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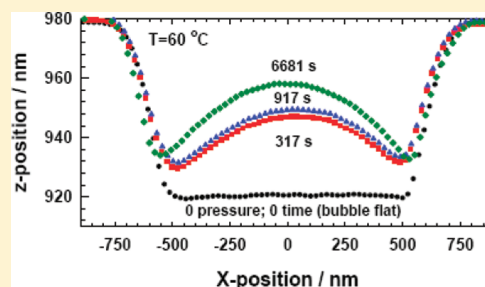
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Exceptional Property Changes in Ultrathin Films of Polycarbonate: Glass Temperature, Rubbery Stiffening, and Flow

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ABSTRACT: The TTU nanobubble inflation method has been used to determine the creep compliance of ultrathin films of polycarbonate over a thickness range of 3–22 nm and a temperature range from ambient (25 °C) to 112 °C. The compliance from the segmental regime through a stiffened rubbery plateau regime was able to be measured for films of thickness from 4.2 nm and above, and the results show a greatly reduced glass temperature and stiffening of the rubbery regime relative to that of the macroscopic material. In the case of the 3 nm film, we found that even at ambient conditions the system is above the enhanced rubbery plateau and is in the terminal flow regime as evidenced by a slope of unity on a double-logarithmic representation of the compliance versus time. The biaxial viscosity of the film at this temperature is $\sim 2.7 \times 10^{11}$ Pa s. We also observed flow behavior in a 9.1 nm thick film that had been heated to 75 °C, i.e., 10 °C above the reduced glass transition of the thin film. These are the first evidence of polymer flow in the equibiaxial deformation geometry in the nanobubble inflation experiments. Interpretation of the results suggests that the glass transition of the 3 nm film is ~ 10 °C below room temperature, which implies a glass transition reduction of 122 °C, which is substantially greater than has been reported previously for any polymer and particularly surprising because the polymer is of relatively low molecular weight, in a regime where one might anticipate a weak dependence of T_g on film thickness. We also observe that the plateau stiffening of the polycarbonate, even to 4.2 nm thickness, falls on the extrapolation of the compliance vs thickness behavior of polystyrene and poly(vinyl acetate) observed previously. This implies a stiffening of over 3 orders of magnitude in the nominal rubbery regime. There is also a stiffening of approximately a factor of 2 in the glassy regime for these films. The results are considered in the context of prior work on ultrathin films.



INTRODUCTION

In past work,^{1–7} we have successfully used the Texas Tech University (TTU) nanobubble inflation device to investigate the viscoelastic creep behavior of nanometric thickness polystyrene (PS) and poly(vinyl acetate) (PVAc) through the glass transition regime and to the rubbery plateau region. In addition, we were successful in the examination of the rubbery plateau behavior of a poly(*n*-butyl methacrylate) (PBMA) above its glass transition regime.⁸ In all of those instances we found, surprisingly, that the rubbery plateau regime exhibited considerable stiffening relative to that of the macroscopic material, with the stiffening following approximately an inverse square law in film thickness for the PS and PVAc, while the stiffening was somewhat less for the PBMA exhibiting a power law closer to 0.83 in film thickness. Along with these findings, we found that the PS exhibited a dramatic reduction in the glass transition temperature, consistent with that seen in other measurements of the T_g reduction in freely standing polystyrene films, though not of the same magnitude. The measurements on PVAc films showed little to no change in the glass transition temperature. A very interesting result in all of those investigations was that we did not see in any circumstance the terminal flow of the material; i.e., the creep compliance did not increase once the rubbery plateau was

achieved even when times longer than the expected reptation time for the material were reached.

In the present work, we enlarge our investigation of materials to polycarbonate ultrathin films and show two landmark results not previously achieved. First, we are able to measure the creep compliance from glassy regime to the rubbery regime for films as thin as 4.2 nm, and there, we observe extreme rubbery stiffening, very large reductions of the glass transition temperature (~ 97 °C), and stiffening of the glassy compliance. Second, we have been able to make measurements on films as thin as 3 nm and evidence continued reduction of the glass temperature as film thickness decreases to this dimension. As we show, the polycarbonate at this film thickness exhibits flow at room temperature, though under conditions of deformation significantly smaller than what would be expected if one were to attain the macroscopic rubbery plateau.

The rest of the paper is organized as follows: after this introduction, we present the experimental materials and methods, we then present the results of the bubble inflation measurements, and follow this with a discussion of the results and an attempt to put them into the context of the current

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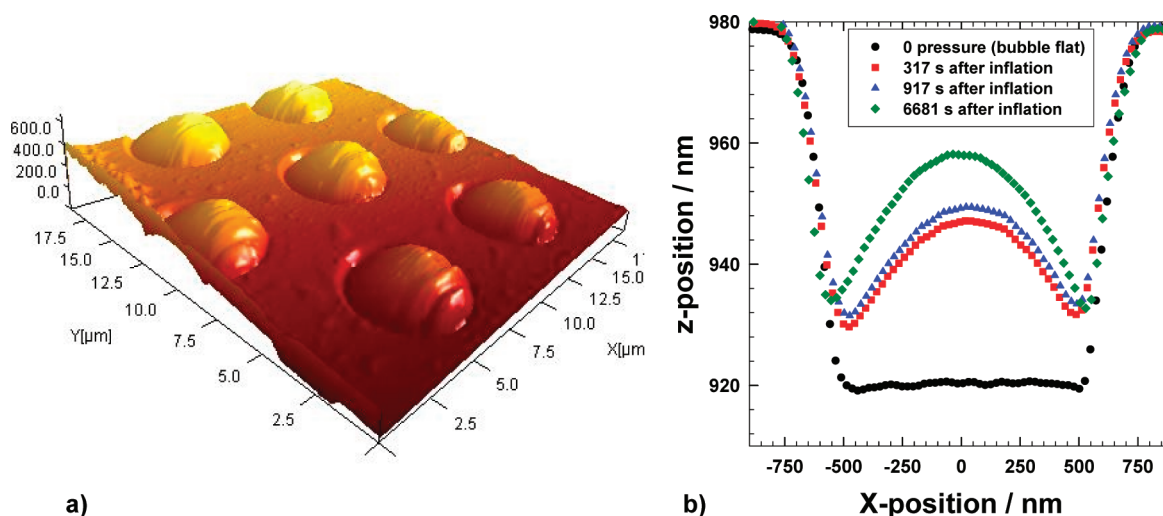


Figure 1. (a) Representative AFM image of 5 μm diameter bubbles for a 15 nm thick polycarbonate film. $P = 3.5$ kPa, inflated at 70 $^{\circ}\text{C}$ and imaged at room temperature. (b) Profiles of bubble shape for a 9.1 nm thick polycarbonate film at 60 $^{\circ}\text{C}$ for different creep times, as indicated. Bubble diameter was 1.2 μm . Pressure was 27.6 kPa.

understanding of the behavior of ultrathin polymer films. We finish with a set of conclusions.

MATERIALS AND METHODS

Materials. The prime material used in the present work was General Electric Lexan LS-2, which is a UV-stabilized, commercial grade bisphenol A polycarbonate⁹ having a weight-average molecular weight of 47 kg/mol with a polydispersity of 2.55. The calorimetric T_g of this material is reported to be 414.2 K (141 $^{\circ}\text{C}$)^{9–11} after rapid cooling and heating at 10 K/min, and the T_g was taken as the midpoint of the measured heat flow signal in the transition region. Our current measurements give a glass transition from the limiting fictive temperature^{12,13} $T_f = 410.1$ K (136.9 $^{\circ}\text{C}$) after cooling at 10 K/min and reheating at 10 K/min. We use this latter value as the T_g throughout the paper. We also use a PVAc from our prior studies^{1–3,5} that has a $T_g = 303.8$ K (30.6 $^{\circ}\text{C}$) from cooling at 10 K/min.¹ The PVAc has a molecular weight of 157 kg/mol and $M_w/M_n = 2.731$.

The polycarbonate films were spin-cast from chloroform solution onto mica sheets at a speed of 2000 rpm for 30 s. The solution concentration determined the final film thickness, which was measured by a method developed in our laboratories² that involves scoring the films and determining the height change with the atomic force microscope. The films were floated from the mica onto a water surface and picked up onto a template containing through holes. The samples were then annealed at the reduced $T_g + 15$ K of the thin film for 15 min to ensure adhesion to the template. As in our in past work we used both 1.2 μm diameter and 5 μm diameter holes. Testing involves placing the templates with the films into a special device built for the purpose that fits into the AFM. By applying pressure across the film membrane at a controlled temperature, one can observe the bubble growth by scanning the template in the AFM. From the membrane approximation for the deformation of thin plates (films) we determine the biaxial creep compliance of the films. In all cases the membrane height was greater than 3 times the membrane thickness; hence, the membrane approximation is valid.^{2,3,14}

Bubble Inflation Experiment. The TTU bubble inflation test method and methods of analysis have been described thoroughly in our prior publications.^{1–8} Briefly, the creep measurements are made by placing a constant pressure across the thin polymer film (on the templates) and measuring the changing bubble height profile. Because the stress in the bubble decreases with increasing bubble height during the test, we apply Boltzmann superposition to the nonconstant stress history and the measured strain history to “back out” the creep compliance, as described previously (see ref 5).

The experiments in the present case were performed for film thicknesses of polycarbonate from 3 to 22 nm. The reason for the limited upper range of thickness is that the high glass transition temperature of polycarbonate in the bulk state, i.e., for thick films, is above the temperature capability of our instrument. However, as we will show, the 22 nm thickness films have a sufficiently reduced glass transition temperature that the creep experiments can be performed at below 112 $^{\circ}\text{C}$ even though the T_g of the PC is 136.9 $^{\circ}\text{C}$. Time–temperature superposition was applied to all film thicknesses to obtain master curves of the creep response from the glassy state through to a rubbery plateau state. Temperature shift factors were obtained, and these are used in the determination of the glass transition reductions. The rubbery plateau compliances found are reported as a function of film thickness.

As part of the present investigation we also carried out creep experiments on films of poly(vinyl acetate) (PVAc) for very long times and at temperatures above the glass transition temperature to determine if we could obtain flow in this material, for reasons to be described below. Macroscopic measurements for the PVAc were obtained in our laboratories using a magnetic bearing torsional creep apparatus available in our laboratories and originally built and developed by Plazek.¹⁵

Importantly, the experiments are performed at stresses that are generally in the linear viscoelastic regime, though in some instances this may be slightly exceeded. Also, we have shown that measurements from bubble diameters of 1.2 and 5 μm give similar results. It is generally advantageous to perform experiments with the smaller diameter bubbles when the film thicknesses are small so that the pressures required to inflate the membranes can be larger, consistent with our bubble inflation pressure control being limited to a minimum of about 0.10 psi (0.4 kPa). We ran our experiments in the present work at conditions similar to the prior work^{1–8} but with smaller strains. The stress levels are time-varying because they decrease as the bubble inflates. This has been discussed in the original publications, but we reiterate it here to emphasize that the stress values, by the time we can measure them, are always sub(macroscopic) yield, and the strains in this study were always less than 1%.

RESULTS AND DISCUSSION

PC Behavior: T_g Reduction and Rubbery Stiffening.

Figure 1a shows a typical AFM bubble inflation image for a 15 nm PC film on a 5 μm hole diameter template. Figure 1b shows height profiles at different times for a 1.2 μm diameter bubble for a 9.1 nm thick film and illustrates how the film creeps. Figure 2 shows the derived creep response for a 22 nm thick

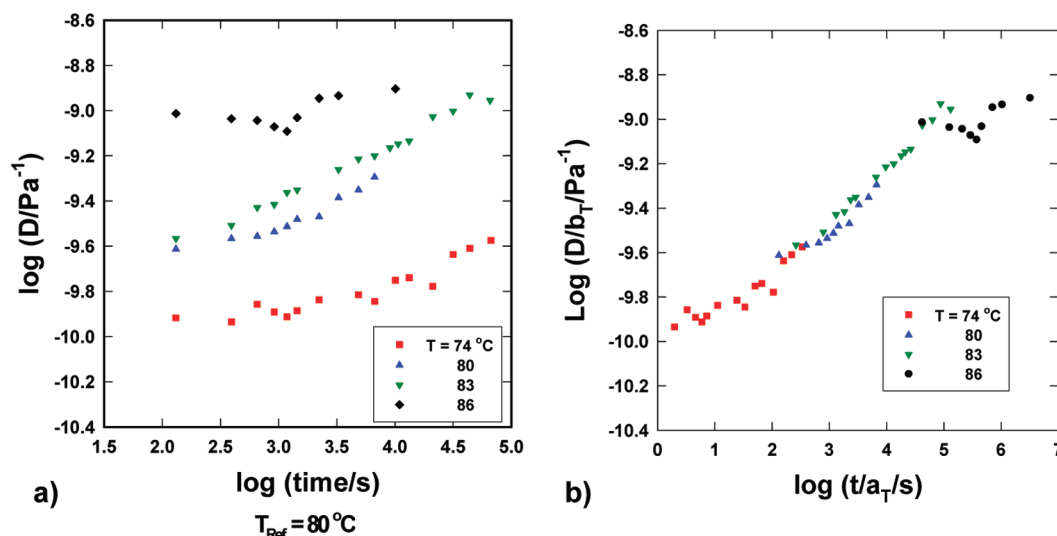


Figure 2. (a) Creep compliance for a 22 nm polycarbonate film at temperatures indicated. (b) Master curve for creep compliance of a 22 nm polycarbonate film with $T_{\text{ref}} = 80\text{ }^{\circ}\text{C}$. Remark that the macroscopic rubbery plateau for polycarbonate is at $\log D = -7.1$ (D in Pa^{-1}).

polycarbonate film at four temperatures as well as the corresponding master curve obtained by time–temperature superposition with a reference temperature of $80\text{ }^{\circ}\text{C}$. In the data we see that one achieves creep from the glassy regime to the rubbery regime at a temperature well below the macroscopic glass transition temperature of $136.9\text{ }^{\circ}\text{C}$. Figure 3 shows the creep master curves for the 22 nm film along with

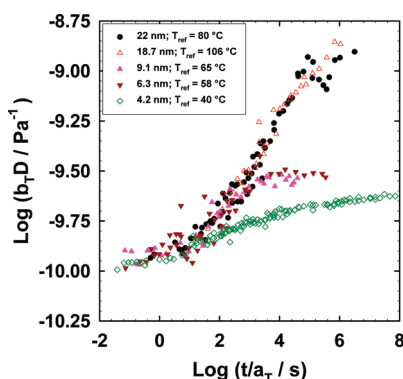


Figure 3. Creep master curves for polycarbonate ultrathin films having thicknesses from 4.2 to 22 nm. Reference temperatures are indicated in the figure.

those for 4 other film thicknesses from 4.2 to 18.7 nm. The temperatures of reference for each master curve are given in the figure. The data of Figure 3 show two clear trends. First, the glass transition temperature for the PC is considerably reduced relative to the bulk temperature, and the amount of reduction in the T_g increases as the films become thinner. We return to the quantitative measure of the reduction in T_g in a subsequent paragraph. The second trend that we see is that the rubbery regime stiffens significantly in these thin films and the compliance is significantly below the expected value for the rubbery plateau of polycarbonate. Neither of these results is *per se* surprising as the results are qualitatively similar to what we have reported previously for polystyrene for the reduction in the T_g as well as for the rubbery stiffening of both PS and PVAc. We will come back to the quantitative comparison subsequently. Perhaps more interesting is the observation we

make that the films down to a thickness of 4.2 nm seem to behave consistently with what we have observed for the other polymers; i.e., they creep from the glass to a rubbery plateau but do not flow. We now turn to the problem of the flow of the ultrathin polymer films.

PC Behavior: Flow. In none of our prior work did we observe flow of our ultrathin polymer films, although the times of some of the experiments were long enough that the bulk material at the same distance above the glass transition temperature would have been well into the terminal flow regime. We see the same behavior in the data presented in Figure 3 for the polycarbonate and for films as thin as 4.2 nm. However, when we carried out our experiments for a film having a thickness of 3 nm, we obtained a surprising result. As shown in Figure 4, we observe flow of the film at the shortest

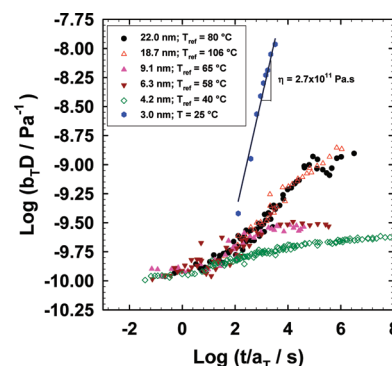


Figure 4. Creep master curves for polycarbonate ultrathin films having thicknesses from 4.2 to 22 nm, as in Figure 3. Hexagons with line show creep/flow response of the 3 nm polycarbonate film at $T = 25\text{ }^{\circ}\text{C}$.

times we could measure ($\approx 100\text{ s}$) and at room temperature ($T = 25\text{ }^{\circ}\text{C}$). The implications of the data are striking. First, we have a film of polycarbonate at $\sim 112\text{ }^{\circ}\text{C}$ below the macroscopic glass transition temperature, and we observe viscous flow as evidenced by the slope of unity drawn through the data and the apparent viscosity of $2.7 \times 10^{11}\text{ Pa s}$, close to what one might expect near to the glass transition temperature for such a low molecular weight, but entangled, polymer. We note that the

molecular weight for entanglement in polycarbonate is ~ 2.5 kg/mol,¹⁶ which gives an approximate entanglement density of M_w/M_e of 19/chain ($M_n/M_e = 7.6$). We also note that the flow is occurring at compliance values much below the rubbery plateau for the macroscopic material. In a sense, it is showing a liquidlike behavior if we did not know that there is a very stiff rubbery plateau compliance in these ultrathin films.

In order to further examine the problem and because we had not previously seen flow in our bubble inflation experiments, we repeated our measurements on the 9.1 nm thick PC film that had an approximate T_g of 65 °C (master curve reference temperature), but now at 75 °C. As we see in Figure 5, where

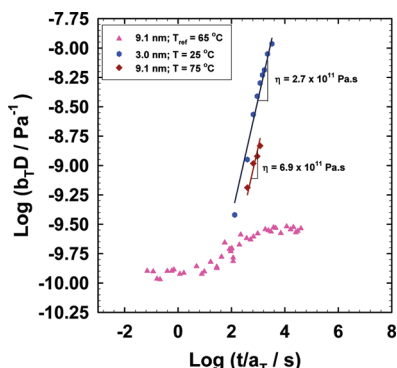


Figure 5. Comparison of flow of PC film of 3 nm thickness with the behavior of the 9.1 nm thickness film. The data for the test at 75 °C correspond to the same time scale as those obtained for the 3 nm film at 25 °C. The lines of slope unity are drawn to indicate that the samples have achieved steady state flow and biaxial viscosities are indicated.

we plot the data as creep compliance vs reduced time, the sample at 75 °C creeps to terminal flow at a similar time to the 3 nm thick film at 25 °C and with a viscosity of $\sim 6.9 \times 10^{11}$ Pa s, not greatly different from that of the room temperature viscosity of the 3 nm thick film. This suggests that the 3 nm film is ~ 10 °C above the glass transition temperature when it is at ambient conditions.

But, if the PC can flow, can we obtain conditions in which, e.g., the PVAc can flow? PVAc has an entanglement molecular weight of 9.1 kg/mol;¹⁷ hence, the PVAc used in our experiments has an entanglement density of approximately $M_w/M_e = 17$ /chain ($M_n/M_e = 6.3$), not dramatically different from the entanglement density for the polycarbonate. In Figure 6, we show the creep response of a 93 nm film of PVAc as a master curve created using temperatures up to 60 °C, which is 30 °C above the macroscopic glass transition of this material. For comparison, we show the creep response obtained from macroscopic rheology for the same material using a conventional rheometer.¹⁵ As seen, the rubbery plateau region is stiffened and no flow occurs for times (reduced times) much longer than the time for which flow would be expected from the data for the macroscopic material. We did not perform further experiments due to issues at long times, such as film rupture, that limited our experimental time window. But it seems that the resistance to flow in the films is greatly enhanced relative to the bulk material. While the polystyrene used in our prior works had a molecular weight of $\sim 10^3$ kg/mol, hence an entanglement density of 55/chain, both the PVAc and the polycarbonate have much lower entanglement densities. Hence, it is unclear why the PC could flow and the PVAc could not. If

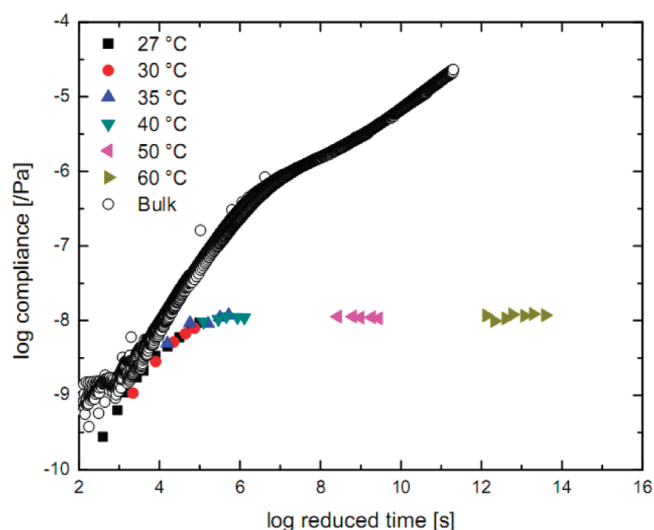


Figure 6. Comparison of creep master curves for poly(vinyl acetate) film having a thickness of 93 nm with the macroscopic behavior of the same material. $T_{ref} = 30$ °C. Figure shows that even for extremely long reduced times the PVAc does not flow, though it is above its glass transition temperature.

the entanglement density is lowered by film confinement,¹⁸ it may simply be that we are able to make thinner films with the PC (we were unable to make films thinner than 24 nm with the PVAc). It would be worth the effort to investigate the flow behavior of the PS thin films that have M_w/M_e similar to the polycarbonate investigated here, though we have not yet successfully made films of PS below 9 nm for the bubble inflation measurements and that was with the 10^3 kg/mol system. Lower molecular weight samples are harder to work with, and we also find that thinner films are prone to rupture. Finally, it is worth remarking that the studies of PBMA,⁸ though all performed above the macroscopic glass transition temperature, also showed no evidence of flow.

PC Behavior: Glassy Compliance. In our prior work with polystyrene,⁵ we reported that the glassy compliance was somewhat stiffened relative to the macroscopic glassy compliance. In the present work, we also find modest stiffening of the glassy compliance with the value being approximately $D_g = 1 \times 10^{-10}$ Pa⁻¹, which corresponds to a modulus of $E_{biax,g} = 10$ GPa. From the known shear modulus at 30 °C,¹¹ assuming that $E_{biax} = 6$ G, we find a conservative value of the corresponding macroscopic modulus of 4.14 GPa. This is consistent with uniaxial moduli reported by Legrand¹⁹ at 0 °C and 10 s of 2.25 GPa. This would give a biaxial modulus, assuming $E_{biax} = 2E$, of 5.5 GPa. Clearly, there is a stiffening of the glassy regime of ~ 2 in these ultrathin polycarbonate films.

Quantitative Analysis of T_g Reduction and Rubbery Stiffening of PC Ultrathin Films. In order to determine the reduction of the glass transition temperature of the ultrathin polycarbonate films, we plotted the temperature shift factors vs reciprocal temperature for each of the film thicknesses. Using the reference temperature as shift factor $\log a_T = 0$ and simply comparing the ΔT_g required to shift the bulk VFT or WLF curve to the reference temperature, we obtain Figure 7. Assuming the macroscopic T_g to be 136.9 °C, we can determine the T_g reduction vs film thickness, as shown in Figure 8. We add that for the 3 nm thick film we have assumed that the T_g is 10 °C below room temperature (for the reasons explained above) in order to include that point on the figure.

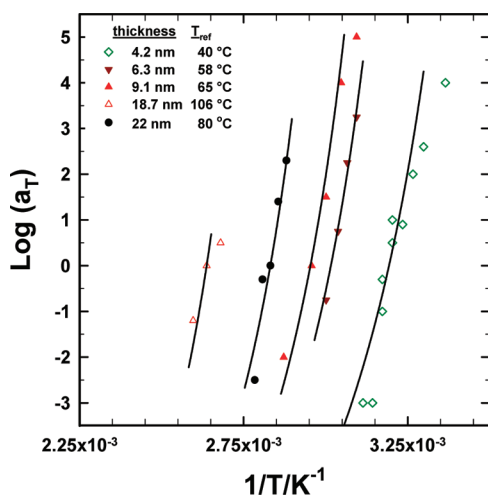


Figure 7. Time–temperature shift factors vs $1/T$ for polycarbonate ultrathin films of different thickness. Solid lines are calculated from the macroscopic VFT behavior shifted to the reference temperatures indicated. The reference temperatures determine the reduced glass transition temperatures.

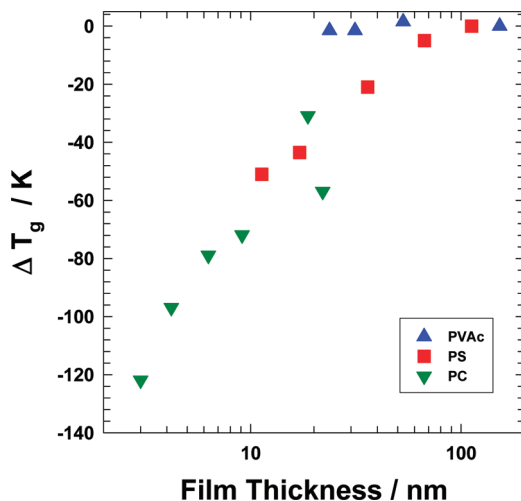


Figure 8. Reduction in the glass transition temperature as a function of film thickness in ultrathin films of polycarbonate (PC), polystyrene (PS), and poly(vinyl acetate) (PVAc).

For comparison, we show the T_g reductions obtained similarly for PS and PVAc from the TTTU bubble inflation experiments. As seen, the T_g decreases for the polycarbonate are very large, perhaps the largest yet observed in polymer thin films. Furthermore, the large reductions become more surprising given that the molecular weight of the polycarbonate is relatively small, and in the seminal work on molecular weight effects in polystyrene,^{20–22} there was no molecular weight effect on T_g reductions until above approximately $M_w = 375\,000$ g/mol.

In the case of the film stiffening in the rubbery regime, it appears that the PC “rubbery plateau” compliance lies on the extrapolation of the compliance lines for PS or PVAc as shown in Figure 9. Hence, the rubbery stiffening is similar to the PS and PVAc^{1,3,5–7} but differs from the poly(*n*-butyl methacrylate),⁸ which has a weaker thickness dependence than the other polymers.

Placing the Results in Context. Freely Standing Films. There is a very broad range of literature on the behavior of

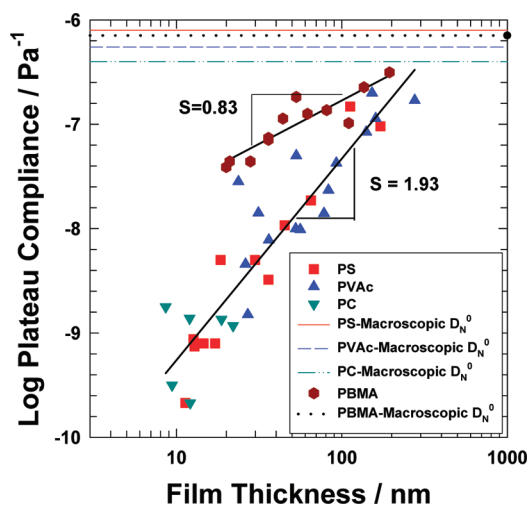


Figure 9. Comparison of the rubbery plateau compliance as a function of film thickness for polycarbonate (this study), polystyrene, and poly(vinyl acetate) (prior work). Also shown are results for poly(*n*-butyl methacrylate), which shows much less film stiffening than do the other polymers.

glass-forming materials, including polymers in film form, at the nanometer size scale.^{21,23–25} Though there is much work in both small molecules in confinement and for supported polymer films, here we discuss the observations on freely standing polymer films as they are more limited and the purpose is to put the present work into that context first. In the next section we discuss briefly results from the supported polymer films and small molecules in confinement.

The first point of importance, then, is the observation of a reduction in the glass transition in freely standing films. The initial reports for polystyrene freely standing films^{20,21} showed significant reductions in the glass transition temperature using Brillouin scattering and ellipsometry in the pseudothermodynamic mode²³ in which a material property is measured as temperature is scanned and an observed change in slope is interpreted as the glass transition temperature. In that work, it was found that the T_g decreased by up to ~ 60 °C for film thicknesses that varied from 20 to 70 nm depending on molecular weight. For molecular weights from 120 to 378 kg/mol there was no molecular weight dependence. In the case of higher molecular weights, the thickness at which such a reduction in T_g was obtained increased, being ~ 70 nm for films of 9100 kg/mol in molecular weight. Other polymers have generally been reported to show weaker reductions in T_g in freely standing films,^{1,5,26,27} though there is not as great a set of measurements of the change in T_g in freely standing films as for supported films. Clearly, the polycarbonate results reported here show much greater reductions in the glass transition than do the polystyrene films (i.e., as much as 122 °C). Furthermore, this is for films having very low molecular mass. It is clear that it would be worth examining the molecular mass dependence of the T_g of polycarbonate. Unfortunately, this requires a synthesis program as readily available commercial PCs of varying molecular mass do not exist.

There are two other sets of measurement that are relevant vis-à-vis the reduction of the glass transition temperature in freely standing films. One is the recent work of Ediger and co-workers,^{28–30} in which a photobleaching technique was used to monitor probe rotational relaxation as a function of temperature in freely standing films. Their results show that there is a

mobile layer at the surface of most films studied and that this layer thickens as the glass transition temperature is approached. This work does not evidence a reduction in the glass transition based on the probe dynamics; rather, they find that there is a bulklike response and a liquid layer response, not a reduced glass transition temperature. Also, the liquid layer thickness varies from zero in the case of poly(α -methylstyrene) to about 10 nm in poly(*tert*-butylstyrene). Polycarbonate was not investigated, and the thickness of the liquid layer in polystyrene was about 6–7 nm at T_g . Such results seem to contradict what we have found for the viscoelastic response of the ultrathin films. If, for example, the PC had a liquid layer thickness the same as that of polystyrene, one would expect the thin film glassy compliance to be much higher for the thinner films as the liquid layer would be less stiff than the glass. The fact that the 4.2 nm thick film and the 9.1 nm thick film both have stiffened glassy compliance values seems to suggest that the surface layer must be much smaller than this. The flow of the 3 nm thick film, however, might suggest a layer thickness of order 1.5 nm; hence, two layers could traverse the film thickness. In the case of polystyrene measurements in prior studies, the smallest film thickness measured was ~ 9 nm, which would still imply for polystyrene that the glassy compliance should be much higher than what was observed, especially since glassy stiffening was observed in that instance as well. The reasons for such discrepancies need further investigation.

The other reports of relevance to the response of freely standing films are those of Bodiguel and Fretigny^{31–33} in which polystyrene thin films are floated onto a glycerol surface where they dewet spontaneously. Using the spreading parameter as the force causing a biaxial compression on the film, they were able to extract the creep compliance in the films for different temperatures. Unlike the bubble inflation measurements here, they observe only a modest increase in polymer mobility, i.e., a 3–4 °C reduction in the glass transition temperature for films ~ 20 nm thick. Why these differences among experimental methods exist remains an open question.

The mechanical properties of ultrathin films that are freely standing have only been measured by ourselves with the nanobubble technique of this paper and by Bodiguel and Fretigny with their liquid dewetting method (assuming that the mobile glycerol/polymer interface is equivalent in that sense to the air/polymer interface). The results contrast significantly. In addition to the issue of the lack of a major reduction of the glass transition in the dewetting experiments, Bodiguel and Fretigny do not observe the rubbery stiffening in the polymer, and the flow behavior that they report is typical of the macroscopic polymer rheology. They do not observe the “rubbery” stiffening reported here, and we remark that other studies from this lab^{3,6,8} have demonstrated fairly conclusively that the stiffening that we observe is not due to the surface tension acting at the film surface. The fact of flow in the 3 and 9.1 nm films evidenced here is further support that the surface tension is not the cause of the rubbery stiffening. Additionally, it is of interest to note that the pressures used to inflate the present 3 and 4.2 nm thickness films should have been too small to inflate the bubbles if the surface tension were the cause of the stiffening. Here, as reported, the polycarbonate seems to flow with a glass-like viscosity approximately 10 °C above the nominal glass transition temperature. These are the first reports of flow in the nanobubble inflation measurements. An interesting observation in recent work by Pye and Roth³⁴ gives an apparent double T_g in high molecular weight

polystyrene films. The observation here of a reduced segmental dynamics followed by the “rubbery stiffening” and terminal flow may suggest that terminal flow dynamics is differently affected by the confinement than are the segmental dynamics. The case of the PVAc, where we did not observe flow even 30 °C above the macroscopic glass transition temperature, however, is not fully consistent with this interpretation, and further study is required. As for why the PVAc behaves differently from the PC, we speculate that the difference between the PVAc and the polycarbonate in this regard is related to the observation by Plazek³⁵ that the rubbery plateau for poly(vinyl acetate) “is too wide” for the molecular weight that he investigated. We postulate the possibility that this effect is magnified by the ultrathin film confinement.

As for the glassy compliance, the liquid dewetting method of measurement does not have sufficient resolution to measure the small deformations that occur in the glassy regime for the small stresses that result from the surface tension acting on the films.

Supported Films and Small Molecule Glass-Formers in Confinement. There is considerably more work on the behavior of supported polymer films and on small molecule glass formers in confinement than on freely standing films. Therefore, we need to be brief. However, it is worth noting that there is a general, but not universal, acceptance that the T_g decreases upon confinement when the interactions with the surface are weak. This is seen in works from the earliest in nanopores^{36,37} in which only modest reductions in T_g were observed, in polymer films on weakly interacting substrates^{38,39} where larger T_g reductions were seen, to the more recent works in pores⁴⁰ where very large reductions of T_g have been reported for large but nonpolymeric molecules. For the case of systems that interact with the confining surfaces,^{23,41,42} such as hydrogen-bonding liquids, the T_g has been reported to either increase, remain the same or decrease modestly. In addition, some works have suggested that the mechanical constraints provided by the confining medium may contribute to observed changes in molecular mobility that lead to the reduced T_g observations.^{43–45} The present work does not directly address these issues, but it is worth noting that the observations of T_g reductions in freely standing films are much stronger than those observed in supported films. Finally, one other work is worth considering in the context of the present study. Torkelson’s work⁴⁶ using fluorescent probe intensity as a function of temperature to obtain the pseudothermodynamic T_g in supported films has led to the suggestion that the polymer chain backbone chemistry (is it rigid?) or how it relates to the macroscopic fragility of the glass-forming system may lead to very strong T_g dependence on film thickness. The limited set of data here comparing the T_g reductions of poly(vinyl acetate), polystyrene, and polycarbonate would fit into this framework. Further work is required to systematically explore this possibility.

SUMMARY AND CONCLUSIONS

The rheological response of a series of polycarbonate films having thicknesses from 3 to 22 nm has been measured using the TTU bubble inflation method. The results show exceptional property changes in the PC relative to those of the material at the macroscale. Reductions in the glass transition are observed that are greater than any previously observed, being ~ 122 °C below the macroscopic T_g for the 3 nm thick film. Furthermore, for the first time we have been able to demonstrate flow in the ultrathin films in the nanobubble

experiment and we observe this flow at $\sim 10^\circ\text{C}$ above the thin film glass transition and for deformations/compliance values well below the macroscopic rubbery plateau value. Also, we observe that the rubbery stiffening of these extremely thin polycarbonate films falls on an extrapolation of the stiffening observed previously for polystyrene and poly(vinyl acetate), suggesting that the observation of the reduced rubbery compliance follows the square of the thickness in these three materials to thicknesses at least as small as 4.2 nm. Finally, we also see an enhancement of the glassy stiffness as evidenced by a reduction of the glassy compliance. Insufficient data are available to provide a trend in the glassy stiffness with film thickness.

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Notes

The authors declare no competing financial interest.

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