Unusual Expansion and Contraction in Ultrathin Glassy Polycarbonate Films

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ABSTRACT: The thermal expansion behavior of thin polycarbonate (PC) films supported on hydrophilic and hydrophobic silicon substrates is studied with specular X-ray reflectivity. These measurements suggest a suppression of the apparent glass transition temperature ($T_g$) with decreasing film thickness on hydrophilic silicon oxide substrates, while no evidence for an $h$-dependent $T_g$ shift is observed on hydrophobic passivated silicon substrates. More interestingly, we find that when $h$ is comparable to the bulk radius of gyration, the expansion becomes nonmonotonic with temperature $T$ in a reversible manner. Cooling one of these ultrathin PC films well below the apparent $T_g$ gives rise to an apparently negative coefficient of thermal expansion (CTE). This unusual behavior stems from the fact that nominally $R_g$-thick glassy films exhibit an appreciable isothermal thickening over extended periods of time, with the propensity for this thickening increasing with the depth of cooling into the glassy state; normal thermal contraction upon cooling becomes convoluted with the sub-$T_g$ thickening phenomenon. This is counterintuitive since deep in the glassy state the molecular mobility is anticipated to be small. The magnitude and rate of the isothermal thickening depend on the ratio of the macromolecular size to the film thickness, suggesting that chain distortion by the film boundaries is associated with this effect. The surface energy of the supporting substrate also influences these unusual behaviors.

Introduction

Nanotechnology demands that materials be utilized at increasingly smaller length scales. For polymers this can be problematic since it is generally understood that material properties in confined geometries and at surfaces or interfaces can deviate from their bulk values. For example, in thin polymer films there are well-documented shifts of the glass transition temperature ($T_g$) as the film thickness approaches the unperturbed dimensions of the macromolecule in bulk. Finite size effects could be of significant impact in fields such as lithography, where crucial properties such as acid diffusivity in a chemically amplified photoresist or polymer viscosity in imprint lithography typically display dramatic changes at $T_g$. Unexpected deviations in various physical properties at increasingly smaller dimensions may very well impede advances in polymer-based nanotechnology.

$T_g$ shifts as a function of thickness are commonly studied in polymer films. Thin film $T_g$'s are normally inferred from changes in a thermodynamic property (i.e., specific heat, thermal expansion, etc.) probed under nonequilibrium conditions. A time scale is always implicit, depending upon the rate at which the property is probed (i.e., heating rate) and the characteristic frequency of the technique. One classic attribute of polymer glasses is a marked thermal history dependence of the physical properties, examples of which include the physical aging and stress relaxation phenomena. However, in the thin polymer film literature these long-term effects have been to a large extent ignored. This is disturbing since there are strong indications that the time scales over which a polymer film equilibrates could be quite different in comparison to the bulk. For example, surface forces apparatus measurements on confined liquid films (both polymer and small molecule) demonstrate that viscoelastic time scales in the bulk and molecularly confined films are not the same. Surface forces measurements are primarily limited to the liquid state, but it is reasonable to anticipate an extension of this behavior into the glass.

In the present paper, we focus on the long-term stability of thin polymer films where the thickness $h$ is comparable to or less than the unperturbed radius of gyration. At these length scales the film thickness should be small enough to induce an in-plane molecular orientation that would seemingly be susceptible to relaxation phenomena. Before discussing our results, it is helpful to briefly summarize preceding relevant observations. Some time ago Reiter annealed thin films of polystyrene (PS) at temperatures ($T$) below $T_g$ and found that the films appreciably thickened with time. At the same time, Orts et al. made the controversial observation that similar sub-$R_g$-thick PS films supported on a silicon (Si) wafer would contract upon heating, prior to dewetting at elevated $T$. Tolan repeated these X-ray reflectivity measurements, confirming the negative coefficient of thermal expansion (CTE) seen by Orts et al. More recently, Kanaya et al. confirmed this negative CTE via neutron reflectivity. Reiter investigated these phenomena further and proposed a sub-$T_g$ elastic dewetting model. In this model, a proliferation and growth of pinholes occurs (below $T_g$) due to the elastic stresses in the PS film. Conservation of mass dictates that as the pinholes grow in diameter with a concomitant thickening of the material between the holes. The rimless pinholes continue to grow (i.e., thickening the film) until the film becomes unstable and completely dewets the substrate.

We will demonstrate that certain parts of the original elastic dewetting mechanism in PS are not general and illustrate several important molecular considerations needed to fully comprehend this curious phenomenon. By studying thin polycarbonate (PC) films, we show that the isothermal thickening is not necessarily a precursor to dewetting. This is already in line with the observa-
tions of Tolan,\textsuperscript{7} who did not observe dewetting when using a higher molecular mass PS than Ort et al.\textsuperscript{6} Mukherjee and co-workers\textsuperscript{10} also find reversible negative CTEs in thin glassy films of both PS and polyacrylamide, just as we have seen similar behavior in thin poly(hydroxystyrene) (PHS) films.\textsuperscript{11} Beyond the similarities with Tolan,\textsuperscript{7} Mukherjee,\textsuperscript{10} and PHS,\textsuperscript{11} we illustrate that the isothermal thickening in PC is not the result of pinhole formation and growth, suggesting that the film density changes with isothermal aging. We also find a thermal history dependence on the negative CTE and isothermal thickening effects that has not yet been observed. Finally, we provide the first kinetic data for these effects and characterize the T, h, and molecular mass dependence of what appears to be a complicated thin film “relaxation” process.

**Experimental Section**

Casting solutions were prepared by dissolving PC into cyclohexanone at mass fractions ranging from 0.25% to 3.00%. In total, four different molecular masses of PC were studied: $M_w = 18 \text{ kg/mol}$, $M_r = 24 \text{ kg/mol}$, $M_w = 36 \text{ kg/mol}$, and $M_r = 64 \text{ kg/mol}$. The solutions were filtered through a 0.45 $\mu$m Teflon filter and spin-cast at 2000 rpm for 40 s onto Si wafers. Two different surface treatments were employed to create wafers with either a native oxide (hydrophilic) or hydrogen passivated (hydrophobic) surface. For the native oxide surfaces, the as-received wafers were etched in O$_2$ plasma for 10 min to remove residual organic contaminants. The original native oxide was then stripped through a 1 min immersion in HF acid (48.8–49.2% HF). After etching, a uniform oxide layer, 5–10 Å thick, was regrown on the clean wafer with a 5 min UV-ozone exposure. The PC solutions were then immediately spin-cast onto the hydrophilic wafer to avoid surface contamination. After spinning, excess solvent is removed from the film by holding the wafer at 200 °C for 12–24 h under a vacuum of 0.1 Pa.

The procedure for creating the hydrogen-passivated wafers was identical to the previous protocol up through the HF acid step. Immediately following the HF etch step, the wafers were immersed in an ammonium fluoride bath (39.0–41.0% NH$_4$F) for 1 min. This passivation temporarily preserves the hydrophobic nature of the oxide-free wafer. The PC solutions were immediately spun-coat onto the wafer and transferred to the high-vacuum chamber of the X-ray reflectometer for both thermal treatment and the ensuing measurements. It took no more than 10 min after creating the hydrophobic passivated surface to transfer the wafer to the vacuum chamber, thereby minimizing the possibility that a hydrophilic oxide could reform on the surface.

Specular X-ray reflectivity measurements are made on a modified diffractometer with Ni-filtered Cu K$_\alpha$ radiation and Soller slit collimation. With these optics coupled to a low-noise solid-state detector we routinely obtain reflectivity data out to a Q vector of 0.35 Å$^{-1}$. The reflectivity measurements are performed under a vacuum of approximately 10$^{-4}$–10$^{-5}$ Pa on a temperature stage that is stable to ±0.2 °C. Prior to collecting reflectivity data, the films first annealed under vacuum at 200 °C (equilibrated well above $T_g$) for 6–12 h to establish a well-defined initial thermal history. The subsequent data are collected on cooling to 20 °C in intervals of 10 °C, with 45 min allowed between steps for thermal equilibration. Each isothermal reflectivity curves require approximately 1 h to obtain, implying that the sample spends 1 h and 45 min at each temperature. Once the sample is cooled to 20 °C, the film is again held for 6–12 h (unless otherwise indicated), after which data are collected in a similar manner upon heating back to 200 °C. At each T, the film thickness is obtained by fitting the reflectivity curves with a nonlinear least-squares routine that uses a recursive multilayer method.\textsuperscript{12}

Atomic force microscopy (AFM) measurements are obtained at room temperature with a Digital Instruments Dimension

![Figure 1](image)

**Figure 1.** Thermal expansion is shown for PC films ranging from approximately 70 to 700 Å thick, supported on Si substrates with either the native oxide (filled triangles) or hydrogen passivated (open circles) surfaces. The expansion is presented in terms of a percent change of thickness (thermal strain), arbitrarily in reference to the film thickness at 180 °C. The curves have been offset vertically for clarity. For each set of films, a dotted line indicates bulklike expansion corrected for the lateral thin film constraints.\textsuperscript{13} The vertical dashed line indicates the position of the calorimetric $T_g$. Error bars, often smaller than the data symbols, indicate the uncertainty as described in the text.

The 3000 instrument operating in the tapping mode. The tapping amplitude is adjusted so as to produce a minimal response in the phase image. The topological information gained is then less dependent on phase information. Multiple scans over the same area are time independent, indicating a lack of surface damage due to interactions of the tip with the sample.

**Results and Discussion**

Figure 1 displays thermal expansion curves for a series of 36 kg/mol PC films supported both the native oxide and hydrogen passivated substrates. Each curve represents an average of two heating and cooling runs, or four data points per temperature. To facilitate comparison of the samples of different h, the expansion data are presented in terms of a percent change, arbitrarily taken in reference to the h at 180 °C. The curves are vertically offset for clarity of comparison. As a subset of four data points is insufficient to obtain a standard deviation, an alternative approach is employed to estimate the uncertainty. For each isothermal data point, the difference between each of the four individual thickness determinations and the average thickness is calculated. The error bars in Figure 1 (and all ensuing thermal expansion plots) indicate the average, taken over all h’s of this difference. Typically this type of uncertainty is ±0.25% or less in terms of an absolute percentage.

There are several features worth noting in Figure 1. First, all of the curves nominally show a marked change in slope in the general vicinity of the PC’s calorimetric glass transition temperature ($T_g = 150 \degree C$). Typically, this characteristic “kink” is identified with the apparent glass transition temperature of the polymer film.\textsuperscript{13} In comparing the two substrates, the apparent $T_g$’s of the films on the hydrogen passivated surface appear to be rather insensitive to h while a noticeable suppression with decreasing film thickness occurs on the native oxide. Previous works on thin polymer films suggest that $T_g$ depressions occur when the interactions with the substrate are unfavorable, while a $T_g$ increase occurs...
on more favorable substrate. This suggests that PC displays more favorable interactions with the hydrophobic or hydrogen passivated surface in comparison to the hydrophilic oxide. This notion is also borne out when comparing the rubbery state expansion for films of equal thickness. The rubbery state CTE is always smaller on the passivated surface. Attractive interactions may be more effective at "pinning" the polymer chains to the rigid substrate, thereby reducing expansion normal to the substrate.

The most striking feature in Figure 1 is an apparently negative CTE below the $T_g$-like kink in the thinnest film on the native oxide substrate, leading to an expansion upon cooling (EUC). For simplicity, the term EUC is used in reference to this effect, but it is understood that EUC also implies a contraction upon heating (EUC). We will illustrate below that this effect is reproducible but time-dependent. While not shown in Figure 1, the magnitude of the upturn (in terms of a percentage of the film thickness) increases as the films become increasingly thinner, with no upturn observed for films nominally thicker than 100 Å (for the 36 kg/mol PC). Note also that the EUC effect is not observed on the passivated substrate, suggesting that the interactions with the substrate are relevant. However, there are instances (specifically higher molecular mass PC) where the EUC can be observed on passivated Si, indicating that the process is very complicated.

To establish that the EUC effect is due to the confined nature of the macromolecule, we compare films of equal h but disparate molecular mass. Figure 2 shows the thermal expansion for 125 Å thick films of 36 kg/mol (bulk $R_g$ of approximately 60 Å) and 64 kg/mol (bulk $R_g$ of approximately 86 Å) PC on the oxide substrate. 125 Å corresponds to a film thickness of 2$R_g$ and 1.5$R_g$ for the low and high molecular mass analogues, respectively. Consistent with Figure 1, the apparent CTE remains positive for the 36 kg/mol film at $h = 2R_g$. However, nearly doubling the molecular mass of the PC increases the degree of macromolecular confinement relative to h, and the EUC effect becomes pronounced at $h = 1.5R_g$. The ratio of the macromolecular size to the film thickness is relevant for understanding this unusual phenomenon. More evidence to this effect is discussed later in the paper.

Attempts to study a 125 Å film of an 18 kg/mol PC on the oxide substrate were not possible. The lower molecular mass films were unstable and dewet within minutes of spin-casting. However, a 125 Å film of the 18 kg/mol PC on the passivated substrate was significantly more stable and did not readily dewet. These films show signs of dewetting only after multiple heating cycles. The smoothing of interference fringes (not shown here) measured in X-ray reflectivity at high $Q$ indicate that increased exposure to temperatures above $T_g$ results in increased film roughness, analogous to previous studies of polymer dewetting.

The enhanced stability of the low molecular mass thin film on the passivated surface in comparison with the oxide is consistent with our contention that the interactions between PC and hydrogen passivated Si are more favorable. However, we emphasize that dewetting was not observed in the 36 kg/mol and higher molecular mass films, regardless of the substrate. If any of the thermal histories described herein are repeated, the expansion/contraction curves are reproducible both well above and below $T_g$, only the 18 kg/mol PC showed irreversible signs of dewetting. It is plausible that the large viscosity in the higher molecular mass films makes dewetting kinetically unfeasible, even if the interactions with the substrate are unfavorable.

The EUC effect has a strong dependence on the thermal history of the film, as illustrated by the following. Figure 3 shows a series of expansion and contraction curves for an ultrathin film of the 36 kg/mol PC on the oxide substrate. The complicated thermal path starts with a long anneal at 200 °C, followed by a slow cool (with data collection) to 20 °C, an extended anneal at 20 °C, slow heating (with data collection) back to 200 °C, followed by a rapid cool (without data collection) to 20 °C again, and finally a slow heating (with data collection) back to 200 °C. When the expansion/contraction data are collected, the sample equilibrates at each $T$ for approximately 1 h, plus 1 h to collect the reflectivity data. This means that the cooling rate for the initial contraction curve (diamonds) is fairly slow. Note that upon this initial cooling the magnitude of the EUC is also moderate. After reaching 20 °C, the film is isothermally held for 12 h before heating back to 200 °C. When the thickness is measured the second time at 20 °C (asterisks), it is evident that the film isothermally thickened. Furthermore, the magnitude of the EUC effect (EUC implies a contraction upon heating here) is enhanced by the isothermal aging in comparison to the
initial slow cooling. It is only above the T_g-like kink that the heating data become comparable to the initial cooling. Once the film reaches 200 °C for the second time, it is then held for another 12 h before quenching back to 20 °C. The term quench is a relative term since it still takes 2 h for the sample chamber on the reflectometer to equilibrate at 20 °C. Nevertheless, this quench is considerably faster than the initial slow cooling rate. Once the film stabilizes at 20 °C, the expansion is measured immediately upon heating (circles). This time the EUC effect is less pronounced. Clearly there is a strong thermal history dependence for the EUC effect, and it is difficult for the films below the apparent T_g to establish a stable state. However, the sample thickness at 200 °C is reproducible between the runs; the film remains intact and does not dewet. It is important to distinguish between reproducibility and stability. The film is unstable in that the thickness slowly evolves in the glassy state. However, if the thermal history is repeated, the data are reproducible. In fact, the data in Figure 3 are an average of two cycles of the entire thermal sequence, with excellent agreement between the cycles.

As seen in Figures 1–3, the absolute magnitude of the EUC is small, corresponding to an increase in thickness of only a few angstroms. This raises valid concerns of whether the effect is an experimental artifact. The most obvious concern is whether the apparent expansion reflects an adsorption/absorption of residual moisture from inside vacuum chamber onto/into the film. Both of these effects would make it appear as if the film were “thickening”. This explanation is somewhat plausible in light of the observation that the effect is more pronounced on the hydrophilic Si substrate. To determine whether there is a propensity for water to accumulate at one of the interfaces, we performed neutron reflectivity measurements in the presence of D2O vapor to a partial pressure of 17 Torr. After 6 h at 200 °C under vacuum (10^{-3} Pa) the neutron reflectivity data were collected, still under vacuum. The time dependence of the EUC in Figure 3 is dramatic. It might also be argued that the EUC is the result of an adsorption or adsorption of other small molecules (other gases, residual casting solvent, vacuum pump oil, etc.) into or onto the sample surface at low T. This scenario was explored in a series of experiments where the partial pressure of the vacuum chamber was simultaneously monitored, using a residual gas analyzer, while the isothermal expansion occurred. While the data are not presented here, we report that the isothermal expansion did not coincide with a decrease in the partial pressure of the vacuum chamber on the reflectometer.

This further indicates that the isothermal expansion is not the result of small molecule adsorption or adsorption. It should also be emphasized that the adsorption mechanism is highly inconsistent with Figure 2 where the EUC occurs only in the high molecular mass films. Adsorption would equally affect the low and high molecular mass films given their equal thickness. Finally, although we do not show the data here, the vacuum chamber on an isothermally expanded film can be broken, and the thickness remains the same after exposure to the atmosphere. In fact, the sample can be cycled back and forth between atmosphere and vacuum without changes in thickness. These observations demonstrate a lack of correlation between the EUC and small molecule adsorption.

The time dependence of the EUC in Figure 3 is curious. To explore this remarkable phenomenon, Figure 5a displays a series of quench and anneal experiments. Here a 64 kg/mol oxide supported film, initially 38–43 Å thick (depending on the run), is annealed for 6 h at 200 °C under vacuum (10^{-5} Pa) on the reflectometer and quenched to 20, 35, or 50 °C. Initially there is a “rapid” isothermal expansion of the film that eventually slows down, appearing to approach saturation at long times to a value that increases decreasing T. This explains why the time-dependent EUC and apparent negative CTE are observed upon cooling in the glassy state. The normal thermodynamic contraction becomes convoluted with this time-dependent (kinetic) expansion deep in the glassy state. However, notice that the time scales for this apparent saturation are long, on the order of 250 h. Furthermore, the relative magnitudes of isothermal expansion are tremendous, reaching 16% for the 43 Å film at 20 °C. Given the magnitude and the time scales of these effects, it is prudent to
verify that film remain intact throughout this extraordinary isothermal expansion.

Figure 5b compares the reflectivity curves at a short (t = 14.5 h), intermediate (t = 158.7 h), and long (t = 327.8 h) time after the quench from 200 °C to 20 °C (+), 35 °C (x), or 50 °C (open diamonds). The solid lines through the data indicate fits to the exponential model indicated. The filled diamonds demonstrate an additional rapid expansion after the film held at 50 °C is quenched again to 20 °C. Part b shows several typical reflectivity curves as a function of the isothermal hold time, clearly indicating an increase in film thickness without an appreciable change in roughness. Part b plots the exponential time constants from the fits in part a in an Arrhenius format to extract an activation energy. Error bars, where indicated, denote the standard uncertainty, which is otherwise less than the size of the data markers.

Figure 5. Part a shows the percent expansion, H, of a 64 kg/mol PC films with an initial thickness on the order of 40 Å. The expansion occurs after the film is quenched from 200 °C to 20 °C (+), 35 °C (x), or 50 °C (open diamonds). The solid lines through the data indicate fits to the exponential model indicated. The filled diamonds demonstrate an additional rapid expansion after the film held at 50 °C is quenched again to 20 °C. Part a indicates the presence of the interference fringes at high Q remains strong. One possible explanation for the increase in film thickness with time is the elastic or “rimless” dewetting mechanism reported by Reiter,9 in this model, pinholes form in the film and grow in diameter. If volume is conserved, the film must thicken in response. Reiter correctly argues9 that if the average distance between the growing pinholes is greater than the coherence length of the reflectometer (estimated to be 10–100 nm for this reflectometer), there will be minimal change in the roughness as long as the regions between the holes remains smooth. To probe this effect, we performed analogous measurements on a higher resolution reflectometer where the coherence length is in the range 0.1–1 mm. These measurements did not reveal increased roughness, suggesting that this explanation is unlikely; the films appear smooth over both coherence length scales.

To further explore the possibility of elastic dewetting, a series of AFM measurements are performed on a 43 Å (initial thickness) film of the 64 kg/mol PC as a function of annealing time at 20 °C on the oxide substrate. The AFM images confirm that the films are smooth and free of pinholes immediately after spin-casting. However, after annealing the film under vacuum at 200 °C and quenching to 20 °C (time t = 0 in Figure 5a), Figure 6a indicates that a number of small holes appear in the film. These pinholes resemble the initial stages of dewetting, as observed by Reiter. We quantify the pinholes by measuring the rms average and standard deviation σ of the feature heights in the AFM image. Holes are defined as any negative deviation from the average height greater than 2σ. The binary image in Figure 6b (black corresponds to holes) demonstrates how this procedure faithfully captures the pinholes perceived in Figure 6a. The average diameter and aerial hole fraction in Figure 6b are 101.0 ± 11.4 nm and 1.69 ± 0.49%, respectively, at times within a few hours of t = 0 h on the expansion curve of Figure 5a. Strikingly, the same analysis 250 h later, when the thickness has increased by 16%, yields the same average hole diameter and aerial hole fraction of 1.26 ± 0.39%; the pinholes did not grow, to within experimental uncertainty, during the isothermal thickening process.

Figure 6. AFM image in part a shows that immediately after quenching from 200 to 20 °C small pinholes appear in the approximately 40 Å film of the 64 kg/mol PC. Part b highlights these holes (dark regions) after the image analysis procedure described in the text.
In the elastic dewetting model, the isothermal increase in the film thickness occurs at a cost of the pinholes increasing their diameter, i.e., conservation of volume. This mechanism cannot be invoked to explain the thickening of our films. To estimate how much hole growth would be needed to account for the observed thickening, we assume that the pinholes are distributed regularly on a cubic array. With an average hole size of 100 nm and an aerial hole fraction of 1.7%, the resulting distance between hole centers would be 700 nm. Comparing with Figure 6, this length scale appears reasonable for such an approximation. If the mechanism of elastic dewetting were responsible for the 16% increase in film thickness, the average hole diameter in the model would have increased from 100 to 300 nm. The AFM analysis confirms that this does not occur, and a different mechanism is required to explain the isothermal thickening.

The AFM measurements presented here are, admittedly, not particularly well suited for characterizing holes diameters that are on the order 10 nm or less. It is possible that there are pinholes or voids length scales not perceived by AFM. However, from an energetic point of view we find it highly unlikely that a large population of such small pinholes would form and then change size reversibly. This would create an enormous interfacial energy that could be reduced by coalescing small voids into larger ones. If the material has the mobility to increase uniformly in thickness by 16%, there would also be sufficient mobility for this coalescence to occur. The reversible nature of this phenomenon is not the consistent since coalescence of small voids would be an irreversible process.

The isothermally thickening of very thin PC films by as much as 16% at room temperature is quite remarkable, if not disturbing. Conservation of mass is an obvious concern; a 16% uniform increase in thickness for a film that is constrained in the lateral directions would seem to require a corresponding reduction of density. Is it possible that isothermal aging leads to large density reductions in these thin films? Unfortunately, there are no direct ways to measure the density of supported thin films with sufficient sensitivity. Therefore, we are looking at possible indirect methods to infer thin film density changes. Specifically, small molecule probe diffusion experiments may be an effective way to probe the molecularly open or heterogeneous regions of the glassy PC structure. A small molecule that absorbs into the film with low levels of solubility should not significantly plasticize or restructure the glassy network; its residency should be limited to the heterogeneous regions or regions of reduced density. For example, free volume models of transport predict that small molecule probe diffusion should be enhanced in a lower density matrix. These experiments, which are currently in progress, look promising and will soon be reported. In brief, they provide evidence for decreased density in the expanded film, as anticipated from the expansion and lack of pinhole growth.

The isothermal expansion effect displays a strong temperature dependence. In addition to the 20 °C expansion data discussed above, Figure 5a displays data for isothermal anneals at 35 and 50 °C. While all of the expansion curves have similar shapes, the amplitude diminishes with T*; a larger expansion is evidenced with deeper cooling. Curiously, note the response when the film originally held at 50 °C for several hundred hours (apparently approaching an asymptotic thickness) is quenched again from 50 to 20 °C (filled diamonds in Figure 5); the expansion rate increases rapidly. The initial expansion rate following this secondary quench from 50 to 20 °C is comparable to rate following the quench from 200 to 20 °C. Also note that for long times after the second quench (50 to 20 °C) the thickness tends toward some asymptotic value for the original quench from 200 to 20 °C. The time-temperature dependence of these expansion curves bears a striking resemblance to either creep (the long-time strain response to a step increase in stress) or stress relaxation (long-time stress relaxation to a step increase in strain) phenomenon common to glassy polymers. The stress relaxation analogy, in fact, may be somewhat appropriate. There is a considerable mismatch in the thermal expansion coefficients between Si and PC. At high temperatures, well above the glass transition, assume that the interface between the polymer and the Si is in equilibrium and stress-free. Upon quenching, the compliant PC film tries to contract by an order of magnitude more than the rigid Si. However, this contraction is prohibited through the continuity at the PC/Si interface, leaving the PC under considerable biaxial tension. In this respect a quench can be viewed as a step increase in strain on the polymer film, which provides a basis for this stress relaxation analogy.

It is difficult to perceive the true stress levels in the PC film, but it is instructive to roughly estimate their contributions. First, it is reasonable to assume that the polymer is in equilibrium at 200 °C and that stress does not accumulate until the film is cooled through the glass transition. Tentatively we assume that the T* is bulklike (150 °C) and ignore the possibility of T* depressions with h. In the continuum limit, the purely elastic stress that would accumulate in the PC upon cooling from 150 to 20 °C is δT*E* α*(−α*)1(δT* + E* α*(−α*) where δT is the temperature difference, δT* is the elastic modulus of the PC (approximately 3.2 GPa20), and the αs are the linear coefficients of thermal expansion for PC and Si, 2.6 × 10−4 °C−121 and 3 × 10−6 °C−122 respectively. The thermal mismatch in the coefficients produces a linear thermal strain of 2.8% for the aforementioned T* jump, which corresponds to an elastic stress of 90 MPa. This would exceed the yield stress of PC, which is closer to 60 MPa22 in uniaxial tension. Of course, this approximation is crude in that it does not account for the thermal dependence of material properties, thin film confinement effects on material properties, viscoelasticity and utilizes a continuum mechanics model in molecularly thin films where the continuum theory is perhaps questionable. Nevertheless, it is safe to assume that significant stresses develop upon cooling, and they are probably capable of film distortion. This effect should be general for high-T* polymers supported on a rigid substrate; cooling deep into the glassy state creates significant biaxial stresses.

The biaxial stresses might help explain why pinholes appear in the AFM images after quenching. The stress in the as-cast film would be low due plasticizing effect of the residual solvent. During spin-coating the viscosity of the film increases as the solvent evaporates, eventually reaching a point where the film becomes glassy. Once the film reaches the glassy state, large amounts of residual solvent can still be trapped in the film. Since the structure of the film is locked once it becomes glassy, the interface between the PC and Si should be relatively
stress-free at the spin-coating T. However, if the film is equilibrated at 200 °C under vacuum, the residual solvent is removed and the effective glass transition temperature increases, setting up the scenario for the biaxial tensile stresses described above. It is possible that pinholes cavitate in the film in response to the biaxial tension. In some respects this a two-dimensional analogue to craze formation in bulk polymers. In fact, the 100 nm average cavity diameter is nominally consistent with small-angle X-ray scattering measurements of the fibril structure in crazed PC.\textsuperscript{24}

It is tempting to use the residual tensile stress arguments, and a time-dependent relaxation thereof, to rationalize the isothermal thickening of the thin films deep in the glassy state. However, it is critical to realize that stress relaxation alone is not sufficient to account for the expansions witnessed here. It is true that the dilatative response of the film in biaxial tension would be a contraction in thickness. A relaxation of this biaxial stress could conceivably lead to an effective expansion of the film. From the bulk CTE mismatch between the Si and PC and the T jump from 150 to 20 °C, we previously approximated a linear strain of 2.8%. If this strain is applied biaxially in the x and y directions parallel to the plane of the film, the dilative response (assuming a Poisson’s ratio of 0.33) in the z direction would be a contraction of 6.7%. If this biaxial stress were to completely relax, continuum mechanics predicts at most a 6.7% expansion. This would probably be an overestimate since such strain levels, if achieved, introduce nonrecoverable plastic deformation. Clearly the mechanism that leads to this 16% expansion is more complex and must relate to the state of thin film confinement. Realize that these biaxial stress relaxation arguments are also applicable to the thick PC films that do not display the EUC or isothermal thickening effects. Along these same lines, we point to thermal expansion measurements of free-standing PS films (floated off a glass slide and placed on a metal razor blade with a large hole in the center) by Tolan.\textsuperscript{7} The films in these experiments would seem to be free of residual tension, but a contraction upon heating was still observed. This suggests that the residual tension may not be central to the EUC or isothermal expansion.

We now consider the kinetics of this film relaxation process. For all three of the quenches in Figure 5a, the time dependence of the isothermal expansion, H, is reasonably fit by an exponential of the form $H = A[1 - \exp(-t/\tau)]$, indicated by the solid lines through the data. The fitted time constants $\tau$ are 99, 88, and 68 h (with corresponding A’s of 17.7, 13.4, and 10.7) for the 20, 35, and 50 °C measurements, respectively, indicating that the rate of expansion increases with T. Figure 5c shows that the T dependence of $\tau$ is approximately Arrhenius, with an apparent activation energy of 10 kJ/mol and a $T_0$ of 1.9 h. These observations are striking since single-exponential relaxations are typically not observed deep in the glassy state; something similar to a stretched exponential is more common. The magnitude of the activation energy appears reasonable given the range of thermally activated processes that occur in a typical polymer glass. Activation energies for glass transitions are usually on the order of 200 kJ/mol, while sub-$T_g$ relaxations (i.e., the so-called beta or gamma relaxations) are closer to 50–75 kJ/mol, and intermolecular hydrogen bonds are typically 10–30 kJ/mol. In this respect the isothermal expansion is consistent with the chains/segments slowly overcoming “soft” local potential such as dipolar interactions, dispersion forces, hydrogen bonds, etc., between their intermolecular neighbors and/or the substrate.

Next, we illustrate that the molecular mass affects the rate of the isothermal expansion. Figure 7 displays curves for 36 and 24 kg/mol PC films of comparable initial thickness, 59 Å vs 63 Å, respectively. If we assume that these films are equal in thickness, the rate of expansion is faster for the lower molecular mass. The exponential time constant is 290 h for the 36 kg/mol film and 111 h for the 24 kg/mol PC films. This points toward chain motions being involved; the relaxation is slower for higher molecular masses, just as viscosity increases with molecular mass. However, it must also be acknowledged that in films of equal thickness the higher molecular mass polymer probably experiences a stronger state of confinement. This might enhance the driving force for relaxation, but it remains to be seen what factors are important for determining the expansion rates. For example, the 64 kg/mol film in Figure 7 has a shorter time constant, $\tau = 244$ h, than the 36 kg/mol film. This is probably because the overall film thickness is much smaller in the 64 kg/mol film (43 Å vs 63 Å), i.e., a stronger state of confinement. A broader range of molecular masses with varying film thickness is required to fully appreciate this aspect of the isothermal expansion.

In a recent paper, Reiter and de Gennes\textsuperscript{25} propose a tentative physical interpretation for the isothermal glassy state expansion in PS. In closing, we reflect upon their stimulating ideas and highlight relevant aspects of our observations in comparison to their arguments. First, we observe reproducible expansion and contraction of the PC films over a large T range, extending from below to well above $T_g$. In the thin PS films the expansion and contraction curves are reproducible only over a narrow T range well below $T_g$, near $T_g$ the films irreversibly dewet. The PC films here are far more stable, and the isothermal thickening is not necessarily a precursor to dewetting. The reason why PC is more stable is not exactly clear. However, we speculate that this reflects the fact that PC is generally a more entangled polymer than PS for a given molecular mass (lower entanglement molecular mass).

The second difference from the model proposed by Reiter and de Gennes is in the context of the network memory effect. During spin-coating the as-cast film establishes a glassy network (with low mobility) at a critical solution volume fraction $\phi_c$ that is often on the order of 0.20. When this residual solvent is removed in
a vacuum, the film further reduces in thickness. Reiter and de Gennes argue that the film retains a memory of the network established at \( T_g \) and that enhanced network rigidity in the thin film creates a driving force to return this state. This expansion of the collapsed film is opposed by a cohesive energy term that does not favor a low-density film. Balancing the energy from these two contributions yields an equilibrium dilation, i.e., a tendency for the film to isothermally thicken. However, in the PC films studied here, the relevance of the network established at \( T_g \) remains to be seen. Unlike the PS, the PC films are heated at least 50 °C above \( T_g \) where the polymer should have sufficient mobility to equilibrate and “erase” the memory of the \( T_g \) network. In this case, a more appropriate memory term might reflect the glassy network that is established upon cooling through \( T_g \). It is hard to see, though, how this memory effect would lead to such large isothermal expansions. A 15% change in thickness is reasonable when extracting the residual solvent from a spin-cast film. However, a 15% change in thickness is unreasonable for cooling any polymer from \( T_g \) to room temperature. How does the isothermal expansion become so amplified in comparison to normal thermal expansion/contraction?

Finally, Reiter and de Gennes observe and predict, using their model, that the amplitude of the isothermal expansion increases with \( T \); isothermal hold closer to \( T_g \) produces a greater expansion/dilation. Figure 6a shows the opposite effect, and the film expands toward a greater asymptotic value at lower \( T \). If the nominally similar isothermal expansions in PS and PC are related, the model of Reiter and de Gennes needs to be modified to account for this final discrepancy. At this time, though, it is not clear how these differences can be reconciled.

In summary, we demonstrate that ultrathin PC films can display both an EUC and a slow (over several hundred hours) isothermal thickening when cooled below \( T_g \). The thickness at which these effects are seen depends on the molecular mass, becoming appreciable when \( h \) is comparable to the bulk \( R_g \). We find that amplitude of both the EUC and the isothermal thickening increases with the degree of undercooling below \( T_g \). However, the rate of the isothermal thickening decreases with the degree of undercooling, in an Arrhenius-like fashion. There also is a substrate surface energy influence on the EUC, with more favorable polymer–substrate interactions tending to reduce the effect. Preliminary measurements suggest that the rate of the isothermal thickening decreases when the molecular mass increases. We emphasize that while all of these unusual phenomena display strong thermal history dependencies, they are reversible and repeatable. This is different from the elastic dewetting mechanism, which is a nonreversible precursor to more conventional dewetting.

References and Notes