Molecular Dynamics Simulation of Planar Extensional and Shear Rheology of Dendritic and Blended Dendrimer-Linear Polymer Melts

by

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Abstract

In this work, the planar extensional rheology of dendrimers and hyperbranched polymers and shear and planar extensional rheology of dendrimer-linear polymer blends are investigated with the aid of nonequilibrium molecular dynamics simulation techniques. Molecules are modelled taking a coarse-grained approach using a bead-spring model. The first objective of this thesis is to analyse the influence of the molecular architecture of dendritic polymers on their planar extensional melt rheology. The second objective is to investigate the miscibility of blends of highly branched dendrimer molecules and linear chain polymers, and to elucidate dendrimer induced conformational changes of linear chains in the blend, and their subsequent effects on the shear and planar extensional rheology of the blends. The strain-rate dependence of the extensional viscosity of linear and hyperbranched polymers shows three distinctive regions, including an initial Newtonian region at low strain-rates, followed by thickening behaviour at medium strain-rates and terminated with a thinning region at very high strain-rates. For dendrimers the viscosity upturn decreases with the generation and completely vanishes for dendrimers of higher generations due to their highly constrained molecular geometry. A thorough structural analysis is performed to correlate the flow-induced structural changes of molecules with their unique rheological behaviour. Analysis of the internal structure of dendrimers and hyperbranched polymers reveals that a typical back-folding phenomenon occurs under planar extensional flow. Moreover, dendrimers show much lower melt viscosities compared to their linear counterparts. Therefore, they can be used as rheology modifier agents. Blend systems of dendrimer molecules of generations 1-4 and linear
chains with 187 beads per chain are modelled. Various radial distribution functions are used to analyse the miscibility of blend systems. All of the blend systems studied form miscible blends. The blend shear and planar extensional viscosities are found to decrease, correlating with the amount and generation of dendrimers in the blend. The viscosity reduction is attributed to the replacement of high molecular weight linear chains with dendrimers of inherently lower melt viscosity and also dendrimer-induced free volume in the system. The globular shape of dendrimers results in a particle-like behaviour of dendrimer molecules when blended with linear polymers. This situation resembles mixtures of polymers and nanoparticles in that nanoparticles cause a reduction in nanocomposite viscosity. Effects of shape, size, molecular mass and mass fraction of dendrimers on inter-penetration between blend species are also studied. Both shear and planar extensional flow enhance the inter-penetration due to dendrimers being stretched and opened up under the flow.
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It would not have been possible to write this doctoral thesis without the help and support of the people around me, to only some of whom it is possible to give particular mention here.

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ending support and encouragement that always believed in me and wanted me to be the best at what I am doing.
Declaration

I hereby declare that this thesis entitled “Molecular Dynamics Simulation of Planar Extensional and Shear Rheology of Dendritic and Blended Dendrimer-Linear Polymer Melts”, is submitted in fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Science, Engineering, and Technology of Swinburne University of Technology, and is my own work. It contains no material which has been accepted for the award of any other candidate for any other degree or diploma, except where due reference is made in the text of the thesis. To best of my knowledge and belief, it contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Elnaz Hajizadeh Darzehkonani
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Journal Publications From This Thesis

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Nonequilibrium molecular dynamics simulation of dendrimers and hyperbranched

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Thesis Outline

In Chapter 1 a short introduction to dendrimer and hyperbranched polymers and their significant differences from their conventional linear polymer counterparts is given. In this chapter, potential applications for dendritic polymers arising from their unique properties also are surveyed. In addition, properties of dendritic-linear polymer blends are discussed at the end of this chapter.

The second chapter gives a brief presentation of polymer physics relevant to this thesis. It covers fundamental theories describing the rheological behaviour of polymer melts. In addition, the rheological and structural properties calculated in this thesis, such as the shear viscosity, the extensional, first and second extensional viscosities, first and second normal stress coefficients and different radial distribution functions are defined.

The molecular dynamics and non-equilibrium molecular dynamics techniques used to simulate the polymeric materials are described in Chapter 3.

Chapter 4 concerns the issue of how the polymer architecture, molecular weight, and flow type influence the rheological behaviour and structural properties of dendrimers and hyperbranched polymers.

Rheological and structural properties and the miscibility of dendrimer-linear polymer blends under shear and planar extensional flow are discussed in Chapters 5 and 6, respectively. The main objective of Chapters 5 and 6 is to determine how the globular and restricted architecture of the small amount of dendrimers added to a
melt of linear polymers can affect the melt rheological behaviour of the blend under different flow conditions. These chapters present a detailed investigation of the miscibility, structural changes and radial distribution functions $g(r)$, which are built on the knowledge gained in Chapter 4.

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## Acronyms

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<th>Abbreviation</th>
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<tbody>
<tr>
<td>DB</td>
<td>Degree of Branching</td>
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<tr>
<td>NMR</td>
<td>Neutron Magnetic Resonance</td>
</tr>
<tr>
<td>SANS</td>
<td>Small Angle Neutron Scattering</td>
</tr>
<tr>
<td>SCF</td>
<td>Self Consistent Field Theory</td>
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<tr>
<td>NEMD</td>
<td>Nonequilibrium Molecular Dynamics</td>
</tr>
<tr>
<td>LLDPE</td>
<td>Linear Low Density Poly(ethylene)</td>
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<tr>
<td>RDF</td>
<td>Radial Distribution Function</td>
</tr>
<tr>
<td>PS</td>
<td>Poly(styrene)</td>
</tr>
<tr>
<td>PE</td>
<td>Poly(ethylene)</td>
</tr>
<tr>
<td>LCT</td>
<td>Lattice Cluster Theory</td>
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<tr>
<td>CCR</td>
<td>Convective Constraint Release</td>
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<tr>
<td>BPW</td>
<td>Branch-Point Withdrawal</td>
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<tr>
<td>SORF</td>
<td>Stretch Orientation Friction Reduction</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
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<tr>
<td>BC</td>
<td>Boundary Conditions</td>
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<tr>
<td>LJ</td>
<td>Lennard-Jones Potential</td>
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<tr>
<td>PBC</td>
<td>Periodic Boundary Conditions</td>
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<tr>
<td>KR</td>
<td>Kraynik-Reinelt</td>
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<tr>
<td>MIC</td>
<td>Minimum Image Convention</td>
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<tr>
<td>WCA</td>
<td>Weeks-Chandler-Anderson</td>
</tr>
<tr>
<td>FENE</td>
<td>Finitely Extensible Nonlinear Elastic</td>
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<tr>
<td>PEF</td>
<td>Planar Elongational Flow</td>
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Notation

Frequently Used Symbols In Order Of Appearance

\( g(r) \)  Radial distribution function
\( g \)  Generation number of dendritic polymer
\( M \)  Molecular mass
\( [\eta] \)  Intrinsic viscosity
\( N \)  Number of beads
\( \nu_x \)  \( x \)-component of the velocity field
\( \nu_y \)  \( y \)-component of the velocity field
\( \nu_z \)  \( z \)-component of the velocity field
\( \eta_0 \)  Zero-shear viscosity
\( \dot{\gamma}(t) \)  Time-dependent shear-rate of the fluid
\( \dot{\epsilon} \)  Extension rate of the fluid
\( \nabla \mathbf{v} \)  Velocity gradient
\( p \)  Isotropic pressure and instantaneous pressure
\( \mathbf{P} \)  Total pressure tensor
\( \delta \)  Identity matrix
\( \pi \)  Extra pressure tensor
\( \sigma \)  Stress tensor
\( P_{ij} \)  Components of the total pressure tensor
\( \pi_{ij} \)  Components of the extra pressure tensor
\( N_1 \)  First normal stress difference
\( N_2 \)  Second normal stress difference
\( \Psi_1 \)  First normal stress coefficient
\( \Psi_2 \)  Second normal stress coefficient
\( \eta_1 \)  First extensional viscosity
\( \eta_2 \)  Second extensional viscosity
\( \eta \)  Shear viscosity
\( \tau_d \)  Reptation (tube disentanglement) time
\( \tau_R \)  Rouse time
\( \Psi_{1,0} \)  Zero-shear rate first normal stress coefficient
\( \Psi_{2,0} \)  Zero-shear rate second normal stress coefficient
\( D \)  Rate of deformation tensor
\( \omega \)  Vorticity tensor
\( \lambda \)  Relaxation time
\( M_c \)  Critical molecular weight
\( M_e \)  Entanglement molecular weight
\( M_x \)  Linear chain unit molecular weight
\( N_e \)  Entanglement length
\( \zeta \)  Monomeric friction coefficient
\( \zeta_R \)  Rouse chain friction coefficient
\( D_R \)  Rouse chain diffusion coefficient
\( \delta \)  Sarkar-Gupta model parameter
\( \lambda_1 \)  First time constant of Sarkar-Gupta model
\( \lambda_2 \)  Second time constant of Sarkar-Gupta model
\( m \)  Sarkar-Gupta model parameter
\( I_2 \)  Second scalar invariant of the strain rate tensor
\( R_g \)  Gyration tensor
\( R_g \)  Radius of gyration
\( r_\alpha \)  Position of monomer \( \alpha \)
\( r_{CM} \)  Position of molecular centre of mass
\( m_\alpha \)  Mass of bead \( \alpha \)
\( L_1 \)  Eigenvalue of the gyration tensor
\( L_2 \)  Eigenvalue of the gyration tensor
\( L_3 \)  Eigenvalue of the gyration tensor
\( L_{12} \)  Ratio of eigenvalues of the gyration tensor
\( L_{13} \)  Ratio of eigenvalues of the gyration tensor
\( L_{23} \)  Ratio of eigenvalues of the gyration tensor
\( g_{\text{core}}(r) \)  Distribution of beads from the core
\( g_{\text{end}}(r) \)  Distribution of end groups from the core
\( g_{DL}(r) \)  Total DL pair distribution function
\( g_{LL}(r) \)  Total LL pair distribution function
\( g_{DD}(r) \)  Total DD pair distribution function
\( g_{c,DL}(r) \)  DL pair distribution function
\( r_{i1} \)  Position of the core
\( r_{i\alpha} \)  Position of the monomer \( \alpha \) on molecule \( i \)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$r$</td>
<td>Separation distance</td>
</tr>
<tr>
<td>$N_D$</td>
<td>Number of dendrimer molecules</td>
</tr>
<tr>
<td>$N_L$</td>
<td>Number of linear molecules</td>
</tr>
<tr>
<td>$N_{s,D}$</td>
<td>Number of beads per dendrimer molecule</td>
</tr>
<tr>
<td>$N_{s,L}$</td>
<td>Number of beads per linear molecule</td>
</tr>
<tr>
<td>$f$</td>
<td>Functionality of end groups</td>
</tr>
<tr>
<td>$b$</td>
<td>Number of spacer</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Van der Waals radius</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Lennard-Jones potential energy</td>
</tr>
<tr>
<td>$r_{ij}$</td>
<td>Distance between the monomers $i$ and $j$</td>
</tr>
<tr>
<td>$R_0$</td>
<td>Finite extensibility</td>
</tr>
<tr>
<td>$k$</td>
<td>Spring constant</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density of the fluid</td>
</tr>
<tr>
<td>$r_i$</td>
<td>Laboratory position of atom $i$</td>
</tr>
<tr>
<td>$p_i$</td>
<td>Peculiar momentum of atom $i$</td>
</tr>
<tr>
<td>$F_i^\phi$</td>
<td>Inter-atomic force on atom $i$</td>
</tr>
<tr>
<td>$L_k$</td>
<td>Box lattice vectors</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume of the system</td>
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<tr>
<td>$t$</td>
<td>Time</td>
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<tr>
<td>$\alpha$</td>
<td>Thermostat multiplier</td>
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<tr>
<td>$\dot{\zeta}$</td>
<td>Dilation rate</td>
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<tr>
<td>$Q_p$</td>
<td>Damping factor</td>
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<tr>
<td>$p_0$</td>
<td>Target pressure</td>
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<tr>
<td>$D$</td>
<td>Dendrimer polymer</td>
</tr>
<tr>
<td>$H$</td>
<td>Hyperbranched polymer</td>
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<tr>
<td>$L$</td>
<td>Linear polymer</td>
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<tr>
<td>$\Delta t$</td>
<td>Time step</td>
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<tr>
<td>$r_c$</td>
<td>Cutoff distance</td>
</tr>
<tr>
<td>$\bar{\eta}$</td>
<td>Extensional viscosity</td>
</tr>
<tr>
<td>$\eta_u$</td>
<td>Uniaxial extensional viscosity</td>
</tr>
<tr>
<td>$\tau_p$</td>
<td>Relaxation time obtained from reciprocal of the strain-rate</td>
</tr>
<tr>
<td>$\tau_m$</td>
<td>Relaxation time obtained from the Sarkar-Gupta model</td>
</tr>
<tr>
<td>$\tau_\nu$</td>
<td>Relaxation time obtained from zero-shear rate data</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
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Chapter 1

Dendrimers, Hyperbranched Polymers and Dendrimer-Linear Polymer Blends

1.1 Dendrimers and Hyperbranched Polymers

Polymers can be categorized into four classes based on their molecular architecture, comprising linear, branched, cross-linked, and dendritic polymers. Dendritic polymers, consisting of four subclasses, (1) dendrimers, (2) dendrons, (3) dendrigrafts, and (4) random hyperbranched polymers, are identified as the fourth main category of polymeric architecture [1]. Dendritic macromolecules are tree-like structures consisting of several branched layers. They may be produced as monodispersed assemblies of perfect and precisely defined architecture (known as dendrimers) or as imperfect structures (known as random hyperbranched polymers). Dendrimers and hyperbranched polymers are distinguishable based on the symmetry of their branching pattern [2]. Although the theoretical rationale to generate highly branched polymers was conceptualized by Flory in 1952 [3], the synthesis of hyperbranched polymers was not reported until the late 1970’s. Buhleier et al. [4] devised a syn-
Dendritic polymers (Fig. 1.1) are unique tree-like structures and unlike linear chain polymers, have three structural elements in their architecture: namely, (1) a core (central atom(s)), (2) generations \( (g) \) (concentric shells around the core), and (3) end functional groups. The characteristic feature of the core is its functionality which dictates the number of chemical bonds via which it can generate the first shell of the molecule. This generates a molecule of star type, or dendrimer of generation zero. Since each arm has a multifunctional unit at its end, by adding shells of linear units to the end groups of the lower shell, higher generations are generated.

The molecular shape of dendrimers strongly depends on their generation number due to the congestion of branches at the molecular surface upon increasing the generation number. They change from flat and loose conformations to globular and restricted conformations as the generation number increases [7]. The shape crossover was successively proven by different measurements [8, 9]. It is now fully understood
that core multiplicity plays an interesting role in producing such a congestion, which will result in the shape crossover occurring at lower molecular weight (generation).

1.1.1 Properties

Dendrimers and hyperbranched polymers are similar to linear chain polymers in terms of their chemical composition. Hence, the unique properties of dendritic polymers arise from their tree-like topology. Several research groups have studied molecular shape, mass distribution within the molecule, and location of terminal groups of dendrimers and hyperbranched polymers [10–14]. We will review the observations of some of these experimental studies here, but predictions based on theoretical studies and simulations of dendritic polymers will be discussed later in Section 1.1.2.

Dendrimers are synthesized by stepwise methods, which results in perfectly branched globular polymers, while hyperbranched polymers are prepared by a random polycondensation reaction, which results in highly, but imperfectly branched polymers. The structural perfection of hyperbranched polymers is calculated by the degree of branching (DB) criterion which, by definition, is 0 for a linear polymer and 1 for a perfect dendrimer. Subsequently, the DB of hyperbranched polymers falls between 0 and 1. In early works, DB was calculated as a function of the population of dendritic, terminal and linear units in the molecules, obtained from integration of the relevant signals in NMR–spectra [15, 16]. Later, Höltner and Frey [17] modified DB calculations, considering the ratio of perfectly and imperfectly branched units in hyperbranched polymers for $AB_2$, $AB_3$ and $AB_m$ based systems (where $m$ is the number of active groups in monomer type $AB_m$). Based on kinetic considerations of enhanced reactivity of linear compared to terminal groups, the modified formula for $DB$ is given as

$$DB = \frac{2D}{2D + L},$$

where $D$, and $L$ are the fractions of dendritic and linear monomers in the hyperbranched polymers.
Hölter and Frey [17] showed that the maximum DB value reachable from the dilute/slow addition method is 0.67 for $AB_2$ monomers. Therefore, this method leads to a significantly larger DB compared to that obtained from a single-step polymerization, which is 0.5 [17].

The molecular shape of dendrimers and hyperbranched polymers is one of their most interesting characteristics. X-ray and small angle neutron scattering (SANS) experiments reveal that dendrimers possess spherical conformations, contrary to hyperbranched polymers that show globular structures [18, 19]. In addition, Tomalia et al. [20] showed that the molecular shape of a dendrimer depends on its molecular weight, such that it changes from extended structure for low molecular weight into a spherical shape at higher molecular weight. The radius of gyration can be used to characterize the size of the dendrimers and hyperbranched molecules. The dependence of the molecular size on the molecular mass $M$ can be complex, but for lower generations it can be described by

$$R_g \propto M^\nu.$$  \hspace{1cm} (1.2)

In preliminary investigations by Aharoni and Murthy [21], they reported that the exponent in Eq. (1.2) is roughly equal to 1/3, revealing a uniform distribution of mass within the dendrimer molecule. More detailed studies on the size dependence on mass for a number of dendrimer systems were performed by Prosa et al. [18]. It was observed that dendrimers of lower generations are less dense than those of higher generations. However, after the few first generations, the average density becomes independent of the generation number.

The chain conformation and particularly the location of end functional groups is a key factor in determining the potential applications of dendrimers and hyperbranched polymers. The properties of dendrimers and hyperbranched polymers (such as reactivity, intermolecular interactions, and conformation) are different when the end groups are distributed through the whole interior of the molecule, instead of being localised only on or close to the surface. There has been disagreement in both experimental and theoretical investigations of dendritic polymers on this
matter. Topp et al. [22] performed SANS experiments on polyamidoamines (PA-MAM) dendrimers of generation 7 to determine the distribution of terminal groups. They observed that the end groups were primarily localised near the outer shell. However, a computational investigation by Lescanec and Muthukumar [11] found inward back-folding of end groups resulting in a density maximum close to the center of the molecule. Scherrenberg et al. [19] predicted a strong back-folding of branches. Mansfield and Klushin [23] conducted Monte Carlo simulations and found that end groups are distributed through the whole interior of the molecule and may even be found close to the core. Chai et al. [24] performed NMR experiments and concluded that in good solvents conformations with extended outward facing branches are in majority, while in poor solvents conformations with folded branches are dominant. Later, back-folding was confirmed by several authors for dendrimers and hyperbranched polymers under shear [25, 26].

One of the most fascinating characteristics of dendritic polymers is their significantly different rheological properties compared to their linear counterparts, both in solution and in the melt [2, 26–28], which is due to their highly branched and constrained molecular architecture. Linear chains form flexible coils in solution, whereas dendritic polymers form tightly packed structures. This significantly alters their rheological behaviour. Dendrimer solutions have drastically lower viscosity compared to linear polymers of the same molecular weight [2, 29]. When the molecular weight of dendrimers increases, their intrinsic viscosity versus molecular weight passes through a maximum and then starts to decrease [11, 30]. For traditional linear polymers the intrinsic viscosity increases monotonically with molecular weight. That is, the intrinsic viscosity of dendritic polymers does not obey the well known Mark-Houwink-Sakurada equation, $\eta_p = K[M]^a$. This behavior is attributed to the crossover from an extended structure for lower molecular weights to globular shapes at higher molecular weights [2, 27, 31–33]. Furthermore, the melt viscosity of linear chain polymers increases linearly up to a critical molecular weight where the viscosity significantly increases due to the entanglement of polymer chains. However, this crossover of melt viscosity dependence on molecular weight is not reported for dendrimers or hyperbranched polymers, which shows that there are no entanglements
developing between branches of dendritic molecules [2, 27].

1.1.2 Theoretical Models

The earliest work on the theoretical investigation of the structure of dendrimers goes back to 1983, when de Gennes and Hervet [34] employed a mean field approach. They assumed that the branches of dendrimers always extend outwards while growing and also that the building units belonging to the same generation are located in concentric layers. These assumptions generated molecules possessing hollow flexible inner cores and densely-packed outermost layers. Accounting for excluded volume effects, they predicted the so-called dense-packed generation, for PAMAM dendrimers, at which perfect branching cannot occur any more [34]. This arises because accessible peripheral area becomes too restrained for the mathematically calculated number of surface cells to occupy, and generates a “closed geometric structure”. The surface is “crowded” with functional end groups, that although chemically active, are sterically restricted from engaging in ideal growth of dendrimer molecules. Steric congestion which is a consequence of the excluded volume associated with the core, interior, and surface branched layers, is expected to be a crucial effect [35].

Later, numerical self-consistent field (SCF) methods were formulated by several authors [14, 36, 37] and, as opposed to the findings of de Gennes [34], it was observed that the preferred configuration for dendrimers of higher generations is one with a dense core and terminal groups were found through the whole molecular interior. The Boris and Rubinstein model [36] was modified by Lyulin et al. [38] to incorporate solvent and electrostatic charge related effects on the structure. Another mean-field model was proposed by Muthukrishnan et al. [39] for hyperbranched polymers, in which the polymers were built as a bead-rod model. Later, Konkolewicz et al. [40] adapted a mean-field approach to account for the Flory-Huggins type interactions for both dendritic and any arbitrary disordered polymers.

Several theoretical models for dynamical behaviour of conventional linear polymers were adapted and applied to dendritic polymers. La Ferla et al. [37, 41] extended the Rouse-Zimm hydrodynamic model [42] to complement any arbitrary
molecular architecture and employed it in investigating dynamic properties of dendrimers in dilute solution. Cai and Chen [43] employed Rouse dynamics without hydrodynamic interactions and excluded volume effects to elaborate the dynamics of dendrimers. Both the Rouse and Zimm models were later modified to incorporate the local geometry features such as angles between adjacent units in the molecule (von Ferber and Blumen [44]).

A number of computational approaches have been proposed to elaborate dendrimer conformation. Lescanec and Muthukumar [11] performed atomistic simulation using a self-avoiding walk, kinetic-growth method and predicted a density maximum at the core of model dendrimers with radially distributed end groups at higher generations of dendrimer. Later, this idea was supported using atomistic (Gorman and Smith [45]) and coarse-grained molecular dynamics simulations (Murat and Grest [46]). Mansfield and co-workers developed a technique to study dendrimers by Monte Carlo simulations [23, 47, 48]. Other equilibrium molecular simulation studies have investigated the properties of isolated dendrimers [7, 49–51]. The current consensus on dendrimer structure in all of these studies predicts a dense core, highly back-folded branches, and functional end groups distributed throughout the dendrimer interior.

Although there is now qualitative agreement on the structural characteristics of dendrimers, there are notable quantitative disagreements between the proposed models. These disagreements depend strongly on the structural details of the studied dendrimers and the physical conditions they are exposed to. This can be further explored by looking at the quantitative difference between the reported scaling behaviour of the radius of gyration (dendrimer size) in terms of the number of monomers, by different studies of dendrimers. For instance, the radius of gyration has been reported to scale as $N^{0.22}$ [11], or $N^{0.3}$ [46, 52].

One of the earliest attempts in numerical analysis of hyperbranched polymers was performed by Aerts [53]. In this attempt, configurations of hyperbranched polymers were modelled employing the bead model of Lescanec and Muthukumar [11] and the intrinsic viscosities were computed. They reported that there is an upturn in
intrinsic viscosity plotted against molecular weight but the upturn occurs at higher intrinsic viscosity values compared to dendrimers. Additionally, the viscosity upturn for hyperbranched solutions was shifted to higher molecular weights and occurs at higher intrinsic viscosity values compared to dendrimers [53].

The majority of theoretical and computational investigations of dendrimeric polymers focus on the isolated molecules or molecules in dilute solution. The first atomistic simulations of dendrimers in the melt addressed the morphology of poly(propyleneimine) dendrimers [54]. An increase of back folding of branches with the number of generations was reported. The results of this study support the picture of dendrimers of high generations as compact space-filling molecules. It was observed that the radius of gyration depended on the number of beads per molecule as $N^{0.29}$ [54].

Hyperbranched polymer solutions undergoing shear flow were studied using Brownian dynamics techniques [55]. In this work, hydrodynamic and excluded volume interactions were explicitly taken into account. All the simulated hyperbranched polymer solutions showed a shear thinning behaviour. For hyperbranched polymers analogous to dendrimers, the zero shear-rate intrinsic viscosity showed an upturn and then started to decrease, as the molecular weight increased. Accordingly, it was reported that the peak was weakened (or disappeared) as DB decreased. This suggested that DB was an adequate criterion to be used to qualitatively distinguish different intrinsic viscosity patterns.

Konkolewicz et al. [40] and Watts et al. [56] applied reverse Monte Carlo methods to study randomly branched polymers possessing different molecular architectures and sizes. They reported that the radius of gyration increases logarithmically as polymer molecular weight increases.

The flow properties of dendrimers [25, 28], hyperbranched polymers [26], and linear polymer melts [57–59] have been studied previously using nonequilibrium molecular dynamics (NEMD) simulation techniques. Kröger et al. [57, 60] in their NEMD studies of the shear melt rheology of linear chains observed that the zero-shear-rate viscosity increases linearly up to chain length of 60 beads. They showed
that there is an upturn of the viscous properties for chain length of 100 beads, which is in agreement with the entanglement length reported earlier by Kremer and Grest [61]. Under shear, similar to the conventional linear chain polymers, dendrimers in the melt underwent a transition from the Newtonian regime to the non-Newtonian shear-thinning regime [28]. The onset of shear thinning for dendrimers occurred at higher strain rate, and the rate of shear thinning was smaller [25, 28] compared to the linear chain polymers of the same molecular weight. Bosko et al. [62] calculated the shear-rate dependent radius of gyration for dendrimers and showed that shear-induced stretching was particularly significant for large dendrimers. The onset of both shape deformation and shear thinning occurred at the same value of shear-rate, which depended on the generation of the dendrimer [62]. Therefore, they suggested that the flow-induced molecular deformation is mainly responsible for the observed shear thinning of the dendrimer melt.

There have only been a few studies on the elongational rheology of dendrimers and hyperbranched polymers due to the difficulties involved in the generation and stabilization of these types of flows. Neelov and Adolf [63] employed Brownian dynamics simulations of hyperbranched polymers up to the sixth generation undergoing elongational flow, in which they studied statistical and rheological properties of a bead-rod model of hyperbranched materials. They suggested that dendritic molecules orient at low strain-rates as a whole along the flow direction without any significant deformation and local orientation. It is only at high strain-rates that local orientation at the monomeric level occurs, leading to a significant global deformation of dendrimer and hyperbranched molecules [63]. Daivis et al. [58, 64] performed the first NEMD simulations coupled to the Kraynik-Reinelt periodic boundary condition [65] to study the planar elongational melt rheological behaviour of linear polymer melts. Compared to the shear behaviour of polymer melts, they reported the appearance of an extra thickening region in the extensional viscosity versus strain-rate plot, which is more evident for high molecular weight linear polymer chains [58]. Hunt and Todd [66, 67] conducted several NEMD simulations to study the self-diffusion tensor, velocity autocorrelation functions, and rheology of model unentangled linear chain polymers under both shear and planar extensional flows. They found that the
alignment of the molecules is a key property which affects their diffusive behaviour [66]. Planar extensional rheology of dendrimers and hyperbranched polymer melts is studied in this thesis for the first time and is the subject of Chapter 4.

1.1.3 Applications

Dendrimers have unusual architectural features which include nanoscopic size, ellipsoidal shape, controllable reactivity of the surface, and voids and cavities inside the molecule. As a consequence of this topology, dendrimers display unusual physical properties: soft interior with congested outer shell, large number of terminal groups which can be functionalised, self-assembling properties, etc.

Some researchers [68–70] introduced the idea of a dendrimer box. Dendrimers have the ability to encapsulate certain molecules for later separation and release into another environment. They could be used as vehicles for delivering genetic material or drugs into cells. Small guest molecules can penetrate the interior of dendrimers of small generations. However, the addition of another generation creates a dense shell that becomes impenetrable for the guest molecules that becomes encapsulated. Later, a controlled removal of the external shell could enable the release of the encapsulated guest. Alternatively, dendrimers can be used to carry other molecules or particles attached to their surfaces [68–72]. Hyperbranched polymers and their substitutes can also be used as nanomaterials for host-guest encapsulation [73–76] fabrication of organic-inorganic hybrids [77–79] and nanoreactors [80].

A post-synthetic functionalisation of dendrimers makes them very useful and promising catalysts. The catalytic sites can be located either on the surface, inside internal cavities, or at the central unit. An extensive review of this kind of use of dendrimers is given elsewhere [81].

Dendrimers are considered to be ideal functional building blocks for the creation of nanostructures due to their self-assembly properties [12, 82]. Controlled surface reactivity, uniform shape, and chemical stability make dendrimers promising materials in the production of liquid crystals and mono- or multilayered films [83, 84].
Hong et al. [85] found that small amounts (500-1000 ppm) of hyperbranched polymer added to linear low density polyethylene (LLDPE) results in a reduced viscosity of the melt and as a consequence significantly eliminates surface defects, such as sharkskin without any need to change typical processing conditions. They also showed that the output-rate improved via addition of hyperbranched polymers to the melt while lower extrusion power was needed. Such dual functionality has not been observed for any of the traditional processing aid agents. Their study supported Kim and Webster’s [86] conclusion that the presence of branches in polymer architecture significantly changes polymer properties, and highly branched polymers can be used as rheology modifier materials. Hong et al. [85] showed that hyperbranched polymers in the melt of LLDPE have a tendency to segregate from the bulk and migrate to the surface. They suggested that hyperbranched or a hyperbranched-rich mixture on the surface forms a lubricating layer, which can be responsible for sharkskin elimination. Since this pioneering work, hyperbranched polymers have been extensively used as rheology modifiers or blend components [85, 85, 87–92].

Compared to dendrimers, the synthesis of hyperbranched polymers costs less and, owing to their well-defined architecture having multifunctional terminal groups and narrow polydispersity characteristics, they have become widespread in biomaterials applications, as biocarriers and biodegradable materials [26, 73, 93–95]. Owing to their large number of functional groups and enhanced optical, electrochemical, and mechanical properties, patterning of hyperbranched polymer films has become widespread [78, 96–98]. Due to their high solubility, low viscosity and large number of functional groups, hyperbranched polymers have also been widely employed as the base for various coating resins [99], including powder coatings [100], flame retardant coatings [101] and barrier coatings for flexible packaging [26, 102].

1.2 Dendrimer-Linear Polymer Blends

Blending is an enabling technique to develop and improve materials for a specific application with desirable properties, which are not available in a single material. Nowadays, mostly all categories of commercial polymers are mixed with other poly-
Dendrimers And Their Blends With Linear Polymers

mers to improve a variety of physical and chemical properties of the end product, such as strength, toughness, processability, barrier properties, and chemical activity.

In 1992 Kim and Webster [86] reported that the melt viscosity of a polystyrene melt decreased in the presence of a small amount of bromo-functional hyperbranched polymer. However, they did not discuss the phase behaviour of the blend system. A similar reduction in viscosity was observed for a solution of hyperbranched polymers and their blends with linear polymers. Nunez et al. [103] suggested that the reduction in viscosity, which is partly due to replacement of linear chains with hyperbranched polymers of lower viscosity, is also a consequence of reduction in the number of entanglements between linear chains in the presence of hyperbranched polymers. However, they did not quantify this claim. A few years after Kim and Webster's observation, it was reported that the addition of small perfect dendritic polyesters [104] to poly (ethylene terephthalate), can yield miscible blends. Massa et al. [105] studied the miscibility of blends of both hydroxyl-terminated and acetate-terminated hyperbranched polyesters and linear polymers. They showed that the chemical structure and interaction, and the architecture of the species in the blend both play a role in polymer miscibility.

Fredrickson and Liu [106] incorporated entropic corrections to the Flory-Huggins theory of polymer blends in order to take into account the architectural and conformational effects of blend species on the free energy of mixing. Based on their modified theory for conventional mixtures of linear and star polymers with modest numbers of truly polymeric arms, they predicted that phase separation due to architectural differences alone is unlikely.

The effect of hyperbranched polymer content on the blend viscosity and miscibility of a polyamide 6 and hyperbranched aramid blend at 5 to 30 wt% of hyperbranched polymer was investigated by Monticelli et al. [107]. Viscosity and glass transition $T_g$ data of the blends proved the miscibility of the components in the composition range studied. They attributed the observed miscibility to the possible hydrogen bonding between amide groups and hyperbranched functional end groups. In recent work, Li et al. [108] investigated the melt rheology and mechanical properties of blends of
linear poly (ether ether ketone) and hyperbranched poly (ether ether ketone). They reported that the blend shows only one glass transition temperature, indicating single phase (miscible) blend formation. They suggested that this is due to the similar chemical structure of the two blend species.

In addition to experimental observations there have been a few computational studies using different simulation techniques to study the miscibility and rheological properties of blends of dendritic and linear polymers. For example, Lee and McHugh [109] applied Brownian dynamics simulations to study the effect of the mole fraction of linear segments in the hyperbranched polymers on the rheological properties of linear-hyperbranched polymers. They found that the first normal stress difference is more sensitive to the addition of linear segments in the perfectly branched architecture than the zero-shear viscosity. In addition, they observed that there is a crossover in rheological behaviour from hyperbranched-like behavior (low viscosity) to linear-chain like behaviour (high viscosity) at a transitional mole fraction of linear segments of 0.8.

Theodorakis et al. [110] studied the influence of chain architecture on the miscibility of symmetric linear/linear and star/star polymer blends using Monte Carlo simulations. They found that star/star blends are more miscible than linear/linear ones, at least for short chains. They also reported that an increase in the number of arms enhanced the miscibility significantly. They suggested that this comes mainly from the shielding effect of the star cores, and consequently reduced number of heterocontacts. Consequently, there was a smaller reduction in size of the star polymer compared to their unperturbed state than there was in the size of linear/linear blends.

In order to take advantage of potential applications of dendrimers and hyperbranched polymers upon blending, one should be able to predict the phase behaviour of these blends. Freed and Dudowicz [111] extended the Flory-Huggins theory for linear chains to account for the chain architecture effect on the phase behaviour of the system, with the so-called lattice cluster theory (LCT). Enders et al. [112] applied LCT to predict the phase behaviour of blends of linear and hyperbranched...
polymers. The theory predicts large demixing regions and a small mixing gap, which depends on different structural parameters. However, the LCT needs to be validated by comparing with experimental results because there have been several cases where dendritic and linear polymers form miscible blends [104, 108].

Akten and Mattice [113] proposed a method to assess the miscibility of linear binary systems by calculating the intermolecular radial distribution functions (RDFs). They stated that if the intermolecular RDFs of unlike pairs are higher than those of like pairs, the systems are miscible; otherwise, the systems are immiscible. This concept has now been used by several authors [114, 115].

Kosmas and Vlahos [116] included long range interactions in the Flory-Huggins model where the excluded volume interactions between units belonging to different chains are not cancelled and might lead to a non-random mixing or even demixing. They applied their new model to analyse the stability of blends of chemically identical and different homopolymers in the bulk and in a film. They successfully explained some of the experimentally observed phase diagrams in 2D and 3D systems. In another work, Vlahos and Kosmas [117] applied this approach to study the effective interaction parameters for star/star, ring/ring, and ring/linear blends of chemically identical nature. They found no phase separation in 3D for blends composed of ring/ring and ring/linear chains at any disparity or volume fractions. The same was found for star/star or star/linear polymer blends with a few to moderate number of arms, which was in agreement with experimental and theoretical results.

Mackay et al. conducted several experiments in order to study viscosity [118], miscibility [119], and structural changes of linear polystyrene molecules [120] in the presence of spherical cross-linked polystyrene (PS) and dendritic polyethylene (PE) nanoparticles. They observed a very surprising result that although linear PS - linear PE blends are a classic phase-separating system, branched PE nanoparticles disperse homogeneously in PS and form a single phase system. This means architecture and size both make a clear difference in the miscibility of this system. They showed that when the radius of gyration of the linear polymer is greater than the radius of the nanoparticle, a thermodynamically stable dispersion of nanoparticles into the
polymeric liquid was achieved [119]. Addition of nanoparticles to polymer reduced the blend viscosity, which they found scales with the change in the free volume introduced by the nanoparticles and not with the decrease in entanglement. They reported that the entanglement was not affected at all, suggesting an unusual polymer dynamics [118]. Additionally, they observed a 10%–20% increase in the radius of gyration of PS when the nanoparticles are uniformly dispersed in the polymer. The uniform dispersion occurred only when the radius of gyration of the polymer was larger than the nanoparticle radius [120]. Their studied system composed of PS nanoparticles dispersed in the linear PS resembles our blend systems composed of dendrimer molecules and linear chains of the same chemical nature. The similarity arises due to the globular and constrained topology of dendrimers that result in particle-like behaviour of dendrimers.
Chapter 2

Rheology and Structure of Polymeric Fluids

2.1 Viscoelastic Response of Polymeric Fluids

Owing to their viscoelastic characteristics, polymeric fluids can show significantly different flow behaviour from that of Newtonian fluids [121]. Viscoelastic behaviour indicates that, depending on the circumstances (i.e. extent and rate of imposed deformation), and relaxation characteristics of the polymeric fluids, they can show either solid-like (energy storage) or liquid-like (energy dissipation) behaviour. The macromolecular character of polymeric molecules together with physical interactions called “entanglements” result in elastic behaviour, which is associated with the memory of the material. Deformed molecules are forced by thermal motions and restorative forces to revert to their undeformed conformations, leading to the bulk fluid elastic recovery.
2.2 Material Functions for Viscoelastic Fluids

2.2.1 Kinematics

Two types of flows are applied to analyse polymeric fluids: shear and extensional flows. Occasionally, polymer processes are a combination of these flows or often are dominated by one type or the other. The velocity field for rectilinear shear flow can be written as [121–123]

\[ \nu_x = \dot{\gamma}(t)y \quad \nu_y = \nu_z = 0, \]

(2.1)

where the shear rate, \( \dot{\gamma}(t) \) can be either time-dependent or independent of time. The velocity field for extensional flows can be written in a general format as

\[ \nu_x = \dot{\epsilon}x \quad \nu_y = -\frac{1}{2}\dot{\epsilon}(1 + b)y, \quad \nu_z = -\frac{1}{2}\dot{\epsilon}(1 - b)z, \]

(2.2)

in which \( \dot{\epsilon} \) is the extension rate and \( b \) is a constant that takes either 0 or 1 values. When \( b = 0 \) and \( \dot{\epsilon} > 0 \), the flow defines a uniaxial extensional flow. For \( b = 0 \) but \( \dot{\epsilon} < 0 \), the flow is called equibiaxial extensional flow. When \( b = 1 \) and \( \dot{\epsilon} > 0 \), the flow is a planar extensional flow.

Polymeric fluids exhibit significantly different behaviour under different types of elongational deformations, and each of these deformations impact macromolecular orientation in a distinct way. For instance, uniaxial and planar extensional flows induce considerable molecular orientation in polymer molecules during flow compared to shear flows. Biaxial extensional flow is a weak flow and causes a slight molecular orientation [122, 123]. In addition, the rheological behaviour can be very different for a polymer under extensional flow compared to shear flow condition. These differences are illustrated later in this chapter.

The velocity gradient tensor corresponding to simple planar shear, with flow in
the $x$-direction and velocity gradient in the $y$-direction is given as \cite{121-123}

$$\nabla v = \begin{pmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$ \quad (2.3)

Note that diagonal components of this tensor are zero. In a Newtonian liquid, the viscosity obtained under shear flow can be employed to describe the stress in other flows. However, this is not strictly true for complex fluids. The rheological behaviour of a polymeric fluid under steady extensional flow, especially of high molecular weight polymers, is often substantially different from that under shear flow.

The velocity gradient tensor for extensional flows can be written as \cite{122, 123}

$$\nabla v = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\frac{1}{2}\dot{\epsilon}(1 + b) & 0 \\ 0 & 0 & -\frac{1}{2}\dot{\epsilon}(1 - b) \end{pmatrix}$$ \quad (2.4)

Contrary to the shear case, here only diagonal components are non-zero. The physical significance of these velocity gradient tensors is that they reveal that in shear flow the velocity gradient is perpendicular to the flow direction while in extensional flows it is in the same direction as the flow itself \cite{122, 123}.

2.2.2 Pressure Tensor Components

Pressures that exist in addition to a hydrostatic pressure are expressed as the extra pressure tensor, $\pi$. Thus pressure tensor equals $P = \pi + p\delta$, where $\delta$ is the identity matrix and $p$ is the isotropic (equilibrium pressure \cite{122}. Therefore, the total
pressure of a flowing material in rectangular Cartesian coordinates is given as

\[
\begin{pmatrix}
\pi_{xx} + p & \pi_{xy} & \pi_{xz} \\
\pi_{yx} & \pi_{yy} + p & \pi_{yz} \\
\pi_{zx} & \pi_{zy} & \pi_{zz} + p
\end{pmatrix}
\quad (2.5)
\]

By the convention used here, a positive stress \( \sigma \) is equivalent to a negative pressure \( P \). Hence, the components \( \sigma_{xx} = -(\pi_{xx} + p) \), \( \sigma_{yy} = -(\pi_{yy} + p) \), and \( \sigma_{zz} = -(\pi_{zz} + p) \) are the normal stresses. In addition, \( -\pi_{xx}, -\pi_{xy}, \) and so on are assigned as the extra, or molecular stresses, and

\[
\sigma_{xx} = -P_{xx} = -(\pi_{xx} + p) \quad \sigma_{xy} = -P_{xy} = -\pi_{xy} \quad \sigma_{xz} = -P_{xz} = -\pi_{xz} \quad \text{etc.} \quad (2.6)
\]

are termed the total stress components.

Using symmetry arguments, it can be proved that for a viscoelastic fluid undergoing shear flow, the pressure tensor is of the form [123]

\[
\begin{pmatrix}
\pi_{xx} + p & \pi_{xy} & 0 \\
\pi_{yx} & \pi_{yy} + p & 0 \\
0 & 0 & \pi_{zz} + p
\end{pmatrix}
\quad (2.7)
\]

It is notable that under shear flow, additional normal stresses are developed, which do not occur for a Newtonian fluid. Three distinct quantities of stress of rheological importance are

\[
\sigma_{xy} = \sigma_{yx} = -P_{xy} = -P_{yx},
\quad (2.8)
\]

\[
\sigma_{xx} - \sigma_{yy} = P_{yy} - P_{xx} = \pi_{yy} - \pi_{xx} = N_1,
\quad (2.9)
\]

and

\[
\sigma_{yy} - \sigma_{zz} = P_{zz} - P_{yy} = \pi_{zz} - \pi_{yy} = N_2,
\quad (2.10)
\]

where \( P_{xy} = P_{yx} = -\eta \dot{\gamma}(t) \), and \( N_1 \) and \( N_2 \) are called the first and second normal stress differences, respectively. These additional quantities are related to phenomena such as die swell, elastic recoil, and rod climbing and therefore are connected to the
concept of elasticity.

Similar to shear flow, using symmetry arguments for extensional flows, it can be shown that the pressure tensor takes the form

\[
\begin{pmatrix}
\pi_{xx} + p & 0 & 0 \\
0 & \pi_{yy} + p & 0 \\
0 & 0 & \pi_{zz} + p
\end{pmatrix}
\]  

(2.11)

For incompressible polymeric fluids in elongational flow there exist two normal stress differences of rheological significance

\[
P_{yy} - P_{xx}, \quad \text{and} \quad P_{zz} - P_{yy}.
\]  

(2.12)

When \( b = 0 \) in Eq. (2.2), then there is only one quantity of rheological significance

\[
P_{yy} - P_{xx}.
\]  

(2.13)

Being generated under different flow conditions, it is important to note that these normal stress differences are not the same as the previously defined \( N_1 \) and \( N_2 \).

2.2.3 Material Functions for Shear Flow

Different types of shear flow experiments are conducted to characterize the flow behaviour of polymeric fluids. For constant \( \dot{\gamma}(t) \), where \( \dot{\gamma}_{yx} = \dot{\gamma} \), one can define three material functions for steady shear flow

\[
P_{xy} = -\eta(\dot{\gamma})\dot{\gamma},
\]  

(2.14)

\[
P_{yy} - P_{xx} = \Psi_1(\dot{\gamma})\dot{\gamma}^2,
\]  

(2.15)

\[
P_{zz} - P_{yy} = \Psi_2(\dot{\gamma})\dot{\gamma}^2,
\]  

(2.16)
in which $\eta$ is the shear viscosity, $\Psi_1$ is the first normal stress coefficient, and $\Psi_2$ is the second normal stress coefficient. $\Psi_1$ is typically more shear-rate sensitive than is $\eta$. In addition, it is noted [122, 123] that $-\Psi_2/\Psi_1$ usually takes the values in the range of 0.1 to 0.2.

### 2.2.4 Material Functions for Extensional Flow

Analogous flow histories for extensional flows can also be employed. For steady simple (i.e., homogeneous deformation) extensional flows, based on the two normal stress differences given in Eq. (2.12), two viscosity functions, $\eta_1$, and $\eta_2$ are defined as

\[
P_{yy} - P_{xx} = \eta_1(\dot{\epsilon}, b)\dot{\epsilon},
\]

(2.17)

\[
P_{zz} - P_{yy} = \eta_2(\dot{\epsilon}, b)\dot{\epsilon}.
\]

(2.18)

For a uniaxial extensional flow where $b = 0$ and $\dot{\epsilon} > 0$, $\eta_2 = 0$, and $\eta_1$ is called the uniaxial elongational viscosity, $\eta_u$,

\[
\eta_u(\dot{\epsilon}) = \eta_1(\dot{\epsilon}, 0).
\]

(2.19)

### 2.3 Typical Rheological Behaviour of Polymer Melts

#### 2.3.1 Shear Flow Behaviour

As opposed to Newtonian fluids with viscosities independent of the flow rate, entangled polymer melts show shear-rate dependent viscosity, so-called shear thinning behaviour. Shear thinning is an effect where the viscosity of a fluid decreases with increasing shear rate (Fig. 2.1). Polymeric fluids show shear thinning effects at high shear rates, which are more significant for polymers of high molecular weights. For an entangled polymer chain, shear thinning arises from the stretching of the chains
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Figure 2.1: Typical steady-state shear viscosity versus shear rate for an entangled polymer.

to an “oriented” state when the applied shear rate is higher than a certain critical value [122].

2.3.2 Elongational Flow Behaviour

Fig. 2.2 shows the predicted steady-state elongational viscosity versus elongation rate by standard molecular theories of an entangled polymer melt [124]. Marrucci and Ianniruberto [124] explained this behaviour in terms of the stretching and orientation of the polymer chains along their tube. In region I, where strain rate is smaller than tube disentanglement time $\tau_d$ ($\dot{\epsilon} < 1/\tau_d$), polymer chains keep their equilibrium conformation and consequently viscosity is constant at the Trouton value, which is 3 for uniaxial elongation flow and 4 for planar elongational flow. In zone II, where $1/\tau_d < \dot{\epsilon} < 1/\tau_R$, and $\tau_R$ is the Rouse time, chains are oriented along the flow direction. However, chains are not stretched and reptation is still frozen. Hence, they still carry their equilibrium stress and consequently elongational viscosity decreases with the strain-rate. By further increasing the strain-rate chains stretch and
Figure 2.2: Steady-state elongational viscosity versus elongation rate as predicted by standard molecular theories of entangled polymers.
stress increases, which leads to viscosity upturn (thickening region). Based on predictions of Marrucci and Ianniruberto [124], there is a plateau region at very high strain-rates where chains are fully stretched. However, they did not incorporate the finite extensibility of the chains in their model. Kisbaugh and McHugh [125] studied the effect of this parameter on flow behavior of polymer solutions under shear flow. They showed that in the case of no finite extensibility (Hookean potential), viscosity will increase indefinitely as a function of strain rate, and there will be no thinning region after viscosity upturn occurs. For finitely extensible polymer chains there will be another thinning region at very high flow rates, presumably due to fully aligned chains along the flow direction.

Steady-state elongational viscosity of polymer melts is hard to obtain experimentally and most of the data available in the literature focuses on the transition behaviour of polymer melts undergoing elongational flows. However, Marrucci and Ianniruberto [124] compared their model with data reported by Bach et al. [126] for a nearly monodispersed polystyrene melt. They found a significant disagreement on the value of the slope of the thinning region, which is 1 (given by the model) versus 1/2 (found by Bach et al.). Marrucci and Ianniruberto suggested that this discrepancy can be corrected via incorporation of interchain repulsive interaction due to thermal pressure exerted by the chain segments against the tube wall. For more details, the reader is referred to their original paper [124].

2.3.3 Normal Stress Differences

When a fluid shows shear thinning behaviour one cannot conclude that the fluid is viscoelastic [122]. A fluid is considered viscoelastic when it is able to store elastic energy. The appearance of normal stress differences under shear flows strongly demonstrates the viscoelasticity of the fluid. The stress tensor for an incompressible isotropic fluid and under shear flow has at least two nonzero elements, \(-P_{xy} = -P_{yx}\), along with an isotropic pressure contribution. For a Newtonian fluid, the stress tensor has no other nonzero elements, while a non-Newtonian fluid has other nonzero elements. These are the normal stresses, which are discussed above.
In addition to the shear viscosity $\eta = -P_{xy}/\dot{\gamma}$, the stress coefficients discussed above often have constant values at low shear rates and are called the zero-shear-rate values, $\eta_0$, $\Psi_{1,0}$, and $\Psi_{2,0}$.

At low shear rates, the constitutive equation of a Newtonian fluid can be applied to a viscoelastic “simple” fluid with fading memory [122]

$$\pi = -2\eta D$$

(2.20)

where $D$ is the rate of deformation tensor (i.e., the symmetric part of the velocity gradient tensor).

$$2D = \nabla \mathbf{v} + (\nabla \mathbf{v})^T$$

(2.21)

The antisymmetric part of the velocity gradient tensor, which is called the vorticity tensor, is given as

$$2\omega = \nabla \mathbf{v} - (\nabla \mathbf{v})^T$$

(2.22)

The vorticity tensor is related to the angular velocity of the fluid element. For flows with no rotation, such as the extensional flows, $\nabla \mathbf{v}$ is symmetric and the vorticity tensor is zero [122].

### 2.3.4 Stress Relaxation

If the stresses in a fluid last after the termination of deformation, it is definitely classified as a viscoelastic fluid. The time over which considerable stresses persist after termination of deformation gives an approximation of the relaxation time ($\tau_r$) of the fluid material. Based on molecular theory for melts $\tau_r$ can be defined by the ratio $\Psi_{1,0}/2\eta_{1,0}$ in the low shear rate limit where $\Psi_{1,0}$ and $\eta_{1,0}$ both reach a constant value [127].
2.4 Theoretical Models of Polymer Dynamics

2.4.1 Linear Polymer Chains

The standard model describing the complex rheological behaviour of entangled linear polymers is based on the well-known tube model of Doi and Edwards [42]. The original model includes: (1) the tube (fixed diameter), accounting for the constraints (entanglement) imposed on a single chain by its surrounding chains, (2) an instantaneous retraction of the chain within the tube in order to preserve the constant length of the tube, and (3) a randomization of the tube conformation (relaxation) via 1D diffusion of the chain out of the old tube (de Gennes [128] called this process reptation). Improvements have been made on the original model, including: chain-end fluctuations [129], which explain the observed 3.4 power law dependence of the viscosity on molecular weight in contrast to the third power law predicted by the original model, and constraint release [130] as a result of thermal motion of the surrounding chains, which is an additional relaxation time and is particularly important for polydisperse systems. Mechanisms that are important in the non-linear regime (large and fast deformations or fast flows) are chain stretch [42], which is due to friction of the chain retracting in its tube and convective constraint release (CCR) [131], which contributes to tube randomization. Models accounting for these mechanisms were successively developed, and validated with experimental data in the nonlinear regime [132–134].

2.4.2 Branched Polymers

The majority of commercially available polymers belong to the broad class of branched polymers. The great impact of branching on the rheology of polymeric fluids, particularly on their extensional behaviour, has extensively been observed.

The nonlinear viscoelasticity of polymers with long branches can be described by the Pom-Pom model of McLeish and Larson [135]. In the Pom-Pom model, these authors focused on a simple architecture that consists of two star polymer (arms)
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connected by a linear one (backbone). The Pom-Pom model includes: (1) arm retraction [136], (2) tube dilation for the arm retraction [137], (3) reptation of the backbone after the arm retraction (hierarchical relaxation) [138], (4) chain stretching of the backbone [124], and (5) branch-point withdrawal (BPW) [139]. However, they did not consider the stretching of the arms because their focus was on the intermediate flow rates lying between the widely separated relaxation rates of arm and backbone, respectively. Recently, Masubuchi et al. [140] performed primitive chain network simulations to investigate the details of molecular motion under uniaxial elongation. They included CCR and stretch-orientation/induced friction reduction (SORF) in their simulations, which was missing in the original Pom-Pom model. They showed that the BPW is the dominant mechanism among all others [140].

One of the most significant transitions in the dynamics of polymers occurs at the crossover to the entanglement regime. For the case of mono-disperse linear polymer melts, it is conclusively proved that chain length or molecular weight $M$ governs the crossover to entanglement and the transition occurs at $M = M_e \approx 2M_c$, where $M_e$ is the entanglement molecular weight, which is a material characteristic parameter [141, 142]. However, the crossover to entanglement for branched polymers is a much more complex matter. The complexity arises as there are several length scales in their architecture, and it should be clarified which of these control the entanglement transition. Buzza and co-workers [143] considered three potential candidates consisting of “the branch length $M_x$ (i.e., the molecular weight of chain portions between branch points), the span length (i.e., the molecular weight of the longest linear path through the branched molecule) and the total molecular weight, all appropriately averaged over the ensemble”, for hyperbranched polymers. They found that $M_x$ controls the entanglement transition occurrence for the hyperbranched polymers and the crossover happens around $M_x \approx M_e$.

Branching has a profound impact on the extensional rheology of polymer melts. It has been observed that branching increases strain-hardening (the increase in the stress with increase in the strain at the post-yield region (high strains) of polymer stress-strain response due to molecular orientation) under extensional flow. However, there are no particular relationships available between the rheological properties and
the degree and/or length of the branches [123].

2.5 The Rouse Model: Linear Versus Branched Polymers

Rouse [144] developed the first successful molecular model of dynamical response of polymers. In this model, $N$ beads linked by springs of size $b$ represent the polymer chain. Interaction between beads is only allowed via their linked springs. The friction coefficient $\zeta$ of each bead contributes to the total friction coefficient of the Rouse chain as [145]

$$\zeta_R = N\zeta.$$  \hspace{1cm} (2.23)

If the chain is dragged with velocity $v$, the viscous frictional force on the chain is $-N\zeta v$. The diffusion coefficient of the Rouse chain according to the Einstein relation is

$$D_R = \frac{kT}{\zeta_R} = \frac{kT}{N\zeta}.$$  \hspace{1cm} (2.24)

The polymer diffuses a distance of the order of its own size $R$ during a characteristic time, called the Rouse time, $\tau_R$

$$\tau_R \approx \frac{R^2}{D_R} \approx \frac{R^2}{kT/(N\zeta)} = \frac{\zeta}{kT}NR^2.$$  \hspace{1cm} (2.25)

The Rouse time has a significant importance. The polymer chain shows viscoelastic behaviour for available response times less than the Rouse time. On the other hand, the chain moves effectively in a diffusive mode, for available response time longer than the Rouse time [145].

A randomly branched polymer with $N$ monomers in $d$-dimensional space occupies volume proportional to $R^d \propto N^{d/D}$, where $D$ is the fractal dimension. In the critical percolation class, hyper-scaling [145] demands polymers of a constant size only overlap with molecules of smaller size. Considering the rapid relaxation of these
shorter polymers, one can conclude that each polymer molecule relaxes without any effective topological constraints [145].

Any polymer relaxing with no topological constraints and no hydrodynamic interactions - despite its complex architecture - is well represented by the Rouse model, with friction proportional to molar mass. In order to predict the terminal response of randomly branched polymers, this reasoning is applied to the given branched polymer with friction coefficient $\zeta$ consisting of $N^*$ monomers. The diffusion coefficient of these chains is given by the Einstein relation [145].

$$D_R \propto \frac{kT}{N^*\zeta}, \quad (2.26)$$

which is analogous to Eq. (2.24) for a linear polymer. The Rouse relaxation time of this given polymer $\tau^*$ is the longest relaxation time in the ensemble of branched polymers. It is determined as the time required for the given polymer to move a distance of order of its own size $R$

$$\tau^* \propto \frac{R^2}{D_R} \propto \frac{\zeta}{kT} N^* R^2, \quad (2.27)$$

which is analogous to Eq. (2.25) for a linear polymer. This simple argument can be generalized for the relaxation time of any polymer regardless of its architecture [145].

For randomly-branched polymers the correlations between viscosity and relaxation time with weight-average molar mass are given as [145]

$$\eta \propto M_w^{0.75}, \quad \tau^* \propto M_w^{2.2}. \quad (2.28)$$

which agree quite well with experimental data.

The Rouse model is the most simple and straightforward molecular model that predicts an essential distribution of polymer relaxation times. In fact, real polymeric liquids exhibit numerous relaxation modes. Nevertheless, in most polymer liquids, the relaxation modes observed do not correlate well enough to the mode distribution
predicted by the Rouse theory [145]. For dilute polymer solutions, *hydrodynamic interactions* exist that influence the viscoelastic properties of the solution which are neglected in the Rouse theory. In most concentrated solutions or melts, *entanglements* between long polymer molecules significantly retard polymer relaxation, which is also neglected in the Rouse theory.

Melts consisting of fairly short polymer chains, with molecular weights lower than the *entanglement threshold* $M_e$ (which is commonly in the range $\approx 2000-30,000$), are assumed to be characterized by the Rouse theory at low or moderate frequencies [146]. Nevertheless, for these liquids, there exist *high-frequency* relaxation modes that are not explained by the Rouse model, which includes rotations and coordinated movements of several backbone atoms [146, 147]. These motions are normally called "glassy modes" as they account for much of the relaxation that occurs at the glass transition temperature.

Some polymer melts, such as commercial low-density polyethylene, possess irregularly spaced long side branches. Here "long" means that the branches are longer than $M_e$, and hence are capable of being entangled with surrounding chains. Branches much shorter than this influence the friction coefficient but otherwise do not affect reptation [145]. The effects of long side branches on rheological properties are profound, and are difficult to consider theoretically, especially when compounded by irregularity in side-branch length and spacing along the backbone. In low-density polyethylene, the long side branches can themselves have long branches, thus forming tree-like structures [148, 149]. Such structures are also present in partially *cross-linked* polymers. Polymer strands that terminate in a branching point at one end but are free at the other cannot reptate, but they can still undergo retraction. The contributions of such a polymer strand to the *nonlinear* properties of the melt are expected to be similar to those of a freely reptating chain. The contributions to the linear properties are, however, greatly affected by the presence of a branch point at only one end of the chain.

Strands that terminate with a branch point at both of its ends can neither reptate nor completely retract. Relaxation of such strands presumably occurs by more
complex hierarchical processes discussed by McLeish [148]. Here we simply note that the presence of branch points at both ends of a strand leads to much more strain hardening in extensional flows [150, 151]. Low-density polyethylenes (LDPEs), which are highly branched, are well known for their extreme strain hardening behavior in extensional flows [152, 153].

Early attempts to identify the entanglement crossover for bead-spring model polymers were done by Kremer et al. [154–156], where they performed extensive equilibrium simulations to investigate the different regimes of the diffusive motion of polymer chains. According to their calculations for model polymers of different lengths, the entanglement length $N_e$ was identified to be approximately 35 beads. However, they did not determine the zero-shear viscosity for which a corresponding crossover of the scaling behaviour is predicted for chains with $N_c$ beads, whereby $N_c$ should be greater than the entanglement length $N_e$. Later, Kröger et al. [57] extended this approach to study fluids under flow. In their simulations, the zero-shear-rate viscosity was found to scale linearly with the number of beads $N$ up to chains with $N = 60$. A weak upturn of the viscosity per bead for $N = 100$ was found, which they suggested can be indicative of the onset of the reptation regime.

2.6 Empirical Models

The Carreau-Yasuda model has been used over the past few decades to model the strain-rate dependent steady shear viscosity for polymeric melts. We refer the reader to the book by Bird et al. [121] for details. Sarkar and Gupta [157] modified this model for the elongational melt viscosity by incorporating one extra term for the thickening phenomenon which is observed in the elongational behaviour of polymer melts. We use the Sarkar-Gupta model in our studies and calculate the adjustable parameters of the model by fitting them to our simulation data. The longest relaxation times were further approximated for the systems under study.
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2.6.1 Carreau-Yasuda Model

The Carreau-Yasuda model [121] expresses the shear viscosity as

$$\eta = \eta_0 \left[ 1 + (\lambda \dot{\gamma})^2 \right]^p,$$

(2.29)

where $\eta_0$ is the zero shear viscosity, $\lambda$ is defined as the relaxation time of the system, and $p$ is the power law exponent, used to fit the data points. The exponents in the power law region are obtained from the linear region in the log-log plot of the viscosity versus strain rate curve.

2.6.2 Sarkar-Gupta Model

Sarkar and Gupta [157] used a modified version of the Carreau model [121] for shear viscosity in order to describe the elongational viscosity as

$$\eta_1 = \eta_0 \left[ 4 + \delta \left( 1 - \frac{1}{\sqrt{1 + (\lambda_1 I_2)^2}} \right) \right] \left[ 1 + (\lambda_2 I_2)^2 \right]^{m-1}$$

(2.30)

For $\delta = 0$, the elongational viscosity in Eq. (2.30) reduces to the Carreau model with the elongational viscosity parameters $\lambda_2$ and $m$, respectively, replacing $\lambda$ and $p$ in the shear viscosity model. $I_2$ is the second scalar invariant of the strain rate tensor and is equal to $8\dot{\epsilon}^2$ for planar elongational flow and $2\dot{\gamma}^2$ for shear flow. Physically, $I_2$ is a measure of the rate of viscous heat dissipation in steady state flow. The parameter $\lambda_1$[158] (first time constant) in Eq. (2.30) dictates the value of $I_2$ for the transition between Newtonian and elongation thickening regions of the viscosity against strain-rate curve, whereas $\delta$ characterizes the total increase in viscosity in the elongation thickening region. Parameter $\lambda_2$ (second time constant) specifies the value of $I_2$ for the transition between elongation-thickening and the power-law regions, and $m$ is the power-law index for elongational viscosity. Both $\lambda_1$ and $\lambda_2$ are time constants, corresponding to different relaxation mechanisms, i.e. stretching and alignment of the molecules, respectively.
2.7 Structural Analysis

The extension of a molecule in space can be characterized by its radius of gyration. The average tensor of gyration is given by the expression [26, 28]

\[
R_g(R_g) = \frac{\sum_{\alpha=1}^{n} m_{\alpha}(\mathbf{r}_{\alpha} - \mathbf{r}_{CM})(\mathbf{r}_{\alpha} - \mathbf{r}_{CM})}{\sum_{\alpha=1}^{n} m_{\alpha}}
\]

(2.31)

where \( \mathbf{r}_\alpha \) is the position of monomer \( \alpha \), \( \mathbf{r}_{CM} \) is the position of the molecular centre of mass and the angle brackets denote an ensemble average. The value of the squared radius of gyration, which is defined as the trace of the tensor of gyration \( R_g^2 = Tr(R_gR_g) \), characterizes the size of the molecule and can be compared with the experimentally measured radial sizes of dendrimers and hyperbranched molecules.

Further analysis of the tensor of gyration can provide insights into the shape and orientation of the molecules. For each system mentioned above, the eigenvalues of the tensor of gyration (in descending order, \( L_1, L_2, \) and \( L_3 \)) were computed for each molecule and then averaged over the ensemble. These eigenvalues can be interpreted as the linear dimensions of the ellipsoid occupied by the average molecule, regardless of its orientation [26, 28]. Changes in these values with \( I_2 \) quantitatively describe the flow induced stretching of the molecules. In addition, the asymmetry of molecules is characterized by the ratio of the eigenvalues of the average gyration tensor, which we define here as \( L_{12} = L_1/L_2, L_{13} = L_1/L_3, \) and \( L_{23} = L_2/L_3 \). If the ratios of the eigenvalues are closer to 1, the molecules have greater spherical symmetry. If \( L_1 > L_2 \approx L_3 \) then the shape is prolate and if \( L_1 \approx L_2 > L_3 \) the shape is considered as oblate.

To analyse the distribution of mass within the molecule, we calculate the distribution of the monomers from the core (central monomer), defined by

\[
g_{\text{core}}(r) = \frac{\sum_{i=1}^{N} \sum_{\alpha=2}^{N_\alpha} \delta(r - r_{i1,\alpha})}{4\pi r^2 N}
\]

(2.32)

where \( r_{i1,\alpha} = | \mathbf{r}_{i\alpha} - \mathbf{r}_{i1} | \), \( \mathbf{r}_{i1} \) is the position of the core and \( \alpha \) runs over all the
monomers belonging to the same molecule [26, 28].

One of the characteristic features of dendrimers and hyperbranched polymers is the large number of their terminal groups. Their number doubles with every generation, and their chemical activity can be controlled in the process of synthesis of the molecule. From the configurational point of view, it is important to understand the spatial distribution of these groups because the location of these groups over the molecule affects its chemical activity and physical properties. Similar to the bead distribution function presented earlier, the distribution of terminal groups is defined by

\[
g_{\text{end}}(r) = \left\{ \frac{\sum_{i=1}^{N} \sum_{\alpha} \delta(r - r_{i,\alpha})}{4\pi r^2 N} \right\}
\]

where in this case \( \alpha \) runs over outermost monomers only [26, 28].

### 2.7.1 Blend Miscibility Analysis

In order to investigate the miscibility and inter-penetration of blend species, a series of different pair distribution functions \( g(r) \) are commonly employed [113–115]. These functions represent the probability of finding a pair of atoms at a separation \( r \) relative to the bulk phase in a completely random distribution. This can provide insights into the specific atomic and/or molecular arrangements in the blend melt. Three different pair distribution functions were used to analyse the miscibility of dendrimer/linear (D/L) blend systems. The \( g_{DL}(r) \) function is defined as

\[
g_{DL}(r) = \left\{ \frac{V \sum_{i=1}^{N_D} \sum_{\alpha} \sum_{j=1}^{N_L} \sum_{\beta=1}^{N_{\beta}} \delta(r - r_{i\alpha,j\beta})}{4\pi r^2 N_D N_{s,D} N_L N_{s,L}} \right\},
\]

where \( r_{i\alpha,j\beta} = |r_{j\beta} - r_{i\alpha}| \), \( r_{i\alpha} \) is the position of bead \( \alpha \) in dendrimer molecule \( i \) and \( r_{j\beta} \) is the position of bead \( \beta \) in linear molecule \( j \). \( N_{s,D} \) and \( N_{s,L} \) are the number of beads for the dendrimer and linear species, respectively. \( N_D \) and \( N_L \) are the number of dendrimer and linear molecules in the blend, respectively. \( V \) is the averaged volume of the system. In this function the distribution of the beads of linear chains from the
beads of the dendrimers is calculated. In this way, the mixing of beads belonging to the dendrimer molecules and beads belonging to linear molecules can be analysed.

In addition, we define the \( g_{LL} \) distribution function as

\[
g_{LL}(r) = \frac{V \sum_{i=1}^{N_L} \sum_{\alpha=1}^{N_L} \sum_{j \neq i} N_L \sum_{\alpha \neq \beta} \delta(r-r_{j\beta,i\alpha})}{4\pi r^2 N_L N_s,L}, \tag{2.35}
\]

where \( r_{j\beta,i\alpha} = |r_{j\beta} - r_{i\alpha}|, \) \( r_{i\alpha} \) is the position of bead \( \alpha \) on a linear molecule \( i \) and \( r_{j\beta} \) is the position of bead \( \beta \) in other linear molecules \( j \).

Similarly, the \( g_{DD} \) distribution function is defined as

\[
g_{DD}(r) = \frac{V \sum_{i=1}^{N_D} \sum_{\alpha=1}^{N_D} \sum_{j \neq i} N_D \sum_{\alpha \neq \beta} \delta(r-r_{j\beta,i\alpha})}{4\pi r^2 N_D N_s,D}, \tag{2.36}
\]

where \( r_{j\beta,i\alpha} = |r_{j\beta} - r_{i\alpha}|, \) \( r_{i\alpha} \) is the position of bead \( \alpha \) on a dendrimer molecule \( i \) and \( r_{j\beta} \) is the position of bead \( \beta \) in other dendrimer molecules \( j \).

To describe interpenetration between molecules in the melt we define a modified version of the radial distribution function previously proposed for pure dendrimer systems [28]. It is defined as

\[
g_{c,DL}(r) = \frac{V \sum_{i=1}^{N_D} \sum_{\alpha=1}^{N_L} \sum_{j \neq i} \sum_{\alpha \neq \beta} \delta(r-r_{i1,j\alpha})}{4\pi r^2 N_D N_s,D N_L}, \tag{2.37}
\]

where \( r_{i1,j\alpha} = |r_{j\alpha} - r_{i1}|, \) \( r_{i1} \) is the position of the core of dendrimer molecule \( i \) and \( r_{j\alpha} \) is the position of bead \( \alpha \) in linear molecule \( j \). \( N_s,D \) is the number of beads for the dendrimer species. \( N_D \) and \( N_L \) are the number of dendrimer and linear molecules in the blend, respectively. In this function the distribution of the beads of linear chains from the core bead of the dendrimers is calculated. In this way, the penetration of the beads belonging to linear molecules toward the interior of dendrimer molecules is analysed. The derivation for the general distribution function for single and two-component systems is given in the Appendix.
Chapter 3

Molecular Dynamics Simulation

3.1 Introduction

Computer simulation has emerged as a recognized method of research in science and an effective tool in solving specific scientific and engineering problems. With the introduction of high-powered supercomputers, the impact of the application of computer simulation on many research areas has increased colossally over the past decades [159, 160].

Polymer science benefits from this development in a distinct way; the intricate macromolecular chemical architecture, the immense variability of physical properties and the pervasive range of applications involve many inter-related scientific questions. Theoretical methods usually enforce unrefined mathematical approximations, the validity of which is hard to determine in general. Along with the limitation that unknown parameters introduce, the predictive capability of such methods is often rather restricted. In contrast, computer simulation can enable the study of models of complex many-body systems in full detail without requiring such mathematical approximations. Therefore, one can check the validity of approximate calculations and methods, without unknown parameters blurring a meaningful comparison. Simulta-
neously, comparing with experiment helps to validate and systematically refine the model. In principle, use of computer simulation in this way is an iterative process by which complex materials and processes can be understood in stages [159].

In light of these specific conceptual and practical benefits, computer simulations of polymers have gained significant interest, and different complementary techniques have been established. Nevertheless, it should be noted that simulations of polymers involve specific challenges, considering the vast spread of length scales and time scales invoked by the characteristics of polymeric materials [159].

The molecular dynamics (MD) simulation technique is fundamentally straightforward. It is a deterministic approach where the system tracks a well determined path (or trajectory) in phase space. Presuming the applicability of classical mechanics, MD involves the simultaneous solution of Newton’s equations of motion for a system of particles interacting in accordance with a predefined force field and considered thermodynamic states [159, 160]. Generally, the applied equations of motion are deterministic coupled ordinary differential equations selected according to the statistical ensemble examined. MD provides one with the information on how microscopic structures and their variations can influence macroscopic properties of the simulated system and is the most accurate simulation method for computing time-dependent properties of materials. It is presumed that ensemble averages of properties of the simulated fluid are equal to time averages of the same properties [161], i.e. the systems are ergodic.

Simulating homogeneous polymeric flows far from equilibrium (i.e., undergoing planar shear or planar elongational flows) by applying non-equilibrium molecular dynamics techniques is the subject of the current chapter. This chapter covers a detailed description of the model used to represent dendrimer, hyperbranched and linear polymers. Non-equilibrium molecular dynamics simulation techniques including the isothermal-isobaric (NPT) ensemble implementations of planar shear and planar elongational flow algorithms for molecular fluids are presented in this chapter.
3.2 Model Polymers

Model dendrimers and hyperbranched polymers were generated based on a coarse-grained uniform bead-spring model. Beads represent the linear segments or branching units of the molecular structure and treelike topologies are created by a layered arrangement of inter-connected beads. The only feature that differentiates the beads from each other is their position in the molecule. The total number of monomers in a dendrimer can be calculated using the formula,

\[ N = fb((f - 1)^{g+1} - 1)/(f - 2), \]

in which \( f \) presents the functionality of end groups, \( b \) is the number of monomers in the linear spacers, and \( g \) is the generation number. Having set \( f = 3 \) and \( b = 2 \), dendrimers of generation 1, 2, 3, and 4 will possess 19, 43, 91, and 187 monomers, respectively [28]. To compare our simulation results for hyperbranched polymers with results for dendrimers, we chose a specific architecture of hyperbranched polymers in our simulations [26]. They are dendrimers with trifunctional end groups (\( f = 3 \)) and two monomers in the chain units (\( b = 2 \)) that have one imperfect branching point \( f = 2 \) [26]. As our hyperbranched polymers have the same number of monomers as the dendrimers but fewer branches at one branching point, extra monomers are added in the outermost layer of the molecules with \( f = 3 \) and \( b = 2 \) (see Fig. 3.1). Models of linear polymers of length 19, 43, 91, and 187 have been built by successively attaching the same monomers. Only bond and pairwise interactions are considered in this model.

Monomers in the melt interact via the Weeks-Chandler-Anderson (WCA) [162] potential (which is a shifted and truncated Lennard-Jones (LJ) potential) and also a finitely extensible nonlinear elastic (FENE) potential (details can be found in papers by Kroger and Hess [57] and also Kremer and Grest [155]). The WCA potential is given as

\[
U^{WCA}_{ij} = \begin{cases} 
4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] + \epsilon & \text{for } \frac{r_{ij}}{\sigma} < 2^{1/6}, \\
0 & \text{for } \frac{r_{ij}}{\sigma} \geq 2^{1/6}
\end{cases}
\]

(3.1)

in which \( r_{ij} \) represents the distance between the monomers \( i \) and \( j \), \( \epsilon \) is the potential well depth, and \( \sigma \) is the effective diameter of the monomers. This potential gives purely repulsive forces that include the effect of excluded volume [26, 28].
Figure 3.1: Schematic representation of model hyperbranched and dendrimer molecules of generation 1, (19 beads per molecule), revealing functionality, length of the spacing of both hyperbranched and dendrimer molecules ($f = 3$ and $b = 2$), and position of the missing branch for hyperbranched molecule.
The FENE potential is expressed as

\[ U_{ij}^{FENE} = \begin{cases} 
-0.5kR_0^2ln[1 - (r_{ij}/R_0)^2] & \text{for } r_{ij} \leq R_0 \\
\infty & \text{for } r_{ij} \geq R_0 
\end{cases} \] (3.2)

in which \( R_0 \) represents the finite extensibility of the bond and \( k \) represents the spring constant. In this work, \( R_0 \) and \( k \) were chosen to take their typical values, 1.5 and 30 respectively [57, 155]. This choice of parameters provides the maximum extension of the bonds to be short enough to prevent branches from crossing each other, while the magnitude of the bonding force is small enough to enable using relatively large time steps for simulations.

Nonbonded monomers only interact via the WCA potential while bonded monomers interact with both FENE and WCA potentials which results in a potential well for the flexible bonds that builds the molecular architecture of interest [26, 28].

In this thesis, all quantities are presented in terms of site reduced units where the reduction parameters are the Lennard-Jones interaction parameters \( \epsilon \) and \( \sigma \) and the mass, \( m_{i\alpha} \) of bead \( \alpha \) in molecule \( i \). The reduced temperature is given by \( T^* = k_BT/\epsilon \), the density by \( \rho^* = \rho\sigma^3 \), the pressure tensor by \( P^* = P\sigma^3/\epsilon \), and strain rate by \( \dot{\gamma}^* = \dot{\gamma}(m\sigma^2/\epsilon)^{1/2} \). For simplicity of notation, the asterisk has been excluded from now on [26, 28]. In all simulations we set \( \sigma = \epsilon = m_{i\alpha} = k_B = 1 \).

### 3.3 Nonequilibrium Molecular Dynamics Simulation

In real physical systems, flows far from equilibrium can be actuated by moving boundaries (e.g., Couette flow). Flows driven by the boundaries, where walls are explicitly implemented in the simulation, can induce strong density inhomogeneities into the fluid. This inhomogeneity prevents calculation of meaningful bulk properties, such as transport coefficients.

During the early work on simulation of fluids under flows, Lees and Edwards [163]
used a method to drive the flow by adapting appropriate periodic boundary conditions to the simulation. This method was successful in generating a linear streaming velocity profile for weak Couette flow [163]. Nevertheless, this approach has its own inadequacy. Firstly, this method has no connection with response theory, and consequently, is difficult to connect with statistical mechanics. Secondly, this method will not immediately generate the desired linear streaming velocity and it will take a sufficiently long time before it can reach its target value. This comes from the fact that diffusion of transverse momentum from the boundaries to the whole fluid is a time-consuming process. As a result, investigation of time-dependent transport properties using this method is difficult [164]. Later, Gosling, McDonald, and Singer [165] employed a sinusoidal transverse force to generate a spatially periodic velocity profile.

To generate steady shear flow, Ashurst and Hoover [166] employed the idea of external reservoirs, comprising particles which are separated from the bulk fluid. In this approach the temperature of the reservoir was kept constant, allowing the removal of dissipated heat from the bulk fluid.

Later, Hoover et al. [167] proposed a method based on the DOLLS Hamiltonian. Substitution of the external thermodynamic environment by internal controlling variables was the main idea behind their new approach. Particularly, a fictitious external field mimics the effect of a boundary that triggers the flow. The external field has the characteristic that it maintains the desired streaming velocity profile indefinitely. Although this method works well in the linear response limit, Evans and Morriss [168] showed that it produces errors in nonlinear flow properties, which are calculated at strong fields.

The correct set of equations of motion (the so-called SLLOD equations of motion) were proposed by Evans and Morris [169] for atomic fluids and later proved by Daivis and Todd [170] for generalised homogeneous flows, and by Ladd [171] for molecular fluids and are given for atomic fluids as (molecular version will be addressed later
in this chapter)

\[
\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{v}
\]

\[
\dot{\mathbf{p}}_i = \mathbf{F}^\phi_i - \mathbf{p}_i \cdot \nabla \mathbf{v}
\]  

(3.3)

in which \(\mathbf{p}_i\) and \(\mathbf{r}_i\) represent the peculiar momentum and the laboratory position of atom \(i\), respectively. \(\nabla \mathbf{v}\) presents the gradient of the streaming velocity \(\mathbf{v}\). The thermal velocity relative to the streaming velocity of the fluid is called the ‘peculiar’ velocity. \(\mathbf{F}^\phi_i\) is the inter-atomic force on atom \(i\) imposed by all other atoms in the system [164].

Although the SLLOD equations of motion lead to the correct velocity gradient, it is necessary to use compatible periodic boundary conditions (PBCs) with the flow field to eliminate the perturbation of particle trajectories due to PBCs. The Lees and Edwards [163] scheme is suitable for shear flow. For planar elongational flow, the so-called Kraynik-Reinelt (KR) [65] boundary condition scheme needs to be implemented for NEMD simulations [172–174] to obtain steady-state values for the flow properties.

### 3.4 Periodic Boundary Conditions and the Minimum Image Convention

To build models of molecular fluids, usually a limited number of model molecules are generated in a simulation box. As a result of such a small sample, which corresponds to only a nanoscopic droplet of fluid, surface effects would be significant. In order to obtain bulk properties of the model polymers and overcome this issue, the standard method is to surround the simulation box with periodic images of itself in all directions, known as periodic boundary conditions (PBCs). Permitting molecules at the boundaries to interact with images of other particles makes it possible to remove the surface effects. The position of a particle which exits one side of the simulation box, is replaced by its periodic image entering via the opposite surface [58]. This
gives the constant particle number condition while the molecules are free to travel throughout the fluid. Although using PBCs makes it possible to calculate infinite bulk behaviour of the fluid using a small number of molecules, there is a restriction on the minimum number of molecules that can be used. For the case of short ranged potentials, such as the LJ potential used in this thesis, the size of the simulation box should be constructed such that \( r_c \leq L_{\text{min}}/2 \), where \( L_{\text{min}} \) is the minimum length of the system in any direction, and \( r_c \) is the cut off radius for the LJ potential [58].

The minimum image convention (MIC) states that a molecule should only interact with the closest image of any other molecule. As long as the above condition for minimum size of the simulation box holds true, i.e. \( r_c \leq L_{\text{min}}/2 \), a molecule will only be able to interact with one image of any other molecule [58].

Here we discuss the implementation of compatible periodic boundary conditions (PBCs) with the SLLOD equations of motion for homogeneous flows. The only restraining principle is the time evolution of the boundaries, which must be in line with the enforced streaming velocity profile. To clarify how this principle can be handled, we start with the strain rate tensor [164]

\[
\nabla \mathbf{v} = \begin{pmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_y}{\partial x} & \frac{\partial v_z}{\partial x} \\ \frac{\partial v_x}{\partial y} & \frac{\partial v_y}{\partial y} & \frac{\partial v_z}{\partial y} \\ \frac{\partial v_x}{\partial z} & \frac{\partial v_y}{\partial z} & \frac{\partial v_z}{\partial z} \end{pmatrix}
\]  

(3.4)

Particle (total laboratory) velocities from the SLLOD equation of motion are

\[
\mathbf{\dot{r}}_i = \frac{p_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{v}
\]  

(3.5)

This equation has two terms, one for the thermal velocity \( \frac{p_i}{m_i} \) relative to the streaming velocity and the second one for the streaming velocity at particle \( i \)'s position \( \mathbf{r}_i \cdot \nabla \mathbf{v} \). For the boundaries, thermal velocity has no contribution, therefore the time evolution of the boundaries is governed by

\[
\mathbf{\dot{L}}_k(t) = \mathbf{L}_k(t) \cdot \nabla \mathbf{v}
\]  

(3.6)
where \( \mathbf{L}_k(t) = (L_{kx}(t), L_{ky}(t), L_{kz}(t)) \) are the set of box lattice vectors, which specify the box vertices for \( k = 1, 2, 3 \) \[164\]. Therefore, the time evolution of the boundaries is determined by integrating Eq. (3.6) \[164\].

### 3.4.1 Shear Flow

The time evolution of the lattice vectors for planar shear flow with the flow in the \( x \)-direction and velocity gradient \( \dot{\gamma} \) in the \( y \)-direction, are given as \[164\]

\[
\begin{align*}
\frac{dL_{kx}(t)}{dt} &= L_{ky}(t)\dot{\gamma}dt \\
\frac{dL_{ky}(t)}{dt} &= 0 \\
\frac{dL_{kz}(t)}{dt} &= 0
\end{align*}
\tag{3.7}
\]

Integrating Eq. (3.7), gives \( L_{kx}(t) = L_{ky}(t)\dot{\gamma}t \) and the second and third lines in Eq. (3.7) indicate that during the simulation time, there is no evolution for the box vectors in \( y \) and \( z \), i.e. \( L_{ky}(t) = L_{ky}(t = 0) = L_{ky} \) (equivalently for \( L_{kz} \)) \[164\].

### 3.4.2 Elongational Flow: Kraynik-Reinelt Periodic Boundary Condition

Kraynik and Reinelt \[65\] showed that by using lattice structures one can generate PEF, preserving spatial and temporal periodicity \[164\]. The heart of their technique is the determination of a discrete “magic” angle, upon which the simulation box can be mapped into its original shape. More importantly, the simulation box boundaries are permitted to evolve in accordance to the flow. After one Hencky strain period elapses, the lattice repeats itself, as is shown in Fig. 3.2. The Hencky strain period is the time duration required for the structure to repeat itself spatially and is dependent on the “magic” angle upon which the simulation box is transformed at a certain elongation rate \[164\]. Once one Hencky strain (here 0.5) has passed, the only thing that is needed is that the simulation box boundaries should be re-set to \(-0.5\). More details of this method can be found in Kraynik and Reinelt’s original work \[65\].
Although Kraynik and Reinelt focussed on lattice structures in their paper, their technique similarly can be applied to systems comprising of moving particles which are periodic in space [164]. Todd and Daivis [172] and, independently, Baranyai and Cummings [175] showed that the reproducibility of KR lattice structures can be exploited to design a new algorithm for NEMD simulations of indefinite PEF. Later, Todd and Daivis [173] established an efficient algorithm for PBC’s which can be applied to both the sliding brick [163, 164] and deforming box methods applicable for shear flow [173, 176, 177].

The simulation box for implementation of Kraynik-Reinelt (KR) PBCs is typically initially rotated by the magic angle and through the rotation the principal lattice vectors $L_1$, and $L_2$ are no longer parallel to the $x$- and $y$-axes, which are the directions of expansion and contraction, respectively [164]. The strain rate tensor for planar
elongation flow under this geometrical condition, (Eq. 3.4) becomes

$$\nabla \mathbf{v} = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

(Eq. 3.8)

Eq. (3.6), therefore reduces to

$$\begin{align*}
\frac{dL_{kx}(t)}{dt} &= L_{kx}(t) \dot{\epsilon} dt \\
\frac{dL_{ky}(t)}{dt} &= -L_{ky}(t) \dot{\epsilon} dt \\
\frac{dL_{kz}(t)}{dt} &= 0
\end{align*}$$

(3.9)

the solution for which would be the exponential growth/contraction of lattice vectors for planar elongation,

$$\begin{align*}
L_{kx}(t) &= L_{kx}(0) \exp(\dot{\epsilon} t) \\
L_{ky}(t) &= L_{ky}(0) \exp(-\dot{\epsilon} t) \\
L_{kz}(t) &= L_{kz}(0)
\end{align*}$$

(3.10)

Therefore, the simulation box evolves (stretching in $x$ and contracting in $y$) until the time required for the total strain to reach the periodic strain amplitude, $\epsilon_p = 0.5$, after which the simulation box is set back into $-0.5$ [164].

### 3.4.3 Periodic Boundary Conditions for Arbitrary Parallelepiped Boxes

So far we showed that different flow conditions need different PBCs to be implemented for NEMD simulations, but if there were a unique scheme to be used regardless of flow type, it would be very useful.

The scheme explained below is a general method applicable for any arbitrarily flow fields. We used this method in our implementation of NEMD techniques in this work [164].

The key idea behind this scheme is the representation of the particle position as
a linear combination of the box vectors $\mathbf{L}_1$, $\mathbf{L}_2$, and $\mathbf{L}_3$, which are not necessarily mutually perpendicular

$$\mathbf{r}_i = a_i \mathbf{L}_1 + b_i \mathbf{L}_2 + c_i \mathbf{L}_3 \quad (3.11)$$

The values of $a_i$, $b_i$, and $c_i$, are real numbers and their fractional parts are the coefficients of vectors $\mathbf{L}_1$, $\mathbf{L}_2$, and $\mathbf{L}_3$ that locate the image particle in the original simulation box [164]. By determining the scalar product of both sides of Eq. (3.11) with a vector that is orthogonal to both $\mathbf{L}_2$, and $\mathbf{L}_3$,

$$\mathbf{r}_i \cdot \mathbf{L}_2 \times \mathbf{L}_3 = a_i \mathbf{L}_1 \cdot \mathbf{L}_2 \times \mathbf{L}_3 \quad (3.12)$$

the value of $a_i$ is calculated

$$a_i = \frac{\mathbf{r}_i \cdot \mathbf{L}_2 \times \mathbf{L}_3}{\mathbf{L}_1 \cdot \mathbf{L}_2 \times \mathbf{L}_3} = \frac{\mathbf{r}_i \cdot \mathbf{L}_2 \times \mathbf{L}_3}{V} \quad (3.13)$$

in which it is presumed that the box vectors are defined in a way that the volume $V = \mathbf{L}_1 \cdot \mathbf{L}_2 \times \mathbf{L}_3$ is positive. Analogously, $b_i$, and $c_i$ are found

$$b_i = \frac{\mathbf{r}_i \cdot \mathbf{L}_3 \times \mathbf{L}_1}{\mathbf{L}_2 \cdot \mathbf{L}_3 \times \mathbf{L}_1} \quad c_i = \frac{\mathbf{r}_i \cdot \mathbf{L}_1 \times \mathbf{L}_2}{\mathbf{L}_3 \cdot \mathbf{L}_1 \times \mathbf{L}_2} \quad (3.14)$$

Therefore, the position vector of the image of particle $i$ that is located in the original simulation box is found to be

$$\mathbf{r}'_i = \mathbf{r}_i - ([\text{nint} (a_i - 0.5)] \mathbf{L}_1 + [\text{nint} (b_i - 0.5)] \mathbf{L}_2 + [\text{nint} (c_i - 0.5)] \mathbf{L}_3) \quad (3.15)$$

in which $\text{nint}(x)$ is the closest integer to $x$ [164].

We conclude that under both types of flow, i.e. shear flow and PEF, the box vectors are evolved exactly like the position vectors, except that they don’t have a thermal velocity. After one strain period of 0.5, they are reset to a strain of −0.5 and then start again to minimize the contraction of the shortest box dimension [164].
It is important to note that NEMD simulations of elongational flows are unstable over long simulation times [177]. The exact equations of motion do conserve the momentum, provided that $\sum p_i = 0$ at $t = 0$. However, momentum in the contracting direction is not conserved, due to the exponential growth of numerical error. This had initially been unseen, mainly due to restricted simulation time. Todd and Daivis [177] showed that there are two ways to prevent this effect, firstly, re-zeroing the total momentum in the $y$-direction periodically, and secondly, employing a non-holonomic Gaussian constraint to the total linear momentum in the $y$-direction. The first method is used here [58].

## 3.5 Constant Temperature and Pressure Simulations

Normally, real physical systems are not isolated from their surrounding environment and consequently are usually maintained at constant temperature and/or pressure. During a simulation, the temperature will rise from its initial value as a consequence of viscous heating due to work done by the stress. Viscous heating occurs whether the source of the work is an external field (e.g., SLLOD algorithm) or the boundaries (e.g., shear flow generated by moving boundaries). This excess heat must be removed from the system in order to keep the system at a thermodynamic steady-state [164]. By employing appropriately formulated thermostats, constant temperature simulations are usually accomplished. Since 1980 several thermostats have been formulated. The Gaussian isokinetic thermostat [178] and the Nosé-Hoover thermostat [179–181] are the most suitable ones for NEMD simulations.

### 3.5.1 Gaussian Thermostat

In our simulations we use a Gaussian thermostat [178]. The SLLOD equations of motion for a system under the effect of an external field and coupled to a Gaussian
thermostat, where the strain rate tensor is independent of time, are [164]

\[ \dot{r}_i = \frac{p_i}{m_i} + r_i \cdot \nabla v \]

\[ \dot{p}_i = F^\phi_i - p_i \cdot \nabla v - \alpha p_i \]

(3.16)

with

\[ \alpha = \frac{\sum_i \frac{p_i}{m_i} \cdot \left( F^\phi_i - p_i \cdot \nabla v \right)}{\sum_i \frac{p_i^2}{m_i}} \]

(3.17)

In the case of planar shear flow, the Gaussian-thermostatted SLLOD equations of motion are written as below [164]

\[ \dot{r}_i = \frac{p_i}{m_i} + \dot{\gamma} y_i \]

\[ \dot{p}_i = F^\phi_i - \dot{\gamma} p_{yi} + \alpha p_i \]

(3.18)

where the thermostat multiplier, \( \alpha \) is

\[ \alpha = \frac{\sum_i \frac{p_i}{m_i} \cdot \left( F^\phi_i \cdot p_i - \dot{\gamma} p_{xi} p_{yi} \right)}{\sum_i \frac{p_i p_{xi}}{m_i}} \]

(3.19)

For the Gaussian-thermostatted planar elongational flow, the governing SLLOD equations are [164]

\[ \dot{r}_i = \frac{p_i}{m_i} + \dot{\epsilon} (ix_i - jy_i) \]

\[ \dot{p}_i = F^\phi_i - \dot{\epsilon} (ip_{xi} - jp_{yi}) - \alpha p_i \]

(3.20)

with

\[ \alpha = \frac{\sum_i \frac{1}{m_i} \left( F^\phi_i \cdot p_i - \dot{\epsilon} [p_{xi}^2 - p_{yi}^2] \right)}{\sum_i \frac{p_i p_{xi}}{m_i}} \]

(3.21)
Gaussian constraints have one unsatisfactory feature, which happens when \( t \to \infty \). At large \( t \), the constrained quantity (here the temperature) may deviate from its desired value due to the accumulation of numerical errors. This is true for equilibrium and non-equilibrium conditions. To overcome this issue Baranyai and Evans [182] proposed a proportional feedback term added into the force equation (second equation in Eq (3.16)) using a modified thermostat multiplier as below [164]

\[
\alpha \rightarrow \alpha + \alpha' \left[ \left( \sum_i \frac{p_i^2}{m_i} \right) \left( dN - N_c \right) k_B T - 1 \right]
\]

(3.22)

in which \( \alpha' \) acts as a weighting term chosen so that it is large enough to correct for deviation from the desired value, but not so large that the equations of motion become stiff. Usually \( \alpha' \) varies between 0.1-10. The term in square brackets gives the proportion of deviation of the actual kinetic temperature from the desired target temperature \( T \). If there is no deviation of the kinetic temperature from the target temperature, the second term in Eq (3.22) is zero meaning no feedback is applied. Otherwise, the amount of feedback proportional to the deviation is added into the constraint term [164].

3.5.2 Barostat

In this thesis, the constant pressure simulations are accomplished by applying an NPT version of an NEMD method that employs an extended system technique. This method has been earlier applied in order to investigate flow properties of molecular fluids [183]. Briefly, the method works by adjusting the volume of the simulation box at each time step such that the pressure is altered to fluctuate about a specified target value [161, 168, 184]. This is accomplished by coupling the equations of motion to a barostat, and adding an additional equation of motion for the system volume. Equations of motion for the NPT version of the NEMD algorithm are given in Sections 3.7 and 3.8.
3.6 Integration Scheme

In MD simulations, the equations of motion are solved numerically by integrating particle positions and velocities over time. MD simulations normally involve a large number of time steps; therefore, it is essential that an integration algorithm conserves quantities such as momentum and energy. In addition, time-reversible integration is needed for theoretical handling of a deterministic set of equations. In the end, a large time step is desirable, without too much loss of accuracy. The error of an integration scheme is a combination of the step size $\Delta t$ and the order $b$ of the algorithm, hence the total error scales as $O((\Delta t)^b)$. Considering the fact that we are often interested in averages rather than individual trajectories, a large step size is often chosen over a high accuracy [185].

Several factors influence the selection of a proper simulation time step $\Delta t$ to integrate the equations of motion. The simulation time step has to be selected in a way that the fastest microscopic processes can be computed with a reasonable time resolution. In addition, the time step has to be such that the integrator stays stable. Time steps of approximately $\Delta t = 0.001\tau - 0.005\tau$ are frequently employed, depending on the integrator, the required accuracy and the details of the simulation, where $\tau$ is the reduced time unit. The integration time step for molecular fluids may need to be smaller. If bond lengths and angles are flexible, they are often responsible for the fastest modes in the system [160].

3.6.1 The Gear Predictor Corrector Integration Scheme

There are a few types of numerical methods for integrating Newton’s equations, such as Verlet, leapfrog, 4th order Runge-Kutta, and the predictor-corrector algorithm. In our implementation we used the Gear predictor-corrector method because it is easy to implement while using the Gaussian thermostat. In addition, due to the presence of a higher order derivatives of particle coordinates, one can use longer time steps with this algorithm and can achieve higher order of accuracy for a given time
3 NEMD Algorithm

The Verlet algorithm is fast and time-reversible but it is not easy to implement while using a Gaussian thermostat, as it does not give the momenta to the same order of accuracy as the positions, which is also essential to obtain the pressure in NEMD methods. The key idea behind the Gear method is to use the information about the position and its first \( n \) derivatives at time \( t \) to arrive at a prediction for the position and its first \( n \) derivatives at time \( t + \Delta t \) [160]. Then one can compute the forces, and associated accelerations, at the predicted positions. From the discrepancy between these observed accelerations with those have been predicted, estimations of positions and its derivatives should be improved (the so-called corrector part of the algorithm) [160].

In order to predict the position at time \( t + \delta t \), fourth-order Taylor series expansions are employed to the atomic positions at time \( t \). The Taylor expansion of the position \( r \) denotes the \( x \), \( y \), and \( z \) components) of a given atom at time \( t + \delta t \) is

\[
r(t + \delta t) = r(t) + \delta t \frac{dr}{dt} + \frac{\delta t^2}{2!} \frac{d^2r}{dt^2} + \frac{\delta t^3}{3!} \frac{d^3r}{dt^3} + \frac{\delta t^4}{4!} \frac{d^4r}{dt^4} + \ldots
\]

(3.23)

Using the notation

\[
\begin{align*}
  r_0(t) &= r(t) \\
  r_1(t) &= \delta t \frac{dr}{dt} \\
  r_2(t) &= \frac{\delta t^2}{2!} \frac{d^2r}{dt^2} \\
  r_3(t) &= \frac{\delta t^3}{3!} \frac{d^3r}{dt^3} \\
  r_4(t) &= \frac{\delta t^4}{4!} \frac{d^4r}{dt^4}.
\end{align*}
\]

(3.24)
One can write predictions for \( r_0(t + \delta t) \) through \( r_3(t + \delta t) \)

\[
egin{align*}
    r_0(t + \delta t) &= r_0(t) + r_1(t) + r_2(t) + r_3(t) + r_4(t) \\
    r_1(t + \delta t) &= r_1(t) + r_2(t) + r_3(t) + r_4(t) \\
    r_2(t + \delta t) &= r_2(t) + r_3(t) + r_4(t) \\
    r_3(t + \delta t) &= r_3(t) + r_4(t) \\
    r_4(t + \delta t) &= r_4(t).
\end{align*}
\] (3.25)

Then from the particles' position at time \( t + \delta t \), one can compute the forces at the predicted position, and thus compute the corrected value for the acceleration \( r_2(t + \delta t) \) [160]. The corrector step has the form

\[
\begin{pmatrix}
    r_0(t + \delta t) \\
    r_1(t + \delta t) \\
    r_2(t + \delta t) \\
    r_3(t + \delta t) \\
    r_4(t + \delta t)
\end{pmatrix} =
\begin{pmatrix}
    r_0^p(t + \delta t) \\
    r_1^p(t + \delta t) \\
    r_2^p(t + \delta t) \\
    r_3^p(t + \delta t) \\
    r_4^p(t + \delta t)
\end{pmatrix} + \begin{pmatrix}
    c_0 \\
    c_1 \\
    c_2 \\
    c_3 \\
    c_4
\end{pmatrix} \delta r_2
\] (3.26)

where \( \delta r_2 \) is the difference between the observed and predicted accelerations at time \( t + \Delta t \). In the corrector part of the algorithm, a set of Gear coefficients \( c_i \) is employed [160, 185] to correct all of the predicted derivatives of the motion, based on the discrepancy between the predicted and corrected accelerations. These Gear coefficients are selected in a way that they optimize the stability and accuracy of the trajectories. They depend both on the number of derivatives and the order of the differential equation used in the Taylor series prediction of the positions. As proposed by Gear [186], for the fourth-order algorithm applied to the first-order differential equation, the best choice for Gear coefficients are: \( c_0 = 251/720, c_1 = 1, c_2 = 11/12, c_3 = 1/3, c_4 = 1/24 \) [186]. This method is flexible and leads to good stability, due to the feedback mechanism associated with the corrector step, which dampens instabilities imposed by the predictor. For computing particle trajectories at small time-steps, this algorithm gives more accurate results than the Verlet algorithm [187].
3.7 Molecular SLLOD: Shear Flow

Our NEMD simulations of shear flow are based on the molecular version of the homogeneous isothermal-isobaric SLLOD equations of motion (details can be found in [164])

\[
\dot{r}_{i\alpha} = \frac{p_{i\alpha}}{m_{i\alpha}} + \mathbf{r}_i \cdot \nabla \mathbf{v} + \dot{\zeta} \mathbf{r}_i, \\
\dot{p}_{i\alpha} = F_{i\alpha} - \left( \frac{m_{i\alpha}}{M_i} \right) \mathbf{p}_i \cdot \nabla \mathbf{v} - \alpha \left( \frac{m_{i\alpha}}{M_i} \right) \mathbf{p}_i - \dot{\zeta} \left( \frac{m_{i\alpha}}{M_i} \right) \mathbf{p}_i,
\]

where \( r_{i\alpha} \) and \( p_{i\alpha} \) represent the position and thermal momentum of monomer \( \alpha \) on molecule \( i \), \( \nabla \mathbf{v} \) is the strain rate tensor; \( \mathbf{r}_i = \sum_{\alpha=1}^{N_i} m_{i\alpha} \mathbf{r}_{i\alpha} / M_i \) is the position of the molecular centre of mass of molecule \( i \), \( M_i = \sum_{\alpha=1}^{N_i} m_{i\alpha} \) is the mass of molecule \( i \), and \( \mathbf{p}_i = \sum_{\alpha=1}^{N_i} \mathbf{p}_{i\alpha} \) is the momentum of the molecular centre of mass of molecule \( i \) [26, 28]. Constant temperature simulations were accomplished by employing a molecular version of the Gaussian thermostat with a constraint multiplier \( \alpha \) given as [26, 28]

\[
\alpha = \frac{\sum_{i=1}^{N} (F_i \cdot p_i)/M_i - \dot{\zeta} \sum_{i=1}^{N} (p_{ix} p_{iy})/M_i}{\sum_{i=1}^{N} p_i^2 / M_i - \dot{\zeta}},
\]

where \( N \) is the number of molecules in the system. The thermostat contains the molecular kinetic temperature \( T_M \) of the system defined by [164]

\[
\sum_{i=1}^{N} \frac{p_i \cdot p_i}{2M_i} = \frac{3N - 3}{2} k_B T_M.
\]

This formula for \( \alpha \) is the result of Gauss’s principle of least constraint and employed to maintain \( T_M \) constant.

Constant pressure simulations were performed by coupling the system to an extended degree of freedom \( \dot{\zeta} \) depending on the fluctuations of the volume of the simulation box, rather than the pressure [164]. The Nosé-Hoover integral feedback mechanism has been implemented in this work [183, 188]. The time evolution of \( V \)
is regulated by the variable $\dot{\zeta}$ according to the equation below

$$\dot{V} = 3\dot{\zeta}V,$$

(3.31)

where $\dot{V}$ is the first time derivative of the cell volume. To maintain the target pressure, the lattice vectors have to be rescaled such that the volume of the unit cell is compatible with the equations of motion. Each time the rescaling process takes place, it is necessary to consider the lattice cell evolution for shear. In order to calculate the dilation rate, an additional differential equation (Eq. (3.32)) needs to be solved, which depends on the difference between the instantaneous and target pressures imposed,

$$\dot{\zeta} = \frac{(p - p_0)V}{Q_p N k_B T},$$

(3.32)

where $Q_p$ is a damping factor, and its optimal value depends on the type of system studied, $p$ is the instantaneous isotropic pressure $p = \frac{1}{3} \text{Tr}(P^M)$ and $p_0$ is the target pressure.

The molecular pressure tensor is computed as

$$P^M = \frac{1}{V} \left( \sum_{i=1}^{N_m} \frac{P_i P_i}{M_i} - \frac{1}{2} \sum_{i=1}^{N_m} \sum_{j=1}^{N} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} r_{ij} F_{i\alpha j\beta} \right),$$

(3.33)

where $r_{ij} = r_j - r_i$ and $F_{i\alpha j\beta}$ is the inter-molecular force on monomer $i\alpha$ due to monomer $j\beta$. Hence the total number of differential equations to be solved is $6N + 2$, including $3N$ for the monomer positions, $3N$ for the peculiar momenta, one for the dilation rate and one for the system volume [164].

### 3.8 Molecular SLLOD: Planar Elongational Flow

Our NEMD simulations of planar elongational flow are also based on the molecular version of the homogeneous isothermal-isobaric SLLOD equations of motion (details
can be found in [164])

\[
\dot{r}_{i\alpha} = \frac{p_{i\alpha}}{m_{i\alpha}} + \dot{\epsilon}(ix_{i\alpha} - jy_{i\alpha}) + \dot{\xi} \frac{m_{i\alpha}}{M_i} r_i \tag{3.34}
\]

\[
\dot{p}_{i\alpha} = F_{i\alpha} - \dot{\epsilon}(ip_{x_{i\alpha}} - jp_{y_{i\alpha}}) - \alpha \frac{m_{i\alpha}}{M_i} p - \frac{m_{i\alpha}}{M_i} \dot{\zeta} p_i \tag{3.35}
\]

where \(\dot{\epsilon}\) is the elongational strain rate. Our geometry is such that expansion occurs in the \(x\)-direction, whereas contraction occurs in the \(y\)-direction. The thermostat multiplier is given as [164]

\[
\alpha = \frac{\sum_{i=1}^{N}(F_{i\alpha} p_i - \dot{\epsilon}(p_{x_{i\alpha}}^2 - p_{y_{i\alpha}}^2))/M_i}{\sum_{i=1}^{N} p_i^2 / M_i} - \dot{\zeta} \tag{3.36}
\]

The pressure is maintained at its target value in an analogous way to that described for shear in the previous section [164].
Chapter 4

Dendrimer and Hyperbranched Polymer Melts Under Planar Elongational Flow

4.1 Simulated Systems

In Chapter 3 the coarse-grained bead-spring model of dendrimer, hyperbranched and linear polymers applied in this study was described in detail. In addition, nonequilibrium molecular dynamics techniques used in our simulations were also explained. To perform simulations of dendrimers, hyperbranched and linear polymers under planar elongational flow (PEF), samples of dense fluids were generated. Collections of dendrimers with trifunctional end groups \( (f = 3) \), spacers composed of two beads \( (b = 2) \), and generations of 1-4 (D19, D43, D91, and D187) were generated at low density. Analogously, collections of hyperbranched polymers with trifunctional end groups \( (f = 3) \), spacers composed of two beads \( (b = 2) \), with one imperfect branching point \( (f = 2) \) and generations of 1-4 (H19, H43, H91, and H187) were also generated at low density. Each sample consisted of 125 molecules of generations 1-4, having 19, 43, 91, and 187 beads per molecule, respectively. Systems of linear polymers
with the same number of beads as dendrimers and hyperbranched polymers (L10, L43, L91, and L187) were also prepared for comparison purposes.

Systems of 125 molecules generated at low density were compressed to the monomer number density of $\rho = 0.84$. Afterwards, the barostat was switched on and the systems were equilibrated for typically several million time steps and the pressure was plotted against time to check if the system had reached equilibrium. The field was then applied until the system had reached steady-state. Ensemble averages of all properties of interest were calculated by averaging over typically 30 NEMD steady-state trajectories. The temperature and pressure were fixed at 1.25 and 5.42, respectively (in reduced units) for all systems studied.

Our simulations span over a wide range of strain rates. However, there are two technical limitations in our NEMD simulations. One occurs at very low strain rates and the other at very high strain rates, especially for high molecular weight systems. The first limitation results in poor statistics for the properties calculated at very low strain rates. To obtain better statistics, one needs to run the simulations for very long times, which is not practical from a computational point of view. The second limitation is that at extremely high strain rates the algorithm fails. This comes from the fact that at very high strain rates, bonds between the monomers are fluctuating very fast and the integration time step is larger than the inverse rate of these fluctuations. As a result, the equations of motion become stiff. In order to overcome this limitation, one should reduce the integration time step, which again will demand a higher amount of computational time. Thus in the end a compromise must be made between the competing demands of strain rate range and computational time accessible.

4.2 Rheology

The rheological properties of molecular melts are typically analysed using standard material functions. To characterize the melt rheological properties of dendrimers, hyperbranched polymers of generation 1-4, and their linear polymer counterparts
with 19, 43, 91 and 187 monomers per molecule under steady planar extensional flow, we compute the first extensional viscosity $\eta_1$, second extensional viscosity $\eta_2$ and normalized first extensional viscosity $\bar{\eta}$, which are expressed in terms of the components of the molecular pressure tensor $P^M$ calculated as below

$$\eta_1 = \left( \frac{P_{yy} - P_{xx}}{\dot{\epsilon}} \right)$$  \hspace{1cm} (4.1)$$

$$\eta_2 = \left( \frac{P_{yy} - P_{zz}}{\dot{\epsilon}} \right)$$  \hspace{1cm} (4.2)$$

$$\bar{\eta} = \frac{\eta_1}{4}$$  \hspace{1cm} (4.3)$$

The extensional viscosity is often non-dimensionalized with respect to the shear viscosity. This ratio is called the Trouton ratio. In Eq. (4.3), the factor four comes from the Trouton ratio for planar flows. This implies that in the Newtonian regime the planar extensional viscosity $\bar{\eta}$ is comparable to the shear viscosity and the first planar elongational viscosity $\eta_1$ is four times the shear viscosity.

Fig. 4.1 shows the extensional viscosity $\bar{\eta}$ versus extension rate $\dot{\epsilon}$ in the form of a logarithmic plot for dendrimer, hyperbranched and linear polymers with 19, 43, 91 and 187 monomers per molecule. The overall trend includes three distinct regions: an initial plateau Newtonian behaviour followed by a deformation thickening region, terminated by a considerable deformation thinning tail. The first important issue to discuss here is the influence of the finite extensibility parameter of the FENE potential on the rheological behaviour of our model polymer melt. Kisbaugh and McHugh [125] studied the effect of this parameter on the flow behaviour of polymer solutions under shear flow. They showed that in the case of infinite extensibility (Hookean potential) the viscosity will increase indefinitely as a function of strain rate and there will be no thinning region after viscosity upturn occurs. This suggests that finite extensibility leads to a second relaxation mechanism of the chain after being fully extended, namely the overall alignment of the molecules with respect to
the flow fields at higher strain rates.

In order to discuss the occurrence of these regions for different molecules we subdivide our systems into (a) linear molecules with entanglement (L187) (according to Kroger et al. [57, 60] the entanglement molecular weight for linear molecules starts at approximately 100 monomers per chain), and linear molecules below the entanglement molecular weight (including L19, L43, and L91), (b) dendrimers and hyperbranched molecules (D19, D43, D91, D187, H19, H43, H91, and H187).

For category (a), and generally for linear chains except L19, there is an extra elongation-thinning region at low strain rates before the appearance of thickening behaviour (Fig. 4.1(b-d)), and we suggest that this comes from the fact that linear chains can align themselves more easily along with the flow field than constrained dendritic structures even at fairly low strain rates. The intensity of this initial thinning increases with molecular weight, and as such we do not see it for the L19 system, whereas there is a very strong initial thinning for the L187 system. It should
be mentioned that for the L187 system at the available strain-rate window presented in Fig. 4.1(d), only the initial thinning region has been captured. Newtonian behaviour for the L187 system happens at much lower strain rates and is not captured in this work due to the technical limitations mentioned in the previous section. This trend is already reported in an experimental paper by Bhattacharjee et al. [158] for entangled polymer solutions under uniaxial elongational flow. They suggested that for entangled polymers as $\dot{\epsilon}$ increases, the polymer chains become significantly aligned with the principal axis of strain, but they do not stretch, which causes the extensional viscosity to decrease. Once chain stretching begins, the viscosity upturn shows up. Therefore, thinning at lower values of $\dot{\epsilon}$ is characteristic of polymeric melts with a considerable number of entanglements per chain. For unentangled polymer melts or solutions, extensional viscosity increases monotonically from the limiting Trouton value of $4\eta_0$ under PEF with increasing $\dot{\epsilon}$ to a maximum value and terminates with a thinning region at higher strain-rates [158].

In the case of dendrimers and hyperbranched molecules, we might be able to interpret their elongational behaviour based on their constrained topology which prevents them from being fully stretched and fully oriented along the flow direction. In addition, based on structural analysis later in this chapter, we find that dendrimers and hyperbranched molecules change their size, shape and orientation in the melt while undergoing elongational flow. We suggest that the stretched backbone/branches may be responsible for the thickening behaviour at intermediate strain rates for linear/hyperbranched molecules, and global alignment is responsible for the thinning region for both dendrimers and hyperbranched molecules. In Fig. 4.1 one can also see that there is a significant difference between hyperbranched and dendrimer behaviour under PEF, namely the missing thickening region for dendrimers compared to hyperbranched molecules. This implies that imperfection in the microstructure of the hyperbranched molecules introduces some free space throughout the interior of the molecules which facilitate the motion of branches in the hyperbranched structure compared to dendrimer architecture, in which the tightly packed structure prevents branches being stretched very easily under PEF. Hence, due to the very globular structure and constrained geometry of dendrimers, their rheological behaviour in-
volves Newtonian behaviour at low strain rates, with a weak viscosity upturn at moderate strain rates followed by a thinning region. The viscosity upturn decreases with increasing molecular weight and completely vanishes for the high molecular weight dendrimers for the strain rates studied here. Neelov and Adolf studied the intrinsic viscosity of dendrimers [189] and hyperbranched polymer [190] solutions under elongational flow using Brownian dynamics simulations. They suggested that “as \( \dot{e} \) increases, dendritic molecules first orient at low \( \dot{e} \) as a whole along the flow axis without significant deformation and local orientation. Increasing \( \dot{e} \) leads to local orientation at the level of the monomer leading to significant global deformation of dendrimer and hyperbranched molecules.” [189].

Fig. 4.2 shows the second extensional viscosity \( \eta_2 \) versus extension rate \( \dot{e} \) in the form of a logarithmic plot for dendrimer, hyperbranched and linear polymers with 19, 43, 91 and 187 monomers per molecule. One can see that the start of the thinning region for the two lowest molecular weight systems is approximately around \( \dot{e} = 0.001 \), which suggests that the elongation thinning behaviour of \( \eta_2 \) is not sensitive to the molecular weight for these lower weight systems. The second planar elongational viscosity is very rarely measured, and the only available data are, e.g. Matin et al. [58], Laun and Münstedt [191], and Baig et al. [192] for linear polymers. Our \( \eta_2 \) results are in qualitative agreement with the data of these papers.

We used the Sarkar-Gupta model [157] to fit our data, see Fig. 4.3(a-d). The model parameters for our model dendrimers and hyperbranched polymers of length 19, 43, and 91 are provided in Table 5.3.

<table>
<thead>
<tr>
<th>System</th>
<th>( \delta )</th>
<th>( \lambda_1 )</th>
<th>( \lambda_2 )</th>
<th>( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEN19</td>
<td>0.1</td>
<td>0.11</td>
<td>43.08</td>
<td>0.8</td>
</tr>
<tr>
<td>DEN43</td>
<td>0.07</td>
<td>0.12</td>
<td>92.89</td>
<td>0.76</td>
</tr>
<tr>
<td>DEN91</td>
<td>0.2</td>
<td>116.52</td>
<td>142.98</td>
<td>0.7</td>
</tr>
<tr>
<td>HYP19</td>
<td>2.1</td>
<td>965.14</td>
<td>20.93</td>
<td>0.85</td>
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<tr>
<td>HYP43</td>
<td>2.49</td>
<td>4905.12</td>
<td>52.94</td>
<td>0.782</td>
</tr>
<tr>
<td>HYP91</td>
<td>2.38</td>
<td>11905.11</td>
<td>169.92</td>
<td>0.654</td>
</tr>
</tbody>
</table>

62
Fig. 4.2: Strain-rate dependence of second extensional viscosity for linear (L), hyperbranched (H) and dendrimer (D) molecules with 19 (a), 43 (b), 91 (c), and 187 (d) monomers per molecule. Symbols in each subplot represent: L, H, D.

Fig. 4.3 reveals interesting aspects of elongational behaviour of our studied systems. As opposed to shear flow, there is not just one time constant to define a single Weissenberg number. Here we defined two Weissenberg numbers using two different time constants $\lambda_2$ and $\lambda_1$. Figures 4.3(a, b) show normalized extensional viscosity versus $\lambda_2 I_2$ for dendrimer and hyperbranched systems, respectively. Figures 4.3(c, d) show normalized extensional viscosities against $\lambda_1 I_2$ for dendrimers and hyperbranched systems, respectively. The former Weissenberg number $\lambda_2 I_2$ makes the thinning tail of the plots fall on a single plot (partly only), while the latter $\lambda_1 I_2$ makes the thickening region of the plots collapse on a single plot (partly only). This is a very important aspect of the elongational flow, namely that there is no single Weissenberg number to be used in order to plot a master curve. A combination of time constants will also merely show the plots in accord to the relative weightings of the constants and would be an arbitrary measure.

It is also important to note that, as discussed before, by increasing the perfection
Figure 4.3: Normalized extensional viscosity for dendrimers (a and c) and hyperbranched polymers (b and d) with 19, 43, and 91 monomers per molecule as a function of $\lambda_2 I_2$ (a-b), and $\lambda_1 I_2$ (c-d), respectively. Dashed lines - - show fitted data to the Sarkar-Gupta model. Symbols for each generation of dendrimers and hyperbranched molecules are as follows: 91 beads ◇, 43 beads ■, 19 beads ●.
Figure 4.4: The relaxation times obtained from the Sarkar-Gupta model parameters against molecular weight (in reduced unit) for dendrimers and hyperbranched molecules of generations 1-3. Symbols are as follows: dendrimers (D), hyperbranched (H). Dashed lines are quadratic fits to the data, and the predicted relation is $\tau \propto M^2$.

In the architecture of dendrimer molecules compared to hyperbranched polymers with imperfect structures, the thickening region tends to moderate and disappear for dendrimer systems by increasing the generation number. This is indicative of the constrained internal structure of these molecules that suppresses stretching of the branches along the flow lines.

In order to find the viscous relaxation time under shear flow it is common to use
the following expression [127, 193]

\[ \tau_v = \frac{\Psi_{1,0}}{2\eta_0} \]  (4.4)

where \( \Psi_{1,0} \) is defined as the zero-shear rate first normal stress coefficient. We used data available in Le et al. [26], and Bosko et al. [28], for \( \Psi_{1,0} \) and \( \eta_0 \) and calculated \( \tau_v \) using Eq. (4.4). For more details see Table 4.2. These values are in good agreement with our elongation data calculated from the reciprocal of the strain-rate at which the thinning region begins (\( \tau_p \)). Le et al. [26], and Bosko et al. [28] used the Carreau-Yasuda model to fit their shear-rate dependent shear viscosity data for hyperbranched polymers and dendrimers of generation 1-4, respectively, and calculated the adjustable parameters of the model. Values obtained for the time constant of this model only gave an approximation of the relaxation times and were of the same order of magnitude as the relaxation times calculated from the reciprocal of the strain-rate at which thinning begins. Likewise, values obtained for \( \lambda_2 \) from the Sarkar-Gupta model here (\( \tau_m \)), are shown in Table 4.2, and are within the same order of magnitude of the viscous relaxation times calculated from Eq. (4.4), and also the reciprocal of the strain-rate at which thinning begins (\( \tau_p \)) (for the extensional viscosity versus strain-rate plot). Unfortunately, the \( \Psi_{1,0} \) and \( \eta_0 \) values are not available for all the systems under study due to poor signal to noise quality for these properties at very low strain-rates.

In addition, the relaxation times obtained from the Sarkar-Gupta model parameters are shown in Fig. 4.4 as a function of molecular weight for dendrimers and hyperbranched molecules of generation 1-3. Both dendrimers and hyperbranched molecules show approximately quadratic dependence on the molecular weight under PEF, which confirms theoretical predictions \( \tau \propto M^{2.2} \) for short branched polymers [145]. This relation can be used to predict the approximate longest relaxation time for dendrimers and hyperbranched molecules with any molecular weight. Furthermore, the strain rate at which thinning behaviour starts is obtainable from the reciprocal of this relaxation time. This trend is consistent with Bosko et al. [62] for dendrimers under shear flow.
Figure 4.5: Normalized planar elongational ($\eta_i = \bar{\eta}$) and shear viscosities ($\eta_i = \eta_s$) for hyperbranched molecules of generations 1-4 versus $\lambda_1 I_2$. The coincidence of the zero shear rate viscosity and the zero extension rate viscosity in the Newtonian regime indicates the validity of our extensional flow simulations. Symbols under PEF are as follows: H187 ●, H91 ●, H43 ■, H19 ◆. Open symbols identify correspondent molecules under shear flow.
Table 4.2: Relaxation times calculated from Eq. (4.4), $\tau_v$, reciprocal of $\dot{\epsilon}$ at which thinning region starts, $\tau_p$, and the Sarkar-Gupta model parameters, $\tau_m$.

<table>
<thead>
<tr>
<th>System</th>
<th>$\tau_v$</th>
<th>$\tau_p$</th>
<th>$\tau_m$</th>
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<tr>
<td>DEN19</td>
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<td>50</td>
<td>43.08</td>
</tr>
<tr>
<td>DEN43</td>
<td>-</td>
<td>90</td>
<td>92.89</td>
</tr>
<tr>
<td>DEN91</td>
<td>-</td>
<td>125</td>
<td>169.98</td>
</tr>
<tr>
<td>HYP19</td>
<td>25(3)</td>
<td>25</td>
<td>20.93</td>
</tr>
<tr>
<td>HYP43</td>
<td>67(7)</td>
<td>66.7</td>
<td>52.94</td>
</tr>
<tr>
<td>HYP91</td>
<td>-</td>
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<td>100</td>
<td>-</td>
</tr>
</tbody>
</table>

In order to compare differences in melt behaviour of our systems under PEF with shear flow, we plot the normalized extensional viscosity $\bar{\eta}/\eta_0$ and corresponding shear viscosity results for hyperbranched molecules of generation 1-4 along with dendrimer and linear counterparts under PEF as a function of $\lambda_1 I_2$ in Fig. 4.5. We find that for both PEF and shear flow under Newtonian flow the expected normalized viscosity of 1 is obtained. Secondly, nonlinear behaviour under both types of flow starts at the same $\lambda_1 I_2$ value. This confirms the general knowledge that the Weissenberg number at the onset of extension thickening in PEF is roughly the same as the Weissenberg number at which the shear viscosity begins to shear thin under shear flow [121].

4.3 Structural Analysis

Fig. 4.6 illustrates the changes in shape and orientation of dendrimers with 91 monomers per molecule from $\dot{\epsilon} = 0$ up to $\dot{\epsilon} = 0.08$ under planar elongational flow. Although one snapshot of a molecule is not compelling enough to draw any conclusion on flow-induced molecular deformation, but for visualization purposes one can see that at equilibrium the molecule has its own natural globular configuration and under PEF branches of the molecule stretch in the $x$ direction and compress in the $y$ direction. This results in the molecules becoming more flat and ellipsoidal in
shape rather than spherical. More evidence for the tendency to become ellipsoidal in shape is given later in this section by calculating the eigenvalues of the tensor of gyration and also by schematic 3D representations of dendrimer, hyperbranched and linear molecules under PEF and shear flow.

Fig. 4.7 shows the molecular mass dependence of the radius of gyration of dendrimer and hyperbranched polymers of generation 1-4 at equilibrium. The data reveals a \( R_g \propto M^{1/3} \) relationship for both dendrimer and hyperbranched polymers, which agrees with results reported earlier [21] and confirms a uniform distribution of mass within the dendrimer and hyperbranched molecules at equilibrium.

Fig. 4.8 presents the dependence of the radius of gyration normalized with respect to its value at equilibrium \( \langle R^2_0 \rangle \) for dendrimer, hyperbranched, and linear polymers with 19, 43, 91, and 187 monomers per molecule as a function of \( I_2 \) for elongational flow, and also as a comparison for hyperbranched molecules undergoing shear flow. \( I_2 \) is \( 8\dot{\varepsilon}^2 \) for PEF and \( 2\dot{\gamma}^2 \) for shear flow. Physically, \( I_2 \) is a measure of the rate of viscous heat dissipation in steady state flow, and accommodates the comparison between different flow types. Under PEF, the molecular size increases with \( I_2 \) for all the studied systems, and tends to saturate at higher \( I_2 \) values. The results show
Figure 4.7: Molecular mass dependence of the equilibrium radius of gyration of dendrimer and hyperbranched polymers.

that even at low $I_2$ values, molecules are stretched under PEF which reveals the strong effect of the PEF flow field on molecular deformation. Under shear flow for all studied systems, at small values of $I_2$ the averaged size of the polymer molecules fluctuates around a constant value. It is only at intermediate to high $I_2$ that the molecular size increases, but it is always smaller than its corresponding value under PEF. Differences between molecular size for hyperbranched molecules under PEF and shear flow become smaller as generation increases. This suggests that for higher generations of hyperbranched molecules the type of flow becomes less influential on molecular size. As the generation number is increased the interior of the molecule becomes increasingly crowded which makes stretching difficult. Comparing different architectures reveals that linear molecules are always larger in size than dendritic molecules and this difference in size increases as molecular weight increases (see subplots of Fig. 4.8). The higher the generation number is, the more crowded the outer shell of the molecule becomes, which results in limited movement of the branches under both types of flow. The result is a smaller increase in size for high molecular weight dendrimer and hyperbranched melts under any type of flow.
Figure 4.8: Normalized mean squared radius of gyration of linear, hyperbranched and dendrimer polymers with 19 (a), 43 (b), 91 (c), and 187 (d) monomers under PEF at different $I_2$, and also hyperbranched molecules under shear flow. Symbols represent: L △, H •, D ◆, and + for hyperbranched molecules under shear flow.
Hyperbranched molecules show a larger radius of gyration than their corresponding dendrimer molecules. This was expected due to imperfection in hyperbranched molecule architecture compared to the perfect globular architecture of dendrimers. Imperfection gives hyperbranched molecules the opportunity to use the available free volume in their interior to move and stretch more freely compared to constrained dendrimer microstructures, which results in their relatively larger size.

Neelov and Adolf [189, 190] studied structural properties of dendrimers and hyperbranched solutions under elongational flow using Brownian dynamics simulations. Their results are in qualitative agreement with data presented here for radius of gyration variations of both dendrimer and hyperbranched polymers. They found that the increase/upturn in the radius of gyration with the strain-rate is less pronounced for dendrimers than for hyperbranched molecules and less pronounced for hyperbranched molecules compared to linear counterparts, which is comparable to our findings.

As the radius of gyration is an averaged quantity over the three directions, we
can further investigate the deformation of molecules under both types of flow by calculating ratios of different eigenvalues of the tensor of gyration, which follows.

Further analysis of the tensor of gyration can provide insights into the shape and orientation of the molecules. For each system mentioned above, the eigenvalues of the tensor of gyration (in descending order, $L_1$, $L_2$, and $L_3$) were computed and averaged over the ensemble. Figures 4.9-4.11 show the changes in three different ratios of the eigenvalues as a function of $I_2$. As one can see, all these three ratios are constant at small $I_2$ values and tend to increase at higher $I_2$. At very high $I_2$ values, they tend to decrease slightly. These results reveal a very interesting point here, which is that under PEF even at low strain-rates the molecules start to deform and align themselves along the flow field (without a significant stretching) and as the strain-rate is increased the alignment occurs at shorter length scales [57] in the molecular architecture along with the stretching (leading to an increase in molecular size). Ultimately, molecules under PEF reach a state that further alignment and stretching is not possible and the eigenvalue ratios reach a plateau region. In addition, linear polymers compared to dendrimers and hyperbranched molecules show sharper increase, especially for the $L_{13}$ ratio (Fig. 4.10). This arises because dendrimers and hyperbranched polymers are structurally constrained and are not able to become fully stretched compared to linear chains. In addition, hyperbranched molecules show higher $L_{ij}$ values compared to dendrimers which implies they have a more flattened ellipsoidal shape than dendrimers.

We find that, at low to intermediate $I_2$ values, hyperbranched molecules show much lower $L_{ij}$ values under shear flow in comparison to PEF. Under shear flow and at lower $I_2$ values, these three ratios are closer to 1, which means they have a more spherical shape at low $I_2$. Under PEF, even at very low $I_2$ values, the molecules have an elongated shape and stretched configuration, contrary to the spherical shape under shear flow. By further increasing $I_2$, under both types of flow the molecules become more elongated. Only at very high $I_2$ values do the eigenvalue ratios under shear flow exceed their corresponding values under PEF. It should be noted that at high values of $I_2$, molecules are at their fully stretched and aligned states under shear flow (see Fig. 4.5 for shear thinning region under shear flow). Additionally, for
linear molecules the existence of such a sharp increase in their size is a consequence of the coiled to stretched transition which is missing in the dendritic architecture. It is important to note that higher $L_{ij}$ ratios under shear flow at very high $I_2$ compared to PEF does not imply larger hyperbranched molecules under shear flow compared to PEF. Under shear flow the molecules start to deform from a spherical shape to an ellipsoidal shape at these high values of $I_2$, which leads to a sharp increase in the $L_{ij}$ values. In contrast to shear flow, under PEF molecules are already ellipsoidal, even at lower $I_2$ values, which leads to a gradual increase in $L_{ij}$ values. Consequently, $L_{ij}$ values under PEF are smaller than their corresponding values under shear flow, at very high $I_2$.

We find that there is a specific strain rate at which these ratios start to increase. The value of this strain rate decreases as the molecular weight increases. These values are listed in Table 4.3 and will be discussed in greater detail in what follows. Also, we find that the magnitude of the increase in $L_{13}$ is much higher than for $L_{12}$ and $L_{23}$. It means that the difference between the smallest ($L_3$) and largest ($L_1$)
Figure 4.11: $L_{23}$ ratios for linear, hyperbranched, and dendrimer polymers with 19 (a), 43 (b), 91 (c), and 187 (d) monomers per chain over a wide range of $I_2$ values. Also hyperbranched molecules under shear flow. Symbols under PEF are as follows: L ▲, H ●, D ◆, and + for hyperbranched molecules under shear flow.

dimensions of the molecules becomes larger as strain rates increases. This is evidence that as the strain rates increases, the molecules become much more elongated and flattened in shape.

We can correlate the flow-induced molecular deformation with the viscoelastic behaviour of the studied systems. Comparing the $I_2$ at which the eigenvalue ratios start to rise (see Table 4.3) with the $I_2$ at which the viscosity upturn occurs provides us with very important information. We find that viscosity upturn occurs approximately at the same $I_2$ value where the eigenvalues start to rise. This indicates that the onset of molecular deformation under PEF coincides with the crossover from the Newtonian plateau to the non-Newtonian region in the viscosity curves. In addition, $\langle R_g^2 \rangle$ saturates at $I_2$ values comparable to the $I_2$ at which the ratios of different eigenvalues reach their maximum plateau. At this state, as has already been discussed, the molecules have a flattened ellipsoidal configuration. Also, thinning occurs at higher $I_2$ values when deformed molecules align themselves more strongly with the flow direction. Bosko et al. [28] studied dendrimers under shear flow and found
the same behaviour. They concluded that flow-induced deformation is the major mechanism for the observed non-linear behaviour of these molecules under shear, and molecular alignment, which occurs at all $I_2$ values, is a less effective mechanism at low to intermediate $I_2$ values.

Table 4.3: Strain-rates at which thinning $\dot{\epsilon}_{th}$, and upturn starts to occur for elongational viscosity $\dot{\epsilon}_{ut}$, ratios of different eigenvalues $\dot{\epsilon}_{L_{12i}}$, $\dot{\epsilon}_{L_{13i}}$, $\dot{\epsilon}_{L_{23i}}$, and also strain-rate at which thinning occurs in which they show maximum or a plateau behaviour $\dot{\epsilon}_{L_{12m}}$, $\dot{\epsilon}_{L_{13m}}$, and $\dot{\epsilon}_{L_{23m}}$.

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<th>$\dot{\epsilon}_{ut}$</th>
<th>$\dot{\epsilon}<em>{L</em>{12i}}$</th>
<th>$\dot{\epsilon}<em>{L</em>{13i}}$</th>
<th>$\dot{\epsilon}<em>{L</em>{23i}}$</th>
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<th>$\dot{\epsilon}<em>{L</em>{13m}}$</th>
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<td>-</td>
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<td>-</td>
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In Fig. 4.12 we visualize the flow-induced deformation of dendrimers and linear molecules under PEF, and hyperbranched molecules under both shear and PEF in terms of $L_i$ values as linear dimensions of the ellipsoid occupied by the average molecule. Dendrimer molecules under shear flow have a more spherical shape at low $I_2$, and at high $I_2$ deform to a prolate shape. Hyperbranched molecules under PEF, even at low $I_2$, have an ellipsoidal shape which becomes more flattened and prolate at higher $I_2$ values. While hyperbranched molecules have the same trend under PEF, they are more flattened compared to dendrimer molecules under the same flow conditions. By comparing different eigenvalue ratios, we find that linear molecules at low $I_2$ have a prolate shape which changes to a much more flattened ellipsoidal shape as $I_2$ increases. Hyperbranched molecules under shear flow have a more spherical shape at low $I_2$, and at high $I_2$ deform to a prolate shape. Hyperbranched molecules under PEF, even at low $I_2$, have an ellipsoidal shape which becomes more flattened and prolate at higher $I_2$ values. While dendrimers have the same trend under PEF, they are less flattened compared to hyperbranched molecules under the same flow conditions.

The distribution of mass from the central unit (core) for hyperbranched and dendrimer molecules with 19, 43, and 91 monomers per molecule at the high strain-rate of $\dot{\epsilon} = 0.004$ is shown in Fig. 4.13. The first thing to note is the correlation between the position of the core and its neighbour, which is evident through a strong peak at the distance equal to the averaged bond length for all the generations. Secondly, by increasing the generation number (i.e., layers of branches of the microstructure of dendrimers and hyperbranched molecules) we see multiple peaks in the distribution from the core, which is more significant in the case of dendrimer molecules, and is indicative of tree-like growth of layers in these molecules. For example, regardless of the first peak we see one more peak for hyperbranched and dendrimer molecules with 19 beads (representing generation 1), and so on. These peaks are due to layers of monomers within the interior of the molecular architecture of dendritic molecules. The difference between dendrimer and hyperbranched molecules is that hyperbranched molecules show a broader distribution than dendrimers i.e., the distribution is extended toward the higher distances. This stems from the fact
Figure 4.12: Schematic ellipsoids for dendrimer, hyperbranched, and linear chains with 91 monomers under PEF at low (left column) $I_2 = 8 \times 10^{-8}$ and high (right column) $I_2 = 0.0512$. For comparison we also show the hyperbranched system under shear flow at the same $I_2$ values.
**Figure 4.13:** Distribution of monomers from the core for dendrimer (a), and hyperbranched (b) with 19, 43, and 91 monomers at $\dot{\varepsilon} = 0.004$. Symbols used for different generations are as follows: 19 beads $\bullet$, 43 beads $\circ$, and 91 beads $\triangledown$.

that hyperbranched molecules can become stretched more easily than dendrimers due to their more open structure. In addition, as we already mentioned in Chapter 3, the extra monomers (beads) of hyperbranched polymers are added to the outermost shells of their structure that can further result in their extension toward higher distances.

Fig. 4.14 shows the distribution of the monomers from the core for (a) D43 and (b) H43 molecules at three different strain rates corresponding to the three different regions of rheological behaviour. It is clear that hyperbranched molecules are more strain-rate sensitive compared to dendrimers. The distribution function shifts toward the higher distances when the strain-rate is increased, which is a consequence of molecular deformation and stretched branches. This is more significant for hyperbranched molecules than it is for dendrimers. We suggest that this is also a
consequence of the perfection and constrained geometry of dendrimers that prevents them from becoming stretched as easily as hyperbranched molecules. Furthermore, one can see that the distribution of mass at $\dot{\varepsilon} = 0.004$ is significantly different from that at $\dot{\varepsilon} = 0.01$, and this is only the case for the hyperbranched system. It is important to note that this coincides with the viscosity upturn or stretching, while for dendrimers there is no maximum for the viscosity at this strain rate. These results are in full agreement with previous results reported by Le et al. [26] and Bosko et al. [28].

One of the characteristic features of dendrimers and hyperbranched polymers is the large number of their terminal groups. Their number doubles with every generation, and their chemical activity can be controlled in the process of synthesis of the molecule. From the configurational point of view, it is important to understand...
the spatial distribution of these groups because their location affects the molecule’s chemical activity and physical properties.

In Fig. 4.15, we present the distribution of terminal groups from the central unit for dendrimers and hyperbranched polymers with 19, 43, and 91 monomers per molecule at strain rate of $\dot{\epsilon} = 0.01$. For all the systems, secondary maxima are observed in the plot which indicates that not all of the end groups are located on the surface of the molecules, but rather that they can be found across the full range of distances from the central unit due to backfolding. This means that terminal groups exist everywhere throughout the interior of the molecules. This is consistent with other experimental results by Silva et al. [194] and simulation results by Timoshenko et al. [50], Le et al. [26] and Bosko et al. [28] under shear flow that
have shown similar backfolding behaviour with peaks observed in the plot of end
groups. Fig. 4.15 also shows that the intensity of the secondary and tertiary peaks
are higher for the hyperbranched polymers than for dendrimers. This suggests that
structural imperfection and existence of open spaces in the molecular structure of
hyperbranched polymers facilitate the backfolding and give rise to the corresponding
peaks.

4.4 Conclusion

The planar elongational melt rheology and structural properties of dendrimers
and hyperbranched polymer melts of different molecular weights (generations 1-
4) and their linear counterparts have been studied using a coarse-grained model and
nonequilibrium molecular dynamics (NEMD) simulation techniques coupled with the
so-called Kraynik-Reinelt periodic boundary conditions in the isothermal-isobaric
(NPT) ensemble. According to the above rheological results, it is clear that den-
drimers and hyperbranched polymers, due to their unique and compact structures,
show much lower melt viscosities in comparison to their linear counterparts, which
make them potentially useful candidates as flow modifiers and flow aid agents. The
rheological properties, including extensional viscosity and second extensional vis-
cosity, were calculated. Similar to previous experimental and simulation data for
linear polymer melts, the elongational viscosity showed three distinctive regions of
behaviour for dendrimers and hyperbranched melts: an initial Newtonian region
followed by a thickening region and terminated by a thinning region at high strain-
rates. Dendrimers, contrary to hyperbranched molecules, did not show a thickening
region in their rheological behaviour at the rates of strain studied. We related this
phenomenon to the structural perfection of dendrimers compared to hyperbranched
molecules, which caused reduced mobility of the branches and also reduced flow-
induced stretching and alignment of the molecules. Imperfection in the architecture
of hyperbranched molecules introduced some free volume that facilitated the move-
ment and stretching of the branches. We suggest that this stretching is responsible
for the thickening behaviour of hyperbranched molecules. Furthermore, the termi-
nal thinning behaviour is related to the finite extensibility of the FENE potential and flow-induced alignment. In addition, we fitted our simulation results with the Sarkar-Gupta model to calculate the adjustable parameters of this model from our normalized extensional viscosity data over a wide range of strain-rates. The longest relaxation times for dendrimers and hyperbranched molecules were calculated from the model parameters and were in a good agreement with those calculated from the zero-shear rate normal stress coefficients.

In addition to the rheological behaviour, structural changes under PEF and shear flow were analysed using different standard distribution functions, and also the eigenvalues of the tensor of gyration. The ratios of the eigenvalues demonstrated that, under shear flow, hyperbranched molecules change their shape from a more spherical conformation to a prolate ellipsoidal conformation as the strain rate increases. Under PEF, even at low strain rates, molecules were ellipsoidal in shape and by increasing the elongation rate they became much more flattened and prolate. Dendrimers showed the same changes in their shape but they were less flattened. Linear molecules were more elongated compared to hyperbranched and dendrimer molecules at low elongation rates, while changing to a much more flattened ellipsoidal shape at higher strain rates. We also studied the distribution of monomers from the core of the molecules under PEF at three different strain rates corresponding to the three different regions of the rheological behaviour of dendrimers and hyperbranched molecules. Generally, the distance of monomers from the core increases more significantly for hyperbranched molecules than for dendrimers. This arises from the fact that hyperbranched molecules can stretch and align themselves in the flow direction more easily than dendrimers due to their less constrained molecular architecture. Finally we showed the existence of the typical backfolding phenomena for dendrimers and hyperbranched polymers under PEF. End groups were found across the full range of distances within the interior of the molecules rather than just at the outermost regions of the molecules.
Chapter 5

Dendrimer-Linear Polymer Blends Under Shear Flow

5.1 Dendrimer-Linear Blend Model

In this chapter, the nonequilibrium molecular dynamics (NEMD) simulation results for the miscibility, structural properties, and melt rheological behaviour of polymeric blends under shear flow are presented. The polymeric blends consist of linear polymer chains (187 monomers per chain) and dendrimer polymers of generations \( g = 1-4 \). The number percentage \( x \) of the dendrimer species is varied (4%, 8%, and 12%) in the blend melt.

Blend systems of 125 molecules were generated at low density, they were compressed to the monomer number density of \( \rho = 0.84 \). Afterwards, the barostat was switched on and the systems were equilibrated for typically several million time steps and the pressure was plotted against time to ensure the system had reached equilibrium. Finally, shear flow was applied, and after reaching the nonequilibrium steady state, ensemble averages of all properties of interest were calculated by averaging over typically 30 independent NEMD steady-state trajectories. In order to make
sure that simulation runs are long enough for phase separation to occur between dendrimer and linear species, we examined the diffusion coefficient $D$ of dendrimer species in the blend melt via velocity autocorrelation calculations. For example, for the blend system $12D187B$ the diffusion coefficient is $D = 9.6 \times 10^{-4}$, which means it takes dendrimers around 15,000 time unit to diffuse across the box. Therefore, 30 million simulation steps (where, time step $\Delta t = 0.001$) equal 30,000 time units, which is twice the required time for the phase separation to occur. However, we did not see any sign of phase separation or aggregation of dendrimers in our visualizations. In addition, we used some quantitative methods to investigate the phase stability of dendrimer/linear blend melts, which are discussed later in the next section. The temperature and pressure were fixed at 1.25 and 5.42, respectively (in reduced units) for all systems studied.

Details of blended systems can be found in Table 5.1.

Fig. 6.1 shows snapshot configuration of the blend system $12D187B$ (notation as given in Table 5.1) at equilibrium and under shear, where one can see how the box becomes deformed in the flow direction, and how the chains themselves stretch under flow.

### 5.2 Free Volume Calculations

Table 5.2 presents the volume per monomer in the pure melt of dendrimers $V_{m,D}$ of generation 1-4 and the volume per monomer in the linear polymer (with 187 beads per chain) melt $V_{m,L}$ at equilibrium. In the last column of the Table 5.1 the volume of the blend systems obtained from the MD simulations are shown. We used a simple mixing rule for the volume of the blend systems, $V_B = N_D V_{m,D} + N_L V_{m,L}$, where $N_D$ and $N_L$ are the total number of monomers, which belong to dendrimers and linear species, respectively in the blend. The mixing rule predicts 22468, 22899, 23749, and 25462 values for the volume of the blend systems $12D19B$, $12D43B$, $12D91B$, and $12D187B$, respectively. These predicted values for the volume of the blend systems are less than those values obtained from the MD simulations. This difference reveals
Figure 5.1: Snapshot configuration of blend system 12D187B, at (a) equilibrium and (b) $\dot{\gamma} = 0.0001$. Red balls represent beads of dendrimer molecules while the blue ones show beads of linear chains.
Table 5.1: Number, reduced molecular mass of blend species, dendrimer number percentage $x$ and mass percentage $c$, blend species equilibrium size ratio $R_g,L/R_g,D$, and volume $V$ for all the simulated systems. The leading number in the first column is the number percentage of dendrimers in the blend system.

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<th>$N_L$</th>
<th>$M_D$</th>
<th>$M_L$</th>
<th>$x$</th>
<th>$c$</th>
<th>$R_g,L/R_g,D$</th>
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the development of free volume in the blend due to the presence of dendrimer species in the melt of dendrimer-linear blend systems. More importantly, the difference between the predicted and simulation results are 2380, 2369, 2368, and 2357 for the blend systems 12D19B, 12D43B, 12D91B, and 12D187B, respectively. This means that the amount of dendrimer-induced free volume in the blend is higher for blends containing dendrimers of lower generations. This is an extremely important result as the amount of the free volume in the system determines the level of the molecular motion, inter-penetration of the blend species, and even the viscosity of the blend system.

In addition, in order to investigate the effect of dendrimer concentration on the free volume of the system, we calculated the volume of the blend systems 4D187B,
8D187B, and 12D187B according to the mixing rule, where we obtained 25250, 25356, and 25461, respectively. Consequently, the difference between the volume obtained from the MD simulations and the mixing rule calculations are 2146, 2260, and 2357 for the blend systems 4D187B, 8D187B, and 12D187B, respectively. Therefore, we can conclude that higher concentration of dendrimer in the blend produces more free volume in the system.

Table 5.2: Volume per monomer in pure dendrimer $V_{m,D}$ and linear $V_{m,L}$ polymer melts at equilibrium.

<table>
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<tr>
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<th>D91</th>
<th>D187</th>
<th>L187</th>
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<td>1.1889</td>
<td>1.1887</td>
<td>1.0757</td>
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</table>

### 5.3 Miscibility and Interpenetration

Fig. 5.2 represents the $g_{DL}$, $g_{LL}$, and $g_{DD}$ distribution functions (defined in Chapter 2) at equilibrium for blend systems 12D19B and 12D187B, where the notation is as defined in Table 5.1. Fig. 5.2a shows that for the blend system containing the lowest generation of dendrimer (D19), and at smaller separations, $g_{DL}$ is greater than both $g_{LL}$ and $g_{DD}$. According to Akten and Mattice [113], this implies the formation of a miscible blend. On the other hand, for the blend containing the highest generation of dendrimer (D187), only after a specific distance (approximately, equal to the radius of gyration of the dendrimer, see Fig. 5.7), does $g_{DL}$ become greater than both $g_{LL}$ and $g_{DD}$, which reveals a very interesting aspect of the architecturally different D/L polymer blend species (Fig. 5.2b). In addition, for the 12D19B system and at higher distances ($r > R_g$), $g_{DD}$ is greater than $g_{DL}$, and for 12D187B, at lower distances, $g_{LL}$ is higher than $g_{DL}$. These trends are expected due to the tree-like architecture of dendrimer molecules and do not necessarily indicate the immiscibility of the blend species. In addition, based on the analytical studies of Vlahos and Kosmas [117] for chemically identical blend species with different architecture, no phase separation is predicted for star/linear blends, and one might be able to extend their approach
for dendrimer/linear blends, especially for blends containing dendrimers of lower generations which are architecturally more similar to star polymers.

In order to investigate the effect of dendritic architecture and generation of dendrimer species on blend miscibility and distribution functions, the $g_{DD}$ distribution for blends containing the same number percentage ($x = 12\%$) of dendrimers but different generations are presented in Fig. 5.3. This figure shows that the height of the peaks decreases upon increasing the generation (or molecular weight) of the dendrimer. The peaks tend to move toward higher values of the separation and become weaker for higher generations. The location of the second peak correlates approximately with the radius of gyration of the dendrimer molecules (see Fig. 5.7) in the blend. This observation, in combination with the fact that dendrimers have a crowded surface due to the high number of end groups which doubles with each gen-

Figure 5.2: The $g_{DL}$, $g_{LL}$, and $g_{DD}$ distribution functions for blend systems of (a) 12D19B and (b) 12D187B, at equilibrium.
eration, suggest that dendrimer beads (more specifically, higher generations) are not inter-penetrating deeply toward the lower shells of the other dendrimer molecules and are correlated only at higher separations. This also makes it difficult for linear chains to penetrate into the interior of dendrimer molecules of higher generations. Consequently, it leads to the higher $g_{LL}$ than the $g_{DL}$ at low distances for 12D187B blend system, as linear chains do not have such an architectural barrier for inter-penetration. Therefore, a higher $g_{LL}$ or $g_{DD}$ than $g_{DL}$ at some specific distances does not necessarily imply that D/L blends are not miscible. More importantly, our dendrimer and linear molecules have the same chemical nature and there are no energy differences between these two species (athermal limit) to cause immiscibility. Based on the above arguments, we conclude that our systems form miscible blends. This is supported by the fact that at long distances all of the distribution functions approach 1, as there are no long-range correlations, implying the absence of phase-separated regions. Additionally, Mackay et al. [119] derived a polymer radius of gyration - branched polymeric nanoparticle radius phase diagram, in which they highlighted the importance of the size ratio between the linear and branched polymeric nanoparticle in phase-separation, that $R_{g,L} > R_{g,D}$ is necessary to obtain a miscible blend. It is important to note that dendrimers, due to their globular constrained shape and unique inter-connected structure, show particle like behaviour along with their macromolecular characteristics. The blend species size ratio $R_{g,L}/R_{g,D}$ (presented in Table. 5.1) for our blend systems locates in the miscible region of the phase diagram reported in a work by Mackay et al. [119] and which supports our argument.

Fig. 5.4 compares the $g_{c,DL}$ function (defined in Chapter 2) for blends with dendrimers of different generations; 12D19B, 12D43B, 12D91B, and 12D187B, at equilibrium. It shows that the interpenetration between D-L pairs strongly depends on the molecular weight of the dendrimer species in the blend and increases when the generation of dendrimer species in the blend is reduced. As already mentioned, the surface of dendrimer molecules become more compact with increasing generation number [28]. With the increase in the density of the outermost shell of a dendrimer with generation number due to the high number of end groups, the interior becomes less accessible. This explains why the peaks become weaker in the $g_{DL}$ distribution
Figure 5.3: The $g_{DD}$ distribution functions for blend systems of (a) 12D19B, (b) 12D43B, (c) 12D91B, and (d) 12D187B at equilibrium.
upon increasing the generation (molecular mass) of the dendrimer species in the DL blend systems. In addition, as first predicted by Goddard et al. [195], dendrimers are subject to a congestion-induced molecular shape transform from flat, loose conformations to robust spheroids as the generation number increases. The shape crossover was succeeding proven by different measurements (Turro et al. [196], and Hawker et al. [197]), which further supports a reduced chance of inter-penetration due to the increased generation (molecular mass). In addition, based on our volume calculations we showed that blends containing dendrimers of lower generations possess more free volume compared to those containing dendrimers of higher generations, which can facilitate molecular motion and hence inter-penetration.

Fig. 5.5 shows the effect of shear rate (\(\dot{\gamma}\)) on \(g_{c,DL}\) for the 12D187B blend system. It reveals that the \(g_{c,DL}\) distribution is much greater for blend systems under
Figure 5.5: The $g_{c,DL}$ distribution functions for blend system of 12D187B at equilibrium and different shear rates.

The influence of shear compared to its value at equilibrium, and inter-penetration increases upon increasing $\dot{\gamma}$, which is evident through the larger first peak. Under shear, the dendrimer molecules become stretched, therefore more open, and parts of other molecules can come closer to their centres. In addition, it shows that when the shear rate is increased, the secondary and tertiary peaks at higher distances tend to disappear while the first peak increases, and this is because lower distances become more accessible for linear chains.

### 5.4 Structural Analysis

One of the characteristic features of dendrimers is the large number of their terminal groups. Fig. 5.6 shows the $g_{\text{end}}(r)$ distribution functions (defined in Chapter 2) for dendrimer molecules in the blend systems: 12D19B, 12D43B, 12D91B, and 12D187B, at $\dot{\gamma} = 1 \times 10^{-5}$. The inset plot shows the $g_{\text{end}}$ distribution function for dendrimer molecules of generation 2 in their pure melt, at the same shear rate. The
Figure 5.6: Distribution of terminal groups $g_{\text{end}}$ of dendrimer molecules in the blend systems; $12D19B$, $12D43B$, $12D91B$, and $12D187B$, at $\dot{\gamma} = 1 \times 10^{-5}$. Inset shows the $g_{\text{end}}$ of dendrimer molecules of generation 2 in their pure melt.

The most significant feature of these distribution functions is that comparing the end group distribution for dendrimers of generation 2 in the pure melt (inset plot) to its distribution in the blend melt reveals that back-folding is suppressed significantly upon blending dendrimers with linear chains. This further confirms the opened up configuration of dendrimers in the presence of linear chains and that interpenetration is higher when blending linear chains with dendrimers of lower generations. Similar suppressed backfolding was reported by Chai et al. [24] for dendrimers in good solvent.

In Fig. 5.7 the radius of gyration of both linear and dendrimer molecules in the blend melt at constant monomer number density $\rho = 0.84$ are normalized with their corresponding value $R_{g,0}$ in the pure melt of the linear and dendrimer molecules at constant number density $\rho = 0.84$, respectively and are plotted against the number percentage of the dendrimer in the blend. It is clear that the radius of gyration of linear molecules increases in the presence of dendrimers. This increase is less when the content of dendrimer increases in the blend. The amount of size increase for
Figure 5.7: Radius of gyration for $L_{187}$ and dendrimer species in the blend normalized with their corresponding values in their pure melt against dendrimer number percentage in the blend, at equilibrium. $L_{187}$, $D$. (a) $xD_{19}B$, (b) $xD_{43}B$, (c) $xD_{91}B$, (d) $xD_{187}B$. 
linear molecules is higher when blended with dendrimers of lower generations. On the other hand, dendrimer molecules are slightly contracted compared to their size in their pure melt at low $x$ and increases when their content increases in the blend. Qualitatively, the dendrimer molecules behave as a solvent to swell the polymer chains, which is correlated with the molecular mass and the number percentage of the dendrimers in the blend. This means that the low dendrimer mass fractions and lower generations promote swelling of the linear molecules, presumably due to being a better solvent in this limit. These trends resemble the trends observed for the dendritic PS nanoparticles dispersed in the linear PS reported by MacKay et al. [120]. They attributed this behaviour to the excluded volume effects and nanoparticle mobility and mixing entropy in the system. A similar mechanism would be attributed to our athermal blend systems. Nakatani et al. in their study of polysilicate nanoparticles blended with PDMS also noted that the condition $R_{g,L} > R_{g,D}$ is necessary for chain swelling and they also observed that low nanoparticle concentrations promote chain swelling, probably due to better dispersion of nanoparticles at lower concentrations [198].

Fig. 5.8 shows the radius of gyration as a function of shear rate for $L_{187}$ species and dendrimers of generation 1-4 (a-d) in the blend systems; $12D_{19}B$, $12D_{43}B$, $12D_{91}B$, and $12D_{187}B$. At lower shear rates, the size of both dendrimer and linear molecules tend to fluctuate around a constant value and after a certain shear rate, which corresponds to the shear rate at which viscosity shear thins (see Fig. 5.11) their size increases. Constant size at lower shear rates can be explained in terms of competing mechanisms i.e., rotation due to vorticity and stretching. Apparently, at lower shear rates these mechanisms compensate each other’s effects on molecular size, and only at higher shear rates does the molecular size increase. The shear-induced chain expansion is more significant for linear chains than for dendrimers, because it is much easier to deform linear chains compared to constrained globular shape dendrimers [28, 59]. In addition, the shear rate at which the radius of gyration increases, decreases by increasing the generation number.

The shear rates at which stretching occurs for both linear and dendrimer species at $x = 12\%$ can be compared with their corresponding values in their pure melt.
Figure 5.8: Root mean-squared radius of gyration for $L_{187}$ and different generations of dendrimer against the strain rate in the blend systems at equilibrium. $L_{187}$ $D$ $12D19B$, (b) $12D43B$, (c) $12D91B$, (d) $12D187B$. 
5 Dendrimer-Linear Polymer Blends Under Shear Flow

The results reveal that stretching starts approximately at the same shear rate, dendrimer molecules are more stretched in the blend than they are in their pure melt, but linear molecules have approximately the same size.

Fig. 5.9 shows the shear-rate dependent size ratio between linear and dendrimer molecules for the blend systems at $x = 12\%$; 12D19B, 12D43B, 12D91B, and 12D187B. It is clear that the size ratio first slightly decreases and then increases as the shear rate increases. However, this is only true above a critical strain rate for each system. The shear-induced increase in size ratio moves our blend systems further toward the miscibility region in the Mackay et al. [119] phase diagram. Therefore, this suggests that shear flow improves the miscibility.

We further examine changes in $L_{13}$ as a function of $\dot{\gamma}$ for linear molecules in the blend systems 12D19B, 12D43B, 12D91B, and 12D187B in Fig. 5.10. The value of $L_{13}$, which can be interpreted as the aspect ratio of the molecules, decreases at small $\dot{\gamma}$ values and tends to increase at higher $\dot{\gamma}$ values. Rotation of the molecules
Figure 5.10: The $L_{13}$ values of the tensor of gyration for linear molecules against the shear rate for blend systems at constant dendrimer number percentage $x = 12\%$ (a) 12D19B, (b) 12D43B, (c) 12D91B, and (d) 12D187B.

at lower shear rates is responsible for the initial decrease in $L_{13}$, and the following increase suggests that after a certain shear rate (corresponding to the shear rate at which thinning occurs), stretching is the dominant phenomenon under shear flow. Both the $L_{12}$ and the $L_{23}$ show similar patterns as $L_{13}$ does, which for the sake of space are not shown here.
5.5 Rheological Behaviour

5.5.1 Shear Viscosity

The shear viscosity and first and second normal stress coefficients are defined in Chapter 2. In Fig. 5.11, the shear viscosity is plotted against shear-rate for dendrimer-linear blend melts. Blends are composed of linear chains with 187 beads per chain and dendrimers with (a) 19, (b) 43, (c) 91, and (d) 187 beads per molecule at three different number percentage (x) of 4%, 8%, and 12%. For comparison, the shear viscosity data for the melt of pure linear (L187) and pure dendrimers (D19, D43, D91, and D187) are also presented. All of the systems studied exhibit a transition from the Newtonian regime at small shear rates to the non-Newtonian regime at high shear rates. Melt rheological properties including the shear viscosity (Fig. 5.11) and first (Fig. 5.14) and second (Fig. 5.15) normal stress coefficients obtained from constant pressure simulations were found to fall into the range between those of pure dendrimer and pure linear polymer melts. Replacing linear polymers with dendrimers in blends results in a drastic reduction in the blend viscosity. We suggest that two factors can be responsible for this reduction. The first and most important factor is related to the replacement of high molecular weight linear chains with dendrimers of lower viscosity. The second factor involves the increased free volume in the system introduced by the dendrimers, along with their effect on the change in the conformation of linear chains (discussed earlier). Mackay et al. [118] observed a similar reduction in viscosity in the presence of branched polymer nanoparticles. They reported that entanglement did not change at all, suggestive of unusual polymer dynamics induced by nanoparticles [118]. In addition, Merkel et al. [199] also reported the critical role of the free volume on determining the rheological behaviour of their nanocomposite system [199]. They showed that the fractional free volume due to the addition of nanoparticles is approximately ${3}\phi\Delta/R_{np}$, where $\Delta$ is the thickness of an assumed spherical excluded volume around each nanoparticle, $R_{np}$ is the radius of the nanoparticle and $\phi$ is the volume fraction of nanoparticles in the system. An analogous relationship can be assumed for dendrimer-linear blends, where we
replace the radius of the nanoparticles with the radius of gyration of the dendrimer molecule. Consequently, the fractional free volume is increased by approximately \(3\phi\Delta/R_{g,D}\) [118], where \(\Delta\) is the thickness of an assumed spherical excluded volume around each dendrimer, \(R_{g,D}\) is the radius of gyration of the dendrimer and \(\phi\) is the volume fraction of dendrimers in the system. It is clear that the fractioned free volume increases in the system when the size of the dendrimer decreases. This further supports our viscosity data showing that lower generations of the dendrimers are more effective in reducing the blend viscosity and the reduction in viscosity is higher for blends containing a higher volume fraction of the dendrimers.

In Fig. 5.12 the Carreau-Yasuda model [121] is fitted to the data points. 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. Their values as well as the zero-shear rate viscosities for all studied systems are presented in Table 5.3. For all the blend systems, the exponents in the power law region increase with the molecular mass of the dendrimer \((M_D)\) in the blend at all the \(x\) values, which is in agreement with the results obtained by Bosko et al. [28] for pure dendrimer melts. We also observed that the higher values of \(x\) for the dendrimers in the blend result in the lower power law exponent values for the blend. In other words, this trend confirms findings of other authors that the absolute values of the power law exponents are larger for linear polymers compared to dendrimers [28, 57, 200, 201]. Therefore, based on these findings we can conclude that by increasing the amount of the dendrimers in the blend shear thinning behaviour becomes less pronounced compared to a pure linear melt.

Although the absolute values of the viscosity depend on the actual thermodynamic state point, the flow curves can be superimposed on one master curve [121, 202] as also shown in Fig. 5.12. Therefore, though the simulations were performed only at one single thermodynamic point (single pressure, temperature), the results obtained are characteristic for particular molecules comprising the fluid. Fig. 5.12 shows the shear viscosity normalized by its corresponding zero-shear rate viscosity against Weissenberg number \((Wi = \lambda\dot{\gamma})\) and also fitted to the Carreau-Yasuda model for different dendrimer-linear blends. For better clarity the master curve has been
Figure 5.11: Strain-rate dependence of shear viscosity for pure linear (L187), pure dendrimer (D), and for L/D blend systems for 4%, 8%, and 12% of dendrimer molecules with 19 (a), 43 (b), 91 (c), and 187 (d) monomers per molecule. Symbols in each subplot represent: L +, 4DgB ◦, 8DgB ●, 12DgB ◆, pure D ▲.
Table 5.3: Carreau-Yasuda model parameters for pure D and L melts and DL blend systems.

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divided into 4 sub-figures (each sub-figure corresponds to blends composing different number percentage of a specific generation of dendrimer). The most important feature of these plots is that the non-linear shear thinning regions for the blend systems are not collapsing on top of each other (compared to the pure melts of dendrimers of generations 1-4 (previous chapter)), revealing that the mass fraction of dendrimer in the blend has a great impact on the rheological behaviour of these blend systems. One should note that the strain-rate has been normalized with respect to the longest relaxation time of the blend to define a single Weissenberg
number, and this Weissenberg number is not correlated with the relaxation of any of the single components in the blend.

Another interesting feature of the shear viscosity versus shear rate for blend systems is that the blend melts have smaller relaxation time (presented in Table 5.3) compared to pure linear (not captured but approximately $\lambda \gg 1,000$) and longer compared to corresponding pure dendrimer melts (70, 350, 570, and 1422 for dendrimers of generation 1-4, respectively). Dendrimer-induced free volume manifests itself through reduction in longest relaxation time of the system compared to the pure linear melt. Fig. 5.13 presents the time constants obtained from the shear viscosity data fitted to the Carreau-Yasuda model [121] versus number percentage of the dendrimers in the blend. The time constant is proportional to the longest relaxation time of the molecules composing the fluids [28]. Fig. 5.13 shows that by increasing the number percentage of dendrimers in the blend the relaxation time decreases. This further implies the importance of increase in the free volume of the system which is directly related to the number and molecular weight of dendrimer molecules in the blend.

5.5.2 Normal Stress Coefficients

In Fig. 5.14 the log-log plot of the dependence of the first normal stress coefficient on strain rate for dendrimer-linear blends and pure systems of linear polymer L187 and dendrimers of generations 1-4 is shown. Fig. 5.15 illustrates the second normal stress coefficient versus strain rate for the same systems. For all systems the normal stress coefficients have large power law regions. Linear functions were fitted to the data in the power law region, and from the slopes, the exponents of the asymptotic dependences

$$\Psi_1 \propto \dot{\gamma}^{-\alpha}$$  \hspace{1cm} (5.1)

and

$$|\Psi_2| \propto \dot{\gamma}^{-\beta}$$  \hspace{1cm} (5.2)
Figure 5.12: Normalized shear viscosity against Weissenberg number for pure linear (L187), pure dendrimer (D), and for L/D blend systems for 4%, 8%, and 12% of dendrimer molecules with 19 (a), 43 (b), 91 (c), and 187 (d) monomers per molecule. Symbols in each subplot represent: L +, 4DgB ◀, 8DgB ●, 12DgB ◆, pure D ◆.
were derived. The values obtained are presented in Table 5.4. The absolute values of the first and second normal stress coefficients are usually smaller for dendrimers than for linear molecules [28]. A similar decrease in the normal stresses of branched polymers, compared to linear polymers, was also observed by Jabbarzadeh et al. [203]. This can be attributed to the globular shape of the dendrimers and their internal bond constraints, which prevent large stretching of the molecules and in turn lead to smaller differences between the diagonal elements of the stress tensor. Table 5.4 shows that these exponents for the blend systems compared to the pure linear system are slightly affected by the addition of the dendrimers and decrease with increasing $x$ of the dendrimers in the blend and also increase with the mass (or generation number) of the dendrimers. The values of these two exponents lay in the range reported for linear chains by Kroger et al. [57] and Bosko et al. [25].
Figure 5.14: First normal stress coefficient against shear rate for L/D blend systems for 4%, 8%, and 12% of dendrimer molecules with 19 (a), 43 (b), 91 (c), and 187 (d) monomers per molecule. Symbols in each subplot represent L+, 12DgB ●, 8DgB ●, 4DgB ●, pure D ●.
Figure 5.15: Second normal stress coefficient against shear rate for L/D blend systems for 4%, 8%, and 12% of dendrimer molecules with 19 (a), 43 (b), 91 (c), and 187 (d) monomers per molecule. Symbols in each subplot represent: L+, 4DgB, 8DgB, 12DgB, pure D. 

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Table 5.4: 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 DL blends and pure systems ($\rho = 0.84, T = 1.25$).

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<td>1.483</td>
</tr>
</tbody>
</table>

5.6 Conclusion

We used nonequilibrium molecular dynamics simulations to investigate the miscibility, structural properties, and rheological behaviour of polymeric blends composed of linear polymer chains (187 monomers per chain) and dendrimer polymers of generations ($g$) 1-4 at different number percentage of dendrimers ($x$) (4%, 8%, and 12%) undergoing shear flow in the NPT ensemble [204]. We calculated the dendrimer-induced free volume in the blend from the difference between the volume calculated from a mixing rule and data obtained from the equilibrium simulations. Free volume data revealed that blends containing higher number of dendrimers of lower generations possess more free volume in their melt, which significantly affects the molecular motion, inter-penetration, and viscosity of the blend systems. We studied the miscibility of the blends, using the radial distribution function $g_{DL}$, $g_{LL}$, and $g_{DD}$
obtained from configurational snapshots after reaching a steady state. For all the systems studied, $g_{DL}$ was higher than both $g_{LL}$, and $g_{DD}$ at some specific distances, which demonstrates that linear chains and dendrimers under the conditions investigated are miscible. The size ratio between linear and dendrimers is a determining parameter on blend miscibility, which has been reported earlier by several authors [118, 198]. The $R_{g,L} > R_{g,D}$ condition is required to get a miscible blend, which was the case for all our blend systems. From a thermodynamic point of view, since our blend species had the same chemical nature, the entropy of mixing was a dominant term in the free energy of mixing, which has been promoted in the presence of lower molecular weight dendrimers. The $g_{c,DL}$ pair distribution functions were analysed to study the effect of dendrimer molecular mass and shear rate on interpenetration of linear chains toward the dendrimer interior. We observed higher interpenetration between linear and dendrimer molecules for lower generations of dendrimer, due to the surface congestion effect and a higher amount of back-folding for higher generations. In addition, shear flow increased the inter-penetration between linear and dendrimer species, as stretched dendrimer molecules have more open spaces compared to their undisturbed architecture. We further studied flow-induced molecular deformation of both linear and dendrimer molecules by calculating the radius of gyration and eigenvalues of the tensor of gyration under shear flow. Shear-induced molecular deformation is a consequence of competition between two effects; rotation and stretching. We observed that at lower shear rates, molecular rotation dominates and the molecular aspect ratio decreases, but after a certain shear rate, stretching is dominant and the molecular size increases at a greater rate for linear chains compared to dendrimers. This was expected, as we showed in our previous paper [59] that linear molecules can be stretched more easily compared to dendrimers of more constrained geometry. Melt rheological properties including the shear viscosity and first and second normal stress coefficients obtained from constant pressure simulations were found to fall into the range between those of pure dendrimer and pure linear polymer melts. A small amount of dendrimer added to the melt of the linear chains significantly reduced the shear viscosity of the blend system compared to the pure high molecular weight linear melt. This drop in the viscosity was correlated with the number percentage of dendrimers in the blends and also with the geometry
and generation of the dendrimer molecules. Blends containing a higher amount of dendrimer molecules of lower generations show much lower melt viscosities. The free volume introduced by the globular shape dendrimers in the system was found to be an important factor in reducing the blend viscosity and was reported earlier by Mackay et al. [118] and Merkel et al. [199] for similar systems. The amount of the dendrimer-induced free volume in the system is higher for dendrimers of lower generations, which further explains trends observed in the rheological behaviour of dendrimer/linear blend systems.
Chapter 6

Dendrimer-Linear Polymer Blends Under Planar Elongational Flow

6.1 Dendrimer-Linear Blend Model

In this chapter the structural origin of the planar elongational rheology of model polymer blends are investigated through nonequilibrium molecular dynamics (NEMD) simulations. Details of the blend systems are the same as in the previous chapter.

Fig. 6.1 shows the schematic configuration of the blend system 12D187B (notation as given in Table 5.1) at equilibrium, and under low and high extensional strain rates, where one can see how the box becomes deformed and stretched along the flow direction by applying the planar elongational flow.
Figure 6.1: Illustration of stretched configurations for the blend system 12D187B, at (a) equilibrium, (b) $\dot{\epsilon} = 0.00001$, and (c) $\dot{\epsilon} = 0.0004$. Red spheres represent beads of dendrimer molecules and the blue ones show beads belonging to the linear chains.
6.2 Structural Analysis

Several authors have conducted experimental and molecular dynamics studies to investigate the volumetric and rheological dilatancy in dense atomic and molecular fluids [58, 167, 205]. Knauss and Emri [205] discussed the nonlinear viscoelastic behaviour of dense polymer melts in terms of the stress-induced dilation, which affects the mobility of molecular chains through changes in the free volume in the polymer. Daivis et al. [64] studied both shear and planar extensional rheology of their model linear chain polymers under both constant volume and constant pressure conditions. They showed that at sufficiently low reduced strain-rates, the pressure was quadratic in the strain rate for shear and elongational flows. In Fig. 6.2 variations in the volume are presented against the second scalar invariant of the strain-rate tensor $I_2$, for blends undergoing (a) PEF and (b) shear flow. Fig. 6.2 shows that under PEF, the volume of the blend is constant at low values of $I_2$, and beyond a critical value $I_{2,c} = 3.2 \times 10^{-9}$ increases rapidly. Under shear flow, the volume is constant at low $I_2$ values and starts to decrease slightly beyond a critical value $I_{2,c} = 7.2 \times 10^{-7}$ for each system. It is important to note that the $I_2$ value at which the volume increases under PEF is smaller than the $I_2$ value at which volume decreases under shear flow, because different mechanisms are responsible for each of these phenomena. Under PEF the critical $I_{2,c}$ coincides with the viscosity upturn while under shear flow the $I_{2,c}$ coincides with the start of the shear thinning phenomenon. We can say that for both flows the critical $I_{2,c}$ where volume of the system starts to deviate from its equilibrium value, corresponds to the start of a non-linear effect (i.e. elongation-thickening and shear-thinning under PEF and shear flow, respectively) for the blend melts.

Following from the above discussion, it is crucial to investigate the effect of dendrimer concentration in the blend on the variations of the system volume. For this reason, Fig. 6.3 presents the $I_2$ dependent volume of the melt for blends composed of linear polymers and dendrimers with 187 beads per molecule at different number percentage $x = 4\%, 8\%$, and $12\%$ of the dendrimer in the blend. Blends containing the higher amount of dendrimer show higher volume under both flow conditions.
Figure 6.2: The $I_2$ dependent system volume at equilibrium for blends composed of linear polymers with 187 beads per chain and dendrimers of generations 1-4. (a) Under PEF and (b) Under Shear flow.
We suggest that the increase in the volume of the system is a result of the increase in the free volume of the system due to the presence of the dendrimer molecules. Dendrimers, particularly of higher generations (which is the case in this plot) have a globular shape that is similar to spherical nanoparticles. Increased free volume in the system in the presence of nanoparticles have been previously reported by several authors [118, 199] and plays a crucial role in determining the rheological properties of our blend systems, which are discussed in more detail in Section 6.3.

Fig. 6.4 compares the $g_{c,DL}$ function for the blend systems 12D187B, 8D187B, and 4D187B, at $\dot{\varepsilon} = 2 \times 10^{-4}$. It shows that as the number percentage of dendrimer species in the blend is increased, the initial peak tends to increase. Merkel et al. [199] showed that the fractional free volume due to the addition of nanoparticles is approximately $3\phi \Delta /R_{np}$, where $\Delta$ is the thickness of an assumed spherical excluded volume around each nanoparticle, $R_{np}$ is the radius of the nanoparticle and $\phi$ is the volume fraction of nanoparticles in the system. An analogous relationship can be assumed for dendrimer-linear blends, where we replace the radius of the nanoparticles with the radius of gyration of the dendrimer molecule. It is clear that fractional free volume increases in the system when the volume fraction of dendrimers increases in the blend. Therefore, an increased number of dendrimer species in the blend leads to an increase in the fractional free volume of the system [199], which can facilitate linear chains motion in the blend melt, and consequently leads to more interpenetration. This can be further explained in terms of the dendrimer induced free volume in the system that we showed (previous chapter) as the number percentage of the dendrimer is increased the amount of the dendrimer-induced free volume is increased that enhances motion of the chains in the blend.

Fig. 6.5 compares the $g_{c,DL}$ function for blend systems; 12D19B, 12D43B, 12D91B, and 12D187B, at $\dot{\varepsilon} = 1 \times 10^{-5}$. It shows that inter-penetration increases when the generation of the dendrimer in the blend decreases, which is evident through the increased intensity of the first peak. Under PEF compared to the equilibrium and shear flow (for equilibrium and shear results, we refer the reader to the previous chapter) the molecules become stretched and possess a more open configuration, which is more significant for dendrimers of lower generations at the same
Figure 6.3: The $I_2$ dependent system volume at equilibrium for blends composed of linear polymers and dendrimers with 187 beads per molecule at different number percentage of dendrimers in the blend. (a) Under PEF and (b) Under Shear flow.
Figure 6.4: The $g_{c, DL}$ distribution for the blend systems; 12D187B, 8D187B, and 4D187B, at $\dot{\epsilon} = 2 \times 10^{-4}$. 
Figure 6.5: The $g_{c,DL}$ distribution for the blend systems; 12D19B, 12D43B, 12D91B, and 12D187B, at $\dot{\epsilon} = 1 \times 10^{-5}$. 
Figure 6.6: Comparison of the $g_{c,DL}$ distribution for the blend system 12D187B, under both PEF and shear flow, at $I_2 = 8 \times 10^{-8}$.

strain-rate. This is due to the more crowded surface of the dendrimer of higher generation (possessing a higher number of end groups), which prevents other molecules from penetrating closer to its interior. Similar trends were observed for the same systems at equilibrium in the previous chapter. However, initial peaks are increased under PEF compared to equilibrium and confirm the positive influence of the PEF on inter-penetration.

Fig. 6.6 compares the influence of different flow fields, i.e. PEF and shear flow on the interpenetration between the blend species, at constant $I_2 = 8 \times 10^{-8}$. It is clear that PEF is more effective than shear flow in enhancing the interpenetration, which is evident through the strong initial peak. This can be attributed to the flow-induced deformation of both species under different flow fields. In the previous chapter, we showed that dendrimer molecules are more stretched and opened up under PEF than they are under the shear flow [59]. In addition, linear chains are also more stretched.
Figure 6.7: The root mean-squared radius of gyration for $L_{187}$ molecules and different generations of dendrimer species against $\dot{\epsilon}$ in the blend, at fixed $x = 12\%$. (a) $12D_{19}B$, (b) $12D_{43}B$, (c) $12D_{91}B$, and (d) $12D_{187}B$. $L_{187}$, $D$. Open symbols show the corresponding values at their pure melt. Error bars are smaller than the symbol size for some data presented here.
and elongated under PEF than under shear flow conditions [59]. This leads to a more accessible interior of dendrimers under PEF compared to shear flow, which gives rise to the penetration of linear chains toward the core of dendrimers under PEF. Additionally, the occurrence of the volumetric dilatancy under PEF, which is absent under shear flow, significantly facilitates the chain motion and hence the inter-penetration under PEF compared to the shear flow condition.

We showed in the previous chapter that the radius of gyration of linear molecules (at equilibrium) increases in the presence of dendrimers, which is correlated with the generation and concentration of the dendrimer in the blend. It was explained that dendrimers act as a good solvent for linear chains in the studied limit. Fig. 6.7 shows the strain rate dependent radius of gyration for dendrimers of generations 1-4 and linear molecules in the blend (filled symbols) and also in their pure melt (open symbols). It shows that the size of both linear and dendrimer molecules is increased by increasing the strain rate, due to stretching under the flow, and this increase is higher for linear molecules than for dendrimer molecules, as we showed previously for pure systems [59]. The strain rate at which the radius of gyration increases, is decreased by increasing the generation number and the amount of increase in size for linear molecules is lower when they are blended with higher generations of dendrimers. In addition, the values of the strain rate at which stretching occurs
(i.e. the radius of gyration starts to increase) for both linear and dendrimer species are smaller than their corresponding values in their pure melt and interestingly molecules are more stretched in the blend than they are in their pure melt, which we suggest is a consequence of the solvating effect of the dendrimers. This means that the presence of dendrimers in the blend changes the quality of the surrounding environment of each linear chain and dendrimers act as a good solvent for linear molecules; hence dendrimers promote swelling of the linear chains in the blend. Fig. 6.8 illustrates the stretched configuration of an isolated linear chain and a dendrimer molecule in the blend system 12D187B, at high elongational strain rate.

Fig. 6.9 shows radius of gyration against $I_2$ for the linear and dendrimer molecules in the blend systems containing different number percentage of dendrimer species in the blend, undergoing PEF and shear flow. For all the systems, the size of both linear and dendrimer molecules increases upon increasing $I_2$. It is important to note that increasing the number percentage of dendrimer molecules in the blend leads to less increased size of the linear molecules in the blend. This observation, in combination with the pair distribution function results, suggests that higher dendrimer concentration leads to a smaller increase in the molecular size for the linear chains, which also can be explained in terms of the solvent quality effect of dendrimer molecules in the blend, and that the higher amount of dendrimers in the blend makes them a less good solvent for linear chains. Another feature of this plot is the size comparison of both species under different flow types. It is clear that under PEF, both linear and dendrimer molecules are larger compared to their size under shear flow, meaning they are more stretched and deformed. This further promotes higher interpenetration between the blend species under PEF compared to shear flow.

Fig. 6.10 presents the strain-rate dependent size ratio, $R_{g,L}/R_{g,D}$ between linear and dendrimer molecules for the blend systems; 12D19B, 12D43B, 12D91B, and 12D187B. It shows that contrary to shear flow (previous chapter), under PEF the size ratio is decreased by increasing the strain rate. However, this is only true beyond a critical strain rate for each system. It is clear in Fig. 6.7 that at low to medium strain rates, the linear chains stretch more than the dendrimers, and at higher strain rates their size reaches a plateau value. However, dendrimers (specifically lower
Figure 6.9: Comparison of changes in radius of gyration for $D_{187}$ and $L_{187}$ species in the blend at different concentrations $x$ of dendrimer species against $I_2$. (a) $4D_{187}B$, (b) $8D_{187}B$, and (c) $12D_{187}B$, under PEF and shear flow. Symbols present: $L_{187} \bigstar, D_{187} \bullet$. Open symbols represent the corresponding data under shear flow.
Figure 6.10: Size ratio between blend species against \( \dot{\epsilon} \), for blend systems; (a) 12D19B, (b) 12D43B, (c) 12D91B, and (d) 12D187B.

generations) show their maximum increase in size at high strain rates. This explains the reduced trend observed for the size ratio in Fig. 6.10, because the radius of gyration of the dendrimers starts to rise at strain-rates where the linear chains have reached their plateau region (maximum extension). It is important to note that the size ratio is still larger than unity and even under PEF the blend systems are in the miscibility region of the phase diagram reported by Mackay et al. [119].

As an example, changes in \( L_{13} \) as a function of \( \dot{\epsilon} \) for both dendrimer and linear molecules in the blend (filled symbols) and in their pure melt (open symbols) for blend systems 12D19B, 12D43B, 12D91B, and 12D187B are shown in Fig. 6.11. The values of \( L_{13} \), which can be interpreted as the aspect ratio of the molecules, fluctuate around a constant value at small \( \dot{\epsilon} \) values and tend to increase at higher \( \dot{\epsilon} \) values. It is interesting to note that for all the blend systems, the aspect ratio
Figure 6.11: $L_{13}$ ratios of the tensor of gyration for dendrimer molecules of generation 1-4 and $L_{187}$ against the strain rate in the blend. (a) $12D19B$, (b) $12D43B$, (c) $12D91B$, and (d) $12D187B$. Symbols are as follows: $L_{187}$ $•$, $D$ $•$. Open symbols represents the corresponding values for their pure melt.

is lower for molecules in the blend compared to their corresponding values in their pure melt. This suggests that the observed increase in the size for linear chains is also an overall solvent-quality-induced swelling along with being stretched in the flow direction. $L_{12}$ and $L_{23}$, which for the sake of conciseness are not shown here show similar patterns as $L_{13}$.

6.3 Rheology

The rheological properties of molecular melts are typically analysed using standard material functions. To characterize the melt rheological properties of DL blend
melts, we compute the first extensional viscosity $\eta_1$ and second extensional viscosity $\eta_2$, which are expressed in terms of the components of the molecular pressure tensor as defined in Chapter 4.

Fig. 6.12 shows the first extensional viscosity versus strain-rate for DL blend systems. Note that the linear limit is not captured here due to the poor signal to noise ratio at very low strain-rates. All the blend systems have lower first extensional viscosities compared to the pure melt of linear polymer over the examined strain rates in this study. Replacing linear polymers with dendrimer polymers in the blend results in the reduction in the first extensional viscosity of the blend. Compared to the shear viscosity data (previous chapter) the same mechanisms are responsible here for the reduction in the extensional viscosity, namely, (1) replacement of high molecular weight linear chains with dendrimers of inherently lower viscosity, and (2) increased free volume in the system introduced by the dendrimers. Analogous reductions in viscosity due to increased system free volume in the presence of branched polymer nanoparticles were previously observed by several authors [118, 199]. According to the relationship between the fractional free volume and size of the dendrimer, it is clear that fractional free volume increases in the system when the size of the dendrimer decreases. Therefore, lower generations of dendrimers are more effective in reducing the blend viscosity, and the reduction in the extensional viscosities is higher for blends containing a higher volume fraction of the dendrimers.

Dendrimer-induced free volume also manifests itself through reduction in the relaxation time of the system compared to the pure linear melt. Table 6.1 presents the time constants obtained from the reciprocal of the extension rate at which the first extensional viscosity starts to increase for each blend system. Table 6.1 shows that increasing the number percentage of dendrimers in the blend decreases the relaxation time. This further demonstrates the importance of increase in the free volume of the system which is directly related to the number and molecular weight of dendrimer molecules in the blend. Increased free volume in the system facilitates the motion of the molecules in the system, which leads to a decreased relaxation time for the blend melt. In addition, the observed dilatancy in the blend melt is also responsible for the reduced relaxation time in the presence of dendrimers under
Figure 6.12: First extensional viscosity for blends of dendrimers with 19, 43, 91, and 187 beads and linear polymer of length 187 beads over a wide range of strain rates. Symbols represent +L187, △4%, ● 8%, ◆12%. Inset, * pure D.

PEF, through increasing the free volume in the system and therefore facilitating the molecular chain motion in the blend melt.

In the second column of the Table 6.1, the power law exponents $n$ defined by $\eta_1 \propto \dot{\varepsilon}^{-n}$ for the DL blend systems in the thinning region, are presented. It shows that increasing the number percentage of the dendrimers in the blend decreases the power law exponent. This means that the elongation thinning phenomenon becomes weaker in the presence of the dendrimers. It is known that molecular alignment is responsible for the thinning region in the elongational viscosity-strain rate plots [206]. We showed in Chapter 4 that dendrimer molecules cannot easily align themselves with the flow field compared to linear chain polymers, which is due to the confined globular architecture of the dendrimers.

Fig. 6.13 shows the second extensional viscosity versus strain-rate for DL blend systems. Blend systems have lower second extensional viscosity compared to the pure melt of linear polymer over the strain rates examined in this study. Addition
of dendrimer molecules to the pure high molecular weight linear melt reduces the second extensional viscosity in a similar way to the first extensional viscosity as explained above. The second planar elongational viscosity is very rarely measured, and the only available data that we are aware of are in Daivis et al. [58, 64], Laun and Münstedt [191], and Hajizadeh et al. [59] for dendrimers and hyperbranched polymers. Our $\eta_2$ results for blends are in qualitative agreement with the data of these papers.

### 6.4 Conclusion

We used nonequilibrium molecular dynamics simulations to investigate the structural - rheology relationship for polymeric blends composed of linear polymer chains.
Figure 6.13: Second extensional viscosity for blends of dendrimer polymers with 19, 43, 91, and 187 beads and linear polymer of length 187 beads over a wide range of strain rates. Symbols represent: +L187, ◤ 4%, ◤ 8%, ◤ 12%. Inset, ◤ pure D.

(187 monomers per chain) and dendrimer polymers of generations (g) 1-4, at different number percentage of dendrimer (x) (4%, 8%, and 12%) undergoing planar elongational flow, in the NPT ensemble. We observed a volumetric dilatancy under PEF as opposed to shear flow where there is a decrease in the volume as a function of the shear rate, which is a key for many of their important differences. The stretched molecular conformation along with facilitated motion of the molecules in the melt due to volumetric dilatancy resulted in a higher inter-penetration between linear and dendrimer species under PEF compared to shear flow. The $g_{c,DL}$ pair distribution functions were analysed to study the effect of dendrimer molecular mass and number percentage, and also strain rate on interpenetration of linear chains towards the dendrimer interior. We observed that interpenetration between linear and dendrimer molecules is increased at higher dendrimer concentrations and lower dendrimer generations. We explained this in terms of the dendrimer - induced free volume in the blend, which is proportional to the mass fraction of the dendrimer in the blend and is inversely proportional to the size of the dendrimer molecules in the
blend. Therefore, a higher number of dendrimers of lower generations introduces more free volume in the system. In addition, the congested surface of dendrimers of higher generations is another important factor in prohibiting the interpenetration between the blend species.

We also studied flow-induced molecular deformation of both linear and dendrimer molecules by calculating the radius of gyration and eigenvalues of the tensor of gyration under PEF, and compared them with their corresponding values under shear flow. We observed that the molecular size increases for both linear and dendrimer molecules, which is higher for linear chains compared to dendrimers. This was expected, as we showed in Chapter 4 that linear molecules can be stretched more easily compared to dendrimers of more constrained geometry. In addition, both species were larger in size under PEF compared to their size under shear flow, which is a consequence of the intensity and geometry of the PEF.

Finally, we showed that the flow-induced molecular deformation plays an important role in determining the rheological behaviour of polymer blends under PEF, particularly the existence of the thickening region of the strain-rate dependent first extensional viscosity. Melt rheological properties including the first and second extensional viscosities obtained from constant pressure simulations were found to fall into the range between those of pure dendrimer and pure linear polymer melts. A small amount of dendrimer added in the melt of the linear chains significantly reduced the first and second extensional viscosities of the blend systems compared to the pure high molecular weight linear melt. This drop in the viscosity was correlated with the number percentage of dendrimers in the blends and also with the geometry and generation of the dendrimer molecules. Blends containing a higher amount of dendrimer molecules of lower generations show much lower melt viscosities. The free volume introduced by the globular shape dendrimer molecules in the system was found to be an important factor in reducing the blend viscosity in agreement with results reported earlier by Mackay et al. [118] and Merkel et al. [199] for similar systems. The amount of the dendrimer-induced free volume in the system is higher for dendrimers of lower generations, which further explains the trends observed in the rheological behaviour of our dendrimer-linear blend systems.
Chapter 7

Conclusions and Future Work

7.1 Conclusions

In this thesis we presented results for the planar extensional rheology and structural properties of pure dendrimer and hyperbranched polymer melts and the miscibility, structural properties, and shear and planar extensional rheology of dendrimer-linear polymer blends. Dendrimer, hyperbranched, and linear chain molecules were modelled using a coarse-grained bead-spring model, accounting for the bond and pairwise interactions by applying the WCA and FENE potentials. The NEMD simulations were based on the isothermal-isobaric SLLOD equations of motion, coupled with the KR periodic boundary condition for PEF and the Lees-Edwards periodic boundary conditions for shear.

It was found that the architecture of dendrimers and hyperbranched polymers, which is branched and highly constrained compared to conventional linear chain polymers, is responsible for their unique macroscopic properties. The short linear units between the branching points and branch-on-branch structure of dendrimers and hyperbranched polymers prevents branches from undergoing intermolecular entanglement. Therefore, opposed to linear chains that show both the Rouse and
reptation dynamics, the rheological behaviour of dendritic polymers is expected to be effectively explained by Rouse dynamics. The strain-rate dependence of the extensional viscosity of linear and hyperbranched polymers showed three distinctive regions, including an initial Newtonian region at low strain-rates, followed by thickening behaviour at medium strain-rates and terminated with a thinning region at very high strain-rates. For dendrimers the viscosity upturn region vanished, which was attributed to their highly constrained molecular topology. The structural perfection of dendrimers compared to hyperbranched molecules caused reduced mobility of the branches and also reduced flow-induced stretching and alignment of the molecules. Imperfection in the architecture of hyperbranched molecules can introduce free spaces in the molecular interior, accommodating the movement and stretching of the branches. We suggested that stretching and molecular deformations are responsible for the thickening behaviour of hyperbranched molecules. Furthermore, the terminal thinning behaviour was related to the finite extensibility of the FENE potential and flow-induced alignment.

A structural analysis was performed to correlate the flow-induced structural changes of the molecules to their unique rheological behaviour. The ratios of the eigenvalues demonstrated that, under shear flow, hyperbranched molecules change their shape from an almost spherical conformation to an ellipsoidal conformation as the strain rate increases. Under PEF, even at low strain rates, the hyperbranched molecules were ellipsoidal in shape and by increasing the elongation rate they became much more flattened. Dendrimers showed the same changes in their shape but they were less flattened. Linear molecules were more elongated compared to hyperbranched and dendrimer molecules at low elongation rates, while changing to a much more flattened ellipsoidal shape at higher strain rates. Comparing the strain-rate at which the eigenvalue ratios started to rise with the strain-rate at which viscosity upturn occurred provided us with very important information. We found that the viscosity upturn occurs approximately at the same strain-rate where the eigenvalues start to rise. This indicates that the onset of molecular deformation under PEF coincides with the crossover from the Newtonian plateau to the non-Newtonian region in the viscosity curves. Analysis of the internal structure of dendrimers and hyper-
Conclusions and Future Work

branched polymers revealed that a typical back-folding phenomenon occurs under planar extensional flow.

Dendrimers showed much lower melt viscosities compared to their linear counterparts, suggesting that they can be used as a rheology modifier. Therefore, blend systems of dendrimer molecules of generation 1-4 and linear chains with 187 beads per chain were simulated. Various radial distribution functions were used to analyse the miscibility of blend systems. All blend systems studied in this thesis formed miscible blends. The blend shear and planar extensional viscosities were found to decrease, correlating with the amount and generation of dendrimers in the blend. The viscosity reduction was attributed to the replacement of high molecular weight linear chains with dendrimers of inherently lower melt viscosity and also dendrimer-induced free volume in the system. Interestingly, the globular shape of dendrimers resulted in a particle-like behaviour of dendrimer molecules when blended with linear polymers. For this reason, our results for dendrimer-linear blend systems were consistent with results obtained for mixtures of polymers and nanoparticles that lead to a reduction in nanocomposite viscosity.

Effects of shape, size, and molecular mass and number percentage of dendrimers on inter-penetration between blend species were also studied. Shear flow increased the inter-penetration between linear and dendrimer species, as stretched dendrimer molecules have more open spaces compared to their undisturbed architecture. In addition, we observed higher interpenetration between linear and dendrimer molecules for blends containing dendrimers of lower generations. We explained this in terms of the surface congestion effects of end groups for higher generations. We further studied flow-induced molecular deformation of both linear and dendrimer molecules by calculating the radius of gyration and eigenvalues of the tensor of gyration. Shear-induced molecular deformation is a consequence of competition between two effects: rotation and stretching. We observed that at lower shear rates, molecular rotation dominated and the molecular aspect ratio decreased, but after a certain shear rate, stretching was dominant and the molecular size increased at a greater rate for linear chains compared to dendrimers.
We calculated the dendrimer-induced free volume in the blend from the difference between the volume calculated from a mixing rule and data obtained from the EMD simulations. Free volume data revealed that blends containing higher number of dendrimers of lower generations possess more free volume in their melt, which significantly affects the molecular motion, inter-penetration, and viscosity of the blend systems. We observed a volumetric dilatancy under PEF as opposed to shear flow where there is a slight decrease in the volume with increasing the shear rate, which is a key for many of their important differences.

Under PEF, molecular size increased for both linear and dendrimer molecules, which was higher for linear chains compared to dendrimers. This was expected, as we showed in Chapter 4 that linear molecules can be stretched more easily compared to dendrimers of confined geometry. In addition, both species were larger in size under PEF compared to their size under shear flow, which is a consequence of the intensity and geometry of the PEF. The stretched molecular conformation along with the facilitated motion of the molecules in the melt due to the volumetric dilatancy resulted in a higher inter-penetration between linear and dendrimer species under PEF compared to shear flow. In addition, we observed that the higher the number percentage of dendrimer was, the higher the interpenetration between linear and dendrimer molecules were which was higher for lower generations of dendrimers compared to higher generations. We explained this in terms of the dendrimer-induced free volume in the blend, which is proportional to the mass fraction of the dendrimer in the blend and is inversely proportional to the size of the dendrimer molecules in the blend. Therefore, higher number of dendrimers of lower generations introduced more free volume in the system.

7.2 Future Work

Blends of different polymer species are of major scientific and industrial attractions. One of the crucial issues to be addressed when dealing with blends consisting of architecturally different blend species, is to investigate under which conditions a miscible and stable blend forms. A thermodynamically stable blend is a direct result of com-
petition between the enthalpic effects associated with van der Waals attractions, Coulombic forces, and/or specific polymer-polymer attractive interactions, and the entropic packing constraints due to repulsive forces between species of different size and architecture. Therefore, key system variables are polymer radius of gyration, size ratio between blend species, polymer concentration, and solvent quality [207]. In athermal blends (entropic limit), where there are no interactions between blend species, the intrinsic density fluctuation correlation length of the dense polymer melt (typically a few monomer diameters) dictates the range of the repulsive forces [207]. Polymer blends consisting of highly branched and linear chains of the similar chemistry is the closest realization of such an athermal blend. Therefore, from a theoretical point of view, understanding the pure packing of these blends is always an important issue to investigate.

Dendrimers and linear chain polymers in this study were modelled as a generic coarse-grained model of flexible molecules, because our focus was on the architectural effects rather than the chemical details of each molecule. Therefore, a more realistic model is required to be able to directly correlate results with experimental data and study the effect of chemical nature of the end groups of the dendrimers on the miscibility of the blend species.

One of the fascinating features of dendritic molecules is their encapsulating capability, which is important in their drug delivery applications. We suggest this work can be extended to blends of dendrimer and linear chains where linear chains are smaller in size than dendrimers and chemical details are incorporated. In this situation, one can study the effective architecture and parameters on controlled encapsulating and subsequent delivering of the drug.

Commercially available hyperbranched polymers are polydisperse due to the single-step polymerization. Therefore, it would be interesting from both academic and industrial aspects to study rheological and structural properties of polydisperse hyperbranched systems.
Appendices
Appendix A

Derivation of Pair Distribution Function

The density distribution function for an inhomogeneous two components system, \( \langle \rho_1(r)\rho_2(r') \rangle \) is defined by

\[
\langle \rho_1(r)\rho_2(r') \rangle = \rho_1(r)\rho_2(r')g_{12}(r,r') = \left( \sum_i \sum_j \delta(r-r_i)\delta(r'-r_j) \right)
\]  \hspace{1cm} (A.1)

Therefore, the pair correlation function for an inhomogeneous two components system \( g_{12}(r,r') \) becomes

\[
g_{12}(r,r') = \frac{1}{\rho_1\rho_2} \left( \sum_i \sum_j \delta(r-r_i)\delta(r'-r_j) \right)
\]  \hspace{1cm} (A.2)

Let \( \Delta r = r' - r \), which gives \( r' = \Delta r + r \). Therefore,

\[
g_{12}(r,r + \Delta r) = \frac{1}{\rho_1\rho_2} \left( \sum_i \sum_j \delta(r-r_i)\delta(r+\Delta r-r_j) \right)
\]  \hspace{1cm} (A.3)
If the system is homogeneous, we can integrate over \( r \)

\[
\int g_{12}(r, r + \Delta r)dr = g_{12}(\Delta r) \int dr = V g_{12}(\Delta r)
\]  

(\text{A.4})

Defining \( r_{ij} = r_j - r_i \), and using the identity \( \int \delta(x-a)\delta(x-b)dx = \delta(b-a) \) gives

\[
g_{12}(\Delta r) = \frac{1}{\rho_1 \rho_2 V} \left( \sum_i \sum_j \delta(\Delta r - r_{ij}) \right)
\]  

(\text{A.5})

Since the system is homogeneous, we now define \( \Delta r = r \) for simplicity.

To change to spherical polar coordinates, we take

\[
\delta(r) = \delta(x)\delta(y)\delta(z) = \frac{\delta(r)\delta(\theta)\delta(\phi)}{|J|}
\]  

(\text{A.6})

where \(|J|\) is the Jacobian of the coordinate transformation and

\[
|J| = r^2 \sin(\phi)
\]  

(\text{A.7})

Hence, the pair correlation function in spherical polar coordinates, \( g_{12}(r, \theta, \phi) \) is

\[
g_{12}(r, \theta, \phi) = \frac{1}{\rho_1 \rho_2 V} \left( \sum_{ij} \delta(r - r_{ij}) \delta(\theta - \theta_{ij}) \delta(\phi - \phi_{ij}) \right)
\]  

(\text{A.8})

If \( g_{12}(r) \) is isotropic,

\[
g_{12}(r) = \frac{1}{4\pi r^2 \rho_1 \rho_2 V} \left( \sum_i \sum_j \delta(r - r_{ij}) \right)
\]  

(\text{A.9})

To numerically evaluate \( g_{12}(r) \), we assume it is uniform over a small histogram in \( r \), giving

\[
\int_{r_L}^{r_U} g_{12}(r)dr \approx \frac{1}{3}(r_U^3 - r_L^3)g(r_b)
\]  

(\text{A.10})

where \( r_b = \frac{r_U - r_L}{2} \), and \( r_U \) and \( r_L \) are upper and lower limits of the integral.
On the other hand
\[
\int_{r_L}^{r_U} \sum_i^{N_1} \sum_j^{N_2} \delta(r - r_{ij}) \, dr = N_b \tag{A.11}
\]
where $N_b$ is the number of pairs with separation $r_L < r_{ij} < r_U$. Therefore, for a single-component system, where $\rho_1 = \rho_2 = \frac{N}{V}$
\[
\frac{4\pi}{3} (r_U^3 - r_L^3) g(r_b) = \frac{V}{N^2} N_b \tag{A.12}
\]
and finally the pair distribution for a single component system is,
\[
g(r_b) = \frac{3N_b}{4\pi\rho(r_U^3 - r_L^3)} \tag{A.13}
\]
For a two-component system, we have $\rho_1 = \frac{N_1}{V}$ and $\rho_2 = \frac{N_2}{V}$, and substituting in Eq. (A.9) one gets
\[
g_{12}(r_b) = \frac{3N_b V}{4N_1 N_2 \pi (r_U^3 - r_L^3)} \tag{A.14}
\]
Bibliography


Bibliography


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