

Brillouin light scattering studies of the mechanical properties of thin freely standing polystyrene films

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We have used Brillouin light scattering (BLS) to measure the room-temperature, high-frequency mechanical properties of thin freely standing polystyrene (PS) films. We have investigated the effects of chain confinement and the free surface on the mechanical properties by measuring the velocity of film-guided acoustic phonons in films with thicknesses ranging from less than to greater than the average end-to-end distance of the unperturbed molecules R_{EE} . We find that the measured, room-temperature sound velocities are the same, to within $\pm 1\%$, for all films that have glass transition temperatures that differ by as much as 65 K. Our results, which differ markedly from those of recent picosecond acoustic measurements, are discussed in terms of models proposed to explain anomalous glass transition behavior in thin polymer films. A careful analysis of the BLS data reveals that, at room temperature, the mechanical stiffness, mass density, and thermal expansion of thin, freely standing PS films in the glassy state are consistent with bulk values for all film thicknesses.

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INTRODUCTION

To fully realize the potential of polymer films in technological applications it is necessary to have a detailed understanding of their physical properties. This has led to a recent surge in both experimental and theoretical studies of these systems. Thin polymer films have properties that may deviate from their bulk values for a number of different reasons. For a thin film supported on a substrate, the properties of the thin film may depend sensitively on the polymer-substrate interaction because of the high surface-to-volume ratio for thin films. In addition, for polymer films with film thickness $h < R_{EE}$ ($R_{EE} \sim 2R_g$ is the average end-to-end distance of the polymer molecules and R_g is the radius of gyration), chain confinement effects may affect the physical properties of the film. The glass transition temperature T_g of thin polymer films has proved to be a sensitive probe of both surface and chain confinement effects in thin polymer films. Keddie *et al.* [1] showed that the T_g value of thin polystyrene (PS) films on Si substrates decreased as the thickness was lowered below about 400 Å. Several different experiments involving PS films supported by oxidized Si and hydrogen-passivated Si surfaces have shown quantitatively similar results [1–5]. To isolate and investigate the separate effects of surface interaction and chain confinement, Brillouin light scattering (BLS) and ellipsometry techniques have been combined to measure the glass transition temperature of freely standing and supported PS films [5–7]. In the measurements on the freely standing films, T_g reductions were observed that were

much larger than for supported films of the same thickness, e.g., $\Delta T_g \simeq -60$ K for a PS film with thickness $h = 290$ Å and molecular weight $\bar{M}_w = 767 \times 10^3$. The T_g reductions in freely standing films also depended strongly on M_w , unlike the behavior observed for supported films. The M_w dependence observed for freely standing films provides strong evidence that polymer chain confinement is important in explaining the observed T_g reductions. Collectively, these studies have shown the large effect of both the free surface [5–7] and the polymer-substrate [2,5,8] interaction in determining the measured T_g value.

To probe the effect of confinement on the mechanical properties of polymers, we have used BLS to study the room-temperature mechanical properties of multilayered samples comprised of alternating layers of PS and polyisoprene (PI) films supported by a Si substrate [9]. In these experiments, we probed the mechanical properties of the individual layers with thicknesses as small as 160 Å $\sim R_{EE}/3$. The analysis of the data in terms of an effective medium approach showed that the high-frequency mechanical properties of such samples were the same as the bulk values to within the experimental uncertainty of 20%. The rather large uncertainty estimates resulted from the complicated nature of the sample geometry and the data analysis. Because of the presence of the PI layers, the multilayered samples could not be fully annealed after preparation and it was not possible to estimate the T_g values of the constituent layers. This ruled out the possibility of establishing a correlation between the occurrence of T_g reductions and the occurrence of significant changes in mechanical properties.

Recent work using picosecond acoustic techniques has suggested that the longitudinal sound velocity increases dramatically for single poly(methyl methacrylate) (PMMA) [10] or PS films [11] of thickness less than 400 Å supported on

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Al-coated Si substrates. The results of the experiments were interpreted as a threefold increase in the longitudinal sound velocity and an approximately tenfold increase in the longitudinal modulus over the bulk values for PMMA films with $h \approx 200$ Å. Because the picosecond acoustic measurements are based on a time-of-flight principle, there are difficulties in the interpretation of the data for very thin films. A complicated overlap of the incident and reflected acoustic pulses is obtained for film thicknesses less than 400 Å [see Fig. 2(b) of Ref. [10]]. Similar picosecond acoustic measurements by other researchers studying PMMA films suggest only a 10–20% increase in the longitudinal phonon velocity for film thicknesses less than 600 Å [12]. In this case the modest enhancement of the longitudinal phonon velocity was attributed to the uncertainty in the determination of the film thickness.

Qualitative differences exist between the results obtained for supported films using BLS [9] and picosecond acoustic measurements [10] that extend beyond the differences in the samples and there is disagreement between the results of the two picosecond acoustic studies. It is evident that a thorough and accurate study of the high-frequency mechanical properties of submicrometer-thick films is necessary to resolve the ambiguities that currently exist in the literature.

In both the BLS and picosecond acoustic measurements, the mechanical properties of the thin films are probed by direct measurement of acoustic wave velocities. The velocities are given by the square root of the ratio of the mechanical stiffness (elastic constants) to the mass density. Very small decreases in the mass density ($\leq 2\%$) relative to the bulk value would explain the large reductions in T_g that have been observed for both supported and freely standing films. It is reasonable to expect the mass density may differ by such a small amount in very thin polymer films relative to that of the bulk. Unfortunately, sufficiently accurate direct measurements of mass density in thin films have not yet been realized. However, several techniques have been used to obtain indirect measurements of the mass density in thin polymer films. Reiter [13] has used the results of x-ray reflectivity experiments to infer that PS films with $h \leq R_{EE}$ have a qualitatively lower mass density than in bulk. In neutron reflectivity measurements of very thin polymer films [14,15], the neutron scattering length density has been observed to differ from that of bulk polymer and this has been used to infer deviations in the mass density from its bulk value (of the order of 5%), with both increases [14] and decreases [15] reported for decreasing film thickness. Very recently, neutron reflectivity has been used to show that the mass density of supported PS films agrees with the bulk value to within 1% for films as thin as 65 Å [16]. We note that an alternate explanation has been proposed to explain the T_g reductions in thin polymer films: the presence of a less-dense, mobile surface layer. However, experimental evidence for this explanation has been contradictory [4,17,18].

Brillouin light scattering [7,19] and other acoustic techniques [20] have been used to probe the glass transition of bulk and thin film polymer samples through measurement of high-frequency acoustic phonons. These techniques are very sensitive to changes in the mass density, through both a direct dependence on the mass density and a strong nonlinear dependence of the elastic constants on mass density. For

many fragile [21] glass-forming materials such as polymers, the elastic constants depend sensitively on the mass density [19,22]. Thus the acoustic techniques provide an indirect, though potentially very sensitive, probe of the mass density in thin polymer films.

The present work describes BLS experiments in which high-frequency acoustic phonons in thin freely standing PS films are measured. For thin films, the mechanical boundary conditions at the two film interfaces give rise to a series of film-guided acoustic modes. These modes are of mixed polarization, having both transverse and longitudinal components. For freely standing films the velocity dispersion relations describing the allowed film-guided phonon velocities as a function of the product $Q_{\parallel}h$ are relatively easy to calculate. For the case of an isotropic film, analytic expressions can be obtained for the velocities of two different families of phonon modes [23], denoted as symmetric (*S*) or antisymmetric (*A*) with respect to the midplane of the film. An excellent discussion of the properties of the film-guided acoustic modes in freely standing films can be found in Ref. [23].

Previous studies of PS films supported on Si(001) [24] substrates, as well as supported PS/PI multilayered films [9], suggest that the mechanical properties of thin films (even those with $h \leq R_{EE}$) can be treated as isotropic to a very good approximation. This isotropy in the high-frequency mechanical properties also extends to micrometer-thick spin coated polyimide films [25] in which the molecules have a much less flexible polymer backbone than for PS. For the case of isotropic films, the velocity dispersion curves are completely determined by the longitudinal and transverse elastic constants c_{11} and c_{44} and the mass density ρ or, alternatively, in terms of the bulk longitudinal and transverse velocities v_L and v_T [23]. For thick supported films ($h > 1700$ Å), the room-temperature values of v_L and v_T have been found to be independent of the M_w value of the polymer in the range $30 \times 10^3 < M_w < 600 \times 10^3$ [24].

In the present study, we use BLS to measure the phonon velocities in freely standing PS films with thicknesses ranging from less than to greater than the size of the unperturbed molecules R_{EE} . Because of the simple sample geometry of the freely standing films, BLS measurements of the velocity of the lowest-order, symmetric film-guided S_0 mode are accurate to within $\pm 1\%$ for all values of the film thickness. In addition, for very thin films, the S_0 mode velocity measured using BLS is insensitive to uncertainties in the film thickness. Most importantly, we use freely standing PS films with very well-defined thermal histories for which the glass transition temperature has been well characterized and has been shown to be dramatically reduced from the bulk value [5,7]. Because of all of these reasons, we are able to comment confidently on possible correlations between anomalous T_g behavior and the high-frequency mechanical properties of the glassy phase of thin PS films.

EXPERIMENT

The preparation of freely standing films has been discussed in detail previously [6] and will only be described

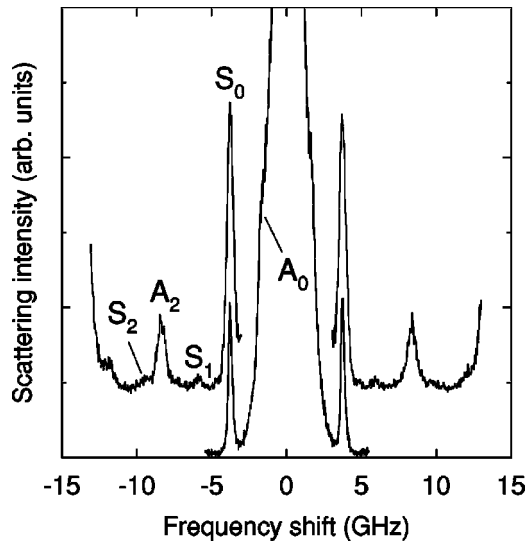


FIG. 1. Room-temperature BLS spectra for a freely standing PS film ($\bar{M}_w = 767 \times 10^3$) with thickness $h = 1900$ Å, collected using an angle of incidence of $\theta_i = 30^\circ$. The top and bottom spectra were collected for free spectral range values of 15.00 GHz and 7.50 GHz, respectively. The laser power was 50 mW and the data collection time per channel was approximately 3.2 s and 1.6 s for the top and bottom spectra, respectively. The peaks corresponding to the film-guided phonon modes are labeled as symmetric (*S*) or antisymmetric (*A*) with the corresponding mode number index.

briefly here. Solutions of polymer molecules [26] ($\bar{M}_w = 767 \times 10^3$, $R_{EE} \approx 570$ Å or $\bar{M}_w = 2240 \times 10^3$, $R_{EE} \approx 970$ Å) in toluene were spin coated onto clean glass slides. The films were annealed and then transferred, using a water surface transfer technique, to a sample holder containing a small (4-mm-diam) aperture. Similar pieces of the same floating films were transferred to a Si(001) wafer for thickness measurement using ellipsometry.

The BLS measurements were performed using a tandem, $3 \times (1+1)$ Fabry-Pérot interferometer. Laser light of wavelength $\lambda = 5145$ Å was focused onto the film surface and the backscattered light was collected and collimated by the same lens used for focusing the incident light. For room-temperature measurements, the angle of incidence was varied between 10° and 70° . A slit was placed in the path of the collimated light to reduce the line broadening due to the nonzero light collection aperture. Conservation of momentum in the plane of the film determines the phonon wave vector $Q_{\parallel} = (2\pi/\lambda)(\sin \theta_i + \sin \theta_s)$, where θ_i is the angle of incidence and θ_s is the angle of the scattered light ($\theta_s = \theta_i + \delta$, where δ is determined by the position of the slit [27]). The frequency shift f measured in the BLS experiment is used to calculate the phonon velocity $v = 2\pi f/Q_{\parallel}$. BLS measurements at temperatures greater than room temperature were performed with the sample placed in an optical furnace using a fixed angle of incidence $\theta_i = 45^\circ$.

RESULTS AND DISCUSSION

Shown in Fig. 1 are typical BLS spectra for a freely standing PS film with thickness $h = 1900$ Å, collected using an

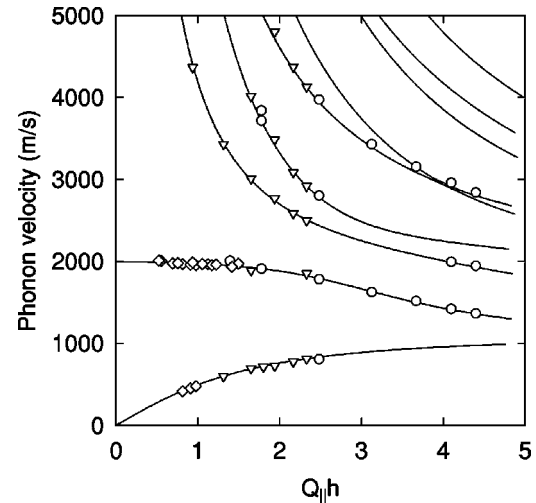


FIG. 2. Velocity dispersion curves for freely standing PS films. The data were collected for two thick PS films ($\bar{M}_w = 767 \times 10^3$): $h = 1000$ Å (open inverted triangles) and $h = 1900$ Å (open circles). The solid lines were calculated using $c_{11} = 5.65$ GPa and $c_{44} = 1.40$ GPa and the bulk value of the mass density $\rho = 1.056$ g/cm³. In addition to the data for the two thick films, we have also shown data collected for a large number of thinner films (open diamonds) for which $Q_{\parallel}h < 1.6$ (see Fig. 3 caption for details).

angle of incidence $\theta_i = 30^\circ$. The two spectra were collected using different values of the Fabry-Pérot interferometer free spectral range to measure both low- and high-frequency peaks. In the figure the peaks have been labeled as symmetric (*S*) or antisymmetric (*A*) together with the index number of each mode. Each peak is fit to an instrumental response function using a nonlinear, least-squares fitting routine. The resulting peak center frequency values are used to calculate the phonon velocities. Velocities determined in this way are accurate to within $\pm 1\%$. In Fig. 2 we show the measured room-temperature phonon velocities for two thick films ($h = 1000$ Å and $h = 1900$ Å; $\bar{M}_w = 767 \times 10^3$) with $10^\circ < \theta_i < 70^\circ$. For these two samples, $h \gg R_{EE}$ and the T_g values are the same as that of bulk PS [7]. To compare the high-frequency mechanical properties of the thick films with those of bulk PS, we examine the dispersion of the film-guided mode velocities. Only two quantities (v_L and v_T) are required to uniquely determine the velocity dispersion curves, but it is more common to write these in terms of the moduli $c_{11} = \rho v_L^2$ and $c_{44} = \rho v_T^2$. We assume that the mass density of the thick films is the same as that of bulk PS, realizing that any changes in the density will produce corresponding changes in the calculated elastic constants. In fact, only two parameters are needed to fully describe the velocity dispersion and it is not often noted that independent measurement of the mass density is required in *any* acoustic measurement to uniquely determine the elastic moduli. To relate our BLS measurements for thick PS films to those for bulk PS, we independently measured the velocity v_L of the pure longitudinal phonon in a bulk sample. Using this value for v_L , we simply adjusted the one remaining parameter v_T until a best fit with the observed mode velocities was obtained. The solid

lines in Fig. 2 show the calculated velocity dispersion curves for the best fit parameters of $c_{11} = \rho v_L^2 = 5.65 \pm 0.09$ GPa and $c_{44} = \rho v_T^2 = 1.40 \pm 0.03$ GPa, using the bulk value of the mass density $\rho = 1.056$ g/cm³ [28]. The c_{11} and c_{44} values are in excellent agreement (identical within error) with previous BLS studies of thick ($h > 1700$ Å) PS films supported by Si(001) substrates [24]. With this encouraging agreement between measured and calculated velocity dispersion, it is reasonable to extend the measurements and analysis to films of smaller thickness, for which large T_g reductions have been observed. Also shown in Fig. 2 are velocity dispersion data collected for films for which reduced T_g values were observed ($h < 1000$ Å, ΔT_g as low as -65 K). It is obvious that the data are very well described by the velocity dispersion curves calculated using the mechanical properties determined for thick films. This excellent, quantitative agreement between the results for thick and thin films is consistent with the conclusions of our previous BLS studies on highly confined molecules [9].

At this point we consider the comparison of our experimental results obtained using BLS with those obtained using picosecond acoustic techniques in Ref. [10] to see if the present results are consistent with their conclusions. Unfortunately, it is not possible to compare directly the sound velocities because the film-guided modes have different character in the two experiments: in the BLS experiment, the modes are hybridized longitudinal-transverse waves, whereas in the picosecond acoustic technique, a purely longitudinal phonon is probed [10]. In the BLS experiments, the S_0 mode velocity depends on both v_L and v_T and as $Q_{\parallel}h \rightarrow 0$, $v_{S_0} \rightarrow 2v_T[1 - (v_T/v_L)^2]^{1/2}$. This relation holds at $Q_{\parallel}h = 0$ and the relative contributions of v_L and v_T to the S_0 mode velocity depend on the value of $Q_{\parallel}h$. While coincidental cancellation of large changes in both v_L and v_T may occur for a particular value of $Q_{\parallel}h$, it is unlikely that such cancellation will occur for an extended range of $Q_{\parallel}h$ values. The excellent agreement between the calculated and measured S_0 mode velocities demonstrates that the values of v_L and v_T do not depend on film thickness. In sharp contrast, the picosecond acoustic measurements on films with thicknesses $h < 400$ Å are interpreted as a threefold increase in the longitudinal sound velocity and a corresponding tenfold increase in the longitudinal modulus (since they assumed that the mass density was independent of film thickness). Considering the differences in sample type and physical quantity probed, it is not possible to compare directly the two sets of results. However, despite these differences, it is unlikely that a threefold increase in v_L with decreasing h should exist for supported PMMA films (for which there are only small changes in other quantities such as T_g [2]) without a corresponding change in v_L with h for freely standing PS films (for which the T_g reductions are large [5,7]).

The disagreement between the results of these two studies is striking. In both experiments, the mechanical moduli are studied at frequencies in the gigahertz range and yet they appear to differ by an order of magnitude. Unlike the BLS technique, the picosecond acoustic technique is a time-of-flight technique and therefore suffers a loss of accuracy for very small film thicknesses. This is evident from the increasing size of the error bars as the film thickness is decreased in

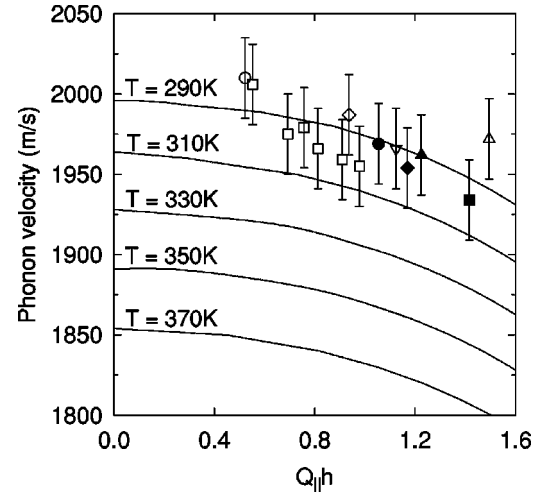


FIG. 3. Magnified S_0 mode velocity dispersion curve. The solid curves were calculated for the temperatures indicated beside each curve. Each symbol corresponds to room-temperature data for a different film, with open symbols used for films with $\bar{M}_w = 767 \times 10^3$ and solid symbols used for films with $\bar{M}_w = 2240 \times 10^3$: open circles, $h = 290$ Å and $\Delta T_g = -66$ K; open squares, $h = 420$ Å and $\Delta T_g = -44$ K; open diamonds, $h = 520$ Å and $\Delta T_g = -33$ K; open inverted triangles, $h = 620$ Å and $\Delta T_g = -11$ K; open triangles, $h = 830$ Å and $\Delta T_g = 0$ K; solid circles, $h = 586$ Å and $\Delta T_g = -61$ K; solid diamonds, $h = 650$ Å and $\Delta T_g = -41$ K; solid triangles, $h = 680$ Å and $\Delta T_g = -16$ K; solid squares, $h = 774$ Å and $\Delta T_g = -13$ K.

Ref. [10]. Also, unlike the BLS measurements, the picosecond acoustic technique is sensitive to errors in the film thickness. The BLS measurements on very thin, freely standing films offer the advantages of insensitivity to film thickness and very high sensitivity to changes in the elastic constants and density.

For BLS measurements of very thin films (with correspondingly small $Q_{\parallel}h$ values), only the A_0 and S_0 mode velocities do not diverge to large values. Because the velocity of the A_0 mode vanishes for small $Q_{\parallel}h$, it is impractical to study this mode in detail. Only the S_0 mode can be used for detailed comparison. Shown in Fig. 3 is the S_0 mode velocity dispersion curve in which the vertical scale has been magnified. In this figure the data points correspond to many different PS films with T_g reductions ranging from 0 K to 65 K. Representative BLS spectra for the film with $h = 540$ Å and $\bar{M}_w = 767 \times 10^3$ are given in Fig. 1 of Ref. [5]. Details of the properties of the individual films (thickness, \bar{M}_w , and T_g) are given in the figure caption. The upper solid curve in Fig. 3 was calculated using the same “thick film” parameters used to calculate the dispersion curves shown in Fig. 2. The data for the thin films are, to within experimental error, identical to the calculated values corresponding to the upper solid curve. In particular, we note that the film with $h = 586$ Å, $\bar{M}_w = 2240 \times 10^3$ has the same S_0 mode velocity as the film with $h = 620$ Å, $\bar{M}_w = 767 \times 10^3$ film. Because the molecules in the former film have a much larger (by a factor of 1.7) R_{EE} value than for the latter film and both films are comparable in thickness, the molecules are much more

strongly confined in the former film. The quantitative agreement between the room-temperature phonon velocities measured for all of the films shows that chain confinement does not affect the measured phonon velocities. It is evident from Fig. 3 that all films, regardless of their respective T_g reductions (up to 65 K) and extent of chain confinement, have the same room-temperature, high-frequency phonon velocities, to within the experimental uncertainty of $\pm 1\%$. In addition, the velocity values and their dispersion are accurately described by the bulk values of the mass density and high-frequency mechanical moduli.

Given the excellent agreement between the high-frequency phonon velocities of the thick and very thin films, it is instructive to estimate the effect that the small changes in density suggested for T_g reductions would have on the measured velocities. To do this we consider the effect of raising the temperature and the resulting effect of the thermal expansion on the film-guided mode velocities because of the known change in density accompanying thermal expansion. For this calculation we use the well-studied temperature dependence [6,20] of the longitudinal and transverse velocities to calculate film-guided phonon velocities as a function of temperature. The different solid curves in Fig. 3 correspond to the calculated S_0 mode velocity as a function of temperature from room temperature up to the bulk glass transition temperature $T_g^{\text{bulk}} \sim 370$ K. The changes in the S_0 mode velocity with temperature are due primarily to the temperature dependence of the mass density and the resulting dependence of the mechanical moduli. The value of the bulk density at $T = T_g^{\text{bulk}}$ is approximately 2% lower than at room temperature [28]. This produces a corresponding decrease in the S_0 mode velocity of 8% for the same change in temperature (see Fig. 3). The S_0 mode velocity values are measured to within an experimental uncertainty of $\pm 1\%$. This means that the error bars for the measured velocity values span less than one-quarter of the total shift in velocity due to the change in density in heating bulk PS from room temperature to T_g . This allows us to state that we can observe density changes of the order of 0.5% in our measurements. If the T_g reductions observed in very thin PS films were due to a reduced value of the mass density, then one would expect that as the film thickness is decreased and certainly as the T_g reduction becomes larger, the measured room-temperature phonon velocities would decrease towards the $T = T_g^{\text{bulk}}$ dispersion curve. Clearly this is not the case. Our results for all films are consistent with the bulk value of the mass density and the bulk values of the mechanical moduli. The above analysis has assumed that the same relationship between the modulus and density exists in films as does in the bulk (the same assumptions are necessarily made in Refs. [10] and [25]). This assumption is almost certainly valid since the dependence of modulus on density is determined by the anharmonic intermolecular potential, which has a characteristic length scale that is small enough as to be unaffected by changes in the film thickness.

While all of the measurements discussed above were performed at room temperature, we can also raise the temperature and compare the measured temperature dependence of the S_0 mode velocity to that calculated using the procedure described above: $dv/dT = -1.7 \pm 0.35$ (m/s)/K. If the density at T_g is the same for all films, the thermal expansion as

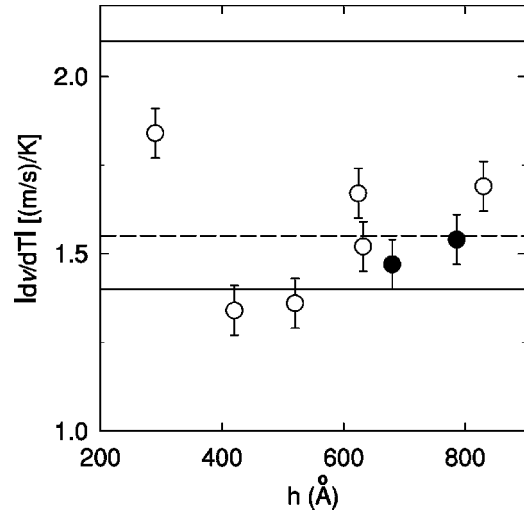


FIG. 4. Magnitude of the derivative of the S_0 mode velocity with respect to temperature dv/dT in the glassy phase as a function of the film thickness h . Data are shown for both \bar{M}_w values: open circles for $\bar{M}_w = 767 \times 10^3$ and solid circles for $\bar{M}_w = 2240 \times 10^3$. The solid lines correspond to the upper and lower bounds on the calculated value; the calculation is described in the text. The dashed line corresponds to the average of the measured dv/dT values.

measured using dv/dT would have to increase with decreasing film thickness. Shown in Fig. 4, for different values of h , are the measured values of the change in the S_0 mode velocity with temperature dv/dT in the glassy phase, together with the upper and lower bounds on the calculated value, neglecting the small change in film thickness. Data points are shown for all films, except that with $h = 586$ Å and $\bar{M}_w = 2240 \times 10^3$, which was omitted from Fig. 4 because of the limited number of measurements in the glassy phase for this film. It is evident that the agreement between measurement and calculation is very good, and that no systematic differences are observed for films that have large differences in ΔT_g . The variations with h of the data in Fig. 4 are more likely due to slight differences in the thermal history of the films. The result of this calculation suggests that, in addition to the room-temperature density, the thermal expansion of these glassy PS films is also independent of the film thickness and ΔT_g .

The robust conclusion of the above results is simply that the high-frequency mechanical properties of thin freely standing polymer films are unaffected by both chain confinement and T_g reductions. The simple analysis performed regarding the mass density suggests that the density of all of the films at room temperature is indistinguishable from the bulk value to within 0.5%. While BLS does not give a direct, absolute measure of the mass density, the relative density values are at least as accurate as those determined using x-ray reflectivity or neutron reflectometry. In addition, the thermal expansion of the films in the glassy phase shows no obvious film-thickness dependence and is consistent with the bulk value. Taken together, these results and analyses suggest that each of the films with a reduced T_g value undergoes the glass transition at a different value of the mass density. This is a surprising observation and it is important to find other evidence to either support or refute this claim.

SUMMARY AND CONCLUSIONS

A detailed understanding of the physical properties of thin polymer films includes knowledge of their high-frequency mechanical properties. We have used BLS to investigate the high-frequency mechanical properties of thin freely standing polystyrene films in the glassy state. Such measurements are a sensitive, though indirect, probe of the mass density. We have found that the measured velocities of the film-guided phonons for thick ($h \geq 1000 \text{ \AA}$) films are consistent with elastic constant values measured previously for supported PS films. By extending this comparison to very thin PS films for which large T_g reductions have been observed, we find that the data for all films are described within experimental error by the same velocity dispersion curves determined for thick

PS films. A careful analysis of the BLS data reveals that, at room temperature, the mechanical stiffness, mass density, and thermal expansion of thin, freely standing PS films in the glassy state are consistent with bulk values for all film thicknesses.

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