# Role of Molecular Architecture on the Vitrification of Polymer Thin Films

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We show that thin film star-shaped macromolecules exhibit significant differences in their average vitrification behavior, in both magnitude and thickness dependence, from their linear analogs. This behavior is dictated by a combination of their functionality and arm length. Additionally, the glass transition temperature at the free surface of a star-shaped molecule film may be higher than that of the interior, in contrast to their linear analogs where the opposite is true. These findings have implications for other properties, due largely to the origins, entropic, of this behavior.

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The role of thickness confinement on the vitrification of thin polymer films has garnered widespread interest from researchers in various communities [1–12]. Simulations and experiments reveal that the average glass transition temperature $T_g$ of thin films depends on thickness $H$ when $H$ is thinner than a few tens of nanometers [8,9]. While the average $T_g$ of freely standing thin linear chain polymer films decreases with decreasing $H$ [1], the average $T_g$ of supported films is influenced by the nature of the intermolecular interactions at the interfaces [2,3]. For weak, nonwetting, interactions between the polymer segments and substrates, the average $T_g$ of the film decreases with decreasing $H$, $\Delta T_g < 0$ [5–7,12], whereas for strong interactions (e.g., hydrogen bonding), the $T_g$ increases with decreasing $H$, $\Delta T_g > 0$ [10–13]. Despite significant activity in this area, many issues, particularly in relation to implications of these findings, remain unclear.

Fundamentally, the central issue is beyond whether the $T_g$ increases or decreases with $H$ in a specific system but about the underlying processes that lead to these effects and the broader implications to the properties of thin polymer films. The earliest conjecture regarding the decreasing $T_g$ with decreasing $H$, from Keddie, Jones, and Cory [6], presupposes the existence of a liquidlike layer at the free surface of the film. Experimental evidence, based on the use of a fluorescent dye as a probe, suggests the existence of a low surface $T_g$ [4]. Additionally, molecular dynamics simulations show evidence of higher chain segmental mobilities, implying increased configurational freedom, and lower $T_g$, in the vicinity of the free interface, compared to the interior of the film [14,15]. Idealized mean field models that account for the effects associated with interactions between polymeric constituents and surfaces on the glass transition generally predict results that are consistent with the experimental observations [16–19].

The requirement for cooperativity in the segmental dynamics, monomer segmental packing in the vicinity of an interface and associated effects over different length scales within the material, would lead to different average thin film $T_g$'s, depending on the material or interface system. To this end, it might be anticipated that the architecture of the molecule would be important; entropic interactions between a macromolecule and an interface are sensitive to the architecture of the molecule, leading to changes in adsorption interactions and interfacial tension [20–24]. In light of these effects associated with interfacial processes, the natural question would be how molecular architecture might affect the vitrification behavior of polymers subject to thickness constraints. We show that, depending on the functionality and the length of the arm chain, the supported thin film of star-shaped polystyrene (PS) molecules can have significantly different vitrification behavior from that of their linear analogs. In addition, we show for the first time that the $T_g$ at the surface of star-shaped PS films can be higher than the bulk; the opposite is true for linear chain PS molecules on the same substrates.

Films of a series of linear and star-shaped PS molecules (star PS) with different functionalities ($f = 3, 4, 8$) and different molecular weights (purchased from Polymer Source Inc.) were prepared by spin-coating filtered solutions onto oxidized ($\sim 2$ nm native oxide layer), $\langle 100 \rangle$ oriented, silicon substrates (purchased from Wafer World Inc.). The samples were then annealed in vacuum at ~40 °C above their bulk $T_g$'s; films thicker than 50 nm were annealed for more than 24 hours, and films thinner than 50 nm were annealed for 12 hours.

The $T_g$'s of the films were determined from measurements of the film thickness as a function of temperature (Fig. 1) by using a variable angle spectroscopic ellipsometer (J. A. Woollam Co., Inc. M-2000D) [5,8,25]. The $T_g$'s of thick supported films ( $\sim 350$ nm) were determined at different depths beneath the surface of the films, by using depth-profiling positron annihilation lifetime spectroscopy (PALS) [26,27]. Through control of the implantation energy of the positrons from 0.7 to 3.2 keV, mean

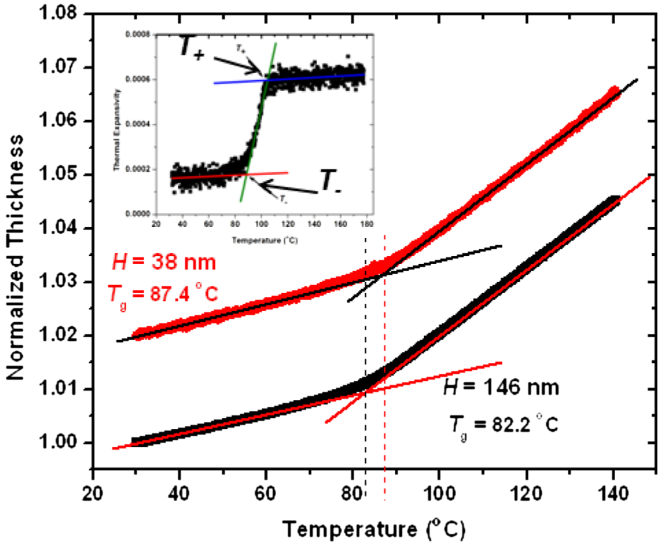

FIG. 1 (color online). Film thickness dependence on temperature, normalized by the thickness of the film at 30 °C, of star PS, 8 arms, $M_w{}^{\mathrm{arm}} = 10$ kg/mol films with $H = 146$ nm and $H = 38$ nm. The inset is the temperature dependence of the thermal expansion of the $H = 146$ nm thick film.

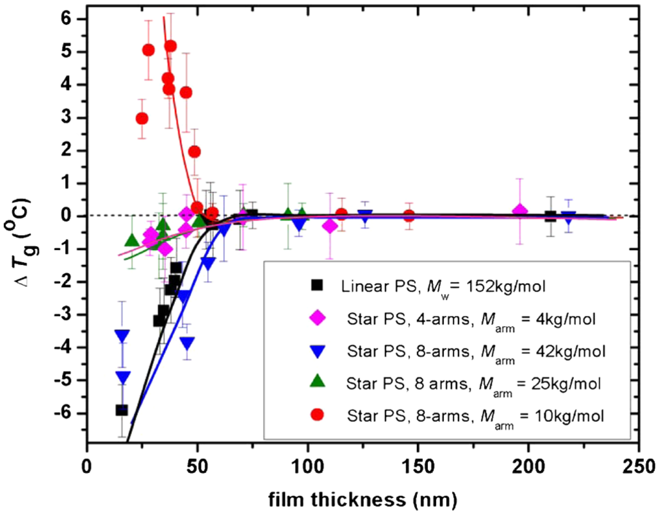

FIG. 2 (color online). $T_g$'s as a function of film thickness for linear PS (black squares), 8-arm star PS with $M_w{}^{\mathrm{arm}} = 42$ kg/mol, $M_w{}^{\mathrm{arm}} = 25$ kg/mol, $M_w{}^{\mathrm{arm}} = 10$ kg/mol, and 4-arm with $M_w{}^{\mathrm{arm}} = 4$ kg/mol. The lines are guides to the eyes.

implantation depths ranging from 16 to 180 nm were achieved. Each sample was first heated at 170 °C, and subsequently cooled, at 10° steps, to 40 °C, with a final run at 25 °C; PALS spectra were taken for 40 minutes at each $T$. More than one scan was performed for each sample. The free volume void sizes were determined directly by analyzing positron lifetimes, as a function of $T$, by using the well-established extended Tao-Eldrup relationship. The apparent $T_g$ for each energy (i.e., at each implantation depth) was deduced by using methods described elsewhere [28,29].

The effects of architecture of the molecule on the average $T_g$ of thin films are summarized in Fig. 2. The $T_g$ of linear chain PS is shown to decrease with decreasing $H$ ($\Delta T_g < 0$), a fact that is well known for this system, regardless of the degree of polymerization of the PS chains [8,9]. We note that the average $T_g$'s of star molecules of $f = 3$ (with $M_{\mathrm{arm}} = 19$ and of $M_{\mathrm{arm}} = 110$ kg/mol) exhibited the identical $T_g$-vs-$H$ dependence as the linear PS molecules (data not shown for the $f = 3$). However, $T_g$'s of the $f = 4$ with $M_{\mathrm{arm}} = 4$ kg/mol exhibited a significantly weaker dependence on $H$ than those of linear PS chains. We further investigated the $T_g$ dependencies on $H$ for a star-shaped molecule possessing a higher functionality, $f = 8$. The $T_g$'s of the longest 8-arm star-shaped molecules ($M_{\mathrm{arm}} = 42$ kg/mol) exhibited the same dependence on $H$ as did the linear chains. However, when the arm molecular weight decreases to $M_{\mathrm{arm}} = 25$ kg/mol, the $T_g$ exhibited a similar dependence on $H$ to that of the $f = 4$ ($M_{\mathrm{arm}} = 4$ kg/mol) star polymer. In contrast, the $T_g$'s of the 8-arm molecule possessing arms of lower molecular weight $M_{\mathrm{arm}} = 10$ kg/mol increased with decreasing $H$ ($\Delta T_g > 0$). Clearly, the transition from $\Delta T_g < 0$ to $\Delta T_g > 0$ is not abrupt; it is gradual and occurs with increasing functionality and/or decreasing arm length. The increase of functionality appears to have a stronger effect on the observed trends than the length of the arm.

Self-consistent field calculations reveal that star polymers exhibit significant interfacial activity in relation to their linear analogs [20]. They suffer a significantly lower entropic penalty than their linear analogs upon adsorption to an interface [21]. In fact, simulations also show that the number of segments of a star molecule in contact with an interface is large compared to linear chains of the same total degree of polymerization, $N$ [22]. Moreover, the frustrated segmental packing in the bulk is responsible for the decrease in the cohesive energy density of star molecules; together with an enhanced adsorption of chain ends at the free surface, star macromolecules possess lower surface tensions than their linear chain counterparts of the same $N$ [23,24].

Simulations show that by confining the film between impenetrable and repulsive, or noninteracting, walls $\Delta T_g < 0$, whereas $\Delta T_g > 0$ when the molecule or wall interactions are attractive [30]. Theories based on dynamic percolation, wherein the behavior of the system is characterized by transient regions of "fast" and "slow" dynamics, have also been proposed to explain the $H$-dependent $T_g$ in thin films [18,19]. The presence of attractive interactions with a "wall" increases the fraction of slow domains leading to the increase of the $T_g$ with decreasing $H$.

Having demonstrated the effect of architecture on the average $T_g$ of the film, it would be important to examine the data further to learn more about the breadth of the transition and implications for the $T_g$ near the free interfaces. We accomplish this by following a strategy, first demonstrated by Kawana and Jones [5], that includes numerically differentiating the data to determine the thermal expansion $\alpha(T)$. The data in the inset in Fig. 1 are typical of all our samples, where a stepwise change in $\alpha(T)$ occurs. This "jump" is characteristic of the glass transition; the onset of the transition is denoted by $T_+$, and the end of the transition is denoted by $T_-$. The significance of this analysis is that different regions of a film "fall" out of equilibrium at different temperatures. It is evident from Fig. 3, for linear chains, that the magnitude of the decrease of $T_-$ with decreasing $H$, $|\Delta T_-|$, is appreciably larger than the increase of $T_+$, $|\Delta T_+|$, over the same thickness range. $T_-$ is the glass transition of the surface region, which clearly occurs at a $T$ below the bulk $T_g$. Since $|\Delta T_-| > |\Delta T_+|$, then the average $T_g$ of the sufficiently thin film decreases. Of course, for thick films the bulk $T_g$ is always recovered because the interior of the film accounts for most of the volume of the system. Our results are consistent with those of Kim *et al.* [31]. The behavior of the star molecules can be quite different; both $T_+$ and $T_-$ of the 8-arm star with $M_{\text{arm}} = 10$ kg/mol increase with decreasing $H$, indicating that the transitions at both interfaces occur at higher temperatures than the bulk $T_g$. The behavior of the star molecule with arms of $M_{\text{arm}} = 25$ kg/mol represents the intermediate case.

While evidence of depth-dependent $T_g$'s in these systems is based on interpretation of the thermal expansion data, PALS provides more direct information. The use of a variable energy focused beam of positrons beam source is particularly powerful as it is reliably used to implant positrons at specific depths within a sample, through control of the incident energy, within a sample. We examined thick films, $H \sim 350$ nm, in order to avoid the influence of the substrate in order to determine the $T_g$ of the free surface. The data for the linear PS and 8-arm star PS in Fig. 4 reveal that the $T_g$ at the free surface of the linear chain PS system is lower than that of the interior of the sample. In contrast, the "surface" $T_g$ of the star is larger than the bulk and decreases gradually to its bulk value with depth.

The differences in the depth dependence of the linear and star molecules may be rationalized in terms of two possible processes. One is related to a mechanism proposed by de Gennes describing the transport of free volume along the contour of linear chains at the free surface, in an effort to rationalize the low surface $T_g$ [32]. The basic idea is that a segment of a chain forming a loop that begins at one location at the free interface and extends below the surface and reaches the surface in another location would be a source for the transport of "free volume." Specifically, "kinks" necessarily would exist along such loops and the motion of the kinks, which

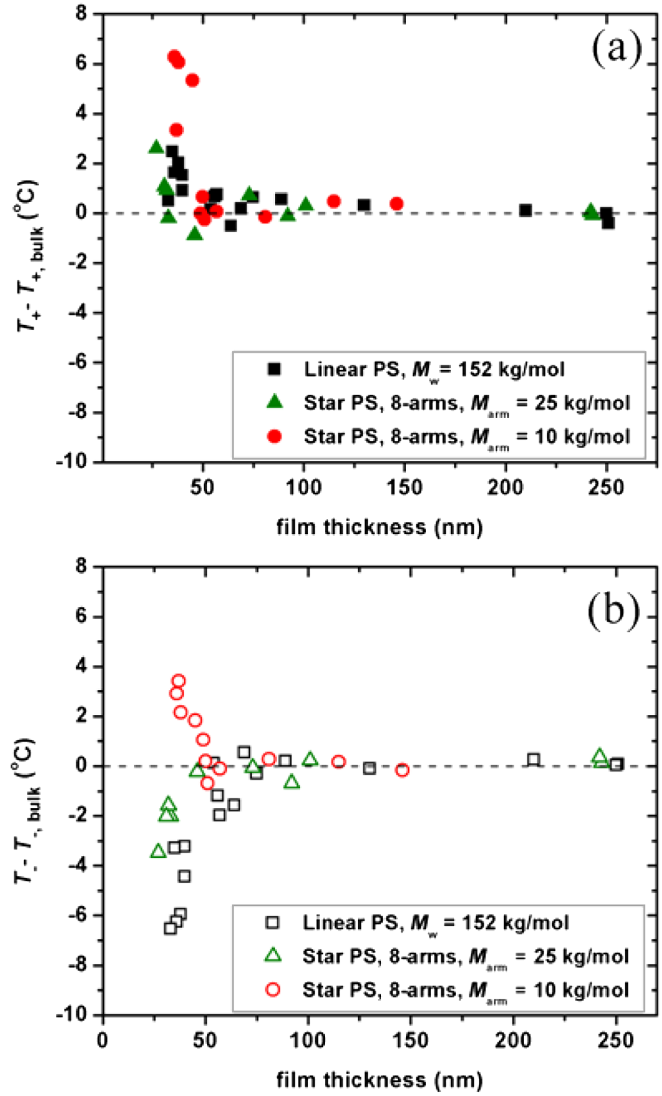

FIG. 3 (color online). Thickness dependence of (a) $T_+$ and (b) $T_-$ for linear PS , 8-arm star PS with $M_w{}^{\text{arm}} = 25$ kg/mol, and $M_w{}^{\text{arm}} = 10$ kg/mol.

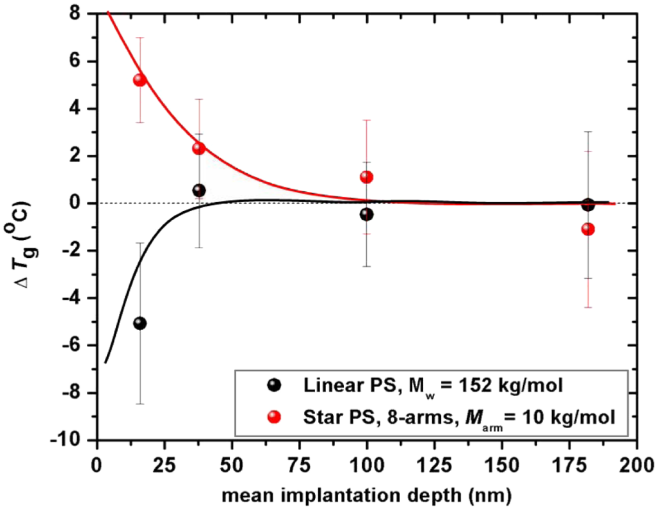

FIG. 4 (color online). From PALS measurements as a function of the mean implantation depth for linear PS and 8-arm star PS, $M_w{}^{\text{arm}} = 10$ kg/mol. The lines are guides to the eyes.

occurs with very low activation energy, would be the source of transport of free volume. Recent work by Milner and Lipson further developed this conjecture to clearly demonstrate the quantitative influence of this mechanism on the $T_g$ of thin films [33,34]. Such a mechanism would necessarily be suppressed in star molecules, of sufficiently small $N$, due largely to their architecture. Furthermore, the star molecules exhibit a tendency to organize more efficiently at interfaces than linear chains, with a smaller loss of entropy for chains of the same $N$. This might affect the local free volume in the vicinity of the free surface and hence the dynamics associated with the $T_g$. The fact that the $T_g$ of the surface region of stars is higher than the bulk also rules out reasons associated with the role of chain-end effects, at least for this system, which is often invoked as a reason for reductions in $T_g$ of thin linear polymer films.

Our primary finding is that by changing the architecture of the molecule, going from linear chains to star-shaped macromolecules, the glass transition temperature increases with decreasing film thickness $H$ ($\Delta T_g > 0$). This is in contrast to the well known behavior of linear chain PS macromolecules, on the same substrates, where the $T_g$ decreases with decreasing $H$ ($\Delta T_g < 0$). Previously, the increase in $T_g$ with decreasing $H$ would have been believed to be due only to specific, strong or enthalpic, interactions between the substrate and the polymer. In our case, the increase of the average $T_g$ of the film was due largely to the fact that the surface $T_g$ of the star molecule is higher than the bulk. The enhanced entropic attraction of the star macromolecules to both interfaces, compared to linear chains, could account for the observation that the $T_g$'s, $T_+$ and $T_-$, are higher than the bulk $T_g$. Notably, the transition from $\Delta T_g < 0$ to $\Delta T_g > 0$ for the star molecules occurs gradually with increasing $f$ and/or decreasing $N_{\mathrm{arm}}$. In the case of low $f$ or/and large $N_{\mathrm{arm}}$, the behavior is identical to that of linear PS. That the surface $T_g$ of a polymer system is higher than the interior (or bulk), associated with the star-shaped architecture of the polymer, is important because until now the generally accepted view was that the surface $T_g$ of a polymer should always be lower than the interior (or bulk).

These results now clearly demonstrate, for the first time, the role of the architecture of the macromolecule on the thickness dependence of $T_g$ and the interfacial $T_g$'s. This has important implications regarding conjectures or theories for vitrification in materials. In principle, one might anticipate that other properties such as the wetting properties as well as structural relaxation processes associated with physical properties such as aging might also be influenced. Preliminary experiments in our laboratory suggest that such may be the case.

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