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Dielectric and ellipsometric studies of the dynamics in thin films of isotactic poly(methylmethacrylate) with one free surface

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We have performed dielectric loss measurements at 1 kHz on thin films of isotactic poly(methyl methacrylate). A key distinction of our studies is that the samples measured were supported films with one free surface rather than films that have metallic electrodes covering both surfaces. This unique sample geometry allows us to eliminate any effects due to evaporation of metal onto the top film surface and provides a unique opportunity to make direct comparisons between dielectric loss and glass transition measurements. Film thicknesses in the range from 6 μm to 7 nm were prepared on Al coated substrates. The dielectric loss peak and ellipsometric glass transition temperature of all films were measured. The dielectric loss was found to exhibit no discernible film thickness dependence in either the temperature of the maximum loss value or the shape of the loss curve. In contrast, the measured T_g values were found to decrease with decreasing film thickness with a maximum shift of 10 K for a 7-nm film. Dielectric measurements were also made on Al coated films and these samples also showed no shift in the temperature of the loss peak. Finally, the T_g measurements were also made on Si substrates. These values exhibited an increasing T_g value with film thickness with a maximum increase of $\simeq$15 K being measured for a 7-nm film.

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I. INTRODUCTION

Technology and science are placing increasing importance on the study and application of very small systems. As technological trends tend towards systems of nanometer size, it becomes imperative to gain a complete understanding of how the properties of such small systems might differ from those of bulk systems. An example of such an area where the properties at the nanometer length scale exhibit significant deviations from bulk properties is the study of thin polymer films [1,2]. In particular, studies of the glass transition and dynamics in thin polymer films offer great promise to increase our understanding of dynamics in polymeric systems and in glass forming systems in general. In recent years, there has been a strong focus on studies of anomalous dynamics in such samples [3,4]. Many such studies focus on the glass transition temperature T_g of thin films and the dynamics at temperatures near T_g. The nature of the glass transition is an important and unsolved problem and a proper explanation of the thin film data may provide an elucidation of fundamental physics behind the glass transition.

A crucial point arising from recent reports of contradictions between experiments is that great care must be taken in making comparisons between results that measure different physical properties. This is true even if these different properties are both probes of the dynamics of the system. Perhaps the most striking example of such behavior occurs for thin films of polystyrene (PS). For this polymer, measurements of the T_g (and segmental dynamics) indicate an enhancement of the dynamics, whereas measurements of the whole chain mobility exhibit exactly the opposite behavior [3].

Early thin film experiments focused on measurements of the glass transition temperature T_g. This temperature is an important and convenient parameter describing the structural relaxation of a material. Most measurements of T_g in thin polymer films involve measurement of the film thickness (or density) as a function of temperature. The slowing down of dynamic processes in the glassy state results in the ‘‘freezing out’’ of certain types of motion. These motions no longer make contributions to properties such as thermal expansion in the material. The glass, therefore, has a smaller thermal expansion coefficient than the liquid. As a result of this the T_g is manifested as a ‘‘kink’’ in the temperature dependent film thickness data. Since the first detailed study of T_g in thin films by Keddie, Jones, and Cory [5], there have been a large number of studies focused on polystyrene. Only recently has there been enough data that a reasonably clear picture has evolved even for this single material. For PS films on a variety of different substrates, the T_g value is film thickness dependent with a T_g, which is reduced below the bulk value for films with thickness less than $\sim$40 nm. This behavior does not exhibit a discernible dependence on the M_w value of the polymer, nor a strong dependence on the substrate used. Even though the details of the polymer-substrate interaction do not seem important in thin PS films the presence of a substrate is important. This is illustrated by the fact that freely standing PS films exhibit a fascinating behavior [6] with much larger T_g reductions than supported films of similar thickness. Freely standing films also display a complicated M_w dependence [7–10]. Despite the relatively strong agreement between different studies of PS films as well as recent attempts at modeling [8,11–13], an explanation of the observed behavior remains elusive.

Measurements of the T_g value of a material are, at best, indirect probes of the dynamics. More seriously, such measurements are sensitive to the thermal and preparation his-

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*Author to whom correspondence should be addressed. Email address: jforrest@uwaterloo.ca tory of the sample. The indirect nature of glass transition measurements has prompted a number of studies aimed at more direct measurements of the dynamics. Some of these measurements including dielectric studies [14] and quartz crystal microbalance measurements [15], exhibit a film thickness dependence of the relaxation, which is quantitatively consistent with the measured lower T_g values. Some studies derived from measures of whole chain motion, on the other hand, indicate that such motion is actually slowed down in thin films compared to the bulk [16]. This stark contrast illustrates some of the difficulties faced in the thin film measurements. Even though measurements of two different dynamical probes (such as segmental versus chain motion) may be used almost interchangeably in bulk systems, the same is not true for thin films. One example of why this may occur was given by Semenov [17]. This particular example brings up a more fundamental question concerning the coincidence of different experimental probes of the dynamics in thin films [2]. The resolution of this question is one of the most important issues in the study of thin film dynamics. In many thin film experiments it is not always clear what is being probed. Comparison between experiments is obviously crucial to develop an understanding of the underlying physics, and in thin film samples such comparisons may not be as valid as they are in bulk materials.

One of the experimental details which has been discussed in detail concerns the degree to which the polymer dynamics are dependent on the substrate that the thin film is prepared upon. While for the case of PS, the substrate seemed to be of minimal importance, extension to other polymer systems has revealed that many polymers display a sensitivity to the substrate material. The earliest indication of this was the work by Keddie, Jones, and Cory with atactic poly (methylmethacrylate) (PMMA) [18]. That work revealed that the T_g value of a thin PMMA film could actually be increased (on SiO_x) or decreased (on Au coating) from the bulk value depending on the substrate used. Fryer *et al.* [19] have also reported a strong sensitivity of T_g values for thin PMMA films in this case between SiO_x substrates and those coated with hexadimethylsilazane. More recent ellipsometry studies have suggested much larger effects depending strongly on the tacticity of the polymer. An example of this is the recent work by Grohens *et al.* on stereoregular PMMA thin films [20]. This work shows a fascinating film thickness dependence of the T_g value on the polymer tacticity with *i* PMMA on Si substrates showing strong increases in the T_g ($\approx$50 K for a 20 nm film) while *s* PMMA on the same substrate material shows significant decreases ($\approx$34 K for a 20 nm film).

Some recent experimental efforts have focused on a particular system that brings both of these key issues to the forefront, and needs to be clearly resolved. Thin films of isotactic PMMA have been measured by Hartmann *et al.* using broadband dielectric spectroscopy [21]. The dielectric loss in these studies appears to have little, if any, film thickness dependence for frequencies greater than about 10^3 Hz, but at lower frequencies the relaxation exhibits a film thickness dependence such that at a given temperature, thin films have a shorter relaxation time. This was used to define a *dielectrically defined* T_g, T_g^{diel} as the temperature where the relaxation peak is at 10^{-2} Hz. This is done by a slight extrapolation of the relaxation curves (approximately one order of magnitude extrapolation on data over more than seven orders of magnitude). The so-defined T_g values decrease with decreasing film thicknesses for films thinner than 100 nm. The magnitude of the effect is such that the thinnest film (18 nm) has a T_g^{diel} reduced by $\sim$12 K from the bulk value. These results are then compared with ellipsometric measures of the T_g^{diel} for the same polymer on Si substrates. The comparison is striking in that the T_g values actually increase with decreasing film thickness. The magnitude of this effect is also remarkable with a measured T_g value 50 K greater than the bulk value for an 18-nm film. The discrepancy between these two measures of the dynamics is clearly significant, and there are two possibilities why such a discrepancy may exist. One possibility is that dielectric spectroscopy and ellipsometry actually probe dynamics in sufficiently different ways that it is not possible to learn from comparisons between these two measures of the dynamics. An alternative possibility is that the observed differences are due to the slight differences in sample geometry between the two studies. Samples for the dielectric study are spincast onto Al coated substrates, and have Al evaporated on the top surface; while the samples measured with ellipsometry were cast onto Si substrates. Either of these effects (the different substrate, or the evaporation onto the top surface) could potentially affect the result.

Clearly, the above results suggest that we have to either give up the assumption that we can compare different types of measurements, or we have to concede such a strong sensitivity to sample details as to make comparisons between different samples tenuous. Both of these suggestions place strong limitations on the usefulness of thin film studies, and we have set out to make a detailed quantitative comparison between systems, where it is reasonable to make and have confidence in such comparisons. In this paper, we present a study of thin supported films of *i*-PMMA. We are able to measure dielectric loss in thin supported films by incorporating the films into an air-gap capacitor. We are also able to do ellipsometry on the exact same sample geometry (*i*-PMMA on Al coated substrates). This provides us with the opportunity to make detailed quantitative comparisons between the results. For completeness, we have also made dielectric loss measurements on *i*-PMMA films that have had an Al layer evaporated on top (to determine any effects due to thermal evaporation) as well as ellipsometry on *i*-PMMA films on Si substrates.

II. EXPERIMENT

Dielectric studies of isotactic poly(methylmethacrylate) (*i*-PMMA) were performed using a home-built capacitance cell. The capacitor plates used in these experiments were prepared by polishing 3-mm-thick, 20-mm-diameter stainless steel disks using a series of four different aluminum oxide slurries (with particle sizes from 1 to 0.05 μm) (Mark V Laboratories) The resulting surfaces were then cleaned by rinsing first in deionized water and then in chloroform. A

1.9-μm-thick layer of aluminum was then thermally evaporated onto one side of the plates using an evaporation rate of $30\ \mathrm{nm\,s^{-1}}$ at an ambient pressure of 4×10^{-6} Torr. This procedure typically produced structureless surfaces with an rms roughness of 5 nm (measured on an atomic force microscope over a $50\times50\ \mu\mathrm{m}^2$ area).

The *i*-PMMA used in this work was obtained from polymer source ($M_w=212\,400$, $M_w/M_n=1.21$) and had an isotactic content $>98\%$. Films of *i*-PMMA were prepared by spin coating the polymer from solutions in toluene onto the aluminum coated capacitor plates. All of the films used in this study were produced using a spin speed of 3000 rotations per minute on a home-built spin coater. The film thickness was controlled by changing the concentration of the solution. Films with thicknesses in the range 7–200 nm were produced using this method.

The coated capacitor plates were annealed under vacuum for 15 h at 90 °C (bulk $T_g=47\,^\circ\mathrm{C}$), removed and allowed to cool to room temperature. They were then loaded into the dielectric measurement cell with a second capacitor plate (also polished and coated with Al). The two plates were spaced using four $3\times3\text{-mm}^2$, 10-μm-thick polytetrafluoroethylene (PTFE) spacers that had been cut from a large sheet (goodfellow) and cleaned in chloroform. This resulted in capacitance values in the range 140–170 pF. An important distinction between these samples and those involving electrodes coated onto the polymer film surfaces is that in the present case the capacitor used in each film is essentially the same, with the actual polymer film being a relatively small perturbation. An additional advantage of using such a large spacer, relative to the thickness of the films being studied, is that this method reduces the size of the electric field in the samples. This eliminates any possibility of nonlinear effects that may possibly be caused by large electric fields, and prevents the difficulties associated with dielectric breakdown in very thin films. The second "reference" plate was used to measure the temperature during the experiment. A thermocouple was fixed (with omegabond 200 thermal epoxy) into a hole in the plate on the side facing away from the polymer film. This was done so that the thermocouple was in intimate thermal contact with, but electrically isolated from, the actual electrode. The voltage on the thermocouple was measured with a HP34401 multimeter. A nitrogen purge was used to gently flush the dielectric measurement cell prior to and during the experiment. This served to remove any atmospheric water vapor on either the cell or the capacitor plates. This dry gas purge was essential to decrease the background loss to values low enough to allow measurement of the very thin films. For the bulk sample measurement, the cell was suspended in nitrogen vapor (from liquid boil off), which allowed the dielectric loss measurements to be extended to temperatures as low as −150 °C.

All of the dielectric measurements were performed using an Andeen Hagerling 2500A 1-KHz ultraprecision capacitance bridge. This instrument is capable of obtaining a precision of 10^{-6} pF in the capacitance and 10^{-8} in the dielectric loss tangent. The instruments were controlled and the data collected using custom software written in national instruments labview. This equipment was used to simultaneously measure the capacitance C and dielectric loss tangent $\tan\delta=\epsilon''/\epsilon'$ of the system as a function of the sample temperature. The lowest room temperature loss tangent measured was 1.85×10^{-6}, which was obtained for the empty cell. To obtain the temperature dependence of the dielectric loss, the temperature of the samples was increased from 25 °C to 140 °C using a ramp rate of $10\ \mathrm{K\,min^{-1}}$. They were then allowed to slowly cool at $2–3\ \mathrm{K\,min^{-1}}$. The temperature was then cycled between 30 °C and 130 °C using heating and cooling rates of $2–3\ \mathrm{K\,min^{-1}}$. The dielectric loss tangent $\tan\delta$ and capacitance C of the system were averaged and recorded every 2 sec. Ellipsometry measurements were also performed on *i*-PMMA films that had been spin coated onto aluminum coated substrates. The aluminum substrates for the ellipsometry studies were prepared by thermally evaporating a 1.9-μm-thick layer onto $2\times2\text{-cm}^2$ silicon wafers ([100] orientation, compart technology). The evaporation rate used in the deposition of this aluminum layer was the same ($30\ \mathrm{nm\,s^{-1}}$) as that used to coat the capacitor plates, and produced an aluminum surface with a roughness essentially the same as that on the steel capacitor plates.

Films of *i*-PMMA were spin coated onto the aluminum coated silicon wafers, annealed under vacuum at 90 °C for 15 h, allowed to cool to room temperature and then placed on the ellipsometer sample stage. An Exacta 2000 nulling ellipsometer (Waterloo Digital Electronics) using a laser wavelength of 633 nm and an incident angle of $60.0°\pm0.1°$ was used for the ellipsometry studies. The values of the zone-averaged polariser P and analyser A angles required to obtain a null value at the photodiode detector were recorded as a function of temperature. The zone averaging compensates for imperfections in the optical components, and is meant to provide a more reliable absolute value in the final quantities. The samples were cooled from 80 °C to 10 °C in steps of 2 °C. At each temperature interval, the samples were allowed to equilibrate for 1–2 min before data were collected. This gave an effective cooling rate of $0.2\ \mathrm{K\,min^{-1}}$. The P and A data obtained from the ellipsometry experiments were converted to thickness and refractive index, using the semi-infinite slab approximation for a film on an oxide coated substrate, described by Azzam and Bashara [22]. A transfer matrix method was used to construct the fresnel coefficients (r_p and r_s) for the p and s components of the reflected light from the film. These were then used to construct a second expression for the complex quantity $\rho=r_p/r_s$. An experimental value of ρ was then constructed using the relation $\rho_{exp}=\tan(A)\exp[i(2P+\pi/2)]$ and the quantity ZZ^* minimized using a Nelder-Mead unconstrained nonlinear simplex optimization method, where $Z=\rho-\rho_{exp}$ and Z^* is its complex conjugate. The only fit parameters in this procedure were the thickness and refractive index of the polymer film. Table I gives a list of the other parameters used in the fitting procedure along with the references used to source the information. In each case, the thickness of the oxide layer was determined by using the substrate values of P and A and assuming a thin unform slab of oxide on a semi-infinite medium of the substrate material. This procedure of using the multilayer technique was found

TABLE I. Parameters used in ellipsometry inversion calculations

Substrate	n	n_{oxide}	h_{oxide} (nm)
Aluminum	$1.300-6.500i$ [23]	1.765 [24]	8.8 ± 0.1
Silicon	$3.860-0.019i$ [24]	1.460 [24]	1.8 ± 0.1

to provide much more reliable data than the use of an "effective substrate" method where an effective index of the substrate including oxide layer is used in the calculation. In contrast to many polymer/substrate systems, it was necessary to do the inversion before trying to extract T_g values. The reason for this is that in the PMMA/AlO_x/Al system, the changes in the ellipsometric angles P and A are strong functions of the refractive index n, and film thickness h. For such strong dependence, linear changes in h and n do not lead to linear changes in P and A even for the small ranges considered in a typical cooling run. The ellipsometry for the capped films was more involved. Given the larger number of unknowns in that case, it was not possible to reliably invert the data, so T_g values could not be determined using ellipsometry.

III. RESULTS

A. Dielectric measurements

After the first heating and cooling cycle, the values of tan δ and the position of the maximum of the α loss peak were reproduced to within $\pm2\,°\mathrm{C}$ between temperature cycles. The background signal in the first heating cycle was found to be significantly larger than in subsequent cycles. This may be due to the presence of small molecules (most likely water molecules) adsorbed on to capacitor plates and cell that are removed during the first heating cycle. The use of dry purge gas prevents reformation of a water layer. The data obtained for tan δ as a function of temperature are plotted in Fig. 1. Also shown, in Fig. 1(b), are the results of the same measurements performed on films of *i*-PMMA that have had a 30-nm layer of aluminum evaporated on top of the polymer using an evaporation rate of $3\ \mathrm{nm\,s^{-1}}$. This second set of experiments was performed so that a comparison could be made between the samples described above (i.e., having one free surface) and those with an aluminum capping layer. The aluminum capped films are similar to those studied previously [25,21] where it was suggested that evaporation of the second aluminum electrode could be responsible for the anomalous results obtained in these studies. In the present study, the second evaporated layer does not act as the electrode because the 10-μm PTFE spacers were placed on top of this layer to isolate it and the polymer film from the reference plate. While it may be preferable in some way, it was not possible to use the same evaporation condition for the top layer as was used for the underlying layer. The reason for this is that in order to maintain the possibility to perform subsequent ellipsometric studies, it is necessary that the Al layer not be so thick that there is no optical penetration into the polymer. The value of 30 nm was chosen as it allows a reasonably thick Al coating while still being thin enough for ellipsometry studies (even though inversion of the ellipsometric data for the capped films was not eventually achieved). In order to have reasonable control over the reproducibility of the experiment for a 30-nm capping layer, it is necessary to employ the low evaporation rates used in these studies.

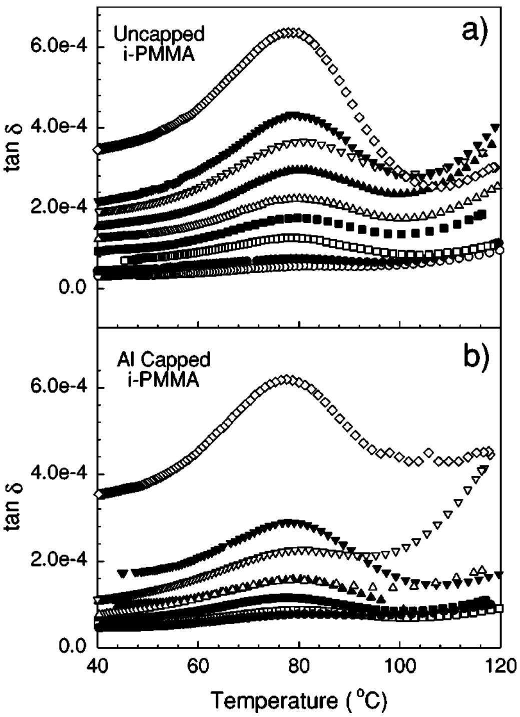

FIG. 1. Dielectric loss tangent tan δ as a function of temperature for thin films of *i*-PMMA ($M_w=212\,400$). Data are shown for films supported on aluminum substrates with (a) one free surface, and (b) with a 30-nm aluminum capping layer. The data shown correspond to film thicknesses of (○) 7 nm, (●) 29 nm, (□) 33 nm, (■) 42 nm, (△) 67 nm, (▲) 78 nm, (▽) 89 nm, (▼) 127 nm, and (◇) 259 nm.

The α-relaxation data shown in Fig. 1 for *i*-PMMA sit on a background that for the thinner films studied make determination of the peak position less obvious. To make more detailed analysis, it is necessary to remove the background. An empty cell run was taken with the same experimental conditions (e.g., cooling rates) as the runs involving thin films. This empty cell spectrum was simply scaled by a multiplicative factor to make the high temperature values of tan δ (where there is no relaxation) equal to that of the data file, and then subtracted from the data. This was done for all the film thickness studied, except the 6-μm-thick (bulk) film. In the case of the 6-μm-thick film, the contribution due to the background was negligible and correction of the data was not necessary. Under normal circumstances, subtraction of tan δ values is not a valid method for performing background corrections. The correct way to perform the background substraction is to correct the ϵ' and ϵ'' by their background values [21,25] and then take the ratio to determine the corrected value of tan δ. The geometry of the air-gap capacitors used in this study allows us to make a number of approxi-

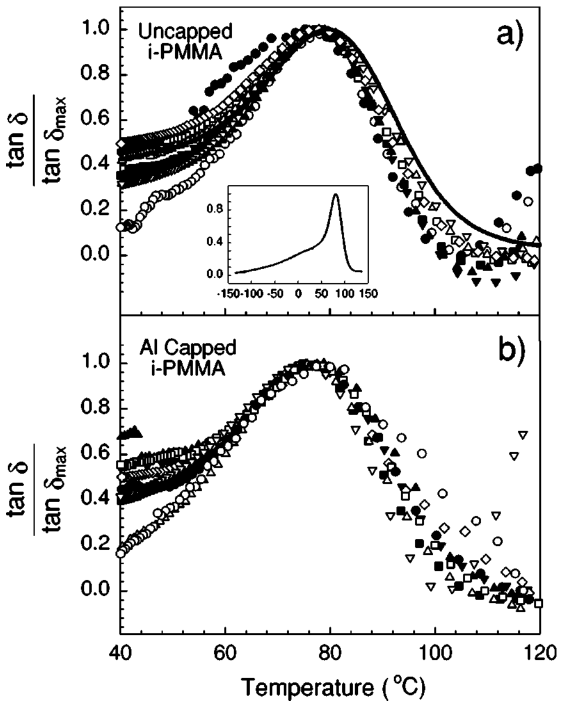

FIG. 2. Corrected dielectric loss data for thin films of *i*-PMMA ($M_w = 212\,400$). The data are scaled by the maximum value of the α loss peak (tan δ_{max}) so that a comparison of the peak shapes for the different film thicknesses studied can be made (see text). Data are shown for *i*-PMMA films with (a) one free surface and (b) with a 30-nm-thick capping layer. The *i*-PMMA film thicknesses studied are (○) 7 nm, (●) 29 nm, (□) 33 nm, (■) 42 nm, (△) 67 nm, (▲) 78 nm, (▽) 89 nm, (▼) 127 nm, and (◇) 259 nm. The solid line is the scaled data obtained for a bulk sample (6.3 μm). The inset shows a plot of the data collected for the bulk sample, taken over a wider temperature range.

mations that makes the subtraction of tan δ values equivalent to subtracting ϵ'' values. This is because the measured ϵ' values are given by an average of the ϵ' values for the polymer and the air gap, weighted by their thickness. The measured capacitance changes in a typical experiment were of the order of 3–4 pF (a typical measured capacitance value was 150 pF) for all the film thickness studied. After correcting for the thermal expansion of the PTFE spacers, the data were inverted to extract values of ϵ'. The resulting values were found to be dominated by the properties of the air gap and ϵ' was determined to be close to one for all temperatures in the range $50°\mathrm{C} < T < 130°\mathrm{C}$. The measured ϵ' was found to be weakly dependent upon temperature in this range. The ϵ' values obtained for the empty cell showed similar behavior. The similar behavior of ϵ' for the data collected from the *i*-PMMA films and from the empty cell means that subtracting the tan δ values of the empty cell behavior from the data collected for the *i*-PMMA films is approximately equivalent to subtracting ϵ'' values. Below 50 °C, the values of ϵ' obtained, show a stronger temperature dependence. This may explain the lack of systematic variation in the data in Fig. 2 for temperatures < 50 °C. The remaining deviations at high temperatures are due to small changes in the background that occur upon different assemblies of the capacitor. The validity of the background subtraction procedure is confirmed by the comparison performed below of the scaled tan δ values obtained in the present study with those of Hartmann *et al.* [21] and Wübbenhorst *et al.* [25].

Figure 2 shows the ratio of tan δ to tan δ_{max} for the corrected data, where tan δ_{max} is the value of tan δ at the maximum value of the α relaxation peak. The solid line is for a 6-μm (bulk) sample and the inset shows an extension of the measurement on the bulk sample over a temperature range large enough to encompass the entire β relaxation peak. The data shown are again for films with one free surface in Fig. 2(a) and for aluminum capped films in Fig. 2(b). All of the data shown were taken from the second cooling of the samples though any subsequent cooling cycle could also have been used. Perhaps the most obvious feature of this figure is that there is no discernible shift in the dielectric relaxation peak at a measurements frequency of 1 kHz for *i*-PMMA films with a thickness as low as 7 nm. This observation is in agreement with the results of Hartmann *et al.* [21] where for films of *i*-PMMA ($M_w = 164700$) with thickness as low as 20 nm there was no observed shift in the 1-kHz data. Closer inspection of the data in Fig. 2 reveals that there is also no discernible change in the peak shape. The small differences at higher temperatures are due to subtleties in removing the background, but what is clear is that in the low temperature loss (where enhanced dynamics in thin films would be observed) there is no evidence for a change of behavior in the thinner films. A distinct possibility has been raised previously that the evaporation of a metal layer on top of the polymer film may actually modify the film properties. This has been discussed as a potential explanation between differing results in dielectric studies of *i*-PMMA systems. We investigate that possibility by also studying PMMA films that have had an Al coating evaporated on top of the film. Figure 2(b) shows the scaled dielectric loss (after removal of the background) as a function of temperature for these samples. As in the previous plot, the most obvious feature of the data in Fig. 2(b) is that the position of the loss peak for this system also displays no dependence on film thickness for films in the entire film thickness range. Though the capped systems exhibit more scatter, there is no monotonic shift in the position of the loss peak maximum.

In producing the scaled data of Fig. 2, one also obtains the actual magnitude of the maximum value of the dielectric loss tangent as a function of the film thickness. Since the film is part of an air-gap capacitor which is, to a good approximation, not varying between samples, we can expect the real peak value of the dielectric loss to be proportional to the film thickness h. Figure 3 shows a plot of the value of tan δ_{max} as a function of the film thickness. One noteworthy point of this data is the small magnitude of tan δ_{max}. All films with $h \simeq 100$ nm have a tan $\delta_{max} < 1 \times 10^{-4}$, and the smallest films have a tan δ_{max} of less than 2×10^{-5}. These small values of tan δ_{max} require the ability to measure changes in tan δ of about 1×10^{-6}. By using spacer layers of smaller thickness, one could relax this requirement. If we extrapolate these lines to the value of the spacer (10 μm) and compare this to the bulk value of tan δ at 1 kHz, we find that the extrapolated

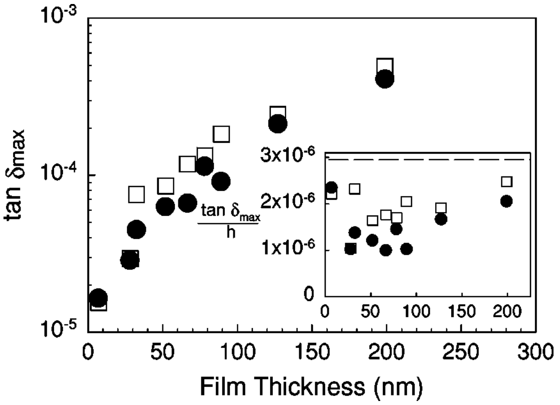

FIG. 3. Variation of tan δ_{max} with film thickness for *i*-PMMA ($M_w = 212\,400$) films supported on aluminum substrates with (□) one free surface and (●) with a 30-nm capping layer of aluminum. The inset shows the value of tan δ_{max}/h as a function of film thickness for both the uncapped and capped films (nm^{-1}). The dashed line represents the value obtained for a 6.3-μm-thick film (bulk sample).

tan δ values derived from the data in Fig. 3 are still lower than expected [25]. This effect is examined in more detail in the inset of Fig. 3, where we plot tan δ_{max}/h as a function of film thickness. Also shown in the inset to Fig. 3 is a dashed line corresponding to the value of tan δ_{max}/h for the 6 μm film. The simple argument given above leads to the suggestion of a constant value of tan δ_{max}/h. All of the thin film data are clearly below the value for the "bulk" sample, and with the exception of the data points for the thinnest films, there is a trend of decreasing values of tan δ_{max}/h as the film thickness is decreased. The very thinnest films are most subject to small quantitative errors after the background substraction; and so the two observations above suggest a slight decrease in the relaxation strength as the film thickness decreases. An interesting point of the data in Fig. 3 is that the value of tan δ_{max} is very similar for both the supported and the Al capped films. In recent dielectric studies of thin polymer films [14,21], it has been suggested that the film thickness dependence of the relaxation strength is due to the presence of *dead layers* near the interfaces that do not contribute to the relaxation. The quantitative coincidence we observe between films with one free surface and those with no free surfaces does not support the suggestion of these *dead layers* as the principal reason for the observed film thickness dependence of the relaxation strength.

B. Ellipsometry measurements

As mentioned previously, the use of ellipsometry for PMMA on Al substrates is not as straightforward as it is for some other systems [5]. As a result, it is not always possible to extract a T_g from raw ellipsometric data. In this case it is necessary to invert the data, within the context of some model, to film thickness and refractive index. Figures 4 and 5 show the raw P and A data for two different *i*-PMMA films (127-nm-thick film and a 32-nm-thick film) supported on Al coated substrates as well as the thickness and refractive index obtained from the numerical inversion. The glass transition is determined in this case by manually fitting the two straight line regions on either side of the transition. For the data used in this experiment, the transition contrast is high enough that this procedure is relatively insensitive to small

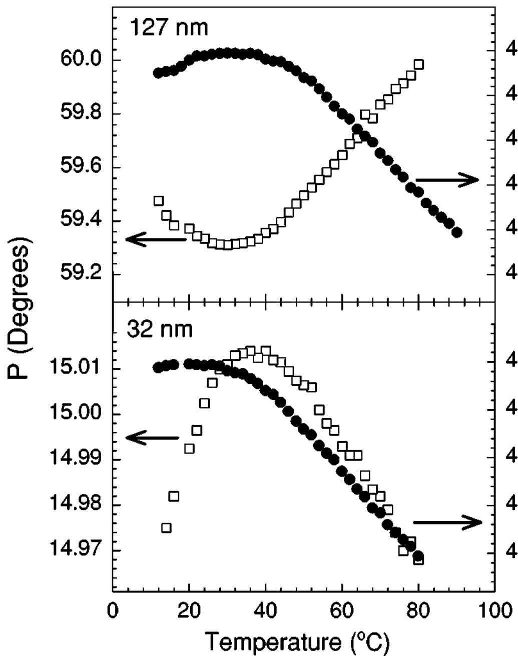

FIG. 4. Plots showing the zone-averaged P (□) and A (●) ellipsometry data as a function of temperature. Data are shown for both a 127-nm and a 32-nm-thick *i*-PMMA film supported on aluminum substrates. All data were collected with an effective cooling rate of 0.2 K min^{-1}.

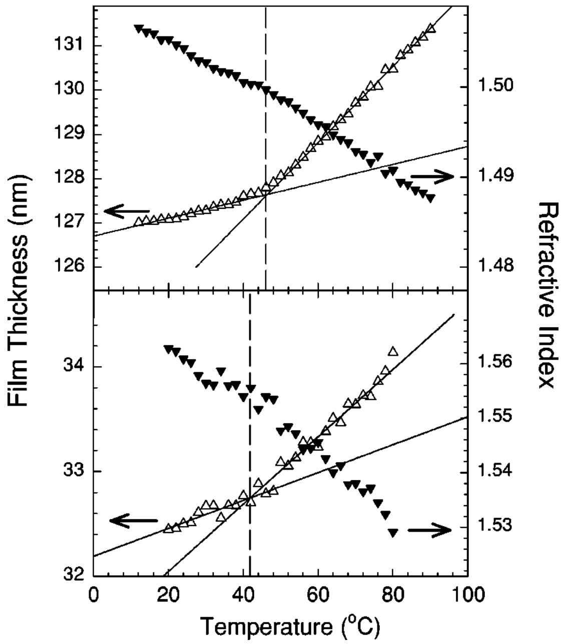

FIG. 5. The fitted values for the thickness (△) and refractive index (▼) of *i*-PMMA films as a function of temperature. The T_g of the polymer is defined as the temperature at which the linear constructions to the film thickness data intersect.

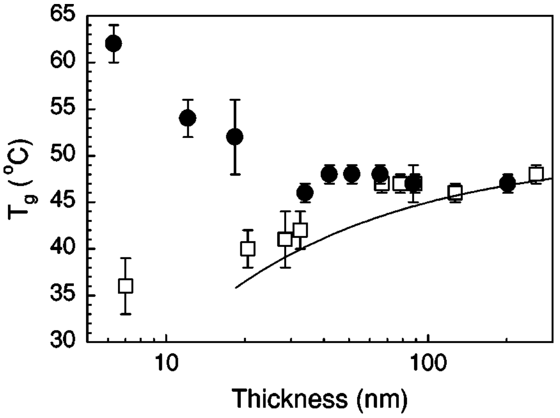

FIG. 6. Thickness dependence of the glass transition temperature (T_g). Data are shown for *i*-PMMA films ($M_w = 212\,400$) supported on aluminum substrates with (□) one free surface. Data are also shown for uncapped films of *i*-PMMA ($M_w = 212\,400$) supported on (●) silicon substrates. The solid line shows the dielectric T_g data for supported films of *i*-PMMA ($M_w = 164\,000$) on aluminum with a thin aluminum capping layer, taken from Ref. [21]. These data are shifted for comparison with the present work.

variations in choice of which points constitute the glassy and melt regions. Figure 5 also shows the fits to these two linear regions on either side of the glass transition. Not only can we use these straight lines regions to determine T_g, but we can also use the values of the slope that correspond to the expansion coefficients of the glassy and melt state of the polymer as a check on the validity of the fitting routines used to derive *h* and *n*. Typical values for the expansion coefficients of the PMMA films were determined to be $1.99 \pm 0.70 \times 10^{-4}$ K^{-1} in the glassy state and $7.82 \pm 0.55 \times 10^{-4}$ K^{-1} in the melt state. These values are both consistent with literature values of the expansion coefficient of PMMA [26]. One point worth noting is that the *absolute values* of the refractive index and film thickness are highly sensitive to the incident angle, and as a result inaccuracies in the incident angle tend to lead to errors in the absolute fit values of *h* and *n* (but not in the relative changes and hence the T_g). This problem is more severe for the thinnest films, and can sometimes lead to fractional errors in the absolute value of the refractive index by as much as 10%. Another effect that leads to quantitative (but not qualitative) discrepancy at small film thicknesses is the assumption used in the model calculation. The interfaces in the system are assumed to be perfectly flat, when we know they have a roughness of a few nanometers. For thick films this has no effect, but when the film thickness approaches the surface roughness, quantitative discrepancies may arise in the absolute values of any derived physical quantities.

As in any dilatometric method, the T_g is determined from a break in the thickness (refractive index) versus temperature plots shown in Fig. 5, by the temperature where the two constructed lines intersect [4]. Figure 6 shows measured T_g values as a function of film thickness for *i*-PMMA films on Al coated substrates, as well as *i*-PMMA films on Si wafers with the native oxide layer intact. The most obvious aspect of the data is the qualitative change in the measured T_g values on the different substrates. For the case of Al coated substrates, the T_g decreases with decreasing film thickness, while for the Si substrates, the T_g increases with decreasing film thickness. This observation is very similar to that observed by Keddie *et al.* for the case of atactic PMMA on SiO$_x$ and Au coated substrates, where it was observed that the T_g decreased on Au coated substrates but increased on SiO$_x$ [18]. This difference between the T_g values on different substrates, and especially the observation of a decreasing T_g with film thickness for the case of Al substrates is of importance in this case as it is the difference between the ellipsometric and dielectric studies of Ref. [21] that has become a focus for discussion. The new ellipsometric results presented in Fig. 6 agree at least qualitatively with the estimated T_g values in Ref. [21], determined using extrapolation of dielectric relaxation studies that were performed on thin *i*-PMMA films capped with a thermally evaporated Al layer. A more quantitative measure of agreement is provided by comparing the data in Fig. 6 to the solid line that fits to the data of Ref. [21] with a constant shift applied to the solid line to allow for coincidence of the values at large values of the film thickness. This comparison leads to a quantitative agreement on the extent of the T_g shift using the two different dynamical probes (dielectric and T_g) within the uncertainty of the measurements. The magnitude of difference in the the measured T_g values between the two substrates becomes as large as 27 K for the thinnest film of 7 nm. This difference is larger than that observed by Keddie *et al.*, but a detailed comparison is not warranted as the tacticity is different in the two different studies. Grohens *et al.* have recently shown that tacticity can have a significant effect on the T_g value [20]. Comparisons can also be made to recent measurements of *i*-PMMA on Si substrates. The results of the *i*-PMMA on oxide coated Si can be compared with other recent studies [20,21]. While the results for Si shown in Fig. 6 agree qualitatively with these previous studies, there are significant quantitative differences.

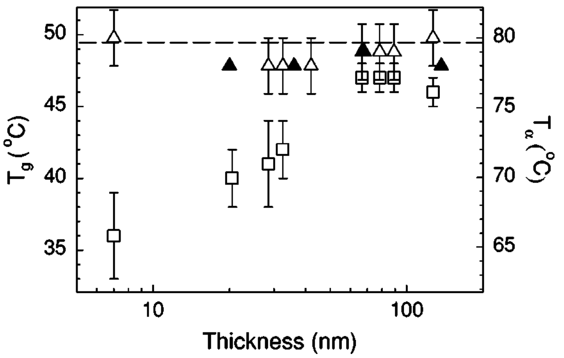

FIG. 7. Comparison of the thickness dependences of the ellipsometric T_g (□) and T_α, the position of the α loss peak (△) in *i*-PMMA ($M_w = 212\,400$) measured at 1 KHz. This plot also shows the position of the 1 kHz loss peak for *i*-PMMA ($M_w = 164\,000$) taken from the data in Ref. [21] (▲). The dashed line represents the position of T_α for a 6.3-μm-thick film (bulk sample).

A summary of the results for the case of *i*-PMMA films on Al-coated substrates is shown in Fig. 7. The hollow triangles (corresponding to the right-hand axis) in this figure indicate

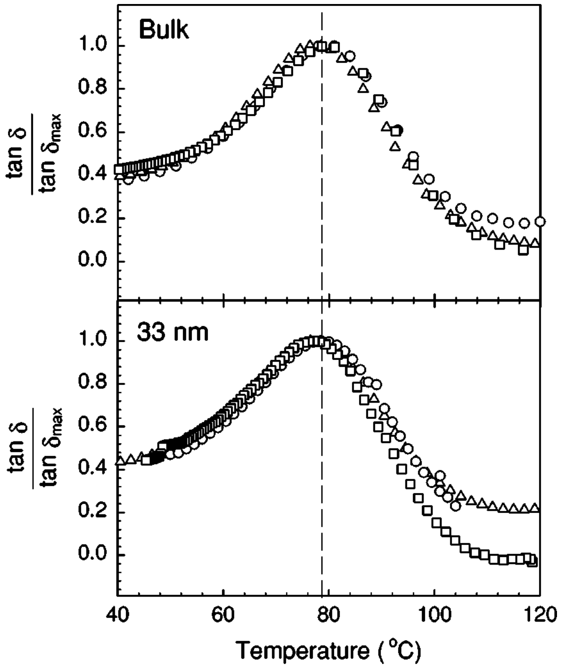

FIG. 8. Scaled peak shapes for the α loss peak. The data shown are taken from this study (□), Ref. [25] (△) and Ref. [21] (○). Data are shown for 6.3-μm (bulk) and 33-nm-thick films, respectively. The dashed vertical line marks the position of tan δ_{max} (T_α) for the α loss peak in the bulk sample.

the temperature of the maximum value for the 1-kHz dielectric loss as a function of the film thickness. As a comparison, the dashed line gives the peak position for a 6-μm bulk sample. The data show that in the entire range of film thickness from 6 μm to 7 nm (i.e., almost three orders of magnitude in film thickness), the peak of the 1-kHz dielectric loss peak occurs at the same temperature. The data are compared to, and are seen to agree quantitatively with, the 1-kHz data of Hartmann *et al.* which is given by the solid symbols. Given sometimes significant discrepancies between different studies, this level of agreement between studies from different laboratories is encouraging. Agreement between the dielectric data of the supported films in this study and the capped films used in other dielectric studies is clear not only in the peak position, but also in the entire peak shape. Figure 8 shows a comparison between the results of our study on supported films, the study of Ref. [21], and Ref. [25]. The comparison in Fig. 8(a) is for *bulk* samples and shows excellent agreement. Even more remarkable is the fact that this level of agreement is still observed for the case of the 33-nm films from each study. In this case, there are small differences only at the highest temperatures. The mutual consistency between the results of the present study and other studies, in terms of the thickness dependencies of the T_g and 1-kHz α peak is encouraging.

Returning to Fig. 7, the temperature of the dielectric loss peak can also be compared to the measured T_g value given by the hollow squares. The separation between the 1-kHz loss peak temperature and the ellipsometric T_g was shown in Fig. 6 to agree with the observation in Ref. [21] that only at low frequencies $\sim 10^{-2}$ Hz do the dielectric loss values show a film thickness dependence. This behavior places some limitations on what sort of an effect can be responsible for the observed T_g reductions. For instance, one way in which the T_g can be changed is through a simple change in the T_0 value of the Vogel Fulcher Tamman relation $\tau = \tau_0 \exp^{B/(T-T_0)}$. A shift in T_0 was suggested to explain observations in photon correlation experiments on free standing PS films [15]. A simple calculation using B and T_0 values consistent with the data of Ref. [21] shows that a change in the T_0 value will produce a change in the relaxation time at 10^3 Hz essentially the same as that at 10^{-2} Hz.

One explanation that is consistent with the data involves the existence of a dynamical correlation length [4]. The effect this has on the dynamics is not described simply by a change in the Vogel-Fulcher parameters. The argument is that the correlation length is a function of temperature as proposed initially by Adam and Gibbs. While it is generally agreed that this dynamic correlation length ξ has a temperature dependence. There are few estimates as to an approximate value for ξ, or for its temperature dependence. One idea is that at sufficiently high temperatures, particle motion is noncooperative, but as the temperature is lowered there is a cooperativity onset temperature T_{ons} and the dynamic correlation length $\xi \sim (T_{ons} - T)^\alpha$, where α is a power that depends on certain assumptions about the dimensionality of the cooperatively rearranging regions. For compact regions, Donth finds that the cooperativity volume $V_\alpha \sim (T_{ons} - T)^2$ [27]. Using a fluctuation model to analyze calorimetric data, Donth [27] has provided estimates of the magnitude of ξ as well as its temperature dependence. For many polymers, the value of ξ near the bulk T_g is a few nanometers [28], and for the case of *a*-PMMA ξ is given as 1.3 ± 0.2 nm [29]. This order of magnitude is also suggested in NMR experiments [30], where a correlation length of 3 nm at $T_g + 10$ K was suggested . In this case we can see that near T_g, the dynamic correlation length is a few nanometers, but at the high temperature of the 1-kHz loss peak (i.e., $T_g + 30$ K) the length scale will be much smaller, reaching a minimum value (of the order of the polymer persistence length) at T_{ons}. Clearly the onset of any finite size effects requires that the sample size be comparable to the value of ξ. At lower peak relaxation frequencies this condition will be satisfied for much thicker films than at higher frequency simply because a higher frequency peak relaxation necessarily occurs at a higher temperature. The result is that as one increases the measurement frequency, the largest film thickness where anomalies will be observed will decrease. This argument is similar to those described by Kremer *et al.* [31] and Anastasiadis *et al.* [32]. It provides one qualitative explanation why one would observe deviations from bulk dynamics using T_g measurements or low frequency dielectric studies, but not observe deviations in the higher frequency dynamics of the same films.

IV. CONCLUSIONS

We have performed a detailed study on thin films of *i*-PMMA using dielectric loss measurements and ellipsometry. By studying supported films on the same substrate material, we are able to make detailed comparisons between dielectric loss measurements and ellipsometrically determined T_g values. The temperature corresponding to the peak in the 1-kHz dielectric loss was found to be independent of film thickness. Al coated samples were also studied and found not to exhibit a discernible difference in the dielectric loss peak from supported films. Ellipsometric studies on both Al and Si substrates show a qualitative change in the T_g behavior with substrate similar to that demonstrated in other studies. Finally, we demonstrate reasonable quantitative agreement between the ellipsometry measurements on Al substrates, and the extrapolation of dielectric measurements reported by Hartmann *et al.*

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