

Chapter 1. Introduction

Dendrimers are a special class of synthetic highly branched polymers with unique tree-like architecture (Tomalia *et al.* 1990). Due to their topology, the properties of dendrimers significantly differ from those of polymers with more traditional topologies. Their capability to encapsulate or attach to the surface of other molecules makes them potential vehicles for the delivery of drugs, whereas their self-assembly properties make them promising nano-scale building blocks. Through control of their structure and composition their properties can be fine tuned to suit a particular application.

Many studies, both experimental (Hawker *et al.* 1995; Stechemesser and Eimer 1997; Farrington *et al.* 1998; Scherrenberg *et al.* 1998; Uppuluri *et al.* 1998; Bodnár *et al.* 2000; Uppuluri *et al.* 2000; Prosa *et al.* 2001; Mallamace *et al.* 2002) and theoretical (de Gennes and Hervet 1983; Boris and Rubinstein 1996; Cai and Chen 1997; La Ferla 1997; Lue and Prausnitz 1997; Chen and Cai 1999; Ganazzoli *et al.* 2001; Mansfield and Jeong 2002), were devoted to understanding properties of single dendrimers or their diluted solutions. However, the topology of these molecules also affects the way they interact with each other when coming into contact in concentrated solutions or melts. For example, flow properties of dendrimers were found to be significantly different from the behaviour of traditional polymeric systems, typically composed of linear chain molecules. This creates new opportunities for the application of dendrimers as nano-scale lubricants or rheology modifiers. Full exploitation of them, however, requires an understanding of correlations between the macroscopic behaviour of dendrimer melts or solutions and underlying phenomena occurring at the micro-scale. The latter ones are related to the internal molecular structure and intramolecular interactions.

A valuable theoretical approach to study material properties at the atomistic level is through molecular simulations (Allen and Tildesley 1987; Evans and Morriss 1990; Sadus 1999). Dendrimers and other polymeric systems have been extensively studied with the aid of Monte Carlo (MC), molecular dynamics (MD) or other simulation techniques. However, most of these attempts address properties of isolated molecules or molecules in solution in thermodynamic equilibrium. Only a few computational studies apply to properties of dendrimers away from equilibrium (Lyulin *et al.* 2000; Lyulin *et*

al. 2001; Sheridan *et al.* 2002), and none of them studied the behaviour of dendrimers in the melt.

The aim of this work is to investigate viscoelastic properties of dendrimers in the melt undergoing planar shear and in particular to determine the influence of the molecular topology on the micro- and macroscopic properties of the systems. To achieve this goal, the flow of dendrimer melts is studied with the aid of nonequilibrium molecular dynamics (NEMD) techniques. The response of dendrimers to shear is compared to the behaviour of melts composed of traditional linear chain polymers. As the main interest is in the influence of the internal molecular structure on the properties of the melt, a generic coarse-grained model is used to represent dendrimers and linear chain polymers. Molecular simulations provide information on dynamics of the studied systems at both the atomic/molecular and, through application of the laws of statistical physics, macroscopic level. Therefore, the results of simulations can be used to derive material functions characterising the flow behaviour of studied systems. These include shear viscosity and normal stress differences and the way they depend on the shear rate, molecular size, or architecture. On the other hand, the conformations and dynamics of molecules composing melts are analysed to determine flow-induced changes in the molecular shape, mass distribution, alignment and motion, as well as intermolecular interactions like entanglement, interpenetration, and spatial arrangement.

The structure of dendrimers, the history that lead to development of synthesis techniques, as well as some of the properties of dendrimers are described in Chapter 2. A review of the theoretical studies of dendrimers is also included in this chapter. Chapter 3 is devoted to the viscoelastic properties of macromolecular fluids. After giving a general introduction to the field of rheology, the behaviour of dendrimers under shear is described. Details of a coarse-grained model used in this study to represent dendrimers and linear chain polymers are presented in Chapter 4. These are followed by description of the nonequilibrium molecular dynamics techniques used to simulate melts under shear. Results of the simulations and their discussion are given in Chapter 5 and Chapter 6. The former describes macroscopic flow properties of the melts, whereas the latter one is devoted to the microscopic analysis of the molecular structure and dynamics. Some conclusions and recommendations for further work will be given in Chapter 7.