonstrates that while segmental mobility is enhanced in thin films, the resulting chain mobility may not necessarily be similarly enhanced. The suggestion of a large length scale determining the T_g reductions for thin polymer films is consistent with the M_w dependence of these T_g reductions discussed in Ref. [4].

We have examined the relaxation behavior of ultrathin films of polystyrene. For freely standing films we have measured a stretched relaxation function with the same shape ($\beta \approx 0.40$) as that of bulk PS, suggesting that the microscopic dynamics are not affected in samples exhibiting T_g reductions as large as 75 K. Supported polymer films also exhibit a thickness dependent enhanced segmental mobility consistent with a reduced T_g value. Collectively the data, which encompass five orders of magnitude in time, suggest that the VTF relation for bulk PS may be applied to thin film samples as long as a shift in T_0 is introduced; this shift is determined by the observed shift in T_g . This provides compelling evidence that cooperativity need not be invoked to explain the anomalous T_g behavior observed for such samples, and that a different physical phenomenon with a much larger length scale than that of local segmental relaxation is instead responsible for the observed T_g reductions.

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