Dynamic heterogeneity and collective motion in star polymer melts

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Jinpeng Fan 📵, Hamed Emamy 📵, Alexandros Chremos 跑, Jack F. Douglas 跑, and Francis W. Starr 跑

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AFFILIATIONS

¹Department of Physics, Wesleyan University, Middletown, Connecticut 06459-0155, USA

²Department of Chemical Engineering, Columbia University, New York, New York 10027, USA

³Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg,

Maryland 20899, USA

a) Author to whom correspondence should be addressed: fstarr@wesleyan.edu

ABSTRACT

While glass formation of linear chain polymer melts has widely been explored, comparatively little is known about glass formation in star polymer melts. We study the segmental dynamics of star polymer melts via molecular dynamics simulations and examine the cooperative nature of segmental motion in star melts. In particular, we quantify how the molecular architecture of star polymers, i.e., the number of arms and the length of those arms, affects the glass transition temperature T_g , the non-Gaussian nature of molecular displacements, the collective string-like motion of monomers, and the role of chain connectivity in the cooperative motion. Although varying the number of arms f and the molecular mass M_a of the star arms can significantly influence the average star molecular shape, all our relaxation data can be quantitatively described in a unified way by the string model of glass formation, an activated transport model that derives from the Adam–Gibbs model, where the degree of cooperative motion is identified with the average length L of string-like particle exchange motions observed in our simulations. Previous work has shown the consistency of the string model with simulations of linear polymer–surface interactions, where there are likewise large mobility gradients as in the star polymer melts studied in the present paper.

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I. INTRODUCTION

There is a growing interest in controlling the molecular topology of polymers in order to control the properties of polymer materials for the diverse technological applications of this broad class of materials and for the intrinsic insights that variations of topology can make into the nature of chain entanglement, polymer crystallization, glass formation, etc. "Regular star" polymers, consisting of multiple linear chains of the same length grafted onto a core monomer or monomer scale core particle represent perhaps the simplest non-linear chain topology and many of the structural and dynamical properties of this class of polymers in both solution and the melt state have been studied in previous work.^{1–10} For a large number of arms f, star polymers often behave in many ways, more like "soft" particles or colloids rather than linear chains due to their progressively spherical shape and increasingly dense packing within the core of these molecules as f becomes large.^{1,3,11} Increasing falso leads to a progressive rigidification of star polymers,^{1,3,4} while increasing the molecular mass M_a of the star arms, having f fixed and large, tends to make the stars "softer."^{7,9} Unlike linear chains, many arm star polymers exhibit a gradient of mobility from their core to their periphery, which can be observed experimentally by selectively labeling sites along the star arm.¹⁰

The glass transition temperature T_g is a key property for the processing and manufacture of polymer-based materials and T_g of star polymer melts can exhibit nontrivial dependence on star molecular parameters.^{7,9,12} While previous work has discussed the effect of star architecture on T_g defined by the relaxation of the core particle near the center of mass of the star polymer,⁷ there has been little work on how the star size and shape influence the overall

segmental dynamics within the star polymer. It is widely appreciated that polymeric glass-forming materials are generally dynamically heterogeneous upon approaching T_g ,^{13,14} but the excluded volume interactions within the star can be expected to alter the dynamics of star polymers in comparison with their linear chain polymer counterparts having the same mass and chain backbone chemical structure. In particular, it has been confirmed by experiments and computer simulations that particles with extreme mobility or immobility relative to the mean form dynamic clusters, and clusters of mobile particles can be further decomposed into subsets of particles exhibiting string-like cooperative replacement motion having direct significance for understanding the dynamics of glass-forming liquids.^{15–20} Therefore, it is natural to ask how the chain topology influences this collective motion, and how this phenomenon dovetails with the intra-molecular mobility gradient within star polymers.

Although the glass transition has been a subject of intense study for decades, the origin of the rapidly increasing relaxation time and viscosity approaching T_g remains a subject of active debate. On cooling toward T_g , the relaxation can be described by an increasing activation free energy barrier for molecular rearrangement.^{21,22} Approaching T_g , the effective activation energy can become even higher than that of the chemical bonds, which naturally leads to an interpretation of the activation process as the reorganization of multiple atoms or molecules. Supporting this interpretation, Adam and Gibbs²³ (AG) proposed a theory in 1965 that relates the relaxation time to the size of hypothetical "cooperatively rearranging regions" (CRRs). Specifically, AG proposed that the activation energy for relaxation is proportional to the number of rearranging atoms in a CRR; however, they provided no molecular definition for these regions. The string model of glass formation builds on these ideas, and identifies string-like cooperative motion with the CRRs of the AG model, where the average number of segments in these welldefined dynamical structures is taken to be the "degree of cooperativity" z of the AG model. This string model has been validated for a range of polymeric glass-forming systems-polymers at constant volume and pressure^{24,25} and variable polymer cohesive interaction strength,²⁶ and this model has been very successful in describing the dynamics of thin supported films of variable thickness and polymer nanocomposites of variable concentration and variable polymer surface interaction strength.^{27–29} The results for supported polymer films and polymer nanocomposites are encouraging for the present study on polymer melts since these polymer materials exhibit large gradients in mobility as in the case of star melts. The novel feature of star melts, however, is that the mobility gradients exist within the molecules due to the molecular topology rather than due to the presence of interfacial interactions as in the case of nanoparticles. The investigation of the application of the string model to polymer melts provides a test of the generality of the predictions of the string model of relaxation.

The properties of star polymers in bulk and at interfaces have been studied extensively by both experiments^{6,10,30,31} and simulations.^{2,7,8,31} Here, we briefly highlight some observed trends in the bulk properties that are relevant to our study of the star polymer melts as the number of arms f and number of segments in the arms M_a are varied. Chremos and co-workers have previously shown^{7,8} that there is a counter-intuitive inversion in the molecular mass dependence of the average segmental density ρ with increasing f.

Specifically, ρ changes from increasing with M_a for linear polymer chains, as one anticipated from the observations of Fox and Flory, 32,33 to decreasing with M_a for star polymers when f is larger than a value $f \approx 5-6$.^{7,8,34} Chremos and Douglas have also shown that this density inversion coincides with the progressive change in the average shape of star polymers in the melt from a relatively anisotropic form for linear polymer chains to a more spherical one with increasing f and decreasing M_a .^{8,34} This type of crossover is reflected in other basic material properties, such as isothermal compressibility and isobaric thermal expansion.³⁴ These changes in basic thermodynamic properties of star polymers are all consequences of how the topological parameter f influences the molecular packing in the melt state through changes in the molecular shape and rigidity. We naturally expect the dynamical properties of such molecules to also be greatly affected. This expectation has already borne out by simulations estimates of star polymer melts, where an inversion of the mass dependence of $T_g(f)$ is observed for $f \approx 5-6$ arms, similar to average segmental density.^{7,8} The present work expands upon this analysis of star polymer melt dynamics by examining how the star architecture influences the dynamic heterogeneity and collective motion within star polymer melts. We confirm the previous findings of Chremos and co-workers⁷ for the trend of T_g with the number of star arms and further show that the relaxation dynamics of these melts can be described in a unified way by the string model of glass formation. Recent work has also examined the role of knot complexity in glass formation in ring polymer melts, where variation in the average knot crossing number was indicated to give rise to similar variations in the melt dynamics and thermodynamics of polymer melts as varying the number of arms of star polymers.35

In this paper, we study segmental dynamics and the associated dynamical heterogeneity of star polymer melts with various architectures at a broad range of temperatures via molecular dynamics (MD) simulations using the same coarse-grained bead-spring model studied in the previous work.⁷ In doing so, we contrast star segmental dynamics with dynamics of the star center of mass, and compare dynamical heterogeneity of star polymers with that of their linear counterparts. As a first step toward a comprehensive understanding of the dynamics of star polymer melts, we examine the mean segmental dynamics of star polymers with different geometries at various temperatures. We find that the relaxation time τ exhibits large sensitivity to the number of arms f when the arm mass M_a is relatively small and a large sensitivity to M_a when f is large. These findings can be attributed to the crowding effect near the star core at large *f*, which leads to a much slower relaxation near the star core. We find that the overall behavior of T_g for segmental motion as a function of the number of arms f and molecular mass M_a is similar to that previously found for the star core. However, T_g of the star segmental relaxation for the longer arm length M_a is less sensitive to the number of arms f compared with that of the core when M_a is large. As the system consists of more monomers at large M_a , the crowding near the center is averaged among all segments and hence a less rapid change of T_g , which accounts for the difference from the core particle behavior. By applying the same methods that are frequently employed in the study of other dynamically heterogeneous glass-forming systems, we investigate how the architecture affects spatial heterogeneity of star polymers approaching T_g . We find that the sensitivity of the strength of heterogeneity to f and M_a

results from central crowding as well, which then indicates that the mobility gradient near the star core controls the architecture dependence of both segmental relaxation and dynamical heterogeneity. This intramolecular mobility gradient also gives rise to features that do not occur for linear polymers. Finally, we test the validity of the string model in star polymer systems and find that relaxation time τ is consistent with the AG approach, regardless of the star geometry.

II. MOLECULAR MODEL AND SIMULATION PROTOCOLS

We perform molecular dynamics simulations for systems consisting of 400 star polymers. We use a coarse-grained model, in which each star polymer is modeled as a core particle with f attached arms and M_a monomers per arm, where we investigate a range of architectural parameters: f = 2, 3, 4, 5, 6, 8, 12, and 16 and M_a = 5, 10, 20, and 40. Chains of the star polymers are described by "bead-spring" interactions, and we use the model and initial configurations from our previous work.⁷ More specifically, interactions between non-bonded monomers are described by the Lennard-Jones (LJ) potential; bonds between monomers within a star polymer are described by a harmonic potential. Distances are defined relative to the LJ diameter σ of the polymer beads, and the core particle has half the diameter of a polymer bead. We set the mass of polymer beads and cores to be m_h and $m_c = 0.125m_h$, respectively, so that the mass scales linearly with the volume. The LJ potential between beads along the arms has a cutoff distance r_c = 2.5σ to include attractions; the core-core and core-monomer interactions are modeled as a purely repulsive Weeks-Chandler-Andersen potential³⁶ with cut-off distances $r_c \approx 0.62\sigma$ and $r_c \approx$ 0.87σ , respectively, to take into account the difference in particle sizes between cores and monomers.³⁷ The harmonic bond potential is given by $V_{H} = (K/2)(r - r_0)^2$, where the spring constant $K = 5000\epsilon/\sigma^2$, the equilibrium position between the core and its neighbors is $r_0 = 0.75\sigma$ and $r_0 = 0.99\sigma$ between the monomers along each arm. Energy is defined relative to the LJ energy parameter ϵ and we use the same energy and interaction range parameters for all interactions so that $\epsilon = \epsilon_{cc} = \epsilon_{cb}$ and $\sigma = \sigma_{cc} = \sigma_{cb}$. All units are reported in standard reduced LJ units, which are given in terms of strength ϵ and size σ_{bb} of non-bonded polymer interactions. Accordingly, T is given by $\epsilon/k_{\rm B}$, where $k_{\rm B}$ is Boltzmann's constant, and time is given in units of $(m\sigma^2/\epsilon)^{1/2}$, where *m* is the mass. Reduced units can be mapped to physical units with a size of chain segments $\sigma \approx 1$ nm–2 nm, time is in ps, and $\epsilon \approx$ 1 kJ/mol.

To examine the nature of glass-formation, we investigate a broad range of temperatures *T* from 0.425 to 2.0. We simulate systems using the large scale atomic/molecular massively parallel simulator (LAMMPS) developed at Sandia National Laboratories.³⁸ Simulations are performed in a cubic box with length *L*, and periodic boundary conditions are applied in all three directions. Simulations consist of equilibration runs (*NPT* ensemble) performed at *P* = 0 and temperature *T*; these simulations are followed by data production runs (*NVT* ensemble), where the volume is determined by the mean volume from the *NPT* equilibration run. We choose *P* = 0, since atmospheric conditions correspond to a small external pressure.

To briefly illustrate the structural properties of the model, we present the structure factor $S_c(q)$ of central beads and segmental structure factor S(q) for star polymers with various number of arms f and the arm length $M_a = 5$ at temperature T = 0.5 (Fig. 1). At small f, $S_c(q) \approx 1$, which suggests that such stars behave akin to an ideal gas in terms of segmental distribution; S(q) exhibits a peak at $q \approx 7$, which corresponds to the length scales of the nearest neighbors. We note that $S_c(q)$ at f = 2shows a small peak at $q \approx 7$. This observation can be attributed to the fact that the cores of linear chains are only neighbored by two monomers and packed closely to cores from other chains; thus, $S_c(q)$ has a more ordered structure at $q \approx 7$, where S(q) reaches its peak. As f increases, $S_c(q)$ resembles a segmental structure factor with the exception that the first peak occurs at a smaller $q \approx 1.5$, indicating the soft-particle behavior of stars at large f. This feature is also reflected in the S(q) such that S(q) for large f displays an additional peak at $q \approx 1.5$. The structural properties shown in $S_c(q)$ and S(q) are consistent with observations in our previous work.

We emphasize that the observed crossover to "soft-particle" behavior around $f \approx 6-8$ is distinct from the emergence of particle like structures having a dense core for much larger *f*. Specifically,



FIG. 1. (a) Structure factor $S_c(q)$ for core particles and (b) segmental structure factor S(q) for star polymers with various number of arms *f* and the arm length $M_a = 5$ at T = 0.5. At f = 16, $S_c(q)$ resembles S(q) and exhibits a peak at $q \approx 1.5$, where S(q) shows an additional peak, indicating a soft-particle behavior for stars having such a large *f*.

the emergent soft-particle behavior discussed above corresponds to a transition in the average molecular shape from the relatively anisotropic shape of linear polymers to the more symmetric average shape for stars having a moderate number of arms ($f \approx 6-8$). We may view these moderate number of arm stars as being highly deformable or "ultra-soft" particles.³ At larger f than we investigate, it is widely appreciated that stars develop a dense core starting around $f \gtrsim 24$.^{40–42} Thus, there are two distinct structural transitions in star polymers in the melt with increasing f that can be associated with the emergence of particle like attributes. Each of these transitions in the star structure is reflected in both thermodynamic and dynamic property changes in star polymer melts. Specifically, significant changes in the rheological properties⁴³ of star polymer melts have been observed for $f \gtrsim 8$, and molecular dynamics simulations have further indicated that the density and glass transition are equal or somewhat above their bulk values for low molecular mass stars having f values in this range.⁶ These property changes derive from the relatively efficient packing of these highly deformable or "soft" particles.³ Measurements also point to changes in dynamics and equilibrium properties in the many arm ($f \gtrsim 24$) limit, where the stars acquire a dense core. For example, Glynos et al.⁴⁴ found that T_{q} of star films for such many arm star melts was nearly the same as for linear chains in the high mass limit. Although stars in this large f regime are more comparable to polymer-grafted nanoparticles or colloidal particles than soft spheres, many arm stars do not tend to crystallize^{40,45} until f > 100 because of softness of the star interfacial regions. The present work focuses on the computationally accessible problem of stars having a moderate number of arms.

III. RESULTS

A. Mean segmental dynamics

Previous work⁷ considered the glass formation associated with the dynamics of the star core. We first contrast the glass formation based on mean segmental motion with that of the star core, which approximates the dynamics of the star center of mass. To quantify the mean dynamics, we evaluate the coherent density-density correlation function,

$$F(q,t) = \frac{1}{NS(q)} \sum_{j=1}^{N} \sum_{k=1}^{N} \langle e^{-iq(r_j(t) - r_k(0))} \rangle$$

where *N* is the number of monomers in the system and $r_j(t)$ represents the position of monomer *j* at time *t*, for star polymers with different topologies. F(q, t) is also known as the intermediate scattering function. We study F(q, t) at the wave vector q_0 corresponding to the nearest neighbor molecular spacing of the static structure factor S(q), and we define the relaxation time τ as $F(q_0, \tau) = 0.2$. This criterion is useful to probe the α -relaxation time, as opposed to the fast β -relaxation, since we are interested in the slow relaxation of the



FIG. 2. (a) and (b) show the coherent density-density correlation function $F(q_0, t)$ for star polymers with various number of arms f and $M_a = 5$ and 20 at T = 0.5. (c) and (d) show $F(q_0, t)$ for star polymers with f = 3 and 12 and various arm length M_a at T = 0.5.

system that defines the glass formation. The α -relaxation and fast β -relaxation should not be confused with the "slow" or Johari–Goldstein β -relaxation process, which is not observed in our intermediate scattering function data.⁴⁶

Since we study a broad range of temperatures, f, and M_a values, we present data for $F(q_0, t)$ along several slices of the parameter space. In particular, we emphasize extreme values of f and M_a that span the range from nearly linear polymers to the case of soft-particles (large f and M_a). To illustrate how the number of arms affects relaxation, we show $F(q_0, t)$ for various M_a at low T = 0.5 in Fig. 2; these data show that the segmental dynamics are more sensitive to functionality when the arm length is short. The difference in sensitivity to f can be understood by the differences in segmental relaxation near the core vs far from the core. As shown in Ref. 7, when f is large, there is substantial crowding near the core of a star polymer, which leads to a substantial increase in τ for inner monomers as compared to those far from the core. This phenomenon is again illustrated in Fig. 3, where such a large mobility gradient is also observed in interfacial regions of polymer thin films⁴⁷ and nanoparticles in a polymer matrix.^{48,49} When changing f at fixed M_a , the effect of this core crowding is, thus, most apparent when the core dominates the average, i.e., small M_a . We can see this sensitivity over the whole range of temperatures we have studied by plotting the relaxation time τ of $F(q_0, t)$ (Fig. 4).

Similarly, we can see the sensitivity to the arm length M_a by comparing systems with fixed f = 3 and f = 12 at T = 0.5 with variable M_a . We find that $F(q_0, t)$ shows large sensitivity to the arm length for systems with larger f (Fig. 2). As the effects of crowding near the star



FIG. 3. The mobility gradient of relaxation as a function of distance from the star core. We plot the relaxation time τ , scaled by the relaxation time τ_{α} at large distances from the star core, as a function of the molecular mass scaled distance $r/M_a^{0.2}$ from the star core. The data shown are for star polymers with f = 12, various M_a , and T = 0.5. The mass scaling exponent does not vary significantly with T or f. The value of the mass scaling exponent does not vary significantly with T or f. The value of the mass scaling exponent is not immediately obvious and is different from the mass scaling of the radius of gyration (see Fig. 2 in the supplementary material). The inset illustrates this mobility gradient for a star polymer with f = 12, and $M_a = 10$, where the color of the monomer reflects its relaxation time; blue shows the slowest relaxation (large τ) and red shows the fastest relaxation (small τ).

core are weaker when f is small, the $F(q_0, t)$ is only weakly dependent on M_a at small f, whereas, the relaxation time becomes increasingly large as M_a decreases when f is large due to crowding of the chain segments about the core region. Hence, the segmental dynamics are more sensitive to the arm length when f is large. By plotting τ , we can demonstrate this trend for the entire range of temperatures (Fig. 4).

The collected data for τ can be used to evaluate key dynamical properties of the star polymer melts. First, we consider the behavior of the high-temperature activation energy. This is a fundamental material property of the dynamics since it largely controls the temperature dependence of relaxation in the high temperature regime. By fitting the τ data for T > 1 to the Arrhenius form, i.e., $\tau \sim \exp[\Delta H/T]$, we can extract the enthalpy ΔH of activation. Figure 5 shows how ΔH varies with f for two representative molecular masses. Generally speaking, we expect crowding at the core to increase the barrier to rearrangement. For small M_a , the effect on ΔH with increasing f is apparent; in contrast, for large M_a , the relative impact of the core is diminished so that ΔH is essentially independent of functionality f. The data for τ also allow us to estimate T_g of the segmental relaxation over the entire range of f and M_a . We define the glass transition temperature (on the computationally accessible time scale) by the fixed dimensionless time scale, $\tau(T_{g}) = 10^{4}$. Figure 6 shows that the variation of T_{g} with f and M_{a} is very similar to that which was previously reported for the core of star polymers.⁷ This finding is not obvious since the dynamics of segments far from the core can differ by several orders of magnitude from that of the core monomer. This difference helps us to explain the minor differences in T_g between what we report and what was reported in Ref. 7. Specifically, for large M_a (long arms), the T_g that we report is less sensitive to f for large f; the weaker sensitivity can be explained by the fact that the central monomer that defined T_g in Ref. 7 is strongly affected by the crowding near the center of the star, but this effect is less pronounced when we average over all segments. Figure 6 also shows that T_g becomes nearly independent of f at large f, in-line with experimental observations at larger f.⁴⁴ That said, we do see a "dip" in T_g for the largest M_a for f = 16 although we emphasize that such large (f and M_a) stars are difficult to fully equilibrate and, thus, have the greatest uncertainty in our simulations. From Fig. 3, we see that dynamics are substantially slower near the core region and weakly enhanced near the free ends. Thus, it is possible that there are particular f and M_a values for which the effects may compensate each other and make T_g or local dynamics "constant." That said, we cannot expect such effect to arise for arbitrary f and M_a values and leave the precise determination of this "compensation point" for future work.

B. String-like motion

It has been demonstrated in many prior works that atoms or molecules with enhanced mobility are highly spatially correlated.⁵⁰ Furthermore, it has been shown that these clusters of highly mobile particles can be decomposed into subsets that move via a cooperative replacement mechanism.¹⁶ This naturally leads to linear "polymeric" structures typically referred to as "strings." In particular, it is of interest to ask whether chain connectivity favors formation of the strings. Furthermore, the size of these collective motions can be used to describe the temperature dependence of the activation



FIG. 4. (a) and (b) show the relaxation time τ , defined by $F(q_0, \tau) = 0.2$, as a function of 1/T for star polymers having a different number of arms and 5 and 20 beads per arm. τ is sensitive to *f* for star having a small arm length, but insensitive when the arm length is large. (c) and (d) show τ as a function of 1/T for star polymers with 3 and 12 arms and different arm lengths. τ is sensitive to the arm length when *f* is large, while τ is insensitive to the arm length for stars having a small number of arms.

free energy of the relaxation time. In the context of Adam–Gibbs (AG) inspired theories, these strings, thus, describe the "cooperatively rearranging regions" (CRRs) anticipated for glass-forming fluids.



FIG. 5. The enthalpy ΔH , obtained from high temperature Arrhenius fit, as a function of *f* for star polymers with $M_a = 5$ and 40. The sharp change in ΔH for $f \approx 5$ at low M_a nearly coincides with the random coil–particle transition in molecular shape, density, and T_g of star arms observed in previous work by Chremos and Douglas.^{8,34}

Accordingly, in this section, we examine the nature of cooperative dynamics to test if such string-like motion is also prevalent in the segmental dynamics of star polymers, and if the same relationship to relaxation is valid. To define string-like replacement motion, we use the criteria previously developed for a very similar model of coarsegrained polymer.²⁰ Specifically, we consider two mobile monomers *i* and *j* to be in the same string if

$$\min[|\boldsymbol{r}_i(t) - \boldsymbol{r}_i(0)|, |\boldsymbol{r}_i(t) - \boldsymbol{r}_i(0)|] < \delta,$$

which means that one monomer has replaced the other within a radius of $\delta = 0.55$ over a time interval *t*.

As done previously for the relaxation, we examine the behavior of the string size L(t) over a range of f and M_a values. First, we consider the variation of L(t) with number of arms f at a fixed $M_a = 5$ or 20 and T = 0.5 (Fig. 7). For low molecular mass $(M_a = 5)$, we observe that the characteristic size L, defined by the peak string size L(t), increases significantly as f increases; in contrast, for larger molecular mass $(M_a = 20)$, the increase in L with increasing f is very modest. We attribute this difference in sensitivity to f again to the fact that crowding effects near the star core dominate behavior when M_a is small. For $M_a = 5$, the enhanced crowding with increasing f at the core leads to slower relaxation, which we expect requires a greater degree of cooperativity. Clearly, this effect is diluted when $M_a = 20$ since most monomers are far from the core region. This same effect can be seen when considering the dependence of L(t) for



FIG. 6. Computational glass transition temperature T_g of segmental relaxation, defined by $\tau(T_g) = 10^4$, as a function of the arm length M_a and number of arms *f*. The behavior of the segmental T_g is very similar to that reported for the star core.⁷ However, we note that the specific value of T_g differs primarily because we chose a different fixed time scale defining T_g .

star polymers with fixed number of arms f and variable M_a (Fig. 7). Specifically, for small f = 3 (where crowding is minimal), L is nearly independent of M_a . Conversely, at large f = 12 (where crowding at the core is significant), L is the largest when M_a is small, and diminishes with increasing M_a . In addition to the mean string length *L*, we evaluate the distribution of observed string lengths *P*(*l*). We find that *P*(*l*) exhibits exponential behavior for all cases [specifically, $P(l) = 1/\langle l \rangle \exp(-l/\langle l \rangle)$, where $\langle l \rangle = L$], characteristic of equilibrium polymerization of linear chain polymers.⁵¹ This observation is consistent with



FIG. 7. (a) and (b) show the string L(t) for star polymers with various f and $M_a = 5$ or 20 at T = 0.5. L(t) shows the similar sensitivity to f as observed in the coherent density-density correlation function $F(q_0, t)$. (c) and (d) show L(t) for star polymers with f = 3 or 12 and various M_a at T = 0.5.

many earlier studies of string-like collective motion in polymer melts and metallic glass materials.^{16,20,52,53} This distribution is essentially invariant to molecular topology, confinement in thin films, the addition of nanoparticles to make composite materials, variable pressure, variable cohesive interaction, and the type of fluid (e.g., polymeric vs metallic glass materials).

Given that the temperature dependence of the string size is very similar to that found for other glass-forming systems (see Fig. 3 in the supplementary material), we now test whether L can be similarly used to explain the variation of the relaxation time, as described by the string model for glass formation,^{28,54} inspired by the AG approach.²³ Briefly, AG proposed that, on cooling toward T_g , relaxation is controlled by activated barrier crossing, and that the activation free energy $\Delta \mu$ is proportional to the size of the hypothetical cooperatively rearranging regions (CRRs), where particle reorganization occurs. Accordingly, AG heuristically argued that $\tau \propto e^{\frac{2\pi i \mu}{T}}$, where z is the number of rearranging monomers in a hypothetical CRR, and z was assumed to scale inversely to the fluid configurational entropy. In the string model generalization of the AG model,²⁸ z is identified with L/L_A , where L is the average number of segments observed in clusters defined by their cooperative rearrangement motion and $L_A \equiv L(T_A)$. In the original AG model, $\Delta \mu$ was approximated by the enthalpy of activation, i.e., the entropy of activation energy was assumed to be equal 0, while the string model avoids this unwarranted approximation so that $\Delta \mu = \Delta H - T \Delta S$.



FIG. 8. Relaxation time τ/τ_0 as a function of $\Delta\mu(L/L_A)/k_BT$ for star polymers, where L is the characteristic string size and $\Delta\mu$ is the activation free energy. The collapse of relaxation time indicates the consistency between our data and the string model of structural relaxation. The inset shows the linear behavior of ΔH as a function of ΔS for all systems of star polymers.

The string model also accounts for the fact that collective motion does not completely disappear in the temperature range above the onset temperature T_A for glass formation, where relaxation becomes Arrhenius to a good approximation. The string length is determined



FIG. 9. (a) and (b) show the string of contiguous segments $L_{seg}(t)$ for star polymers with various "functionality" *f* and the arm length $M_a = 5$ or 20 at T = 0.5. Qualitatively, $L_{seq}(t)$ shows a similar sensitivity to *f* as observed in L(t). (c) and (d) show $L_{seq}(t)$ for star polymers with *f* = 3 or 12 and various arm mass M_a at T = 0.5.

in our simulations to have the length L_A , and this quantity along with the relaxation time at T_A plays an important role in the string model of relaxation. Notably, AG did not identify z with an average scale of collective motion, as in the case of the string model, but this quantity was, instead, identified with some unspecified minimal scale of collective motion. Nonetheless, the string model preserves the spirit of the AG model, while involving changes in detail informed by direct simulation observation of cooperative motion. Accordingly, the structural relaxation time of the string model is written as

$$\tau = \tau_0 \, \exp\left[\frac{L(T)}{L_A} \frac{\Delta \mu(T)}{k_B T}\right]. \tag{1}$$

Equation (1) at T_A suggests that τ_0 is not a free parameter but, instead, determined by

$$\tau_0 = \tau_A \, \exp\left[-\Delta\mu(T_A)/k_B T_A\right],$$

where $\tau_A \equiv \tau(T_A)$. The string model of structural relaxation can then be formulated as

$$\tau = \tau_A \, \exp\left[\frac{L(T)}{L_A} \frac{\Delta\mu(T)}{k_B T} - \frac{\Delta\mu(T_A)}{k_B T_A}\right],\tag{2}$$

where τ only depends on the enthalpic ΔH and entropic ΔS contributions to $\Delta \mu$. Figure 8 demonstrates the validity of this relationship over the entire range of f and M_a values. Thus, the applicability of this approach is not sensitive to the star geometry, or to the significant mobility gradient that exists near the star core for large f. This is similar to the observation that this same approach is robust in polymer thin films and composites, where there can also be substantial gradients in interfacial mobility.²⁷⁻²⁹ Similar to these other systems, we find that the enthalpy ΔH and entropy ΔS are not independent, but, instead, show a compensatory behavior, resulting in a linear parametric relationship shown in the inset.

C. Chain connectivity

It is worth noting that the string-like cooperative motion refers to the coordinated motion of polymer segments, in which monomers are not necessarily bonded, so it should not be confused with reptation-like motion of polymer chains. In particular, Ref. 20 has shown that the string-like collective motion is not strongly correlated with chain connectivity in a bulk system of polymer chains. Therefore, to investigate the role of chain connectivity in strings in the star polymer melts, we follow the same procedure as in the previous work.²⁰ Specifically, we evaluate the average string length $L_{seg}(t)$ of contiguous segments of mobile monomers in a chain and investigate the star architecture effect on $L_{seg}(t)$ by examining $L_{seg}(t)$ with fixed M_a and variable f as well as fixed f and variable M_a (Fig. 9). Similar to the temperature dependence (see Fig. 4 in the supplementary material), $L_{seg}(t)$ has a qualitatively similar dependence on star architecture as the overall L(t), but its variation on f and M_a is less pronounced than that of L(t) (observed in Fig. 7). In order to understand the role of chain connectivity in strings explicitly, we evaluate the ratio L_{seg}/L , where the characteristic string length L_{seg} formed by contiguous chain segments is defined by the peak string size of $L_{seg}(t)$, for star polymers with various f and M_a at T = 0.5, as shown in Fig. 10. A ratio close to one would indicate that chain connectivity



FIG. 10. (a) The ratio of L_{seg} and L for star polymers with various arm length M_a at temperature T = 0.5 as a function of f. (b) The ratio of L_{seg} and L for star polymers with various f at T = 0.5 as a function of arm mass M_a . The ratio of L_{seg} and L has a similar sensitivity to star architecture as observed for L(t).

controls the formation of strings, while a small value of the ratio suggests that connectivity plays little role in string formation. For star polymers having various architectures at relatively low temperature, i.e., T = 0.5, the ratio L_{seg}/L varies approximately from 0.45 to 0.75, implying a substantial contribution of chain connectivity to cooperative motion. However, the ratio is significantly less than unity, indicating that mobility is not concentrated along the backbone of chains. Furthermore, we notice that the ratio also exhibits a similar sensitivity to star geometry as found previously, i.e., L_{seg}/L is sensitive to *f* at small M_a and sensitive to M_a at large *f*. In particular, for star polymers with a small arm length, L_{seg}/L decreases drastically as the number of arms increases; for star polymers with many arms, L_{seg}/L increases rapidly as the arm length increases. Based on this sensitivity, we again attribute to segmental crowding around the core polymer segment.

D. Heterogeneity of segmental dynamics

To investigate the spatial heterogeneity of segmental dynamics, we further assess the degree to which molecular displacements deviate from simple Brownian motions. In particular, we study the non-Gaussian parameter,

$$\alpha_2(t) = \frac{3\langle r^4(t) \rangle}{5\langle r^2(t) \rangle^2} - 1, \tag{3}$$

as an indicator of the deviation of displacement from a Gaussian distribution. Figure 11 shows $\alpha_2(t)$ at various *T* for star polymers with f = 16 and $M_a = 5$ and f = 16 and $M_a = 40$. The behavior of $\alpha_2(t)$ is similar to that observed for many glass-forming fluids. More specifically, α_2 exhibits a peak at intermediate time, which grows in both time scale and amplitude as *T* decreases, just as observed for numerous glass-forming fluids; such behavior typically arises from an increasing degree of spatial correlation of motion on cooling.

We also note an additional feature of $\alpha_2(t)$ not typically seen in simple glass-forming fluids. Specifically, at large t, α_2 exhibits a second peak, observable only at those T, where runs extend to nearly 10^6 time units. The time of the second peak of α_2 increases modestly on cooling, but its amplitude is nearly T independent. What is the origin of this additional feature? Naturally, it must relate in some way to the fact that the star polymers are complex molecules. A clue comes from the observation (Fig. 11) that the second peak of $\alpha_2(t)$



FIG. 11. The non-Gaussian parameter $\alpha_2(t)$ at various *T* for star polymers with f = 16 and $M_a = 5$ and f = 16 and $M_a = 40$. At each *T*, $\alpha_2(t)$ shows a first peak due to the correlated motion of monomers. For star polymers with large M_a , $\alpha_2(t)$ shows a second peak due to the gradient in relaxation of monomers away from the star center.

is absent for star polymers with small M_a . As we discussed above, monomers along the arms relax at different rates due to the crowding near the center. This gradient in relaxation time of monomers along the arm is another form of heterogeneity that can contribute to α_2 . To isolate the origins of the two peaks, Fig. 12 shows $\alpha_2(t)$ for individual monomers at different distances from the core; none of the data for α_2 restricted based on the monomer position show a second peak. We can more clearly demonstrate that the second feature in α_2 arises from the mobility gradient by considering a simplified model for the contribution to α_2 from superposition of Gaussian displacements, since the sum of Gaussians with different means will not result in a Gaussian. The assumption of Gaussian displacements at a given distance from the core requires that $\langle r_n^4 \rangle = \frac{5}{3} \langle r_n^2 \rangle^2$, where $\langle r_n^2 \rangle$ is the mean-square displacement at position *n*. Summing over monomer positions n and plugging into Eq. (3) yields the following approximation:[°]

$$\alpha_2(t) = \frac{M_a \sum_{n=1}^{M_a} \langle r_n^2 \rangle^2}{(\sum_{n=1}^{M_a} \langle r_n^2 \rangle)^2} - 1.$$

This approximation quantifies the contribution to the total α_2 arising from the mobility gradient alone. The comparison between $\alpha_2(t)$ for all monomers in system f = 16 and $M_a = 40$ at T = 0.75 and the Gaussian superposition model is shown in Fig. 12. The second peak of $\alpha_2(t)$ arising from the mobility gradient in the Gaussian model nearly coincide, demonstrating that the second peak arises primarily from the gradient of segmental mobility that occurs for large f and M_a .

We continue by more thoroughly examining the dependence of α_2 on the star polymer structure. Figure 13 demonstrates the characteristic time scale t^* of the peak of $\alpha_2(t)$, and the amplitude of the peak $\alpha_2(t^*)$ increases on cooling presumably due to increasing cooperativity of the motion. Moreover, $\alpha_2(t)$ has sensitivity to functionality f and the arm length M_a that is similar to that of $F(q_0, t)$ and L(t), as shown in Figs. 2 and 7. In particular, the characteristic time



FIG. 12. The non-Gaussian parameter $\alpha_2(t)$ at T = 0.75 for all monomers in the system with f = 16 and $M_a = 40$, monomers at different distances r = 5, 10, 20, and 40 from the core, and the Gaussian superposition model (corresponding to the dashed line). $\alpha_2(t)$ for all monomers shows a second peak that cannot be found in $\alpha_2(t)$ for individual monomers.



FIG. 13. (a) and (b) show the non-Gaussian parameter $\alpha_2(t)$ for star polymers with various functionality *f* and the arm length $M_a = 5$ or 20 at T = 0.5. $\alpha_2(t)$ is more sensitive to number of arms for star polymers having shorter arms. (c) and (d) show $\alpha_2(t)$ for star polymers with functionality *f* = 3 or 12 and various arm mass M_a at T = 0.5. $\alpha_2(t)$ is more sensitive to arm mass for star polymers having more arms.

scale t^* and the amplitude $\alpha_2(t^*)$ are more sensitive to functionality f for systems with a shorter arm length M_a and are more sensitive to the arm length M_a for systems with larger functionality f. The origin of this behavior derives from the increased crowding near the core for large f, just as in the case of the variations we found for $F(q_0, t)$.

IV. CONCLUSIONS

We employed a bead-spring coarse-grained model to examine the effect of star polymer architecture on dynamical properties of star polymer melts via molecular dynamics simulations. In doing so, we compared the dynamics of star polymers with various functionality f and arm length M_a with those of linear analogs and contrasted the segmental dynamics with the dynamics of the polymer center of mass. We found that the segmental dynamics displays different sensitivity to star architecture over the entire temperature range studied by evaluating the relaxation time and glass transition temperature. In particular, the relaxation time shows a large sensitivity to f for small M_a and small sensitivity to M_a for small f. This difference in sensitivity can be attributed to the crowding near the core at large f. Compared with dynamics of large M_a stars, segmental dynamics of small M_a are dominated by the central crowding when f is large, thus exhibiting a larger sensitivity to f. Since the crowding is less pronounced at small f, the relaxation time is less

J. Chem. Phys. **152**, 054904 (2020); doi: 10.1063/1.5135731 Published under license by AIP Publishing sensitive to M_a . The slight deviation of the glass transition temperature considering all monomers rather than just the core particles is also justified by the same logic. This observation indicates that variation of the segmental dynamics due to star geometry is closely related to the crowding near the central beads of the star polymers.

In order to interpret the dynamical heterogeneity of segmental dynamics quantitatively, we further explored the nature of spatially correlated and cooperative motion by assessing the non-Gaussian parameter and string-like collective motion. Besides the well-known features observed in many other glass-forming liquids, we found that the non-Gaussian parameter exhibits an additional characteristic peak. The consistency in both time scale and strength between the secondary feature and the model of Gaussian superposition approximation implies that this extra peak results from the intra-molecular heterogeneity, i.e., the mobility gradient along the polymer chain. In the analysis of non-Gaussian parameter and string-like motion, we noted that the structural dependence of the characteristic time scale, the strength of spatial correlations, and the strength of cooperativity are all qualitatively similar to that observed in the segmental relaxation: more sensitive to f at small M_a and more sensitive to M_a at large f, demonstrating that the architecture effect on the heterogeneity of segmental dynamics is related to the crowding at the star core for large f. Additionally, we studied the role of chain connectivity in strings and concluded that

while chain connectivity influences the extent of string-like motion and thus the fragility of glass formation, the actual form of collective motion is not strongly correlated with the chain connectivity. Furthermore, we used the string model generalization of the Adam–Gibbs approach to test the robustness of these predictions for the dynamics for a range of star polymer architectures. The validity of this approach for all architectures provides another test of the string model. The success in the presence of an intramolecular mobility gradient within the star polymers complements earlier successful comparisons to other complex polymer materials, such as polymer thin films and composites, where mobility gradients also occur.^{28,49,56}

In summary, we have investigated how the star polymer architecture, i.e., the number of arms and arm length affects the segmental dynamics of star polymer melts. While the temperature dependence of the dynamical properties are similar to what is observed for other polymer systems, the variations due to star architecture are dominated by segmental crowding near the core region at large f. Based on the string model and its antecedent AG theory, we are able to establish a relationship between the star melt structural relaxation and the scale of collective motion that holds regardless of star geometry. Throughout our study, we have demonstrated quantitatively that the star architecture has a great effect on segmental dynamics and dynamical heterogeneity. This work should be useful in future work aimed at material design efforts exploiting the manipulation of molecular topology and for giving general insights into how molecular topology influences the dynamics of polymeric materials.

SUPPLEMENTARY MATERIAL

See the supplementary material for additional information on the temperature dependence of the intermediate scattering function $F(q_0, t)$, the string size L(t), the string size of contiguous star segments $L_{seg}(t)$, the second peak of the non-Gaussian parameter $\alpha_2(t)$, and the mass scaling of the radius of gyration R_g .

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