

Two Simultaneous Mechanisms Causing Glass Transition Temperature Reductions in High Molecular Weight Freestanding Polymer Films as Measured by Transmission Ellipsometry

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We study the glass transition in confined polymer films and present the first experimental evidence indicating that two separate mechanisms can act simultaneously on the film to propagate enhanced mobility from the free surface into the material. Using transmission ellipsometry, we have measured the thermal expansion of ultrathin, high molecular-weight (MW), freestanding polystyrene films over an extended temperature range. For two different MWs, we observed two distinct reduced glass transition temperatures (T_g 's), separated by up to 60 K, within single films with thicknesses h less than 70 nm. The lower transition follows the expected MW dependent, linear $T_g(h)$ behavior previously seen in high MW freestanding films. We also observe a much stronger upper transition with no MW dependence that exhibits the same $T_g(h)$ dependence as supported and low MW freestanding polymer films.

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The study of the glass transition in confined geometries is an active field of research in polymers [1–8], small molecules [9–11], colloids [12,13], and simulations [14–18]. Confinement is seen as a method of perturbing the length scales associated with cooperativity in order to gain insight into the size, arrangement, and correlation of cooperatively rearranging regions (CRRs) [1,5,13]. Polymer systems have been studied to the greatest extent because of the ease with which ultrathin films of known thickness can be made, and for their technological importance in applications such as microelectronics and gas separation membranes. The observations and understanding of how the glass transition temperature (T_g) can increase or decrease by many tens of Kelvin near a boundary in polymer systems has influenced studies in colloids [12], small molecules [11], and optoelectronics [19]. Of particular interest is the mechanism(s) by which the enhanced mobility near a free surface is propagated into the material over large distances of several tens of nanometers, demonstrating that dynamics in neighboring CRRs can be correlated over large distances [5,20,21].

In polymer systems, reductions in T_g observed with decreasing film thickness h can be classified into two qualitatively different behaviors [1,22,23]. Supported films [3,5,24–26], and freestanding films of low molecular-weight (MW) chains [22,23], exhibit decreases in T_g that follow an empirical relation [24]: $T_g(h) = T_g^{\text{bulk}}[1 - (A/h)^\delta]$. T_g reductions of ~ 25 K for 15 nm thick polystyrene (PS) films supported on silica are typical, with no MW dependence observed in supported films for M_n ranging between 5 and 3000 kg/mol [25,26]. Low MW ($M_n < 350$ kg/mol) freestanding PS films show qualitatively the same $T_g(h)$ reduction as supported films, but the presence of two free surfaces results in T_g reductions that

are essentially twice as large for a given film thickness [22]. Originally proposed by Keddie, Jones, and Cory, this functional form was based on the notion that some region of the film near the free surface would experience faster dynamics [24]. This initial assumption has since been experimentally confirmed [5], with results indicating a gradient in dynamics emanating from the free surface that extends several tens of nanometers into the material, and appears to be correlated with cooperative motion [21,22,25]. This gradient in dynamics manifests itself as a broadening of the glass transition with decreasing film thickness, and its effects have been linked to other properties such as changes in physical aging rate [20,21] and modulus [27] with decreasing film thickness. There is no chain connectivity associated with this mechanism and similar effects are seen in colloidal systems [12] and small molecules [9–11]. The most promising theoretical model for this behavior is a percolation model proposed by Long and Lequeux [28] that has since been further refined for thin films [14] and polymer nanocomposites [18].

In contrast, high MW freestanding films exhibit a qualitatively different behavior with a MW dependent linear reduction in T_g below some critical thickness h_0 : $T_g(h) = T_g^{\text{bulk}} - \alpha(h_0 - h)$, for $h < h_0$ [1,22,23,29–32]. The slope α of the linear decrease, as well as h_0 , both depend on MW, and the transition itself always appears sharp. T_g reductions as large as 85 K have been measured for 35 nm thick freestanding films of PS ($M_w = 1250$ kg/mol) [31]. This mechanism clearly depends on chain connectivity, but no direct correlation with chain size has yet been found [1]. The only theoretical model that has been proposed for this behavior is the suggestion by de Gennes of a possible “sliding mode” available to chain segments occurring between mobile surface layers that could impart faster

dynamics from the free surface deeper into the film [33,34].

This strong qualitative difference between the two observed $T_g(h)$ dependencies has led some to propose that two separate mechanisms could be responsible for this behavior [22,23,28]. In fact, Long and Lequeux suggested that the “... de Gennes sliding effect, which applies for large polymer chains, and our proposed mechanism are compatible and can take place simultaneously ...” [28]. Here, we report the first experimental evidence of two separate mechanisms occurring simultaneously in high MW freestanding films. Using transmission ellipsometry to measure the thermal expansion of high MW freestanding PS films over an extended temperature range, we have observed two separate and distinct glass transitions acting simultaneously within high MW freestanding PS films of $M_n = 820$ and 1928 kg/mol. Both T_g 's are reduced from the bulk value. The lower transition is linear in $T_g(h)$ and shows the anticipated MW dependence previously observed in these films [6,22,29–31,35–38]. The upper transition, not previously seen in these films, is much stronger and follows the Keddie-Jones-Cory functional form [24] with $T_g(h)$ values in agreement with those expected for low MW freestanding PS films [22]. We envision these dual T_g 's as reflecting two separate population dynamics within the film resulting from two separate mechanisms simultaneously imparting enhanced mobility from the free surface deeper into the material.

High MW polystyrene with number-average molecular weight $M_n = 820$ kg/mol and polydispersity $M_w/M_n = 1.14$, or $M_n = 1928$ kg/mol and $M_w/M_n = 1.17$, were dissolved in toluene and spin coated onto freshly cleaved mica. Samples were vacuum annealed at ~ 405 K ($> T_g^{\text{bulk}} + 30$ K) for at least 16 h, followed by a slow cool (< 0.5 K/min) to room temperature. Although there have been renewed concerns regarding whether such annealing is sufficient [39], we note that our procedure is comparable to the annealing protocol used in the original studies and previously deemed to be sufficient [1,22,29–31]. Films were subsequently floated onto stainless steel sample holders to create freestanding films across a 4.7 mm opening. Transmission ellipsometry was used to measure the temperature dependence of the film thickness $h(T)$ and index of refraction $n(T)$ of the freestanding films. Temperature ramps consisted of an initial heat to 383 K (391 K for bulk films) to remove wrinkles and obtain flat films, followed by multiple ramps at 0.5 K/min. Typically the temperature was ramped several times through the lower T_g , with a limited number of ramps through the higher temperature T_g where hole formation is more prevalent [40,41]. The T_g values were determined by fitting each transition independently to the same functional form used by Dalnoki-Veress *et al.* [31] (the fitting equation and other experimental details are provided in the Supplemental Material [42]). The width of the transition was fixed to 2 K for the lower

temperature T_g (following Ref. [31]) and 10 K for the higher temperature T_g , representative of the broadening typically associated with this mechanism [26]. The T_g of the film was taken as the weighted average of typically 4–7 ramps for the lower T_g and 2–4 ramps for the upper T_g . We also fit the upper transition using the more common method of finding the intercept of two linear fits above and below the transition [5,6,22–24,26,29,30,32,38], which resulted in T_g values that were within experimental error of the first fitting method. The bulk value of T_g , $T_g^{\text{bulk}} = 373 \pm 2$ K, was determined from the average of films with thicknesses > 150 nm.

Figure 1 graphs the thickness-temperature profiles for three representative freestanding films of PS with $M_n = 820$ kg/mol for thicknesses of 166.5, 54.7, and 33.3 nm, all measured on cooling. The thickest film has only a single bulk $T_g = 370 \pm 2$ K, while the thinnest films exhibit two reduced glass transitions of $T_g = 364 \pm 2$ and 338 ± 3 K for the 54.7 nm thick film and $T_g = 351 \pm 3$ and 308 ± 3 K for the 33.3 nm thick film. The lines shown in the figure are drawn to correspond to the slopes obtained from the fitting equation with the lines extended beyond the transition to indicate where they cross. The Supplemental Material [42] includes a figure showing both $n(T)$ and $h(T)$ for the 33.3 nm thick film, demonstrating that the lower and upper T_g 's are observed at the same temperature in both the index of refraction and film thickness. Also included are $n(T)$ and $h(T)$ data for a 53.2 nm thick freestanding PS film with $M_n = 1928$ kg/mol, demonstrating that ultrathin freestanding films of this MW likewise exhibit two reduced T_g 's.

Figure 2 plots all of our measured T_g values relative to T_g^{bulk} as a function of film thickness for both MWs, $M_n = 820$ (triangles) and 1928 (squares) kg/mol. There are two reduced T_g 's for each individual thin film with $h < 70$ nm. The lines and curves in the figure are not fits, but represent the existing literature data for freestanding PS films. The solid black lines represent the expected $T_g(h)$ data for the two MWs, calculated for $M_w = 934$ and 2257 kg/mol based on the scaling analysis provided by Dalnoki-Veress *et al.* in Ref. [31]. We note that the empirical scaling used by Dalnoki-Veress *et al.* [31] to collapse these MW dependent T_g reductions only scales with the *weight-average* MW (M_w), and not the *number-average* MW (M_n), suggesting a connection to chain length for this mechanism. The dashed curve is a fit of the Keddie-Jones-Cory functional form to the low MW freestanding PS film $T_g(h)$ data by Mattsson *et al.* [22]. Our data for the lower T_g values exhibit a MW dependence and are in excellent agreement with the anticipated high MW $T_g(h)$ data from Ref. [31] that have been previously observed in these films [6,22,29,30,35–38]. The upper T_g values that correspond to the much stronger transition not previously observed in these films are in excellent

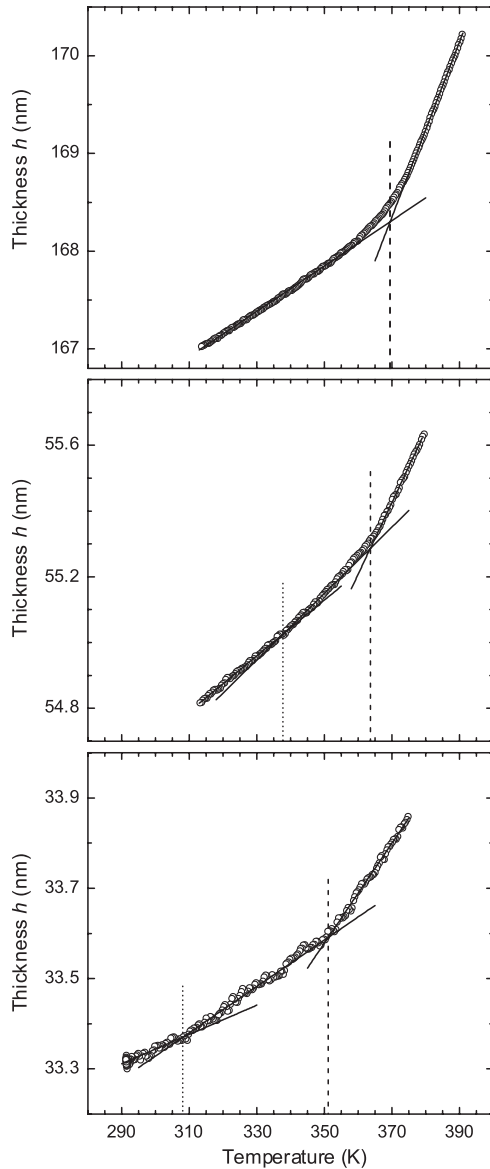


FIG. 1. Film thickness as a function of temperature for three high MW ($M_n = 820$ kg/mol) PS freestanding films of thicknesses 166.5, 54.7, and 33.3 nm. The vertical dashed lines indicate the measured T_g of 370 ± 2 K for the bulk 166.5 nm thick film and the two reduced T_g 's for the thinner films: 364 ± 2 and 338 ± 3 K for the 54.7 nm thick film, and 351 ± 3 and 308 ± 3 K for the 33.3 nm thick film. The fit lines are described in the text.

agreement with the T_g reductions from Ref. [22], which have been previously observed in only low MW freestanding PS films. We have highlighted as solid symbols the two T_g 's measured for a single film of $M_n = 820$ kg/mol that is 32.9 nm thick, $T_g = 353 \pm 1.0$ K and 294 ± 4.5 K, and for a single film of $M_n = 1928$ kg/mol that is 53.2 nm thick, $T_g = 370 \pm 1.5$ K and 310 ± 2.0 K. For both films, the two independent, reduced T_g 's are separated by nearly 60 K.

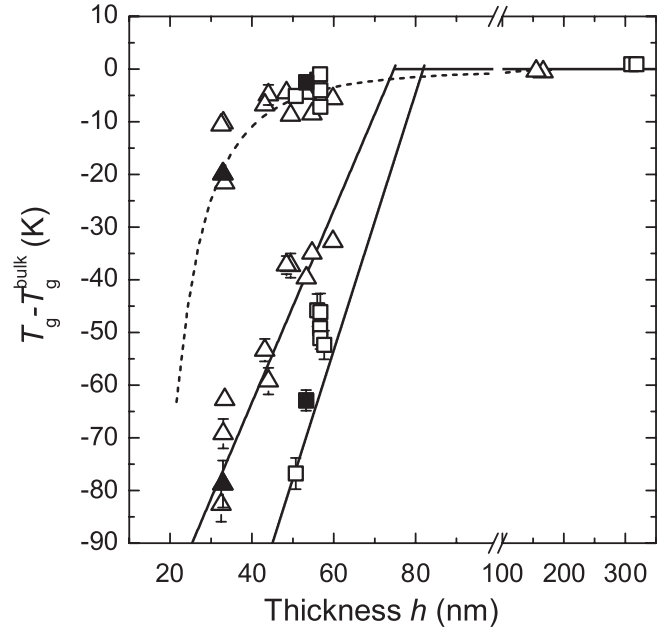


FIG. 2. $T_g - T_g^{\text{bulk}}$ as a function of film thickness for high MW freestanding PS films, $M_n = 820$ (triangles) and 1928 (squares) kg/mol. Two reduced T_g 's for each ultrathin film <70 nm thick are shown; the error is the size of the symbols or smaller except where shown. Highlighted as solid symbols are the two T_g 's, separated by nearly 60 K, measured for a single film: solid triangles correspond to a 32.9 nm thick film of $M_n = 820$ kg/mol, with $T_g = 353 \pm 1.0$ K and 294 ± 4.5 K, and solid squares correspond to a 53.2 nm thick film of $M_n = 1928$ kg/mol, with $T_g = 370 \pm 1.5$ K and 310 ± 2.0 K. The solid black lines represent the anticipated $T_g(h)$ for our MW, calculated for $M_w = 934$ and 2257 kg/mol based on the scaling analysis provided by Dalnoki-Veress *et al.* in Ref. [31]. The dashed curve is a fit of the Keddie-Jones-Cory functional form to the low MW freestanding PS film $T_g(h)$ data by Mattsson *et al.* [22].

For both MWs, the lower transition (which is quite weak and narrow) is in excellent agreement with the anticipated MW dependent T_g 's for these films based on the original work [22,29–31], and since verified by others [6,35–38], for high MW freestanding films. However, for all films, we unmistakably observe a much stronger upper T_g that is broader. Based on the change in slope, i.e., thermal expansion coefficient of the material, we determine that upon cooling from the melt to the glass, the majority of the film ($\sim 90\%$) solidifies at the upper transition, while only a small fraction ($\sim 10\%$) remains mobile to much lower temperatures, solidifying at the lower transition. These two T_g 's do not simply correspond to values representing the free surface and interior of the film. The free surface region is represented in the breadth of the upper transition that follows the Keddie-Jones-Cory functional form [24], and has been previously correlated with a gradient in dynamics originating from the free surface that encompasses both the free surface region and the interior of the

film [5,6,21,22]. This reasoning is most clearly supported by the layer model analysis of Ref. [22] where the reduced $T_g(h)$ observed in low MW freestanding films, which is in quantitative agreement with our upper transition, was interpreted as corresponding to a measured average of a reduced surface T_g and a bulklike interior film T_g . Further support is obtained from recent fluorescence anisotropy measurements on freestanding films by Paeng *et al.*, who observed two dynamical populations in the segmental dynamics in ultrathin freestanding films, both found to be independent of MW and within the temperature range of the upper transition [7]. They attributed the faster population as corresponding to the free surface region. We note, all their measurements on high MW films were at temperatures significantly above that where the lower, MW dependent transition occurs. Thus, their measurements would not have been sensitive to dynamics associated with the mechanism corresponding to the lower transition. The breadth of the upper transition corresponds to the solidification of $\sim 90\%$ of the film (matrix), while the lower MW dependent transition represents some smaller $\sim 10\%$ fraction of the material with extremely fast dynamics. At present, we cannot provide information as to the location of this faster population within the film, but the cause of this very fast population is related to the chain connectivity of the polymer resulting in faster dynamics for higher MWs. In addition, the narrow temperature range associated with this transition suggests a rather homogeneous dynamical population.

Our results measuring two independent, reduced glass transitions in ultrathin high MW freestanding polymer films, a strong upper transition with no MW dependence and a much weaker lower transition with a distinct MW dependence, represent the first experimental evidence of two separate mechanisms acting *simultaneously* to impart enhanced dynamics to these nanoconfined films. Previous studies have only observed a single glass transition [6,22,29–31,35–38,43,44], with the lower (weaker) transition being the “accepted” T_g for high MW freestanding films [6,22,29–31,35–38]. However, there are a few studies that have observed dynamics consistent with the presence of the upper transition in high MW films [7,43–47]. Svanberg used broadband dielectric spectroscopy to measure the α relaxation (T_g) of high MW ($M_w = 767$ k) freestanding PS films surrounded by ethylene glycol [43]. Surprisingly, the film thickness dependence of the α relaxation was found to follow the $T_g(h)$ dependence of the upper transition consistent with low MW freestanding films. The nanobubble inflation method of McKenna and co-workers [44,48], which measures the overall compliance of the film, also obtained $T_g(h)$ values for high MW ($M_w = 994$ k) freestanding PS films consistent with the upper transition [44]. More recently, Napolitano and Wubbenhorst observed in high MW ($M_w = 932$ k) freestanding films evidence of a gradient in dynamics typically

associated with the broad T_g that follows the Keddie-Jones-Cory function form [45]. In addition, the recent fluorescence anisotropy measurements of Ediger and co-workers [7,46,47], which measure the rotational reorientation time of dyes known to be sensitive to the segmental dynamics, observed faster segmental dynamics attributed to the free surface in high MW ($M_n = 984$ and 7370 kg/mol) freestanding PS films within the temperature range of the upper transition. It appears likely that the discrepancies between studies are caused by the various experimental techniques being sensitive to different dynamical populations with the film [3,26]. Interestingly, Baljon *et al.* carried out molecular dynamics simulations on exceedingly thin low MW freestanding films and found that $T_g(h)$ followed the high MW behavior of the lower transition when the film thickness was comparable to the chain size [15]. (A more extended comparison with the literature, discussing why previous studies have not observed these two transitions simultaneously, is provided in the Supplemental Material [42].)

To date, no single theory has been able to capture the two qualitatively different $T_g(h)$ dependences [14,16,17,28,33,34]. Our results indicate that two separate mechanisms can propagate enhanced mobility from the free surface into the film simultaneously. Thus, we recommend that future theories incorporate more than one mechanism to explain the observed phenomena. We note that our results do not directly support any of the existing mechanisms that theorists have suggested for either the upper or lower transition [14,16,17,28,33,34]. Here, we simply articulate the experimental observations of both transitions that should be incorporated into future theoretical efforts. The upper transition appears to be present in *all* films, with $T_g(h)$ following the Keddie-Jones-Cory functional form. This mechanism acts uniformly across the entire free surface of the film causing a gradient in enhanced dynamics with depth that transitions to bulklike dynamics across a length scale of several tens of nanometers [5,6,21,22]. This mechanism appears to control the dynamics of the majority of the film, effectively forming the matrix that dictates the compliance [44,48] and hole formation [40,41] properties. In contrast, the lower transition with a MW dependent, linear $T_g(h)$ appears to only be present in high MW freestanding films resulting in a small fraction of the material exhibiting extremely fast dynamics.

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