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Viscoelastic properties of dendrimers in the melt from nonequlibrium molecular dynamics

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The viscoelastic properties of dendrimers of generation 1-4 are studied using nonequilibrium molecular dynamics. Flow properties of dendrimer melts under shear are compared to systems composed of linear chain polymers of the same molecular weight, and the influence of molecular architecture is discussed. Rheological material properties, such as the shear viscosity and normal stress coefficients, are calculated and compared for both systems. We also calculate and compare the microscopic properties of both linear chain and dendrimer molecules, such as their molecular alignment, order parameters and rotational velocities. We find that the highly symmetric shape of dendrimers and their highly constrained geometry allows for substantial differences in their material properties compared to traditional linear polymers of equivalent molecular weight. © 2004 American Institute of Physics. [DOI: 10.1063/1.1818678]

I. INTRODUCTION

Dendrimers constitute a novel class of highly branched synthetic polymer. Developments in the synthesis of dendrimers over the last decade¹ allows the creation of dendrimers with almost full control over their structure and functionality. The unique molecular architecture of dendrimers makes their use for the design of novel materials very promising. For example, controlling surface reactivity can be used to make chemical sensors, and the ability of dendrimers to encapsulate other molecules means that they might be used as molecular delivery vehicles. Encapsulation in combination with the self-assembling behavior of dendrimers makes them a candidate for the fabrication of novel nanoscale materials.

The distinctive transport properties of dendrimers are a source of potentially useful applications. The high degree of symmetry of high-generation dendrimers and the decreased entanglement in the melt causes significantly different flow properties compared with the behavior of traditional polymer fluids such as linear polymers. Understanding the structureproperty relationships for dendrimers in the melt or in solution would enable full application of these materials as rheology modifiers, processing aids, or nanoscale lubricants.

For the case of dendrimer solutions, the intrinsic viscosity has been determined experimentally and reported for several dendrimers.² It has been observed that, unlike linear polymers that obey the Mark–Houwink equation³ [η]= $K \cdot M^a$ (where M is the molecular mass, and K, a are constants), the intrinsic viscosity of dendrimers reaches a maximum at a certain generation, beyond which it decreases with molecular mass. Many theoretical studies^{4–6} have been devoted to understanding the flow properties of dendrimer solutions.

One of the properties that distinguish dendrimers from

cosity on molecular mass. For linear chain polymers this dependence is described by⁷ $\eta_0 = KM^{\alpha}$ (Rouse theory), where α is ~1.0 for short chains (Rouse nonentanglement regime), and approaches 3.4 for long chains when entanglement becomes more significant (reptation regime). This behavior was experimentally observed³ and confirmed by computer simulation.^{8,9} The flow behavior of dendrimers is different because of the dominant influence of their dense surface and globular structure in comparison to their entanglement effects. There have been only a few experimental studies of concentrated solutions or melts of dendrimers.¹⁰⁻¹² These investigations report that dendrimers do not show a change in slope when the zero-shear viscosity is plotted against the molecular mass. Instead, the viscosity steadily increases with the molecular mass with a decreasing slope, reaching a value of 1.1¹⁰ or unity¹¹ at high molecular weights.

traditional polymers is the dependence of the zero-shear vis-

In contrast to the work in the literature on solutions, our work focuses on flow properties of dendrimers and their linear counterparts at relatively high densities. Previously we have studied¹³ the internal structure of dendrimers in the melt under shear. The aims of our current work are to characterize the viscoelastic properties of dense model dendritic fluids, compare them with the behavior of fluids composed of linear chain molecules, and finally to correlate the macroscopic properties of melts with the underlying dynamics and structural changes of the individual constituent molecules.

II. SIMULATION METHOD

A. Model

Dendrimers were modeled at the coarse-grained level using uniform beads corresponding to either monomers or constituent parts of the molecule. The excluded volume of beads was incorporated using the purely repulsive Weeks– Chandler–Anderson (WCA) potential¹⁴ of the form

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FIG. 1. Dendrimers of generations 1-4 modeled using freely jointed uniform beads. The dendrimer molecules are composed of 19, 43, 91, and 187 beads, respectively.

$$U_{ij}^{\text{LJ}} = 4 \epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \epsilon \quad \text{for } r_{ij} / \sigma < 2^{1/6},$$

$$U_{ij}^{\text{LJ}} = 0 \quad \text{for } r_{ij} / \sigma \ge 2^{1/6},$$
 (1)

where: r_{ij} is the separation between beads *i* and *j*, ϵ is the potential well depth and σ is the effective diameter of the beads. We assign ϵ and σ to unity and, adopting common practice, all quantities are expressed in reduced units relative to the Lennard-Jones (LJ) parameters: $r_{ij}^* = r_{ij}/\sigma$, density $\rho^* = \rho\sigma^3$, temperature $T^* = k_B T/\epsilon$, pressure tensor $\mathbf{P}^* = \mathbf{P}\sigma^3/\epsilon$, strain rate $\dot{\gamma}^* = (m\sigma^2/\epsilon)^{1/2}\dot{\gamma}$, and viscosity $\eta^* = (\sigma^4/m\epsilon)^{1/2}\eta$. For simplicity of notation, hereafter the asterisk will be omitted.

In addition to the WCA potential, we modeled chemical bonds between beads to maintain molecular topology with the finitely extensible nonlinear elastic (FENE) potential¹⁵ of the form

$$U_{ij}^{\text{FENE}} = -0.5kR_0^2 \ln[1 - (r_{ij}/R_0)^2] \quad \text{for } r_{ij} < R_0,$$

$$U_{ii}^{\text{FENE}} = \infty \quad \text{for } r_{ij} \ge R_0.$$
(2)

Setting $R_0 = 1.5$ and k = 30, the average distance between the connected beads at equilibrium and at a temperature T = 1.25 is ~0.97. A review of realistic intermolecular potentials is available elsewhere.¹⁶

We modeled dendrimers with tri-functional cores and 2 beads separating the branching points. As illustrated in Fig. 1, this model results in 19, 43, 91, and 187 beads per single dendrimer of generation 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. For simulations involving either D2G1 or 19-mers, a system of 256 molecules was used, whereas in all other cases 125 molecules were used. In all cases, the system was first constructed at low density and then gradually compressed to a

reduced density of 0.84. The compression was achieved using the SLLOD algorithm¹⁷ with nonzero diagonal elements of the velocity gradient tensor, thus ensuring the system remained homogeneous in space and hence reducing the overall equilibration time.

B. Equations of motion

To simulate shear flow of the melts we applied the molecular version of the homogenous isothermal shear algorithm (SLLOD)¹⁷ in conjunction with standard Lees– Edwards periodic boundary conditions.¹⁸ The equations of motion for bead α in molecule *i* are given by

$$\dot{\mathbf{r}}_{i\alpha} = \frac{\mathbf{p}_{i\alpha}}{m_{i\alpha}} + \mathbf{i}\dot{\gamma}y_i$$

$$\dot{\mathbf{p}}_{i\alpha} = \mathbf{F}_{i\alpha} - \mathbf{i}\frac{m_{i\alpha}}{M_i}\dot{\gamma}p_{yi} - \zeta^M \frac{m_{i\alpha}}{M_i}\mathbf{p}_i,$$
(3)

where $\mathbf{r}_{i\alpha}$ and $\mathbf{p}_{i\alpha}$ represent the position and thermal momentum of bead α on molecule *i*, \mathbf{p}_i is the momentum of the molecular center of mass of molecule *i* and M_i is the mass of molecule *i*. The strain rate is defined by $\dot{\gamma} = \partial u_x / \partial y$, where $\mathbf{u} = \mathbf{i} u_x$ is the fluid streaming velocity in the *x*-direction. The streaming velocity of the molecule is determined by the position of its center of mass and has the form $\mathbf{i} \dot{\gamma} y_i$, where y_i is the position of the molecular center of mass; no further assumptions are made on the rotational degrees of freedom of the molecules. The simulations were performed at constant temperature using a molecular version of the Gaussian thermostat with a constraint multiplier ζ^M given by

$$\zeta^{M} = \frac{\sum_{i=1}^{N} (\mathbf{F}_{i} \cdot \mathbf{p}_{i} - \dot{\gamma} p_{xi} p_{yi}) / M_{i}}{\sum_{i=1}^{N} \mathbf{p}_{i}^{2} / M_{i}}, \qquad (4)$$

where N is the number of molecules in the system. The thermostat constrains the molecular kinetic temperature of the systems defined as

$$\sum_{i=1}^{N_m} \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2M_i} = \frac{3N-4}{2} k_B T_M.$$
⁽⁵⁾

All simulations were performed at a molecular temperature $T_M = 1.25$. The algorithm has been discussed in detail previously by Edberg *et al.*¹⁹ The justification for using the molecular version of the SLLOD algorithm with a thermostatted molecular kinetic temperature has been discussed in detail by Travis *et al.*²⁰

The equations of motion of all beads were integrated using a fifth-order Gear predictor corrector differential equation solver²¹ with reduced time step $\Delta t = 0.001$. After achieving steady state (typically several million time steps), the bead trajectories were accumulated and ensemble averages were calculated.

C. Viscoelastic properties

The rheological properties of molecular melts are typically analyzed using standard material functions. To characterize the rheological properties of the dendrimer melt under steady shear flow we compute the shear viscosity $\eta(\dot{\gamma})$, first



FIG. 2. Comparison of the various extrapolation schemes used to obtain the zero-shear viscosity with simulation data (\blacksquare) for a generation 1 dendrimer (D2G1): (a) $\eta = \eta_0 - A \dot{\gamma}$ (...), $\eta = \eta_0 - B \dot{\gamma}^2$ (...-), $\eta = \eta_0 - C \dot{\gamma}^{1/2}$ (...); (b) $\eta^{-1} = \eta_0^{-1} - DP_{xy}$. The estimated values of the zero-shear viscosity are 9.22, 9.09, 9.42, and 9.24, respectively. The average value is 9.24.

 $\Psi_1(\dot{\gamma})$ and second $\Psi_2(\dot{\gamma})$ normal stress coefficients. All the viscometric functions are expressed in terms of the components of the molecular pressure tensor \mathbf{P}^M calculated as

$$\mathbf{P}^{M}V = \sum_{i=1}^{N} \frac{\mathbf{p}_{i}\mathbf{p}_{i}}{M_{i}} - \frac{1}{2}\sum_{i=1}^{N} \sum_{\alpha=1}^{n} \sum_{j\neq i}^{N} \sum_{\beta=1}^{n} \mathbf{r}_{ij}\mathbf{F}_{i\alpha j\beta}, \qquad (6)$$

where \mathbf{r}_{ij} is the center of mass separation of molecules *i* and *j*, $\mathbf{F}_{i\alpha j\beta}$ is the force on site α in molecule *i* due to site β in molecule *j*, and *n* is the total number of interaction sites in a molecule.

The shear viscosity is defined as

$$\eta = \left\langle -\frac{P_{xy} + P_{yx}}{2\dot{\gamma}} \right\rangle,\tag{7}$$

whereas the first and second normal stress coefficients are

$$\Psi_1 = \left\langle \frac{P_{yy} - P_{xx}}{\dot{\gamma}^2} \right\rangle, \quad \Psi_2 = \left\langle \frac{P_{zz} - P_{yy}}{\dot{\gamma}^2} \right\rangle. \tag{8}$$

III. RESULTS AND DISCUSSION

Our simulation studies allow us to examine both the macroscopic flow properties of dendrimers and microscopic properties such as the effect of molecular shape, alignment,



FIG. 3. Zero-shear viscosity vs molecular mass for dendrimers and linear chain molecules. Results for chains are combined with those reported by Kröger and Hess (Ref. 9). Lines with slope 1 (Rouse regime) and 3 (reptation regime) are fit to the data points for linear chain molecules. A single line is fit to the data for dendrimers with a slope of 0.65.

and dynamics. We have reported a detailed analysis of the shape of dendrimer molecular melts under shear in a pervious paper.¹³

A. Macroscopic properties

1. Viscosity

All of the systems studied exhibit the transition from the Newtonian regime for small strain rates to the non-Newtonian regime for high strain rates. The flow curves can be characterized by the zero-shear viscosity $\eta_0 = \lim_{\dot{\gamma} \to 0} \eta$, and the value of an exponent in the power-law region $\eta \propto \dot{\gamma}^{-n}$. Although the absolute values of viscosity depend on the actual thermodynamic state point, the flow curves can be superimposed on one "master curve."^{3,22} Therefore, the results obtained are characteristic for the particular molecules composing the fluid.

There are several ways in which the zero-shear viscosity of a fluid can be obtained through molecular-dynamics (MD) simulations. The most commonly used method is to perform Green-Kubo equilibrium MD simulations and compute the zero-shear viscosity from the stress autocorrelation function. Alternatively, a less used but more efficient method is to compute the shear viscosity as a function of strain rate via NEMD simulation and then extrapolate to zero strain rate to extract η_0 . This is the method we use. However, accurate determination of the melt viscosity at very small shear rates can be a tedious and computationally expensive task, especially for systems composed of large molecules. The values obtained are also often associated with a large degree of uncertainty. Several extrapolation schemes have been proposed to derive the value of η_0 from the flow curve. These include fitting of linear $(\eta = \eta_0 - A\dot{\gamma})$ or quadratic $(\eta = \eta_0 - B\dot{\gamma}^2)$ functions²³ to the values of the viscosity obtained at the smallest shear rates. The latter dependence is also known as the retarded motion expansion³ for a third-order fluid. Alternatively, Evans et al.²⁴ proposed a square root dependence



FIG. 4. Comparison of shear viscosity vs strain rate for dendrimers and linear chains of equivalent molecular weight (i.e., same number of beads in the molecule). Solid lines represent fitting with the Carreau–Yasuda (Ref. 3) model: $\eta = \eta_0 / [1 + (\lambda \dot{\gamma})^2]^p$ Parameters obtained from this fit are in agreement with results presented in the text.

 $(\eta = \eta_0 - C \dot{\gamma}^{1/2})$ for the asymptotic behavior of the fluid. Recently Ge *et al.*²⁵ have demonstrated that the exponent dependence of the transport properties of simple fluids is a linear function of density and temperature; such a dependence has yet to be determined for more complex molecular fluids. The dependence of the inverse viscosity on the shear stress $(\eta^{-1} = \eta_0^{-1} - DP_{xy})^{26}$ can also be used to estimate η_0 . We determined the zero-shear viscosity as the average of the values obtained using all four of these extrapolation schemes. Details of this averaging procedure are given elsewhere.^{9,27} The quality of the fit to the simulation data for these various extrapolation schemes is compared in Fig. 2 for a generation 1 dendrimer.

Figure 3 shows the dependence of the zero-shear viscosity on the molecular mass for dendrimers and linear chain molecules. We combined our results for the linear chain molecules with the NEMD results obtained by Kröger and Hess.⁹ For the short chains, in agreement with the Rouse model, we observe an almost linear dependence ($\eta_0 \propto M^{0.95}$), which for the larger molecules tends to a power law with the exponent >3 (reptation regime). In contrast, for dendrimer melts a



FIG. 5. Exponent of the viscosity vs. strain rate curve in the shear-thinning region plotted against molecular weight.

similar crossover has not been observed. Instead, the relationship satisfies a power law with a single exponent that is smaller than that for unentangled chain molecules ($\eta_0 \propto M^{0.646(2)}$). Our results are in qualitative agreement with experimental observations,^{10,11} however the absolute value of the exponent is much smaller than the one determined experimentally. This discrepancy could be attributed to the assumptions made in the way we modeled our dendrimers. The freely jointed beads (without constraints on the bond angles) results in molecules that are more flexible than the real ones. This means that our model dendrimer is more prone to fold upon itself when sheared in a dense melt. This could result in lower values of the shear viscosity compared to that observed in real dendrimer melts.

The exponents in the power-law region were obtained from the linear region in the log–log plot of the viscosity versus strain rate curve (Fig. 4). Their values (plotted in Fig. 5) as well as the zero-strain-rate viscosities for all studied systems are presented in Table I. For both dendrimers and linear polymers, the exponents in the power law region of the η versus $\dot{\gamma}$ relationship increase with molecular mass, but the increase is more rapid for linear polymers. Also the absolute values of the exponents are larger for linear chain molecules. This is in agreement with the results of Xu *et al.*²⁸ and Kröger *et al.*,⁸ but in contrast with more recent results reported by Kröger and Hess⁹ who find invariant exponents. However, it should be noted that the determination of these

TABLE I. Estimated values of the zero-shear viscosity (η_0) and exponent ($\eta \propto \dot{\gamma}^n$) in the power law region (shear thinning) for dendrimers and linear chains. Statistical uncertainty (from the standard error of the fit) in the last significant digit is given in brackets.

	Dendrimers		Chain J	polymers
Mass	η_0	n	η_0	n
19	9.2(3)	0.275(3)	12.5(4)	0.321(2)
43	17.4(9)	0.304(3)	27.3(2)	0.413(5)
91	26.9(1)	0.330(3)	82.1(7)	0.523(2)
187	43.1(2)	0.360(8)		0.743(3)

exponents is extremely sensitive to where on the strain rate curve one assumes the power law region is valid. In the absence of a commonly accepted rule for judging the onset of the non-Newtonian region there is some ambiguity in comparing values of exponents. We further note that they use the atomic SLLOD equations of motion with an atomic thermostat and simulate their fluid at a lower temperature than ours, which could also account for differences in trends. A full discussion on the merits and pitfalls of the various forms of the SLLOD algorithm and thermostatting mechanisms is given elsewhere.²⁰ Daivis *et al.*²⁹ also report constant values of exponents, but their estimates were performed at constant pressure, in contrast to our constant volume simulations.

For dendrimers the exponent in the shear-thinning region is close to 1/3 for all generations taken into account. The same scaling was observed by Lyuiln *et al.*⁶ in their simulations of dendrimers in solution. Larger power law exponents for linear chain molecules in comparison to branched alkanes were also reported elsewhere.^{28,30,31}

A direct comparison of the viscosity-strain rate curves for dendrimers with those of traditional linear chain polymers of the same size (at the same density and temperature) is shown in Fig. 4. In all cases, when the fluid is in the Newtonian regime the viscosity of dendrimer melts is lower than that of the linear molecules. Internal branching and the compact globular structure of dendrimers, resulting in suppression of intermolecular entanglement, is responsible for this decrease in viscosity. We previously analyzed the structural changes of dendrimers under shear¹³ and found that the outermost branches, which might participate in entanglement, often fold back and can be found inside the molecule. Therefore they can not interact with branches of other molecules, consequently reducing intermolecular entanglement and hence the shear viscosity. In the non-Newtonian regime the exponent in the power law region is always smaller for dendrimer melts in comparison to linear chain polymers, leading to lower viscosities for linear chains in comparison to dendrimers of the same molecular weight. In this case the branching of dendrimers reduces shear-induced alignment of molecules, which therefore slows shear thinning. Similar behavior has been reported for star-shaped molecules compared to linear chain molecules of the same mass.^{30,32}

2. First and second normal stress coefficients

Figure 6 shows the log–log plot of the first normal stress coefficient vs. strain rate, whereas Fig. 7 shows the dependence of the second normal stress coefficient on strain rate. For all systems the stress coefficients have large power law regions. The exponents of the asymptotic dependences $\Psi_1 \propto \dot{\gamma}^{-\alpha}$ and $|\Psi_2| \propto \dot{\gamma}^{-\beta}$ in the power law region are shown in Table II. In the case of dendrimer melts, the values of the α and β exponents appear to be constant and do not depend on molecular mass. In contrast, for linear chain molecules their values increase with the size of the molecules, in agreement with the observations of Kröger *et al.*⁸ The smaller values of the power law exponents for branched alkanes are also reported by Daivis *et al.*³⁰



FIG. 6. First normal stress coefficient vs strain rate for dendrimers and linear chain molecules of equivalent molecular weight.

linear chain molecules. Jabbarzadeh *et al.*³¹ observed a similar decrease in the normal stresses of branched polymers compared to linear polymers. In Fig. 8 the ratio $|\Psi_2/\Psi_1|$ is plotted against the strain rate. For linear polymers its value is ~5%–15% and is in agreement with experimental results for typical polymers.³ In contrast, for dendrimers this ratio is about 20%. This could be attributed to the spherical shape of the molecules and internal bond constraints which prevent large stretching of the molecules and in turn leads to smaller differences between the diagonal elements of the stress tensor.

3. Pressure

The pressure of the systems undergoing shear flow, calculated as the average of one third the trace of the diagonal elements of the molecular pressure tensor, is shown in Fig. 9. Unlike simple fluids, which have been shown to display a simple power law behavior²⁵ $p = p_0 + b \dot{\gamma}^m$, molecular fluids display a more complex behavior in which the pressure first decreases as a function of $\dot{\gamma}$ down to a minimum, beyond which it increases with a power law behavior. The parameters for the high strain rate power law region $(p = b \dot{\gamma}^m)$ are shown in Table III. Note that the p_0 values here are obtained by extrapolation of low strain rate data to zero strain rate.

We note that Lue⁵ has studied the equilibrium volumetric behavior of athermal dendrimers in solution and compared the results with linear systems. These equilibrium solution



FIG. 7. Second normal stress coefficient vs strain rate for dendrimers and linear chain molecules of equivalent molecular weight.

results indicate that the pressure of high generation dendrimers increases more rapidly with density than is observed for linear systems.

B. Structural properties

In our previous work¹³ we analyzed flow induced structural changes of dendrimers under shear. We showed that the onset of shear thinning is correlated with the onset of stretching of the molecules (changes in shape, fractal dimensionality of dendrimers). We now consider intermolecular correlations: Spatial distribution of molecules, their alignment, as well as the molecular dynamics (spin velocity) underlying macroscopic flow properties of the melts. Figure 10 shows snapshot configurations of a single dendrimer (selected from

TABLE II. Estimated values of the exponents in the power law regions of the first $(\Psi_1 \propto \dot{\gamma}^{-\alpha})$ and second $(|\Psi_2| \propto \dot{\gamma}^{-\beta})$ normal stress coefficients for dendrimers and linear chains.

	Dendrimers		Chain polymers	
Mass	α	β	α	β
19	1.089(6)	0.99(2)	1.175(5)	1.05(2)
43	1.099(4)	1.03(1)	1.228(3)	1.26(2)
91	1.099(4)	1.003(8)	1.306(2)	1.537(9)
187	1.065(4)	1.04(1)	1.448(5)	1.507(9)



FIG. 8. Ratio of the second to first normal stress coefficient vs strain rate for dendrimers and linear chain molecules of equivalent molecular weight.

the melt) under shear at different strain rates. Note the flow induced changes in shape and orientation of the molecule, as discussed in detail below.

1. Radial distribution function of the molecular centers of mass

The radial distribution function (RDF) is defined by

$$g(r) = \frac{\langle \sum_{i=1}^{N} \sum_{j>i}^{N} \delta(|\mathbf{r} - \mathbf{r}_{ij}|) \rangle}{4 \pi r^2 N \rho}, \qquad (9)$$

where \mathbf{r}_{ij} is the distance between the centers of mass of molecules *i* and *j*, *N* is the total number of molecules, and ρ is the density. This function describes the probability of finding two molecules at a separation *r*. In Fig. 11 distribution functions are shown for our dendrimer systems. The first peak corresponds to the shell of the first neighbors and is observed at equilibrium (not plotted) and for relatively small strain rates. Its position is typically at the distance comparable to double the radius of gyration (average diameter of the volume occupied by the molecule). For higher strain rates it disappears due to flow induced stretching and alignment of molecules, which induces an orientational preference for molecular alignment. The radial distribution function, which is spherically averaged over all space, can not account for this without computing the angular dependence



FIG. 9. Molecular pressure of melts composed of dendrmiers and linear chain molecules plotted against the strain rate.

of g(r). However, we analyze the orientational configuration space of our dendrimers by computing order parameters, alignment angles and spin velocities.

2. Molecular orientation

To describe the flow induced alignment of dendrimers we calculated an order tensor defined by

$$\mathbf{S} = \frac{1}{N} \sum_{i=1}^{N} \left(\mathbf{u}_i \mathbf{u}_i - \frac{1}{3} \mathbf{I} \right), \tag{10}$$

where \mathbf{u}_i is the unit vector denoting orientation of the single molecules, and *N* runs over the number of molecules in the system. We assumed that the eigenvector corresponding to the largest eigenvalue of the tensor of gyration denotes the orientation of the molecule. The principal eigenvector of the order tensor indicates the direction in which molecules are aligned. The angle between the flow direction and the align-

TABLE III. Estimated parameters in the shear-dependent pressure of the melt given by $p = p_0 + b \dot{\gamma}^n$.

	Dendrimers			Linear polymers		
Mass	p_0	b	т	p_0	b	т
19	5.546(2)	16.3(1)	2.04(4)	5.599(1)	17(5)	2.3(2)
43	5.420(4)	31.5(1)	1.75(3)	5.4847(1)	29(6)	2.1(1)
91	5.368(3)	74.8(9)	1.643(7)	5.413(2)	51(6)	2.01(6)
187	5.350(3)	156(2)	1.527(7)	5.410(1)	25(11)	1.3(2)



FIG. 10. Configuration of a single dendrimer D2G4 in the melt under shear at strain rate (a) 0.0001, (b) 0.001, (c) 0.01, and (d) 0.1.

ment direction is the birefringence extinction angle χ . The extent of alignment may be described by an order parameter S defined as 3/2 of the principal eigenvalue of the order tensor. The order parameter varies between 0 (in the case of orientational disorder) to 1 (for perfect alignment). The extinction angle and the order parameter for linear chains and dendrimer melts are shown in Fig. 12. In both systems the alignment angle decreases with increasing strain rate, whereas for small strain rates it converges to 45° (expected in the Newtonian regime). The order parameter instead increases monotonically with the strain rate. The alignment angle is always smaller for linear chains than for dendrimers of the same molecular mass, whereas the order parameter is higher for linear chains than for dendrimers. This implies that, for equivalent strain rates, linear chains more easily stretch and align with respect to the flow field than dendrimers of the same molecular weight. As discussed previously, this is a consequence of the compact and constraint limiting geometry of dendrimer molecules compared to the more 'open" less constrained linear molecules.

3. Molecular rotation

Apart from alignment and stretching, shear flow also induces rotation of molecules constituting the fluid. The angular velocity of molecules can be derived by solving the equation

$$\mathbf{L} = \mathbf{I} \cdot \boldsymbol{\omega}, \tag{11}$$

where **L** is the average angular momentum vector of the molecule with reference to its center of mass, **I** is the average moment of inertia tensor, and ω is the average angular velocity vector. Linear nonequilibrium thermodynamics³³ predicts that for planar shear flow the angular velocity should satisfy the relationship $\omega_z = -\dot{\gamma}/2$ in the limit as $\dot{\gamma} \rightarrow 0$.

In Fig. 13 the calculated values of the spin velocity of dendrimers and linear chain molecules are plotted against the strain rate. The angular velocity of dendrimers does not appear to depend on the molecular mass (generation) and its value converges to the 1/2 slope at higher values of $\dot{\gamma}$ than for linear chain molecules. Furthermore, the rotation of linear chain molecules is strongly correlated with the molecular



FIG. 11. Molecular RDF for D2G1 (a), D2G2 (b), D2G3 (c), D2G4 (d), and comparison for the smallest strain rate (e). Plots are shifted along the *y* axis, and fitted lines in each case are g(r)=1. In panels (a)–(d) curves correspond to strain rates 0.1, 0.01, 0.001, and 0.0001 from bottom to top, respectively. In panel (e) the arrows indicate the distance corresponding to the average diameter of dendrimers (twice the radius of gyration).

(a) Linear chains.



FIG. 12. Birefringence extinction angle [top panels in (a) and (b)] and order parameter [bottom panels in (a) and (b)] as a function of strain rate for (a) linear chain molecules and (b) dendrimers.

mass (chain length). The fact that the rotation of dendrimers is less constrained is a direct consequence of the dendrimer architecture, which results in compact and symmetric structures that prevent branch entanglement.

IV. CONCLUSIONS

We have performed nonequilibrium molecular dynamics studies on the viscoelastic properties of coarse-grained den-



FIG. 13. Average angular velocity of dendrimers and linear chain polymers vs strain rate. The line shows the expected linear regime dependence: $\omega = -\dot{\gamma}/2$.

drimer melts and compared their material properties with linear polymer melts of the same molecular weight. We find that the spherical symmetry and highly constrained nature of the molecular architecture of dendrimers results in viscoelastic properties that differ markedly from those of linear chain molecules. The zero shear viscosity of dendrimers exhibits a power law scaling with molecular mass, with an exponent that remains constant for all systems investigated. This is in contrast to traditional linear chain molecules which exhibit two scaling regimes, the Rouse and reptation regions. The architecture of dendrimers and their short branch lengths prohibit reptation dynamics. The shear viscosity of dendrimers and linear chains as a function of strain rate also displayed a universal characteristic: for low strain rates the viscosity of dendrimers of a particular molecular weight is always lower than the viscosity for linear chains of equivalent weight. In the shear-thinning region there is a cross-over point where the trend reverses, i.e., the viscosity for linear chains is lower than that of equivalent mass dendrimers. This is a direct result of the relative enhancement in the transport of linear momentum for linear chains as they align with respect to the flow field, compared to dendrimers that are stretched and aligned to a lesser degree due to their more constrained architecture. We find that the spin angular velocity of dendrimers seems not to depend on the molecular mass and its value converges to the predictions of linear irreversible thermodynamics at higher values of strain rate than for linear chain

molecules of equivalent mass. The rotation of dendrimers is less constrained due to the compact and symmetric architecture that prevents branch entanglement. These interesting features of dendrimers suggest that they may be usefully utilized as additives in blends of traditional linear polymers.

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