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Examination of the influence of cooperative segmental dynamics on the glass transition and coefficient of thermal expansion in thin films probed using poly(*n*-alkyl methacrylate)s

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Abstract

The thermal behavior of thin films of a homologous series of poly(*n*-alkyl methacrylate)s supported on silicon substrates was probed using spectroscopic ellipsometry. Deviations from bulk behavior for the glass transition temperature (T_g) and coefficient of thermal expansion (CTE) were observed for films thinner than approximately 60 nm, consistent with most observations for confinement effects in polymer films. However, the extent of the decrease of CTE and the deviation in T_g are significantly influenced by the alkyl chain length. As the alkyl chain length is increased from methyl to *n*-octyl, the deviation from bulk behavior is significantly suppressed. This behavior is similar to that observed by Torkelson and coworkers (Physical Review Letters 2004; 92: 095702) for polystyrene films as small molecule diluents were added; this behavior was attributed to the decrease in size of the cooperative segmental dynamics, ξ_i(CRR), with addition of solvent. ξ_i(CRR) decreases as the alkyl chain length is increased; this is consistent with the hypothesis for the relationship between ξ_i(CRR) and confinement effects in thin polymer films. However, a two order of magnitude difference between the thickness of nanoconfinement onset and ξ_i(CRR) for poly(*n*-octyl methacrylate) results in uncertainty for ξ_i(CRR) as the origin of the nanoconfinement effect.

Keywords: Thin films; Glass transition; Coefficient of thermal expansion

1. Introduction

The physical behavior of polymers when geometrically confined to the nanoscale has fascinated scientists for more than a decade [1]. Deviations from bulk behavior has been observed for multiple material properties including glass transition [2–5], thermal expansion coefficients [6–8], modulus [9–11], crystallization [12,13], physical aging [14–16], segmental mobility [17,18], and chain diffusivity [19–21] amongst many. The bulk of the published studies of polymer thin films have focused on measuring the glass transition temperature (T_g) due to its strong interdependency with critical material properties such as modulus, diffusivity, and viscosity. These properties in thin films have significant implications for existing and emerging commercial applications including photoresists, hard drive lubricants, and thin film asymmetric membranes. The observed T_g in thin polymer films is dependent upon the interfacial chemistry [5,22–24], polymer tacticity [25], but generally is found to be independent of molecular weight [26–28]. A comprehensive picture to the physical properties of thin polymer films has begun to emerge, but the origins of the nanoconfinement effect are still subject of much speculation [2,29]. Forrest and Dalnoki-Veress suggested that the connection between the size scale of nanoconfinement effects and the fundamental length scale associated with glass formers has not been pursued to the extent necessary to exclude an interrelationship between these two length

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scales as the origin of nanoconfinement [4]. One difficulty in assessing this hypothesis is that a large majority of studies have focused specifically on two polymer systems: polystyrene and poly(methyl methacrylate).

Two studies from Torkelson and coworkers have hinted at the importance of chain stiffness and size scale of cooperative motion on the deviations of T_g from bulk behavior [28,30]. First, a decrease in the 'confinement' effect was observed when a small molecule diluent remains in the film, where bulk-like T_g was observed for all films when 9 wt% diluent was added as measured with fluorescence [30]. This small molecule effect was attributed to the decreased size scale of the cooperative dynamics (ξ_i(CRR)) with added diluent and the confinement size scale. This provided a connection between the nanoconfinement length scale and the size scale of a cooperatively rearranging region (CRR) as defined by Adam and Gibbs [31]. Thus by variation of the chemistry of the polymer segments such that ξ_i(CRR) is modified, the T_g confinement effect should be tunable. Second, a study on the substitution of side groups on styrenic polymers was also performed [28]. By addition of methyl or *tert*-butyl groups, variation in the strength of the T_g nanoconfinement was observed. Unfortunately, no obvious correlation between ξ_i(CRR) and T_g nanoconfinement was obtained, but nanoconfinement effects increased as the chain stiffness increased.

A systematic variation in ξ_i(CRR) with minimal chemistry variation would enable testing of this hypothesis as the origin of the thickness dependent behavior of thin polymer films. One series that meets this criterion is the poly(*n*-alkyl methacrylate)s. Since the 1950's, this series has generated significant interest towards understanding the relaxation properties in bulk polymers [32–34]. The cooperativity (N_α) of the α relaxation in this series decreases systematically as the alkyl chain length is increased from methyl to *n*-hexyl varying from $N_\alpha \approx 35$ to $N_\alpha \approx 1$ [35]. N_i is the number of monomeric units per CRR and is related to ξ_i(CRR) through the repeat molar volume. The wide variance in cooperativity for poly(*n*-alkyl methacrylate)s provides a route to systematically vary ξ_i(CRR) by simply changing the alkyl chain length.

In this paper, we present a systematic investigation of the influence of ξ_i(CRR) on the thermal properties of thin polymer films supported on silicon wafers using a series of poly(*n*-alkyl methacrylate)s. The properties of the thin film are measured using spectroscopic ellipsometry similar to prior studies of polystyrene and poly(methyl methacrylate) [36,37]. The T_g of the films was determined from the discontinuity in thermal expansions. One issue with the poly(*n*-alkyl methacrylate) series is that T_g for the bulk is below room temperature for alkyl chains larger than *n*-propyl. This limits the number of polymer systems that can be examined for deviations in T_g in thin films without the use of significant cooling. However, the coefficient of thermal expansion (CTE) of thin films is generally suppressed in comparison to the bulk, especially in the rubbery regime [7,8]. We thus extend the poly(*n*-alkyl methacrylate) series to higher alkyl groups by only examining the influence of confinement on the CTE of the polymer films. One interesting note on CTE of thin films is that unlike T_g, where positive or negative deviations in comparison to the bulk have been observed, suppression of the CTE has almost always been shown in thin polymer films. The CTE behavior in the glassy regime can show positive deviations or even negative CTE due to unrelaxed thermal stresses [38–41]. As the suppression in CTE in the rubbery regime generally occurs very near the thickness where deviations in T_g are observed [8], we expect that the influence of ξ_i(CRR) on the CTE will mirror T_g. This paper presents a systematic examination of the impact of the cooperative segmental dynamics on the observed confinement effects in polymer thin films.

2. Experimental

2.1. Materials and film preparation

A series of poly(*n*-alkyl methacrylate)s were obtained from Scientific Polymer Products: poly(methyl methacrylate) (PMMA, $M_w = 75{,}000$ g/mol, $T_g = 100.9$ °C), poly(ethyl methacrylate) (PEMA, $M_w = 250{,}000$ g/mol, $T_g = 70.1$ °C), poly(*n*-propyl methacrylate) (PPMA, $M_w = 250{,}000$ g/mol, $T_g = 36.1$ °C), poly(*n*-butyl methacrylate) (PnBMA, $M_w = 180{,}000$ g/mol), poly(*n*-hexyl methacrylate) (PnHMA, $M_w = 400{,}000$ g/mol), poly(*n*-octyl methacrylate) (PnOMA, $M_w = 100{,}000$ g/mol). Since polydispersity and molecular weight do not appear to influence the nanoconfinement effect for polystyrene [28], polydisperse commercial polymethacrylates have been utilized in this study. One relatively monodisperse PMMA sample (denoted as mPMMA, Polymer Source, $M_w = 91{,}000$ g/mol, PDI = 1.3, $T_g = 105$ °C) was used for comparison purposes to determine if polydispersity impacts the thin film behavior. The T_gs listed above were obtained from thick films measured with ellipsometry. These values are in good accord with the nominal T_g listed by the manufacturer. All films were prepared dissolving the poly(*n*-alkyl methacrylate) in toluene (Aldrich) at varying polymer concentration (0.16 wt%–5 wt%) and spin coating on to clean silicon wafers. Prior to spin coating, all silicon wafers were cleaned using piranha solution (30% hydrogen peroxide, 70% sulfuric acid) for 10 min at 90 °C and then rinsed liberally with deionized (DI) water. The polymer films were annealed at 160 °C for 12 h under vacuum to minimize non-equilibrium effects from spin coating.

2.2. Ellipsometry

The thickness and refractive index of the polymer films as a function of temperature were determined using a spectroscopic ellipsometer (M-2000, J.A. Woollam Co., Inc.). A fixed incident angle of 70° was utilized while the elipsometric angles (Ψ and Δ) were measured over the wavelength range from 250 to 1700 nm. Thermal response of the films was measured upon cooling from 160 °C at 1.3 °C/min in a nitrogen purge atmosphere. The measured Ψ and Δ data were fit recursively using a layered model (polymer film: native oxide: silicon) to yield the film thickness and refractive index of the poly(*n*-alkyl methacrylate) film at each measured temperature.

Thermal induced variation in the refractive index of the silicon substrate was included in the model. Fig. 1 illustrates representative experimental ellipsometry curves with the best fit of the PEMA film optical properties and thickness shown by the solid lines. Reproducibility of the film thickness and expansion was within 2% on duplicate samples.

2.3. Glass transition (T_g) and coefficient of thermal expansion (CTE) determination

There have been multiple methods proposed for determining the glass transition temperature (T_g) in thin films. These include the intercept of regression lines in the glassy and rubbery region and full curve fitting using an empirical model [8,27,42–45]. By assuming a tanh(T) profile for the transition between thermal expansion coefficients in the glass and melt, integration yields an empirical expression for determining T_g [4,37]:

$$h(T)=w\left(\frac{M-G}{2}\right)\ln\left(\cosh\left(\frac{T-T_g}{w}\right)\right)+\left(T-T_g\right)\left(\frac{M+G}{2}\right)+c \tag{1}$$

where h is the film thickness, M and G are the linear thermal expansion of the melt and glass, respectively, w is the width of the transition, and c is the value of the film thickness at $T=T_g$. This expression has been applied in the past to determine T_g with w assumed to be 2 °C. We find that there is no difference within error of the glass transition temperature calculated with $w=2$ °C and if w is freely fit. Additionally even for very thin films (<10 nm), the reproducibility of the measured T_g was within one standard deviation (based upon the regression of the fit to Eq. (1)) for multiple heating–cooling cycles. No degradation in the samples during the temperature cycles was readily observed.

To determine T_g using Eq. (1), the expansion of the films in the rubbery and glassy regimes is required. These are determined from linear least squares regression fits of the film thickness versus temperature. Since the longer alkyl chains of the polymethacrylates leads to a decrease in T_g, the glass transition in some of the higher alkyl systems was not measured as T_g was below ambient temperature. However, the coefficient of thermal expansion (CTE) of thin polymer films is also known to be thickness dependent [7,27]; thus providing a route to probe the influence of the alkyl chain length on the physical properties of thin films. To calculate the CTE of the rubbery regime, a reference thickness at 160 °C was used in all cases as this is well above the glass transition temperature. As this is an arbitrary condition, the CTE for the shorter alkyl chain polymethacrylates was also calculated using a fixed reference above T_g (+30 °C) of the film.

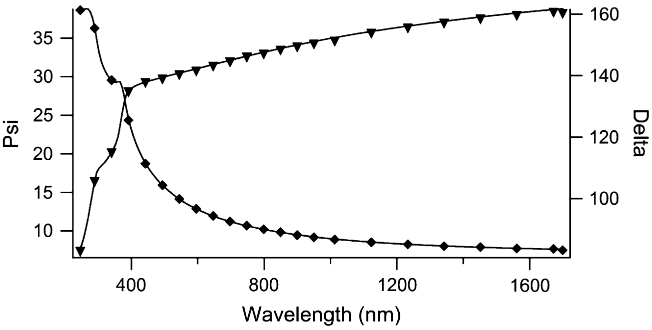

Fig. 1. Representative spectroscopic ellipsometry data at 70° of the ellipsometric angles; Ψ (▼) and Δ (◆). The typical quality of the fit to a layered model is shown by solid lines.

3. Results and discussion

Spectroscopic ellipsometry was used to measure the thermal properties of thin films of poly(n-alkyl methacrylate)s supported on silicon wafers. Previous work by Pochan et al., demonstrated that the CTE of PMMA thin films deviates from bulk behavior below approximately 60 nm [7]. A similar behavior is observed for the entire series of methacrylate polymers examined here. Fig. 2 illustrates the change in CTE of PEMA films as the film thickness is decreased below 60 nm. Two distinct regimes of thermal expansion are observed for all PEMA films corresponding to glassy and rubbery behaviors. There is a dramatic decrease in the CTE of the rubbery region while the glassy region remains approximately constant. A comparison of bulk behavior in the rubbery region is illustrated by dashed lines in Fig. 2. The 196 nm film can be considered a bulk film because there is a universal collapse of physical properties for most polymer films approximately thicker than 100 nm [36,41], except several noted exceptions where deviations can exceed 300 nm [28,46]. The invariance of CTE from near 200 nm–60 nm suggests that the thick films of PEMA behave in a bulk-like manner. Additionally the T_g of these 'thick' films is in agreement with the expected T_g for the bulk. However, when the thickness is decreased to 55 nm, a minor decrease in the CTE of the film is observed in comparison to the bulk. As the film thickness is further decreased to 7 nm, a significant suppression in the CTE in comparison to the bulk is found. This behavior for the PEMA is consistent with the changes in CTE for PMMA observed previously [7].

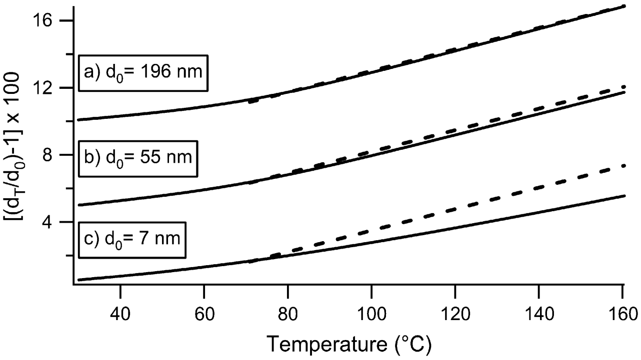

Fig. 2. Thermal expansion of thin PEMA films. As film thickness decreases below approximately 60 nm, deviations from bulk behavior are observed. Solid lines represent data for different film thicknesses; dashed lines represent the thermal expansion behavior of the bulk. The data are offset vertically for clarity.

However, the extent of the suppression of CTE is strongly dependent upon the alkyl chain length as illustrated in Fig. 3. For all of the poly(*n*-alkyl methacrylate) films examined, bulk-like CTE behavior is observed for films thicker than 100 nm, consistent with most observations in the literature. Similarly, there is an increasing suppression of CTE as film thickness decreases below the threshold thickness of 60–100 nm. The extent of this suppression is, however, muted as the *n*-alkyl chain length is increased. A 8.5 nm thick PMMA film has a CTE that is 75.5% of the bulk, whereas the CTE of a PnOMA film of identical thickness is 97% of the bulk CTE of PnOMA. However, the large variation in T_g between these polymethacrylates may lead to some artifacts based upon the use of a constant reference temperature (160 °C) for calculating CTE. For thin polystyrene films, a significant temperature dependence for the CTE as a function of film thickness was found [39]. To avoid ambiguities, an alternative representation for the CTE data is presented in Fig. 3b where the reference temperature for CTE is correlated to the glass transition temperature ($T_g + 30$ °C). This change in reference state does not alter the trend in CTE changes as a function of *n*-alkyl chain length. However, in all cases, temperatures well above T_g are utilized. This systematic variation in confinement behavior of polymer thin films with respect to polymer chemistry provides some insight into the origins of the deviations in physical properties of thin films in comparison to the bulk.

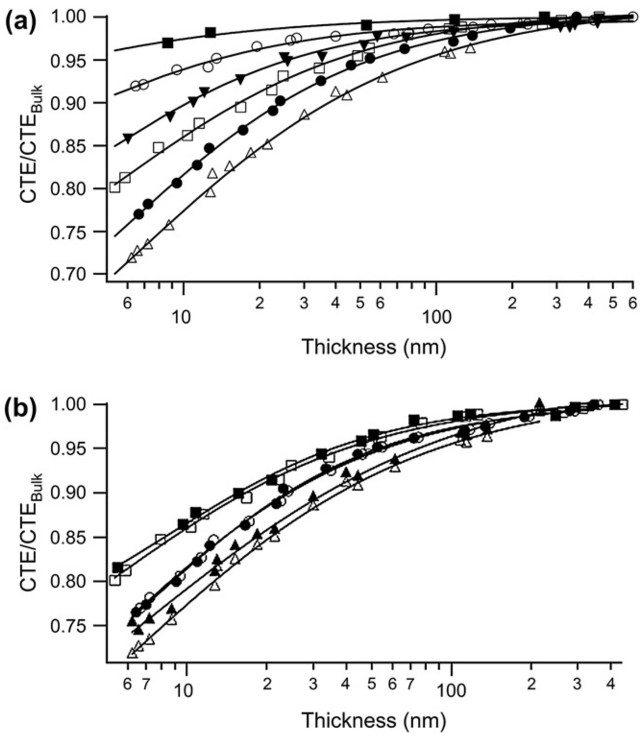

Fig. 3. (a) Effect of film thickness on CTE for PMMA (△), PEMA (●), PPMA (□), PnBMA (▼), PnHMA (○) and PnOMA (■). As alkyl chain length is increased, deviations from bulk behavior are suppressed in the thin films. A constant reference temperature of 160 °C is used; (b) comparison of reference state for CTE on the film thickness effect for PMMA (△, ▲), PEMA (○, ●), PPMA (□, ■) using 160 °C (open symbols) and $T_g + 30$ °C (closed symbols).

Work from Torkelson and coworkers demonstrated that a residual small molecule diluent in thin polymer films can cause a systematic decrease in the 'confinement' effect with concentration; in this case the physical parameter of interest was T_g [30]. At sufficient diluent concentration, T_g was found to be invariant of film thickness. The origin for this effect is correlated to the size scale of cooperative dynamics, ξ_i(CRR), [30] which has been proposed as the intrinsic length scale for nanoconfinement [4,47]. As diluent is added to the system, ξ_i(CRR) decreases such that nanoconfinement is no longer present. Several different polymer systems appear to follow this correlation between ξ_i(CRR) and nanoconfinement effects [48], but it has not been systematically investigated. Although this hypothesis was developed for understanding variations in T_g behavior of thin polymer films, it is equally applicable in elucidating the origins of deviations in CTE. The series of poly(*n*-alkyl methacrylate)s have been studied for many years in attempts to understand T_g and relaxation behavior of bulk polymer systems [32–34]. It is well established that ξ_i(CRR) decreases as the *n*-alkyl chain length is increased; $\xi_{PMMA}(CRR) = 1.71$ nm, $\xi_{PEMA}(CRR) = 1.51$ nm, $\xi_{PnPMA}(CRR) = 1.44$ nm, $\xi_{PnBMA}(CRR) = 1.38$ nm, $\xi_{PnHMA}(CRR) = 0.94$ nm, and $\xi_{PnOMA}(CRR) = 0.62$ nm [35]. An interesting note is that ξ_{PMMA}(CRR) is approximately $(1/2)\xi_{PS}$(CRR) and the nanoconfinement effect for PMMA that is not strongly interacting with a substrate is generally much less than that observed for polystyrene (PS) [42,49]. Thus it appears that longer alkyl side chains on the polymethacrylate have a similar effect to the addition of diluents to polymer thin films, both in terms of suppression of nanoconfinement effects and also a decrease in ξ_i(CRR). The hypothesis that ξ_i(CRR) is correlated with nanoconfinement [30] appears to hold based upon the data presented here for a series of poly(*n*-alkyl methacrylate)s.

However, recently, Torkelson and coworkers examined styrenic analogs with additional methyl or *tert*-butyl groups, either on the vinyl backbone (α-position) or at the *para*-position on the aromatic ring [28]. The glass transition of these materials in thin films was studied using intrinsic fluorescence of the aromatic ring. They observed significant variation in the strength of the T_g confinement based upon the polymer chemistry. However, no obvious correlation between the size scale of cooperative motion, ξ_i(CRR), and the nanoconfinement effect could be determined [28]. Thus, the correlation between ξ_i(CRR) and nanoconfinement does not appear to be universal for all polymer systems. There are several key distinctions between this study of poly(*n*-alkyl methacrylate)s and the styrenic polymers examined by Torkelson and coworkers that could explain this discrepancy. The variation in the later study considered methyl and *tert*-butyl additions to styrene at α- and *para*-position. The steric bulk of the *tert*-butyl group increases the stiffness of the polymer chain, which also has been hypothesized as a key parameter in determining nanoconfinement [8,28]. An increase in the chain stiffness leads to an increase in the extent of nanoconfinement. Further, the difference between α- and *para*-methyl styrene polymers changes the conformation of the polymer chains and interactions with the free surface and substrate. Changes in availability of interacting groups have been attributed to the tacticity dependent behavior of PMMA where an increase in T_g is observed for i-PMMA, while a decrease in T_g is observed for s-PMMA [25]. For the poly(*n*-alkyl methacrylate) series examined in this work, the variation in the chemical structure is simply extending the length of the alkyl side chain. This does not involve any sterically hindered groups, nor is the structure of the polymer backbone altered. One discrepancy is that the nanoconfinement effects begin to manifest at approximately 60–100 nm irrespective of the alkyl methacrylate examined, while ξ_i(CRR) varies by nearly a factor of three (1.71–0.62 nm). Moreover, ξ_i(CRR) is almost two orders of magnitude smaller than the length scale at which nanoconfinement is first observed. This large discrepancy in size scale between the size scale of CRR and nanoconfinement casts some doubt on the direct correlation between these quantities as the origin of these nanoconfinement effects. However, the chain stiffness hypothesis by Torkelson and coworkers [28] is not supported by the data presented here. The persistence length of poly(*n*-alkyl methacrylate) chains increases as the alkyl chain length is increased [50]. The persistence length is generally directly correlated with the stiffness of polymeric chain; thus, the behavior is observed for this poly(*n*-alkyl methacrylate) series is counter to the hypothesis that nanoconfinement effects increase with an increase in chain stiffness.

From the data illustrated in Fig. 2, a discontinuity in the CTE of the films is clearly present and indicative of the glass transition. The intercept of the linear fits of the glassy and rubbery CTE can be used to determine T_g, but deviations from linearity occur near T_g. Thus, the range of data fit to determine CTE can dramatically influence the calculated T_g for the thin films. To avoid arbitrary exclusion of data near T_g, a full fit of the thermal expansion of the films using Eq. (1) was utilized to determine T_g following the procedure of Forrest and Dalnoki-Veress [4]. Following their example, the width of the transition, *w*, was initially fixed to be 2 °C. However, this appeared arbitrary, so *w* was allowed to freely fit along with T_g. This provided a better fit of the data, but the calculated T_g was within error of the value found by fixing *w* at 2 °C. Thus, a fixed *w* for the transition does not artificially influence the calculated T_g. Fig. 4 illustrates the film thickness dependence of T_g for the series of poly(*n*-alkyl methacrylate)s. Similar to the observations for CTE, a decrease in T_g is observed for films thinner than approximately 60 nm and the extent of this depression is suppressed as alkyl chain length is increased. One issue with the poly(*n*-alkyl methacrylate) series is that T_g for the bulk is significantly reduced with increasing chain length. For alkyl chains longer then *n*-propyl, bulk T_g drops below room temperature and were not measured due to lack of cooling capabilities. However, similarities with suppression results in CTE suggest that the observed trend in T_g will continue for higher alkyl groups for poly(*n*-alkyl methacrylate)s. Prior arguments regarding the correlation of ξ_i(CRR) with confinement effects are consistent with the observations of T_g as well.

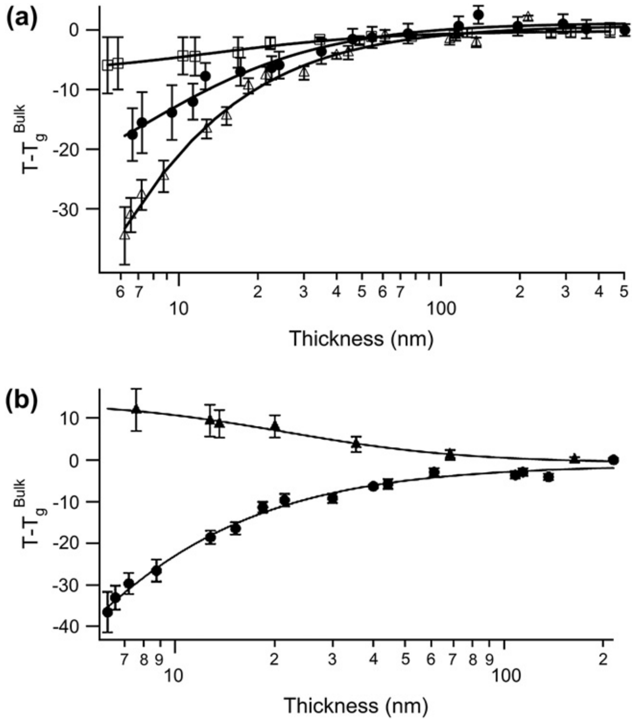

Fig. 4. (a) Effect of film thickness on T_g for an homologous series of methacrylate polymers: PMMA (△), PEMA (●) and PPMA (□). As the local segmental mobility increases, a suppression in the deviation of the glass transition from the bulk ($T - T_g$) was observed. The error bars represent one standard deviation due to experimental uncertainty of the measurement; (b) effect of PMMA source on the thin film behavior. An increase in T_g with decreasing film thickness is observed for the monodisperse PMMA (▲), while a decrease in T_g is found for the polydisperse PMMA (●).

However, the thin film behavior of PMMA on silicon wafers has been studied extensively in the past and almost always an increase in T_g is observed as the film thickness decreases, or T_g is found to be independent of film thickness [5,23,37,51,52]. In one case where a decrease in T_g was observed, the PMMA was syndiotactic [25], while isotactic PMMA has an increase in T_g similar to that observed for the typically studied atactic PMMA [53]. More recently, a decrease in T_g for PMMA supported on a silicon wafer was reported where the polymer was 79% syndiotactic [54]. The commercial PMMA utilized in this study is atactic and thus an increase in T_g would be expected based upon published reports for thin PMMA films. However, there are several notable differences between this PMMA sample and those examined in the literature previously. Due to concerns about molecular weight effects, previous studies utilized monodisperse PMMA [5,23,37,51,52]. To check if this was the source for the discrepancy, the influence of film thickness on T_g for a relatively monodisperse PMMA (mPMMA) was examined. Consistent with prior studies, the T_g of the mPMMA film increases as the film thickness is decreased below approximately 50 nm as illustrated in Fig. 4b.

PMMA films exhibit a rich behavior that is not found for PS as initial reports examining different tacticity have uncovered [53]. However, the polymers examined here are both atactic and thus the observed behavior would not be expected based upon these previous studies. There are other differences between these two PMMA materials that result from their methods of polymerization. These differences could influence the local structure of the PMMA and lead to the decrease in T_g for the polydisperse sample. Likewise, an alternative simple explanation for the differences is the polydispersity of the polymers. However, from these data, it is not possible to determine the exact source for the decrease in T_g for the polydisperse PMMA films. This unusual behavior for PMMA warrants additional studies.

The unusual behavior of the PMMA film in Fig. 4a is reproducible, but not yet understood. However, we can begin to examine the T_g behavior for the series of poly(*n*-alkyl methacrylate)s with confidence as the source for all these polymers is identical. When comparing the architectural effects on T_g of thin films between the series of poly(*n*-alkyl methacrylate)s and different styrenic polymers, one additional striking difference that was not mentioned previously is the thickness where the onset of nanoconfinement occurs. As shown in Fig. 4, although the extent of the T_g depression upon confinement is dependent upon the alkyl chain length, the onset thickness of deviations from bulk T_g is insensitive to the specific chemistry of the poly(*n*-alkyl methacrylate). This transition occurs at approximately 60 nm, which is also the onset thickness for PS. For small segmental variations to PS, the location of the deviation from bulk T_g behavior can be dramatically shifted to larger thickness (90 nm for poly(α-methylstyrene (PαMS) [48,55], >300 nm for poly(4-*tert*-butylstyrene) (P4TBS) [28]). This shift is not correlated with ξ_i(CRR) of the bulk material. One apparent correlation between the extent of T_g reduction and polymer backbone structure is the bulk T_g of the polymer. As bulk T_g is decreased, the nanoconfinement effect is suppressed. This holds not only for the poly(*n*-alkyl methacrylate) series examined here, but also for the styrenic polymers examined previously. T_gs for PS and poly(4-methylstyrene) are similar and their thin film behavior is nearly identical as well [28]. P4TBS and PαMS both have elevated T_gs and exhibit onsets of nanoconfinement at much larger length scales in comparison to PS [28,48]. This is not as elegant as ξ_i(CRR) being the dominant length scale for nanoconfinement, but rather suggests that the local segmental entropy is responsible for nanoconfinement. Studies of issues related to the conformational changes in thin films especially at interfaces and changes in film dynamics near interfaces as a result of nanoconfinement as a function of repeat unit structures are most likely necessary to provide a better understanding of the nanoconfinement effect in thin polymer films.

4. Conclusions

The nanoconfinement of poly(*n*-alkyl methacrylate)s with alkyl chains ranging from methyl to *n*-octyl is investigated through the changes in the thermal properties of these thin films; specifically CTE and T_g. Depression in both CTE and T_g is found for films less than 60 nm, irrespective of the alkyl side chain length for the commercial polymers. The behavior of PMMA can be altered by switching from the polydisperse PMMA to a more monodisperse PMMA, where an increase in T_g is found for thin films. This latter result is consistent with extensive literature on the behavior of PMMA on silicon wafers. The impact of the alkyl side chain length for free radical polymerized poly(*n*-alkyl methacrylate)s can be determined from this study. The extent of the deviation from bulk behavior is strongly dependent upon the repeat unit structure. Longer alkyl side chains mute the nanoconfinement effect.

Chain stiffness has been hypothesized to be responsible for nanoconfinement as well, where increasing chain stiffness results in enhanced nanoconfinement [28]. For the poly(*n*-alkyl methacrylate) series examined, the persistence length, which is generally related to chain stiffness, increases with alkyl chain length; this is inconsistent with the chain stiffness hypothesis. Conversely, the size scale of the cooperative segmental dynamics (ξ_i(CRR)) has also been attributed to the nanoconfinement effect [4]. It is well established that ξ_i(CRR) monotonously decreases with increasing alkyl chain length. Thus, the observed thin film behavior is consistent with this hypothesis for the origins of nanoconfinement. However, the length scales involved for the onset of nanoconfinement versus ξ_i(CRR) differ by 1–2 orders of magnitude; thus, it is unclear if it is reasonable for ξ_i(CRR) to be responsible for nanoconfinement. Additional studies regarding how the local dynamics and interfacial structure change upon nanoconfinement as a function of repeat unit structure are likely necessary to provide improved understanding of the origins of nanoconfinement in thin polymer films.

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