

Analysis of the shape of dendrimers under shear

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Nonequilibrium molecular-dynamics simulations are used to investigate the molecular shape of dendrimers and linear polymers in a melt and under shear. Molecules are modeled at the coarse-grained level using a finitely extensible nonlinear elastic bead-spring model. The shape of dendrimers and linear polymers at equilibrium and undergoing planar Couette flow is analyzed quantitatively and it is related to the shear viscosity. The shape of dendrimers responds differently to the influence of shear compared with linear polymers of equivalent molecular mass. However, in both cases the transition from Newtonian to non-Newtonian viscosity behavior corresponds to significant changes in molecular symmetry. This suggests that a shape analysis could be used to estimate the onset of shear thinning in polymers. © 2006 American Institute of Physics.

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I. INTRODUCTION

Molecular shape can have a significant influence on the physical properties of fluids.¹ For systems away from equilibrium or self-assembling systems, such as liquid crystals,^{2,3} the average shape of molecules determines how these systems align, rotate, entangle, or deform when subjected to external fields. The shape of macromolecules in either solution or in a melt is determined by their overall topology, which influences their macroscopic and microscopic properties. For example, dendrimer melts do not crystallize, whereas crystallization is observed for linear polymers of equivalent molecular mass.

The experimentally determined properties of polymer systems are often orientationally averaged. In the absence of external fields, which can lead to molecular alignment, the results would be consistent with spherical symmetry. In contrast, if the instantaneous shape of molecules without orientational averaging were examined, their symmetry might be far from spherical. This fact is important for phenomena that occur on a time scale that is comparable or smaller than the largest of the molecular relaxation times, namely, the rotational relaxation time. In such situations, the instantaneous shape of the molecules would prevail over the orientationally averaged one and the molecular asymmetry would have to be taken into account. Furthermore, even for phenomena occurring at longer time scales, the interactions, orientation, and alignment of aspherical molecules can affect macroscopic properties.

Asphericity of the linear chain coil was addressed for the first time by Solc and Stockmayer.⁴ They used eigenvalues of the tensor of gyration and relationships between them as a quantitative indicator of molecular shape. The shape of linear chains at equilibrium has been studied extensively^{4–7} using

molecular simulation.⁸ The results indicate that, for long flexible chains, the average shape of the coils does not depend on the chain length but converges to a common limit, which agrees with predictions for Gaussian random-flight chains. The deformation of linear chains under shear has also been studied,⁹ and the molecular shape was analyzed using eigenvalues of the orientationally averaged tensor of gyration. The asymmetric shape of linear polymers and its flow-induced evolution has been related to dynamical properties such as rotation.¹⁰ Mansfield and Klushin¹¹ have analyzed the shape of some model dendrimers at equilibrium.

The flow properties of dendrimers and linear polymer melts¹² and the scaling properties of the dendrimer systems^{13,14} have been studied previously. Like other traditional polymers,¹⁵ dendrimers in the melt undergo a transition from the Newtonian regime characterized by the shear-independent viscosity to the non-Newtonian shear-thinning regime. Molecules rotate and align under shear at all strain rates. However, it is not until the onset of shear thinning that molecules become noticeably stretched and deformed. Compared to linear polymers, highly concentrated dendrimers are more compact and globular, rotate more freely, and entangle less. The comparison with linear polymers also indicates that the viscosity of dendrimers at the same density and temperature is lower in the Newtonian regime, the onset of shear thinning occurs at higher strain rate, and the rate of shear thinning is smaller.

In this work, we present the results of a shape analysis of dendrimers and linear polymers at equilibrium and under steady shear for a wide range of strain rates. We report an analysis of the influence of the molecular topology on the shape anisotropy and study the way the molecules respond to the shear. The results indicate that shape considerations are closely linked to the rheological properties of dendrimers and linear polymers.

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II. THEORY

A. Simulation details

Details of the simulation have been discussed extensively elsewhere.^{12–14} Therefore, only the salient features are summarized here.

In general, the structure of a dendrimer is characterized by the generation number (g), the functionality of the core (f_c), the functionality of the end groups (f), and the number of monomers in the chain units (b). The total number of monomers can be calculated¹⁶ as $N_\alpha = (f_c b (f-1)^{g+1} - 1) / (f-2) + 1$. We modeled dendrimers with trifunctional cores ($f_c=3$) and two beads separating the branching points ($b=2$, $f=3$). This model results in 19, 43, 91, and 187 beads per single dendrimer of generations 1, 2, 3, and 4, respectively. Henceforth, our model dendrimers will be referred to as D2G1, D2G2, D2G3, and D2G4. The length of the linear polymers studied corresponded exactly to the mass (i.e., the number of beads) of the dendrimers. Therefore, the properties of D2G1, D2G2, D2G3, and D2G4 were compared to linear chains of 19-mers, 43-mers, 91-mers, and 187-mers, respectively. The interaction between the beads was obtained using the purely repulsive Weeks-Chandler-Anderson (WCA) potential¹⁷ and the chemical bonds between the beads were modeled using a finitely extensible nonlinear elastic (FENE) potential.¹⁸ For simulations involving either D2G1 or 19-mers, a system of 256 molecules was used, whereas in all other cases 125 molecules were used.

To simulate shear flow of the melts we applied the molecular version of the homogenous isothermal shear algorithm (SLLOD) (Ref. 19) with standard Lees-Edwards periodic boundary conditions.²⁰ The equations of motion of all beads were integrated using a fifth-order Gear predictor-corrector differential equation solver^{8,21} with reduced time step $\Delta t=0.001$. All properties are reported in dimensionless reduced units. The state point used ($T=1.25$, $\rho=0.84$, where T and ρ are the reduced temperature and density, respectively) corresponds to a melt.¹² After achieving steady state (typically several million time steps), the bead trajectories were accumulated and ensemble averages were calculated.

B. Shape parameters

Solc and Stockmayer⁴ were the first to introduce measures to describe the shape of polymers using eigenvalues of the tensor of gyration. The extension of a molecule in space is given by the tensor of gyration:

$$\mathbf{R}_g^2 \equiv \left\langle \frac{\sum_{\alpha=0}^n m_\alpha (\mathbf{r}_\alpha - \mathbf{r}_{CM})(\mathbf{r}_\alpha - \mathbf{r}_{CM})}{\sum_{\alpha=0}^n m_\alpha} \right\rangle, \quad (1)$$

where \mathbf{r}_{CM} is the position of the molecular center of mass, n is the number of beads in molecule, m_α is the mass of a bead, and $\langle \dots \rangle$ denotes an ensemble average. The value of the squared radius of gyration is defined as the trace of the tensor of gyration:

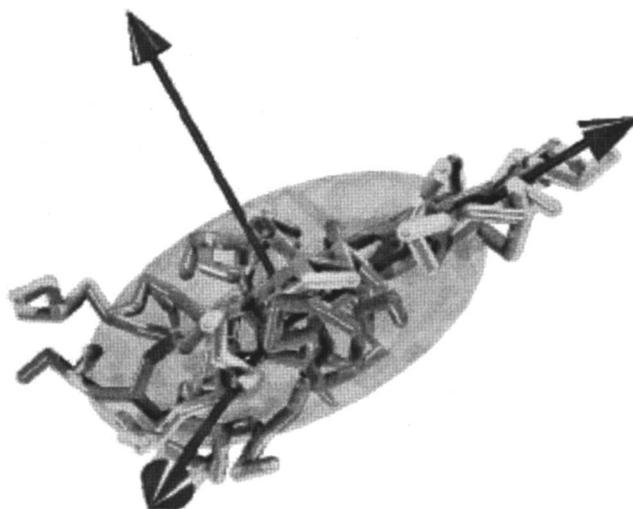


FIG. 1. Mapping of a single dendrimer on a spheroid. The dimensions of the spheroid are determined by eigenvalues of the tensor of gyration, whereas the main axes are aligned with the eigenvector of the tensor of gyration.

$$R_g^2 = \text{Tr}(\mathbf{R}_g^2), \quad (2)$$

which can be compared with experimentally measured radial sizes of the dendrimers. The variation of the radii of gyration and the scaling properties of dendrimers under shear were reported in our earlier papers.^{12,13}

Shape analysis for dendrimers in the melt can be performed in two ways. First, the average tensor of gyration can be calculated for the system of molecules prior to diagonalization: each element of the tensor is separately averaged over all molecules and time. In this approach molecules are analyzed in the fixed laboratory reference frame, and the derived tensor of gyration describes the shape of a mean molecule obtained through superposition of all molecules in the system. Eigenvalues of the average tensor of gyration (L'_1 , L'_2 , and L'_3) can be interpreted as the linear dimensions of the ellipsoid occupied by the orientationally averaged molecule.

Alternatively, the tensor of gyration could be diagonalized separately for each molecule in order to calculate ensemble averages of its eigenvalues (L_1 , L_2 , and L_3). Conceptually, this would correspond to a shape analysis of a system of molecules discarding their orientation. In this approach the real shape of dendrimer molecules can be studied neglecting effects due to the molecular orientation. This method was used in this work. Figure 1 illustrates the mapping of a dendrimer on a spheroid and the relationship of the eigenvectors and the molecular axes.

Asymmetry of dendrimers can be quantitatively described with the ratios of the eigenvalues of the tensor of gyration:¹¹

$$1 \geq \frac{L_2}{L_1} \geq \frac{L_3}{L_1} \geq 0. \quad (3)$$

For spherically symmetric molecules both of these ratios would be equal to 1.

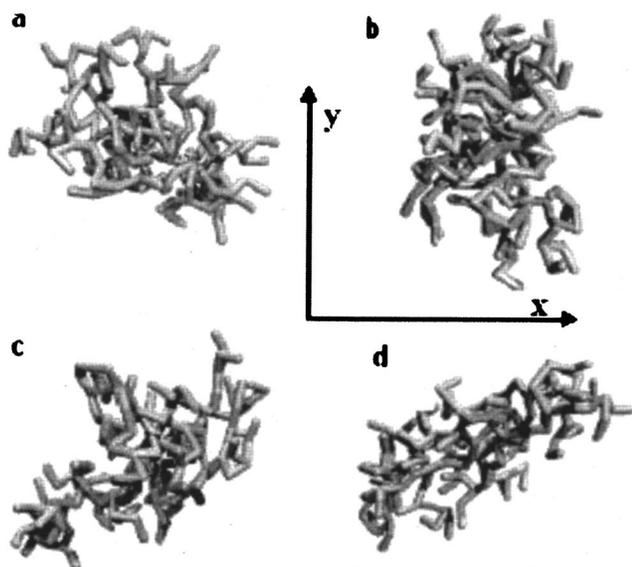


FIG. 2. Configurations of a single D2G4 dendrimer at strain rates of (a) 0.0001, (b) 0.001, (c) 0.01, and (d) 0.1. Notice the flow-induced changes in shape and orientation.

Additional parameters that can be used to describe symmetry of dendrimers are asphericity, acylindricity, and relative shape anisotropy.

The asphericity is defined by¹¹

$$b = L_1 - \frac{1}{2}(L_2 + L_3), \quad (4)$$

acylindricity by

$$c = L_2 - L_3, \quad (5)$$

and relative shape anisotropy by¹¹

$$\kappa^2 = \frac{b^2 + (3/4)c^2}{R_g^4}. \quad (6)$$

For systems with tetrahedral or higher symmetry $b=c=0$ and departs from it when the symmetry is broken. The relative shape anisotropy assumes values between 0 and 1, where 0 corresponds to tetrahedral or higher symmetry, 0.25 for planar structures, and 1 for linear objects, e.g., a rigid-rod molecule. In this work, we have obtained these shape parameters at different strain rates. Equilibrium values were obtained by extrapolating the results to the zero-shear limit.

III. RESULTS AND DISCUSSION

The flow-induced changes in shape and orientation of a dendrimer at different strain rates are qualitatively illustrated in Fig. 2. The dependences of the eigenvalue ratios on strain rate are shown for both dendrimers and linear polymers in Figs. 3 and 4. In each case, as the systems are sheared and molecules are more stretched, the differences between the eigenvalues increase with strain rate. In equilibrium or close to it, long linear polymers have the same eigenvalue ratios irrespective of molecular size, whereas the eigenvalue ratios for dendrimers strongly depend on the generation number. The asymmetry of dendrimers decreases with increasing size. Our equilibrium values for linear polymers of $L_2/L_1 \approx 0.21$

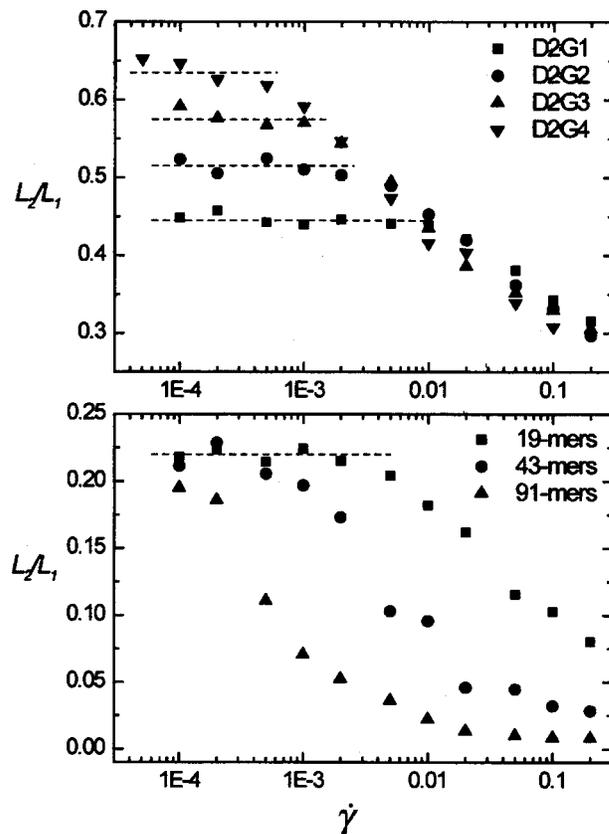


FIG. 3. Ratio of the second (medium) to the first (largest) eigenvalue of the tensor of gyration for dendrimers and linear polymers at different strain rates.

and $L_3/L_1 \approx 0.075$ are in very good agreement with the values of 0.23 and 0.08, 0.22 and 0.074, or 0.21 and 0.065 reported elsewhere.⁴⁻⁶

In Figs. 5 and 6, the variation of the asphericity and acylindricity with the shear rate is presented for dendrimers and linear chain. The shape of dendrimers at or near equilibrium becomes more spherocylindrical with increasing generation number. In contrast, for linear polymers the shape does not depend on the size and for small strain rates $b/R_g^2 \approx 0.66$ and $c/R_g^2 \approx 0.1$. These results are in very good agreement with values of these parameters reported earlier.⁴⁻⁶

Figure 7 shows the relative shape anisotropy for both dendrimers and linear polymers under shear. The anisotropy of both systems increases with the shear rate. However, the anisotropy parameter for linear polymers is much larger than for dendrimers and, at high strain rates, it approaches a value of 1 corresponding to a fully stretched linear configuration. For strain rates close to equilibrium linear molecules converge to 0.42 observed elsewhere.⁴⁻⁶

All of the shape parameters presented here remain unchanged and equal to their equilibrium values until the strain rate attains a value of $\dot{\gamma}_0$, which is a characteristic molecular parameter correlated with the onset of shear thinning. The equilibrium shape parameters for dendrimers are compared to the results obtained for linear polymers in Table I. The values reported here are consistent with estimates derived in the literature²² from Monte Carlo data.¹¹ In contrast to linear polymers, the equilibrium shape of dendrimers varies with

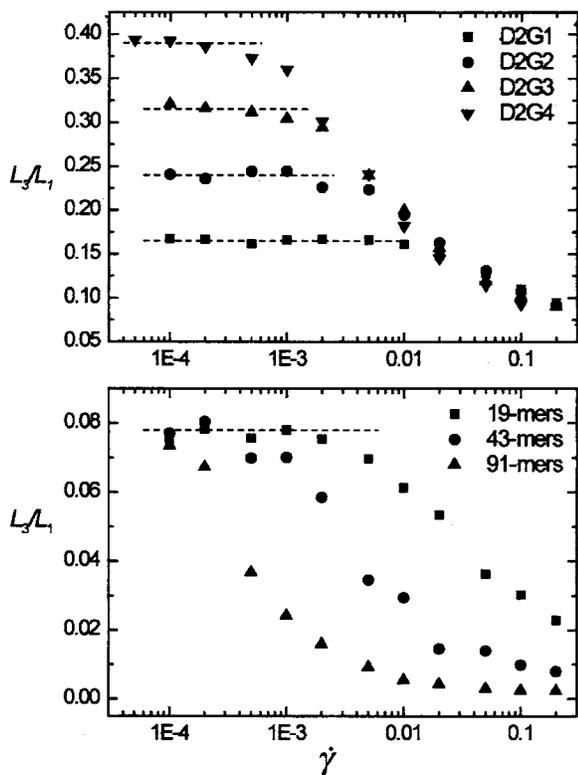


FIG. 4. Ratio of the third (smallest) to the first (largest) eigenvalue of the tensor of gyration for dendrimers and linear polymers at different strain rates.

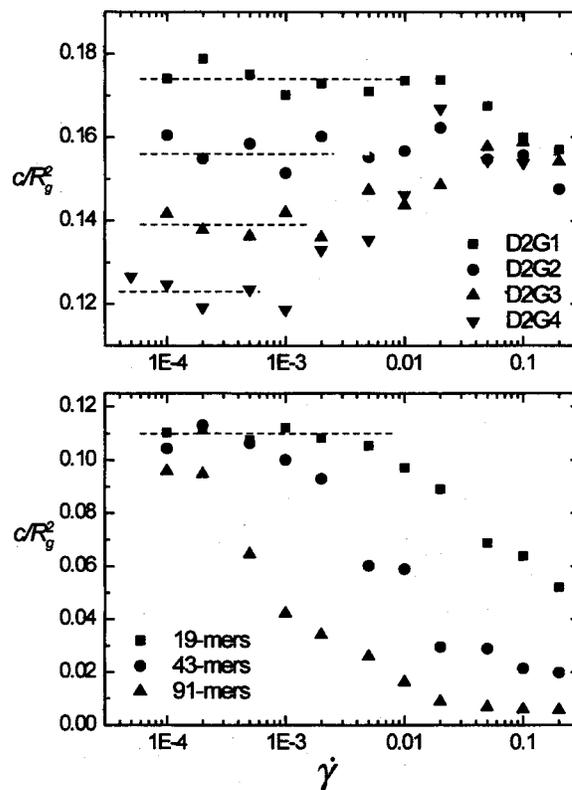


FIG. 6. Flow-induced changes in the acylindricity [as defined by Eq. (5)] of dendrimers (top panel) and linear polymers (bottom panel) at different strain rates.

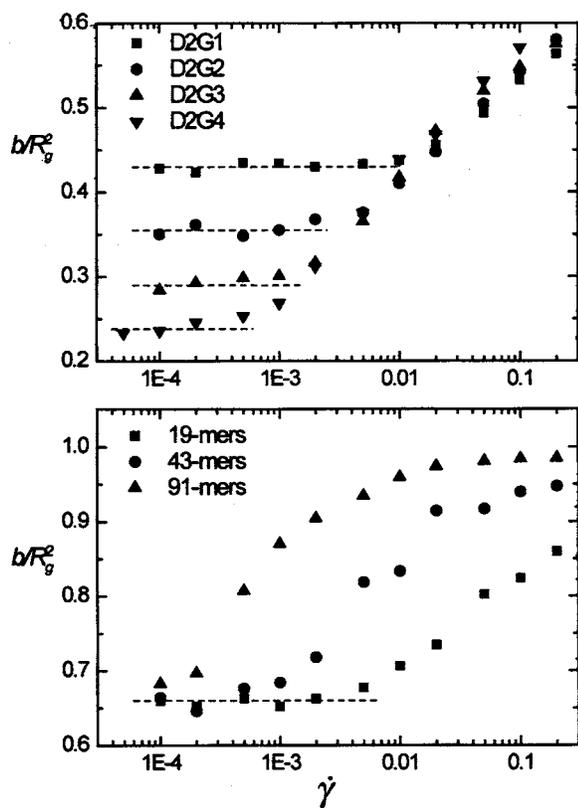


FIG. 5. Flow-induced changes in the asphericity [as defined by Eq. (4)] of dendrimers (top panel) and linear polymers (bottom panel) at different strain rates.

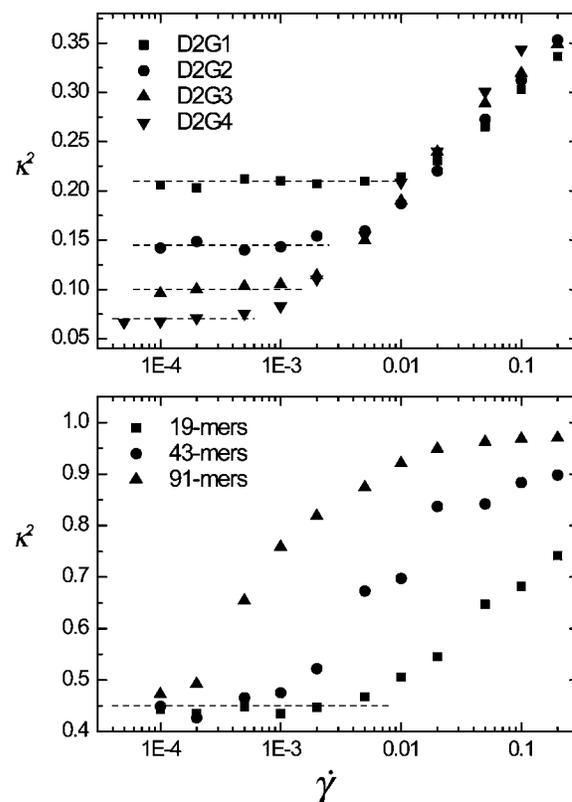


FIG. 7. Flow-induced changes in the relative shape anisotropy [as defined by Eq. (6)] of dendrimers and linear polymers at different strain rates.

TABLE I. Comparison of the equilibrium shape parameters of dendrimers, linear polymers, and ideal spheres.

Shape parameter	D2G1	D2G2	D2G3	D2G4	Linear polymers	Ideal sphere
L_2/L_1	0.445	0.515	0.575	0.635	0.22	1
L_3/L_1	0.165	0.24	0.315	0.39	0.078	1
b/R_g^2	0.43	0.355	0.29	0.238	0.66	0
c/R_g^2	0.174	0.156	0.139	0.123	0.11	0
κ^2	0.21	0.145	0.1	0.07	0.45	0

generation number. The considerable variation of the L_2/L_1 and L_3/L_1 ratios compares with values of 0.33–0.41 and 0.12–0.16, respectively, reported²² for star polymers. In general, the shape anisotropy of dendrimers decreases with the increasing size. This trend can be easily explained by taking into account the topology of dendrimers with branches emanating from the central core and molecules growing concentrically. In combination with excluded volume effects, the structure of dendrimers of higher generations becomes globular and compact resulting in a more spherical shape.

At the highest strain rates considered in this study, dendrimers, due to their topological constraints, remain globular with ratios of the second (L_2) and third (L_3) eigenvalues of the tensor of gyration being still approximately 30% and 10% of the largest eigenvalues (L_1). In the case of linear polymers these ratios drop to much smaller values. This indicates the presence of almost fully stretched molecular coils, which can also be identified through the asphericity or the relative shape anisotropy approaching the value of 1. One can also notice at high strain rates that the anisotropy of dendrimers increases with the generation number, opposite to the trend observed at equilibrium. Such behavior is a result of the increasing number of molecular degrees of freedom and the increasing length of the branches that make the molecule more flexible, thus more susceptible to flow-induced deformation. While not the focus of this work, it is interesting to note that our results can be related to the rheo-optical behavior of shearing molecules.^{12,23}

Molecules with different topologies, sizes, and flexibili-

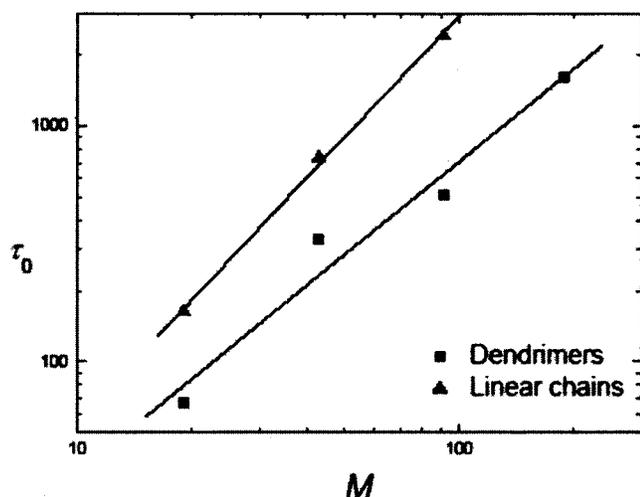


FIG. 8. Relaxation times of dendrimers and linear polymers as a function of molecular mass. The values were obtained from the strain rate corresponding to the onset of shear thinning.

ties are characterized by a number of relaxation times, with the largest being indicated by τ_0 . When the system is sheared at a rate that is small enough to enable structural relaxation, the average shape of molecules remains unchanged and identical to the one observed in equilibrium. In this case alignment and other long- and short-range correlations between molecules can still contribute to the changes in the macroscopic properties of the fluid. However, at shear rates larger than the reciprocal of the maximal relaxation time ($\dot{\gamma}_0 = 1/\tau_0$), apart from being aligned, molecules also become stretched and deformed. We determined values of $\dot{\gamma}_0$ from the onset of shear thinning observed in the shear viscosities.¹² For dendrimers of generations 1–4 these values are 0.015, 0.003, 0.0019, and 0.00062, respectively. In contrast for linear polymers, we determined $\dot{\gamma}_0$ to be 0.0061, 0.0014, and 0.00041 for 19-mers, 43-mers, and 91-mers, respectively. The relaxation times of dendrimers and linear polymers are displayed in Fig. 8 and they are listed in Table II. It should be noted that the nature of the simulation and the difficulty in accurately judging the onset of shear thinning mean that these values should be considered only as approximations.

The data presented in Figs. 3–7 clearly indicate that these values of $\dot{\gamma}_0$ closely coincide with the shear rates at which the shape parameters depart from their equilibrium values. Figure 9 directly compares the asphericity and acylindricity parameters with the shear viscosity reported elsewhere¹² for a 19-mer linear polymer and a first generation dendrimer, respectively. It is apparent from this comparison that the change in the shape parameters corresponds, at least approximately, with the onset of shear thinning.

IV. CONCLUSIONS

It has been demonstrated that the onset of a transition from Newtonian to non-Newtonian viscosity behavior in both linear polymers and dendrimers occurs simultaneously with significant changes in molecular shape. Dendrimers and

TABLE II. Characteristic relaxation times estimated from the strain rate at which onset of shear thinning is observed for dendrimers and linear polymers of the same mass.

Mass	τ_0	
	Dendrimers	Linear polymers
19	66.67	162.95
43	332.23	735.29
91	514.14	2415.93
187	1625.14	

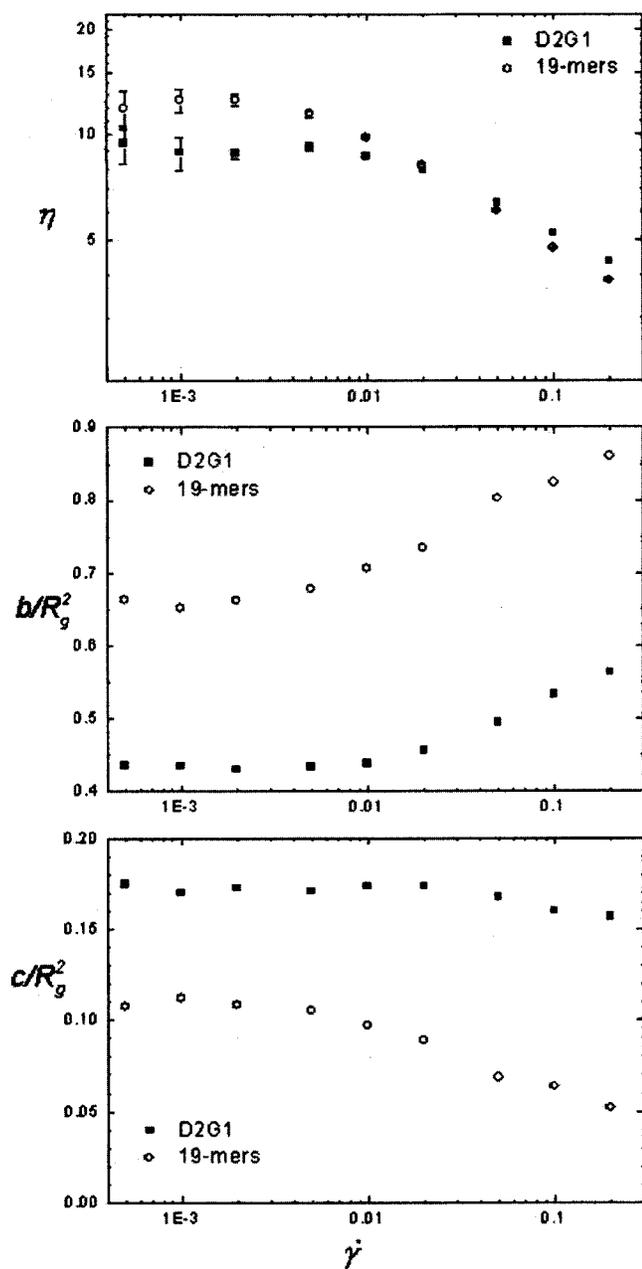


FIG. 9. Strain rate dependence of shear viscosity (Ref. 12), acylndricity, and asphericity for a 19-mer polymer (○) and a dendrimer of generation 1 (D2G1) (squares). It is apparent that the onset of shear thinning coincides with changes in molecular shape.

linear polymers of equivalent size exhibit different shape behavior. At equilibrium, values of the various shape parameters for linear polymers are independent of size whereas a strong size dependency is observed for dendrimers. In both

cases, the shape parameters are strongly strain-rate dependent in the shear-thinning region. The anisotropy of both dendrimers and linear polymers increases under shear. However, for a given strain rate, the change for linear polymers is much more rapid than for dendrimers. The phenomenological similarity between the shear-rate dependence of the shape parameters and the shear-rate dependence of physical properties such as shear viscosity and pressure suggests that the analysis of shape could be used as an alternative indicator of the onset of shear thinning or vice versa.

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