Interfacial Effects and the Glass Transition in Ultrathin Films of Poly(*tert*-butyl methacrylate)

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ABSTRACT: Glass transition studies were performed on ultrathin spin cast films of poly(*tert*-butylmethacrylate) (PtBMA) with thickness values in the range 6−415 nm. Ellipsometry was used to measure the dilatometric properties of uncapped PtBMA films as well as films that had been capped with 5 nm thick evaporated Aluminum (Al) layers . Al-capped films were also prepared using a recently developed $2(h/2)$ sample preparation procedure that is designed to completely remove the effects of the free polymer surface. These studies revealed that the glass transition temperature (T_g) in uncapped PtBMA films is reduced from the bulk value (383 K) by ∼28 K for films as thin as 6 nm. Similar T_g depressions were also reported for Al-capped films that were prepared by thermally evaporating Al directly on to the PtBMA films. However, films that were prepared using the $2(h/2)$ sample preparation procedure displayed bulk like T_gs for films as thin as 6 nm. These experiments illustrate that evaporating metal coatings on polymer films does not necessarily remove the effects of the free surface, but that if care is taken to ensure that the properties of the free surface are removed, the thickness dependence of the T_g in thin polymer films can be suppressed. These combined experiments provide strong evidence that free polymer surfaces are responsible for the T_g reductions that are routinely observed in ultrathin polymer films.

Introduction

The role of surfaces, interfaces, and molecular confinement effects can be extremely important in determining the nanoscale properties of polymeric materials. Previous studies have shown that the physical properties of polymers can change dramatically in systems that are smaller than a few tens of nanometres in size.[1–4] Understanding how these phenomena affect the properties of polymers will clearly be a key factor in developing the next generation of nanoscale polymeric materials and devices.

Ultrathin polymer films provide an excellent model system for developing an understanding of how interfacial and confinement effects influence the properties of polymers . In particular, studies of the film thickness dependence of the glass transition temperature (T_g) in thin polymer films have indicated that surfaces and interfaces can have a significant influence upon the nanoscale properties of these materials.[1,3–6]

The T_g reductions that are routinely observed in these samples have been attributed to the presence of enhanced dynamics at the free surface of the glassy polymer films. Numerous experimental studies have been performed to try to test this hypothesis. Ellison and co-workers used fluorescent probe layers to show that the dynamic properties of glass forming polymers near the free surface are faster than in the bulk.[1] Teichroeb and Forrest also used nanoparticle embedding experiments to show that there is a 3−4 nm thick liquid like region near the free surface of glassy polymers.[7] Studies have also been performed on "free-standing" polystyrene films that have twice the surface-to-volume ratio of simple supported films. These studies showed that the measured reductions in the T_g of free-standing films were larger than those measured in simple supported films of the same thickness.[5,8] They also revealed that free-standing films and supported films with the same surface-to-volume ratio had equivalent T_g values. These experiments strongly suggest that the free surface region plays a significant role in determining the T_g of thin film polymer samples. However, there are also a number of studies that suggest that the dynamics at the free surface do not differ from the bulk polymer dynamics and that

interfacial effects are therefore not responsible for the observed T_g reductions.[9–11] These apparent contradictions have resulted in a significant amount of controversy over the nature of the dynamic properties of polymers near surfaces and interfaces and their relationship to the physical properties of ultrathin polymer films.

Interpreting the wealth of results and resolving the controversy that already exists regarding thin film polymer dynamics has proven to be a challenging task. When comparing techniques that are designed to probe similar properties of these samples, a number of experimental considerations need to be taken into account. For example, great care has to be taken to differentiate between experiments that are designed to probe local segmental relaxations (such as those responsible for the glass transition) and those that are designed to probe the motion of whole polymer chains. Recent reports have provided strong evidence for the existence of a more mobile surface region at the free surface of glassy polymer films[1,7] and the existence a gradient in the dynamics of polymeric materials as we move away from the free surface.[1] These studies suggest that it is likely that there are polymer chains near the free surface that have segments in regions of enhanced mobility near the free surface and that also have parts of the chain buried in glassy regions of the film. These combined experiments suggest that the enhanced surface dynamics that have been reported in recent nanoparticle embedding[7,6] and surface relaxation studies[12] (that probe only the first few nanometers close to the surface of the films) may not be inconsistent with measurements of thin film polymer chain diffusion coefficients that are lower than those observed in the bulk polymer.[10] If a gradient in dynamics exists, then the characteristic relaxation times of the polymer close to the free surface would be expected to vary by orders of magnitudes on length scales that are comparable to the dimensions of a single polymer molecule. These effects are likely to be further complicated by the presence of a substrate. These factors are likely to result in complicated dynamics and the decoupling of segmental and whole chain motion in ultrathin polymer films.

Similar arguments can also be applied in attempt to explain measurements of the rupture and hole formation properties of

thin polymer films. Studies of ultrathin, freely standing polymer films revealed that holes would only form in these samples when they were heated above the bulk T_g of the polymer, even when the measured T_g of the films was ~30 K below the bulk value.[13] At first these results would seem to be highly inconsistent, as a freely standing film that is above its measured T_g would be expected to flow and rupture to form holes under the influence of van der Waals interactions between its two surfaces.[14] However, it is worth noting that the measured T_g in thin polymer films represents a global measure of the dynamics averaged over the entire thickness of the sample. So although the average T_g of the entire film is reduced, the gradient in dynamic properties mentioned above would result in a central layer that behaves like the bulk polymer in films above a critical thickness (~6–8 nm [6]). The films would not be expected to flow and rupture until all the material in this central region was melt-like. As a result, holes would not form until these samples were heated above the bulk T_g of the polymer.

In addition to these factors, other studies have shown that consideration needs to be given to the role of polymer/substrate interactions[15–18] (in the case of supported films) and also to the effective measurement frequency of the probes being used when comparing different measurements of the dynamics in thin polymer films.[19] While the effects of polymer/susbstrate interactions have largely been accounted for, the role of measurement probe frequency in determining the thickness dependence of the dynamic properties of ultra thin polymer films is still a matter of debate.[17,19–21]

A simple way of testing whether or not free polymer surfaces are responsible for the reduced T_g in thin polymer films, is to try to manipulate the free surface and to determine the resulting effect upon the measured thickness dependence of the T_g. Previous attempts to achieve this have produced mixed results. The measured T_g values for SiO_x coated polystyrene (PS) films were found to be essentially the same as those for supported films with one free surface.[22] This result was confirmed in dielectric studies of Al coated PS which also showed T_g behavior the same as that of uncapped films.[23] The comparison between these results and the T_g values measured in free-standing films results in an apparent and striking inconsistency. If the free surface is important in causing reduced T_g values in thin films then eliminating the free surface must have an influence on the measured T_g values. The fact that this does not seem to be the case has proven to be a major obstacle in understanding thin film glass transitions. More recent results have suggested that the structure of the polymer/metal interfaces produced by evaporating different metals on to polymers can play a vital role in determining whether or not the free surface effects are removed.[6] These studies also showed that PS films that are evaporatively capped with Al display a thickness-dependent T_g. However, when almost identical Al-capped PS films were prepared in such a way that great care was taken to ensure that the free polymer surface was removed, the thickness dependence of the T_g was suppressed.

In this article we describe an experimental study of the glass transition in ultrathin spin cast films of poly (*tert*-butyl methacrylate) (PtBMA) supported on Aluminum (Al) substrates. Ellipsometry was used to measure the thickness dependence of the T_g in PtBMA films with thickness values in the range 6–415 nm. Experiments were performed on uncapped PtBMA films, as well as films that were capped with thermally evaporated Al layers and Al-capped films that were manufactured using the previously developed 2(h/2) sample preparation procedure.[4] We show that uncapped and evaporatively capped PtBMA films display depressions of ~28 K relative to the bulk polymer for films as thin as 6 nm. However, Al-capped films that were prepared using the 2(h/2) technique display bulk like T_g's for all the thickness values studied. These experiments confirm that evaporating metal capping layers on to thin PtBMA films does not necessarily remove the effects of the free surface. They also show that it is possible to remove the memory of the free surface using the 2(h/2) sample preparation procedure and that preparing the samples in this way results in bulk-like properties in all measured quantities for films as thin as 6 nm. This study provides strong evidence that free polymer surfaces play a significant role in determining the physical properties of nanoscale polymer samples.

In addition to probing the role of interfacial effects upon the glass transition in thin polymer films, this study serves another purpose. Much of the previous work on thin film polymer dynamics has concentrated on a limited range of polymers, namely, polystyrene, poly(methyl methacrylate), and a few others.[1–19] Studies of the thin film dynamic properties of other polymers (such as PtBMA) are beneficial as they will enable us to rule out any possible effects that could be due to the specific chemistries of the polymers being used. These experiments therefore provide additional evidence that confinement and interfacial effects are a general property of all polymers.

Experimental Section

Thin films of poly (tert-butyl methacrylate) (PtBMA, M_w = 275 KDa, M_w/M_n = 1.30, Polymer Source) were spin coated from solutions in toluene on to 12 mm × 12 mm, 300 μm thick, single crystal silicon wafers (Compart Technology) that had been coated with a 300 nm thick thermally evaporated aluminum (Al, 99.999%, Advent) layer (evaporation rate 5 nm s^{-1}, 1 × 10^{-5} torr). All the silicon wafers used in this study were used as received and as such had the native oxide in tact. All PtBMA films were prepared using a spin speed of 3000 rpm and the thickness of the films (h) was controlled by changing the initial concentration of the polymer solutions.

Three different types of sample were prepared to determine how manipulating the free surface of the films can be used to alter the dynamic properties of these samples. The first set of samples was prepared by thermally evaporating a 5 nm thick Al layer on the top surface of the as spun films (using the same deposition parameters described above). These samples were then annealed at 413 K (Bulk T_g PtBMA = 384 ± 1 K as determined using ellipsometry) under vacuum (1 × 10^{-3} torr) for 10 h. This was done to remove residual solvent and to relax any stresses that were introduced into the films during the spin coating procedure. The second set of samples was prepared in a similar way except that the order of annealing and the evaporation of the top Al layer were reversed. These two sets of samples were prepared to determine if thermally evaporating a metal layer on top of the polymer films can be used to manipulate the material properties of the free surface region. Changing the order of annealing and evaporation of the top layer also served to determine how the effects of using different sample preparation histories changes the material properties of ultrathin polymer samples. During the evaporation of the Al capping layers, a thermocouple was placed close to the samples in the evaporation chamber so that the temperature could be measured. It was found that the temperature of the samples did not exceed 310 K (which is well below the bulk T_g of PtBMA) during evaporation.

A third set of samples was also prepared in an attempt to remove the memory of the free polymer surface that is formed during spin coating. These samples were prepared by spin coating two films of thickness h/2 on two separate substrates and then placing them with their free surfaces in intimate contact to give a film of total thickness, 2(h/2) = h. The first film was prepared by spin coating a solution of PtBMA in toluene on to a 12 mm × 12 mm, Si wafer that had been coated with a 300

nm thick thermally evaporated Al layer (using the same deposition parameters used above). The second film was spin coated on a 10 mm diameter sodium chloride (NaCl) window that had been coated with a 5 nm thick thermally evaporated layer. The film supported on the Al coated NaCl window was then turned upside down and gently placed on top of the film supported on the Al coated Si wafer. A small drop of deionized water (Elga) was then placed at one edge of the NaCl window using a glass pipet. At this point the water was observed to wet the interface between the top Al layer and the NaCl window, causing the PtBMA film and top Al layer to detach from the NaCl window. The resulting wetting front was observed to propagate from one side of the NaCl window to the other. As the PtBMA film and top Al layer detached from the NaCl window, surface forces between this PtBMA film and the PtBMA film supported on the Al coated Si wafer pulled the two polymer films into intimate contact. Removal of the NaCl window and subsequent rinsing of the films in deionized water resulted in flawless Al-capped PtBMA samples that had the same optical appearance and sample geometry (i.e., PtBMA films sandwiched between a 300 nm thick Al substrate and 5 nm thick Al capping layer) as those prepared by thermally evaporating thin Al layers directly on top of Al supported PtBMA films. These $2(h/2)$ samples were then annealed at a temperature of 413 K for 10 h.

Prior to the formation of the thinnest (6 nm thick) $2(h/2)$ composite films, an Asylum Research MFP 3D atomic force microscope was used to image the surface of the two separate (3nm thick) films that were used to manufacture the samples. This was done to ensure that films of this thickness did not dewet and break up to form droplets during spin coating. These images revealed the surface of the 3nm thick film to be uniform with a peak to peak roughness of less than 1 nm. This confirms that the films formed by spin coating PtBMA on to Al substrates were stable and did not break up prior to formation of the composite $2(h/2)$ samples.

The thickness dependence of the T_g in each set of samples was then determined using ellipsometry. Each sample was mounted on the heating block of a Linkam THMS600 Hotstage and attached to the sample stage of a home-built self-nulling ellipsometer. The sample stage was purged with dry N_2 gas to exclude water vapor and oxygen. The PtBMA films were then heated to a temperature of 405 K and allowed to equilibrate. After 20 min, the samples were cooled to a temperature of ~320 K at a cooling rate of 10 K min^{-1}. During cooling the polarizer and analyzer (P and A) angles were varied to obtain a null signal at the photodiode detector on the ellipsometer. The values of P and A obtained at null were recorded as a function of temperature for all samples studied.

Results and Discussion

Figures 1 and 2 show the variation in the polarizer angle P for 6 nm and 270nm thick PtBMA films that were evaporatively capped with Al and prepared using the $2(h/2)$ sample preparation procedure respectively. As the changes in film thickness (h) and refractive index (n) of the PtBMA films are small, the changes in P shown in Figures 1 and 2 are expected to be linear in both of these quantities.

The T_g of each sample was determined by calculating the temperature at which the fits to the two linear regions (corresponding to the thermal expansion coefficients of the melt and glassy regions respectively) intersected (see Figures 1 and 2). This process was repeated for films with thickness values in the range 6–415 nm.

Figure 3 shows the combined results of thin film glass transition studies performed on uncapped ultra thin PtBMA films and films that have been sandwiched between Al layers using different sample preparation procedures. This figure clearly
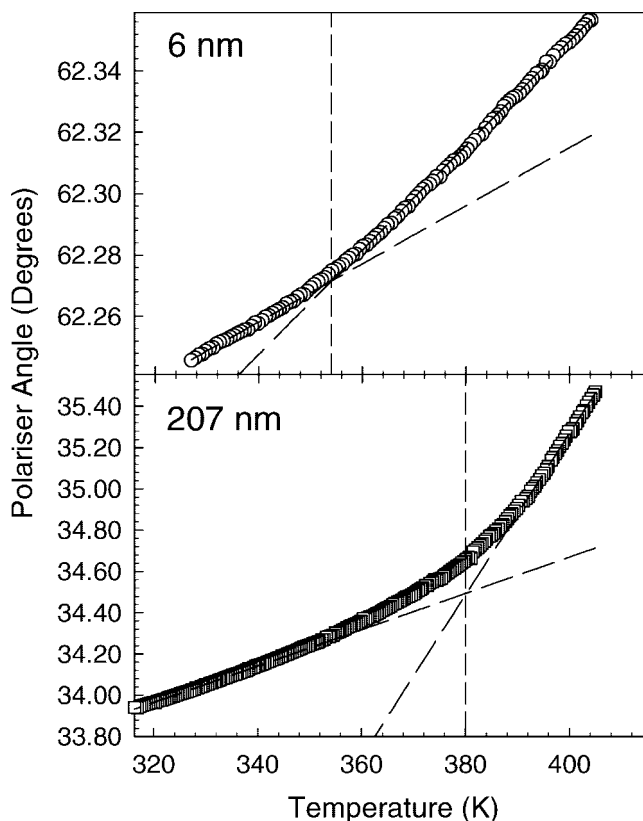

Figure 1. Ellipsometry measurements of the glass transition of thin PtBMA films supported on Al substrates. Data are shown for the variation in the polariser angle (P) as a function of temperature for 6 nm thick (top panel) and 207 nm thick (bottom panel) PtBMA samples that were annealed after being evaporatively coated with a 5 nm thick Al capping layer. The dashed lines represent fits to the melt and glassy expansion regions respectively and the vertical dashed lines mark the position of the T_g for each film.

shows that uncapped films and films that are evaporatively capped display T_g reductions as large as 28 ± 1 K for films as thin as 6 nm. These data show that the T_g reductions occur in films that are less than ~40–50 nm thick and that the reductions that are observed in these data sets are the same within the limits of experimental uncertainty. In addition, the data shown in Figure 3 indicates that the measured T_g in thin films of PtBMA is not influenced by the order of annealing and evaporation when the films are evaporatively capped with thin (5 nm thick) Al capping layers. These results are consistent with those observed in studies of other polymers.[3,4]

A consideration of the data shown in Figure 3 reveals that the T_g reductions reported here for uncapped PtBMA films are smaller than the 60 K shifts reported by See and co-workers[24] for silicon (Si) substrate supported PtBMA films of a similar thickness range and molecular weight. The reason for the discrepancies is not entirely clear. One possible explanation could be related to differences in the polymer–substrate interactions in the two sets of experiments. The thickness dependence of the T_g in thin PtBMA films spin coated on silicon wafers (shown in the inset of Figure 3) reveals that the measured T_g shifts on both Al and Si substrates are the same within the limits of experimental uncertainty. However, it is worth noting that in the present study the native oxide coating on the Si wafers remained in tact, while in the study by See and co-workers, the oxide coating was removed prior to deposition of the polymer films. This is likely to result in some differences between the surface chemistry of the Si substrates used in the two studies and could result in different polymer/substrate interactions. This may explain the measured differences
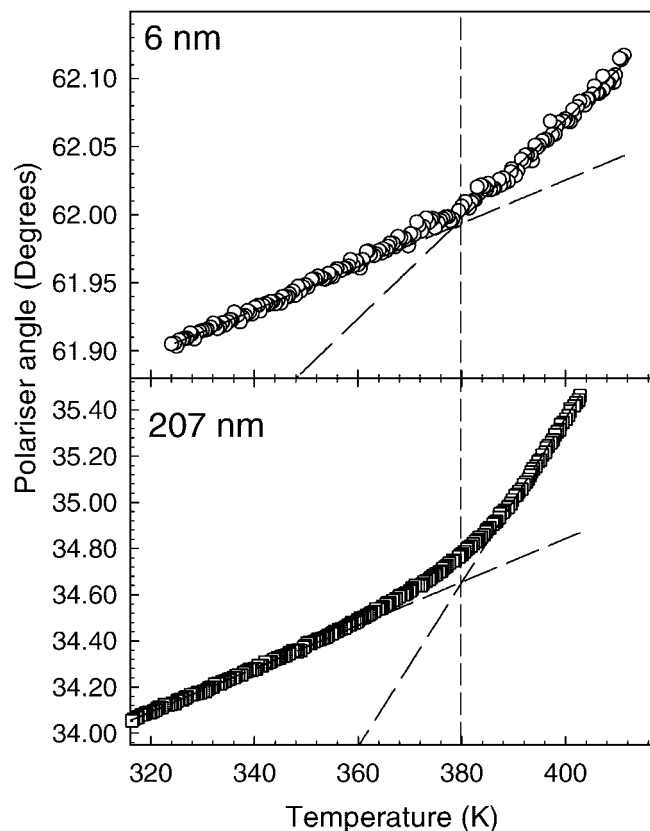
Figure 2. Ellipsometry measurements of the T_g of 2(h/2) PtBMA films. Data are shown for the variation in the polariser angle (P) as a function of temperature for 6 nm thick (top panel) and 207 nm thick (bottom panel) PtBMA films. The dashed lines represent fits to the melt and glassy regions, respectively, and the vertical dashed lines mark the position of the T_g for each film.
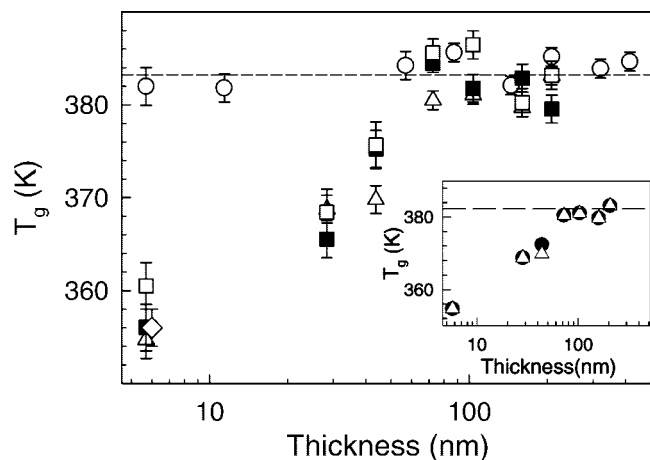

Figure 3. Film thickness dependence of the T_g for PtBMA samples on Aluminium substrates. Data are shown for uncapped films ($\triangle$) and films that were capped with a 5 nm thick thermally evaporated Al layer and annealed before ($\square$) and after ($\blacksquare$) the evaporation of the capping layer. Data are also shown for samples that were manufactured using the 2(h/2) sample preparation procedure ($\bigcirc$), see text. The T_g of these samples is plotted as a function of the total polymer film thickness $h = 2(h/2)$). The open diamond ($\diamond$) shows the measured T_g of the 6 nm thick 2(h/2) film following the removal of the capping layer using 0.1 M NaOH$_{(aq)}$. The inset shows the variation in T_g with film thickness for uncapped PtBMA films on aluminium ($\triangle$) and silicon ($\bullet$) substrates.

in the magnitude of the observed T_g reductions between the two studies.

Regardless of the cause of the discrepancy between the two studies, the high level of reproducibility in the thickness-

dependent T_g values obtained for PtBMA films prepared using different sample preparation procedures gives us confidence in the measurements reported here. Moreover, the magnitudes of the T_g reductions shown in Figure 3 are comparable to those that have been reported for other polymers on similar substrates.[3,4]

The fact that T_g reductions are observed in evaporatively capped PtBMA films appears to contradict the idea that free surfaces are responsible for the thickness dependence of the T_g in thin polymer films. If the free surface of a glassy polymer film has enhanced dynamics relative to the bulk, then we might expect that capping the films with a rigid metal over layer would remove any regions of enhanced mobility at the free surface and result in bulk like dynamics for even the thinnest PtBMA films. Dielectric relaxation studies have also been performed using polymer films that are sandwiched between metal electrodes and these have also been shown to display behavior that is consistent with that reported for uncapped polymer films.[23] However, recent studies have indicated that the structure of the polymer/metal interface formed during evaporative coating of polymers is such that the properties of the free surface are not always modified by preparing the samples in this way.[4,6,25] These studies showed that the polymer/metal interfaces formed by evaporating relatively reactive metals such as aluminum on to polymers are very sharp but that the corresponding interfaces formed by less reactive metals such as gold (Au) are much broader. Measurements of the thickness dependence of the T_g of Al- and Au-capped PS films showed that the thickness dependence of the T_g was suppressed for Au-capped films but not in the case of Al-capped films.[4,6] These combined experiments strongly suggest that the structure of the polymer/metal interface plays an important role in determining whether or not the effects of the free surface are properly removed.

To overcome these potential difficulties and to show that it is possible to produce Al-capped PtBMA films in such a way that any regions of enhanced mobility in the near surface region can be removed, an alternative method of trying to manipulate the free surface properties of these samples needed to be found. One way to do this is to produce samples where the free surfaces produced by spin coating are placed at the center of the films as in the case of the 2(h/2) films described above. Annealing these samples should allow the polymer chains at the interface between the two films to interpenetrate and remove any regions of enhanced mobility caused by the two free surfaces. As a result of preparing the Al-capped films in this way, the polymer/metal interfaces at both the top and bottom surfaces of the films have never been free surfaces and would be expected to behave more like polymer/substrate interfaces. Producing the samples in this way would therefore result in the films being capped with a rigid metal overlayer that would remove any density defects at the free surface that could be the cause of enhanced mobility. This should result in bulk like polymer properties throughout the entire thickness of the samples.[4]

The thickness dependence of the T_g for the 2(h/2) PtBMA films is shown in Figure 3. The data in this figure shows that these samples display bulk like T_g's for films as thin as 6 nm. Comparison of the ratio of the slopes, corresponding to the melt and glassy expansion coefficients (α_{melt} and α_{glass}, respectively, obtained from the data shown in Figures 1 and 2) also provides further evidence that the 2(h/2) PtBMA films display bulk like properties. In Figure 1, the data shown for the evaporatively capped films has a ratio of the slopes for the thick (207 nm) film of $r = \alpha_{melt}/\alpha_{glass} = 3.9 \pm 0.4$, while that for the 6 nm thick film is $r = 1.8 \pm 0.4$. These values are the same as those obtained for uncapped PtBMA films of a similar thickness. Previous studies have interpreted the reduction of this ratio with decreasing film thickness as being due to the presence of a
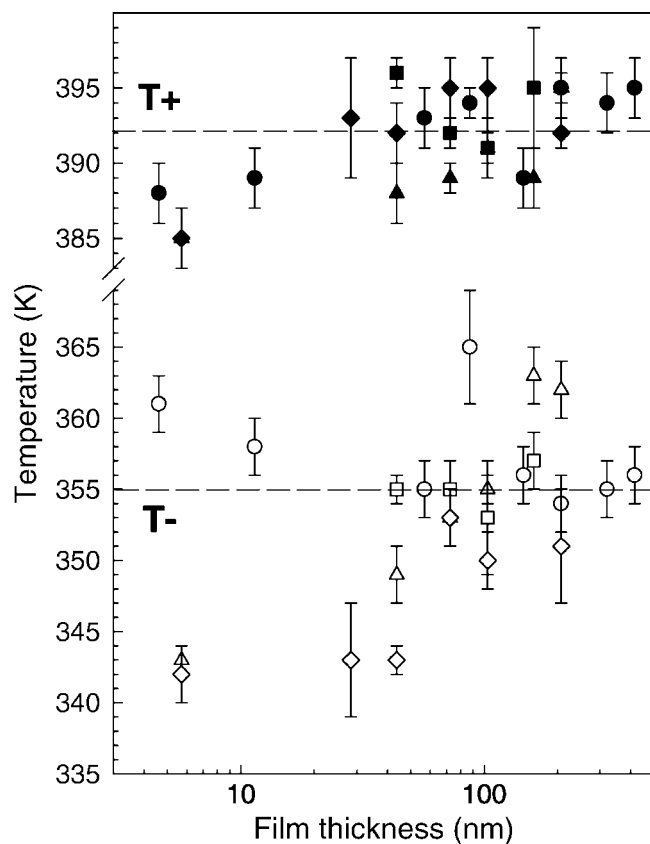
Figure 4. Film thickness dependence of the width of the glass transition in PtBMA films. Data are shown for uncapped PtBMA films (triangles), evaporatively capped films that have been annealed then capped (squares) and capped then annealed (diamonds), and 2(*h*/2) films (circles). The solid symbols mark the position of T_+ and the hollow symbols mark the position of T_- (see text for definitions).

liquid-like layer at the surface of the glassy polymer films.[26] The larger surface-to-volume ratio in thin films is expected to result in an increased contribution from the near surface region with enhanced dynamics. This is manifested as an increase in the effective glassy thermal expansion coefficient of the thin films and a corresponding reduction in the ratio, r. The ratio of the slopes for the 2(*h*/2) PtBMA films obtained from Figure 2 give values of $r = 3.5 \pm 0.4$ and $r = 2.7 \pm 0.4$ for the thick (207 nm) and thin (6nm) films, respectively. These are the same within the limits of experimental uncertainty, indicating that the thinnest 2(*h*/2) films have bulk-like thermal expansion properties.

The width of the glass transition in thin polymer films can also be determined by extracting the temperatures T_+ and T_- at which the linear fits to the melt and glassy slopes deviate from the P vs T data, respectively.[26] Figure 4 shows the thickness dependence of T_+ and T_- for ultrathin PtBMA films. This figure shows that the value of T_+ remains constant over much of the film thickness range studied for all of the PtBMA samples. There is some evidence that the value of T_+ starts to decrease for the thinnest films studied. However, this is difficult to determine within the limits of experimental scatter and uncertainty. The values of T_- shown for the uncapped and evaporatively capped PtBMA films in Figure 4 have a stronger film thickness dependence. The reductions in T_- with decreasing film thickness indicate that the glass transition in these samples experiences a broadening to lower temperatures as the film thickness is decreased. These results are consistent with previous reports of the thickness dependence of the width of the transition in other polymers.[26] The T_- values obtained for the 2(*h*/2) PtBMA films remain constant over much of the range of film

thickness values studied with some possible evidence of a slight increase in T_- for the thinnest films. This analysis reveals that the width of the transition in the thinnest 2(*h*/2) films is the same as that in the thickest (bulk-like) PtBMA samples.

To ensure that the suppression of the thickness-dependent properties of PtBMA is in fact due to the removal of the free surface (and not due to some other aspect of the sample preparation of the 2(*h*/2) films), the Al capping layer on the thinnest 2(*h*/2) sample was removed using a simple chemical treatment. This was achieved by immersing the 2(*h*/2) films in a 0.1 M solution of NaOH $_{(aq)}$ for a few seconds. Removing the capping layer and restoring the free surface in this way should result in the restoration of the free surface and the subsequent recovery of the thickness-dependent T_g that is observed in uncapped PtBMA films.

Following the removal of the capping layer and the restoration of the free surface, the film was rinsed in deionized water and then annealed at 413 K under vacuum (1×10^{-3} torr) for 10 h before being transferred to the sample stage of the ellipsometer, where its T_g was remeasured. The resulting T_g value is shown as the open diamond in Figure 3. As this figure shows, this value is comparable to the measured T_g of a freshly prepared uncapped PtBMA film of the same thickness. Hence restoring the free surface results in the recovery of the thickness-dependent T_g in ultrathin PtBMA films.

One potential concern is that the chemical treatment used to remove the capping layer may be responsible for altering the properties of the thin polymer films. To rule out this possibility, 6 nm thick uncapped PtBMA films were prepared by spin coating on to Al substrates. These were then annealed and immersed in 0.1 M NaOH $_{(aq)}$ for the same period of time as the 6 nm thick 2(*h*/2) sample described above. These samples were then rinsed in deionized water and then annealed at 413 K under vacuum (1×10^{-3} torr) for 10 h before being transferred to the sample stage of the ellipsometer, where their T_g value was determined. These samples were found to have measured T_g's that were identical to uncapped PtBMA films that did not experience the NaOH treatment (data not shown). A similar procedure was also repeated for 6 nm thick films that had been immersed in saturated NaCl $_{(aq)}$ solutions. These NaCl treated uncapped PtBMA films also displayed T_g values that were identical to untreated films of the same thickness (data not shown). These results give us confidence that the chemical treatment used to remove the capping layers and the presence of NaCl during the formation of the 2(*h*/2) films are not responsible for changing the properties of the thinnest polymer films. This indicates that any changes in the thickness dependence of the T_g of the PtBMA films must be due to the manipulation of the free surface.

These simple experiments therefore represent a complete manipulation of the free polymer surface. The production of the 2(*h*/2) films was shown to remove the effects of the free surface and to give rise to bulk like properties in all measured quantities for films as thin as 6 nm. Subsequent removal of the capping layer and restoration of the free surface resulted in thickness-dependent T_g values that are the same as those observed in freshly prepared uncapped PtBMA films.

Conclusions

These studies provide strong evidence that free polymer surfaces are essential for the existence of reduced T_g's in thin poly(tert-butyl methacrylate) films. They show that uncapped PtBMA films display T_g reductions below thickness values of ~40−50 nm that can be as large as 28 ± 1 K for films as thin as 6 nm. Simply coating the polymer films with a thin evaporated metal layer does not alter the thickness dependence of the T_g in these samples and is not sufficient

to remove the memory of the free surface. These results suggest that great care has to be taken when interpreting the results obtained from evaporatively capped polymer films. Samples that were prepared by placing two substrate supported films with their free surfaces in contact showed no T_g reductions for films as thin as 6 nm. This indicates that the $2(h/2)$ sample preparation procedure that was used to prepare these films is capable of removing the effects of the free surface, resulting in bulk like physical properties in nanoscale polymer samples.

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