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Structure and Dynamics of Star Polymer Films from Coarse-Grained Molecular Simulations

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Abstract

We quantify the structure and dynamics in molecular simulations of star polymer films of varying arm mass M_a and number of star arms f on a supporting solid substrate with an attractive interaction and compare to the corresponding properties of thin films of linear polymers. While the spatial variation of segmental density profile is only weakly dependent on star polymer topology, the polymer topology changes both the average rate of relaxation and the spatial variation of the average segmental relaxation time τ_α as function of depth from the film substrate, z . In particular, we observe a general slowing down in the rate of relaxation of the entire film with an increasing functionality f , a general trend attributed to an alteration of the effective cohesive interaction strength when f is increased. The mobility gradients in the film, quantified by the relaxation time obtained from the intermediate scattering function on a layer-by-layer basis, is also significantly altered by f . In particular, the width of the substrate interfacial layer grows with increasing f , saturating in value around $f=12$, while the width of the interfacial zone near the ‘free’ boundary, where the polymer dynamics is greatly accelerated compared to the film interior, is less influenced by changes in polymer topology. These observations are qualitatively consistent with the interpretation of recent X-ray photon correlation spectroscopy on star polymer melt films.

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Introduction

The significant variation in the glass transition temperature T_g of polymeric melts upon varying polymer molecular mass M indicates that structural correlations in polymer liquids associated with chain connectivity can have a large impact on the dynamics of polymer melts. [1]–[5] Although this type of polymer mass dependence of T_g has been interpreted in terms of ‘free volume’ ideas, [6]–[8] this phenomenological approach to glass-formation does not consider how branching, ring formation or other topological constraints alter the average molecular shape, size, and overall molecular rigidity-- molecular properties that are expected to be quite different in general for polymers having different topologies. Recent theoretical modeling based on the generalized entropy theory (GET) [9], [10] indicates that any factor that alters molecular packing efficiency can be expected to alter both the fragility of glass formation and T_g , and, correspondingly, we study how both the structure and segmental dynamics of star polymers in thin films are altered when the number of star arms is varied. In previous papers, we studied linear [11]–[17], star polymers [18] and knotted ring polymer melts in the bulk state [19], providing useful reference points for comparing to our star melt data.

It has been appreciated for some time based on both experimental observation [20], [21] and theoretical arguments [22] that ring polymer melts should exhibit a very different variation of T_g with polymer mass M and molecular dynamics simulation studies by Chremos and Douglas [23] have indicated that these strong changes in the mass dependence of T_g , and many of the other configurational properties of polymer melts, should extend to star polymers. [24]–[27] Vargas et al. [19] have amplified on this similarity in the conformational states of ring and star polymers in the melt and showed quantitatively that the melt dynamics properties of knotted ring polymers having a minimal crossing number m_c (a topological invariant of ring polymers describing their

knot complexity) resemble star polymer melts having a number of arms f , i.e., $f \leftrightarrow m_c + 4$. This approximate correspondence between star polymers and knotted ring polymers also extends to knotted ring and star polymers in solution. [28] Moreover, Chremos and Douglas [23]–[27] found in their simulations that the average conformational structure of bottlebrush polymers resembles ring polymers in a wide range of their molecular parameter space, both in terms both of the average polymer shape and the scaling of the polymer radius of gyration R_g with polymer mass so we may naturally expect the structural and dynamical properties of star and bottlebrush melts to have properties rather similar to ring polymer melts. This expectation runs rather contrary to the heuristic free volume picture of polymer glass-formation where the many free ends of the star and bottlebrush polymers might be expected to lead to a large increase of the melt ‘free volume’ associated with the many chain ends, and a corresponding depression of the glass transition temperature, T_g .

Recent measurements on thin films of star polymers [29]–[32], relatively unknotted ring polymers [33], [34], and bottlebrush polymers [35] have correspondingly indicated significant changes in the effect of film confinement in comparison to linear chain counterparts of the same material so there is clear evidence that molecular topology influences melt dynamics of thin polymer films. In the case of the unknotted ring and bottlebrush melts, the relative sensitivity of the glass transition to film thickness was diminished relative to linear chains, but measurements on the star polymer melts of different f indicate that even the *sign* of the T_g -shift with confinement can be altered by changing the number of arms f of the star when the polymer substrate is fixed. [29]–[31] These experimental observations are broadly in accord with theoretical expectations based on the simulations noted above, which showed a strong similarity between the configurational properties of unknotted rings and bottlebrush polymers, [24], [26] and a strong

upward shift T_g of low molecular mass of the arms of star polymers M_a having a large number of arms, [29]–[31] relative to linear chain polymer melts having the same chain mass as the star arms. Interestingly, the observed shifts in T_g with film thickness h seem to parallel the shifts of T_g with changes in molecular mass of these polymers, the effect of molecular mass and confinement ultimately disappearing when M and h approach infinity when the branching complexity (f , M_a , etc.) is fixed. There are clearly many variations on topological constraints on glass-formation that remain to be studied experimentally and by simulation. As a final point of motivation, we point out that there are an increasing number of technological and bioscience applications of star polymers materials which are excellently reviewed by Ren *et al.* [2]

The present work considers the structural nature (density profiles, etc.) and dynamics of star melt polymer films supported on a solid substrate based on a model extensively studied previously for polymer linear polymer chain melt supported films and for the glassy dynamics of bulk star [18] and knotted ring [19] polymer melts. In addition to the average properties of the film as a whole, we also quantify the density and mobility gradients and the interfacial scales that quantify the gradients at both the supporting and free interfaces of the polymer film as function of the number of chain segments m in the star arms f , and temperature T , utilizing methods described in recent papers on supported thin linear polymer films [11], [14], [16], [36]–[42]. The film thickness studied is well below the film thickness at which the T_g shifts from finite size effect occur [30].

Modeling and Simulation Details

Our results are based on a series of coarse-grained molecular simulations of supported thin star polymer films. We attach f coarse-grained linear polymer ‘arms’ to a core particle to model our star polymers, and we designate the number of beads (or monomers) in each linear polymer

that attached to the core as the arm mass M_a . All polymer chains are fully flexible. In this study, we investigate molecular architectures of star polymer with $f = 2, 4, 6, 8, 12$, and 16 , and $M_a = 5, 10, 20$, and 40 . For detailed description of the molecular modeling and parameters of star polymers, we refer to our previous publication emphasizing the same polymer model in the bulk [18]. The only difference of the star polymer in this study compared to Ref. [18] is that the bond length between the nearest monomers along the linear polymer chain in each arm is slightly smaller. Specifically, we use harmonic bonds with an equilibrium bond length $r_0 = 0.9 \sigma$ to avoid the crystallization of star polymer film (σ denotes the diameter of each monomer or core particle); such crystallization is not an issue for the bulk system. We model the supporting substrate as a single layer representing the 111 face of a face-centered cubic (FCC) lattice (a triangular lattice) with polymer(monomer)-substrate interaction ε_s the same as that of monomer-monomer, $\varepsilon \equiv \varepsilon_s$. For all molecular architectures, we simulate thin film with thickness $\approx 16 \sigma$. The number of star polymer molecules in each system is ranging from approximately 100 to 360, depending on star architecture. All units are expressed in terms of the Lennard-Jones strength ε and length σ parameters for monomer-monomer interactions, so that temperature T is given by ε / k_B , where k_B is Boltzmann's constant, time t is given in units of $(m \sigma^2 / \varepsilon)^{1/2}$, where m is the mass of monomer. Reduced units can be mapped to physical units -- the size of chain segments $\sigma \approx 1 \text{ nm}$ to 2 nm , time is in picosecond, and energy $\varepsilon \approx 1 \text{ kJ/mol}$.

We simulate film thickness $h \approx 16 \sigma$, a value much smaller than the film thickness (65σ) at which the linear chain melt starts were estimated to exhibit significant ($\approx 2 \text{ K}$) changes of its glass transition temperature. [37] We have also employed the polymer-substrate interaction strength ε_s to be moderately attractive ($\varepsilon_s = 1.0$), corresponding to a thermodynamically stable film,

but not so attractive that T_g of the film as whole is shifted upward and non-equilibrium polymer binding near the solid substrate becomes prevalent. [13]

We use periodic boundary conditions in the directions parallel to the substrate. All simulations are performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). [43] The equations of motion are integrated using the reversible reference system propagator algorithms (rRESPA) [44] with 3 bonded interaction updates for each non-bonded interaction update. The inner-most time step is 0.002. We use a canonical (NVT) ensemble for all supported film simulations. To obtain T_g based on quasi-thermodynamic criterion, we performed at least two independent heating and cooling runs for polymer films at a rate of 10^{-5} between $T = 0.01$ and $T = 1.0$. To study the dynamics at a fixed T , we collect trajectories at T ranging from 0.45 to 0.80.

Results

A. Density and Mobility Gradients in Supported Star Polymer Films

We first consider the variation of the monomer density as function of distance from the substrate z in a star and linear polymer film. The comparison of the linear and star-melt segmental density profile $\rho(z)$ in Fig. 1(a) and (c) indicates that the variation of the segmental density is only weakly affected by star polymer architecture. Near the substrate, $\rho(z)$ is highly insensitive to architecture; approaching the free interface, there is a weak enhancement of segmental density at large f , a feature noted in earlier studies [30]. The slight variation of density is also consistent with findings that nanoparticles influence the local packing [39], [45]. In contrast, Figure 1 (b) and (d) shows that the segmental relaxation time profile $\tau_a(z)$ (or “mobility gradient”) in the film is rather sensitive to the star functionality f and arm molecular weight M_a . Specifically, shorter arm length M_a and larger functionalities f result in longer local relaxation time. Taken together, these

data show that a ‘free volume’ theory based solely on the average density profile is not adequate to predict changes in dynamics in polymer materials confined polymer materials, which has been pointed out before for linear polymer films. [36] That said, more sophisticated measures of the local dynamical free volume accessible to a monomer, such as the Debye-Waller factor, can potentially capture these changes in the mobility gradient.

It is apparent from Fig. 1(b) that there is a substantial slowing down of the dynamics of the polymer film with increasing topological complexity (f) throughout the film, except near the free interface where the segmental mobility is nearly independent of the polymer branching. As a second order effect, there is a tendency of the relaxation near the free boundary to exhibit an oscillatory behavior in the relaxation time for very large f , which seems to be associated with a layering of the stars as they become more ‘particle-like’ for large f [3], [4], [46]–[48]; we quantify this effect later when we examine the density profile of the cores of star polymers.

The data for the density and relaxation profiles in Fig. 1 allow us to estimate the changes in the interfacial scale. First, consider that the lack of variation in the density profile in Figs. 1(a) and (c) demonstrates that the scale in interfacial density changes is essentially independent of the star shape. In contrast, it is readily apparent from the $\tau(z)$ profiles that the interfacial scale of dynamical gradients is sensitive to star shape. Qualitatively, it is apparent that the width of the interfacial layer of diminished segmental mobility near the solid substrate increases substantially with f ; at the same time, it appears that the relaxation gradient scale saturates for larger f values. We quantify the temperature dependence of the interfacial layer thickness ξ (or interfacial width, interfacial scale) using the same procedure described at length before for polymer films of linear polymers and polymer nanocomposites [39], [40],

$$\ln \tau_a(z) = \ln(\tau_0) - c_1 \tanh[(z - \xi_{\rho, \text{sub}}) / \xi_{\text{sub}}] - c_2 \tanh[(z - (h - \xi_{\rho, \text{free}})) / \xi_{\text{free}}], \quad (1)$$

where $\zeta_{p,sub}$ and $\zeta_{p,free}$ are the interfacial density scales of the substrate and free surface, respectively; ζ_{sub} and ζ_{free} are the dynamical interfacial scales of the substrate and free surface, respectively; h is the temperature dependent film thickness, defined by the height at which density decreases to 0.05 near the interfaces; c_1 , c_2 , and τ_0 are fitting parameters. We show the result for the interfacial mobility scale of star polymer films from the fits to Eq. 1 in Fig. 2. We find that the interfacial layer thickness (ζ_{sub} for the substrate and ζ_{free} for the free interface) generally increases with *decreasing* T for $T > T_g$, as quantified in Fig. 2. Moreover, the interfacial layer thickness near the substrate ζ_{sub} increases with increasing functionality f at any fixed temperature (Fig. 2a). As for the interfacial layer thickness near the free interface ζ_{free} , its magnitude appears to be less sensitive to the star polymer architecture. For completeness, we note that, like ordinary polymer films [36], [40], the density interfacial scale *grows upon heating rather than cooling* [36], [39] near the free interface for all the films studied in the present paper, demonstrating yet again that average local density not correlate with changes in the dynamics of glass-forming materials.

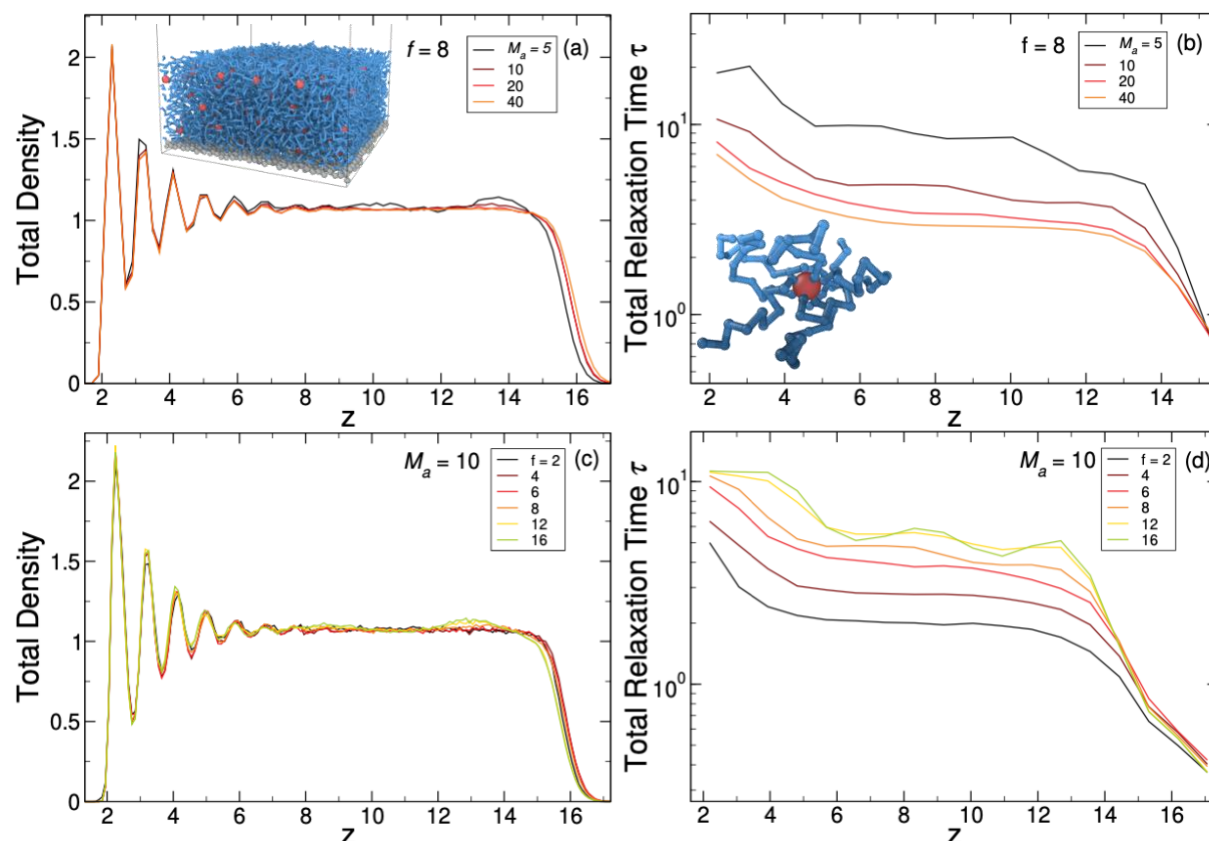


Figure 1. The average segmental density and structural relaxation time of star and linear polymer films as function of distance z from the solid substrate at $T = 0.6$. a), b) Fixed number of arms $f = 8$ and a range of arm lengths, $M_a = 5, 10, 20$, and 40 . c), d) $M_a = 10$ and $f = 2$ (linear polymers), $4, 6, 8, 12$, and 16 . (a), and for various functionality f at a fixed arm length $M_a = 10$ (c). Despite of the difference M_a or f , there is little difference in the average density of star polymer film as function of z . The relaxation time τ_α of star polymer films, on the other hand, is quite sensitive to M_a or f . Pictures in (a) and (b) show the star polymer film and individual star polymer ($f = 8, M_a = 10$), respectively. Images are rendered by OVITO[49].

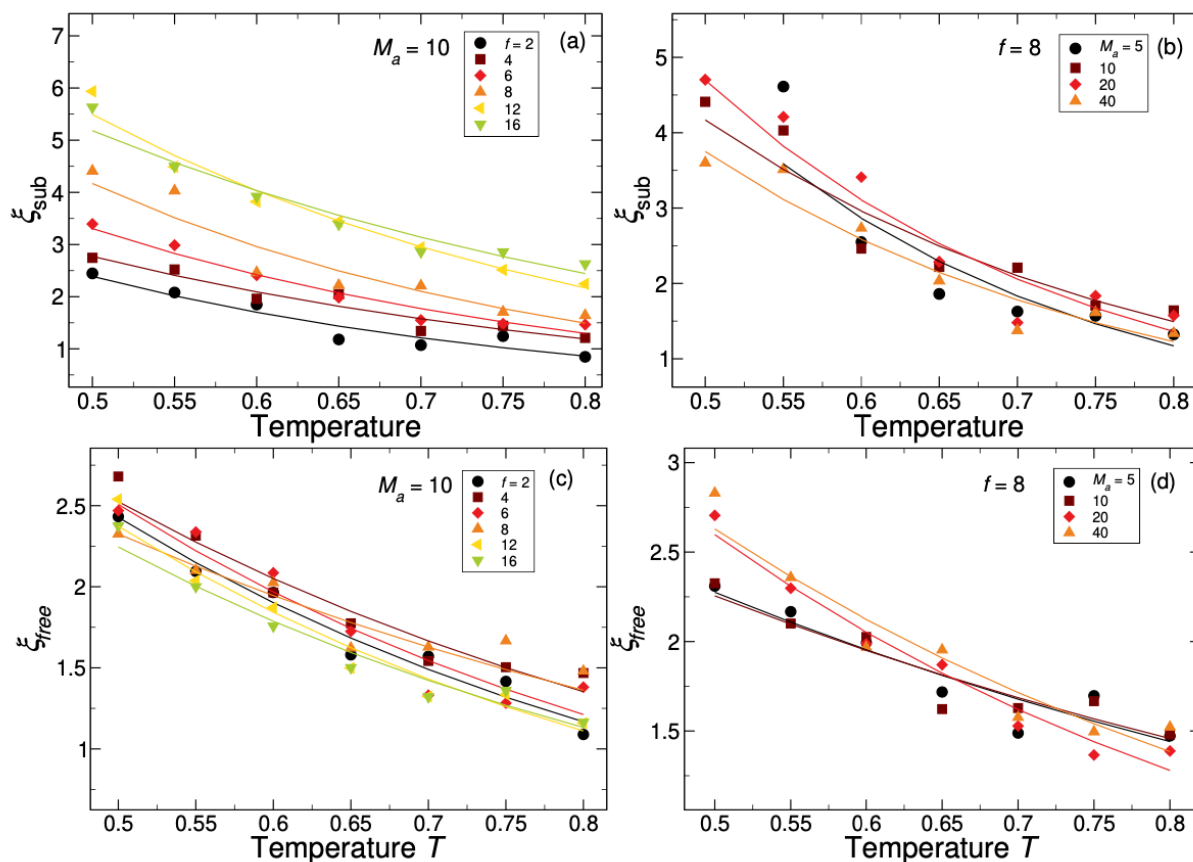


Figure 2. Temperature dependence of mobility interfacial layer thickness near the substrate (ξ_{sub}) and free boundary (ξ_{free}) as a function of arm length m and f . Top figures: Substrate interfacial layer thickness for ξ_{sub} for $M_a = 10$, $f = 2, 4, 6, 8, 12, 16$ and $f = 8$, $M_a = 5, 10, 20, 40$. Bottom figures: Substrate interfacial width estimates scale for ξ_{free} for $M_a = 10$, $f = 2, 4, 6, 8, 12, 16$ and $f = 8$, $M_a = 5, 10, 20, 40$.

Our results are broadly consistent with recent experiments. Similar to our results for the interfacial scale in Fig. 2, recent X-ray photon correlation spectroscopy measurements on thin films of linear polymer melts, as well as ring polymer melts and 4-armed star polymers have indicated evidence for a large gradient of mobility that defines an interfacial zone at the film substrate [50]–[52]; further, they interpret the gradient in terms of significant increase in the thickness of the substrate interfacial layer with increasing T . [50], [51] These works have generally

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3 inferred a significant slowing down of the dynamics of the film as whole with increasing f , in
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5 accord with our simulations.
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8 In addition to a mobility gradient near interfaces, previous studies [1], [18] emphasized
9 that there is a significant gradient of the relaxation times within the star polymers themselves due
10 to crowding near the star core. This intramolecular gradient also varies with molecular topological
11 complexity (f) and arm length m . Since this type of intramolecular mobility gradient also exists in
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13 the thin polymer films, we examine the interplay between these effects in Fig. 3(a). Specifically,
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15 we compare the density and structural relaxation time of the average properties of the entire film
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17 with that of the core or arm end segments for a representative star polymer having an arm length
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19 $M_a = 10$ and $f = 8$. While the overall (total) density near the free interface remains essentially the
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21 same for various star polymer architectures (Fig. 1) considered, we find there is an enhanced
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23 density for the star cores near the free surface, $z \approx 13$ nm, and density of the free end segments of
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25 the star arms peaks nearer the free surface, $z \approx 15.4$ nm. We also see that oscillations of the density
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27 profile of the core segments at large f persists further into the film, symptomatic of the stars
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29 developing a particle-like layering when f is large. This star layering effect and the localization of
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31 the star cores near the free boundary has been emphasized in earlier work by Glynos *et al.* [30]
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33 Despite the heterogeneous distribution of the cores and arm ends of star polymers, the relaxation
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35 time profile of the core and arm segments [Fig. 3(b)] does not reflect the same oscillations that we
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37 see for density. Moreover, the scale of the gradients for each type is similar to that for the relaxation
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39 time profile of all the segments. The relaxation times of the star ends are overall a little smaller,
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41 consistent with the intramolecular mobility gradient of star polymer molecules similarly, and the
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43 core segments exhibit an overall slower relaxation, consistent with the diminished mobility arising
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45 from the intramolecular relaxation gradient.
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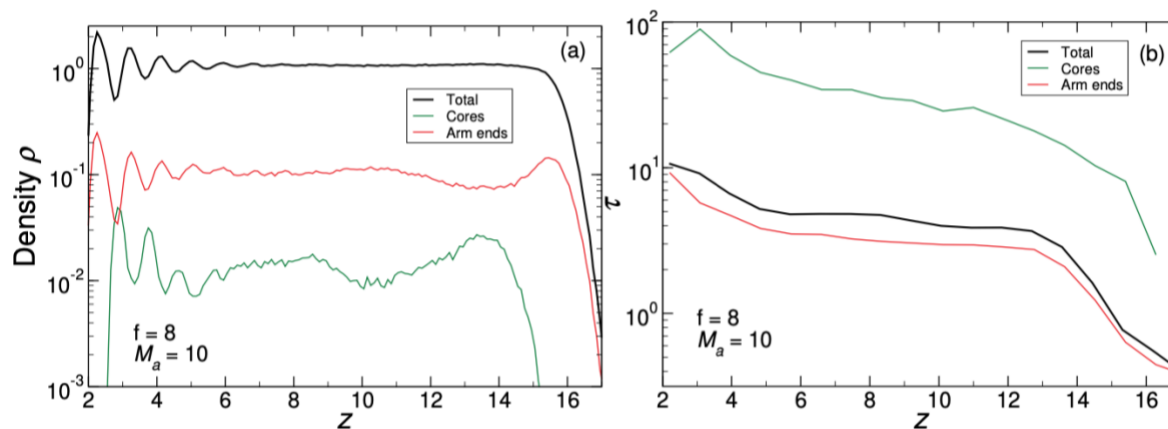


Figure 3. The density profile and segmental relaxation times of core segments, chain end segments and all segments for $f=8$ and $M_a=10$ at $T=0.6$. a) density profiles, b) mobility profiles.

To better understand the distribution (and localization) of star molecules across the film profile, we examine how arm mass M_a and f affects the core density profile and relaxation in Fig. 4. We see from Figs. 4(a) and 4(c) that there is a tendency of the core segments to localize near the solid substrate and free boundary. This progressive delocalization of the core segments near the boundaries correspondingly gives rise to a reduction of the relaxation time of the core segments with increasing M_a [Fig 4(b)]. Increasing the number of star arms f leads to the layering effect mentioned before, and a corresponding substantial increase of the core segmental relaxation time. In contrast to the peaks in the density of the core segments near the free surface, the locations of the peaks near the solid substrate are nearly independent of m , suggesting that the conformation of star polymer is somewhat flattened near the substrate. Furthermore, in contrast to the density profile in Figs. 4 (a) and 4(c), the relaxation profile for core segments in Figs. 4 (b) and 4(d) is larger for star polymers with smaller M_a or larger f .

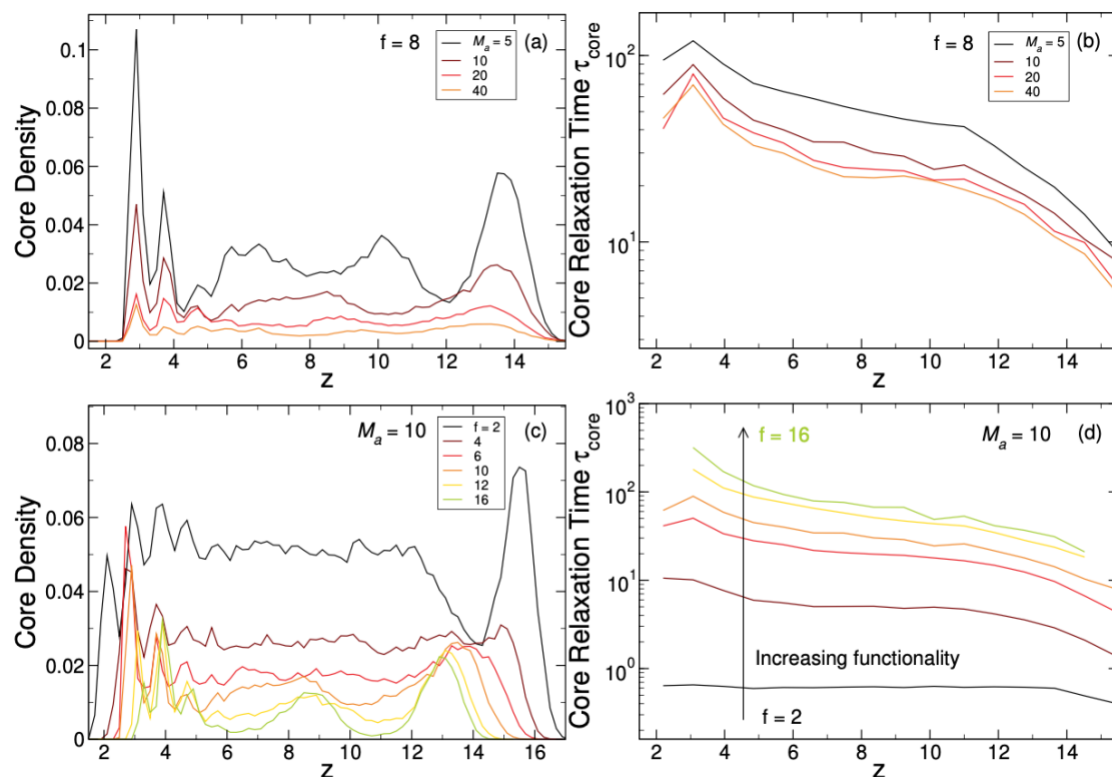


Figure 4. Segmental density and structural relaxation times of core, free end and all segments at $T = 0.6$. (a) The core density of the star polymer film with $f = 8$ and variable M_a (b) The core segment structural relaxation time as function of M_a and $f = 8$. (c) The core segment density for $M_a = 10$ and variable f . (d) The core segment structural relaxation time uniformly throughout the film with increasing f .

B. Dynamics of the Entire Star Melt Film

We next consider how the temperature (T) dependence of the segmental relaxation dynamics of the entire star melt film is altered upon changing the chain functionality f and length m where other molecular and thermodynamic parameters are held fixed. In particular, we focus on the segmental relaxation time determined from the decay of the self-intermediate scattering function $F_s(q_0, t)$ (The Fourier transform of the distribution of the segmental displacements in time from an initial position or the “van Hove self-correlation function”) on a scale $(2\pi/q_0)$

corresponding to a polymer segment size, which in our model corresponds to a scale in the range of 1 nm to 2 nm. The calculation of $F_s(q_o, t)$ is standard and has been described at length in previous works [12], [13], [17]. The segmental relaxation time τ_a is determined at the time scale at which $F_s(q_o, t)$ decays to $1/e$. We show the results for $\tau(T)$ in Fig. 5 for a representative polymer film of thickness $h \approx 16$ at T_g . The simulation data in Fig. 5 indicate that the increasing the number of star arms f with a fixed star arm mass ($M_a = 10$), leads to a substantial slowing down of the relaxation dynamics of the film as whole, an effect seen in Fig. 4(c) on a layer-by-layer basis. This slowing down with increasing f becomes increasingly amplified as T is reduced. A similar slowing of dynamics was observed in the star melt material in the bulk [18] and in ring polymer melts of increasing knot complexity [19]. This slowing down of the dynamics of segmental dynamics of stars is broadly in accord with X-ray photon correlation measurements on star films. [53], [54]

These relaxation time data allow us to estimate how the glass transition temperature of these star films varies with molecular architecture. To do so, we evaluate a “computational” iso-kinetic definition of the glass-transition temperature, $\tau_a(T_g) = 1000$; this is analogous to the experimental convention of defining T_g by the temperature at which relaxation reaches 100s, except that we limit our time scale to those that are close to those accessible to equilibrium simulation. To estimate this temperature fairly precisely, we fit our data to the Vogel-Fulcher-Tammann equation [55], [56] and use the isokinetic criterion; we avoid extrapolation to the experimental time scale, since we have found extrapolations over such a large time scale to be frequently unreliable. From this approach, we estimate the linear polymer $T_g(f = 2) = 0.40 \pm 0.02$, where $\pm$ indicates the range of T_g . Temperature $T = 0.6$ is a representative intermediate temperature between the glass transition range and the high T Arrhenius regime, and our film thickness is also in the middle of the crossover range in which finite shifts of T_g and other properties are exhibited.

Fig 6 shows estimates of T_g using this dynamic definition for variable number of polymer arms f and arm mass M_a . The general trend in the shift of T_g with M_a is consistent with the previous study.[1], [18] However, there is an overall downward shift of all the star melt T_g data. Notice that while T_g approaches a constant value for large M_a . This plateau value of T_g seems to be related to the high mass limit of linear polymer film having the same thickness. As noted above, the situation of brush films as the film thickness grows indefinitely with increasing polymer mass so that the plateau value of T_g approaches a value comparable to the bulk material, although a small shift has been observed in graded polymer layers in the limit of densely grafted polymers[57], an effect which we suggest arises from a rigidification of the polymer chains that may be naturally expected in the dense brush limit. Rigidification from topological interactions was quantified by Vargas-Lara *et al.*[19] in the context of knotted ring polymers where the ring polymers were found to progressively stiffer with increasing knot complexity. A similar effect is expected in stars having many arms.

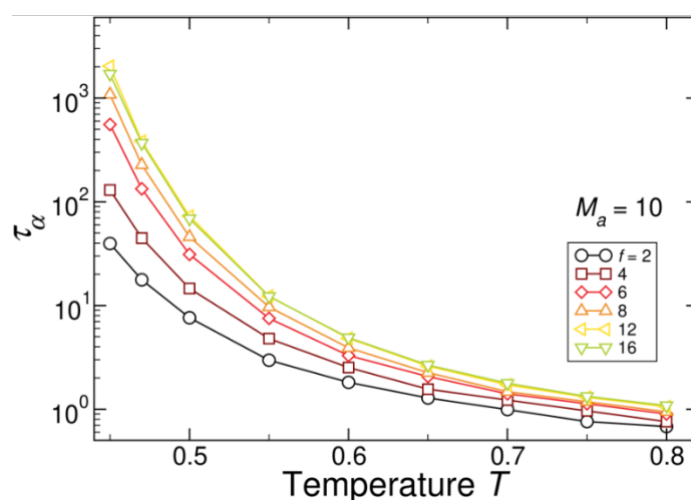


Figure 5. The relaxation time as a function of temperature T for varying functionality and a fixed arm mass $M_a = 10$.

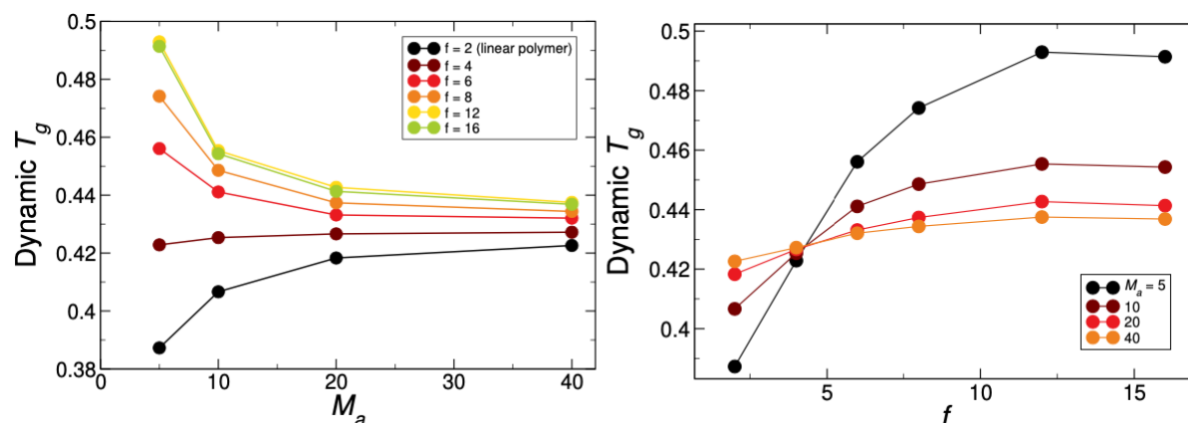


Figure 6. The dynamic T_g of star polymer film as a function of (a) arm mass M_a and (b) functionality f .

A complementary approach to characterize the variation of T_g is through a thermodynamic criterion. In particular, T_g can be alternatively estimated from the ‘kink’ in the T dependence of potential energy (or maximum in the specific heat) of the melt during heating, analogous to experimental DSC measurement where a peak in the specific heat at fixed heating rate defines T_g . This quasi-thermodynamic and the previous dynamic generally coincide in bulk materials, but they can significantly differ in film systems, due to differences in the sensitivity of each method to the mobility gradients across the film [15]. We show the T_g based on this quasi-thermodynamic criterion in Fig. 7, and these alternative T_g estimates are remarkably consistent with those estimated from the kinetic criterion above. Notably the variation of T_g with f is contrary to free volume expectations, in which having larger f leads to a greater free volume due a greater number of chain end-segments and would thus predict a decrease of T_g . This simple argument fails because it does not take into the strong densification of polymers that arises upon increasing branching and subtle effects associated with the alteration of the average shape of polymers as their topology is altered. [24] Note that the shift in T_g with M_a is very weak for $f=4$, where the chain effects and branching

effects on the polymer density compensate, [24] and that for a larger number of arms T_g increases to significantly larger values than linear polymers when the arm length is not very long. Figures 6(b) and 7(b) show how these shifts of T_g at fixed M_a as f is varied, illustrating from a different perspective how increasing the mass of the star arms progressively decreases the effect of polymer branching on T_g . The enhancement of T_g for $f > 4$ is also found for ring melts of increasing topological complexity m_c where the condition $f = 4$ corresponds to unknotted rings, consistent with the approximate ‘mapping’ between knotted ring and star polymers identified previously. [19] As mentioned above the thermodynamic can differ significantly from the kinetic estimate when the interaction strength between the polymer and substrate is large and attractive. Caution is thus advised in the interpretation of thermodynamic estimates of T_g -shifts. However, in the case of relatively weak attractive polymer-surface interaction strengths, the two methods to define T_g appear to be consistent, at least qualitatively.

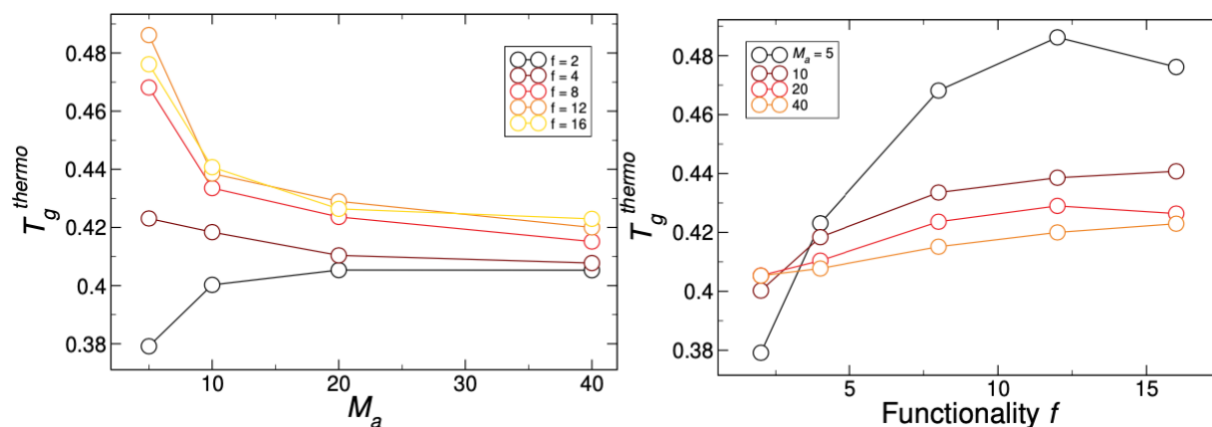


Figure 7. The thermodynamic T_g as a function of arm mass M_a and functionality f at a fixed cooling rate of 10^{-5} .

In previous work, we have shown that the variation of T_g of thin films with confinement can be understood qualitatively from the change of the cohesive interaction energy with

confinement.³⁹ The activation energy ΔH_a for relaxation and diffusion in the Arrhenius regime has long been correlated with the cohesive interaction energy [58], [59] and this scaling relation is supported by simulation studies of a similar coarse-grained model to our own [60], [61] so we may expect to obtain some further insight into our T_g trends from a determination of $\Delta H_a(f, M_a)$. While our ability to accurately estimate $\Delta H_a(f, M_a)$ is limited by the fact that films dewet at high T , we nonetheless see nearly Arrhenius T dependence of relaxation for the highest three temperatures simulated, which we use to estimate $\Delta H_a(f, M_a)$. Figure 8 shows the variation of $\Delta H_a(f, M_a = 10)$ for our polymer melt having a thickness, $h \approx 16$ and we include the variation of the kinetic T_g in the inset to this figure for comparison. Both $\Delta H_a(f, M_a = 10)$ and $T_g(\text{dynamic})$ exhibit a similar variation with f , increasing and then peaking around $f = 12$. Many previous studies have found a near linear variation of T_g and the high temperature activation energy in glass-forming liquids, so this correlation is not really surprising.[62]

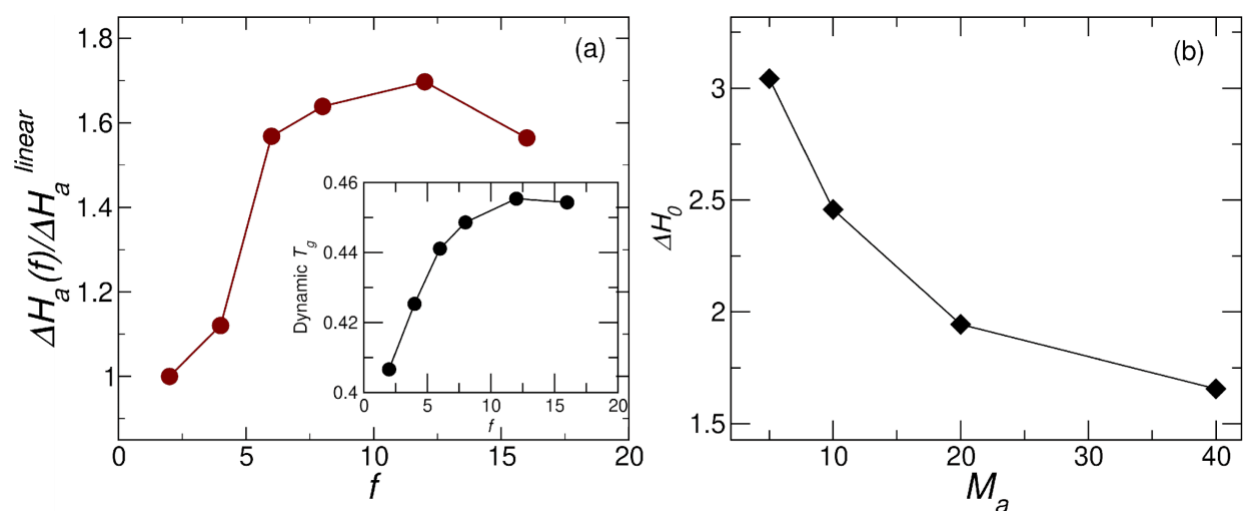


Figure 8. Activation energy as a function of the number of star arms and the length of the star arms. a) High temperature activation energy ΔH_a as a function of f for fixed arm length, $M_a = 10$. Inset shows the dynamic T_g as a function of f for comparison. b) High temperature activation energy ΔH_0 as a function of arm molecular mass M_a for $f = 8$.

As opposed to the well-known increase of the activation energy of polymers with polymer mass [63], [64], the activation energy decreases with the length of the arms for a representative star polymer having a moderate number of arms ($f=10$). This inverted trend is indicated in Fig. 8(b), and is consistent with the decrease of $T_g(M_a)$ observed in Fig. 6(a). A general increase of activation energy with the number of star arms and with random branching in melts of branched polymers has been observed, as reviewed by Graessley and coworkers [65] and others [66], [67]; an increase of activation energy for low molecular mass rings in comparison to linear polymer melts has also been reported. [68]

In many theoretical descriptions for the temperature dependence of dynamics approaching the glass transition, including the Adam-Gibbs approach,[69] the random first-order transition theory [70], the generalized entropy theory [10], and any theory based on activated dynamics, the activation energy $\Delta H_a(f, M_a)$ plays an important role. Thus, the changes in $\Delta H_a(f, M_a)$ that we observe necessarily imply changes in the fragility of these materials. That said, fragility changes can also arise from changes in the degree of collective motion, since the scale of this motion typically scales $\Delta H_a(f, M_a)$. We tested the possibility of changes in collective string-like motion [71], and found that the scale of collective monomer exchanges is not strongly dependent on star architecture (see supplementary information), similar to the findings of Ref. [18]. Hence, changes in $\Delta H_a(f, M_a)$ make the dominant contribution to changes in the fragility of these materials.

Conclusion

We have studied how increasing the number of star arms influences the segmental dynamics of a thin polymer film of intermediate thickness ($h_g \approx 16$ nm) less than the critical thickness (estimated to be 65 nm in laboratory units for linear polymers) at which the glass-

transitions to show appreciable (2 K) deviations from its bulk value. Our study is also limited in scope to star polymer films supported on a substrate having a moderately-attractive polymer substrate so that the film is stable and where equilibrium calculations can be performed at temperatures well above the glass transition temperature. Previous work on linear polymer chains under this type of condition showed that T_g of the polymer film shifted downward [36], [37], [72], as often observed experimentally linear polymer melt films under supported on weakly attractive surfaces. confined linear polymer chain melts is shifted downward. We find that the shift of T_g of the star polymers changes from a negative to a positive value for f near 4, consistent with previous simulation studies on linear polymer melts. [37] The magnitude of this shift is progressively diminished with increasing arm mass and increasing f to large value causes the T_g to have a maximum and presumably the T_g shift also approaches a constant in simulations for very large f , but this limit is not accessible in our simulations. We find that these changes in the strength of the temperature dependence of the segmental relaxation time arise from a convolution of effects- a change of the activation free energy in the Arrhenius regime and rate of change of the degree of collective motion with temperature. Altering molecular topology alters the fundamental nature of the glass-forming material rather than just altering T_g .

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References

- [1] A. Chremos, E. Glynos, and P. F. Green, "Structure and dynamical intra-molecular heterogeneity of star polymer melts above glass transition temperature," *J. Chem. Phys.*, vol. 142, no. 4, p. 044901, Jan. 2015.
- [2] J. M. Ren *et al.*, "Star Polymers," *Chem. Rev.*, vol. 116, no. 12, pp. 6743–6836, Jun. 2016.
- [3] T. Pakula, D. Vlassopoulos, G. Fytas, and J. Roovers, "Structure and dynamics of melts of multiarm polymer stars," *Macromolecules*, vol. 31, no. 25, pp. 8931–8940, Dec. 1998.
- [4] D. Grest, G. S.; Fetters, L. J.; Huang, J. S.; Richter, *Star polymers: experiment, theory, and simulation*, vol. 94. John Wiley & Sons, 2007, p. 67.
- [5] T. Kinsey *et al.*, "Impact of Molecular Architecture on Dynamics of Miktoarm Star Copolymers," *Macromolecules*, vol. 51, no. 14, pp. 5401–5408, Jul. 2018.
- [6] T. G. Fox and P. J. Flory, "The glass temperature and related properties of polystyrene. Influence of molecular weight," *J. Polym. Sci.*, vol. 14, no. 75, pp. 315–319, Sep. 1954.
- [7] J. D. Ferry, *Viscoelastic properties of polymers*. John Wiley & Sons, 1980.
- [8] T. G. Fox and P. J. Flory, "Second-Order Transition Temperatures and Related Properties of Polystyrene. I. Influence of Molecular Weight," *J. Appl. Phys.*, vol. 21, no. 6, pp. 581–591, Jun. 1950.
- [9] E. B. Stukalin, J. F. Douglas, and K. F. Freed, "Application of the entropy theory of glass formation to poly(α -olefins)," *J. Chem. Phys.*, vol. 131, no. 11, p. 114905, Sep. 2009.
- [10] J. Dudowicz, K. F. Freed, and J. F. Douglas, "Generalized entropy theory of polymer glass formation," in *Advances in Chemical Physics*, vol. 137, 2008, pp. 125–222.
- [11] W. Zhang, F. W. Starr, and J. F. Douglas, "Reconciling computational and experimental trends in the temperature dependence of the interfacial mobility of polymer films," *J. Chem. Phys.*, vol. 152, no. 12, p. 124703, Mar. 2020.
- [12] W. Zhang, J. F. Douglas, and F. W. Starr, "Dynamical heterogeneity in a vapor-deposited polymer glass," *J. Chem. Phys.*, vol. 146, no. 20, p. 203310, May 2017.

- [13] W. Zhang, J. F. Douglas, and F. W. Starr, "Effects of a 'bound' substrate layer on the dynamics of supported polymer films," *J. Chem. Phys.*, vol. 147, no. 4, p. 044901, Jul. 2017.
- [14] P. Z. Hanakata, J. F. Douglas, and F. W. Starr, "Interfacial mobility scale determines the scale of collective motion and relaxation rate in polymer films.," *Nat. Commun.*, vol. 5, no. May, p. 4163, Jun. 2014.
- [15] W. Zhang, J. F. Douglas, and F. W. Starr, "Why we need to look beyond the glass transition temperature to characterize the dynamics of thin supported polymer films," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 115, no. 22, pp. 5641–5646, 2018.
- [16] W. Zhang, F. W. Starr, and J. F. Douglas, "Collective Motion in the Interfacial and Interior Regions of Supported Polymer Films and Its Relation to Relaxation," *J. Phys. Chem. B*, vol. 123, no. 27, pp. 5935–5941, 2019.
- [17] A. N. Storey, W. Zhang, J. F. Douglas, and F. W. Starr, "How Does Monomer Structure Affect the Interfacial Dynamics of Supported Ultrathin Polymer Films?," *Macromolecules*, vol. 53, no. 21, pp. 9654–9664, Nov. 2020.
- [18] J. Fan, H. Emamy, A. Chremos, J. F. Douglas, and F. W. Starr, "Dynamic heterogeneity and collective motion in star polymer melts," *J. Chem. Phys.*, vol. 152, no. 5, p. 054904, Feb. 2020.
- [19] F. Vargas-Lara, B. A. Pazmiño Betancourt, and J. F. Douglas, "Influence of knot complexity on glass-formation in low molecular mass ring polymer melts," *J. Chem. Phys.*, vol. 150, no. 10, p. 101103, Mar. 2019.
- [20] P. G. Santangelo, C. M. Roland, T. Chang, D. Cho, and J. Roovers, "Dynamics near the glass temperature of low molecular weight cyclic polystyrene," *Macromolecules*, vol. 34, no. 26, pp. 9002–9005, 2001.
- [21] S. . Clarson, K. Dodgson, and J. . Semlyen, "Studies of cyclic and linear poly(dimethylsiloxanes): 19. Glass transition temperatures and crystallization behaviour," *Polymer (Guildf)*, vol. 26, no. 6, pp. 930–934, Jun. 1985.
- [22] E. A. Di Marzio and C. M. Guttman, "The glass temperature of polymer rings,"

- Macromolecules*, vol. 20, no. 6, pp. 1403–1407, Nov. 1987.
- [23] A. Chremos and J. F. Douglas, “Communication: When does a branched polymer become a particle?,” *J. Chem. Phys.*, vol. 143, no. 11, p. 111104, Sep. 2015.
- [24] A. Chremos and J. F. Douglas, “A comparative study of thermodynamic, conformational, and structural properties of bottlebrush with star and ring polymer melts,” *J. Chem. Phys.*, vol. 149, no. 4, p. 044904, Jul. 2018.
- [25] A. Chremos and J. F. Douglas, “Hidden Hyperuniformity in Soft Polymeric Materials,” *Phys. Rev. Lett.*, vol. 121, no. 25, p. 258002, Dec. 2018.
- [26] A. Chremos and J. F. Douglas, “Influence of Branching on the Configurational and Dynamical Properties of Entangled Polymer Melts,” *Polymers (Basel)*, vol. 11, no. 6, p. 1045, Jun. 2019.
- [27] A. Chremos, C. Jeong, and J. F. Douglas, “Influence of polymer architectures on diffusion in unentangled polymer melts,” *Soft Matter*, vol. 13, no. 34, pp. 5778–5784, 2017.
- [28] F. Vargas-Lara, B. A. Pazmiño Betancourt, and J. F. Douglas, “Communication: A comparison between the solution properties of knotted ring and star polymers,” *J. Chem. Phys.*, vol. 149, no. 16, p. 161101, Oct. 2018.
- [29] E. Glynos, B. Frieberg, H. Oh, M. Liu, D. W. Gidley, and P. F. Green, “Role of Molecular Architecture on the Vittrification of Polymer Thin Films,” *Phys. Rev. Lett.*, vol. 106, no. 12, p. 128301, Mar. 2011.
- [30] E. Glynos, B. Frieberg, A. Chremos, G. Sakellariou, D. W. Gidley, and P. F. Green, “Vitrification of Thin Polymer Films: From Linear Chain to Soft Colloid-like Behavior,” *Macromolecules*, vol. 48, no. 7, pp. 2305–2312, Apr. 2015.
- [31] B. Frieberg, E. Glynos, and P. F. Green, “Structural Relaxations of Thin Polymer Films,” *Phys. Rev. Lett.*, vol. 108, no. 26, p. 268304, Jun. 2012.
- [32] P. von Tiedemann *et al.*, “Tapered Multiblock Star Copolymers: Synthesis, Selective Hydrogenation, and Properties,” *Macromolecules*, vol. 53, no. 11, pp. 4422–4434, Jun. 2020.

- [33] L. Zhang, R. Elupula, S. M. Grayson, and J. M. Torkelson, "Major Impact of Cyclic Chain Topology on the T_g -Confinement Effect of Supported Thin Films of Polystyrene," *Macromolecules*, vol. 49, no. 1, pp. 257–268, Jan. 2016.
- [34] L. Zhang, R. Elupula, S. M. Grayson, and J. M. Torkelson, "Suppression of the Fragility-Confinement Effect via Low Molecular Weight Cyclic or Ring Polymer Topology," *Macromolecules*, vol. 50, no. 3, pp. 1147–1154, Feb. 2017.
- [35] L. Li, Z. Qiang, X. Chen, K. Jin, M. Wang, and J. M. Torkelson, "Impact of bottlebrush chain architecture on T_g -confinement and fragility-confinement effects enabled by thermo-cleavable bottlebrush polymers synthesized by radical coupling and atom transfer radical polymerization," *J. Polym. Sci.*, vol. 58, no. 20, pp. 2887–2905, Oct. 2020.
- [36] P. Z. Hanakata, J. F. Douglas, and F. W. Starr, "Local variation of fragility and glass transition temperature of ultra-thin supported polymer films," *J. Chem. Phys.*, vol. 137, no. 24, p. 244901, Dec. 2012.
- [37] P. Z. Hanakata, B. A. Pazmiño Betancourt, J. F. Douglas, and F. W. Starr, "A unifying framework to quantify the effects of substrate interactions, stiffness, and roughness on the dynamics of thin supported polymer films," *J. Chem. Phys.*, vol. 142, no. 23, p. 234907, Jun. 2015.
- [38] B. A. Pazmiño Betancourt, P. Z. Hanakata, F. W. Starr, and J. F. Douglas, "Quantitative relations between cooperative motion, emergent elasticity, and free volume in model glass-forming polymer materials," *Proc. Natl. Acad. Sci.*, vol. 112, no. 10, pp. 2966–2971, Mar. 2015.
- [39] W. Zhang, H. Emamy, B. A. Pazmiño Betancourt, F. Vargas-Lara, F. W. Starr, and J. F. Douglas, "The interfacial zone in thin polymer films and around nanoparticles in polymer nanocomposites," *J. Chem. Phys.*, vol. 151, no. 12, p. 124705, Sep. 2019.
- [40] W. Zhang *et al.*, "The Interfacial Layers Around Nanoparticle and Its Impact on Structural Relaxation and Glass Transition in Model Polymer Nanocomposites," 2021, pp. 101–131.
- [41] W. Xia, S. Mishra, and S. Keten, "Substrate vs. free surface: Competing effects on the glass transition of polymer thin films," *Polym. (United Kingdom)*, vol. 54, no. 21, pp.

- 5942–5951, 2013.
- [42] D. D. Hsu, W. Xia, J. Song, and S. Keten, “Glass-Transition and Side-Chain Dynamics in Thin Films: Explaining Dissimilar Free Surface Effects for Polystyrene vs Poly(methyl methacrylate),” *ACS Macro Lett.*, vol. 5, no. 4, pp. 481–486, Apr. 2016.
- [43] S. Plimpton, P. S. and S. Plimpton, “Fast parallel algorithms for short-range molecular dynamics,” *J. Comput. Phys.*, vol. 117, no. 1, pp. 1–19, 1995.
- [44] M. Tuckerman, B. Berne, and G. Martyna, “Reversible multiple time scale molecular dynamics,” *J. Chem. ...*, vol. 97, no. 3, pp. 1990–2001, 1992.
- [45] E. Yang, R. J. S. Ivancic, E. Y. Lin, and R. A. Riggleman, “Effect of polymer–nanoparticle interaction on strain localization in polymer nanopillars,” *Soft Matter*, vol. 16, no. 37, pp. 8639–8646, 2020.
- [46] D. Vlassopoulos, G. Fytas, T. Pakula, and J. Roovers, “Multiarm star polymers dynamics,” *J. Phys. Condens. Matter*, vol. 13, no. 41, pp. R855–R876, Oct. 2001.
- [47] D. Vlassopoulos, T. Pakula, G. Fytas, J. Roovers, K. Karatasos, and N. Hadjichristidis, “Ordering and viscoelastic relaxation in multiarm star polymer melts,” *Europhys. Lett.*, vol. 39, no. 6, pp. 617–622, Sep. 1997.
- [48] A. Giuntoli, A. Chremos, and J. F. Douglas, “Influence of polymer topology on crystallization in thin films,” *J. Chem. Phys.*, vol. 152, no. 4, p. 044501, Jan. 2020.
- [49] A. Stukowski, “Visualization and analysis of atomistic simulation data with OVITO—the Open Visualization Tool,” *Model. Simul. Mater. Sci. Eng.*, vol. 18, no. 1, p. 015012, Jan. 2010.
- [50] F. Zhang *et al.*, “Anomalous Confinement Slows Surface Fluctuations of Star Polymer Melt Films,” *ACS Macro Lett.*, vol. 7, no. 7, pp. 834–839, Jul. 2018.
- [51] Q. He, S. Narayanan, D. T. Wu, and M. D. Foster, “Confinement Effects with Molten Thin Cyclic Polystyrene Films,” *ACS Macro Lett.*, vol. 5, no. 9, pp. 999–1003, Sep. 2016.
- [52] O. K. C. Tsui, T. P. Russell, and C. J. Hawker, “Effect of Interfacial Interactions on the Glass Transition of Polymer Thin Films,” *Macromolecules*, vol. 34, no. 16, pp. 5535–

- 5539, Jul. 2001.
- [53] S. Wang, S. Yang, J. Lee, B. Akgun, D. T. Wu, and M. D. Foster, “Anomalous Surface Relaxations of Branched-Polymer Melts,” *Phys. Rev. Lett.*, vol. 111, no. 6, p. 068303, Aug. 2013.
- [54] E. Glynos *et al.*, “Free Surface Relaxations of Star-Shaped Polymer Films,” *Phys. Rev. Lett.*, vol. 119, no. 22, p. 227801, Nov. 2017.
- [55] G. S. Fulcher, “Analysis of Recent Measurements of the Viscosity of Glasses,” *J. Am. Ceram. Soc.*, vol. 8, no. 6, pp. 339–355, Jun. 1925.
- [56] G. Tammann and W. Hesse, “Die Abhängigkeit der Viskosität von der Temperatur bei unterkühlten Flüssigkeiten,” *Zeitschrift für Anorg. und Allg. Chemie*, vol. 156, no. 1, pp. 245–257, Oct. 1926.
- [57] S. Yamamoto, Y. Tsujii, and T. Fukuda, “Glass transition temperatures of high-density poly(methyl methacrylate) brushes,” *Macromolecules*, vol. 35, no. 16, pp. 6077–6079, Jul. 2002.
- [58] R. H. Ewell, “The Reaction Rate Theory of Viscosity and Some of its Applications,” *J. Appl. Phys.*, vol. 9, no. 4, pp. 252–269, Apr. 1938.
- [59] J. F. Kincaid, H. Eyring, and A. E. Stearn, “The Theory of Absolute Reaction Rates and its Application to Viscosity and Diffusion in the Liquid State,” *Chem. Rev.*, vol. 28, no. 2, pp. 301–365, Apr. 1941.
- [60] W.-S. Xu, J. F. Douglas, and K. F. Freed, “Influence of Cohesive Energy on the Thermodynamic Properties of a Model Glass-Forming Polymer Melt,” *Macromolecules*, vol. 49, no. 21, pp. 8341–8354, Nov. 2016.
- [61] W.-S. Xu, J. F. Douglas, and K. F. Freed, “Influence of Cohesive Energy on Relaxation in a Model Glass-Forming Polymer Melt,” *Macromolecules*, vol. 49, no. 21, pp. 8355–8370, Nov. 2016.
- [62] B. Schmidtke, N. Petzold, R. Kahlau, M. Hofmann, and E. A. Rössler, “From boiling point to glass transition temperature: Transport coefficients in molecular liquids follow

- three-parameter scaling,” *Phys. Rev. E*, vol. 86, no. 4, p. 041507, Oct. 2012.
- [63] W. Lauzmann, H. Eyring, W. Kauzman, and H. Eyring, “The Viscous Flow of Large Molecules,” *J. Am. Chem. Soc.*, vol. 62, no. 11, pp. 3113–3125, Nov. 1940.
- [64] C. Jeong and J. F. Douglas, “Mass dependence of the activation enthalpy and entropy of unentangled linear alkane chains,” *J. Chem. Phys.*, vol. 143, no. 14, p. 144905, Oct. 2015.
- [65] J. M. Carella, J. T. Gotro, and W. W. Graessley, “Thermorheological Effects of Long-Chain Branching in Entangled Polymer Melts,” *Macromolecules*, vol. 19, no. 3, pp. 659–667, May 1986.
- [66] P. G. Santangelo and C. M. Roland, “Effect of long-chain branching on the rheology of 1,4-polyisoprene,” *J. Non. Cryst. Solids*, vol. 235–237, pp. 709–716, Aug. 1998.
- [67] A. Munari, G. Pezzin, and F. Pilati, “Linear and branched poly(butyleneisophthalate): Activation energy for melt flow,” *Rheol. Acta*, vol. 29, no. 5, pp. 469–474, Sep. 1990.
- [68] V. Arrighi *et al.*, “Effect of Chain Length and Topological Constraints on Segmental Relaxation in Cyclic PDMS,” *Macromolecules*, vol. 51, no. 18, pp. 7209–7223, Sep. 2018.
- [69] G. Adam and J. H. Gibbs, “On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids,” *J. Chem. Phys.*, vol. 43, no. 1, pp. 139–146, Jul. 1965.
- [70] T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, “Scaling concepts for the dynamics of viscous liquids near an ideal glassy state,” *Phys. Rev. A*, vol. 40, no. 2, pp. 1045–1054, Jul. 1989.
- [71] C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, “Stringlike Cooperative Motion in a Supercooled Liquid,” *Phys. Rev. Lett.*, vol. 80, no. 11, pp. 2338–2341, Mar. 1998.
- [72] C. J. Ellison and J. M. Torkelson, “The distribution of glass-transition temperatures in nanoscopically confined glass formers,” *Nat. Mater.*, vol. 2, no. 10, pp. 695–700, Oct. 2003.

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