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Influence of polymer architecture on diffusion in unentangled polymers melts

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Abstract

Recent simulations have indicated that the thermodynamic properties and the glassy dynamics of polymer melts are strongly influenced by average molecular shape, as quantified by the radius of gyration tensor of the polymer molecules, and that average molecular shape can be tuned by varying molecular topology (e.g., ring, star, linear chain, etc.). In the present work, we investigate if molecular shape is similarly a predominant factor in understanding the polymer center of mass diffusion D in the melt, as already established for polymer solutions. We find that all our D data for unentangled polymer melts having a range of topologies can be reasonably described as a power law of the polymer hydrodynamic radius R_h . In particular, this scaling is similar to the scaling of D for a tracer sphere having a radius on the order of the chain radius of gyration, R_g . We conclude that chain topology influences molecular dynamics in as much as the polymer topology influences average molecular shape. Experimental evidence seems to suggest that this situation is also true for entangled polymer melts.

I. INTRODUCTION

The influence of molecular structure on the dynamics of polymer liquids is a central problem in polymer science. Polymers in solution are known to exhibit near universal scaling properties. For example, chain self-diffusion coefficient, D , is mainly determined by the overall average size and shape of the polymer coil, while D is rather insensitive to the segmental size and shape.^{1,2} Specifically, D of a polymer coil in a dilute solution can be described by the Stokes-Einstein relation:

$$D = \frac{\kappa_B T}{6\pi\eta R_h}, \quad (1)$$

where T is the temperature, κ_B is the Boltzmann constant, R_h is the polymer hydrodynamic radius, and η is the viscosity of the solvent. This relation has been used to estimate and tabulate the effective hydrodynamic radius of numerous systems.³ However, polymer diffusion in polymer melts is usually described by mean field theories emphasizing the

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topology of polymer chains (linear, star, comb, ring, etc.) in relation to their presumed movement through a fixed background representing neighboring chains. In particular, the reptation model^{2,4} and its variants dominate the thinking for linear chains, and arm retraction ideas dominate the modeling of star polymer melts.^{5,6} Despite the wide use of such models in the last three decades, a universal description of the dynamics of polymers with different molecular architectures in melt conditions is lacking.⁷ Recent work has established that the Rouse model is not generally applicable even in the relatively simple case of unentangled polymers^{8–11} so we take a fresh look at the problem of the dynamics of unentangled polymer melts based on established hydrodynamic models and the assumption that continuum hydrodynamic theory is applicable to molecular fluids.

We begin our discussion with some interesting observations by Antonietti and coworkers.¹² They performed a series of experiments to understand the mass scaling of the shear viscosity, η for linear, ring, star, and H-comb polystyrene polymers over a range of polymer masses covering both the entangled and unentangled regimes and found an almost universal scaling of η with the solution viscometric radius (R_v) of all these polymers, see Fig. 1. Even more striking was their finding that the common phenomenology of entangled linear polymer melts can be found in microgel particles, a type of molecule that could not possibly reptate. This data reduction suggests that molecular shape and size are primary factors governing mobility in the melt, as in polymer solutions. This general conclusion also accords with our recent work¹³ pointing to the primacy of molecular shape on the segmental density and the glass transition temperature of linear chain, star, and ring polymer melts.

To obtain deeper insights into this problem, we revisit the observations of Antonietti and coworkers¹² based on molecular dynamics simulations of a coarse-grained bead-spring model. Given the inherent difficulty of calculating the shear viscosities of polymer melts for different polymer model architectures over a large molecular mass range, we initially confine our attention to the polymer self-diffusion coefficient D in the melt and to a mass regime where the polymers are not expected to be entangled. Moreover, we explore melts at relative high temperatures so that the physics of glass-formation does not complicate our discussion, i.e., $T/T_g \approx 2$, where T_g is the glass transition temperature (for more details of the T_g calculation in our model see Refs. 13,14). Additionally, we employ a path-integration algorithm ZENO^{15–17} to calculate and quantify the molecular size and shape of polymer melts having a range of polymer topologies (linear chains, stars, and rings) to determine their potential relation to D . The radius of gyration tensor is also used as a complementary measure of shape anisotropy.

This paper is organized as follows. Section II contains details of the coarse-grained model and simulation methods. Results of the shape characterization and the dynamics of the polymeric materials are presented in Section III. In Section IV, we conclude our work.

II. MODEL AND METHODOLOGY

Our system consists of $N_s = 400$ polymers. A star polymer is represented as a spherical core particle with f attached arms and each arm is composed of M segments with a total number of interaction centers $M_w = fM + 1$. The molecular parameters investigated correspond to

arm lengths having $M = 5, 10, 20$, and 40 segments, and to star functionalities ranging from $f = 2$ to 16 . The longest linear chain used in our study has $M_w = 81$ segments, which is close to the estimated boundary between unentangled and entangled regimes (entanglement length $N_e \approx 85$),¹⁸ so we assume that all our polymer systems are in the unentangled regime. The interactions between polymer segments are described by the cut-and-shifted Lennard-Jones (LJ) potential where ϵ and σ define the units of energy and length, and a cutoff distance $r_c = 2.5 \sigma$. The core-core and core-monomer interactions are modeled as purely repulsive Weeks-Chandler-Andersen potential¹⁹ with modification taking into account the difference in the particle sizes.²⁰ The segments along a chain are connected with their neighbors via a stiff harmonic spring, $V_H(r) = k(r - l_0)^2$, where $l_0 = 0.99 \sigma$ is the equilibrium length of the spring, and $k = 2500 \epsilon/\sigma^2$ is the spring constant. In terms of the units of real polymer chains, the beads should be identified with statistical segments of flexible polymer having a typical scale of 1 nm to 2 nm and the core particle of the stars should have a dimension on the order of polymer monomer and we then take $R_c = 0.5 \sigma$ as representative estimate of the star core size. The energy and interaction range parameters are chosen to be the same for these interactions such that $\epsilon_{cc} = \epsilon_{cb} = \epsilon$ and $\sigma_{cc} = \sigma_{cb} = \sigma$. For a linear chain (denoted as a star polymer with $f = 2$) and a ring, the core particle is taken to be the same type as those of the arms.

Simulations were performed in a cubic box with length L ; periodic boundary conditions were applied in all three directions. We utilized the large-scale atomic/molecular massively parallel simulator (LAMMPS).²¹ Simulations were performed in the NVT ensemble after equilibration in the NPT ensemble at the desired temperature. Time averaging was conducted for $Q(10^8)$ time steps after equilibration. The time step was set to $\delta t = 0.005 \tau$, where $\tau = \sigma(m_b/\epsilon)^{1/2}$ is the unit of time. Temperature and pressure are measured in units of ϵ/k_B and σ^3/ϵ , respectively. All simulations were performed at $T = 0.75$ and $\langle P \rangle \approx 0.1$ in reduced units.

III. RESULTS & DISCUSSION

The first step in our analysis is the determination of the “average size” of our model polymers in the bulk as function of the molecular architecture and molecular mass. In particular, we calculate the average radius of gyration, $\langle R_g \rangle$, the average hydrodynamic radius $\langle R_h \rangle$, and the average viscometric radius $\langle R_v \rangle$; the calculation of $\langle R_h \rangle$ and $\langle R_v \rangle$ is based on the use of path-integration algorithm ZENO, which calculates hydrodynamic, electrical, and shape properties of polymer and particle suspensions.^{15–17}

The program ZENO has been applied to many complex objects to determine the hydrodynamic radius, intrinsic viscosity, radius of gyration and other properties; one recent example is duplex DNA covering a large range of chain lengths where excellent agreement of ZENO with experimental measurements is found.²² Recent studies of the diffusion coefficient of proteins has also shown that ZENO performs very well for these systems.²³ In brief, the computational method used by ZENO for calculating R_h , as well other hydrodynamic properties, involves placing a polymer having a particular molecular conformation inside an enclosing sphere and then launching random walks from the surface of the sphere. The fraction of walks that hit the molecule as opposed to infinity can be

directly related to R_h . We repeat this process for 10^4 distinct molecular conformations and then construct distributions of R_h for each molecular topology and M_w . We also determine the mean and the standard deviation for these distributions. Through an extension of the process just described,¹⁶ which considers both where the launched trajectories initiate on the probing sphere and where they end when they hit the polymer, other basic polymer characterization properties can be estimated from ZENO such as the intrinsic conductivity of conducting particles and the intrinsic viscosity due to the mathematical similarities between electrical and hydrodynamical properties.^{16,24} Although R_h is normally measured by dynamic light scattering in solution, it is possible to estimate this quantity by neutron scattering measurements. In the present work, however, we utilize R_h , formally calculated for polymers under melt conditions, as a metric for determining the size and shape of the polymers to probe how these molecular properties influence polymer molecular dynamics in the melt. We also consider the eigenvalues of the radius of gyration tensor below as a complementary measure of molecular shape.

The mass scaling of the average polymer size as described by R_g and R_h increases with mass as a power law, i.e., $\langle R_g \rangle \propto M_w^\nu$ and $\langle R_h \rangle \propto M_w^\mu$, as expected, see Fig. 2a. The exponents in these power law relations define the “fractal dimension” of the polymers ($d_f = 1/\nu$), e.g., for linear polymer chains in a melt (or in θ -solvent), $\nu = 1/2$, the well-known value for random walks.^{1,25} Increasing the degree of molecular complexity leads to more contracted molecular conformations, meaning that their exponent is smaller than a random walk chain ($\nu = 1/2$), but larger than a fully collapsed polymer in its globular state ($\nu = 1/3$).

We find that both exponents for stars decrease with increasing f up to the functionality $f \approx 6$, beyond which the arms begin to stretch, as in grafted polymer brushes leading to an increase of ν and μ . We see a striking similarity between the star polymers having $f \approx 6$ and ring polymers. We note that the effective scaling exponents determined for R_g and R_h are limited to the range of molecular masses considered in our study. In particular, we estimate $\nu \approx 0.42$ for rings, which is consistent with previous experimental findings²⁶ and computer simulation exponent estimates for relative low M ring melts.²⁷ Our estimated value of μ is 0.43, which is close to our value of ν . This near equality is expected from the relatively compact nature of the melt rings in comparisons to ideal rings without excluded volume interactions. In the limit of extremely long rings in the melt, simulations and theoretical arguments have suggested that ν might approach smaller values, $\nu = 0.36$ or even $\nu = 1/3$,^{27–30} However, proving the exact value of ν is an inherently difficult matter by simulation and we restrict ourselves to the effective exponent values that can be determined by our simulations and measurement. The infinite mass scaling limit is out of the scope of the current study. Our simulations further suggest that there is a reversal in the variation of the exponents with f . In particular, $\nu > \mu$ for $f < 6$, but for $f > 6$ we find $\nu < \mu$, indicating that there may be a different mass dependence between chainlike systems ($f < 6$) and for the particle-like stars having $f > 6$.¹⁴

To probe further the crossover between chain-like ($f < 6$) and particle-like ($f > 6$) systems, we probe the average shape of molecular conformations using the computational measures of shape indicated above. It is well-known that linear polymers exhibit highly anisotropic conformations,^{32,33} and similar calculations have been performed before for star^{34–38} and

ring^{27,34,35,39,40} polymers. As noted above, we use two different approaches to quantify the shape of the molecules. In the first approach, the molecular shape is quantified by the eigenvalues of the radius of gyration tensor S . These eigenvalues are denoted below by λ_1 , λ_2 , and λ_3 and are related to R_g^2 as follows:

$$\text{Tr } S = \langle R_g^2 \rangle = \langle \lambda_1 \rangle + \langle \lambda_2 \rangle + \langle \lambda_3 \rangle, \quad (2)$$

where $\lambda_1 \geq \lambda_2 \geq \lambda_3$ and the brackets $\langle \rangle$ represent to time averages. The eigenvalue data are organized by comparing the two larger eigenvalues with respect to the smallest one. As expected, a sphere has $\langle \lambda_3 \rangle / \langle \lambda_1 \rangle = \langle \lambda_2 \rangle / \langle \lambda_1 \rangle = 1$ and infinite long thin rod has $\langle \lambda_3 \rangle / \langle \lambda_1 \rangle \rightarrow \infty$ and $\langle \lambda_2 \rangle / \langle \lambda_1 \rangle$ is finite. An increase in f leads to a decrease of both $\langle \lambda_3 \rangle / \langle \lambda_1 \rangle$ and $\langle \lambda_2 \rangle / \langle \lambda_1 \rangle$, as illustrated in Fig. 3. Our results are in excellent agreement with the findings by Šolc.³⁴ The variation in the eigenvalue data implies that the molecular conformations of polymers in their melt state range from highly anisotropic structures, as in the case of linear polymers, to relative symmetric, particle-like structures for large f . Curiously, our results on the R_g eigenvalues of star polymers having $f > 2$ suggest that the shape of stars resemble a

soft ellipsoid having dimensions that follow a geometric mean, i.e., $\langle \lambda_2 \rangle \sim \sqrt{\langle \lambda_1 \rangle \langle \lambda_3 \rangle}$; linear chains and ring polymers do not follow this behavior, as seen in the inset of Fig. 3. As demonstrated in our previous work,¹³ unknotted ring polymers have a similar average molecular shape, as defined by the λ_i to star polymers having $f \approx 5$ arms and rings melts. It was also found that unknotted rings and $f = 6$ stars had very similar thermodynamic properties.

We extend this shape analysis by calculating the relative shape anisotropy, κ^2 , which describes the segmental distribution of the molecules:

$$\kappa^2 = \frac{3}{2} \frac{\langle \lambda_1 \rangle^2 + \langle \lambda_2 \rangle^2 + \langle \lambda_3 \rangle^2}{\langle R_g^2 \rangle^2} - \frac{1}{2}. \quad (3)$$

κ^2 is a dimensionless measure of polymer asymmetry that lies in the range, $0 \leq \kappa^2 \leq 1$; $\kappa^2 = 0$ corresponds to a spherical particle and $\kappa^2 = 1$ to a thin rod. Figure 4 again shows that increasing f leads to particles having a more spherical shape. This shape measure exhibits an interesting mass scaling, $\kappa^2 \sim M_w^\gamma$ for stars having fixed M . The exponent γ has a weak dependency on M , ranging from approximately 1.3 to 0.99 for $M = 5$ and 40, respectively. The eigenvalue ratios $\langle \lambda_3 \rangle / \langle \lambda_1 \rangle$ and $\langle \lambda_2 \rangle / \langle \lambda_1 \rangle$ provide complementary measure of polymer size and lead to the general conclusion of shape transition between anisotropic to nearly symmetric particle-like structures in the melt with increasing number of star arms, but ring polymers remain anisotropic in the melt, having a conformation more similar to branched polymers than collapsed globules.⁴¹

In the second approach to quantify the shape of the molecular conformations, we utilize the difference in variation between R_h and R_g . Indeed, the ratio R_h/R_g is often used as a

descriptor to quantify the shape of polymers.^{15,16} The values of R_h/R_g for a smooth sphere is 1.29, for a random walk is 0.79, and for an infinite long rod is 0.^{31,42} As expected, we find the values of $\langle R_h \rangle / \langle R_g \rangle$ of linear chains decrease from the smooth sphere limit (when $M_w = 1$) to the more anisotropic conformations characteristic of polymer random coils. Increasing f leads to molecular conformations that are more compact and spherically symmetric by this measure of shape, Fig. 5. Our results for κ^2 and $\langle R_h \rangle / \langle R_g \rangle$ further support our previous conclusions¹³ that a crossover between linear chain and particle-like conformations occur for $f \approx 6$. The variation of the polymer molecular shape in the melt with f is clearly a general trend that has significant potential importance for polymer thermodynamics and dynamics because of the importance of molecular shape on molecular packing and friction.

The experimental observations of Antonietti and coworkers¹² suggested that the viscosity of polymer melts composed of polymers having different molecular topologies follow a *universal* relation with the viscometric radius R_v , see Fig. 1. For the polymers that we investigate, we find that R_h for a polymer in a melt is proportional to R_v to a good approximation,

$$\langle R_h \rangle \propto \langle R_v \rangle = \left(\frac{3 [\eta] M_w}{4\pi} \right)^{1/3}, \quad (4)$$

where $[\eta]$ is solution intrinsic viscosity;⁴³ see also Fig. 6. $[\eta]$ is estimated from the program ZENO. As we have described above,^{16,24,42} our computations are based on chain computations in the melt, however, $[\eta]$ should be taken as a measure of molecular shape and volume in the melt. We expect estimates of $[\eta]$ in θ -solvents to track our formal melt estimates of $[\eta]$, but these quantities should not be taken as identical because of dimensional changes in the polymer upon going from the solution to the melt state.

To evaluate the validity of the Stokes-Einstein relation in our polymer melt simulations, we investigate the connection between the molecular dimensions of the polymers to D . A direct comparison between D and R_h indicates a nearly universal power law relation between these properties,

$$D \propto R_h^{-\lambda}, \quad (5)$$

where the exponent λ is approximately $\lambda \approx 2.7$ for most polymers that we have examined; see Fig. 7. We find that these properties closely approximate each other for all polymers melts having $f \geq 6$. We find this to be a striking result given that D and R_h are obtained by independent methods. This general conclusion accords well with the experimental findings of Antonietti and coworkers¹² and suggests that molecular size and shape are indeed of primary importance for diffusion in polymer melts. Evidently, molecular topology is important for polymer melt dynamics in as much as it alters polymer molecular shape.

We further observe a systematic variation in the exponent, λ , in Fig. 7 in the case of star polymers having many arms ($f = 16$). A careful examination of the exponent for each

molecular architecture reveals that λ varies from approximately 2.7 for linear chains and low star functionality, $f \approx 4$, to 2.2 for ring polymers and moderately branched stars $f \approx 6$, see inset of Fig. 7. For highly branched stars $f > 6$, λ decreases more strongly and it approaches 1.0 for stars having $f = 16$ arms. These results indicate that molecular architecture not only influences the relative compactness of polymers, but also the mechanism by which polymers diffuse in the melt.

In previous studies, the diffusion data for linear chains are overwhelmingly presented as function of the molecular mass (or the degree of polymerization) and these results are compared to the prediction of the Rouse model $D \sim M_w^{-1}$. It is well established that the Rouse model fails, when the length of the linear chain polymer is long⁴⁴ and at temperatures near T_g .⁴⁵ We find a mass scaling $D \sim M_w^{-1.3}$ for linear chains. This means that even at high temperature $T/T_g \approx 2$, there is significant deviation from Rouse predictions, see Refs.¹¹ for further discussion. Ring polymers diffuse at a higher rate compared to the linear chain analogues, consistent with previous studies.^{46,47}

What is the origin of the apparent power law relation between D to R_h in the polymer melt? Recent simulations^{48,49} and experiments⁵⁰ have shown that the tracer D of nanoparticles having a size R similar or smaller than the R_g of the polymers in the melt scales with a power law relation, $D \propto R^{-3}$ rather than to $D \propto R^{-1}$ relation expected from Stokes law with a fixed solution viscosity. This scaling was rationalized by Wyart and DeGennes,⁵¹ and others following them,^{52–55} as arising from the particles “sensing” a local viscosity distinct from the macroscopic viscosity. These observations suggest that we might think of the polymers in the melt as being similar in a coarse-grained sense to tracer particles having dimensions comparable to the surrounding polymers. This hypothesis accords with our D data.

If we demand that the Stokes-Einstein relation also holds (Eq. 1), then the polymer viscosity must consistently obey the scaling relation, $\eta \sim R_h^{\lambda-1} \sim M_w^{\mu(\lambda-1)}$ and in Fig. 8 we show the corresponding apparent exponent $\mu(\lambda - 1)$ as function of f . We find that this exponent is approximately equal to 0.9 for linear chains ($f = 2$), which is in good agreement with the predictions of the Rouse model since η scales with M_w to a good approximation.¹ This is an apparent agreement, because the Rouse model underestimates the diffusion mass scaling exponent in our model as we discussed above. This suggests that the Rouse model to agree with the experimental observation of $D\eta = \text{constant}$ for unentangled polymers, it overestimates the viscosity mass scaling exponent. As f increases, the exponent exhibits a monotonic decrease to 0 for highly branched stars f . For particle-like polymers having a large f , η is independent of polymer molecular mass, as in hard sphere suspensions. Previous experimental studies^{6,56,57} have shown that η of many-arm stars is independent of molecular mass, consistent with the observed trend in Fig. 8. We thus observe evidence of a crossover between linear chain and particle-like transport with an increased number of star arms.

The Stokes-Einstein relation is often observed to break down in dynamically heterogeneous liquids due to the formation of particle clusters that persist on sufficiently long time scales and this leads to a fractional Stokes-Einstein relation $D \sim \eta^{-\delta}$, where $\delta < 1$.⁵⁸ If we assume

that such a transition to heterogeneous polymer dynamics of the scale of R_g underlies the “entanglement” phenomenon in polymer melts,⁵⁹ then we would expect a transition between $\eta \sim R_h^\lambda$ and $\eta \sim R_h^{\lambda/\delta}$ as the polymer enters the dynamically heterogeneous melt regime. We suggest that the transition between the power law scalings observed by Antonetti et al.¹² for all different polymer architectures can be rationalized as the emergent dynamical heterogeneity that is characteristic of strongly interacting soft particle systems.⁶⁰

The idea that a polymer can be considered as a soft particle is not new, for example Flory and Krigbaum⁶¹ modeled polymers in solution by a mean field Gaussian blob representing a segmental density cloud. Gobush et al.⁶² generalized this picture to more faithfully reflect the average anisotropic shape of flexible polymers. The Gaussian segmental cloud description of polymers has recently reemerged in coarse-graining studies of the thermodynamic and dynamic properties of polymer melts.^{63–65} We think it is entirely reasonable to view polymers *in the melt* as soft particles whose *average shape* can be tuned through the molecular mass and topology.

IV. CONCLUSIONS

In summary, we investigated polymer melts having different molecular topologies (linear chains, stars, and rings) and made a direct comparison between D and R_h , the latter was calculated with the use of a path integration algorithm.^{15–17} We find that there is a nearly universal power law relation between these properties, meaning that molecular size and shape are indeed of primary importance for diffusion in polymer melts so that molecular topology is important in as much as it alters the large scale polymer molecular shape. This general conclusion accords with the former experimental observations of Antonietti and coworkers¹² on the viscosity of melts composed of polymer melts having different topologies. We find that we can rationalize the dependence of D based on the hydrodynamic polymer size by viewing polymers in the melt as being similar to “soft” particles whose average shape is influenced by their molecular topology (e.g., linear chain, star, ring). Our simulations are limited to unentangled polymer melts and it is natural to consider how the present perspective of polymer melt dynamics might be extended to melts of “entangled” polymers having higher molecular mass.

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Fig. 1.

Zero-shear viscosities, η_0 , of different polymer topologies (polystyrenes) for a reference temperature of 443 K as function of viscometric radius, R_v . Data was extracted from Ref. 12 and the lines correspond to power law relations as a guide for the eye.

FIG. 2.

(a) Average radius of gyration, $\langle R_g \rangle$, and hydro-dynamic radius $\langle R_h \rangle$ as function of the molecular mass, M_w , for polymers having different molecular topologies. The error bars represent two standard deviations. (b) The mass scaling exponents ν (circles) and μ , (squares) for R_g and R_h , respectively, as function of functionality, f , filled symbols correspond to linear chain (with $f = 2$) and star polymers and open symbols to ring polymers.

FIG. 3.

Ratio of the eigenvalues, $\langle \lambda_3 \rangle / \langle \lambda_1 \rangle$, of the mean-square radius of gyration of stars in melt as function of functionality, f , at $T = 0.75$. Symbols are the same as in Fig. 2a. Results for different arm lengths, M , are also presented and ring data are indicated at $f = 5$ for comparison. The dashed line corresponds to a fit based on the power relation: $\langle \lambda_3 \rangle / \langle \lambda_1 \rangle - 1 \sim f^{1.22}$. Inset: Ratio of the eigenvalues, $\langle \lambda_3 \rangle / \langle \lambda_1 \rangle$ versus $\langle \lambda_2 \rangle / \langle \lambda_1 \rangle$. The dot-dashed line corresponds to a fit based on the power relation: $\langle \lambda_3 \rangle / \langle \lambda_1 \rangle - (\langle \lambda_2 \rangle / \langle \lambda_1 \rangle)^2$. Reference points from Ref. 31 for random walks ($\square$), lattice animals (∇), percolation clusters (∇), and Gaussian rings ($\circ$) are also presented.

FIG. 4.

Relative shape anisotropy, κ^2 , as function of molecular mass, M_w . The dashed lines corresponds to fits based on the relation $\kappa^2 M_w^\gamma$ for stars having fixed arm length, where γ is a fitting parameter.

FIG. 5. Ratio of the average hydrodynamic radius over the average radius of gyration, $\langle R_h \rangle / \langle R_g \rangle$ as function of the molecular mass, M_w , for polymers having different molecular topologies. The error bars represent two standard deviations.

FIG. 6.

Comparison between the average viscometric radius, $\langle R_v \rangle$, and the average hydrodynamic radius, $\langle R_h \rangle$. The error bars represent two standard deviations. The dashed line is a guide for the eye.

FIG. 7. Center of mass self-diffusion coefficient, D , as function of the average hydrodynamic radius, $\langle R_h \rangle$. The dashed lines represent power law that scales as R_h^{-1} and $R_h^{-2.7}$; error bars represent two standard deviation. Inset: Scaling exponent of Eq. 5. Symbols represent stars (squares) and ring (circles) polymers. The dotted line is a guide for the eye. The ring polymers were placed at $f=5$ given their similarity in molecular shape, see Fig. 5.

FIG. 8.

Product of the hydrodynamic radius mass scaling exponent μ , and the exponent λ obtained from Eq. 5 as function of number of arms, f . Symbols represent stars (squares) and ring (circles) polymers. The dotted line is a guide for the eye. The ring polymers were placed at $f = 5$ given their similarity in molecular shape, see Fig. 5.