

Molecular Dynamics Study of Star Polymer Melts under Start-up Shear

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Abstract It has been established that star polymers with a large number of arms display both the conventional chain relaxation and a slower interchain relaxation due to the formation of hard cores, which is called the local structural relaxation. Here, we demonstrate that this unique relaxation property of multi-arm stars leads to unusual rheological behaviors. We study the response of star polymer melts with various arm numbers to start-up shear flow via nonequilibrium molecular dynamics simulation. Our simulation results indicate that the stress-strain response of multi-arm star polymer melts differs from that of star polymers with a small number of arms in both quantitative and qualitative manners. While the multi-arm star polymer melts exhibit an overshoot peak in the stress-strain curve both at relatively small and sufficiently large shear rates, two overshoot peaks appear when the flow strength is comparable to the relaxation time of the star polymers. This double stress overshoot is absent in linear polymers and star polymers with a small number of arms and is evidently related to the presence of the local structural relaxation in star polymers with a large number of arms. We present a detailed analysis of the conformational and dynamical properties of star polymer melts under start-up shear to gain a molecular understanding of their stress response.

Keywords Simulation; Star polymer; Start-up shear

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INTRODUCTION

Star polymers, consisting of a number of linear arms joined covalently to a central core, have attracted considerable attention from both fundamental and practical points of view due to their unique mechanical, optical, magnetic, electrical, physical, and chemical properties.^[1–7] In particular, star polymers with a large number of arms have been attractive targets in the context of soft deformable materials.^[7–10]

The most remarkable difference between a multi-arm star polymer and a few-arm counterpart is the emergence of the "hard core".^[11–13] This feature is related to the densely packed structure formed in the core region due to the compression by the arms, making it difficult for other chains to enter this region.^[14] Due to the emergence of hard cores, multiarm star polymers possess the dual characteristics of both chain and colloid so that these materials are often called "soft colloids".^[15–21] For the structural properties, the hard cores lead to the mutual repulsion between the adjacent molecular chains of the star polymers, thus resulting in a localized ordered structure similar to the molecular liquid.^[22,23] For the dynamic properties, the hard cores significantly slow down the movement of the surrounding molecular chains, which leads to the movement pattern of the system gradually devi-

ating from the linear polymer system. In particular, in addition to the end-to-end relaxation of the molecular chain, an additional relaxation mode, called local structural relaxation, emerges in multiarm star polymers.^[24–26] The structural and dynamic properties of multiarm star polymers determine their macroscopic mechanical behavior. The study of their structure and dynamics is thus of great significance for the design of new polymeric materials with desired properties.

It is well known that stress overshoot is a nonlinear rheological response of polymer melts under start-up shear. For linear chains, stress overshoot is generally considered to be related to the stretching and orientation of molecular chains in linear polymers.^[27–30] Branched polymers exhibit more complex flow behavior compared to their linear counterparts. For instance, McLeish *et al.* demonstrated that the branches of pom-pom polymer are entangled with the surrounding molecules, so the main chain is easy to stretch in extensional flow, resulting in strain hardening.^[31] However, at the beginning of shearing, the main chain is only temporarily stretched, and finally collapses with the rearrangement of molecules, resulting in strain softening. Due to the nonlinear chain topology, comb polymers exhibit hindered transient stretching in extensional flow.^[32–34] The double stress overshoot behavior of the entangled comb polymer was observed under start-up shear.^[35] The experimental start-up stress-strain curves for highly branched commercial polymers (styrene-butadiene rubber, SBR) displayed multiple peaks.^[36] Moreover, Padding *et al.*^[17] found that the interaction between the cores of the

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star polymers was critical for understanding their flow behavior, which would lead to a significant forward shift of the peak position of stress overshoot. For colloidal spheres, besides one-step yielding, two-step yielding was observed in many soft materials.^[37] One-step yielding is mainly due to the rupture of the cage.^[38–40] The reason for two-step yielding is more complex, and the molecular mechanism appears to be different for different soft materials.^[41,42] Therefore, the primary aim of the present study is to examine whether a more complex response of star polymers emerges with increasing the number of arms and study how the flow behavior of star polymers can be understood at a molecular level.

In the present work, we analyse the stress, structural and dynamic properties of star polymer melts having variable arm numbers under shear flow. We find that the stress-strain response of multiarm star polymer melts differs from that of star polymers with a small number of arms in both quantitative and qualitative manners. First, the 60-arm star polymers exhibit an overshoot peak at the weak shear strength. This feature is absent in the 3- and 20-arm star polymers, thereby implying that the local structural relaxation in multiarm star polymers leads to overshoot even when the shear strength is relatively weak. When the shear strength is comparable to the relaxation time of star polymers, we find that the 60-arm star polymers exhibit a two-step yielding phenomenon, which is again not observed in the 3- and 20-arm star polymers. Finally, all the star polymers show one-step yielding behavior for sufficiently strong shear strengths. We present a detailed analysis of the conformational and dynamical properties of star polymer melts under start-up shear to understand the flow behavior of star polymers at the molecular scale.

The present study is organized as follows. The simulation method and molecular model are described in the second section. The stress-strain behaviors and the structural and dynamic properties of multiarm star polymers are presented in the third section. Finally, the findings of the present work are briefly summarized in the last section.

MODEL AND SIMULATION DETAILS

In our model system, star polymers are composed of $f=3, 20$ or 60 linear polymers with one end linked to a common center, and each arm consists of $N_f=20$ monomers. Inter- and intra-molecular excluded-volume interactions are taken into account by the repulsive, truncated, and shifted Lennard-Jones(LJ) potential:

$$U_{\text{LJ}} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{1}{4} \right] \Theta \left(2^{1/6} \sigma - r \right) \quad (1)$$

where $r = |r_i - r_j|$ denotes the spatial distance between monomers i and j located at r_i and r_j , respectively, and $\Theta(x)$ is the Heaviside function (i.e., $\Theta(x) = 0$ for $x < 0$ and $\Theta(x) = 1$ for $x \geq 0$). The adjacent monomers are connected by the finitely extensible nonlinear elastic (FENE) potential:

$$U_{\text{FENE}} = -\frac{1}{2} k R_0^2 \ln \left[1 - \frac{r^2}{R_0^2} \right] \quad (2)$$

where the spring constant is fixed at $\kappa = 30\epsilon/\sigma^2$ and the maximum bond length is chosen to be $R_0 = 1.5\sigma$, following the previous works.^[43–45] In this model, a coarse-grained monomer

roughly corresponds to a Kuhn segment.^[46] In order to connect a large number of arms, the size of the central monomers is taken to be twice as large as that of a normal monomer.^[47,48] The standard reduced LJ units, in terms of which all physical quantities are expressed, are used in our simulations. Specifically, mass, length, energy, time, and temperature scales are expressed in units of $m, \sigma, \epsilon, \tau = \sqrt{m\sigma^2/\epsilon}$ and $T = \epsilon/k_B$, respectively, where k_B denotes the Boltzmann constant. We set $k_B=1$ for convenience. The number density is: $\rho = 0.85\sigma^{-3}$. The 3-, 20-, and 60-arm star polymer systems consist of 61000, 60150, and 72060 monomers in a cubic box, respectively.

The equilibrium properties of our model star polymers have been investigated in prior works.^[28] In the present work, we focus on the nonequilibrium properties of these star polymers under start-up shear. In our simulations, the Lees-Edwards boundary conditions are employed to induce a shear flow in the x direction, and y, z are the gradient and vorticity directions, respectively.^[49] Within these boundary conditions, a monomer that leaves the simulation box in the gradient direction immediately re-enters the box through the opposite face with the position and velocity displaced appropriately. The flow velocity field is thus given by:

$$v_x = \dot{\gamma}z, v_y = 0, v_z = 0 \quad (3)$$

where $\dot{\gamma}$ denotes shear rate. The DPD thermostat is used to maintain the temperature at the desired value.^[50,51] The equations of motion are integrated by a modified velocity-Verlet algorithm with a time step of $\Delta t=0.01$ for all shear rates considered. After the system undergoes sufficient relaxation, the shear flow field is applied. The relaxation time of the star chain refers to the relaxation of the overall conformation. The relaxation time is almost independent of arm number and has a value about 500τ ($520\tau, 480\tau$ and 525τ for $f=3, 20, 60$, respectively), which is estimated by the autocorrelation function of center-end distance.^[28] For untangled polymers, the relaxation time shows a quadratic dependence on chain length, namely, $\tau \sim N^2$. Hence, we define the Weissenberg number of star polymer as $Wi = 4\dot{\gamma}\tau_{\text{arm}}$, because the end-to-end distance of this type of star polymers is roughly twice the arm length.

RESULTS AND DISCUSSION

Stress-Strain Response

The mechanical behavior of polymer materials is the combination of elasticity and viscosity, which is called viscoelasticity.^[52–55] Therefore, polymers exhibit elastic solid and simple liquid properties. Generally, when the imposed shear rate is greater than the reciprocal of relaxation time, the stress overshoot can be observed in many polymer melts, that is, the shear stress first increases with shear strain, then decreases under large strains, and finally reaches a nonzero plateau value.^[56,57] The characteristic of a star polymer gradually transforms from being polymeric to colloidal with increasing the number of arms. Hence, it can be expected that the structural and dynamic response of star polymers to shear becomes more complex than that of linear polymers. In particular, the multiarm star polymer has the dual characteristics of both "chain" and "colloid", which may lead to interesting stress responses.

Fig. 1 presents the strain dependence of the shear stress for the 3-, 20- and 60-arm star polymers at three different shear

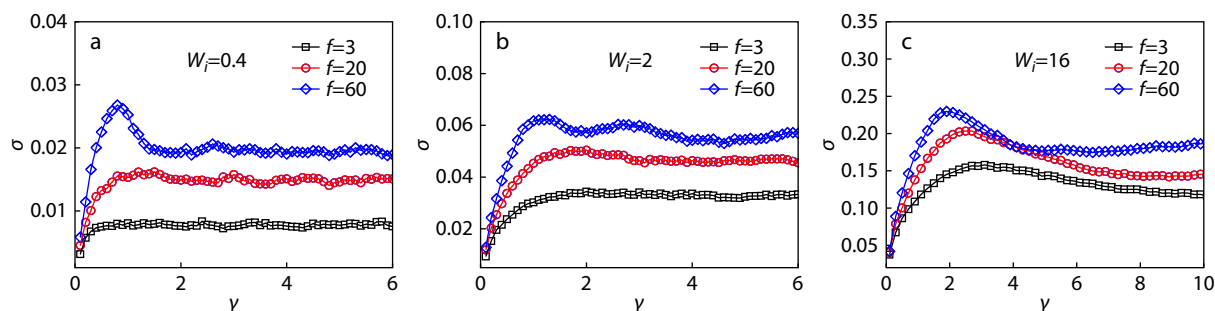


Fig. 1 Shear stress σ as a function of strain γ for the 3-, 20- and 60-arm star polymer melts at various shear strengths of (a) $W_i=0.4$, (b) $W_i=2$ and (c) $W_i=16$, respectively.

rates. These shear rates, $W_i=0.4, 2, 16$, represent the weak, intermediate, and strong shear strengths, respectively. The shear stress σ is obtained using the tensor version of the virial theorem:

$$\sigma = \frac{1}{V} \left\langle \sum_i \frac{P_i P_i}{m} + \frac{1}{2} \sum_{i \neq j} r_{ij} F_{ij} \right\rangle \quad (4)$$

where V denotes the volume of the system and the angular brackets represent a time average over the system trajectory.

At the shear strength of $W_i=0.4$, the stresses of 3- and 20-arm star polymer melts reach the plateau values after a short increase, and there is no overshoot peak, because the shear rate is less than the reciprocal of relaxation time. However, there is an overshoot peak in the 60-arm star polymer melt. The stress-strain curve of the 60-arm star polymer melts increases rapidly at first, indicating that the system has a very strong resistance to the applied shear flow. This behavior probably originates from the fact that the cage starts to be deformed in the initial shear regime, which causes stress storage. Then the stress decreases rapidly after overshoot, which indicates that the energy is released rapidly. Finally, the stress reaches the plateau value in the steady regime. At the same time, the peak stress also appears in a very small strain, the peak shape is narrow, which is different from the stress-strain curve of traditional linear polymers. Therefore, the overshoot mechanism of the 60-arm star polymer melt is different from that of traditional linear polymers, which is related to the local structure of the 60-arm star polymer melt.

At the shear strength of $W_i=2$, the 3-arm star polymer melt does not exhibit overshoot, but the stress corresponding to the plateau value increases in comparison to the case of $W_i=0.4$. The 20-arm star polymer reaches the plateau value after a very small overshoot peak. The shear stress of the 60-arm star polymer melt first increases drastically and then passes through two stress overshoot peaks. This behavior does not appear in the other star polymer melts with a small number of arms. The first stress peak appears at a smaller strain of about $\gamma=1.3$, and the second stress peak appears approximately at $\gamma=2.4$. Then the stress begins to decrease and eventually plateaus. The first overshoot may be due to the cage deformation, and the second overshoot may originate from the collision between 60-arm star polymers. At this shear strength, the stress overshoot peaks of 3-, 20- and 60-arm star polymer melts are from no overshoot to one overshoot, and then to double overshoot, which may be related to the transition from linear chain to colloidal chain.

At the shear strength of $W_i=16$, the stress of all the star polymer melts increases rapidly at first and then decreases after the overshoot point. With the increasing number of arms, the peak stress increases and the peak strain appears on the smaller strain. At the same time, the peak shape of the stress-strain curve becomes narrower. This may be due to the fact that the multiarm star polymer is not easy to stretch and orient.

Here, let us add some remarks on the interesting stress yielding phenomenon of the 60-arm star polymer melt. The one-step yielding behavior may be similar to that of soft colloids under weak shear flow. The mechanism of two-step yielding behavior is more complex, however the two-step yielding phenomenon has been found in different materials. Ahuja *et al.*^[37] summarized the two-step yielding behavior of soft materials and reviewed the research progress of the two-step yielding phenomenon in recent years. Soft materials with different microstructures exhibit two-step yielding, which is usually the double overshoot of stress-strain in the start-up shear experiment. Zhou *et al.* studied the two-step yielding behavior of gel systems with different core/shell ratios.^[42] One-step yielding behavior appeared at low and high core/shell ratios, and two-step yielding behavior was found for medium core/shell ratios. The first step was that particles escape from soft cages and the second yielding was the rupture of hard cages. For glass systems, Koumakis *et al.* studied the yielding characteristics of hard-sphere (HS) glassy systems and reported the two-step yielding of HS glassy systems.^[58] This process of two-step yielding was linked to escape facilitated by the Brownian motion of the particles and shear-induced collision. It is thus clear from the above discussion that although the two-step yielding occurs in different materials, the origins of this intriguing phenomenon are different. Nevertheless, this behavior is related to the existence of two different length scales in the system.^[59–64] With increasing the number of arms, the multi-arm star polymers gradually display the local ordered structure similar to the small molecular liquid. Therefore, the two-step yielding behavior of the multiarm star polymers may be due to the structural response of two levels under shear, namely, the local-level and the chain-level responses. Gury *et al.* studied the jammed behavior of multiarm star polymer and found that the multiarm stars effectively behave like jammed colloids even in the melt state. Multi-arm star polymers exhibit a hybrid viscoelastic response, relaxing stress *via* a fast polymeric arm retraction and a slow colloidal

mode.^[15] Therefore, their structural responses to shear are more complicated than those in traditional polymer melts, including both the local structure and the polymer chain, which may lead to various stress-strain responses. The yielding behavior of multi-arm star polymer melts from the perspectives of structure and dynamics are discussed in detail below.

As discussed above, multi-arm star polymers display two levels of structural response to start-up shear, namely, local-level and chain-level responses. To reveal the relationship between the stress response and local structural evolution, we investigate the local structural details under shear. Generally, star polymers gradually transform from linear chains to soft colloidal spheres with increasing the number of arms, thus resulting in a localized ordered structure similar to the colloid. Hence, we characterize the localized ordered structure by calculating the radial distribution function of the center of mass of the star polymers:

$$G(r) = 4\pi r^2 \rho g(r) \quad (5)$$

Fig. 2 shows the radial distribution function of the center of mass of the 3-, 20- and 60-arm star polymer melts at equilibrium (i.e., $W_i=0$). For the star polymer with few arms, the polymers can be freely penetrable so that a locally ordered structure is not formed. For this reason, no evident peak shows up in $g_{cm}(r)$ for the 3-arm star polymer melt. With increasing the number of arms, the star polymers gradually exhibit the locally ordered structure as in the small molecular liquid, and the position corresponding to the first maximum shifts to larger values. For the peak strength, the 60-arm star polymer melt is much larger than that of the 20-arm star polymer melt.

For the 3-arm star polymer, there is no ordered structure under different shear rates. We further analyse the instantaneous radial distribution functions of the 20- and 60-arm star polymer melts under different shear strengths in Fig. 3. For the 20-arm star polymer melt, the local ordered structure of

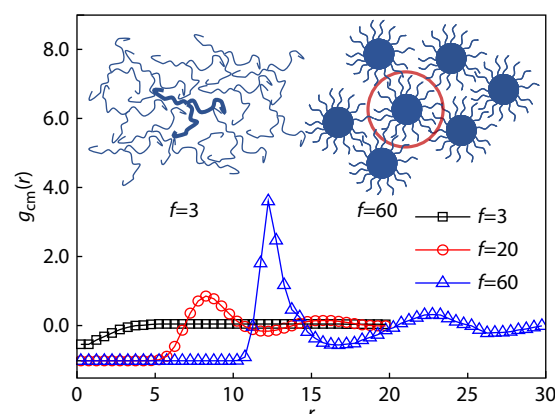


Fig. 2 Radial distribution function of the center of mass of the 3-, 20- and 60-arm star polymer melts at equilibrium. Inset: Illustration of the local structure of the 3- and 60-arm star polymer melts.

the 20-arm star polymer melt remains at the shear strength of $W_i=0.4$. For the shear strength with $W_i > 1$, the local ordered structure gradually disappears as the shear is processed. For the 60-arm star polymer melt, it can be found that the polymer still maintains the local ordered structure for strains up to $\gamma=0.5$ for $W_i=0.4$, but the peak value of the radial distribution function decreased, indicating that the local ordered structure was deformed under shear flow. Therefore, at the shear strength of $W_i=0.4$, the occurrence of stress overshoot may be due to the release of stored energy during local structural deformation. For $W_i > 1$, the local structure first deforms, similar to that for $W_i=0.4$. Before reaching the steady state, the collision between molecular chains and the rearrangement of local structure always exists, so that the peak of the radial distribution function always changes with the shear process. Finally, we also find that the peak of the radial distribution function of the 20-arm star polymer melt gradually

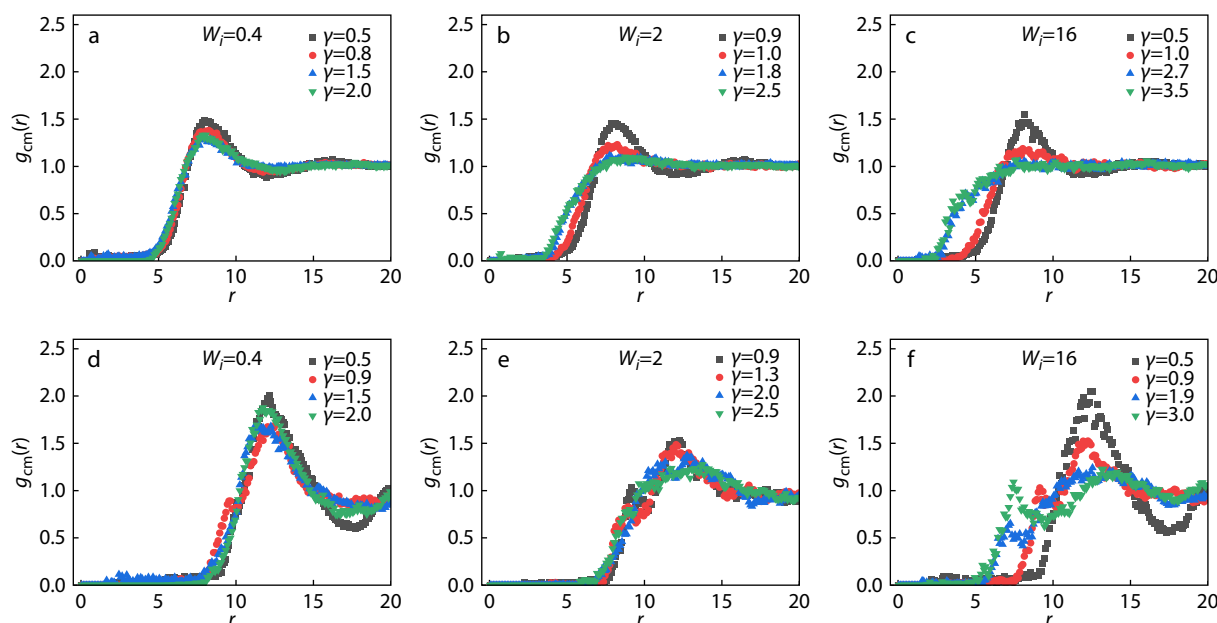


Fig. 3 The instantaneous radial distribution functions of the center of mass of the (a, b, c) 20- and (d, e, f) 60-arm star polymers at various shear strengths of $W_i=0.4$, 2 and 16.

shrinks until it disappears under shear flow, but the 60-arm star polymer melt is different, which may be due to the large volume and internal density of the 60-arm star polymer melt.

To extract a decay of the height of the first peak of $g_{cm}(r)$ under the start-up shear, we calculate the height of the first peak of $g_{cm}(r)$, H_p , and show it as a function of γ in Fig. 4. For the 20-arm star polymer melt, H_p first decreases rapidly until $g_{cm}(r)=1.4$ reaches the plateau value for $W_i=0.4$, and we find that the star polymer still maintains the local ordered structure in Fig. 2. For $W_i > 1$, the change of H_p is basically the same under different shear strengths. First, H_p decreases rapidly until near $g_{cm}(r)=1$ reaches the plateau value, which indicates that the local ordered structure of the 20-arm star polymer melt gradually disappears during the shear process. For the 60-arm star polymer, H_p decreases rapidly at $\gamma < 1$, which indicates that the local structure is strongly deformed at the initial stage of shear.

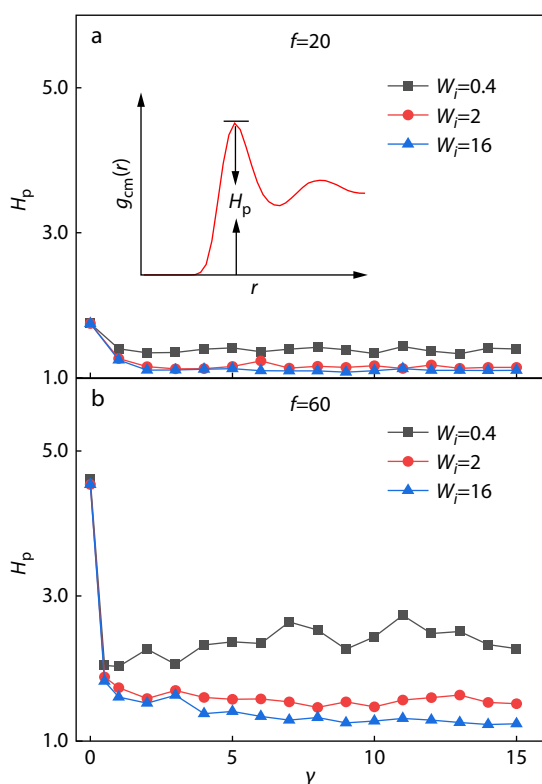


Fig. 4 The height of the first peak of $g_{cm}(r)$ for (a) $f=20$ and (b) $f=60$, respectively, as a function of strain.

Chain Conformation

As we stressed before, multi-arm star polymers display two levels of structural response under start-up shear, namely, local-level and chain-level responses, both of which can determine the macroscopic stress behaviors. Hence, following the localized ordered structure analysis, we investigate the structural properties of the chains. We study the effect of shear flow on the structural properties of star polymer by analysing the stretching and orientation of the chain. Figs. 5(a)–5(c) show the ratio $\langle g_{max} \rangle / \langle g_{min} \rangle$ where $\langle g_{max} \rangle$ and $\langle g_{min} \rangle$ represent the largest and smallest eigenvalues of the radius of gyration tensor,

respectively. The ratio $\langle g_{max} \rangle / \langle g_{min} \rangle$ is generally used to characterize the shape of a polymer and this quantity is equal to unity for a sphere. At equilibrium, star polymers become more spherical with the increase of f .^[22] Figs. 5(d)–5(f) show the ratio $\langle R_g^2 \rangle / \langle R_{g0}^2 \rangle$ of the 3-, 20-, and 60-arm star polymers, where $\langle R_g^2 \rangle$ and $\langle R_{g0}^2 \rangle$ represent the mean square radius of gyration of the whole chain and the mean square radius of gyration of the initial equilibrium melt, respectively. This ratio evidently quantifies the degree of chain deformation. Figs. 5(g)–5(i) show the evolution of the orientation angles of 3-, 20- and 60-arm star polymers with strain, respectively. The orientation of star polymer is described by the following expression:

$$\tan 2\theta = \frac{2G_{xy}}{G_{xx} - G_{yy}} \quad (6)$$

where G_{xy} , G_{xx} and G_{yy} denote the components of the average gyration tensor.

At weak shear strength, the $\langle g_{max} \rangle / \langle g_{min} \rangle$ changes slightly, indicating no obvious change in the shape of the star polymers. The 3-arm star polymer is closer to linear chain, and the 60-arm star polymer is closer to sphere. For the ratio $\langle R_g^2 \rangle / \langle R_{g0}^2 \rangle$ of the 60-arm star polymers, we find that the polymers hardly deform because the shear rate is less than the reciprocal of the relaxation time of the polymer, so the polymer is not stretched under shear flow. At $W_i=0.4$, the polymer is essentially not oriented along the flow field direction. This shows that under weak shear strength, the stress overshoot behavior of star polymer may come from the deformation and collapse of the local structure of the 60-arm star polymer, which is independent of the stretching and orientation of the polymer.

At the intermediate and strong shear strengths, we find that the deformation of star polymers is smaller for star polymers with more arms. For the 60-arm star polymer, the shape gradually changes from spherical to ellipsoidal with the increasing shear strength. At $W_i=2$, we find that the star polymers are only slightly deformed. At $W_i=16$, the $\langle R_g^2 \rangle / \langle R_{g0}^2 \rangle$ curves of 3-, 20- and 60-arm star polymers have similar shapes. More specifically, this ratio first increases rapidly with shear strain, then decreases under large strains, and finally tends to level off, which indicates that the star polymers begin to stretch along the flow field under strong shear flow. Evidently, between the increasing and decreasing regions, an overshoot peak will emerge. At $W_i=2$, we find that the orientation of the star polymer with few arms is basically the same as that of the star polymer with many arms in the flow field, which first decreases with the strain and finally reaches the plateau value near $\theta=30$. In short, at $W_i > 1$, the star polymer begins to stretch and orientation under shear flow. Especially, for 60-arm star polymer, the chain structure begins to affect its stress-strain response and the polymer chain dynamics gradually dominate with the increase of shear strength.

Fig. 6 shows illustrative snapshots of a single star chain under shear flow. We can more intuitively observe the conformational changes of star polymers under different shear strengths. At low shear strength, the 3-arm star polymer remains in the coil state, and the 20- and 60-arm star polymers are spherical. At intermediate shear strength, the 3-, 20- and 60-arm star polymers are slightly stretched, and the 60-arm star

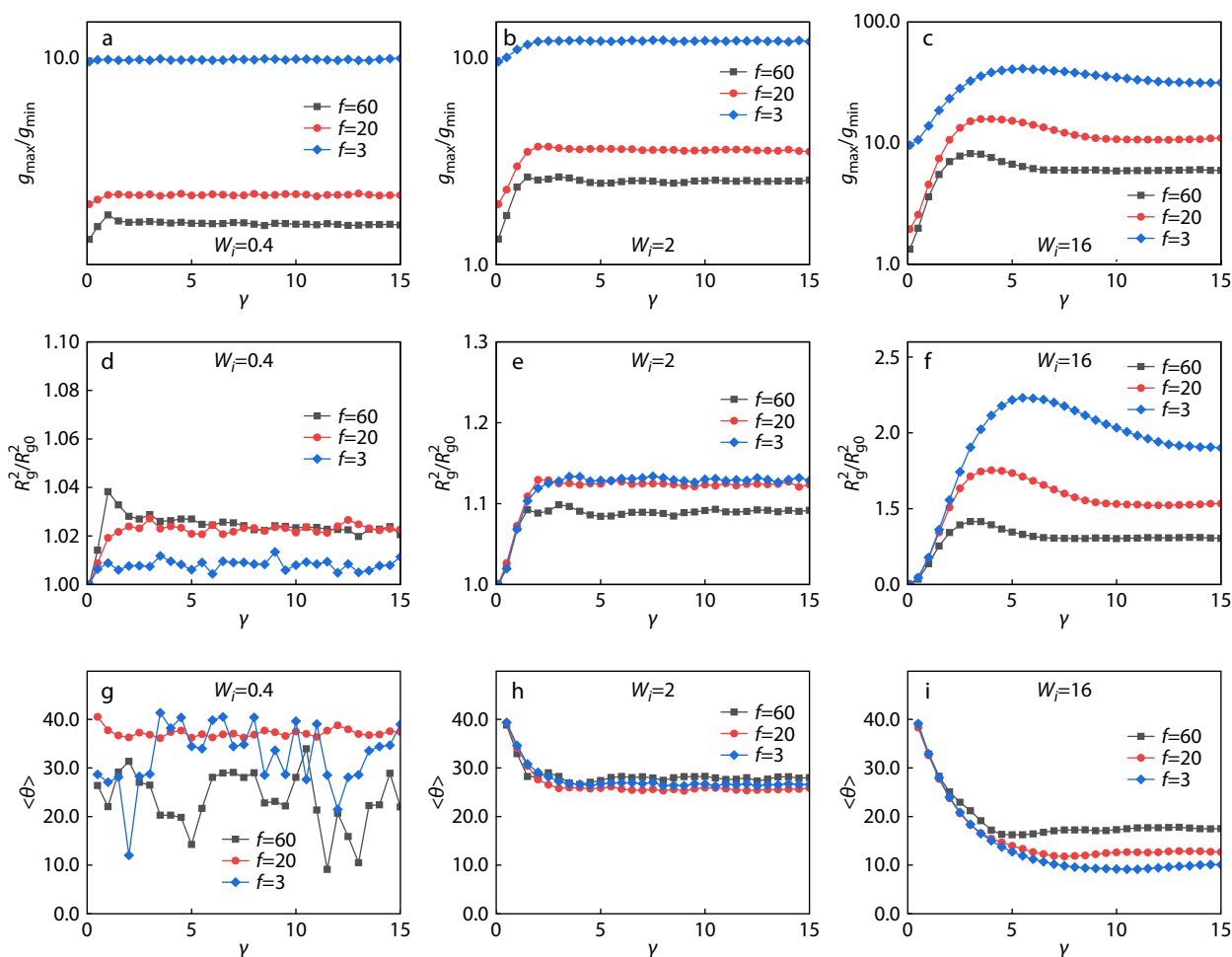


Fig. 5 The ratio $\langle g_{\max} \rangle / \langle g_{\min} \rangle$ for $f=3$, $f=20$ and $f=60$ at various shear strengths of (a) $W_i=0.4$, (b) $W_i=2$ and (c) $W_i=16$, as a function of shear strain. Transient behaviors of $\langle R_g^2 \rangle / \langle R_{g0}^2 \rangle$ for $f=3$, $f=20$ and $f=60$ under various shear strengths of (d) $W_i=0.4$, (e) $W_i=2$ and (f) $W_i=16$. The mean orientation angle of 3-, 20- and 60-arm star polymers under various shear strengths of (g) $W_i=0.4$, (h) $W_i=2$ and (i) $W_i=16$.

polymers are still nearly spherical. Under strong shear strength, the 3-, 20-, and 60-arm star polymers deform greatly under shear flow. Compared with the 20- and 60-arm star polymers, it can be seen that the 60-arm star polymers are more difficult to deform due to higher grafting density, so they are ellipsoidal under high shear strength.

Dynamic Properties

In addition to the structure, we analyse the dynamic properties of star polymers during the start-up shear to better understand their flow behavior. Previously, we learned that the structural response of multiarm star polymer melts differs from that of star polymers with a small number of arms under shear. Similarly, there is a distinct qualitative difference in the nature of diffusion between stars with a small and large number of arms. As discussed earlier, since the core region is described with a density higher than the other regions for the 60-arm star polymers, it is almost impossible for the chains to penetrate each other. Therefore, a local ordered structure similar to that of the small molecular liquid is formed, which makes the motion of stars confined by their neighbors, which is similar to the cage effect in small molecule liquids. Due to the formation of this special ordered structure, the dynamic properties of multi-arm

star polymer are obviously different from those of star polymer with few arms. This leads to an additional dynamic relaxation mode of the star polymer besides the chain relaxation. Pakula *et al.* found that in addition to the arm relaxation of the multiarm star polymer, there is also a slower local structural relaxation. Therefore, the relaxation of this system is not controlled by the star arm relaxation, but by a slower local structure relaxation process, which has been attributed to the cooperative motion of the multiarm star polymers within the ordered state.^[25,26] In addition, the physical description of yielding in the multiarm star polymer system can also be completed by examining chain motions under shear. Hence, we calculate the mean square displacement (MSD) of the center-of-mass of the star polymers under start-up shear in the gradient and vorticity directions as follows:

$$r_{\text{cm}}^2 = \frac{1}{n} \sum_n [r_{\text{cm}}(t) - r_{\text{cm}}(0)]^2 \quad (7)$$

Fig. 7 shows the mean square displacement of the center-of-mass of 3-, 20- and 60-arm star polymers along with gradient and vorticity directions under different shear strengths. The diffusion of the 3-arm star polymer firstly shows a super-diffusion motion at short time, and finally changes to simple

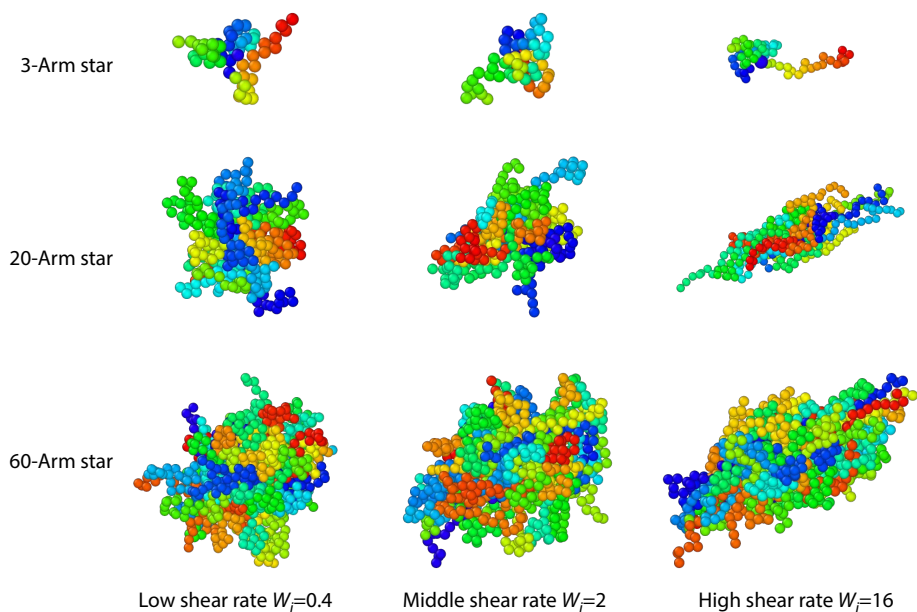


Fig. 6 Snapshots of 3-arm, 20-arm and 60-arm star polymer molecules under different shear strengths.

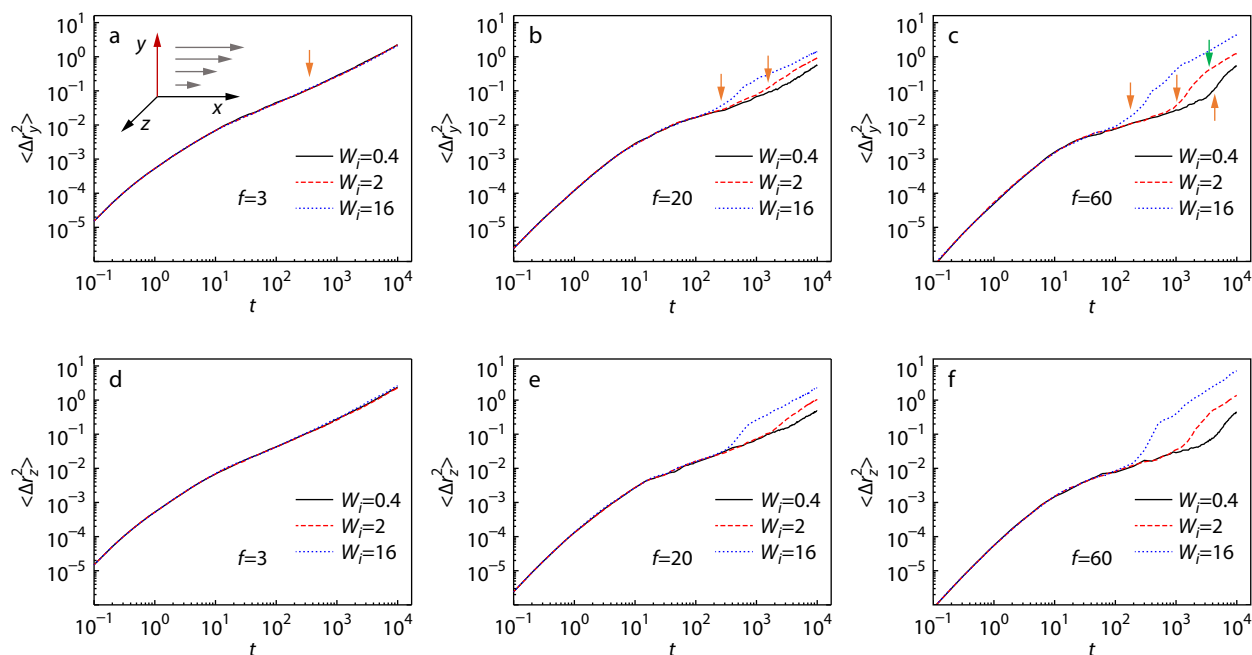


Fig. 7 Mean square displacements of the center of mass of 3-, 20- and 60-arm star polymers in gradient (a, b, c) and vorticity (d, e, f) direction at various shear strengths of $W_i=0.4$, 2 and 16. The orange arrow indicates the stress overshoot point. For the two-step overshoot behavior of 60-arm star polymer at $W_i=2$, the first overshoot is represented by an orange arrow and the second overshoot is represented by the green arrow.

diffusion at long time, which is similar to the diffusion of linear polymers.^[65] With increasing the number of arms, the star polymer is gradually affected by the cage effect similar to colloids, and there will be a sub-diffusion motion before simple diffusion, and this effect will be strengthened with increasing the number of arms. For the 60-arm star polymer, the MSD curves under different shear strengths are basically consistent at short time, and the star polymer shows similar super-diffusion behavior. The same phenomenon is found in the MSD curve along the vorticity direction. Then, the motion of

the polymer chain begins to become the sub-diffusion motion. In this region, the multi-arm star polymer shows an obvious difference under different shear strengths, that is, with the increase of shear strength, the sub-diffusion region gradually shrinks, and this phenomenon is the same as the vorticity direction. With the increase of shear strength, this behavior of super-diffusion occurs in a shorter time scale, which indicates that the shear promotes fast damages of locally ordered structures of multiarm star polymers, which makes star polymers easier to escape from their neighbors. At

longer time, the system reaches the steady state under shear, and the multi-arm star polymer presents simple diffusion.

At short time, the super-diffusion motion of the 60-arm star polymer corresponds to the ballistic motion in the cage, as it occurs around $(\Delta r_y^2)^{1/2} \approx 0.1$. In addition, another important finding is the relationship between stress overshoot and super-diffusive motion. For the 60-arm star polymer, the stress overshoot corresponds to the transition point from sub-diffusion to super-diffusive motion at $W_i=0.4$. There is a long sub-diffusion process before stress overshoot, which may correspond to the deformation process of cages. In this process, the stress accumulated by cage deformation is partially released, and the overshoot peak appears. Similarly, at $W_i=2$, the 60-arm star polymer first goes through the cage deformation process, which may be related to the emergence of the first overshoot peak. The second stress overshoot corresponds to the transition point from super-diffusive to simple diffusion motion. The transient super-diffusion motion may be caused by the fast motion of the molecular chain under the traction of the flow field after the local ordered structure is destroyed, which may be related to the emergence of the second stress overshoot.

CONCLUSIONS

In this study, the stress, structural and dynamic behaviors of star polymer melts with various arm numbers were studied under start-up shear flow via molecular dynamics simulations. The simulation reveals that the shear strength has a great influence on the stress-strain behavior of the multi-arm star polymer. The stress-strain curves, as well as the structural properties that include information of two levels, i.e., local-level and chain-level, are discussed in detail. At the shear strength of $W_i=0.4$, the multi-arm star polymer shows one-step stress overshoot behavior. With the increase of shear strength, the single peak gradually changed to double peaks, and finally showed an overshoot peak under the stronger shear strength. At weak shear strength, the time scale corresponding to the shear rate is between the chain relaxation time and the local structure relaxation time, only slight deformation occurs in the polymer. We found that the local structure of the star polymer underwent large deformation at the initial stage of shear. In this case, the stress-strain response of star polymer may be affected by the local structure. At strong shear strength, the shear rate is greater than the reciprocal of the relaxation time of the chain, and the molecular chain is strongly stretched along the flow field direction, the stress-strain response begins to be dominated by the orientation and stretching of the chain. Finally, we also studied the dynamic properties of the multi-arm star polymer and found that shear promotes fast rearrangement of the star chains. The physical description of yielding in the multi-arm star polymer system can also be completed by examining chain motions under shear. Under weak shear strength, there is a long sub-diffusion process before stress overshoot, which may correspond to the deformation process of cages. In this process, the stress accumulated by cage deformation is partially released, and the overshoot peak appears. In a word, we studied the response of star polymer melts having variable arm numbers to start-up shear flow, and reported the unusual

rheological response of star polymers with a large number of arms to start-up shear, which is a problem of high significance from both fundamental and practical perspectives.

NOTES

The authors declare no competing financial interest.

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