

# Molecular Simulation of Dendritic Systems

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## ABSTRACT

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 non-equilibrium 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.<sup>1,2</sup> Potentially, dendrimers have beneficial applications to many areas. Possible areas of application are nanoscale catalysis,<sup>3</sup> mimics for micelles,<sup>4,6</sup> 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<sup>7</sup> also has potential implications for the fabrication of nanostructures.<sup>8</sup>

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.

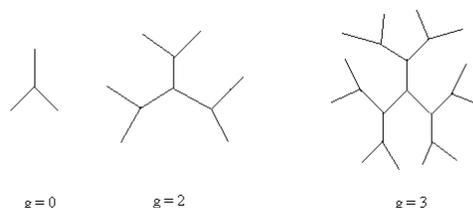


Figure 1. Schematic illustration of dendrimer connectivity with different generation number.

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 Hervet<sup>9</sup> 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<sup>10</sup> 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.

Molecular simulation studies have been reported<sup>10,13-17</sup> to determine the structure of isolated homogeneous dendritic polymers. Off-lattice simulations have been performed<sup>10</sup> 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.<sup>13</sup> applied atomic-scale molecular dynamics simulations of dendrimers with up to seven generations. 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.<sup>9</sup> Wiener et al.<sup>23</sup> used molecular dynamics to study chelate complexes attached to dendrimers.

We<sup>24-27</sup> 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 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

As discussed in detail elsewhere,<sup>24-27</sup> dendrimers were modeled using tri-functional cores ( $f_c = 3$ ) and 2 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<sup>22</sup> and the chemical bonds between the beads will be modeled using a finitely extensible nonlinear elastic (FENE) potential.<sup>22</sup> 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)<sup>28</sup> with standard Lees-Edwards periodic boundary conditions.<sup>22</sup> The equations of motion of all beads were integrated using a fifth-order Gear predictor corrector differential equation solver<sup>22</sup> 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  $\rho$  are the reduced temperature and density, respectively) corresponds to a melt. After achieving steady state (typically several million time-steps), the bead trajectories were accumulated and ensemble averages were calculated.

Solc and Stockmayer<sup>29</sup> 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 centre of mass,  $n$  is the number of beads in molecule,  $m_{\alpha}$  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:

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

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.<sup>24-27</sup>

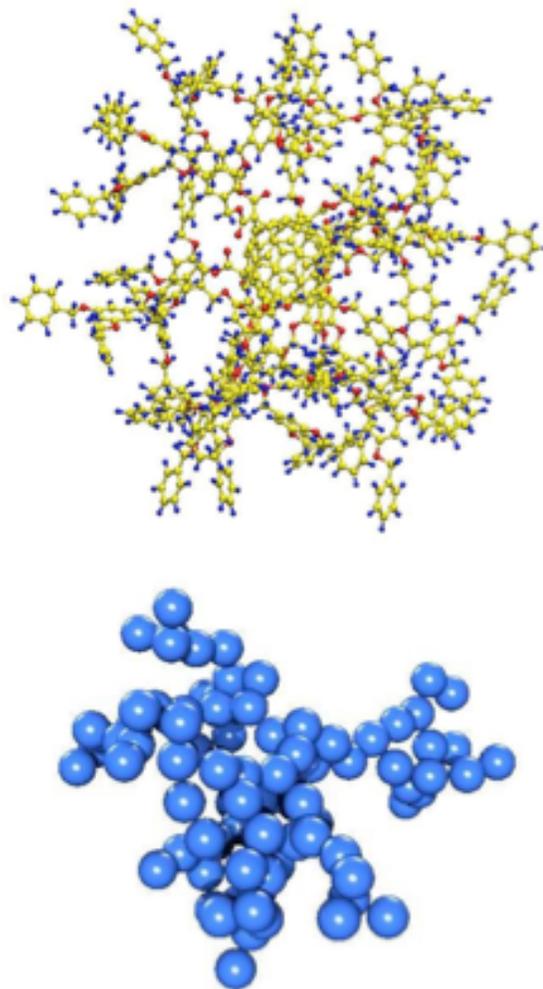


Figure 2. Comparison of a fully atomistic model of a fullerene dendrimer of generation 3 containing 1278 atoms with a coarse-grained generation 3 ( $b = 2$ ) bead-spring model composed of 91 beads.

Asymmetry of dendrimers can be quantitatively described with the ratios of the eigenvalues ( $L_1, L_2$  and  $L_3$ ) of the tensor of gyration.<sup>29</sup>

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

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

Additional parameters that can be used to describe symmetry of dendrimers are asphericity, acylindricity and relative shape anisotropy. The asphericity is defined by:<sup>29</sup>

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

acylindricity by:

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

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.

### 3 RESULTS AND DISCUSSION

Results of simulation studies<sup>24-26</sup> consistently show the onset of a transition from 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<sup>24</sup> 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  $\tau_0$ . 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.

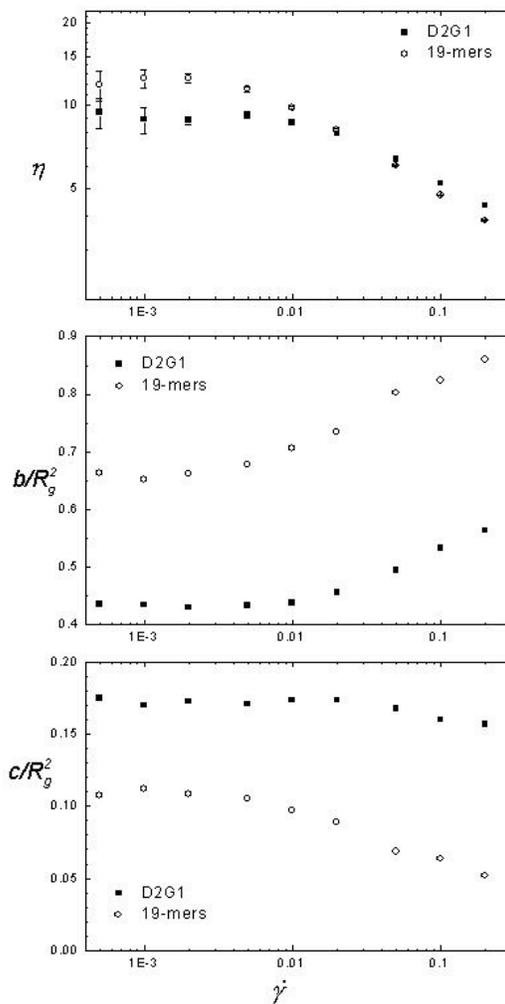


Figure 3. Strain rate dependence of shear viscosity, acylindricity and asphericity for a 19-mer polymer (o) a dendrimer of generation 1 (D2G1) (squares). It is apparent that the onset of shear thinning coincides with changes in molecular shape.<sup>27</sup>

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.<sup>24</sup> For dendrimers of generation 1 to 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 Figure 4.

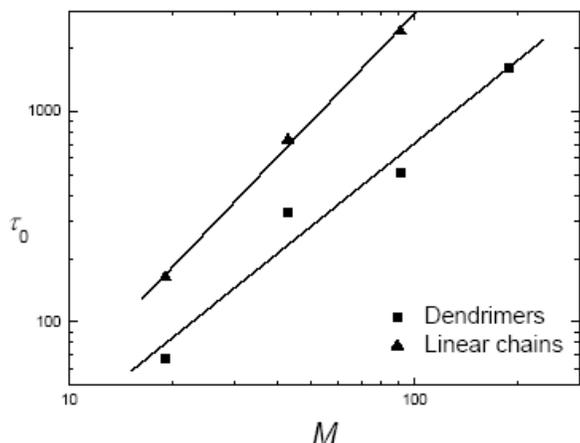


Figure 4. Relaxation times of dendrimers and linear polymers as a function of molecular mass. The values were obtained from the strain rate corresponding to the onset of shear thinning.<sup>27</sup>

#### 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 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.

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