

Thickness dependence of structural relaxation in spin-cast, glassy polymer thin films

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The isothermal structural relaxation of glassy, spin-cast polymer thin films has been investigated. Specifically, the thickness h of freshly cast poly(methyl methacrylate) thin films was measured over time using spectroscopic ellipsometry. The spin-cast films exhibit a gradual decrease in thickness, which is attributed to structural relaxation of the glass combined with simultaneous solvent loss. In all cases, h was found to be greater than the equilibrium thickness h_∞ , which is obtained by cooling slowly from the melt. It is observed that both the rate of the volume relaxation and the fractional departure from h_∞ (referred to as δ_0) increase with increasing film thickness. In the limit of very thin films, the initial h is close to h_∞ , and δ_0 is small, whereas in thick films (>500 nm), a plateau value of δ_0 of 0.16 is observed, which is close to the volume fraction of the solvent at the vitrification point. This dependence of δ_0 on thickness is observed regardless of the substrate, polymer molecular weight, or angular velocity during spin casting. Enhanced mobility near film surfaces could be leading to greater relaxation in thinner films prior to, and immediately after, the vitrification of the polymer during the deposition process.

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I. INTRODUCTION

Structural relaxation of glassy polymers has been widely studied in bulk materials, and it is now well understood [1–5]. Relaxation is important for explaining the long-term changes in physical properties (e.g., elastic modulus, dielectric strength, and refractive index) during the aging of a glass [1,2]. In bulk polymer glasses, temperature-volume relationships have been thoroughly studied and are well documented. When a polymer melt is cooled rapidly through its glass transition temperature T_g to a temperature T_0 a volume of V_0 is obtained. If the glass is annealed at a temperature of T_a , the volume will slowly relax and will approach an equilibrium volume V_∞ over time. V_∞ corresponds to the volume that the supercooled liquid (or glass if it passes through the glass transition) would obtain if it were cooled extremely slowly [3]. Figure 1 schematically shows these relationships between volume and temperature.

The relaxation process can be monitored by measuring after a given time of annealing t the volume of the glass V_t . The relative departure from the equilibrium volume, δ , can then be defined [3,5] as

$$\delta(t) = (V_t - V_\infty)/V_\infty. \quad (1)$$

When a *bulk* polymer is quenched from the melt, δ is typically on the order of 0.01. At macroscopic length scales (several millimeters or more), such small fractional volume changes can be easily measured as a function of temperature and time through standard techniques of dilatometry. Typically, δ approaches 0 over tens of hours.

A conventional way of analyzing relaxation kinetics is to plot δ as a function of the logarithm of relaxation time t . The volume relaxation rate β of a glass is then defined [3,5] from the slope of such a plot:

$$\beta = \frac{d\delta}{d \log_{10} t}. \quad (2)$$

Values of β can be used to compare two different polymers or to examine the effects of temperature or thermal history. A limitation of this type of analysis, however, is that it cannot distinguish a distribution of relaxation times from a time-dependent δ [3]. From measurements of volume in bulk samples of quenched glasses, β has been determined for sev-

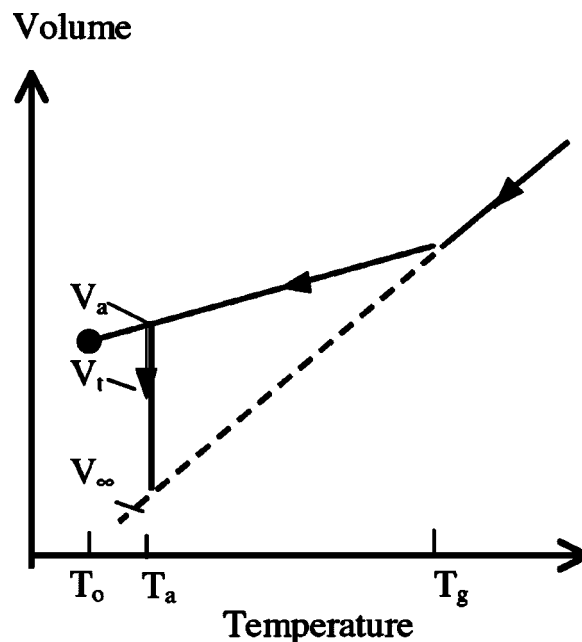


FIG. 1. Schematic illustration of the volume relaxation of a glass at an annealing temperature of T_a [3]. Over a sufficiently long time, its volume will decrease from V_a to V_∞ , which is the volume of the supercooled liquid at T_a .

eral homopolymers [3], including poly(methyl methacrylate) (PMMA) [6], in which $\beta \approx 4 \times 10^{-4}$ when annealed at $T_a = 333$ K after quenching from the melt at 393 K.

Polymer glasses in the form of thin films have numerous technological applications and also constitute ideal systems for fundamental studies of confinement effects in metastable soft matter. The relaxation of volume (or thickness) in thin films of polymer glasses has been observed by several workers [7–12] in neat polymers [7,8] and in polymers containing residual solvent [9–13]. In these previous experiments, measurements of thickness have been made as a function of increasing temperature, and it was observed that the change in thickness (volume) due to relaxation occurs simultaneously with a change resulting from thermal expansivity. Studies of isothermal relaxation in polymer thin films are much more rare [9,10,12]. The possible effects of molecular confinement and attraction to interfaces on the dynamics of relaxation in polymer thin films are largely unexplored.

Thin films are usually deposited by spin casting from a dilute solution in a volatile solvent. During this deposition process, solvent evaporates, and the T_g of the solution increases until it reaches the ambient temperature, at which point the solution vitrifies [14,15]. In a direct analogy to vitrification by reducing the temperature of a polymer melt (i.e., via a thermal quench), the vitrification of a polymer solution occurs by reducing the concentration of the solvent (i.e., via a “solvent quench”). The solvent volume fraction ϕ_{sol} when the T_g of the solution is at the temperature of the solution during casting, designated herein as ϕ_g , can be estimated via an equation derived from free volume arguments [16]. For a PMMA solution in toluene at room temperature (295 K), ϕ_g is estimated to be 0.19, taking the T_g of toluene to be 117 K [17].

It has been argued that when $\phi_{\text{sol}} < \phi_g$, the rate of solvent loss should be considerably slowed down, because to lose further solvent would require either the compression of the glassy matrix or the introduction of voids, both of which have an energetic cost [14]. Specifically, the energy required to compress the glass, E , is proportional to the compressive modulus of the glass, K , as $E \sim K(\phi_g - \phi_{\text{sol}})^2$ [14]. Several authors [11,14,15] have commented that polymer glasses obtained via a solvent quench will undergo a substantial volume change. At the point of vitrification, $\delta \sim \phi_g$. Hence, after a solvent quench of a polymer solution, δ can be much higher than after a thermal quench, in which δ is typically 0.01. If a polymer glass is constrained in one or more dimensions, significant mechanical stress could be generated [10,11,14,15].

Studying the relaxation behaviour in unannealed, spin-cast films is potentially very useful because it may help to explain a number of phenomena such as dewetting [10] and stress relaxation [18]. In our previous experiments [9,10], solvent-cast, glassy polymer thin films have been found to undergo slow relaxation with a reduction in thickness and a corresponding release of solvent. The rate of relaxation is expected to be influenced by the polymer segmental mobility [3]. Hence, measurements of relaxation in spin-cast thin films provide a means of probing molecular mobility in confined systems.

One aim of the present work is to measure β and δ for spin-cast glassy polymer thin films. As these two parameters

are characteristic of molecular mobility, their measurement can then be used as a probe at the molecular level in confined systems. Because data are available for the relaxation of bulk PMMA, it makes an ideal model system. The structural relaxation in thin films is conveniently measured *in situ* using spectroscopic ellipsometry at several wavelengths [9]. The experiments that are described here explore the possible effects of film thickness, interactions with the substrate, and molecular entanglement on the measured parameters β and δ .

II. EXPERIMENTAL PROCEDURE

PMMA (Polymer Laboratories, Church Stretton, U.K.) of several different molecular weights M_w was used: 8.0×10^4 g mol⁻¹ (polydispersity index of $M_w/M_n=1.02$); 1.42×10^5 g mol⁻¹ ($M_w/M_n=1.02$); 7.72×10^5 g mol⁻¹ ($M_w/M_n=1.02$); 1.25×10^6 g mol⁻¹ ($M_w/M_n=1.07$). According to the suppliers, the PMMA was 80% syndiotactic, 16.5% isotactic, and 3.5% atactic. The T_g for the $M_w=1.42 \times 10^5$ g mol⁻¹ polymer was determined by differential scanning calorimetry to be 382 K. Polymer films were spin cast from dilute solutions in AnalaR grade toluene onto (100) silicon wafers. In an effort to study film relaxation at the earliest stages of spin casting, the spin time was set to only 3 s. The films were spin cast at spinning rates between 1900 and 4000 revolutions per minute (rpm), with 2000 rpm being used for most experiments. The film thicknesses were varied by adjusting the polymer volume fraction ϕ_{pol} in the polymer solution between 0.003 and 0.065.

In most experiments, the polished silicon substrates were used as received; the native oxide was intact, and the substrate is referred to here as SiO₂/Si. In some experiments, the surface of the silicon was modified by grafting octyl trichlorosilane onto the native oxide of silicon using standard techniques described elsewhere [19]. This substrate is referred to as C8. In other experiments, a thin film of gold (200 nm thick) was thermally evaporated onto glass slides prior to the PMMA film deposition.

Film thickness as a function of time was determined using a rotating analyzer spectroscopic ellipsometer (J. A. Woollam Co., Inc., Lincoln, NE). To control the temperature, substrates were mounted on a heating stage (Linkam, Tadworth, U.K.) placed in the ellipsometer beam. To measure the fast changes in film thickness immediately after spin casting, ellipsometry parameters (ψ and Δ) were acquired at four different wavelengths as a function of time at intervals of about 20 s. (The use of four wavelengths enables more reliable thickness and index measurements in comparison to data collection at a single wavelength.) When the rate of change of film thickness was slower, spectroscopic scans over the wavelength range from 400 to 800 nm were obtained at regular time intervals, allowing both h and refractive index to be obtained with confidence [9]. In modeling the data, the refractive index dispersion was described by a Cauchy equation [20]. The film thickness h was obtained from the best fit to a model using a Marquardt algorithm [21]. In a one-dimensional analogy to V_∞ , an equilibrium thickness h_∞ was defined as the film thickness that was obtained after heating

the film on the hot stage to a temperature of 423 K (well above T_g) for 10 min and cooling slowly to 298 K at a rate of 2 K min^{-1} . For a thin film, δ is then defined in this work as

$$\delta = (h_t - h_\infty)/h_\infty. \quad (3)$$

In these measurements, the light beam probed the same area of a film when measuring h_t and h_∞ . This methodology ensured that errors were not introduced by any lateral non-uniformity of film thickness. In some preliminary experiments, some films were heated a second time to 423 K for 10 min and then cooled again. It was found that the same or highly similar values of h_∞ (within 0.1% in all cases) were obtained. That is, all of the measured thickness decrease occurred within 10 min of reaching the annealing temperature (423 K); a longer heat treatment did not cause further relaxation. The result was found to be the same for films ranging in thickness from 39 to 640 nm. This finding gave us confidence in referring to the thickness after annealing as h_∞ .

Some experiments to determine β were carried out at room temperature, but because the relaxation was so slow, it took four or more days before h_t approached h_∞ . Most measurements were therefore performed at 328 K. In these experiments, the film was placed on the heating stage immediately after spin casting and heated to 328 K at a rate of 50 K min^{-1} . Data collection was commenced as soon as the experimental temperature was reached. The film was then maintained at the temperature over a period of about 20 h, until the film thickness approached its equilibrium value. After each relaxation experiment was complete, the film was annealed *in situ* at 423 K for 10 min and then cooled slowly to 328 K at a rate of 2 K min^{-1} . A further spectroscopic scan was carried out to determine h_∞ at 328 K.

A special procedure was carried out to obtain an accurate value for the initial thickness, i.e., immediately after spin casting. Dynamic scans were made for 10 min and then followed by a single spectroscopic scan. The Cauchy constants determined from the best fit of the data from the spectroscopic scan were then used to fit the dynamic data. Preliminary experiments justified the modeling of the dynamic data by fixing the value of the Cauchy constants. The refractive indices of toluene and PMMA are very similar. As solvent is lost from the film and the glassy matrix decreases in thickness, independent measurements found that the change in refractive index was negligible because of the index matching. To allow for the variable time lag between initiating the ellipsometry scan and collecting the first data point, the thickness obtained at 2 min after starting the ellipsometer was arbitrarily taken to be the initial thickness h_0 . Using this value of h_0 , the initial departure from equilibrium, δ_0 , could be calculated.

III. RESULTS AND DISCUSSION

A. Relaxation in glassy thin films

An example of a typical dynamic ellipsometry scan is presented in Fig. 2. The ellipsometry parameters ψ and Δ obtained from a PMMA film spin cast from toluene are plot-

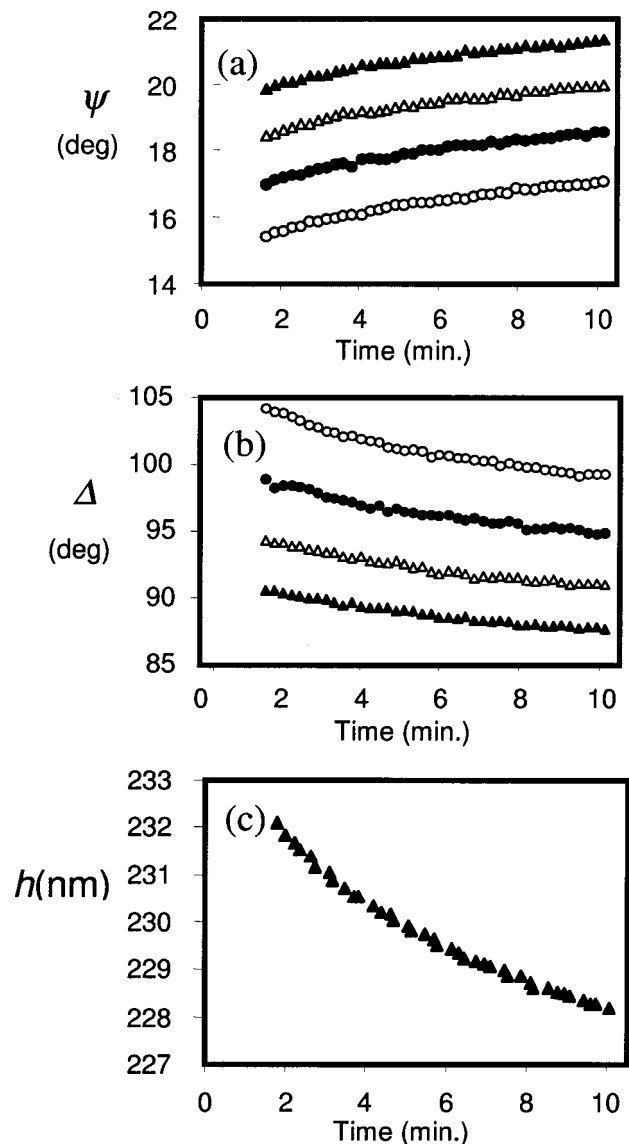


FIG. 2. The evolution of (a) ψ over time and (b) Δ over time for a freshly cast PMMA film ($M_w=142\,000$) deposited on Si from toluene at room temperature (RT), shown at four different wavelengths: 600 nm (unfilled circles); 610 nm (filled circles); 620 nm (unfilled triangles); 630 nm (filled triangles). (c) Corresponding best-fit thickness as a function of time after starting the scan.

ted for the first 10 min after casting (unless stated otherwise, $M_w=1.42 \times 10^5 \text{ g mol}^{-1}$). The standard deviations on ψ and Δ are typically 0.05 and 0.5° , respectively, and so the changes in the parameters are easily resolved in this measurement. Greater confidence in the thickness values is achieved by acquiring measurements at four different wavelengths of light rather than just one. The corresponding best-fit film thickness, which is also shown in the same figure, decreases by 4 nm to a thickness of 228 nm. This decrease in thickness is much greater than the precision of the measurement (about 0.2 nm).

The thicknesses of spin-cast PMMA films were found to continue decreasing over several days. The spectroscopic data in Fig. 3, obtained from the same film on three different occasions, reveal how this thickness decrease can be readily

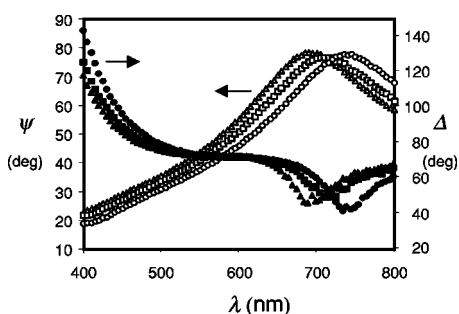


FIG. 3. Ellipsometry spectra showing ψ (unfilled symbols) and Δ (filled symbols) for a PMMA film on Si at RT: 1 h after spin casting (circles); 4 days after spin casting (squares); and after annealing at 423 K for 10 min and cooling at 2 K min^{-1} to RT (triangles). The angle of incidence was 72°.

resolved. An analysis of these and intermediate spectra, using the Cauchy model for the PMMA refractive index, is presented in Fig. 4. It is seen that this particular film was 165.5 nm thick after casting and decreased in thickness to 154.0 nm after four days at room temperature (295 K). Despite this significant decrease in thickness, the film decreased even further to h_{∞} =153.2 nm after heating at 423 K for 10 min and then cooling to room temperature. Using this value of h_{∞} , the measurements of h were converted to δ . The resulting values are presented in the inset of Fig. 4 as a function of the logarithm of the aging time, which is the conventional way of presenting relaxation data [3]. It is seen that δ decreases from an initial value of $\delta_0 \approx 0.10$. At a higher temperature of 328 K, a film with a similar thickness relaxes by the same amount but at a faster rate in comparison to the room temperature measurement, as also shown in the inset of Fig. 4. This result is consistent with experiments on bulk systems [3] in which the maximum value of β is obtained when the annealing temperature is approximately $T_g - 50$ K. An annealing temperature of 328 K for a PMMA film is equivalent to $T_g - 54$ K.

It was not known with certainty whether the large value observed for δ was a general characteristic of PMMA in the

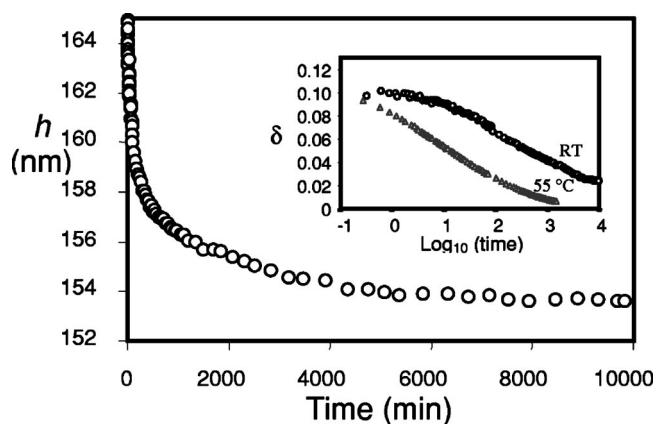


FIG. 4. The continuous decrease in h over time at RT after spin casting for a 150 nm PMMA film. Inset: h as a function of $\log_{10}(\text{time})$ for the same film at RT and compared to a 150 nm film at 328 K. In all plots the number of data points has been reduced for clarity.

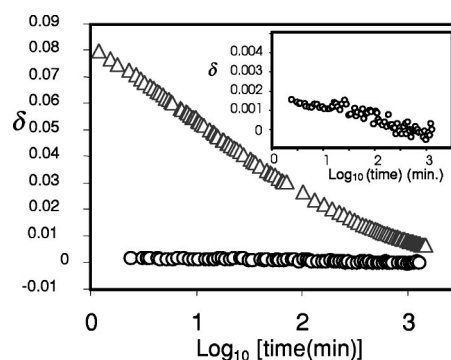


FIG. 5. δ versus the logarithm of time at 328 K for a 150 nm PMMA film (triangles) compared to a 130 nm PMMA film which has been annealed and quenched (circles). The number of data points has been reduced for clarity. Inset: data for annealed and quenched sample plotted on an expanded scale.

form of a thin film or if it is characteristic of the solvent quench during spin casting. A comparison was therefore made between the results for the film shown in Fig. 4 and a film of similar thickness that was quenched from the melt. To prepare a thermally quenched sample, a spin-cast PMMA film was equilibrated on the hot stage at 423 K (well above its T_g) and then quenched by immersion in liquid nitrogen. The comparison of the data is shown in Fig. 5. The thermally quenched film was found to decrease in thickness slowly over time, but the value of δ was much lower in comparison to the solvent-quenched film, with $\delta_0 \approx 0.002$.

From the data in Fig. 5, the relaxation rate β at 328 K for the freshly cast film was calculated to be 2.5×10^{-2} , whereas for the thermally quenched film $\beta = 7.0 \times 10^{-4}$. Solvent quenching results in a relaxation rate that is at least two orders of magnitude greater than what is obtained with thermal quenching. The β value for the thermally quenched thin film is comparable to what has been found elsewhere [6] for bulk samples of thermally quenched PMMA at a similar temperature (333 K), where $\beta = 4 \times 10^{-4}$. Thus it is seen that β for glassy PMMA in a thin film is on the same order of magnitude as in the bulk.

The data in Fig. 5 clearly illustrate that β for a solvent-quenched polymer film is significant, but little is known about what affects β in such systems. Further experiments were therefore conducted to explore the extent to which β in a solvent-quenched film is influenced by the film thickness. Figure 6 compares relaxation data obtained at 328 K from spin-cast PMMA films with three different equilibrium thicknesses: $h_{\infty} = 35, 69, \text{ and } 138$ nm. β was calculated from the initial linear regions of the data, as shown in the figure by the straight lines. The results reveal that β increases with increasing film thickness; β is twice as great in the 138 nm film in comparison to the 35 nm film. But even in the case of the 35 nm solvent-quenched film, β is one order of magnitude higher than in the thermally quenched film.

An obvious explanation for this trend is that the thicker films are observed to have a higher δ_0 . Further experiments on spin-cast films over a wider range of thicknesses going from 30 to 300 nm were conducted, and this trend was supported. As δ_0 increases, β likewise increases, as shown in

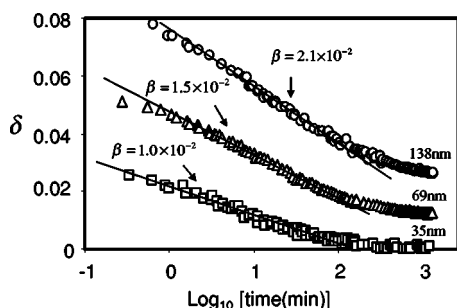


FIG. 6. Relaxation behavior at 296 K for spin-cast PMMA films of different thicknesses: 138 nm (circles); 69 nm (triangles); 35 nm (squares).

Fig. 7. This behavior was predicted by Kovacs [5] who presented a relationship in which δ_0 is proportional, to a first approximation, to β through a constant. This relationship was verified experimentally in bulk samples of poly(vinyl acetate) [5]. Physically, this correlation means that a glass that is further away from its equilibrium volume will relax faster. Hence, in order to understand the observed thickness dependence of β , it is necessary to explain why δ_0 increases with increasing thickness.

B. Thickness dependence of δ_0

The dependence of δ_0 , and hence the structure of the polymer glass, on film thickness is an intriguing result. Further experiments were conducted to understand this phenomenon. One possible explanation could be that the polar methacrylate groups of PMMA are attracted to the native oxide surface of silicon. As a result of this attraction, a denser layer might then be formed along the substrate during the film deposition. Thinner films would have a greater average density, and they would therefore show a smaller fractional decrease in thickness. This hypothesis was tested through the use of two other substrates (Au/Si and C8/Si) that are less attractive to PMMA.

Figure 8 compares measurements of δ_0 at room temperature for spin-cast film on three different types of substrate: Si with a native oxide (SiO₂/Si), C8/Si, and Au/Si. Regardless of the substrate, δ_0 increases with h_∞ in an identical way. The amount of structural relaxation during and after spin casting,

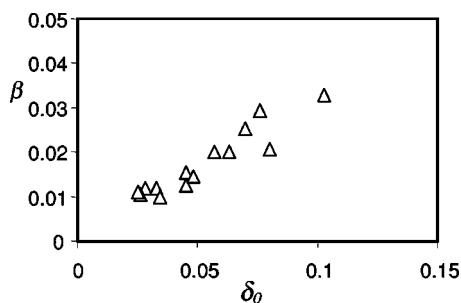


FIG. 7. The dependence of β on δ_0 for PMMA films spin cast on Si substrates. The thicknesses of the films vary from 35 to about 200 nm.

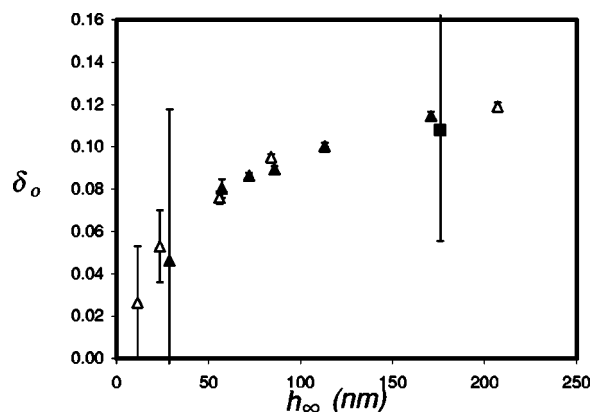


FIG. 8. The thickness dependence of δ_0 for spin-cast PMMA films on three different substrates: SiO₂/Si (unfilled triangles); C8-Si (filled triangles); and Au (filled square). On the Au substrate, there is greater uncertainty in the thickness measurements, resulting in a larger error bar in the plot.

as gauged by δ_0 , is not affected by interactions between the polymer and the substrate.

In previous work, Fernandez *et al.* [13] measured the thicknesses of PMMA films (spin cast from cyclohexanone or *para*-xylene) before and after annealing at 393 K. They likewise observed a thickness decrease upon annealing. Although the number of films studied was limited to seven, there is some evidence for a thickness dependence of δ_0 . For a film with $h_\infty=156.8$ nm, their results are consistent with $\delta_0=0.123$, whereas when $h_\infty=40.0$ nm, $\delta_0=0.048$. These findings are broadly in line with the present results.

The thicknesses of the films in Fig. 8 were adjusted by varying the concentration of the solution used for spin casting. It has been found recently that when glassy polymers are precipitated from dilute solutions, below the polymer overlap volume fraction ϕ^* , their T_g is reduced below the bulk value [22,23]. This result was attributed to a lower extent of entanglement in the polymers obtained from dilute solution. The concept that reduced entanglement density is responsible for a reduction in T_g is not supported by the work of other authors [24,25], however. Nevertheless, it has been pointed out that since the polymer molecules fill all available space, when they are not entangled their conformation will be compacted from a random coil to a smaller, tighter coil [22]. Hence, less entangled PMMA molecules should be more compact and perhaps better able to pack into a dense film during the deposition process. A simple scaling argument [26] predicts that ϕ^* varies with the degree of polymerization N as given by $\phi^* = \nu a^{-3} N^{-4/5}$. Here, ν is the volume of the repeat unit ($\nu=0.147$ nm³ for PMMA), and a is the effective length per repeat unit (reported as 0.65 nm for PMMA [27]). Thus, for $M_w=1.42 \times 10^5$ g mol⁻¹, the prediction is $\phi^* = 1.61 \times 10^{-3}$. Experimentally, it was found that to spin-cast a film thicker than 10 nm, however, ϕ_{pol} must be greater than 3×10^{-3} . Hence, in our experiments, $\phi_{\text{pol}} > \phi^*$, and there is always some molecular overlap in the solutions used for spin-casting PMMA with this N . Thicker films will require solutions that are well within the overlap region.

The thickness of a spin-cast film, h , is predicted [28] to vary as $(1+k/\eta)^{-0.5}$, where k is a constant that depends on

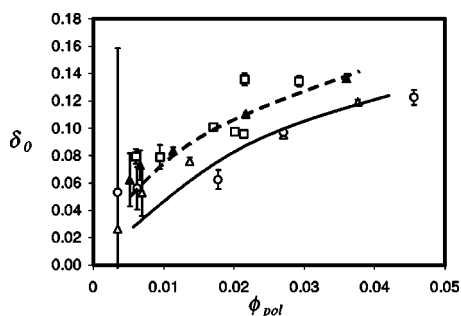


FIG. 9. The variation in δ_0 with the solvent volume fraction (ϕ_{vol}) used in the solutions for spin-casting PMMA films on Si substrates using four different PMMA molecular weights: 8.0×10^4 (circles); 1.42×10^5 (triangles); 7.7×10^5 (filled triangles); 1.25×10^6 (squares) g mol^{-1} . The dashed and solid lines are guides for the eye for the 1.42×10^5 g and the 7.7×10^5 g mol^{-1} data, respectively.

the square of the angular velocity of the spinning and η is the viscosity of the solution (which changes over time). In dilute solutions of a polymer in a solvent with a viscosity of η_{solv} , η will increase with the volume fraction V_f occupied by isolated polymer coils as $\eta = \eta_{\text{solv}}(1 + 2.5V_f)$. In turn, V_f is a function of the number density of molecules ($\sim N^{-1}$) and their volume, which scales with the radius of gyration, and hence scales with N as $(N^{3/5})^3$ [26]. Thus, in the dilute limit, when entanglement effects can be neglected, h has this dependence on ϕ_{pol} and N :

$$h \sim (1 + k/\phi_{\text{pol}}N^{4/5})^{1/2}, \quad (4)$$

indicating that—as is commonly observed in the laboratory—a film of a given thickness h can be cast from a more dilute solution of a high- N polymer or from a more concentrated solution of a low- N polymer. To explore the possible effect of molecular overlap and entanglements, δ_0 was determined for spin-cast films of PMMA with four different N . In these experiments, films of approximately the same thickness were deposited from solutions of different concentration. The experiments are thus designed to separate out the effects of entanglement from true thickness effects.

Data obtained from PMMA of four different molecular weights are shown in Fig. 9. There is a clear trend in which δ_0 increases with increasing ϕ_{pol} for all four N . Although there is some scatter in the data, a second general trend is observed. For a particular range of ϕ_{pol} , a higher N tends to yield a higher δ_0 . In turn, higher N values for a particular ϕ_{pol} result in thicker films, indicating that a thickness dependence is observed in the data. To demonstrate this dependence, the data from Fig. 8 and 9 are replotted in Fig. 10. All of the δ_0 values are seen to follow an identical dependence on film thickness, regardless of the combination of ϕ_{pol} and N .

Although δ_0 is seen to vary with both ϕ_{pol} and h_∞ , the dependence on h_∞ is the dominant factor. The data in Table I illustrate this point for PMMA films cast from low N ($M_w = 8.0 \times 10^4$ g mol^{-1}) and high N ($M_w = 1.25 \times 10^6$ g mol^{-1}) solutions. It is seen that δ_0 is insensitive to changes in ϕ_{pol} when h_∞ is fixed. For instance, films *A* and *B* have quite

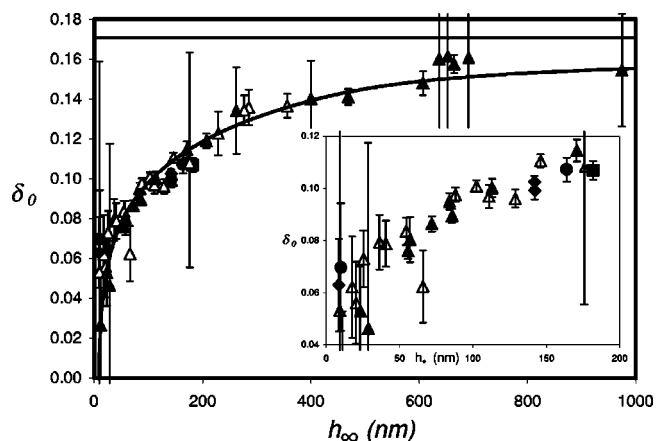


FIG. 10. A summary of the thickness dependence of δ_0 observed for spin-cast PMMA films using a variety of spin speeds, solution concentrations, molecular weights, and substrates: $M_w = 1.42 \times 10^5$ g mol^{-1} , 1900 rpm (filled squares), 2000 rpm (filled triangles), 3000 rpm (filled circles), 4000 rpm (diamonds); other M_w at 2000 rpm (unfilled triangles). The solid line is a guide for the eye. The inset shows the data for thinner films.

different ϕ_{pol} (0.050 and 0.029) but comparable h_∞ (262 and 276 nm). The δ_0 values are identical for *A* and *B* (0.134), indicating that they are not influenced by the difference in ϕ_{pol} . A similar observation can be made when comparing film *C* (111 nm thick) and film *D* (102 nm thick), which have very different ϕ_{pol} but comparable values of δ_0 (0.097 and 0.101). On the other hand, δ_0 is sensitive to changes in h_∞ when ϕ_{pol} is fixed. Films *B* and *C* have nearly the same ϕ_{pol} (0.029 and 0.027) yet very different δ_0 (0.134 and 0.097) and dissimilar h_∞ . Likewise, films *D* and *E* have nearly the same ϕ_{pol} (0.017 and 0.018) yet very different δ_0 (0.101 and 0.062). It is apparent that δ_0 increases when h_∞ increases, even when ϕ_{pol} stays roughly constant.

Nevertheless, entanglement effects cannot be ruled out by the data. To deposit thin films of sufficient thickness, ϕ_{pol} is required to be greater than ϕ^* in all cases (such as illustrated by values listed in Table I). For a given ϕ_{pol} , however, solutions with a higher N are farther from ϕ^* compared to solutions with a lower N . Hence, the lower δ_0 values that are observed for film *C* in comparison to *B*, and also in *E* in comparison to *D*, could be related to the fact that the solutions for *E* and *C* are closer to ϕ^* , and hence the molecules are less overlapped in comparison to the more concentrated solutions.

Further experiments were conducted to determine the reasons for the variation in δ_0 . For a fixed N and ϕ , the thick-

TABLE I. Influence of polymer concentration and film thickness on volume relaxation in spin-cast PMMA thin films.

Film	M_w (g mol^{-1})	h_∞ (nm)	δ_0	ϕ_{pol}	ϕ^*
<i>A</i>	8.0×10^4	262	0.134	0.050	2.6×10^{-3}
<i>B</i>	1.2×10^6	276	0.134	0.029	2.9×10^{-4}
<i>C</i>	8.0×10^4	111	0.097	0.027	2.6×10^{-3}
<i>D</i>	1.2×10^6	102	0.101	0.017	2.9×10^{-4}
<i>E</i>	8.0×10^4	66	0.062	0.018	2.6×10^{-3}

ness of a thin film can also be varied through the rotational velocity of spin casting. Whereas the data presented in Figs. 8 and 9 were obtained from films deposited at 2000 rpm, some of the films in Fig. 10 were deposited at 1900, 3000, or 4000 rpm. Consequently, any dependence on thickness can be attributed neither to differences in ϕ_{pol} nor to entanglement effects. The decrease in h when increasing the speed from 2000 to 4000 rpm is relatively small, but nevertheless there is an observable corresponding decrease in δ_0 that is consistent with the previous findings obtained at varying ϕ_{pol} . This result provides further evidence for a true thickness effect on the value of δ_0 .

Further insight can be obtained from Fig. 10 through the examination of δ_0 in the limits of $h \rightarrow 0$ and $h \rightarrow \infty$ (bulk). In the limit of very thin films, δ_0 approaches zero. Physically, this result makes sense, because it means that films that must consist of a single, flattened layer of molecules will be unable to decrease in thickness after annealing. In an ultrathin film, molecules cannot relax to a flatter conformation. In the limit of thick films, δ_0 is seen to approach a plateau value of 0.16. At the point of vitrification, $\phi_g \approx 0.19$. The loss of this volume fraction of solvent, without the introduction of voids, would yield a fractional volume change of 0.19, which is just slightly higher than what is found for δ_0 in the limit of thicker films. We suggest that the initial conformational state of the films in the thick-film limit corresponds to that at ϕ_g , where the film vitrifies. In a thick film, interfaces will have a diminished influence, and so the state of the film is identical to that at the point of vitrification. This result suggests that thick films display bulk behavior as a result of a diminished influence of interfaces.

Our results are consistent with measurements of density profiles in PMMA thin films, using neutron and x-ray reflectivity and reported elsewhere [29,30]. The density near the interface with the substrate was greater than near the interface with air. A denser structure would be expected to undergo a lesser amount of relaxation. A larger proportion of the molecules in a thinner film are near the substrate, which could provide an explanation for their lower δ_0 values. Our results indicate, however, that any interface effect is insensitive to the composition of the substrate.

During spin casting, a dilute solution is transformed very quickly to a glass. Molecules that are expanded from a random coil conformation in a good solvent are presumed to entangle with others and collapse to a random coil. This transformation requires molecular mobility, and it will cease when mobility is lost at the point of vitrification. A liquidlike layer with enhanced molecular mobility near a film surface, as has been proven conclusively to exist in neat, glassy homopolymer films [31,32], could conceivably result in an enhanced rate of this transformation. The lower δ_0 obtained in thin films could indicate that this transformation goes further to completion prior to vitrification. Alternatively, in thin films there might be some very fast relaxation after vitrification, which takes place prior to the measurement of δ_0 . The thinner films are therefore closer to their equilibrium thickness at the time of the measurement. In any case, these results provide clear evidence for greater stability of film thickness in thinner spin-cast films.

Recent experiments by Grohens *et al.* [33] have found that the T_g of equilibrated syndiotactic PMMA thin films

decreases as the thickness decreases. A decreased T_g in thinner films in our experiments would lead to a decreased value of ϕ_g , which would then presumably result in a decreased δ_0 . As an example, if the T_g of PMMA in the thinnest film is depressed by 30 K from the bulk value (as found by Grohens *et al.*), then it is predicted that ϕ_g decreases from 0.19 to 0.13. Thus, the observed decrease in δ_0 of 0.135 (from 0.161 to 0.026) is even greater than what is predicted from the previous data on $T_g(h)$. Our observations cannot be explained by the effects of $T_g(h)$ alone, although they might play a part.

Grohens *et al.* also reported that the T_g of the PMMA thin films was a strong function of the tacticity and the type of solvent used in film deposition [33]. It was argued that molecular conformations in the solution persisted in the solid films. In the present work, these factors were not explored. Toluene and syndiotactic PMMA were used in all experiments. We point out, however, that the T_g of solvents can span a wide range of values, and hence the value of ϕ_g for a given polymer will vary with the solvent used in the solution. If the argument that δ_0 in the thick-film limit approaches ϕ_g is correct, then one would expect that δ_0 would depend on the solvent in a predictable way. Further work is under way in our laboratory to test this hypothesis.

Our analysis of the ellipsometry data did not consider any gradient in the refractive index (or density) with depth into the film. However, previous studies of spin-cast PMMA films using neutron reflectivity have found that the density of polymer changes with depth into the surface. There are conflicting findings, however, as to whether the denser layer is at the air surface [13] or near the substrate [29] and whether thinner films are more dense [13] or less dense [29] than thicker films. Likewise, there are some theoretical predictions [34] of nonuniformity in solvent concentration in spin-cast films that depend on the conditions of spin casting. The presence of such small variations in refractive index, however, is not expected to alter significantly the values of δ_0 that are obtained in our experiments. In our experiments, an average refractive index for each film was fitted to the data.

IV. CONCLUDING REMARKS

In summary, the magnitude of the structural relaxation in spin-cast films of PMMA, as measured through δ_0 , has been found to depend strongly on the film thickness. In very thin films ($h_\infty < 20$ nm), δ_0 was found to be less than 0.06. The film thickness is relatively stable, and it decreases only slightly after annealing above T_g . In thicker films (> 500 nm), δ_0 reaches a plateau value of 0.16. When a PMMA solution in toluene at a temperature of 295 K passes through the glass transition, ϕ_{sol} will be 0.19. Thus, the observed change in thickness is close to the change expected for the loss of the toluene.

Film thickness was adjusted through ϕ_{pol} , PMMA molecular weight, and the rotational velocity during spin casting. Regardless of how the thickness was adjusted, the thickness dependence of δ_0 was the same. In all cases, the solutions used for spin casting were above the overlap concentration. Thicker films are cast from more concentrated

solutions, however, and one might speculate that this factor plays a role in determining δ_0 . However, the experiments show that δ_0 depends much more strongly on film thickness than on ϕ_{pol} . One explanation for the results is that there is enhanced mobility near the film surface, and during the earliest stages of film deposition the molecules are able to relax to a greater extent.

The same dependence of β and δ_0 on film thickness, although weaker, has likewise been observed in our laboratory in poly(styrene) and in poly(butyl methacrylate), and hence it appears to be a general phenomenon and not specific to PMMA. The fact that the magnitude of δ_0 is found to vary between polymers of different composition gives us confidence that the thickness dependence is real and cannot be attributed to errors in the thickness measurements. This re-

sult has implications for applications that use glassy polymer thin films. The data reveal that thinner films will be more stable and undergo less relaxation in comparison to thicker films. When polymer films are used for lithography and optical coatings, dimensional stability is highly important

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