Role of Molecular Architecture on the Vitrification of Polymer Thin Films

Emmanouil Glynos, Bradley Frieberg, Hyunjoon Oh, Ming Liu, David W. Gidley, and Peter F. Green

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Thin Film Polymer Systems

Emmanouil Glynos[1], Bradley Frieberg[2], Hyunjoon Oh[1], Ming Liu[3], David W. Gidley[3]

and Peter F. Green[1]

[1]*Department of Materials Science and Engineering,* [2]*Macromolecular Science and Engineering,* [3]*Department of Physics, University of Michigan, Ann Arbor, Michigan, USA*

We show that thin film star-shaped macromolecules exhibit significant differences in their average vitrification behavior, both in magnitude and thickness dependence, from their linear analogs. This behavior is dictated by a combination of their functionality, number of arms, and the arm length. Additionally, the glass transition 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.

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, non-wetting, 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 (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 et al. [6], presupposes the existence of a liquid-like 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_gs, depending on the material/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 funactionality and the length of the arm chain, supported thin film of star-shaped polystyrene (PS) molecules can have significantly different vitrification behavior from that of their linear analogues. In addition we show for the first time that near the surface T_g 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 of 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 (~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 $^{\circ}$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 (Figure 1) using a variable angle spectroscopic ellipsometer (J.A. Woollam Co., Inc. M-2000D) [5, 8, 25]. The T_g's of thick supported films (~350 nm) were determined at different depths beneath the surface of the films, 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 implantation depths ranging from 16 to 180 nm were achieved.. Each sample was first heated at 170 $^\circ$C, and subsequently cooled, at ten degree steps, to 40 $^\circ$C, with a final run at 25 $^\circ$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 (Ps) lifetimes, as a function of T, using the well-established extended Tao-Eldrup relationship. The apparent T_g for each energy, (i.e. at each implantation depth) was deduced using methods described elsewhere.[28, 29]

The effects of architecture of the molecule on the average T_g of thin films are summarized in Figure 2. The T_g of linear chain PS is shown to decrease with decreasing H (ΔT_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_{arm}=19 and of M_{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_{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_{arm}=42 kg/mol.) exhibited the same dependence on H as did the linear

chains. However when the arm molecular weight decreases to M_{arm}=25 kg/mol., the T_g exhibited a similar dependence on H to that of the f=4 (Ma=4 kg/mol.) star polymer. In contrast, the T_g·s of the 8-arm molecule possessing arms of lower molecular weight M_{arm}=10 kg/mol. increased with decreasing H (ΔT_g>0). Clearly the transition from ΔT_g < 0 to ΔT_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 (SCF) 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 non-interacting, walls the ΔT_g <0, whereas ΔT_g >0 when the molecule/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 of Figure 1 is 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 Figure 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 $M_{arm} = 10$ 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 $M_{arm} = 25$ 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 Figure 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 deGennes 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 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 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/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_{arm}. In the case of low f or/and large N_{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 is 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/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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Figure legends

Figure 1: Film thickness dependence on temperature, normalized by the thickness of the

film at 30 °C, of star PS, 8 arms, $M_w^{arm} = 10$ 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.

Figure 2: T_g's as a function of film thickness for: liner PS (black squares), 8-arm star PS

with M_w^{arm} =42 kg /mol , M_w^{arm} =25 kg/mol , $M_w^{arm} = 10$ kg/mol , and 4-arm with M_w^{arm}

=4 kg /mol. The lines are guides to the eyes.

Figure 3: Thickness dependence of (a) T_+ and (b) T_- for liner PS , 8 arm star PS with $M_w{}^{arm}$ =25 kg/mol , and $M_w{}^{arm}$ = 10 kg/mol .

Figure 4: from PALS measurements as a function of the mean implantation depth for linear PS and 8 arm star PS, $M_w{}^{arm}$ = 10 kg/mol . The lines are guides to the eyes.
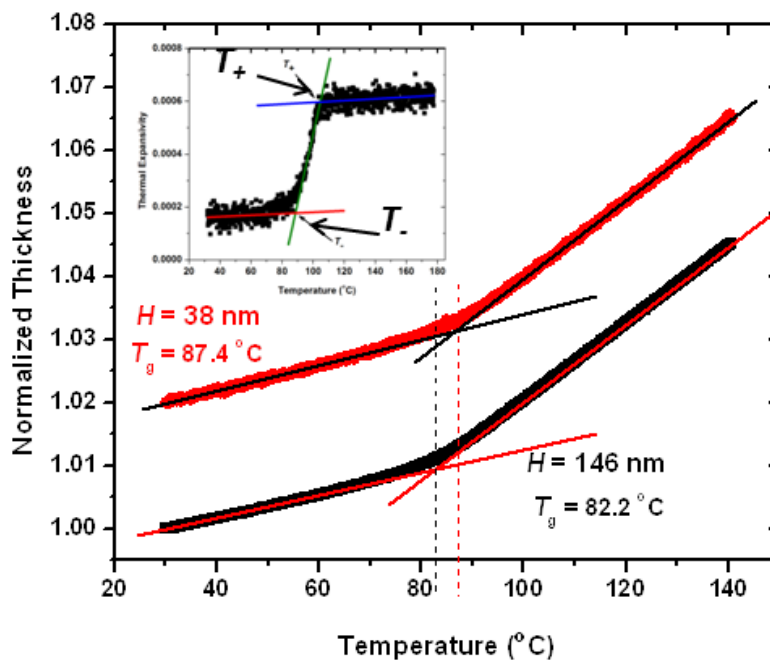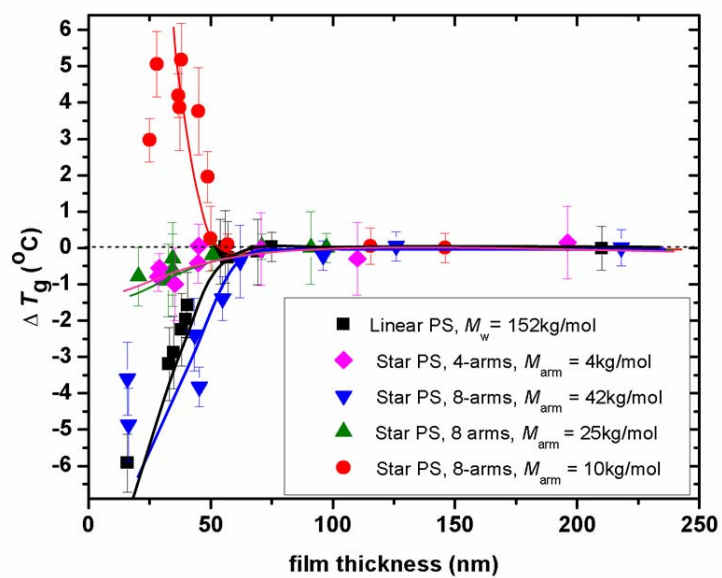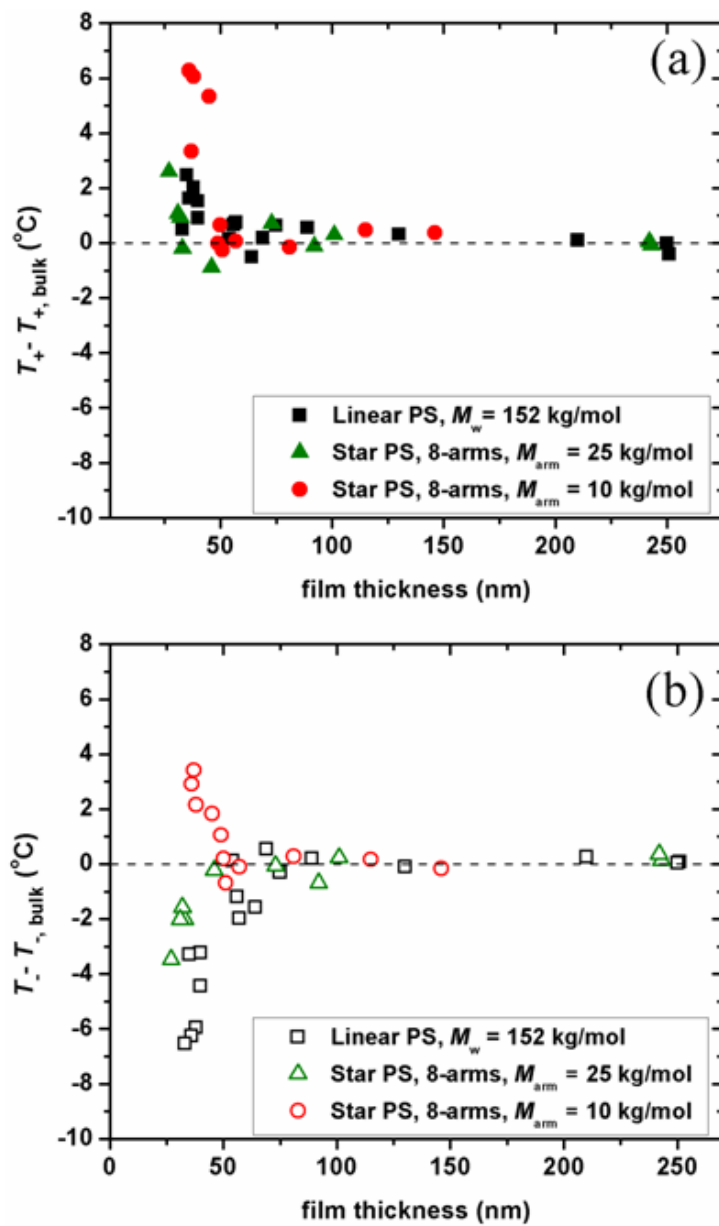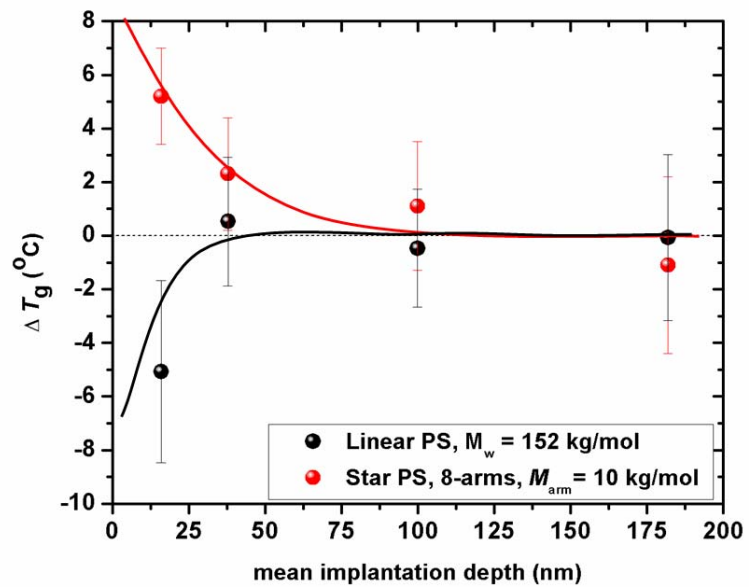
Figures

Figure 1

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