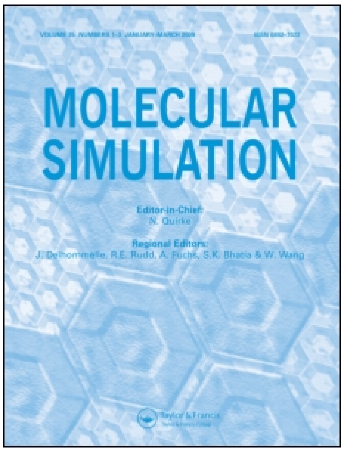

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Molecular simulation of dendritic systems

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Molecular simulation of dendritic systems

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Dendrimers are a new class of highly branched polymers consisting of short chain units with multifunctional groups at both ends. Starting from an initiator core, the successive reaction of the functional groups with other units generates a highly branched chain molecule, which resembles a Cayley tree. We have used nonequilibrium molecular dynamics to examine the viscosity behaviour of dendrimers under shear. The results for dendrimers up to generation number 4 show that there are quantitative differences in the viscoelastic properties of dendrimers compared with linear systems of equivalent size. Here, we review our recent work on dendrimers, which demonstrates that the viscoelastic properties are directly related to molecular shape.

Keywords: Dendrimers; Molecular dynamics; Viscosity; Molecular shape

1. Introduction

Dendrimers are a new class of highly branched polymers consisting of short chain units with multifunctional groups at both ends. Starting from an initiator core, the successive reaction of the functional groups with other units generates a highly branched chain molecule, which resembles a Cayley tree [1,2]. Potentially, dendrimers have beneficial applications to many areas. Possible areas of application are nanoscale catalysis [3], mimics for micelles [4–6], magnetic resonance imaging, adhesives and coatings. Dendrimers are similar in size to biologically important molecules such as enzymes, antibodies, DNA, RNA and viruses, and the structure of dendrimers can be tailored to be cell-specific. Consequently, it may be possible to use dendrimers to deliver drugs or genes into specific cells. The self-assembling properties of some dendrimers [7] also has potential implications for the fabrication of nanostructures [8].

Dendrimer molecules are characterised by the number of generations they contain (g), the functionality of the end groups (b), and the number of monomer segments or separator length (n) between the functional groups. Figure 1 illustrates the generational change of a dendrimer with trifunctional end groups. The number of monomers (N) in a dendrimer grows rapidly with each successive generation obeying the relationship, $N = nb[(b-1)^{g+1} - 1]$. In contrast, the volume available to the dendrimer scales as g^3 inhibiting indefinite growth.

Theoretical work on dendrimers has focused largely on determining the structure of isolated homogeneous dendrimers. The early work concentrated on the application of traditional theoretical methods to dendrimers. De Gennes and Hervert [9] developed a self-consistent mean-field theory for the distribution of polymer segments within the dendrimer molecule. They concluded that a perfect dendrimer can be grown up to a limiting generation number $g \approx 2.88(\ln n + 1.5)$. Biswas and Cherayil [10] reported renormalization-group calculations to determine the dependence of the average centre-to-end distance of a dendrimer on both the generation number and the length of the separator. These theories assume that the separator is extremely flexible, whereas dendrimers are commonly synthesised using non-flexible separator molecules. Numerical self-consistent mean-field calculations have also been performed for individual dendrimers.

Many studies have been reported [10,21] to determine the properties of isolated dendritic polymers. Off-lattice simulations have been performed [10] for randomly grown tangent sphere dendrimers to determine both the density distribution of segments and the dependence of the radius of gyration on the molecular weight and length of the spacer molecule. However, because the dendrimer was grown randomly, these simulations do not represent the real structure of dendrimer molecules in solution. Naylor *et al.* [13] applied atomic-scale molecular dynamics simulations of dendrimers with up to seven generations.

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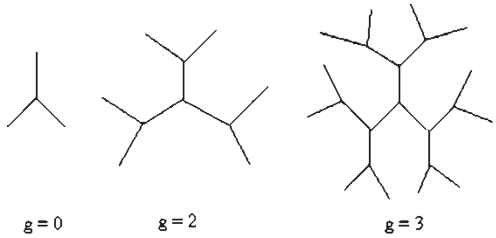

Figure 1. Schematic illustration of dendrimer connectivity with different generation number.

The use of atomic-level force fields yielded detailed information on molecular structure indicating that dendrimers have open structures, in contrast to the concentric shell structure assumed by early theories [9]. Wiener *et al.* [23] used molecular dynamics to study chelate complexes attached to dendrimers.

We [24–27] have recently developed a successful model that appears to adequately describe the salient features of real dendrimers. This model has been used to determine the structural features of dendrimers up to generation number four. It has also been used to determine the properties of dendrimers in response to the application of a shearing force. Here, we discuss the relationship between viscosity and molecular shape.

2. Theory

Details of both the model and simulation techniques have been described extensively elsewhere [24–27]. Therefore, only a brief summary is provided here. Dendrimers were modeled using tri-functional 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 generation 1, 2, 3 and 4, respectively. The interaction between the beads was obtained using the purely repulsive Weeks–Chandler–Anderson (WCA) potential [22] and the chemical bonds between the beads was modeled using a finitely extensible nonlinear elastic (FENE) potential [22]. Figure 2 shows how this simple coarse-grain model captures the salient structural features of a fully atomistic model To simulate shear flow of melts we applied the molecular version of the homogenous isothermal shear algorithm (SLLOD) [28] 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.

Solc and Stockmayer [29] showed that the shape of polymers could be quantified using eigenvalues of the tensor of gyration (R_g). In particular, the asymmetry of polymers can be quantitatively described with the ratios of the eigenvalues (L_1, L_2 and L_3) of the tensor of gyration [29]:

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

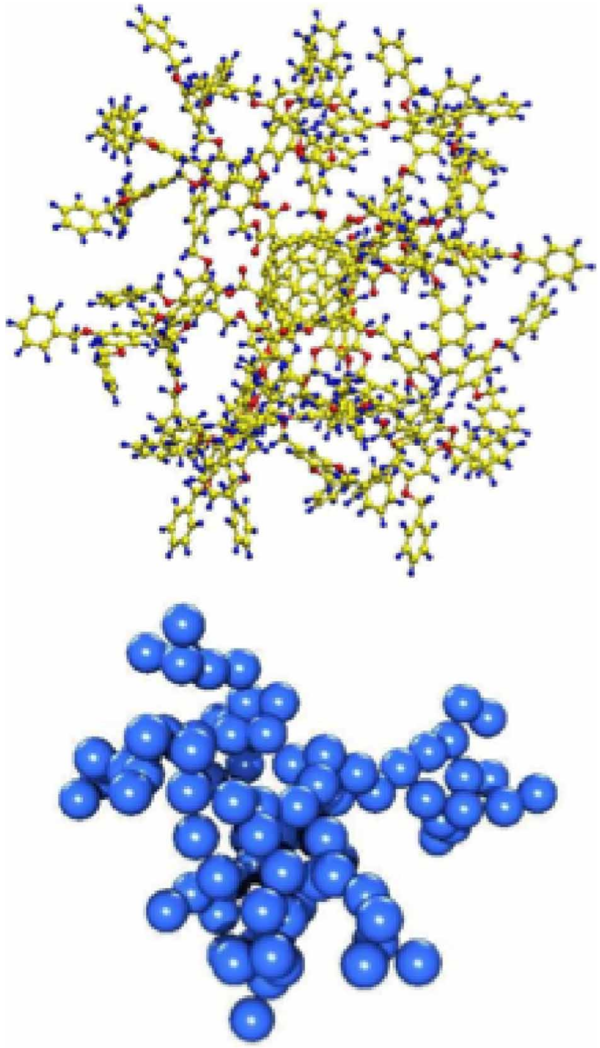

Figure 2. Comparison of a fully atomistic model of a fullerene dendrimer of generation 3 containing 1278 atoms with a coarse-grained generation 3 ($b = 2$) bead-spring model composed of 91 beads.

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

Additional parameters that can be used to describe symmetry of dendrimers are asphericity, acylindricity and relative shape anisotropy. The asphericity is defined by [29]

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

acylindricity by:

$$c = L_2 - L_3 \qquad (3)$$

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.

3. Results and discussion

Our calculations are based on a coarse-grained model of both linear polymers and dendrimers. A coarse-grained model has both advantages and disadvantages compared to genuinely atomistic simulations. The main disadvantage is that the results cannot be directly related to a real system. On the other hand, atomistic models require accurate values of the various inter- and intra-molecular parameters that are often not available. The coarse-grain approach usually requires much less computational resources, which can often make a calculation feasible. However, the main advantage of a course-grain approach is the ability to obtain general conclusions for a well-defined class of molecules. In contrast, both atomistic simulations and indeed experimental investigations are by definition system-specific.

Results of simulation studies [24–26] consistently show the onset of a transition form Newtonian to non-Newtonian behaviour at a threshold value of strain rate ($\dot{\gamma}_0$). Figure 3 directly compares the asphericity and acylindricity parameters with the shear viscosity reported elsewhere [24] 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.

Molecules with different topologies, sizes, and flexibilities 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. However, at shear rates larger then the reciprocal of the maximal relaxation time ($\dot{\gamma}_0 = 1/\tau_0$), apart from being aligned, molecules also become stretched and deformed.

The relaxation times of dendrimers and linear polymers are displayed in figure 4. It is apparent from figure 4 that linear systems and dendrimers have distinctly different relaxation times. This can be directly related to the different shape adopted by the two types of molecules in response to shear. Dendrimers have a much higher degree of spherical symmetry compared with linear polymers of equivalent molecular mass. The application of shear reduces the symmetry but they retain a considerable degree of spherical character compared with linear systems. This is apparent in the variation of the *b* parameter shown in figure 3, which indicates that linear polymers will reach the asymmetric limit at much lower strain rates than dendrimers of equivalent mass. Similarly, at equilibrium, dendrimers have much less cylindrical character than linear polymers. The application of shear (figure 3) induces a more cylindrical shape in both linear polymers and dendrimers. However, the effect is much more pronounced in linear systems, particularly after the onset of shear thinning.

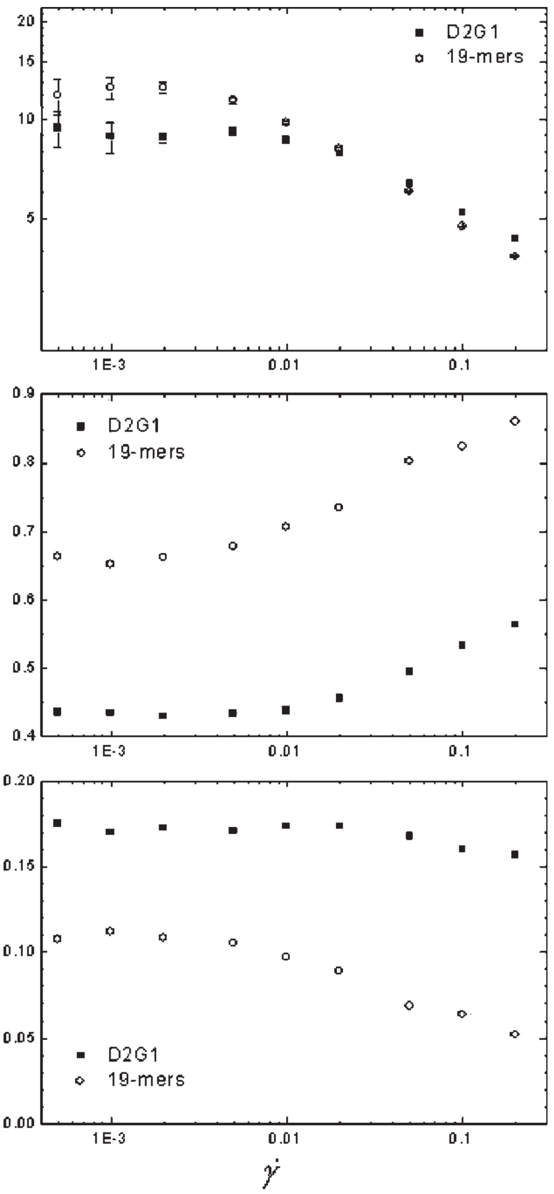

Figure 3. Strain rate dependence of shear viscosity, acylindricity and asphericity for a 19-mer polymer (o) a dendrimer of generation 1 (D2G1) (squares). It is apparent that the onset of shear thining coincides with changes in molecular shape [27].

It should be noted that the traditional method for determining the onset of shear thinning and relaxation time is to examine the flow curves, i.e. the variation of viscosity with respect to strain rate. In some cases, uncertainties in the calculation of viscosities means that it is difficult to accurately determine this point. In such cases, determining the shape parameters could provide an alternative way of locating the onset of non-Newtonian behaviour independently of viscosity data.

4. Conclusions

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 linear polymers of

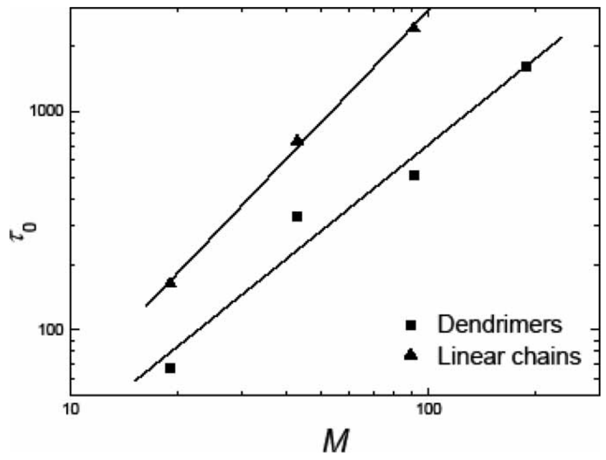

Figure 4. Relaxation times of dendrimers and linear polymers as a function of molecular mass. The values were obtained from the strain rate corresponding to the onset of shear thinning [27].

equivalent size exhibit different shape behaviour. 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. The results highlight the value of coarse-grain models in providing general insights for a class of molecules.

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