

Chapter 7. Conclusions and recommendations

Results of an extensive molecular dynamics study of concentrated dendrimer fluids have been presented in this thesis. A coarse-grained bead-spring model, previously used to simulate linear chain molecules, has been successfully adopted to represent molecules with dendritic architectures. A suite of programs has been written to generate and simulate the behaviour of dendrimer and other polymeric melts, blends and solutions. A molecular version of the homogenous isothermal shearing algorithm (SLLOD) was implemented at both constant volume and constant pressure and used to study the properties of the fluids undergoing planar Couette flow. Dendrimers of generations up to four were studied in a wide range of strain rates, and their properties were compared with melts composed of linear chain molecules of comparable molecular weights. In this way, the direct influence of the molecular architecture on the viscoelastic behaviour was analysed. Moreover, the response of the molecules composing the fluid to the imposed streaming velocity profile was extensively studied to determine correlations between macroscopic and underlying microscopic phenomena occurring within the systems. To the best of author's knowledge, this is the first nonequilibrium molecular dynamics study of dendrimer melts under shear.

The viscoelastic properties of dendrimer melts were derived from NEMD simulations and compared with properties of linear polymer melts of the same molecular weight. It was found that the highly branched, congested structure of dendrimers is responsible for flow properties that differ significantly from those of linear chain molecules. For example, the zero shear viscosity of dendrimers exhibits a power law scaling with the 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, i.e. the Rouse and the reptation regions. The architecture of dendrimers and their short branch lengths result in a suppression of intermolecular entanglement. Therefore, it prohibits reptation dynamics that dominates behaviour of long linear chains. The shear viscosity of dendrimers and linear chains as a function of strain rate displays a universal characteristic: all systems undergo a transition from the Newtonian regime, where viscosity does not depend on the strain rate, to the non-Newtonian region, where viscosity strongly depends on the strain rate. However, the following

trends can be identified when comparing systems at the same thermodynamics steady state but with different molecular topologies:

- for low strain rates the viscosity of dendrimers of a particular molecular weight is always lower than the viscosity of linear chains of equivalent weight;
- the onset of shear thinning (decrease of viscosity with the shear rate) is always shifted towards larger strain rates for dendrimers in comparison to the linear chains;
- in the shear thinning region, the rate at which the viscosity decreases is larger for linear chains than for dendrimers, and in consequence there is a cross-over point where the viscosity for linear chains becomes lower than that of equivalent mass dendrimers.

These observations may suggest the conclusion that the addition of dendrimers to traditional polymeric melts could be used to lower the viscosity of the melts at low strain rates, to delay the onset of shear thinning with increasing strain rate, as well as to decrease the shear thinning effect.

To fully understand how dendrimers would perform as rheology modifiers, a thorough study of the behaviour of polymeric blends containing dendrimers in a wide range of compositions would be required. However, preliminary results of simulations of blends of linear chains and dendrimers (of the same molecular weight) were presented in this thesis (see Section 5.8). As expected, with the ratio of dendrimers to linear chain molecules, the monotonic change in the material functions was observed from those of pure dendrimer melts to those of pure linear chain systems. Further studies are recommended, especially of systems composed of molecules of different sizes (e.g. blends of large dendrimers with short linear chains). Moreover, an extensive study of changes at the microscopic level due to mixing molecules of different architectures would be necessary. This should include the extent to which the addition of dendrimers affects interactions and entanglement of chains in polymeric melt, as these are the effects that dominate the macroscopic flow properties of the fluids.

Results of the simulations performed in this work were used to analyse flow-induced changes in the molecular conformation and in the dynamics of dendrimers and linear chain polymers constituting melts. It was shown that the onset of the shear thinning in fluids is correlated with the deformation of the molecules from the average equilibrium

conformation. In the Newtonian regime the rate of deformation (shearing) is small in comparison to the largest molecular relaxation time, and it enables dendrimers to relax and to assume the optimal equilibrium conformation. As a consequence, the average shape of molecules is the same as in equilibrium, despite flow induced alignment. The latter one is related to and contributes to the macroscopic anisotropy of the fluid. In contrast, at higher strain rates, the molecules are additionally stretched. In experimental characterisations of macromolecular fluids, the separation of effects of molecular alignment and deformation are impossible, and the shape analysis always provides spherically averaged details of the molecular shape. Molecular simulations instead enable the analysis of these effects separately. A detailed analysis of the molecular shape of dendrimers and linear chains in equilibrium and under shear was presented in this thesis. It was shown that, unlike linear chains whose shape in equilibrium does not strongly depend on the length, for dendrimers the asymmetry and the anisotropy change with generations.

The internal structure of dendrimers has been extensively analysed in terms of scaling properties and the distribution of mass and terminal groups. In agreement with other theoretical and computational studies, it was found that in concentrated solutions and melts dendrimers assume compact globular conformations. The fractal dimensionality of dendrimers at equilibrium is close to the dimensionality of the space (3D), which indicates a uniform distribution of mass within the volume of the molecule. The fractal dimensionality decreases with increasing shear rate as the molecules undergo flow-induced deformation and stretching. It was also found that terminal groups are not constrained to the surface of the dendrimer, but are also distributed throughout the interior of the molecule. These two features, i.e. compact structure and folded back branches, are responsible for the suppression of the entanglement between dendrimers, an effect which dominates the viscoelastic properties of long linear chain polymers. It was shown that the interpenetration between molecules does not depend on the molecular weight for linear chains, whereas for dendrimers the rate at which the interior of a molecule is penetrated by parts of other molecules decreases with the increasing congestion of branches with the generation number.

The interactions between dendrimers as well as molecular conformations in solution are different from those in the melt. They strongly depend on the type of solvent used and

the type of interactions between solvent and solute or molecules of solvent. Preliminary results obtained from NEMD simulations of dendrimer solutions were presented in this thesis (Section 5.8). As the size of solvent molecules is much smaller in comparison to the dendrons composing the dendrimer, they can easily penetrate the structure they built leading to the so-called *swelling* of dendrimers. Moreover, the flow properties change with the concentration of dendrimers. It would be worthwhile to thoroughly examine the viscoelastic properties of dendrimer in various solvents. This could provide valuable insight into the effect of the dendrimer-solvent interactions on the molecular conformation and dynamics.

A flow-induced anisotropy of dendrimer and linear chain systems under shear was analysed, and the results were presented in this thesis. The molecular alignment was described in terms of the alignment rate and angle. It was shown that dendrimers, due to their highly branched structure, align at smaller rates than linear chains. The alignment angle is also always larger for dendrimers than for linear polymers.

The response of molecules to the imposed external velocity field was also quantitatively described using angular velocity. As expected, the spheroidal, compact dendrimers spin much easier than entangled chain polymers. The spin velocity of dendrimers was found to be independent of the molecular weight and to be in agreement with the prediction of the linear response theory in a wide range of shear rates. This feature of dendrimers makes them good candidates as rheology modifiers.

The simulations of dendrimers presented in this thesis were performed using a generic coarse-grained model of a flexible dendrimer. The focus of this work was mainly on the effects associated with molecular topology and configuration. In order to obtain quantitative agreement with the properties of real dendrimer molecules observed experimentally, the model would require further modification and fine-tuning. To achieve this, the flexibility and stiffness of dendrimer branches, sizes of monomeric units composing the molecule, etc. would need to be incorporated. A technique of mapping results obtained from the coarse-grained simulations on the real units would also need to be developed.