COMPUTATIONAL SIMULATION OF HYPERBRANCHED POLYMER MELTS UNDER SHEAR

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Abstract

In this work, hyperbranched polymers of different molecular weights and different molecular architectures have been simulated using a coarse-grained model and non-equilibrium molecular dynamics techniques. A number of structural parameters and the rheology of hyperbranched polymer melts under shear were analysed to explain the effect of the molecular structure and molecular weight on microscopic as well as macroscopic properties.

In order to determine the shear-induced changes in the structural properties of hyperbranched polymers, various parameters were calculated at different strain rates. The radii of gyration which characterize the size of the polymer were evaluated. The relationship between the zero shear rate mean squared radius of gyration and the molecular weight as well as the Wiener index was established. The tensor of gyration was analysed and results indicate that hyperbranched polymer molecules have a prolate ellipsoid shape under shear. As hyperbranched polymers have compact, highly branched architecture and layers of beads have increasing densities which might lead to an unusual distribution of mass, the distribution of beads was also studied. The distribution of terminal beads was investigated to understand the spatial arrangement of these groups which is very important for hyperbranched polymer applications, especially in drug delivery. Flow birefringence was characterized by taking into account both form and intrinsic birefringences which result from molecular and bond alignment respectively.

The melt rheology of hyperbranched polymer structures with different molecular weights and different number of spacers was also studied. Systems were simulated over a wide range of strain rates to capture the crossover behaviour from Newtonian to non-Newtonian regimes. Rheological properties including the shear viscosity and first and second normal stress coefficients were computed and the transition to shear thinning was observed at different strain rates for hyperbranched polymers of different sizes and topologies. The results were consistent with findings from NEMD simulations of linear and dendritic polymers. The stress-optical rule was tested and shown to be valid only in the Newtonian regime and violated in the strong flow regime where the rule does not
take into account flow-induced changes of the micro structure. The stress-optical coefficient was found to be independent of the molecular weight and topology of polymers.

Blends of hyperbranched polymers and linear polymers were also simulated and their rheological properties were investigated. Results show that even a small proportion of hyperbranched polymer in a melt of linear chains can reduce the shear viscosity of the whole system. This feature makes hyperbranched polymers a potential candidate as rheology modifiers. However there is no observed limit in the proportion of hyperbranched polymers in the samples above which the viscosity is stabilized. The viscosity drops continuously, correlating with the amount of hyperbranched polymers present.
Acknowledgements

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Finally, my deepest thanks to my family for their endless love, support and encouragement for every step I make in my life.
Declaration

I hereby declare that the thesis entitled “Computational simulation of hyperbranched polymer melts under shear”, and submitted in fulfilment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Information and Communication Technologies of Swinburne University of Technology, is my own work and that it contains no material which has been accepted for the award to the candidate of any other degree or diploma, except where due reference is made in the text of the thesis. To the 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.

Tu Cam Le
December 2009
Publications from this thesis

The following papers have been based on part of this work:


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## Notation

### Abbreviations

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<td>FENE</td>
<td>Finitely Extensible Nonlinear Elastic potential</td>
</tr>
<tr>
<td>LJ</td>
<td>Lennard-Jones potential</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>NEMD</td>
<td>Non-Equilibrium Molecular Dynamics</td>
</tr>
<tr>
<td>WCA</td>
<td>Weeks-Chandler-Anderson potential</td>
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### Latin alphabet

- $b$: *spacer* – number of beads in a linear unit of a dendritic polymer
- $B$: degree of branching
- $d_{ij}$: number of bonds separating site/bead $i$ and $j$ of a molecule
- $D$: number of fully branched units in a hyperbranched molecule
- $D$: rate of strain tensor
- $f$: functionality of the branch groups of a dendritic polymer
- $f_c$: functionality of the core of a dendritic polymer
- $F_i$: force acting on molecule $i$
- $F_{ia}$: force acting on bead $\alpha$ in molecule $i$
- $F_{ia\beta}$: intermolecular force on bead $\alpha$ in molecule $i$ due to bead $\beta$ in molecule $j$
- $g$: generation number of a dendrimer
- $g_A(r)$: atomic radial distribution function
- $g_{CM}(r)$: distribution of beads from the centre of mass
- $g_{core}(r)$: distribution of beads from the core
- $g_{inter}(r)$: interpenetration function
- $g_{term}(r)$: radial distribution of terminal group
- $I$: tensor of inertia, unit tensor
- $k$: spring constant of the FENE potential
- $k_B$: Boltzmann constant
- $K$: consistency index in the Cross model
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<tr>
<td>$l_{bond}$</td>
<td>bond length</td>
</tr>
<tr>
<td>$L$</td>
<td>number of partially reacted units in a hyperbranched molecule</td>
</tr>
<tr>
<td>$L_y$</td>
<td>size of the simulation box along the y axis</td>
</tr>
<tr>
<td>$L_1, L_2, L_3$</td>
<td>mean eigenvalues of the tensor of gyration</td>
</tr>
<tr>
<td>$L_1', L_2', L_3'$</td>
<td>eigenvalues of the mean tensor of gyration</td>
</tr>
<tr>
<td>$m$</td>
<td>mass of a single bead</td>
</tr>
<tr>
<td>$m_C$</td>
<td>power law exponent in the Cross model fitted for shear viscosity data</td>
</tr>
<tr>
<td>$m_p$</td>
<td>power law exponent in the Carreau-Yasuda model fitted to isotropic pressure data</td>
</tr>
<tr>
<td>$m_p$</td>
<td>power law exponent in the Carreau-Yasuda model fitted to reduced bead density</td>
</tr>
<tr>
<td>$M$</td>
<td>mass of a molecule</td>
</tr>
<tr>
<td>$N$</td>
<td>number of molecules</td>
</tr>
<tr>
<td>$N_s$</td>
<td>number of beads composing a single molecule</td>
</tr>
<tr>
<td>$N_t$</td>
<td>total number of beads composing the system</td>
</tr>
<tr>
<td>$N_1$</td>
<td>first normal stress difference</td>
</tr>
<tr>
<td>$N_2$</td>
<td>second normal stress difference</td>
</tr>
<tr>
<td>$p$</td>
<td>isotropic pressure</td>
</tr>
<tr>
<td>$p_\eta$</td>
<td>power law exponent in the Carreau-Yasuda model fitted for shear viscosity data</td>
</tr>
<tr>
<td>$p_{\eta_i}$</td>
<td>power law exponent in the Carreau-Yasuda model fitted to radius of gyration data</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure tensor</td>
</tr>
<tr>
<td>$P^A$</td>
<td>atomic pressure tensor</td>
</tr>
<tr>
<td>$P^M$</td>
<td>molecular pressure tensor</td>
</tr>
<tr>
<td>$P_{xy}$</td>
<td>$xy$ element of the pressure tensor</td>
</tr>
<tr>
<td>$p_i$</td>
<td>momentum of the centre of mass of molecule $i$</td>
</tr>
<tr>
<td>$p_{i\alpha}$</td>
<td>momentum of bead $\alpha$ in molecule $i$</td>
</tr>
<tr>
<td>$Q$</td>
<td>damping factor in the $NpT$ algorithm</td>
</tr>
</tbody>
</table>
\( \mathbf{r}_i \)  position of the centre of mass molecule \( i \)
\( \mathbf{r}_\alpha \)  position of bead \( \alpha \)
\( \mathbf{r}_{\alpha i} \)  position of bead \( \alpha \) in molecule \( i \)
\( \mathbf{r}_{CM} \)  position of the centre of mass
\( \mathbf{r}_{i} \)  position of the core of molecule \( i \)
\( r_{ij} \)  distance between centres of mass of molecule \( i \) and molecule \( j \)
\( R_0 \)  finite extensibility of the FENE spring
\( \mathbf{R}_g^2 \)  tensor of gyration
\( \langle R_g^2 \rangle \)  mean squared radius of gyration
\( \langle R_g^2 \rangle_{0} \)  zero shear rate mean squared radius of gyration
\( R_g \)  radius of gyration
\( \mathbf{S}_m \)  molecular alignment tensor
\( \mathbf{S}_b \)  bond alignment tensor
\( S_m \)  molecular order parameter
\( S_b \)  bond order parameter
\( s_{m,i} \)  eigenvalue of the molecular alignment tensor
\( s_{b,i} \)  eigenvalue of the bond alignment tensor
\( S_{xx} \)  xx component of the alignment tensor
\( \Delta t \)  integration time step
\( T \)  temperature
\( u_x(t) \)  \( x \) component of the streaming velocity vector
\( \mathbf{u}_i \)  unit vector denoting the orientation of molecule \( i \)
\( \mathbf{v}_i \)  unit vector denoting the orientation of bond \( i \)
\( U \)  interaction potential energy
\( U_{ij}^{FENE} \)  FENE interaction energy between beads \( i \) and \( j \)
\( U_{ij}^{LJ} \)  LJ interaction energy between beads \( i \) and \( j \)
\( U_{ij}^{WCA} \)  WCA interaction energy between beads \( i \) and \( j \)
\( V \)  volume of the simulation box
$W$ Wiener index

$Wi$ Weissenberg number

**Greek alphabet**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>power law exponent for first normal stress coefficients</td>
</tr>
<tr>
<td>$\beta$</td>
<td>power law exponent for second normal stress coefficients</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>shear rate</td>
</tr>
<tr>
<td>$\dot{\gamma}_c$</td>
<td>shear rate of the onset of shear thinning</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>LJ energy parameter</td>
</tr>
<tr>
<td>$\dot{\epsilon}_{xx}$</td>
<td>compression rate along $x$ axis</td>
</tr>
<tr>
<td>$\eta$</td>
<td>shear viscosity in the steady shear</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>zero shear viscosity</td>
</tr>
<tr>
<td>$\eta_\infty$</td>
<td>infinite shear viscosity</td>
</tr>
<tr>
<td>$[\eta]$</td>
<td>intrinsic viscosity</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>characteristic strain rate in the flow</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>characteristic time of the fluid</td>
</tr>
<tr>
<td>$\lambda_\eta$</td>
<td>time constant in the Carreau-Yasuda model fitted for shear viscosity data</td>
</tr>
<tr>
<td>$\lambda_p$</td>
<td>time constant in the Carreau-Yasuda model fitted for isotropic pressure data</td>
</tr>
<tr>
<td>$\lambda_{\rho}$</td>
<td>time constant in the Carreau-Yasuda model fitted for reduced bead density data</td>
</tr>
<tr>
<td>$\lambda_{g}$</td>
<td>time constant in the Carreau-Yasuda model fitted for radius of gyration data</td>
</tr>
<tr>
<td>$\rho$</td>
<td>bead concentration/density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>stress tensor</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>LJ length parameter</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>thermostating coefficient</td>
</tr>
<tr>
<td>$\tau_0$</td>
<td>longest relaxation time</td>
</tr>
<tr>
<td>$\chi_m$</td>
<td>molecular alignment angle</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>$\chi_b$</td>
<td>bond alignment angle</td>
</tr>
<tr>
<td>$\psi_1$</td>
<td>first normal stress coefficient</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>second normal stress coefficient</td>
</tr>
</tbody>
</table>
1. General Introduction

Polymers are long chain macromolecules which have drawn considerable interest of both academia and industry. In comparison with other classes of materials, polymers have been found to have one of the widest ranges of applications such as plastics, coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology, and supramolecular science (Gao and Yan, 2004). The main key to a large number of applications of polymers is their special properties, which strongly depend on the molecular topologies. Based on the architecture, polymers are classified as linear, branched and cross-linked polymers. Among these, branched polymers can be further classified as graft, star, comb or dendritic polymers with interesting molecular structures as shown in Figure 1.1.

The branched polymers that have the most complex architecture are dendritic polymers including dendrimers and hyperbranched polymers whose configurations are shown in Figure 1.2. Dendrimers, which are perfectly branched tree-like structures, are more difficult to synthesize due to the requirement of chemical purity and stringent multi-step processing. In contrast, hyperbranched polymers with incompletely or irregularly branched topologies can be prepared easily using “one-pot” techniques that save time and are suitable for large scale, low cost production. Due to the easy synthesis and unique properties, hyperbranched polymers have a wide range of potential applications.
such as rheology modifiers, blend components or tougheners for thermosets (Gao and Yan, 2004). However the easy one-pot synthesis method used to prepare hyperbranched polymers provides a mixture of randomly branched polymers with different size and topology. This leads to difficulties in establishing structure – property relationships experimentally, but it gives simulation a valuable opportunity to shed light on the structure and rheology of monodisperse hyperbranched polymers.

<table>
<thead>
<tr>
<th>Dendritic polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dendrimer</strong></td>
</tr>
<tr>
<td><img src="image1.png" alt="Dendrimer" /></td>
</tr>
</tbody>
</table>

**Figure 1.2.** Comparison between the architecture of a dendrimer molecule and a randomly branched hyperbranched polymer molecule.

<table>
<thead>
<tr>
<th>Year of publication</th>
<th>Number of papers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1992</td>
<td>0</td>
</tr>
<tr>
<td>1996</td>
<td>50</td>
</tr>
<tr>
<td>2000</td>
<td>100</td>
</tr>
<tr>
<td>2004</td>
<td>200</td>
</tr>
<tr>
<td>2008</td>
<td>400</td>
</tr>
</tbody>
</table>

**Figure 1.3.** The number of scientific publications as a function of publication year based on a search by ISI web of science with hyperbranched polymers as the topic.
As shown in Figure 1.3, the number of studies on hyperbranched polymers has increased rapidly in the last twenty years due to their unique chemical and physical properties as well as potential applications. However most of these studies are experimental and focus on the synthesis of these materials.

Although there have been a few papers on hyperbranched polymer simulations, none of them focus on melt rheology of these materials. Hyperbranched polymers in solution have been simulated with the aid of Monte Carlo (Konkolewicz et al., 2007, Widmann and Davies, 1998) and Brownian dynamics techniques (Dalakoglou et al., 2008, Neelov and Adolf, 2004, Sheridan et al., 2002, Lyulin et al., 2001). Therefore the aim of this work is to extend the simulations on hyperbranched polymers further by conducting the first non-equilibrium molecular dynamics simulations of hyperbranched polymers in the melt. Hyperbranched polymers of different molecular weights and architectures have been simulated under shear. The influence of size and topology of these molecules on micro and macroscopic properties of the systems are investigated. Structural properties are studied to characterize the flow-induced changes in the shape, distribution of mass, alignment, spatial arrangement and interpenetration. Furthermore the melt rheology of these materials including shear viscosity and normal stress coefficients are also analysed.

The remainder of this thesis is organized as follows. Chapter 2 introduces the topology, properties as well as the history, synthesis methodology and potential applications of hyperbranched polymers. Reviews of theoretical studies of hyperbranched polymers and experimental studies on the melts of these materials are also included. Chapter 3 gives an overview of the structure and rheology of polymeric fluids. Details of the coarse-grained model and different non-equilibrium molecular dynamics techniques employed to study hyperbranched polymers in this work are presented in Chapter 4. Chapter 5 is devoted to simulation results on microscopic structural properties of hyperbranched polymers in the melt under shear, whereas Chapter 6 presents the macroscopic flow properties of those melts. Conclusions of this work and recommendations for further work are given in Chapter 7.
2. Hyperbranched polymers

2.1. Topology

Hyperbranched polymers belong to a class of synthetic tree-like macromolecules called dendritic polymers (Gao and Yan, 2004). They are polymers with densely branched structure and a large number of end groups. Dendritic polymers include dendrimers which have completely branched star-like topologies and hyperbranched polymers which have imperfectly branched or irregular structures. Both dendrimer and hyperbranched polymer molecules are composed of repeating units emanating from a central core. The core is characterised by its functionality, which is the number of chemical bonds through which it can be connected to the external parts of the molecule. The functionality of the core is normally three (e.g. amine) or four (e.g. ethylenediamine). Through the bonds of the core, the layers of linear units (single monomers or linear chains) are attached to the core and each of these arms is terminated with the multifunctional branched unit. Larger molecules are created by adding shells of linear units to the end groups of the layer beneath. If all of these units are attached to the molecule perfectly, a dendrimer is formed. In contrast, the absence of any of these units in the molecule will result in a hyperbranched polymer structure. A schematic representation of dendrimers and hyperbranched polymers is presented in Figure 2.1.

![Schematic representation of dendrimer and hyperbranched polymer structures](image)

**Figure 2.1.** Schematic configuration of a tri-functional dendrimer of generation 3 and an example of a hyperbranched polymer molecule.

For a given number of monomers and generation, there is only one dendrimer structure but a large number of hyperbranched structures can be formed because of the different
ways of distributing the branched and unbranched monomers. In experiments, due to the “one-pot” synthesis technique, hyperbranched polymers are usually randomly branched and polydisperse systems with different topologies and molecular sizes. Computational simulations have also been performed to create randomly branched hyperbranched polymers (Dalakoglou et al., 2008, Konkolewicz et al., 2007, Konkolewicz et al., 2008, Lyulin et al., 2001, Sheridan et al., 2002, Widmann and Davies, 1998).

Different structural parameters can be used to characterize the topology of hyperbranched polymers. The degree of branching is defined as 
\[ B = \frac{2D}{2D+L} \]
where \( D \) is the number of fully branched units and \( L \) is the number of partially reacted units (Holter et al., 1997). The value of the degree of branching varies from 0 for linear polymers to 1 for dendrimers or fully branched hyperbranched polymers. In addition to the degree of branching, the Wiener index, defined as 
\[ W = \frac{1}{2} \sum_{i<j} N \cdot d_{ij} \]
where \( N \) is the degree of polymerization and \( d_{ij} \) is the number of bonds separating site \( i \) and \( j \) of the molecule, can also be used to characterize the topologies of hyperbranched polymers in greater detail.

### 2.2. History and synthesis methodology

The history of hyperbranched polymers commenced in the 19th century with the report of formation of a resin from tartaric acid (A\(_2\)B\(_1\) monomer) and glycerol (B\(_3\) monomer), followed by the report of the reaction between phthalic anhydride (latent A\(_2\) monomer) or phthalic acid (A\(_2\) monomer) and glycerol (B\(_3\) monomer) in 1901 (Kienle and Hovey, 1929). Kienle et al. (Kienle et al., 1939b, Kienle et al., 1939a, Kienle and Hovey, 1929) then studied this reaction further and found out that the specific viscosity of samples of phthalic anhydride and glycerol was low in comparison with that of other synthetic linear polymers. In 1909, the first commercial synthetic polymers, namely phenolic resins were introduced (Odian, 2004). Just prior to gelation, these polymers are so-called random hyperbranched materials.

In 1952, Flory (Flory, 1952) reported a theory concluding that highly branched polymers can be synthesized without gelation by polycondensation of an AB\(_n\) monomer
(n ≥ 2) in which A and B functional groups can react with each other. It was not until 1978 that the first synthesis of branched systems was reported by Vögtle and co-workers (Buhleier et al., 1978). In 1988, the first hyperbranched polymer was finally synthesized in the form of soluble polyphenylene by Kim and Webster (Kim and Webster, 1992, Kim and Webster, 1990, Kim and Webster, 1988). Since then, hyperbranched polymers have gained considerable attention from both academia and industry due to their unique properties and ease of preparation, hence greater availability compared with dendrimers.

The synthetic techniques for hyperbranched polymers can be divided into two major categories. The first category contains techniques of the single-monomer methodology (SMM), in which hyperbranched macromolecules are synthesized by polymerization of an AB_x, AB^* or a latent AB_x monomer. The second category contains examples of the double-monomer methodology (DMM) in which direct polymerization of two types of monomers or a monomer pair generates hyperbranched polymers (Gao and Yan, 2004).

According to the reaction mechanism, the SMM category includes at least four specific approaches (Yates and Hayes, 2004, Gao and Yan, 2004, Jikei and Kakimoto, 2001):

- **Step-growth polycondensation of AB_n monomers method** is used to prepare a broad range of hyperbranched polymers such as polyphenylenes, polyesters, polyamides and polycarbonates.
- **Self-condensing vinyl polymerization (SCVP) of AB^* monomers technique** is applied to synthesize polystyrenes, poly(methacrylate) or poly(acrylate)s.
- **Multibranching ring-opening polymerization (SCROP) of latent AB_n monomers approach** can be used to obtain polyamines, polyethers and polyesters.
- **Proton-transfer polymerization (PTP)** forms hyperbranched polysiloxanes or polyesters with epoxy or hydroxyl end groups.

**DDM** can be classified into two main subclasses based on the selected monomer pairs and different reaction pathways (Gao and Yan, 2004).
• ‘A$_2$ + B$_3$’ methodology has been applied to synthesize three main polymer architectures including polyamides, polycarbonates and polyureas (Yates and Hayes, 2004).

• Couple-monomer methodology (CMM), which is the combination of the basic SMM and ‘A$_2$ + B$_3$’, is used to prepare many types of hyperbranched polymers such as poly(sulfone amine)s, poly(ester amine)s, poly(urea urethane)s (Gao and Yan, 2004).

2.3. Properties

Hyperbranched polymers have special properties which are the key to their industrial applications.

One of the most interesting physical properties of hyperbranched polymers is their considerably different viscosity characteristics in comparison with their linear analogues (Jikei and Kakimoto, 2001, Malmstrom and Hult, 1997, Yates and Hayes, 2004), which is a consequence of the architecture of the molecules. Hyperbranched macromolecules in solution reach a maximum of intrinsic viscosity as a function of molecular weight as their shape changes from an extended to a more compact globular structure, especially at high molecular weights. The conditions for the existence of this maximum intrinsic viscosity as a function of molecular weight are however still not clear (Lyulin et al., 2001). In addition, for linear polymers, the melt viscosity increases linearly up to a critical molar mass where the viscosity drastically increases as a consequence of the entanglement of polymer chains. However, this phenomenon is not observed for dendrimers or hyperbranched polymers which indicates that minimal entanglement of the branched chains occurs (Yates and Hayes, 2004, Malmstrom and Hult, 1997).

Other interesting characteristics of hyperbranched polymers are their conformation and degree of branching. X-ray and small-angle neutron scattering experiments show that dendrimers have spherical conformations, whilst hyperbranched polymers have globular structures (Prosa et al., 1997). The degree of branching is reflected in the flexibility of the branching components contained within the architecture as well as the intrinsic viscosity of the polymer. Polymers with a higher degree of branching have lower
viscosity. This affects the polymer’s relative solubility in various media (Yates and Hayes, 2004, Jikei and Kakimoto, 2001).

Besides, hyperbranched polymers have high chemical reactivity and enhanced solubility when compared to their linear analogues. They also exhibit enhanced compatibility with other polymers as has been demonstrated by blending studies (Yates and Hayes, 2004).

Hyperbranched materials also have outstanding mechanical properties such as initial modulus, tensile strength and compressive moduli which reflect the compact highly branched structures (Bolton and Wooley, 2002, Jikei and Kakimoto, 2001, Yates and Hayes, 2004). The research of Massa et al. showed that a blend of linear Bisphenol A polycarbonate with an all-aromatic hyperbranched polyester resulted in increased tensile and compressive moduli and decreased strain-to-break and toughness compared to those of polycarbonate (Massa et al., 1995).

2.4. Theoretical models

One of the first numerical studies of hyperbranched polymers was reported by Aerts (Aerts, 1998). Configurations of hyperbranched polymers were modelled using the bead model of Lescanec and Muthukumar (Lescanec and Muthukumar, 1990) and the intrinsic viscosities were calculated. It was shown that there is a maximum of intrinsic viscosity as a function of molecular weight but the maximum is situated at a higher level of intrinsic viscosity and shifted to higher molecular weights in comparison with dendrimers (Aerts, 1998). The limitations of this work are the application of the algorithm with no configurational relaxation and the questionable deduction of the intrinsic viscosity from the radius of gyration for branched structures (Lyulin et al., 2001).

Also with the purpose of determining the intrinsic viscosities, a special class of hyperbranched polymers built by single step-wise addition of AB₂ monomer units to a B₃ core was modelled using a simple hydrocarbon model and the RIS Metropolis Monte Carlo procedure (Widmann and Davies, 1998). This model once again suggested that
hyperbranched polymers should show a maximum in intrinsic viscosity at readily achievable branching ratios. Furthermore, it was found that degree of branching is not an adequate descriptor for the shape of dendritic molecules and the Wiener index of the connectivity tree of a hyperbranched structure shows a near perfect power-law correlation with the simulated intrinsic viscosities of molecules with the same molecular weight but different topologies (Widmann and Davies, 1998). However, a phantom chain model without solvent was applied and this does not take into account excluded-volume effects which increase in highly crowded hyperbranched structures (Lyulin et al., 2001).

In order to address the issues of these papers, hyperbranched polymers in simple shear flow were simulated by Lyulin et al (Lyulin et al., 2001) using Brownian dynamics techniques. This method allows calculation of the intrinsic viscosity of a very dilute solution over a broad range of shear rates. Hydrodynamic and excluded-volume interactions were treated explicitly. Shear thinning effects were observed for all simulated degrees of branching and, similar to dendrimers, as the molecular weight increases, the zero shear rate intrinsic viscosity reaches a maximum and then begins to fall. On the other hand, a reduction or disappearance of the peak was observed when the degree of branching decreased, which suggested that degree of branching was an effective index to distinguish different intrinsic viscosity behaviours on a qualitative basis. Nevertheless, degree of branching only accounts for the relative number of branch points and is insensitive to their distribution within the molecule (Sheridan et al., 2002). Therefore, the Wiener index was used to characterize the different structures in further study (Sheridan et al., 2002). Brownian dynamics simulations of hyperbranched polymers up to the sixth generation under elongational flow have also been reported (Neelov and Adolf, 2004), in which the statistical and rheological properties of a bead-rod model of hyperbranched materials were investigated. With the aid of Brownian dynamics techniques, the structure and transport properties of dendritic polymers in dilute solution subjected to planar shear flow have recently been studied (Bosko and Prakash, 2008).

Konkolewicz et al. (Konkolewicz et al., 2007) reported that reverse Monte Carlo (Watts et al., 2007) was applied to generate randomly branched polymers with different
architectures and sizes in solution. A logarithmic growth of radius of gyration with polymer mass was observed.

One of the most recent reports on hyperbranched polymers simulation was in 2008 (Dalakoglou et al., 2008). Brownian dynamics was applied to simulate complexes formed by hyperbranched polymers with linear polyelectrolytes under steady shear flow. Static and dynamic properties of these complexes were investigated. Another report (Konkolewicz et al., 2008) in 2008 presented Monte Carlo and molecular dynamics simulation results in order to test theoretical models for randomly hyperbranched polymers in solution.

2.5. Applications

Due to their unique properties and easy synthesis, hyperbranched polymers have a wide range of potential applications.


Because of the low cost and well-defined architecture with multifunctional terminal groups and narrow polydispersity, hyperbranched polymers have increasingly attracted attention in biomaterials application, as biocarriers and biodegradable materials (Gao and Yan, 2004, Frey and Haag, 2002, Cosulich et al., 2000, Lim et al., 2001).

Based on their special properties, hyperbranched polymers have been used as rheology modifiers or blend components (Kim and Webster, 1992, Hong et al., 1999, Hong et al., 2000, Mulkern and Tan, 2000, Jang et al., 2000, Ratna and Simon, 2001, Tang et al., 2002), tougheners for thermosets (Mezzenga et al., 2001, Xu et al., 1999, Wu et al., 1999, Gopala et al., 1999, Mezzenga et al., 2000, Boogh et al., 1999, Gryshchuk et al., 2002b, Gryshchuk et al., 2002a), cross-linking or adhesive agents (Oh et al., 2001,
Emrick et al., 2000) and dye-receptive additives for polyolefins (Burkinshaw et al., 2002, Schmaljohann et al., 1999). In the early 1990s, it was found that adding a small amount of hyperbranched polyphenylenes to a polystyrene melt greatly reduced the melt viscosity (Kim and Webster, 1990).

Due to a large number of functional groups and interesting optical, electrochemical, biological and mechanical properties of hyperbranched molecules, patterning of hyperbranched polymer films is receiving increased attention (Crooks, 2001, Lackowski et al., 1999, Ghosh and Crooks, 1999, Ghosh et al., 1999, Aoki et al., 1999, Ghosh et al., 2001).

Depending on the high solubility, low viscosity and abundant functional groups, hyperbranched polymers have been used as the base for various coating resins (Gao and Yan, 2004) including powder coatings (Johansson et al., 2000), flame retardant coatings (Zhu and Shi, 2002) and barrier coatings for flexible packaging (Lange et al., 2001).

Hyperbranched polymers such as poly(phenylenevinylene) and polythiophenes have been used as conjugated functional materials (optical, electronic and magnetic) because of their good solubility and excellent processibility (Gao and Yan, 2004, Lin et al., 2000, He et al., 2001, Dai et al., 2001, Yang et al., 2001, He et al., 2002).

Hyperbranched macromolecules possessing ethylene glycol chains have been designed, prepared and used as novel polymeric electrolytes or ion-conducting elastomers as they meet the requirements of having a high solvating power for appropriate ions, good ion transport and electrochemical stability (Gao and Yan, 2004, Itoh et al., 2001, Itoh et al., 2002, Wen et al., 2000, Itoh et al., 2003, Hong et al., 2002, Wang et al., 2001, Nishimoto et al., 1999).
3. Structure and rheology of polymeric fluids

3.1. Structural properties of polymers

In order to characterize the structure of polymers, different structural parameters need to be taken into account such as the degree of branching, Wiener index, radius of gyration, radial distribution of mass and interpenetration function.

3.1.1. Degree of branching and Wiener index

The topology of a polymer molecule is normally characterized by the degree of polymerization (number of sites), degree of branching and Wiener index. The two latter parameters are of great importance when polymers studied have the same molecular weight. As mentioned in the previous Chapter, the degree of branching, defined as 

\[ B = \frac{2D}{(2D + L)} \]

where \( D \) and \( L \) are the numbers of fully and partially reacted sites respectively, indicates the proportion of perfectly branching units in the molecule. For linear chains, the value of \( B \) is always 0. This value reaches the maximum of 1 for the case of dendrimers or fully branched hyperbranched polymers. Randomly branched hyperbranched polymers have the degree of branching falling between 0 and 1. Figure 3.1 illustrates some examples of polymer architecture with the same degree of polymerization but different degree of branching.

In addition to this structural parameter, the Wiener index is also used to distinguish polymers of different topologies. As previously defined in Chapter 2, 

\[ W = \frac{1}{2} \sum_{j=1}^{N} \sum_{i=1}^{N} d_{ij} \]

where \( d_{ij} \) is the number of bonds between bead \( i \) and \( j \). The Wiener index is important in describing the connectivity within a polymer molecule. Larger Wiener index numbers indicate higher numbers of bonds separating beads in molecules and hence more open structures of polymer molecules. Among non-cyclic polymers of the same molecular weight, linear chains have the largest Wiener index number while star polymers with the core functionality of \( N_s - 1 \) have the smallest value of \( W \). Figure 3.2 shows the Wiener indices of polymers with different architecture but the same degree of polymerization.
Figure 3.1. Degree of branching for different polymer architectures of the same molecular weight (blue beads representing linear units and red beads representing branching units).

Figure 3.2. Wiener index for different polymer architectures of the same molecular weight (10 monomers).
3. STRUCTURE AND RHEOLOGY OF POLYMERIC FLUIDS

3.1.2. Radius of gyration

The size of a polymer molecule can be described by the radius of gyration which is the trace of the tensor of gyration given as:

\[ \langle R_g R_g \rangle = \frac{\sum_{\alpha=1}^{N_i} m_\alpha (r_\alpha - r_{CM})(r_\alpha - r_{CM})}{\sum_{\alpha=1}^{N_i} m_\alpha} \]  \hspace{1cm} (3.1)

where \( r_\alpha \) is the position of site \( \alpha \), \( r_{CM} \) is the position of the molecular centre of mass, \( m_\alpha \) is the mass of site \( \alpha \) and the angle brackets denote an ensemble average. The radius of gyration is thus the average distance from the centre of gravity to the chain segment. It can be measured experimentally using different techniques and is dependent on molecular weight. Polymers with higher degree of polymerization normally have larger radius of gyration. Furthermore for a given value of molecular weight, depending on the branching topology, the value of the radius of gyration for different branched polymers can vary.

3.1.3. Radial distribution of mass

The radial distribution functions can give an extensive profile of the system structure. The distribution of sites from the molecular centre of mass is given as:

\[ g_{CM}(r) = \frac{\sum_{i=1}^{N} \sum_{\alpha=1}^{N_i} \delta(|r - (r_{i\alpha} - r_{CM})|)}{N} \]  \hspace{1cm} (3.2)

where \( N \) is the total number of molecules, \( r_{CM} \) is the position of the centre of mass and \( \alpha \) runs over all other sites belonging to the same molecule. Similarly, the distribution from the central site (the core) can be defined as:

\[ g_{core}(r) = \frac{\sum_{i=1}^{N} \sum_{\alpha=2}^{N_i} \delta(|r - (r_{i\alpha} - r_i)|)}{N} \]  \hspace{1cm} (3.3)

where \( r_i \) is the position of the core. If \( \alpha \) only runs over the outermost layer of each molecule, the distribution of terminal groups can be computed. This is important for the analysis of the entanglement and back folding in molecules.
In order to characterize the internal structure and spatial ordering of sites composing the materials, the atomic radial distribution can be computed as:

\[
g_A(r) = \frac{1}{2} \frac{\sum_{i \neq j} \sum_{i \neq j} \delta(|r - r_{ij}|)}{4\pi r^2 N_{total} \rho}
\]

where \( r_{ij} \) is the distance between the sites \( i \) and \( j \), \( N_{total} = NN_\alpha \) is the total number of sites in the studied system, and \( \rho \) is the density. Results can be compared to those of diffraction experiments.

Another useful function that has been used in this work is the interpenetration function which is defined as:

\[
g_{inter}(r) = \frac{\sum_{i \neq j} \sum_{i \neq i} \delta(|r - (r_{\alpha j} - r_{i i})|)}{4\pi r^2 N}
\]

where \( r_{\alpha j} \) is the position of bead \( \alpha \) in molecule \( j \). This function shows the ability of sites of a molecule to penetrate into the volume occupied by other molecules in the system. Polymers with more open structures have higher values of the interpenetration function as interior parts of molecules are more accessible.

### 3.2. Flow birefringence

Many complex fluids are birefringent because they contain orientable molecules, particles and microstructures that rotate and the index of refraction becomes anisotropic under flow, electric or magnetic fields (Larson, 1999). The birefringence due to the alignment of molecules is called ‘form birefringence’ while that caused by intramolecular bond alignment is called ‘intrinsic birefringence’. For simple polymeric fluids, the birefringence tensor is often proportional to the stress tensor. This relationship is called the ‘stress optical rule’ (SOR).

The form birefringence can be characterized by analysing the molecular alignment tensor given by:
where $\mathbf{u}_i$ is the unit vector denoting the orientation of the single molecules. The direction in which molecules are aligned is indicated by the eigenvectors of this tensor and the eigenvector corresponding to the largest eigenvalue of the tensor of gyration denotes the orientation of the molecule $\mathbf{u}_i$. The molecular alignment angle is the angle between the flow direction and the molecular alignment direction.

The intrinsic birefringence can be described using the bond alignment tensor which can be computed as:

$$
\mathbf{S}_b = \sum_{j} \left( \sum_{i=1}^{N-1} \mathbf{v}_i \mathbf{v}_i^T - \frac{1}{3} \mathbf{I} \right)
$$

where $\mathbf{v}_i$ is the unit vector between neighbouring sites, defined as:

$$
\mathbf{v}_i = \frac{\mathbf{r}_{i+1} - \mathbf{r}_i}{|\mathbf{r}_{i+1} - \mathbf{r}_i|}.
$$

The flow alignment angle and the extent of the bond alignment can be calculated similarly to those of the molecular alignment.

### 3.3. Rheology of polymeric fluids

Polymeric fluids are the most studied of all complex fluids due to their rich rheological behaviour which determines the ease and expense of processing as well as the final properties of different manufactured products. Polymeric fluids are classic examples of ‘viscoelastic’ fluids (Bird et al., 1987). The use of the word ‘elastic’ is to characterize the ability to return to its original state and shape after the release of the applied stress. Because of this property, polymeric fluids which have the elastic property are also referred to as ‘memory’ fluids.

Polymeric fluids often show strong viscoelastic effects which can include shear thinning, extension shear thickening, viscoelastic normal stresses and time-dependent rheology (Larson, 1999). In order to characterize the rheology of polymer liquids, systems of these materials under shearing or extensional flow are studied. There are many possible deformations that can be imposed on a polymeric fluid. Some of the
simple geometries for imposing a shear flow, including sliding plates, concentric cylinders, parallel disks and the cone and plate (Macosko, 1994), are presented in Figure 3.3.

![Simple geometries for producing shear flows](image)

Figure 3.3. Simple geometries for producing shear flows (a) sliding plates (planar Couette geometry), (b) concentric cylinders (cylindrical Couette geometry), (c) parallel disks or plate-and-plate (torsional flow) and (d) the cone-and-plate. (adopted from (Macosko, 1994)).

The simple geometry, sliding plates, experimentally generates planar Couette flow. The polymeric system is placed between two parallel plates moving in opposite directions. The resulting streaming velocity \( v = v(r, t) \) of the molecules has a linear profile as can be seen in Figure 3.4. The velocity gradient tensor is calculated as:

\[
\nabla v = \frac{\partial v}{\partial r}
\]

and the strain rate, which is the symmetric part of this tensor, can be computed as:

\[
\dot{\gamma} = \sqrt{2I_2}
\]

where \( I_2 = \text{Tr}(D \cdot D) \) and \( D = \frac{1}{2} \left( \nabla v + (\nabla v)^T \right) \). This planar Couette geometry has been employed in this work with linear streaming velocity profiles for molecules but with the absence of sliding plates.
3. STRUCTURE AND RHEOLOGY OF POLYMERIC FLUIDS

Figure 3.4. Streaming velocity profile of the polymeric fluid undergoing planar Couette flow.

3.3.1. Shear stress

The shear stress is the force that a flowing fluid exerts on a surface in the direction parallel to the flow. The shear stress $\sigma_{xy}(t)$ is the corresponding off-diagonal element of the stress tensor $\sigma(t)$ which is given by:

$$
\sigma(t) = -\left[ P(t) - \frac{1}{3} \rho I \right]
$$

(3.11)

where $P$ is the pressure tensor, $\rho$ is the hydrostatic pressure and $I$ is a unit tensor. For Newtonian fluids, only the shear stress is nonzero. However for non-Newtonian liquids, all six independent components of the stress tensor may be nonzero. The general form of the stress tensor in planar shear is given as:

$$
\sigma = \begin{bmatrix}
\sigma_{xx} & \sigma_{xy} & 0 \\
\sigma_{yx} & \sigma_{yy} & 0 \\
0 & 0 & \sigma_{zz}
\end{bmatrix}
$$

(3.12)

In all polymeric systems, the stress depends on the conformations of the molecules. After a steady shear flow has been imposed on a fluid for a suitable period of time, the shear stress often converges to a steady state value.
3. STRUCTURE AND RHEOLOGY OF POLYMERIC FLUIDS

3.3.2. Non-Newtonian viscosity

The steady-state shear viscosity is defined as:

$$\eta = \frac{\sigma_{xy}}{\dot{\gamma}}$$  \hspace{1cm} (3.13)

The dependence of viscosity on shear rate is the most characteristic feature of a macromolecular complex fluid. Unlike Newtonian fluids which have constant viscosity, the viscosity of polymeric fluids reaches a plateau in the low strain rate region and decreases at strain rates above a certain value. In some cases, the viscosity drops rapidly and by many orders of magnitude. The decrease of viscosity is called shear thinning and the materials expressing it are referred to as pseudo-plastic. In fact, most of the polymer solutions and melts which exhibit a shear-rate dependent viscosity are shear thinning (Bird et al., 1987). The critical shear rate at which the transition from Newtonian to non-Newtonian flow occurs is related to a relaxation time $\tau_0$ characteristic for the molecules composing the system through the form:

$$\dot{\gamma}_c = \frac{1}{\tau_0}$$  \hspace{1cm} (3.14)

At shear rates above the critical value, the viscosity becomes shear rate dependent.

On the other hand, the shear viscosity for some macromolecular fluids increases with the shear rate. This phenomenon is called shear thickening. Furthermore some fluids can show a region of shear thinning at low shear rates, then shear thickening at higher shear rates and followed by shear thinning again at very high shear rates. This behaviour was found in the flow of dense suspensions (Larson, 1999).

3.3.3. Normal stress effects

The viscoelastic effects of polymeric liquids can be represented by the normal stress differences of the liquid in steady flow. The first normal stress difference, which is defined as:

$$N_1 (\dot{\gamma}) = \sigma_{xx} - \sigma_{yy}$$  \hspace{1cm} (3.15)

where $\sigma_{xx}$ and $\sigma_{yy}$ are the xx and yy components of the stress tensor, is always positive. This implies that there is a higher degree of orientation in the direction of the flow, the x...
3. STRUCTURE AND RHEOLOGY OF POLYMERIC FLUIDS

direction, than in the direction of the velocity gradient, the $y$ direction. In contrast, the second normal stress difference, which is given by:

$$N_2(\dot{\gamma}) = \sigma_{yy} - \sigma_{zz}$$

(3.16)

where $\sigma_{zz}$ is the $zz$ component of the stress tensor, is always negative. This implies that the orientation in the $y$ direction is reduced because of the polymer orientation related to the vorticity $z$ direction (Larson, 1999). Although the second normal stress difference has been studied much less extensively, it was found that the dependence of the second normal stress difference on shear rate is similar to that for the first normal stress difference but smaller by an order of magnitude.

From the first and second normal stress differences, the first and second normal stress coefficients, which are used to describe the behaviour of the molecular fluids, can be calculated using the following equations:

$$\psi_1(\dot{\gamma}) = \frac{N_1}{\dot{\gamma}^2}$$

(3.17)

$$\psi_2(\dot{\gamma}) = \frac{N_2}{\dot{\gamma}^2}$$

(3.18)

Together with the viscosity, the first and second normal stress coefficients are sometimes collectively referred to as the viscometric functions. The positive value of the first normal stress coefficient means that the polymeric fluids exhibit an extra tension along the streamlines in the $x$ direction in addition to the shear stresses. In contrast, the negative and much smaller value of the second normal stress coefficient means that the fluids exhibit a small extra tension in the $z$ direction. (Bird et al., 1987).

3.3.4. Dimensionless groups in non-Newtonian fluid mechanics

Dimensionless groups are useful for scaling arguments and classifying flow regimes (Bird et al., 1987). In Newtonian fluid mechanics, the Reynolds number, which is interpreted as the ratio of the magnitude of inertial forces to that of viscous forces, is generally the most important dimensionless group. For non-Newtonian fluids, the key dimensionless groups are Deborah number and Weissenberg number.
In this work, only the Weissenberg number has been used with the purpose of establishing master curves for shear viscosity data of different hyperbranched polymers. The Weissenberg number is defined as:

\[ Wi = \lambda \kappa \]  

(3.19)

where \( \lambda \) is a characteristic time of the fluid and \( \kappa \) is a characteristic strain rate in the flow.
4. Molecular dynamics simulation

4.1. Brief overview of different computer simulation methods

Computer simulation is a powerful and modern tool for solving scientific problems as numerical experiments can be performed for new materials without synthesizing them. One of the aims of computer simulation is to reproduce experiments to elucidate the invisible microscopic details and further explain experiments. On the other hand, simulation can also be used as a useful predictive tool. The most widely used simulation methods for molecular systems are Monte Carlo, Brownian dynamics and molecular dynamics.

The Monte Carlo method is a stochastic strategy that relies on probabilities (Sadus, 1999). The Monte Carlo sampling technique generates large numbers of configurations or microstates of equilibrated systems by stepping from one microstate to the next in a particular statistical ensemble. Random changes are made to the positions of the species present, together with their orientations and conformations where appropriate. Quantities of interest can be averaged over these microstates. The advantages of the Monte Carlo simulation technique include the ease of extending it to simulate different ensembles, flexibility in the choice of sampling functions and the underlying matrix or trial move which must satisfy the principle of microscopic reversibility as well as time-saving as only the potential energy is required (Allen and Tildesley, 1993).

Brownian dynamics is an efficient approach for simulations of large polymer molecules or colloidal particles in a small molecule solvent. In this approach, the solvent is treated as a viscous continuum which dissipates energy as macromolecules or particles move through it. The Brownian motion of the macromolecules produced by random collisions with solvent molecules is mimicked by a stochastic force generated by pseudo-random numbers.

Molecular dynamics is the most detailed molecular simulation method (Allen and Tildesley, 1987) which computes the motions of individual molecules. Coupled Newton’s equations of motion, which describe the positions and momenta, are solved for a large number of particles in an isolated cluster or in the bulk using periodic
boundary conditions. The equations of motion for these particles which interact with each other via intra- and inter-molecular potentials can be solved accurately using various numerical integration methods such as the common predictor-corrector or Verlet methods. Molecular dynamics efficiently evaluates different configurational properties and dynamic quantities which cannot generally be obtained by Monte Carlo (Haile, 1997).

4.2. **Coarse-grained model**

Early models of liquids (Morrell and Hildebrand, 1936) involved the physical manipulation and analysis of the packing of a large number of gelatine balls, representing the molecules. This resulted in a surprisingly good three-dimensional picture of the structure of a liquid. Later, there was some interest in the study of assemblies of metal ball bearings, kept in motion by mechanical vibration (Pieranski et al., 1978). However the use of large numbers of physical objects to represent molecules can be very time-consuming, there are obvious limitations on the types of interactions between them, and the effects of gravity can never be eliminated. The natural extension of this approach is to use a mathematical, rather than a physical, model, and to perform the analysis by computer (Allen and Tildesley, 1987).

The first computer simulation of liquids was carried out in 1953 (Metropolis et al., 1953). The model was an idealized two-dimensional representation of molecules as rigid disks. Only four years later, the simulation was carried out on the three-dimensional Lennard-Jones fluids (Wood and Parker, 1957) which made it possible to compare data obtained from experiments with computer-generated data. In the late 1950s, the molecular dynamics method was first introduced to study the interactions of hard spheres (Alder and Wainwright, 1957, Alder and Wainwright, 1959).

Nowadays simulation of materials can be performed at different scales, from a coarse-grained approach to a fully atomistic model. Although the fully atomistic method is more accurate, it is computationally expensive due to a large number of degrees of freedom and provides a large amount of data that is sometimes irrelevant to the properties studied. For macromolecular systems, the coarse-grained approach is widely
used as the modeling process is simplified, hence becomes more efficient, and the characteristic topological features of the molecule can still be maintained.

The level of detail for a coarse-grained model varies for different cases. The whole molecule can be represented by a single particle in a simulation and interactions between particles incorporate average properties of the whole molecule. With this approach, the number of degrees of freedom is greatly reduced. Different polymers have been modeled using this method (Bolhuis et al., 2001, Harreis et al., 2003, Likos et al., 2002, Likos et al., 2001, Louis and Bolhuis, 2000). On the other hand, a segment of a polymer molecule can also be represented by a particle (bead). Using this method, branched polymers of different architectures have been successfully simulated (Jabbarzadeh et al., 2003).

The first coarse-grained model, called the ‘dumbbell’ model, was introduced in the 1930s (Bird et al., 1987). This is only a very crude representation of polymers, as can be seen in Figure 4.1. Molecules are treated as a pair of beads interacting via a harmonic potential. However by using this model, it is possible to perform kinetic theory derivations and calculations for nonlinear rheological properties and solve some flow problems. The analytical results for the dumbbell models can also be used to check computer simulation procedures in molecular dynamics and Brownian dynamics (Bird et al., 1987).

![Rigid dumbbell model of length L and orientation given by unit vector \( \mathbf{u} \)](image)

![Elastic dumbbell model with configuration given by vector \( \mathbf{Q} \)](image)

Figure 4.1. The first coarse-grained models – the rigid and elastic dumbbell models.
Some years later, the bead-rod and bead-spring model were introduced to model chainlike macromolecules. Beads in the bead-rod model do not represent the atoms of the polymer chain backbone, but some portion of the chain, normally 10 to 20 monomer units. These beads are connected by rigid and massless rods. While in the bead-spring model, a portion of the chain containing several hundreds of backbone atoms are replaced by a “spring” and the masses of the atoms are concentrated in the mass of beads. Figure 4.2 illustrates the configurations of linear polymers represented by these models.

![Bead-rod chain model with rod orientations given by unit vectors $u_i$](image1)

![Bead-spring chain model with spring configurations given by connector vectors $Q_i$](image2)

**Figure 4.2. The freely jointed bead-rod and bead-spring chain models.**

If the springs are taken to be Hookean springs, the bead-spring chain is referred to as a Rouse chain or a Rouse-Zimm chain. This approach has been applied widely as it has a large number of internal degrees of freedom and exhibits orientability and stretchability. However the disadvantage of this model is that it does not have a constant contour length and can be stretched out to any length. Therefore in many cases finitely extensible springs with two more parameters, the spring constant and the maximum extensibility of an individual spring, can be included so the contour length of the chain model cannot exceed a certain limit.
In this work, hyperbranched polymers have been simulated using coarse-grained uniform beads connecting via finitely extensible springs. These basic units correspond to the linear units or branching points of the molecule and are interconnected to create tree-like structures. Beads along the chain can rotate and vibrate freely. All beads are identical and indistinguishable except for their positions in the molecule.

### 4.3. Intermolecular interaction

The most widely used model to calculate the interactions is the Lennard – Jones (LJ) potential. This model is useful for soft-sphere pair potentials and was introduced in 1924 (Lennard-Jones, 1924a, Lennard-Jones, 1924b):

\[
U_{ij}^{LJ} = k \epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^n - \left( \frac{\sigma}{r_{ij}} \right)^m \right] \tag{4.1}
\]

where

\[
k = \frac{n}{n-m} \left( \frac{n}{m} \right)^{n/(n-m)} \tag{4.2}
\]

This model attempts to account for both short range, repulsive overlap forces, and longer range, attractive dispersion forces. Short range repulsive forces prevent the substance from collapsing onto itself whereas longer range attractions deter disintegration of the substance (Haile, 1997). These forces have the range and strength determined by the values of \(n\) and \(m\). The value of \(m\) is normally chosen to be 6 because the leading term in London’s theory (London, 1930) for dispersion varies as \(1/r^6\) and the value of \(n\) is set as \(n = 2m = 12\). The resulting LJ model is then given as:

\[
U_{ij}^{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] \tag{4.3}
\]

In order to shorten the computer time, the pair interactions beyond the distance of \(r_c\) are neglected. Therefore the LJ potential actually used in simulations is a truncated version defined as:

\[
U_{ij}^{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] \quad \text{for} \quad r_{ij} \leq r_c \tag{4.4}
\]

\[
U_{ij}^{LJ} = 0 \quad \text{for} \quad r_{ij} > r_c
\]
4. MOLECULAR DYNAMICS SIMULATION

$r_c$ is normally chosen to be $2.5\sigma$, at which $U = -0.0163\varepsilon$, hence when $r_{ij} = r_c$, atom $j$ only makes a small contribution to the force on atom $i$ (Haile, 1997).

In this work, the pairwise Weeks-Chandler-Anderson (WCA) (Weeks et al., 1971) potential is used. This is actually a truncated and shifted LJ potential given by:

$$
U_{ij}^{WCA} = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] + \varepsilon \quad \text{for} \quad r_{ij}/\sigma < 2^{1/6} \\
U_{ij}^{WCA} = 0 \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{for} \quad r_{ij}/\sigma \geq 2^{1/6}
$$

where $r_{ij}$ is the separation between the sites represented by beads $i$ and $j$, $\varepsilon$ is the potential well depth, and $\sigma$ is the effective diameter of the beads. This potential results in a purely repulsive force that includes the effect of excluded volume.

For beads with chemical bonds, a finitely extensible nonlinear elastic (FENE) (Grest and Kremer, 1986) potential is added. The FENE potential is given as:

$$
U_{ij}^{FENE} = -0.5kR_0^2 \ln \left[ 1 - \left( \frac{r_{ij}}{R_0} \right)^2 \right] \quad \text{for} \quad r_{ij} \leq R_0 \\
U_{ij}^{FENE} = \infty \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{for} \quad r_{ij} \geq R_0
$$

where $R_0$ is a finite extensibility and $k$ is a spring constant. In this work, these FENE parameters, $R_0$ and $k$, were set to 1.5 and 30 respectively. For this choice of parameters the maximal extent of bonds is short enough to prevent crossing of branches, whereas the magnitude of the bonding force is small enough to enable simulations with relatively large time steps (Bosko et al., 2004a, Kroger et al., 1993). The FENE chain model is not only suitable for entangled and unentangled polymer melts but is also applicable to monodisperse and polydisperse polymers.

Figure 4.3 illustrates the interaction potential between non-bonded and bonded beads. Non-bonded beads only have WCA potential interactions whereas bonded beads have both FENE and WCA interactions which creates a potential well for the flexible bonds that maintains the architecture of the molecules.
4. MOLECULAR DYNAMICS SIMULATION

Figure 4.3. Interaction potential between non-bonded beads which interact via only the WCA potential and bonded beads which interact via both WCA and FENE potential.

From the interaction potentials between beads, the force acting on each bead for the system of beads at position \( \mathbf{r}_i \) can be calculated as:

\[
\mathbf{F}_i = -\nabla_{\mathbf{r}_i} \left( \sum_{\text{bonds}} U_{\text{bond}}(r_{ij}) + \sum_{i=1}^{N_{\text{total}}} \sum_{j>i}^{N_{\text{total}}} U_{\text{non-bond}}(r_{ij}) \right)
\]

where \( N_{\text{total}} \) is the total number of interacting beads. The overwhelming proportion of the computing effort is spent in the calculation of the forces on each atom/bead.

All quantities reported hereafter in this thesis will be presented in reduced LJ units:

\[
\begin{align*}
  r_{ij}^* &= r_{ij} / \sigma, \\
  \rho^* &= \rho \sigma^3, \\
  T^* &= k_B T / \varepsilon, \\
  \mathbf{P}^* &= \mathbf{P} \sigma^3 / \varepsilon, \\
  \dot{\gamma}^* &= (m_0 \sigma^2 / \varepsilon)^{1/2} \dot{\gamma}, \\
  \eta^* &= (\sigma^4 / m_0 \varepsilon)^{1/2} \eta,
\end{align*}
\]

with both \( \varepsilon \) and \( \sigma \) being assigned a value of one, \( \rho \) is the bead density, \( T \) is the kinetic temperature, \( \mathbf{P} \) is the pressure tensor, \( \dot{\gamma} \) is the strain rate, and \( \eta \) is the shear viscosity. In
addition, the mass of the beads was assigned to one. For simplicity of notation, the asterisk will be omitted hereafter.

4.4. Periodic boundary conditions

Molecular dynamics is typically applied to small systems containing thousands of particles. Unless the behaviours near the walls (surface effects) are of interest, they can be eliminated and periodic boundary conditions are employed to simulate the bulk material. Particles are generated in a volume $V$ which is called the primary cell. The bulk is assumed to be composed of the primary cell surrounded by its exact replicas to model a macroscopic sample. The image cells not only have the same size and shape as the primary one but also contain particles that are images of the particles in the primary cell. Cells are separated by open boundaries so particles can freely enter or leave any cell. When particles leave the cell, their images simultaneously enter the cell through the opposite face. Therefore the shape of the cells must be space filling. The number of image cells needed depends on the range of intermolecular forces. When the forces are sufficiently short ranged (e.g. in truncated Lennard-Jones model), only image cells that adjoin the primary cell are needed (minimum image convention). For squares in two dimensions, there are eight adjacent image cells whereas for cubes in three dimensions, the number of adjacent images is 26 (Haile, 1997). Figure 4.4 illustrates the periodic boundary condition in two dimensions with the primary cell surrounded by eight of its image cells.

For simulations of shear flows, the application of the standard periodic boundary condition would lead to a discontinuity in the coordinates and momenta on the edge of the simulation box. Therefore an appropriate modification is necessary in order to maintain a steady linear velocity profile for planar shear flows. In this work, molecules were generated in a cubic simulation box which was surrounded by its periodic images and Lees-Edwards shear boundary conditions (Lees and Edwards, 1972) were applied to eliminate effects associated with surfaces and the small volume of the system.
Figure 4.4. Periodic boundary condition in two dimensions with the primary cell surrounded by its image cells. Molecules that leave the cell will be replaced by their images entering the cell from the opposite side.

It can be seen in Figure 4.5 that for the linear velocity profile with the streaming velocity in the $x$ direction and its gradient in the $y$ direction, the cells in the $x$ and $y$ directions are still periodically repeated. However in the $y$ directions, the image cells are displaced with reference to the central one according to the streaming velocity. The displacement of these cells with reference to the central cell is given by:

$$D = i\gamma L_y$$

(4.14)

where $L_y$ is the size of the simulation box along the $y$ axis in the absence of any other external forces. The motion of the periodic images of particles above and below the simulation box after some time would induce a linear streaming velocity profile.
4.5. **Equations of motion**

There are many ways of writing the equations of motion for systems composed of interacting molecules (Allen and Tildesley, 1987).

The most fundamental form is the Lagrangian equation of motion which is given as:

\[
\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_k} \right) - \frac{\partial L}{\partial q_k} = 0
\]

(4.15)

where \( L(q, \dot{q}) \) is the Lagrangian function defined in terms of kinetic energy \( K \) and potential energy \( U \) as \( L(q, \dot{q}) = K - U \). The Lagrangian is a function of the generalized coordinates \( q_k \) and their time derivatives \( \dot{q}_k \). If a system of particles with mass \( m \), in the Cartesian coordinates \( r_i \), is considered, the Lagrangian equation of motion reduces to Newton’s second-order differential equation of motion:

\[
m \ddot{r}_i = F_i.
\]

(4.16)

Defining the generalized momentum \( p_k \) conjugate to \( q_k \) as:
4. MOLECULAR DYNAMICS SIMULATION

\[ p_k = \frac{\partial L}{\partial \dot{q}_k} \]  

the Hamiltonian is then defined as:

\[ H(p, q) = \sum_k \dot{q}_k p_k - L(q, \dot{q}) \]  

Therefore the Hamiltonian form of the equations of motion is given as:

\[ \dot{q}_k = \frac{\partial H}{\partial p_k} \]

\[ \dot{p}_k = -\frac{\partial H}{\partial q_k} \]  

The advantage of the Hamiltonian equations of motion is that for Cartesian coordinates, Hamilton’s equations reduce to a set of first-order differential equations given by:

\[ \ddot{r}_i = \frac{p_i}{m_i} \]

\[ \dot{p}_i = -\nabla r_i V = F_i \]  

The solution of the Lagrangian and Hamiltonian equations of motion yields the complete dynamics of the system.

For the purpose of simulating systems undergoing shearing flow, therefore away from equilibrium, two different approaches can be applied.

One of the two common methods to derive transport properties is through analyzing the equilibrium correlation functions. The disadvantage of this approach is the significant statistical errors with time correlation functions representing the average response to naturally occurring small fluctuations in the system properties and the unfavorable signal-to-noise ratio at long times, where there may be a significant contribution to the integral defining a transport coefficient. The finite system size also limits the maximum time for which reliable correlations can be calculated (Allen and Tildesley, 1987).

The second method that can be employed to study systems away from equilibrium is to sample a non-equilibrium ensemble directly. A perturbation field is incorporated into the classic molecular dynamics model. The advantages of this approach are a much larger fluctuation induced and dramatically improved signal-to-noise level of the measured response. In order to simulate fluids under shear, two different methods can
be employed. The first one is called a boundary-driven algorithm in which the periodic boundary conditions are modified to simulate systems far from equilibrium. The most useful of these is the Lees-Edwards boundary conditions. However this algorithm has two serious shortcomings (Allen and Tildesley, 1987). Firstly there is no connection with response theory, hence links to the statistical mechanics of transport are not possible. Furthermore long times are required for the effects of translation of atoms between boundaries to communicate throughout the fluids or through the simulation cell. Therefore a linear streaming velocity will only evolve after a sufficiently long time and time-dependent transport properties cannot be studied (Todd and Daivis, 2007). Alternatively a synthetic field method such as the SLLOD algorithm (Evans and Morriss, 1990) can be used to study systems under shear. The history of this algorithm can be traced back to 1980 when the first homogenous NEMD algorithm, the DOLLS Hamiltonian, was invented (Hoover et al., 1980). In this approach, the effect of a boundary that drives the flow is replaced by a fictitious external field which is designed to guarantee that the required streaming velocity profile is maintained indefinitely. The flow field is incorporated into the equations of motion which are given as:

\[
\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{r}_i \cdot \mathbf{\nabla} \mathbf{u} \tag{4.21}
\]

\[
\mathbf{p}_i = \mathbf{F}_i - \mathbf{\nabla} \mathbf{u} \cdot \mathbf{p}_i
\]

where \( \mathbf{r}_i \) and \( \mathbf{p}_i \) are the position and thermal momentum of an atom/bead \( \alpha \) in molecule \( i \), \( \mathbf{F}_i \) is the interatomic force on atom \( i \) and \( \mathbf{\nabla} \mathbf{u} \) is the velocity gradient tensor which takes the form:

\[
\mathbf{\nabla} \mathbf{u} = \begin{pmatrix}
\dot{\gamma}_{xx} & \dot{\gamma}_{xy} & \dot{\gamma}_{xz} \\
\dot{\gamma}_{yx} & \dot{\gamma}_{yy} & \dot{\gamma}_{yz} \\
\dot{\gamma}_{zx} & \dot{\gamma}_{zy} & \dot{\gamma}_{zz}
\end{pmatrix}
\tag{4.22}
\]

This algorithm is suitable for simulating flows in the linear response limit but not for generating physically realistic shear flow at high field strengths (Evans and Morriss, 1984). It was then proposed that the correct set of equations of motion was given by:

\[
\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{r}_i \cdot \mathbf{\nabla} \mathbf{u} \tag{4.23}
\]

\[
\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \mathbf{\nabla} \mathbf{u}
\]

and named SLLOD to indicate the transpose of DOLLS.
In this work, the SLLOD algorithm has been applied to simulate hyperbranched polymer fluids under shear. Depending on the velocity gradient tensor, the SLLOD algorithm will correspond to different forms of flow.

When only diagonal elements of the velocity gradient tensor are nonzero (either positive or negative), the equations of motion will correspond to the expansion or compression at a steady state.

\[
\begin{align*}
\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m} + \mathbf{r}_i \cdot \nabla \mathbf{u} \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{u} \\
\mathbf{u} &= \begin{pmatrix} \dot{\varepsilon}_{xx} & 0 & 0 \\ 0 & \dot{\varepsilon}_{yy} & 0 \\ 0 & 0 & \dot{\varepsilon}_{zz} \end{pmatrix}
\end{align*}
\] (4.24)

This approach is used in this work to prepare the initial configuration for simulations of polymer melts under shear. Systems of polymer molecules are first generated at a low density and then compressed until the required density is achieved.

When only one off-diagonal element of the velocity gradient tensor is nonzero, the SLLOD algorithm corresponds to planar Couette flow:

\[
\begin{align*}
\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m} + \mathbf{r}_i \cdot \nabla \mathbf{u} \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{u} \\
\mathbf{u} &= \begin{pmatrix} 0 & 0 & 0 \\ \dot{y}_{ys} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
\frac{\partial u_x}{\partial y} &= \dot{y}_{ys}
\end{align*}
\] (4.25)

This is the standard approach employed in this work to study the melts of different hyperbranched polymers under shear.

Using the SLLOD algorithm has many advantages (Allen and Tildesley, 1987, Allen and Tildesley, 1993). Firstly, the SLLOD equations of motion only involve the coordinates and the peculiar momenta of the particles. Furthermore the thermostat, internal energy and pressure involve peculiar, rather than laboratory velocities. Secondly, the SLLOD momenta are continuous as particles leave and enter the primitive cell, so the calculation is more stable than it otherwise might be. Finally, the SLLOD equations transform a boundary driven system into one with an external field, which makes the system more amenable to theoretical analysis.

However in order to apply the above atomic SLLOD algorithm for molecular systems, the equations of motion need to be redefined as the streaming velocity is imposed on the molecule and all its parts according to the position of its centre of mass. This is different
from the atomic SLLOD where the linear velocity profile is imposed on atoms/beads according to their current position. Nevertheless, in the steady state, both atomic and molecular methods produce the same results if the atomic/bead streaming velocity is correctly accounted for (Edberg et al., 1986, Edberg et al., 1987).

The atomic version of the SLLOD equations of motion for molecular systems is given as:

\[
\dot{r}_{ia} = \frac{p_{ia}}{m_{ia}} + r_{ia} \cdot \nabla u \\
\dot{p}_{ia} = F_{ia} - p_{ia} \cdot \nabla u
\]  

(4.26)

where \( r_{ia} \) and \( p_{ia} \) are the position and momentum of an atom/bead \( \alpha \) in molecule \( i \) and \( m_{ia} \) is an atomic mass.

The molecular version of the SLLOD equations of motion, which is the form of the algorithm used in this work, is given by:

\[
\dot{r}_{ia} = \frac{p_{ia}}{m_{ia}} + r_{i} \cdot \nabla u \\
\dot{p}_{ia} = F_{ia} - (m_{ia} / M_i) p_{i} \cdot \nabla u
\]  

(4.27)

where \( N_s \) is the number of atoms/beads in a molecule, \( M_i \) is the molecular mass, \( r_{i} \) is the position of the molecular centre of mass, and \( p_{i} \) is momentum of the molecule. These quantities can be defined as:

\[
M_i = \sum_{\alpha=1}^{N_s} m_{ia} \\
\]

(4.28)

\[
r_{i} = \sum_{\alpha=1}^{N_s} m_{ia} r_{ia} / M_i \\
\]

(4.29)

\[
p_{i} = \sum_{\alpha=1}^{N_s} p_{ia} \\
\]

(4.30)

In constant temperature simulations, the equations of motion are modified and given by:

\[
\dot{r}_{ia} = \frac{p_{ia}}{m_{ia}} + r_{i} \cdot \nabla u \\
\dot{p}_{ia} = F_{ia} - (m_{ia} / M_i) p_{i} \cdot \nabla u - \zeta (m_{ia} / M_i) p_{i}
\]  

(4.31)
where $\zeta$ is the thermostat constraint multiplier which is given as:

$$
\zeta = \frac{\sum_{i=1}^{N} \mathbf{F}_i \cdot \mathbf{p}_i - \gamma \sum_{i=1}^{N} p_{ix} p_{iy}}{\sum_{i=1}^{N} \mathbf{p}_i^2}
$$

(4.32)

This molecular version of the Gaussian isokinetic thermostat $\zeta$ is used to keep the translational kinetic temperature fixed. $\zeta$ is determined by the condition that the molecular kinetic energy is constant and the deviations of the trajectories from the unthermostated ones is minimized. The justification for using the molecular thermostat algorithm is discussed in detail elsewhere (Todd and Daivis, 2007).

For constant pressure simulations, the equations of motion (Todd and Daivis, 2007) are given by:

$$
\mathbf{r}_{ia} = \frac{\mathbf{p}_{ia}}{m_{ia}} + \mathbf{r}_i \cdot \nabla \mathbf{V} + \mathbf{\varepsilon} \mathbf{r}_i
$$

$$
\dot{\mathbf{p}}_{ia} = \mathbf{F}_{ia} - \left(\frac{m_{ia}}{M_i}\right) \mathbf{p}_i \cdot \nabla \mathbf{V} - \zeta \left(\frac{m_{ia}}{M_i}\right) \mathbf{p}_i - \dot{\varepsilon} \left(\frac{m_{ia}}{M_i}\right) \mathbf{p}_i
$$

(4.33)

$$
\dot{\mathbf{V}} = 3\dot{\varepsilon} \mathbf{V}
$$

where $\varepsilon$ is the multiplier which depends on the difference between the instantaneous pressure $p$, the required pressure $p_0$ and a damping factor $Q$ chosen by trial and error to give good damping of the pressure fluctuations as follows:

$$
\varepsilon = \frac{(p - p_0) V}{Q N k_B T}
$$

(4.34)

In all constant pressure simulations of hyperbranched polymers in this work, the damping factor was chosen to be 1000 to minimize the effect of unphysical oscillations of volume and molecular pressure caused by coupling the simulated system to the barostat. Therefore the melts are allowed to relax to compensate for the flow-induced changes in the pressure.

### 4.6. Integration

As the most computationally intensive component of the computation is the force evaluation, any integration method requiring more than one such calculation per time-step is wasteful unless it can deliver a proportionate increase in the size of the time-step.
4. MOLECULAR DYNAMICS SIMULATION

$\Delta t$ while maintaining the same accuracy. Therefore the well-known Runge-Kutta method is not suitable as it is unable to enlarge the time-step beyond the limit of $\Delta t$ due to the strongly repulsive force at short distances in the Lennard-Jones potential (Haile, 1997, Rapaport, 1995). The multiple time-step algorithms (Tuckerman et al., 1992), in which the potential is divided into the short range interactions with a shorter time step and the long range interactions with a much longer time step, have been shown to be efficient in molecular dynamics simulations (Frenkel and Smit, 1996).

There are two common algorithms, which are used to solve the equations of motion, namely the Gear predictor-corrector and the Verlet algorithms, as both of these algorithms require only one evaluation of the forces at each time step.

The Verlet algorithm uses information from the current and previous time steps to advance the atomic positions (Allen and Tildesley, 1993). The algorithm can be constructed by considering the two Taylor expansions from $t$ to $t + \Delta t$ and $t - \Delta t$. Adding or subtracting these equations produces the equation for advancing the positions or velocity. Some modifications to the Verlet scheme, such as ‘leap-frog’ and ‘velocity-Verlet’ algorithms, have been suggested to try to improve the method of handling the velocities. These algorithms are simpler to use and require less memory than the Gear predictor-corrector (Allen and Tildesley, 1987, Allen and Tildesley, 1993).

The Gear predictor-corrector method is composed of three steps (Allen and Tildesley, 1987, Allen and Tildesley, 1993). From a significant number of time derivatives of the atomic positions at time $t$, fourth-order Taylor series expansions are used to predict the position at time $t + \Delta t$. For the first-order differential equation:

$$\dot{\mathbf{r}} = f(\mathbf{r})$$

the predictor step would have the form:

$$
\begin{bmatrix}
\mathbf{r}_0''(t + \Delta t) \\
\mathbf{r}_1''(t + \Delta t) \\
\mathbf{r}_2''(t + \Delta t) \\
\mathbf{r}_3''(t + \Delta t) \\
\mathbf{r}_4''(t + \Delta t)
\end{bmatrix} =
\begin{bmatrix}
1 & 1 & 1 & 1 & 1 \\
0 & 1 & 2 & 3 & 4 \\
0 & 0 & 1 & 2 & 3 \\
0 & 0 & 0 & 1 & 2 \\
0 & 0 & 0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
\mathbf{r}_0''(t) \\
\mathbf{r}_1''(t) \\
\mathbf{r}_2''(t) \\
\mathbf{r}_3''(t) \\
\mathbf{r}_4''(t)
\end{bmatrix}
$$

(4.36)
where \( r_i \) are the scaled time derivatives: 
\[
\begin{align*}
  r_1 &= \delta t \left( \frac{dr_0}{dt} \right), \\
  r_2 &= \frac{1}{2} \delta t^2 \left( \frac{d^2 r_0}{dt^2} \right), \\
  r_3 &= \frac{1}{6} \delta t^3 \left( \frac{d^3 r_0}{dt^3} \right) \quad \text{and} \\
  r_4 &= \frac{1}{24} \delta t^4 \left( \frac{d^4 r_0}{dt^4} \right).
\end{align*}
\]

The order of the method depends on the number of elements taken into account in the expansion.

In the evaluation step which is the most time consuming, the forces at \( t + \Delta t \) are computed using the series of predicted positions and their derivatives to give accelerations. The difference between the predicted value of the first scaled derivative \( r_1^p \) and the correct one \( r_1^c \) calculated by the substitution of \( r_0^p \) into the equation of motion (the right side of the equation) can be derived from:
\[
\Delta r = r_1^c - r_1^p \tag{4.37}
\]

and used in the corrector step.

In the final step, the corrected values at the end of the integration step take the form:
\[
\begin{pmatrix}
  r_0(t + \Delta t) \\
  r_1(t + \Delta t) \\
  r_2(t + \Delta t) \\
  r_3(t + \Delta t) \\
  r_4(t + \Delta t)
\end{pmatrix} = \begin{pmatrix}
  r_0^p(t + \Delta t) \\
  r_1^p(t + \Delta t) \\
  r_2^p(t + \Delta t) \\
  r_3^p(t + \Delta t) \\
  r_4^p(t + \Delta t)
\end{pmatrix} + \begin{pmatrix}
  c_0 \\
  c_1 \\
  c_2 \\
  c_3 \\
  c_4
\end{pmatrix} \Delta r \tag{4.38}
\]

The difference between the predicted and corrected accelerations is used with a set of Gear coefficients \( c_i \) to correct all of the predicted derivatives of the motion. These Gear coefficients are chosen to optimize the stability and accuracy of the trajectories. They depend on the order of the differential equation and the number of derivatives used in the Taylor series prediction of the positions. Gear has discussed and proposed the best choice, and for the fourth-order algorithm applied to the first-order differential equation the values are: \( c_0 = 251/720 \), \( c_1 = 1 \), \( c_2 = 11/12 \), \( c_3 = 1/3 \), \( c_4 = 1/24 \) (Gear, 1971).

This method offers great flexibility and good stability as the corrector step amounts to a feedback mechanism that can dampen instabilities that might be introduced by the predictor. For computing particle trajectories using small time-steps, this algorithm is more accurate than the Verlet algorithm (Haile, 1997).
4. MOLECULAR DYNAMICS SIMULATION

4.7. Simulation conditions

In this work, melts of hyperbranched polymers of different molecular weights and architecture have been simulated. The original program for simulating our polymer melts was written by Bosko (Bosko, 2005) and modified in this project to model a variety of hyperbranched polymers and their blends with linear chains. Samples of these dense fluids are prepared and modelled under shear. For polymers of the smallest size, the sample consists of 216 molecules whereas for all other polymers, the sample comprises 125 molecules. The total number of beads in the simulation box varies from approximately 4000 to 23,500. The system is first generated at low density and then compressed until the desired density is achieved. The SLLOD algorithm with equal negative diagonal elements of the velocity gradient tensor has been applied during this density equilibration phase.

Constant temperature simulations were performed at the constant density of 0.84 and temperature of 1.25. The reason for choosing these parameters is that at this thermodynamic state point, the monomer WCA fluid is a dense fluid. This suggests that the molecular WCA fluid is also a liquid under the same conditions (Bosko, 2005).

Constant pressure simulations were performed at the pressure of 5.42. This is the equilibrium pressure of the generation 2 dendrimer melt at the density of 0.84. Modelling hyperbranched polymers with the same conditions allows comparison between our results with those for dendrimers and linear polymers reported previously (Bosko et al., 2005).

In this work, hyperbranched polymers of different molecular weights were simulated using the NVT ensemble. Hyperbranched polymers of the same molecular weight but with different architectures were modelled using both NVT and NpT ensembles. NpT simulations were also performed for the blends of hyperbranched polymers and linear chains composed of the same number of particles.

The SLLOD equations of motion were integrated with a time-step $\Delta t = 0.001$ in reduced units using a fourth-order Gear predictor corrector differential equation solver. This value of the time-step is sufficiently small to ensure that the simulation results do not depend on it.
The range of strain rates was chosen to be from 0.0001 up to 0.2 as with this wide range, the transition of the polymeric fluid from Newtonian to non-Newtonian regimes can be captured.
5. Structural properties of hyperbranched polymers

5.1. Conformation of simulated hyperbranched polymers

In this work, two series of hyperbranched polymers were simulated using the coarse-grained uniform bead model in order to characterize the effect of molecular weight and inter-branch spacing on structural and rheological properties of hyperbranched polymer melts. This model has been successfully used in an NEMD study of dendrimers (Bosko et al., 2004a).

The first series of simulated hyperbranched polymers have molecular weights corresponding to those of tri-functional dendrimers as this allows a comparison between our simulation data and previously reported results for linear polymers and dendrimers (Bosko et al., 2004a, Bosko et al., 2004b, Bosko et al., 2005, Bosko et al., 2006). The total number of beads in dendrimers can be defined as:

\[ N_s = fb((f - 1)^{e+1} - 1)/(f - 2) + 1 \]  \hfill (5.1)

where \( f \) is the functionality of end groups, \( b \) is the number of monomers in the chain units and \( g \) is the generation number. With the choice of \( f = 3 \) and \( b = 2 \), dendrimers of generation 1, 2, 3 and 4 will have 19, 43, 91 and 187 beads respectively. Therefore the hyperbranched polymer chains generated in this work are composed of 19, 43, 91 and 187 interconnected beads. A simple specific architecture of hyperbranched polymers has been chosen. They are dendrimers with trifunctional end groups (\( f = 3 \)) and two beads in the chain units (\( b = 2 \)) that have one imperfect branching point (\( f = 2 \)). As our hyperbranched polymers have the same number of beads as dendrimers but fewer branches at one branching point, extra beads are added in the outer-most layer of the molecules with \( f = 3 \) and \( b = 2 \). The schematic configuration of these hyperbranched polymers (type A) is presented in Figure 5.1 and their typical instantaneous configurations in comparison with dendrimers and linear polymers are shown in Figure 5.2.
5. STRUCTURAL PROPERTIES OF HYPERBRANCHED POLYMERS

Figure 5.1. Schematic architectures of type A hyperbranched polymers of different molecular weights.
Figure 5.2. Configuration of type A hyperbranched polymers with different molecular weights in comparison with dendrimers and linear polymers.

The hyperbranched polymers of the second series have the same molecular weight but different chain lengths between branches. They all have the same degree of polymerization $N_s$ of 187, as for a perfect dendrimer of generation 4, and one imperfect branching point with the functionality of end groups $f = 2$. The only difference in their architectures is the number of spacer units. Hyperbranched polymers of type A as mentioned above have two beads in the chain units ($b = 2$) while polymers of type B, C and D have three, four and five beads, respectively, in the chain units. The schematic configuration of these hyperbranched polymers is presented in Figure 5.3 whereas their typical instantaneous configurations are shown in Figure 5.4.
Figure 5.3. Schematic architectures of hyperbranched polymers of the same molecular weight of 187 beads but different number of spacers.
Figure 5.4. Configurations of hyperbranched polymers comprising 187 beads but with different number of spacers.
The structure of hyperbranched polymers of the same molecular weight can normally be characterized by two different structural parameters, the degree of branching and the Wiener index. These values for simulated hyperbranched polymers with different numbers of spacers are shown in Table 5.1.

**Table 5.1. Degree of branching and Wiener index for hyperbranched polymers of the same molecular weight of 187 beads but with different number of spacers.**

<table>
<thead>
<tr>
<th>Type of hyperbranched polymers</th>
<th>Degree of branching</th>
<th>Wiener index</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.9920</td>
<td>123,194</td>
</tr>
<tr>
<td>B</td>
<td>0.9920</td>
<td>153,122</td>
</tr>
<tr>
<td>C</td>
<td>0.9836</td>
<td>174,986</td>
</tr>
<tr>
<td>D</td>
<td>0.9836</td>
<td>193,770</td>
</tr>
</tbody>
</table>

The degree of branching, as previously mentioned, can be calculated as:

\[
B = \frac{2D}{2D + L}
\]

where \(D\) is the number of fully branched beads and \(L\) is the number of partially reacted beads. The value of the degree of branching varies from 0 for linear polymers to 1 for dendrimers or fully branched hyperbranched polymers. As all simulated systems have only one imperfect branching point, the value of \(L\) is always 1. Hyperbranched polymers of type A and B have the same number of fully branched beads of 61 hence they have the same degree of branching of 0.992. Polymers of type C and D have the same number of fully branched beads of 30. Therefore they have the same degree of branching of 0.9836. The same values of the degree of branching for different hyperbranched polymers indicate that this parameter only characterizes the extent of unbranched content within a hyperbranched molecule and does not fully describe the architecture of the systems. This is in agreement with many other reports (Neelov and Adolf, 2004, Sheridan et al., 2002, Lyulin et al., 2001, Widmann and Davies, 1998) on hyperbranched polymers.
In addition to the degree of branching, the Wiener index, defined as:

\[
W = \frac{1}{2} \sum_{j<i} \sum_{k<i} d_{ij}
\]  \hspace{1cm} (5.3)

where \( N_s \) is the number of beads per molecule and \( d_{ij} \) is the number of bonds separating bead \( i \) and \( j \) of the molecule, was calculated to characterize the topologies of simulated hyperbranched polymers in greater detail. This parameter only describes the connectivity and is not a direct measure of the size of the molecules. For polymers of the same molecular weight, the linear chain has the largest value of \( W \) whereas the star polymer with branch length of 1 and the core functionality of \( N_s - 1 \) has the smallest value of \( W \). In this work, the Wiener index is largest for the type D system which has the longest linear chain in between branching points (number of spacers \( b=5 \)) and smallest for the type A system which has the shortest linear chain between branching points (\( b=2 \)). With increasing number of spacers from 2 to 5, the values of the Wiener index for hyperbranched polymers comprising 187 beads increase and fall in the range between 123,194 and 193,770. Polymer systems with higher number of spacers or higher Wiener index have more open structure and larger topological separation of beads.

Figure 5.5. Configuration of type A hyperbranched polymer with 187 monomers at strain rates of (a) 0.0001, (b) 0.001, (c) 0.01 and (d) 0.1.
In contrast to all previous studies which addressed the simulation of hyperbranched polymers in solution, this work focuses on the properties of these macromolecules in the melt away from equilibrium. Hyperbranched polymers were simulated over a wide range of strain rates so the change in the behaviour of these polymers under shear, including different structural and rheological properties, can have been analysed. Figure 5.5 illustrates the changes in shape and orientation of hyperbranched polymers with 187 monomers at the strain rates of 0.0001, 0.001, 0.01 and 0.1. It can be seen that at higher strain rates, hyperbranched polymer molecules are more stretched, as is to be expected.

5.2. Radius of gyration

The mean square radius of gyration of molecules, which is a measure of the extension of a molecule in space, can be calculated according to the formula:

$$\langle R_g^2 \rangle = \frac{\sum_{\alpha=1}^{N_s} m_\alpha (r_\alpha - r_{CM}) (r_\alpha - r_{CM})}{\sum_{\alpha=1}^{N_s} m_\alpha}$$

(5.4)

where $r_\alpha$ is the position of bead $\alpha$, $r_{CM}$ 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 is defined as the trace of the tensor ($R_g^2 = Tr\left(\langle R_g R_g \rangle\right)$). These simulated values are often compared to experimental results using light scattering, small-angle neutron scattering and small-angle X-ray scattering methods which are well-established in polymer science. In this work, as only idealized hyperbranched architectures with one specific imperfect point are examined, the radius of gyration results cannot be compared directly to experimental data for a randomly branched polydisperse system. However the analysis of the radius of gyration gives significant information about the mean spatial distribution inside the molecules regardless of their shapes.

5.2.1. Radius of gyration of hyperbranched polymers with different molecular weights

Figure 5.6 presents the dependence of the radii of gyration for the type A hyperbranched polymers of different molecular weights on strain rate. For all studied systems, at small
strain rates, the size of the polymer remains constant but for large values of strain rate, the values of $<R_g^2>$ increase which indicates that molecules are stretched under shear. For a given value of strain rate, the extent of shear induced stretching increases with the number of beads. In order to compare the results for the type A hyperbranched polymers to those for dendrimers (Bosko et al., 2004a) and linear polymers, the values of the mean square radii of gyration for these polymers are plotted against the strain rate as shown in Figure 5.7. As can be seen, the radii of gyration for hyperbranched polymers are always in the range between those of dendrimers and linear polymers. This can be explained by the architecture of the molecules. With the same number of monomers, dendrimer structures on average have the most compact geometry with the smallest spatial separation of monomers, whereas hyperbranched polymers are less compact while linear polymers have the largest distances between monomers.

![Figure 5.6. Mean squared radii of gyration of the type A hyperbranched polymers of different molecular weights at different strain rates.](image_url)
Figure 5.7. Comparison of radii of gyration for type A hyperbranched polymers, dendrimers and linear polymers.
5. STRUCTURAL PROPERTIES OF HYPERBRANCHED POLYMERS

5.2.2. Radius of gyration of hyperbranched polymers with different numbers of spacers

Figure 5.8 presents the mean squared radius of the gyration for hyperbranched polymers with the number of beads per molecule of 187 but different numbers of spacers. At low strain rates, the value of $\langle R_g^2 \rangle$ remains constant while at high strain rates where the molecules are stretched, $\langle R_g^2 \rangle$ increases rapidly. Furthermore as type A molecules have the most dense and rigid structure while type D molecules have the most open and flexible architecture, the radius of gyration rises the least steadily for type A hyperbranched polymers and the most steadily for type D polymers. The ratio of the radii of gyration at strain rates of 0.0001 and 0.1 is 1.34 for type A, 1.52 for type B, 1.81 for type C and 2.08 for type D polymers. In addition, hyperbranched polymers of type A have the most compact architecture with the least extension of molecules in space. Hence at a given strain rate, the radius of gyration is lowest, whereas hyperbranched polymers of type D with the greatest spatial separation of beads have the highest value of the radius of gyration.

Figure 5.8. Dependence of the radius of gyration on strain rate for hyperbranched polymers with the same molecular weight of 187 beads but different numbers of spacers.
5. STRUCTURAL PROPERTIES OF HYPERBRANCHED POLYMERS

Data for the radii of gyration for different hyperbranched polymers were fitted using the Carreau-Yasuda model (Bird et al., 1987) which is usually used for viscosity data, given as

\[
\langle R_g^2 \rangle = \frac{\langle R_g^2 \rangle_0}{\left[ 1 + \left( \frac{\dot{\gamma}}{\dot{\gamma}_c} \right)^2 \right]^{\frac{1}{p_{R_g}}}}
\]

where \( \lambda_{R_g} \) is a time constant and \( p_{R_g} \) is the power law exponent. Results for the zero shear rate radii of gyration were plotted against the Wiener index as shown in Figure 5.9. The exponential function gives a very good fit to the zero shear rate mean square radius of gyration data. The dependence of \( \langle R_g^2 \rangle_0 \) on the Wiener index was found to be

\[
\langle R_g^2 \rangle_0 = 61(15) - 85(5) \times e^{-W/(10(5))} \]

where the number in brackets shows the statistical uncertainty from the standard error of the fit.

![Figure 5.9](image)

**Figure 5.9.** Dependence of zero shear rate radii of gyration on Wiener index for 187 bead hyperbranched polymers with different numbers of spacers (the solid line representing fitting with the exponential function).

The relationship between the radius of gyration and molecular weight for dendrimers was suggested to be a complex function of the generation number, the order of the dendra and the functionality of the core (LaFerla, 1997). However for hyperbranched polymers, the power law scaling is the most common approach because of its sufficiency in characterizing the dependence of the radius of gyration on molecular weight for hyperbranched polymers with different levels of imperfectness or irregularity. If a power law function is used to fit the \( \log \langle R_g^2 \rangle_0 \) data, the zero shear rate mean squared radius of gyration scales as \( \langle R_g^2 \rangle_0 \sim W^{1.20(6)} \). The power law exponent of
1.20(6) for these hyperbranched polymers in NEMD simulations is close to the value of 1.0 found for phantom chains neglecting long-range excluded volume interactions and the correction term \( R(n_{ij}) \) in the calculation of the end-to-end distance between two segments. This correction term is given as \( \left\langle R^2_{ij} \right\rangle_0 = C_\infty n_{ij} \left\langle I^2 \right\rangle + R(n_{ij}) \) where \( C_\infty \) is the characteristic ratio of an infinite chain, \( n_{ij} \) is the number of bonds between segments \( i \) and \( j \) and \( \left\langle I^2 \right\rangle \) is the mean-squared bond length (Widmann and Davies, 1998).

Brownian dynamics simulations (Neelov and Adolf, 2004, Sheridan et al., 2002) which take into account the excluded volume and hydrodynamic interactions also showed a power law exponent of approximately 1.0 for hyperbranched polymers of different molecular weights. Specifically the Brownian dynamics results showed that the zero shear rate radius of gyration scales as \( \left\langle R_s \right\rangle_0 \sim W^{0.5} N_s^{-0.85} \) which means that the squared radius of gyration scales as \( \left\langle R^2_s \right\rangle_0 \sim W N_s^{-1.7} \). It is interesting that this relationship for hyperbranched polymers is very similar to that for linear chains in good solvents \( \left\langle R^2_s \right\rangle_0 \sim W N_s^{-1.824} \) which results from \( W \sim N_s^{3} \) for linear polymers and \( \left\langle R_s \right\rangle_0 \sim N_s^{0.588} \) for linear molecules in good solvents (Doi and Edwards, 1986). In ideal solvents or melts, the squared radius of gyration for linear polymers scales as \( \left\langle R^2_s \right\rangle_0 \sim N_s \) hence the relationship between \( W, R_s \) and \( N_s \) is expected to be \( \left\langle R^2_s \right\rangle_0 \sim W \times N_s^{-2.0} \). Furthermore, it was found that at high elongation rates, the dependence of the limiting (plateau) mean squared radius of gyration on Wiener index for hyperbranched polymers is close to \( W^{3} \) (Neelov and Adolf, 2004).

In order to clarify the relationship between \( W, R_s \) and \( N_s \), radius of gyration data for the type A hyperbranched polymers with different molecular weights in Figure 5.6 were fitted using the Carreau-Yasuda equation and the zero shear rate radii of gyration were plotted against the number of beads per molecule, as shown in Figure 5.10. The dependence of \( R_s \) on \( N_s \) was found to be \( \left\langle R^2_s \right\rangle \propto N_s^{0.773(6)} \). On the other hand, the Wiener index for these systems scales as \( W \propto N_s^{1.6(1)} \), as presented in Figure 5.11. Therefore the relationship between \( W, R_s \) and \( N_s \) for the short branch polymer
molecules simulated is $\langle R_g^2 \rangle_0 \sim W \times N_s^{-0.9}$. Taken together these results shows that more work is needed to understand the relationship between the Wiener index, radius of gyration and molecular weight for hyperbranched polymers.

Figure 5.10. Dependence of zero shear rate radii of gyration on the number of beads per molecule for type A hyperbranched polymers.

Figure 5.11. Dependence of the Wiener index on the number of beads per molecule for short branch hyperbranched polymers of type A.
5. STRUCTURAL PROPERTIES OF HYPERBRANCHED POLYMERS

5.2.3. Radius of gyration of blends composed of hyperbranched polymers and linear chains of equivalent molecular weight

As hyperbranched polymers have a promising application as rheology modifiers, blends of these polymers and linear chains have been simulated in this work. Hyperbranched polymers of type A and D comprising 187 beads per molecule were mixed with linear analogues of the same molecular weight. The proportions of hyperbranched polymers in these mixtures were chosen to be 4%, 8%, 12%, 16% and 20%. The simulation box contains 125 molecules in which 5, 10, 15, 20 and 25 molecules respectively are hyperbranched polymers of type A or D.

Figure 5.12 shows the mean squared radii of gyration for blends comprising 187 bead type A or D hyperbranched polymers and linear chains of equivalent molecular weight at different strain rates. For all blends, the radii of gyration remain constant at low strain rates and increase rapidly at high strain rates. Furthermore an increase in the proportion of hyperbranched polymers in the blends leads to a decrease in the value of the squared radius of gyration due to the compact structure of hyperbranched molecules. On the other hand, the presence of type A hyperbranched polymers in the blends reduces the mean squared radii of gyration of the system more than that of type D polymers. This is in accordance with the smaller values of $\langle R_g^2 \rangle$ for type A hyperbranched polymers in comparison with that for type D polymers at all strain rates considered as discussed in the previous section. The radius of gyration data for blends of hyperbranched and linear polymers were fitted with the Carreau–Yasuda equation and results on the zero shear rate squared radius of gyration are presented in Table 5.2. Furthermore the mean squared radii of gyration for only linear chains or only hyperbranched polymers in the blends do not differ from those for pure linear chain melts or pure hyperbranched polymer melts.

<table>
<thead>
<tr>
<th>Hyperbranched polymer fraction in blends</th>
<th>Type A</th>
<th>Type D</th>
</tr>
</thead>
<tbody>
<tr>
<td>4%</td>
<td>49(7)</td>
<td>50(6)</td>
</tr>
<tr>
<td>8%</td>
<td>48(6)</td>
<td>49(7)</td>
</tr>
<tr>
<td>12%</td>
<td>47(6)</td>
<td>48(6)</td>
</tr>
<tr>
<td>16%</td>
<td>45(6)</td>
<td>47(6)</td>
</tr>
<tr>
<td>20%</td>
<td>44(5)</td>
<td>45(6)</td>
</tr>
</tbody>
</table>
Figure 5.12. Mean squared radii of gyration for blends of 187 bead linear polymers and hyperbranched polymers of (a) type A, (b) type D with different hyperbranched polymer fractions and (c) type A and D with hyperbranched polymer fraction of 20% and squared radii of gyration for pure 187 bead linear polymers.
5.3. Tensor of gyration

The tensor of gyration is a useful parameter to characterize the structural properties and alignment of molecules. By studying the tensor of gyration, the shape of hyperbranched polymers can be investigated. The ensemble averaged eigenvectors and eigenvalues ($L_1$, $L_2$ and $L_3$) of the tensor of gyration were derived to analyse flow-induced changes in the shape of the molecules, as the flow induced stretching of hyperbranched polymers together with molecular alignment can lead to the macroscopic anisotropy of the material (Bosko et al., 2004a). In order to calculate these ensemble averaged eigenvalues, the tensor of gyration was diagonalized separately for each molecule in the system. Using this approach, the shape of the hyperbranched polymer molecule can be studied disregarding the molecular orientation. The ratios of these eigenvalues, which describe the asymmetry of hyperbranched polymers, were also calculated. Results of the ensemble averaged tensor of gyration prior to its orthogonalization have also been computed and the corresponding eigenvalues ($L'_1$, $L'_2$ and $L'_3$) were analyzed. In this approach, all elements of the tensor of gyration are averaged over all molecules and time separately, the shape of a mean molecule is obtained from superposition of all molecules in the system and these eigenvalues can be considered as the linear dimensions of the ellipsoid occupied by the orientationally averaged molecule (Bosko et al., 2006).

![Figure 5.13. Averaged eigenvalues of the tensor of gyration for type A hyperbranched polymers of different molecular weights.](image)
As mentioned above, the mean shape of a polymer molecule in the system is characterized by the ensemble average eigenvalues $L_1$, $L_2$ and $L_3$ of the tensor of gyration which was diagonalized separately for each molecule. These values were computed for hyperbranched polymers of different molecular weight and plotted against the strain rate. As shown in Figure 5.13, for all type A hyperbranched systems simulated, the values of $L_1$ are always much higher than $L_2$ and $L_3$ which are very similar. This indicates that hyperbranched polymers have a prolate ellipsoid shape. In comparison with dendrimers and linear polymers (Bosko, 2005, Bosko et al., 2004a), the eigenvalues of the tensor of gyration for hyperbranched polymers are in the range between those of linear polymers and dendrimers but slightly higher than the eigenvalues for dendrimers. This shows that the prolate ellipsoid shape of hyperbranched polymer molecules is very similar to dendrimers but somewhat flatter. The variation of these values is related to the stretching of the molecules and becomes significant at high strain rates. The comparison of average eigenvalues of the tensor of gyration for different hyperbranched polymers is also presented. These values for hyperbranched polymers with different chain lengths show very similar trends.

The asymmetry of hyperbranched polymers is characterized by the ratios of the eigenvalues of the average gyration tensor. If the ratios of the eigenvalues are closer to 1, the molecules have greater spherical symmetry. Like dendrimers and linear polymers, hyperbranched polymer molecules are stretched under shear. The differences between the eigenvalues of the tensor of gyration increase with the increase in strain rates and there is a noticeable change in the slopes of these ratios at similar strain rates as can be seen in Figure 5.14. Previous investigations have shown that for dendrimers, with increasing number of beads, the molecules become more spherical and for linear polymers, an opposite trend is observed (Bosko et al., 2006). It is interesting that smaller molecules of hyperbranched polymers become aspherical under shear more slowly than larger molecules of hyperbranched polymers. In other words, small hyperbranched chains tend to retain their cross-section when stretched, while larger chains extend by contracting in their smallest dimension (i.e. they become flatter).
Figure 5.14. Ratios of averaged eigenvalues of the tensor of gyration for type A hyperbranched polymers with different molecular weights.
Figure 5.15. Eigenvalues of the average tensor of gyration for type A hyperbranched polymers of different molecular weights.

The eigenvalues of the average tensor of gyration for hyperbranched polymers, which was calculated prior to diagonalization, also reflect the degree of orientation of the molecules. They can be interpreted as the linear dimensions of the prolate ellipsoid occupied by the orientationally averaged molecule. For hyperbranched polymers, the eigenvalues of the average tensor of gyration are equal at equilibrium because of orientational disorder and depart from this equilibrium value right from the smallest strain rates, as shown in Figure 5.15. This demonstrates the onset of flow-induced molecular deformation. It can also be seen from Figure 5.14 that the eigenvalues of the average tensor of gyration for hyperbranched polymers of different size have very similar trends due to their similar behaviour under shear flow.

Ratios of the eigenvalues of the average tensor of gyration can be found in Figure 5.16. The ratios $L_i' / L_j'$ and $L_3' / L_1'$ both decrease with increasing strain rates. An opposite trend was observed for the ratio between $L_2' / L_1'$ which increase with increasing strain rates. These behaviours are caused by the fact that hyperbranched polymers become more stretched along the flow axis and lead to the faster growth of $L_1'$ with strain rates compared to the increase of $L_2'$ and $L_3'$. These ratio values for hyperbranched polymers are again in the range between those for linear polymers and dendrimers due to their molecular topologies. Unlike the case of the average
eigenvalues of the tensor of gyration, the eigenvalues of the average tensor of gyration show very similar trends for dendrimers, linear and hyperbranched polymers.

Figure 5.16. Ratios of eigenvalues of the average tensor of gyration for type A hyperbranched polymers in comparison with those of dendrimers and linear polymers.
5.4 Distribution of mass

Hyperbranched polymers have a compact, globular structure due to their densely branched architecture. This might lead to an unusual distribution of mass. To analyse the distribution of mass within the molecule, two forms of intra-molecular radial distribution function have been used. The first function, which measures the distribution of beads from the central bead (the core), is defined as:

\[ g_{\text{core}}(r) = \frac{\sum_{i=1}^{N} \sum_{\alpha=2} \delta(r - (r_{\alpha} - r_i))}{N} \]  \hspace{1cm} (5.5)

where \( r_i \) is the position of the core and \( \alpha \) runs over all other beads belonging to the same molecule. The second function, which measures the distribution of beads from the molecular centre of mass, is defined as:

\[ g_{\text{CM}}(r) = \frac{\sum_{i=1}^{N} \sum_{\alpha=1} \delta(r - (r_{\alpha} - r_{\text{CM}}))}{N} \]  \hspace{1cm} (5.6)

where \( r_{\text{CM}} \) is the position of the centre of mass.

5.4.1. Distribution of mass for hyperbranched polymers of different molecular weights

The distribution of mass from the central unit (core) for different type A hyperbranched polymer systems at the strain rate of 0.0001 and 0.1 can be found in Figure 5.17, whereas the distribution of mass from the centre of mass at those strain rates is shown in Figure 5.18. In all cases, the distributions of mass for polymers with different chain lengths always show a similar trend. The correlation between the position of the core and its first neighbours expresses itself through a strong peak at the distance equal to the average bond length. At high strain rates, as the molecules are stretched in the flow, the distribution of mass becomes broader and the average distance of beads from the centre of mass increases with the strain rate. For the largest strain rates considered, the maximum distance between beads and the centre of mass is comparable to the lengths of fully stretched arms of the polymers.
Figure 5.17. Distribution of beads from the core for type A hyperbranched polymers of different molecular weights at strain rates of (a) 0.0001, (b) 0.1 and (c) for type A hyperbranched polymers with 91 monomers at various strain rates.
Figure 5.18. Distribution of beads from the centre of mass for type A hyperbranched polymers of different molecular weights at strain rates of (a) 0.0001, (b) 0.1 and (c) for type A hyperbranched polymers with 91 monomers at various strain rates.
**5.4.2. Distribution of mass for hyperbranched polymers with the same molecular weight of 187 beads but different numbers of spacers**

Figure 5.19 presents the distribution of beads from the molecular centre of mass for hyperbranched polymers of the same molecular weight of 187 beads but with different numbers of spacers. With increasing number of spacers, the distribution of mass becomes broader and the average distance of beads from the centre of mass increases. This is in accordance with the topologies of hyperbranched polymer systems simulated. Furthermore the shear-induced behaviour of the distribution of mass for different hyperbranched polymers shows a similar trend. At higher strain rates, the curves become wider and the peaks shift towards larger distance as molecules are stretched under shear flow. This behaviour was also observed in Brownian dynamics simulations for charged hyperbranched polymers (Dalakoglou et al., 2008).

The distribution of beads from the central bead (the core) for hyperbranched polymers with different numbers of spacers is presented in Figure 5.20. Strong peaks at the distance equal to the average bond length which are observed for all systems correspond to the first neighbours of the core. The same height of these peaks for different hyperbranched polymers is due to the same number of beads around the core in the inner-most shell of the molecules. In contrast, in the outer shells of the molecules, the separation of beads around the core is lowest for the system of type A and highest for the system of type D. Therefore the distribution of beads from the core is the most narrow for type A polymers and broadest for type D polymers. Similar to the radial distribution of beads from the centre of mass, the distribution of beads from the core for all hyperbranched polymers under shear flow becomes wider as molecules in the systems are stretched.
Figure 5.19. Distribution of mass from the centre of mass for hyperbranched polymers of the same molecular weight of 187 beads but with different numbers of spacers (a) at strain rate of 0.0001, (b) at strain rate of 0.02 and (c) hyperbranched polymer of type B at strain rate of 0.0001 and 0.02.
Figure 5.20. Distribution of mass from the core for hyperbranched polymers of the same molecular weight of 187 beads but with different numbers of spacers (a) at strain rate of 0.0001, (b) at strain rate of 0.02 and (c) hyperbranched polymer of type B at strain rate of 0.0001 and 0.02.
5.4.3. Distribution of mass for blends of hyperbranched polymers and linear polymers of the equivalent molecular weight

The distribution of beads from the centre of mass was computed for different blends of type A and type D hyperbranched polymers and linear chains of the same molecular weight of 187 beads. The distribution of beads from the centre of mass for blends comprising type A hyperbranched polymers is presented in Figure 5.21(a) whereas that for blends composed of type D hyperbranched polymers is shown in Figure 5.21(b). A comparison between the bead distribution functions of blends containing type A and type D hyperbranched polymers with the proportion of hyperbranched polymers of 20% can be found in Figure 5.21(c). All these results are for systems at the strain rate of 0.0001.

As can be seen from Figure 5.21(a), the distribution of beads from the centre of mass for blends composed of at least 12% type A hyperbranched polymers shows a peak at the distance of approximately 4 which is also the distance at which a peak is observed for the bead distribution function of pure type A hyperbranched polymers. The distribution of beads from the centre of mass for blends comprising less than 12% of the short branch type A hyperbranched polymers reaches the highest value when the distance $r$ is about 5. At this distance from the centre of mass, the largest number of beads can be found in the melts of pure or blends mainly containing linear polymers.

In Figure 5.21(b), the distribution of beads from the centre of mass for blends composed of type D hyperbranched polymers is presented. A peak at the distance of approximately 5 is observed for blends with different ratios of hyperbranched and linear polymers. This is also the distance at which the largest number of beads is found for pure long branch type D hyperbranched polymers.

Figure 5.21(c) shows a clearer picture of the bead distribution functions for blends with the same proportion of hyperbranched polymers of type A or type D. As type A hyperbranched molecules have shorter branches and a larger number of branching points, a peak at a smaller distance from the centre of mass can be found.
Figure 5.21. Distribution of mass from the centre of mass for blends of 187 bead hyperbranched polymers and linear chains of equivalent weight at strain rate of 0.0001. (a) Blends with different fractions of type A hyperbranched polymers, (b) Blends with different fractions type D hyperbranched polymers and (c) Blends with 20% hyperbranched polymers of type A or D.
Figure 5.22. Distribution of terminal groups for type A hyperbranched polymers of different molecular weights at strain rates of (a) 0.0001, (b) 0.1 and (c) hyperbranched polymers with 91 beads at various strain rates.
5. STRUCTURAL PROPERTIES OF HYPERBRANCHED POLYMERS

5.5. Distribution of terminal groups

One of the special properties of hyperbranched polymers is the large number of terminal groups, from which hyperbranched polymers are characterized as active molecules. This leads to a number of applications, especially in drug delivery. Therefore, the radial distribution function of the terminal groups with reference to the central bead was also investigated to analyze the entanglement and back folding in the molecules. This is defined as:

\[
g_{\text{term}}(r) = \frac{1}{4\pi r^2 N} \sum_{i=t}^{N} \sum_{a=\{\text{term}\}}^{N} \delta(|r - (\mathbf{r}_{ai} - \mathbf{r}_{ai})|)
\]

(5.7)

where \( \alpha \) runs over the outermost beads only.

In Figure 5.22, we present the distribution of terminal groups from the central unit at the strain rate of 0.0001 when the system is close to equilibrium and at a high strain rate of 0.1 for type A hyperbranched polymers with different molecular weights. In all cases, the end groups can be found at any distance from the centre unit. This means that reactive groups exist everywhere throughout the interior of the molecules. Similar behaviour has been observed previously for dendrimers (Timoshenko et al., 2002, Lescanec and Muthukumar, 1990, Bosko et al., 2004a).

5.6. Atomic radial distribution function

The atomic radial distribution function is defined by:

\[
g_{A}(r) = \frac{1}{4\pi r^2 N_{\text{total}} \rho} \sum_{i=1}^{N_{\text{total}}} \sum_{j\neq i}^{N_{\text{total}}} \delta(|\mathbf{r}_{ij}|)
\]

(5.8)

where \( \mathbf{r}_{ij} \) is the distance between the beads \( i \) and \( j \). \( N_{\text{total}} = NN_j \) is the total number of beads in the studied system, and \( \rho \) is the density. It is extensively used to study the internal structure and spatial ordering of atoms (beads) composing materials. The function \( g_{A}(r) \) shows the probability of finding two beads at the separation \( r \). The atomic
radial distribution simulation results can be directly compared to results of diffraction experiments.

The atomic radial distribution functions for hyperbranched polymers of different molecular weights as well as those for polymers of different numbers of spacers are indistinguishable. Therefore Figure 5.23 only shows the distribution function for polymers with different spacer lengths.

![Figure 5.23](image)

**Figure 5.23.** The atomic radial distribution function for 187 bead hyperbranched polymers with different numbers of spacers at the strain rate of 0.0001.

For blends of 187 bead hyperbranched polymers and linear chains of equivalent molecular weight, the atomic radial distribution functions are also not distinguishable when the proportion of hyperbranched molecules in the system changes. This can be seen from Figure 5.24.

The distribution function at different shear rates is shown in Figure 5.25. In all cases, only the first few peaks which correspond to the shells of near neighbours can be observed. No significant changes could be distinguished in the atomic radial distribution functions of hyperbranched polymers with their size, and the distributions of different hyperbranched polymers almost overlap. It can also be seen that the shear does not
significantly change the distribution function: the first peak becomes slightly wider whereas the second peak is shifted towards smaller distances. The first peak, which is also the strongest peak of the atomic radial distribution, consists of contributions from two types of first neighbours. The first type includes beads that are chemically bonded to the central one and interact via both WCA and FENE potentials, whereas the second type refers to all other beads that are close to the core and interact via only the WCA potential.

Figure 5.24. Atomic radial distribution function for blends of 187 bead linear polymers and hyperbranched polymers of (a) type A and (b) type D.
5.7. Interpenetration

In order to characterize the interpenetration of the volume occupied by the molecule by beads of other molecules, the interpenetration function, defined as:

\[ g_{\text{inter}}(r) = \frac{\sum_{i=1}^{N_i} \sum_{j=1}^{N_j} \sum_{\alpha=1}^{N_{\beta}} \delta \left( \left| r - (r_{j\alpha} - r_i) \right| \right) }{4\pi r^2 N} \]  

(5.9)

where \( r_i \) is the position of the core of molecule \( i \) and \( r_{j\alpha} \) is the position of bead \( \alpha \) in molecule \( j \), was used and results are shown in Figures 5.26 and 5.27.

5.7.1. Interpenetration function for hyperbranched polymers of different molecular weights

As can be seen from Figure 5.26, the interpenetration function for hyperbranched polymers strongly depends on the molecular weight. The function decreases with
increasing number of beads per molecule. This is due to the architecture of these short branch polymers. With increasing molecular weight, the polymeric structure becomes more compact and the number of beads in the outer-most layers increases rapidly. Hence the bead density of these layers rises steadily and the interior becomes less accessible.

Figure 5.26. Interpenetration in the melts of type A hyperbranched polymers of different molecular weights at the strain rate of (a) 0.0001 and (b) 0.1.
5.7.2. Interpenetration function for hyperbranched polymers with different numbers of spacers

![Figure 5.27](image)

Figure 5.27. Comparison of the interpenetration function for hyperbranched polymers of the same molecular weight of 187 beads but with different numbers of spacers (a) at strain rate of 0.0001, (b) at strain rate of 0.02 and (c) type A hyperbranched polymer at strain rate of 0.0001 and 0.02.
In Figure 5.27, it can be clearly seen that the interpenetration function for hyperbranched polymers increases with the increase of the number of spacers. The system of type A has the lowest interpenetration function while the system of type D has the highest interpenetration function. This is because polymer molecules with longer linear chains between branching points are more open and freely accessible by beads of other molecules, whereas polymers with short chains between branching points have more compact structures which reduce the probability of finding parts of other molecules within the interior of a polymer molecule. Furthermore, under shear flow, the interpenetration increases with the increase of strain rate as molecules are stretched and become more open. Hence parts of other molecules can access closer to the core of the hyperbranched polymer molecule.

5.8. Flow birefringence

In the presence of a velocity gradient, the statistical distribution of a flexible polymer is deformed from the equilibrium isotropic state and the refractive index of the medium becomes anisotropic. This phenomenon is called flow birefringence or the Maxwell effect. As mentioned in Chapter 3, the birefringence of a polymer system due to the alignment of the intramolecular bonds is called intrinsic birefringence whereas that caused by the alignment of the whole molecules is called form birefringence (Doi and Edwards, 1986). The contribution to the birefringence effect from the alignment of molecules is more important in the case of solutions and arises due to the differences between the polarisability of the molecules and the solvent.

5.8.1. Form birefringence

In order to characterise the flow induced molecular alignment of hyperbranched polymers, the molecular order tensor $S_m$ has been computed as:

$$S_m = \sum_{i=1}^N \left( u_i u_i - \frac{1}{3} I \right)$$

(5.10)

where $u_i$ is the unit vector denoting the orientation of the single molecules and $N$ is the total number of molecules in the system. The direction in which molecules are aligned is indicated by the eigenvectors of the order tensor. The eigenvector corresponding to
the largest eigenvalue of the tensor of gyration denotes the orientation of the molecule $u_i$ and the birefringence extinction angle is the angle between the flow direction and the molecular alignment direction.

![Graph showing molecular alignment angle for hyperbranched polymers](image)

**Figure 5.28.** Molecular alignment angle for hyperbranched polymers of (a) type A with different molecular weights and (b) the same molecular weight of 187 beads but different numbers of spacers.

Figure 5.28 shows the molecular alignment angle which is the average angle between the flow direction and the molecular alignment direction for hyperbranched polymers of different molecular weights and different numbers of spacers. It can be seen that all
simulated systems reach the Newtonian region with the alignment angle of 45° in the range of considered strain rates. The 45° angle is expected for systems in the Newtonian regime due to the non-uniform spin angular velocity of molecular rotation in shear flow (Doi and Edwards, 1986). Furthermore Figure 5.28(a) shows that the alignment angle of large hyperbranched polymers departs from 45° at low strain rates whereas the alignment angle of small polymers remains close to 45° until higher strain rates are reached because these small polymers can rotate with the flow more easily. In comparison with other NEMD simulation data, our alignment angles in the non-Newtonian region are smaller than those for dendrimers and larger than those for linear polymers of the same molecular weight. This is because dendrimers have the most compact and constrained structure while hyperbranched polymers have less rigid architecture and linear polymers can stretch and align more easily with respect to the flow field, leading to anisotropic friction (Doi and Edwards, 1986). In Figure 5.28(b), it can be seen that at high strain rates where systems are in the non-Newtonian regime, hyperbranched polymers of type A have the highest values of the alignment angles $\chi_m$ while polymers of type D have the lowest values of $\chi_m$. This again can be explained by the topologies of these systems. Type A hyperbranched polymers with the smallest number of spacers have the most compact and constrained structure. With increasing number of spacers, polymer architectures become less rigid, hence molecules and bonds can stretch and align more pronouncedly with respect to the flow field.

The order parameter $S_m$, which describes the extent of the molecular alignment, can be defined as 3/2 of the largest eigenvalue of the order tensor, which is a measure of the anisotropy of the average inertia tensor of a flexible molecule caused by the shear field (Doi and Edwards, 1986). This parameter equals 0 in the case of orientational disorder and reaches 1 for perfect alignment. Figure 5.29 presents the molecular order parameter of hyperbranched polymers with different molecular weights and different number of spacers. In all cases, the order parameter remains constant at low strain rates and rapidly increases in the high strain rate regions. This indicates that the orientational ordering increases and the alignment of the polymeric chains is more pronounced at higher strain rates. From Figure 5.29(a), it can also be seen that for any given strain rate, larger $N$ polymer systems have larger values of $S_m$ in comparison to smaller $N$ polymer systems. However when the number of beads increases, the gap between the values of $S_m$ for
hyperbranched polymers decreases. For the two largest systems of simulated hyperbranched polymers, the order parameter curves almost overlap. Furthermore, at the highest strain rate of 0.2, the order parameters for polymers comprising 43, 91 and 187 beads reach the same value of approximately 0.73.

Figure 5.29. Order parameter of the molecular alignment tensor for hyperbranched polymers of (a) type A with different molecular weights and (b) the same molecular weight of 187 beads but with different numbers of spacers.
Figure 5.30. The eigenvalues of the molecular alignment tensor for hyperbranched polymers with the same molecular weight of 187 beads but different numbers of spacers.
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Figure 5.30 presents the comparison of the eigenvalues of the molecular alignment tensor for hyperbranched polymers with different number of spacers. As can be seen, in all cases, the second and third eigenvalues are about half of the largest eigenvalues indicating weaker ordering in the other two directions. Such ordering is consistent with the prolate ellipsoid molecular shape characterized by the eigenvalues of the gyration tensor as discussed in the previous section.

5.8.2. Intrinsic birefringence

In order to characterize the intrinsic birefringence of hyperbranched polymer systems, the flow induced bond alignment has been analysed. The bond alignment tensor can be calculated as:

\[
S_b = \frac{1}{N} \left\langle \sum_{i=1}^{N-1} v_i v_i - \frac{1}{3} \right\rangle
\]  

(5.11)

where \(\langle \ldots \rangle\) denotes an ensemble or time average and \(v_i\) is the unit vector between neighbouring beads which can be defined as:

\[
v_i = \frac{r_{i+1} - r_i}{|r_{i+1} - r_i|}.
\]  

(5.12)

The flow alignment angle and the extent of the bond alignment can be calculated similarly to those of the molecular alignment in the previous section.

Figure 5.31 presents the bond alignment angle results for different hyperbranched polymers and linear polymers of equivalent molecular weight. As can be seen, the range of considered strain rates is wide enough for all hyperbranched polymer systems to reach the Newtonian regime where the bond alignment angle \(\chi_b\) is 45°. In contrast, for large linear polymers of 91 and 187 beads per molecule, the bond alignment angle cannot reach 45° in the considered range of strain rate. In order to reach the alignment angle of 45°, the systems would have to be simulated at lower strain rates. It can also be seen that in the non-Newtonian region, the bond alignment angle decreases with increasing strain rate. At a given strain rate, the bond alignment angle of larger molecules is smaller than that of the smaller ones. Our data for linear polymers are in good agreement with other NEMD simulation results (Kroger et al., 1993) which
indicated that the bond alignment of systems comprising no more than 60 beads can reach the Newtonian regime in the range of strain rates we have investigated.

Figure 5.31. Bond alignment angle for (a) linear polymers and (b) type A hyperbranched polymers of different molecular weights.
Figure 5.32. Bond alignment angle for hyperbranched polymers with the same molecular weight of 187 beads but different numbers of spacers.

Figure 5.32 illustrates the bond alignment angle which is the angle between the flow direction and the bond alignment direction for hyperbranched polymers with different number of spacers. Similar to hyperbranched polymers of different molecular weights, at low strain rates where polymer systems are in the Newtonian regime, the bond alignment angles reach 45° and decrease at higher strain rates where systems are in the non-Newtonian regime. In comparison with the molecular alignment angle, at high strain rates, the bond alignment angle is always higher than the molecular alignment angle of the same polymer type. This is due to the packing constraints around branching points which prevent the simultaneous alignment of all bonds in the system, especially for the highly branched type A molecules.
Alignment in the shear plane can be characterised by the values of $S_b$ which are shown in Figure 5.33. $S_b$ is defined as $3/2$ of the largest eigenvalue of the bond alignment tensor. These order parameters are a measure of the anisotropy of the average inertia tensor of flexible molecules or bonds caused by the shear field (Doi and Edwards, 1986). From Figure 5.33, it can be clearly seen that for both hyperbranched and linear polymer systems, all these values increase with increasing strain rates, and at the same strain rate, values for larger polymers are always higher than those for smaller polymers. This implies that for a given strain rate, the chain segments in large
molecules can more easily stretch and align with respect to the flow field. The $S_b$ function of shear rate is monotonically increasing, but at high strain rates the values of $S_b$ become the same for all hyperbranched polymer systems while those values are much higher for large linear polymers in comparison with small ones. Furthermore, at a given strain rate, the alignment parameter for hyperbranched polymers is always lower than that for linear polymers. This is because it is more difficult for hyperbranched chain segments to stretch and align with respect to the flow field as they have a more compact and constrained architecture. Our alignment results for linear polymers show good agreement with other NEMD simulation results (Kroger et al., 1993) although our data show slightly stronger alignment due to the difference in temperature and chain length of the systems.

![Order parameter of the bond alignment tensors for hyperbranched polymers with the same molecular weight of 187 beads but different numbers of spacers at different strain rates.](image)

**Figure 5.34.** Order parameter of the bond alignment tensors for hyperbranched polymers with the same molecular weight of 187 beads but different numbers of spacers at different strain rates.
Figure 5.35. The eigenvalues of the bond alignment tensor for hyperbranched polymers with the same molecular weight of 187 beads but different numbers of spacers.
Figure 5.34 presents the bond order parameter $S_b$ of hyperbranched polymers with different spacer lengths. Similar to the data for hyperbranched polymers of different molecular weights, in all cases, the order parameter remains constant at low strain rates and increases at high strain rates. This indicates that for all hyperbranched polymers, the orientational ordering increases and the alignment of bonds is more pronounced at high strain rates. It can also be seen that with increasing number of spacers, the order parameter increases. The alignment parameter for hyperbranched polymers with smaller number of spacers is always lower than that for polymers with larger number of spacers, because they have more compact and constrained structures and it is more difficult for the chain segments to stretch and align with respect to the flow field. Furthermore, in comparison to the molecular order parameter, the bond order parameter is always much lower due to the high level of branching of hyperbranched polymers and the excluded volume effect.

Figure 5.35 illustrates the comparison between eigenvalues of the bond alignment tensor for hyperbranched polymers with different spacer lengths. Similar to the case of the eigenvalues of the molecular alignment tensor, the second and third eigenvalues of the bond alignment tensor are only about half the magnitude of the largest eigenvalues. This shows that not only the molecular ordering but also the bond ordering in the other two directions is less pronounced.
6. Rheology of hyperbranched polymer melts

6.1. Introduction

The rheological properties of hyperbranched polymer fluids under shear flow, such as the shear viscosity and first and second normal stress coefficients, can be calculated from the components of the molecular pressure tensor (Todd and Daivis, 2007) given by:

\[ P^M = \left\{ \sum_{i=1}^{N} \frac{\mathbf{p}_i \mathbf{p}_i}{M_i} - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} \mathbf{r}_{ij} \mathbf{F}_{i\alpha j\beta} \right\} \]  (6.1)

where \( \mathbf{p}_i \) represents the total peculiar centre of mass momentum of molecule \( i \), as defined by the equations of motion, \( \mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i \) is the centre of mass separation of molecule \( i \) and \( j \), \( \mathbf{F}_{i\alpha j\beta} \) is the intermolecular force on bead \( \alpha \) in molecule \( i \) due to bead \( \beta \) in molecule \( j \) and \( N_s \) is the total number of interacting beads in a molecule. The angular brackets denote an average over the non-equilibrium steady state.

The time average of the molecular pressure tensor is symmetric and equal to the time average of the atomic pressure tensor which is given by:

\[ \mathbf{P}^A = \left\{ \sum_{i=1}^{N} \sum_{\alpha=1}^{N} \frac{\mathbf{p}_i \mathbf{p}_i}{m_{i\alpha}} - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} \mathbf{r}_{i\alpha j\beta} \mathbf{F}_{i\alpha j\beta} \right\} \]  (6.2)

where \( \mathbf{r}_{i\alpha j\beta} \) is the separation between bead \( \alpha \) in molecule \( i \) and bead \( \beta \) in molecule \( j \) and \( \mathbf{p}_{i\alpha} \) represents the atomic momentum. In this work, only the molecular pressure tensor has been calculated.

The non-Newtonian shear viscosity of hyperbranched polymer fluids subject to planar shear flow, where the fluid flows in the \( x \) direction with velocity gradient in the \( y \) direction, can be calculated from the components \( P_{xy} \) and \( P_{yx} \) of the molecular pressure tensor \( P^M \) as:

\[ \eta = -\left( \left\langle P_{xy} \right\rangle + \left\langle P_{yx} \right\rangle \right) / 2\dot{\gamma} . \]  (6.3)

The first and second normal stress coefficients can be computed as:

\[ \psi_1 = \frac{\left\langle P_{yy}^M \right\rangle - \left\langle P_{xx}^M \right\rangle}{\dot{\gamma}^2} \]  (6.4)

\[ \psi_2 = \frac{\left\langle P_{zz}^M \right\rangle - \left\langle P_{yy}^M \right\rangle}{\dot{\gamma}^2} \]  (6.5)
whereas the isotropic hydrodynamic pressure of the system is obtained from:

\[ p = \frac{1}{3} \text{Tr}(\mathbf{P}_m) = \frac{1}{3} \left( \langle P^M_{xx} \rangle + \langle P^M_{yy} \rangle + \langle P^M_{zz} \rangle \right) \]  

(6.6)

6.2. Shear viscosity

6.2.1. Shear viscosity for hyperbranched polymers of different molecular weights

The viscosities at various shear rates computed for type A hyperbranched polymers of different molecular weights using NVT simulations are presented in Figure 6.1. As can be seen, at the same strain rate, larger hyperbranched polymers always have higher viscosity values. It can also be seen that the range of strain rates considered is large enough to capture the shear thinning behaviour of all simulated hyperbranched polymer systems. At low strain rates, the viscosities remain constant whereas at high strain rates, these values decrease rapidly. This property of polymeric fluids is very important for many engineering applications.

![Figure 6.1. Dependence of shear viscosity on strain rate for type A hyperbranched polymers of different molecular weights (solid lines representing fitting with the Carreau-Yasuda model).](image-url)
Shear viscosity data for different hyperbranched polymers in Figure 6.1 were fitted using the Carreau-Yasuda model (Bird et al., 1987) which is given by:

\[
\eta = \eta_0 \left[ 1 + \left( \frac{\dot{\gamma}}{\lambda} \right)^{\frac{1}{p}} \right]^{1/p_\eta}
\]  

(6.7)

where \( \eta_0 \) is the zero shear viscosity, \( \lambda \) is a time constant and \( p \) is the power law exponent.

The fitting parameters obtained for simulated type A hyperbranched polymers of different molecular weights are presented in Table 6.1.

### Table 6.1. Parameters of the Carreau-Yasuda model fitted to the shear viscosity versus strain rate dependence of type A hyperbranched polymers.

<table>
<thead>
<tr>
<th>Number of beads</th>
<th>( \eta_0 )</th>
<th>( \lambda_\eta )</th>
<th>( p_\eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>10(2)</td>
<td>101(8)</td>
<td>0.138(1)</td>
</tr>
<tr>
<td>43</td>
<td>18(3)</td>
<td>378(237)</td>
<td>0.143(5)</td>
</tr>
<tr>
<td>91</td>
<td>31(11)</td>
<td>1069(299)</td>
<td>0.148(8)</td>
</tr>
<tr>
<td>187</td>
<td>48(6)</td>
<td>1422(615)</td>
<td>0.158(2)</td>
</tr>
</tbody>
</table>

Apart from using the Carreau-Yasuda model, an alternative way to obtain the zero shear rate viscosity is by using the Cross equation (Cross, 1965), given as:

\[
\eta = \eta_\infty + \left( \eta_0 - \eta_\infty \right) \left( 1 + (K \dot{\gamma})^{mc} \right)^{-1/m_c}
\]  

(6.8)

where \( \eta_\infty \) is the infinite shear viscosity, \( K \) is the consistency index and \( m_c \) is the power law index. The disadvantage of the Cross model is that in experiment, it is difficult to measure the infinite shear rate viscosity \( \eta_\infty \), therefore it is often set to be a very small value (Yasuda, 2006). Cross equation fitting parameters for shear viscosity data are shown in Table 6.2. The zero shear viscosities for hyperbranched polymers composed of 19, 43 and 91 beads obtained from Cross equation fitting are quite similar to those from the Carreau-Yasuda model.
Table 6.2. Parameters of the Cross equation fitted to the shear viscosity versus strain rate dependence for type A hyperbranched polymers.

<table>
<thead>
<tr>
<th>Number of beads</th>
<th>$\eta_0$</th>
<th>$\eta_\infty$</th>
<th>$K$</th>
<th>$m_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>10 (2)</td>
<td>4(1)</td>
<td>24(9)</td>
<td>1.3(4)</td>
</tr>
<tr>
<td>43</td>
<td>18.6(3)</td>
<td>3.2(9)</td>
<td>60(10)</td>
<td>0.78(9)</td>
</tr>
<tr>
<td>91</td>
<td>35(1)</td>
<td>2(1)</td>
<td>178(20)</td>
<td>0.56(5)</td>
</tr>
<tr>
<td>187</td>
<td>53(2)</td>
<td>6(1)</td>
<td>310(41)</td>
<td>0.71(8)</td>
</tr>
</tbody>
</table>

Figure 6.2 presents the fitted lines obtained from the Cross equation in comparison with the Carreau-Yasuda equation for shear viscosity data of type A hyperbranched polymer comprising 187 monomers. It can be seen that these two models agree very well. Fitted lines are slightly different at very high shear rates, in the transition region from Newtonian to non-Newtonian and at very low shear rates.

Figure 6.3 presents the dependence of the zero shear rate viscosity on the number of beads per molecule for different hyperbranched polymers. The zero shear rate viscosity scales as $\eta_0 \propto N_s^{0.657(2)}$ where $N_s$ is the number of monomers/beads per molecule. The exponent of
the power law for hyperbranched polymer melts is consistent with that for dendrimers which were found to have $\eta_0 \propto N_s^{0.646(2)}$ (Bosko et al., 2004b) due to similar molecular structures. Furthermore, our results suggest that hyperbranched polymers are free of entanglements as the dependence of viscosities on the number of monomers does not break into two regions at low and high number of monomers, whereas most of the linear analogues have viscosity dependencies given as $\eta_0 \propto M_w$ at low molecular weights and $\eta_0 \propto N_s^{3.4}$ at high molecular weights where the polymer chains entangle (Doi and Edwards, 1986). However as WCA and FENE potentials were employed to simulate hyperbranched polymers, beads along the polymer chain can vibrate and rotate freely. This results in a polymer model that is more flexible than typical real materials and model molecules in shearing dense fluids may fold upon themselves more than in reality. It has been found experimentally that the value of the power law exponent for dendrimers is approximately 1.1 (Hawker et al., 1995, Farrington et al., 1998, Uppuluri et al., 2000) which is quite high compared to that from NEMD simulations which was found to be 0.646(2). Therefore higher shear viscosity and higher values of the power law exponent are expected in experiments on common hyperbranched polymers.

![Figure 6.3. Zero shear viscosity vs. number of beads per molecule for hyperbranched polymers of type A.](image)

The time constant $\lambda$ in the Carreau-Yasuda model fitted to the simulation data is also the longest relaxation time of molecules composing the fluids. Although the longest relaxation
time $\tau_0$ can be the rotational relaxation time or the reptation relaxation time, $\tau_0$ can be considered to be the rotational relaxation time as there is no entanglement in these hyperbranched polymer systems and hence there is no reptation relaxation time. On the other hand, the inverse of the time constant $\lambda$ is the strain rate $\dot{\gamma}_0$ at which the onset of shear thinning is observed. For type A hyperbranched polymers with 19, 43, 91 and 187 beads, the values of $\dot{\gamma}_0$ are $9.9(5)\times10^{-3}$, $2.6(4)\times10^{-3}$, $9.35(3)\times10^{-4}$ and $7.032(2)\times10^{-4}$ respectively. The shear thinning behaviour occurs at lower strain rates for large hyperbranched molecules in comparison with small hyperbranched polymers. This can be explained by relaxation times, the deformation and tendencies to align with the shear flow. Shear thinning occurs due to the deformation and increased alignment of the molecules to the flow field, which is directly related to the relaxation time $\tau_0$ (Kioupis and Maginn, 1999). At shear rates higher than the inverse of $\tau_0$, molecules are stressed and in order to reduce the stress, the molecules extend, deformation occurs and alignment increases, the fluid moves into the non-Newtonian regime and the new structural configuration results in lower viscosity. Because larger molecules have longer relaxation time $\tau_0$, the value of $1/\tau_0$ is smaller than that of small molecules and the fluids composed of large polymers exhibit the crossover from Newtonian to non-Newtonian behaviour at lower strain rates. The stretching caused by the applied shear results in a more asymmetric ellipsoidal configuration of hyperbranched polymers which has been discussed in detail in the previous Chapter.

Figure 6.4 presents the dependence of longest relaxation times $\tau_0$ on the number of beads per molecule $N_s$ for four type A hyperbranched polymer systems. The logarithm of $\tau_0$ for hyperbranched polymers composed of 19, 43 and 91 beads has a linear relationship with the logarithm of the number of beads $N_s$. The relaxation time for these systems scales as $\tau_0 \propto N_s^{1.4(2)}$. The exponent value of 1.4(2) for hyperbranched polymers is consistent with previous NEMD simulation results which found that the exponent value is 1.7 for linear polymers and 1.3 for dendrimers (Bosko, 2005). Our exponent result is lower than those predicted by the Rouse model which gives $\tau_0 \propto M^2$ (Doi and Edwards, 1986). On the other hand the value of $\tau_0$ for the largest hyperbranched polymer system comprising 187 beads does not follow the same trend of
the smaller polymers. The main causes might be the increase of structural rigidity with the number of beads \( N_s \) and the flow-induced stretching behaviour of hyperbranched polymers which results in the more aspherical shape of small molecules and more spherical shape of large molecules. This is opposite to the behaviour of linear molecules. For long linear polymers above the critical value of \( N_s \), the longest relaxation time, which is predicted to scale as \( N_s^3 \) by the reptation theory, results from the entanglement of long chains (Doi and Edwards, 1986). This is less likely to be the case for hyperbranched polymers with short branches and a large number of terminal groups. Furthermore our computed values of the longest relaxation time have large uncertainties due to the multi-step procedure used to obtain them.

![Figure 6.4](image_url)  
**Figure 6.4. Longest relaxation time versus number of beads per molecule for type A hyperbranched polymers.**

The Weissenberg number \( Wi \) is a dimensionless number that can be calculated from the longest relaxation time by the definition \( Wi = \gamma \tau_0 \). Unlike the Deborah number which is used to describe flows with a non-constant stretch history, the Weissenberg number describes the flow with a constant stretch history. Figure 6.5 presents the dependence of the ratio of shear viscosity and zero shear rate viscosity on the Weissenberg number for different hyperbranched polymers. It can be seen that the ratios of shear viscosity to zero shear rate viscosity obtained from NEMD simulations for four hyperbranched polymer systems show a significant degree of consistency with a single master curve.
At $Wi = 1$, the value of $\eta/\eta_0$ for all polymers starts to decrease. The computed data were fitted with the Carreau-Yasuda model and give a dependence of $\eta/\eta_0$ on the Weissenberg number as $\eta/\eta_0 = 0.996(9)/\left[1 + (1.1(1) \times Wi)^2\right]^{0.143(6)}$. Using the master curve established, the shear rate dependence of the viscosity of other hyperbranched polymers in this series could be predicted.

![Figure 6.5. Dependence of the ratio $\eta/\eta_0$ on the Weissenberg number for type A hyperbranched polymers of different molecular weights.](image)

6.2.2. Shear viscosities for hyperbranched polymers with different numbers of spacers

Shear viscosity data at different strain rates obtained from $NpT$ and $NVT$ simulations for hyperbranched polymers with the same molecular weight of 187 beads but different numbers of spacers are presented in Figure 6.6. As can be seen, the shear thinning behaviour is captured within the considered range of strain rates for hyperbranched polymers of all types. The viscosities reach a plateau at low strain rates then decrease rapidly at high strain rates. Furthermore, the viscosities of simulated fluids increase with increasing number of spacers. Hyperbranched polymers of type A possess the lowest shear viscosities whereas polymers of type D have the highest viscosities. This is because hyperbranched polymers with a larger number of spacer units have longer branches and more open structure, which can lead to more entanglement in the systems and result in higher values of viscosity.
Figure 6.6. Shear viscosities versus strain rate for 187 bead hyperbranched polymers (a) of different types in $NVT$ simulations, (b) of different types in $NpT$ simulations and (c) of type A in $NVT$ and $NpT$ simulations (solid lines representing fitting with the Cross model).
Results obtained from NVT and NpT simulations only differ from each other at high strain rates as they apply to different state points. Viscosities in the high strain rate region obtained from constant pressure simulations are lower than those from constant volume simulations. The reason for the more pronounced shear thinning behaviour in NpT simulations is because of the ‘shear dilatancy’ – the density decreases as the shear rate increases. However NpT and NVT simulation results will be the same if the same state point is investigated by setting the required pressure in NpT simulations equal to the pressure obtained from NVT simulations at a given strain rate (Daivis and Evans, 1994).

Viscosity data for these polymers were fitted using the Cross equation, as given in Eq. 6.8. Fitting parameters are shown in Table 6.3. The NpT simulation zero shear rate viscosities obtained from the Cross equation fit are then plotted against the number of spacers and results are shown in Figure 6.7. It can be clearly seen that zero shear rate viscosities correlate linearly with the number of spacers \( b \) in the hyperbranched polymer systems simulated. The slope of the linear fit is found to be 7.3(2). The linear dependence of \( \eta_0 \) on number of spacers has also been found in Brownian dynamics simulations (Lee and McHugh, 2001) for hyperbranched polymers comprising 66 beads per molecule and in experiments (Markoski et al., 2001) for hyperbranched aromatic etherimide copolymers.

### Table 6.3. Parameters of the Cross model fitted to the shear viscosity versus strain rate dependence for 187 bead hyperbranched polymers with different numbers of spacers.

<table>
<thead>
<tr>
<th>Type of hyperbranched polymers</th>
<th>NVT</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>NpT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \eta_\infty )</td>
<td>( \eta_0 )</td>
<td>( K )</td>
<td>( m_c )</td>
<td>( \eta_\infty )</td>
<td>( \eta_0 )</td>
<td>( K )</td>
<td>( m_c )</td>
</tr>
<tr>
<td>A</td>
<td>7(2)</td>
<td>53(2)</td>
<td>322(46)</td>
<td>0.74(9)</td>
<td>3(2)</td>
<td>52(1)</td>
<td>241(24)</td>
<td>0.72(7)</td>
</tr>
<tr>
<td>B</td>
<td>7(1)</td>
<td>61(1)</td>
<td>374(28)</td>
<td>0.86(6)</td>
<td>4(1)</td>
<td>60(1)</td>
<td>336(25)</td>
<td>0.81(6)</td>
</tr>
<tr>
<td>C</td>
<td>7(1)</td>
<td>67(1)</td>
<td>391(30)</td>
<td>0.90(7)</td>
<td>3(1)</td>
<td>67(1)</td>
<td>347(21)</td>
<td>0.82(5)</td>
</tr>
<tr>
<td>D</td>
<td>8(2)</td>
<td>74(2)</td>
<td>408(30)</td>
<td>1.01(8)</td>
<td>5(1)</td>
<td>74(2)</td>
<td>380(30)</td>
<td>0.96(8)</td>
</tr>
</tbody>
</table>
Figure 6.7. Dependence of zero shear rate viscosities on the number of spacers for 187 bead hyperbranched polymers.

Viscosity data were also fitted using Carreau-Yasuda equation, given by
\[ \eta = \eta_0 \left[ 1 + \left( \frac{\gamma_c}{\lambda_\eta} \right)^2 \right]^{\lambda_p}. \]

The fitting parameters for all simulated hyperbranched polymer systems are presented in Table 6.4. The inverse of the time constant \( \lambda_\eta \) is the critical strain rate \( \dot{\gamma}_c \) at which the onset of shear thinning is observed. As the values of \( \lambda_\eta \) increase with increasing number of spacers, the critical strain rate \( \dot{\gamma}_c \) is lowest for hyperbranched polymers of type A with the lowest Wiener index and highest for polymers of type D with the largest Wiener index. A similar behaviour of the critical strain rate was found for hyperbranched polymers under elongational flow in Brownian simulations (Neelov and Adolf, 2004). Furthermore the time constants in the Carreau-Yasuda model fitted to the shear viscosity data from \( NpT \) simulations are always lower than those from \( NVT \) simulations. Therefore the value of the critical strain rate for a given hyperbranched polymer system at constant pressure is always higher than that at constant volume. The advantage of \( NpT \) simulations over \( NVT \) simulations is that \( NpT \) data are more comparable to experiments. However, as mentioned above, \( NVT \) and \( NpT \) algorithms will give the same results if the same state point is investigated.
Table 6.4. Parameters of the Carreau-Yasuda model fitted to the shear viscosity versus strain rate dependence for 187 bead hyperbranched polymers with different numbers of spacers.

<table>
<thead>
<tr>
<th>Type of hyperbranched polymers</th>
<th>$NVT$</th>
<th>$NpT$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\eta_0$</td>
<td>$\lambda_\eta$</td>
</tr>
<tr>
<td>A</td>
<td>48(6)</td>
<td>1422(615)</td>
</tr>
<tr>
<td>B</td>
<td>57.5(4)</td>
<td>1524(87)</td>
</tr>
<tr>
<td>C</td>
<td>63(5)</td>
<td>1612(93)</td>
</tr>
<tr>
<td>D</td>
<td>75(19)</td>
<td>1918(1268)</td>
</tr>
</tbody>
</table>

The time constant $\lambda_\eta$ in the Carreau-Yasuda model fitted to the viscosity data is also the longest relaxation time $\tau_0$ of molecules composing the fluids, from which the Weissenberg number $Wi$ can be calculated by the definition $Wi = \dot{\gamma}\tau_0$. As shown in the previous section, using the Weissenberg number, a master curve can be established and the shear rate dependence of the viscosity for hyperbranched polymers of different molecular weights in the same series could be predicted. With the same purpose, the ratios of shear viscosity and zero shear rate viscosity for hyperbranched polymers of four different architectures are plotted against the Weissenberg number and results are shown in Figure 6.8. However results show that using the Weissenberg number calculated from the time constant in the Carreau-Yasuda model and normalized viscosity is not sufficient to eliminate the differences between different architectures. Therefore the time constant in the Cross model is used to compute the Weissenberg number and viscosity data were normalized using different parameters in the Cross models. Although this gives a better result in eliminating the differences between simulated architectures, a master curve still cannot be established, as shown in Figure 6.9.
Figure 6.8. Shear viscosities versus Weissenberg number calculated from the time constant of the Carreau-Yasuda model for 187 bead hyperbranched polymers with different numbers of spacers in $NVT$ and $NpT$ simulations (solid lines representing fitting with the Carreau-Yasuda model).
Figure 6.9. Shear viscosities versus Weissenberg number calculated from the time constant of the Cross model for 187 bead hyperbranched polymers with different numbers of spacers in $NVT$ and $NpT$ simulations (solid lines representing fitting with the Cross model).
6.2.3. Shear viscosity of hyperbranched polymer blends

Figure 6.10 presents the shear viscosity of blends of hyperbranched and linear polymers of the same molecular weight at different strain rates in $NpT$ simulations. Due to statistical uncertainty in the low strain rate region, only results at strain rates from 0.001 are shown. It can be seen that for both type A and D hyperbranched polymers, at lower strain rates, the blend viscosities decrease with increasing proportion of hyperbranched polymers. This suggests fewer entanglements in the system occurred due to the presence of hyperbranched polymers. These findings are in good agreement with previous simulation and experimental results for dendritic polymers (Bosko, 2005, Nunez et al., 2000, Uppuluri et al., 1998). On the other hand, as can be seen from Figure 6.10(c), in the lower strain rate region, the introduction of type A hyperbranched polymer with short branches leads to lower shear viscosity than that for type D polymer with long branches between branching units. This might be due to the larger number of end groups together with a more compact structure, globular molecular shape and lower interpenetration function of type A polymer. However, at higher strain rates, an opposite trend is observed, higher proportion of hyperbranched polymers in the blend results in higher viscosities. This is simply a mixing effect in the blends of hyperbranched polymers and linear chains. At low strain rates, the viscosities of hyperbranched polymers are lower than those of linear chains with equivalent molecular weight whereas at high strain rates, linear chains possess lower viscosities due to stronger chain alignment with the flow. Other authors (Daivis et al., 1992) also observed the same trends where a faster rate of shear thinning for linear molecules leads to a lower viscosity for the linear melt in the high strain rate region. Therefore a combination of hyperbranched polymers and linear analogues has higher shear viscosities than pure hyperbranched polymers and lower viscosities than pure linear chains in the low strain rate region, and vice versa at high strain rates. This can be clearly seen in Figure 6.11 which shows the comparison of the shear viscosity results for the blend of 20% type A polymer with pure hyperbranched and linear polymer melts of equivalent molecular weight of 187 beads per molecule. The value of the blend viscosity always falls in the range between those for hyperbranched and linear chains. The drop of blend viscosities in the Newtonian regime can be attributed to the globular shape of hyperbranched molecules.
Figure 6.10. Shear viscosity of blends of hyperbranched and linear polymers composed of 187 beads per molecule at different strain rates. (a) Hyperbranched polymer of type A with different blend proportions. (b) Hyperbranched polymer of type D with different blend proportions (solid lines representing fitting with the Carreau – Yasuda equation). (c) Hyperbranched polymers of type A and D with the blend proportion of 20%.
Shear viscosity data in Figure 6.11 were fitted using the Carreau – Yasuda equation and fitting parameters for blends comprising type A and type D hyperbranched polymers are presented in Tables 6.5 and 6.6 respectively. These data were also fitted using the Cross equation and fitting parameters are shown in Table 6.7 and 6.8. As computed viscosities in the low strain rate region were not considered, the zero shear rate viscosities predicted using the Carreau – Yasuda and the Cross models are quite different. However both of these models suggest that the zero shear rate viscosity value decreases with increasing hyperbranched polymer fraction in the blends. Furthermore the longest relaxation time obtained from the Carreau – Yasuda fit for blends comprising more hyperbranched polymers is higher than that for blends composed of less hyperbranched polymers. In other words, the critical strain rate, at which the transition from Newtonian to non-Newtonian regime occurs, is lower for blends with smaller proportion of hyperbranched polymers. This is in accordance with lower critical strain rate of linear chains compared to hyperbranched polymers of the same molecular weight.
Table 6.5. Carreau – Yasuda fitting parameters for shear viscosity data of blends of the type A hyperbranched polymers and linear chains of equivalent molecular weight of 187 beads.

<table>
<thead>
<tr>
<th>Hyperbranched polymers fraction</th>
<th>$\eta_0$</th>
<th>$\lambda_\eta$</th>
<th>$p_\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4%</td>
<td>71(3)</td>
<td>723(109)</td>
<td>0.37(2)</td>
</tr>
<tr>
<td>8%</td>
<td>70(3)</td>
<td>727(107)</td>
<td>0.36(2)</td>
</tr>
<tr>
<td>12%</td>
<td>68(3)</td>
<td>730(105)</td>
<td>0.36(2)</td>
</tr>
<tr>
<td>16%</td>
<td>67(3)</td>
<td>733(101)</td>
<td>0.35(2)</td>
</tr>
<tr>
<td>20%</td>
<td>66(2)</td>
<td>735(99)</td>
<td>0.34(2)</td>
</tr>
</tbody>
</table>

Table 6.6. Carreau – Yasuda fitting parameters for shear viscosity data of blends of the type D hyperbranched polymers and linear chains of equivalent molecular weight of 187 beads.

<table>
<thead>
<tr>
<th>Hyperbranched polymers fraction</th>
<th>$\eta_0$</th>
<th>$\lambda_\eta$</th>
<th>$p_\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4%</td>
<td>74(3)</td>
<td>731(112)</td>
<td>0.37(2)</td>
</tr>
<tr>
<td>8%</td>
<td>73(3)</td>
<td>744(112)</td>
<td>0.37(2)</td>
</tr>
<tr>
<td>12%</td>
<td>72(2)</td>
<td>758(113)</td>
<td>0.36(2)</td>
</tr>
<tr>
<td>16%</td>
<td>71(3)</td>
<td>772(114)</td>
<td>0.35(2)</td>
</tr>
<tr>
<td>20%</td>
<td>71(3)</td>
<td>786(114)</td>
<td>0.35(2)</td>
</tr>
</tbody>
</table>

Table 6.7. Cross fitting parameters for shear viscosity data of blends of type A hyperbranched polymers and linear chains of equivalent molecular weight of 187 beads.

<table>
<thead>
<tr>
<th>Hyperbranched polymers fraction</th>
<th>$\eta_\infty$</th>
<th>$\eta_0$</th>
<th>$K$</th>
<th>$m_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4%</td>
<td>2(3)</td>
<td>88(17)</td>
<td>467(174)</td>
<td>1.0(2)</td>
</tr>
<tr>
<td>8%</td>
<td>2(3)</td>
<td>86(16)</td>
<td>462(168)</td>
<td>1.0(2)</td>
</tr>
<tr>
<td>12%</td>
<td>2(2)</td>
<td>85(15)</td>
<td>456(161)</td>
<td>1.0(2)</td>
</tr>
<tr>
<td>16%</td>
<td>2(2)</td>
<td>83(14)</td>
<td>450(154)</td>
<td>1.0(2)</td>
</tr>
<tr>
<td>20%</td>
<td>2(2)</td>
<td>81(13)</td>
<td>442(146)</td>
<td>1.0(2)</td>
</tr>
</tbody>
</table>
Table 6.8. Cross fitting parameters for shear viscosity data of blends of the type D hyperbranched polymers and linear chains of equivalent molecular weight of 187 beads.

<table>
<thead>
<tr>
<th>Hyperbranched polymers fraction</th>
<th>$\eta_\infty$</th>
<th>$\eta_0$</th>
<th>$K$</th>
<th>$m_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4%</td>
<td>1(3)</td>
<td>93(19)</td>
<td>532(224)</td>
<td>1.0(2)</td>
</tr>
<tr>
<td>8%</td>
<td>1(3)</td>
<td>92(18)</td>
<td>517(213)</td>
<td>1.0(2)</td>
</tr>
<tr>
<td>12%</td>
<td>1(3)</td>
<td>91(18)</td>
<td>504(203)</td>
<td>1.0(2)</td>
</tr>
<tr>
<td>16%</td>
<td>1(3)</td>
<td>91(18)</td>
<td>493(195)</td>
<td>1.0(2)</td>
</tr>
<tr>
<td>20%</td>
<td>1(3)</td>
<td>90(18)</td>
<td>482(187)</td>
<td>1.0(2)</td>
</tr>
</tbody>
</table>

The results show that adding hyperbranched polymers in the melts of linear chains of the same molecular weight does not significantly reduce the viscosity of the system. The shear viscosities of blends drop slightly with increasing proportion of hyperbranched polymers. The reason is that hyperbranched and linear polymers composing the blends have equivalent molecular weight of 187 beads of the same type. In experiments where the presence of a small amount of hyperbranched molecules leads to a substantial drop of viscosities, the molecular weight of linear chains is typically much higher than that of hyperbranched polymers (10 to 40 times higher) (Nunez et al., 2000, Mulkern and Tan, 2000, Hong et al., 1999). On the other hand, our results shows that the viscosity decreases proportionately with the increase of hyperbranched polymer fraction in the blend, whereas some experimental studies found that the viscosity is stabilized after the critical concentration of hyperbranched polymers is reached. In those studies, this limit is caused by the cross-linking and molecular weight buildup due to compatibilization reaction occurring in the blends (Fowler and Baker, 1988, Mulkern and Tan, 2000). The blends in these cases are called reactive blends. In this work, hyperbranched and linear polymers do not have chemical interactions, hence the blends are unreactive and hyperbranched polymers only act as a lubricant. Therefore the viscosities only drop in proportion to the amount of hyperbranched polymers in the blends. This is in agreement with experimental results on hyperbranched polyols and linear styrene maleic anhydride resins (Mulkern and Tan, 2000).

In order to establish a relationship between shear viscosity and blend proportion, viscosities of different blends at different strain rates were plotted against the
hyperbranched polymer fraction in the blends, as presented in Figure 6.12. A linear function, \( \eta = a + c \times H \% \), was used to fit the data and fitting parameters \( a \) and \( c \) are shown in Tables 6.9 and 6.10. Using these parameters, the blend viscosity at the strain rates considered can be predicted if the value of hyperbranched polymer fraction between 0% (pure linear polymers) to 100% (pure hyperbranched polymers) is given.

Figure 6.12. Shear viscosity versus hyperbranched polymer fractions for blends of (a) type A and (b) type D hyperbranched polymers and linear chains of equivalent molecular weight of 187 beads at different strain rates.
6. RHEOLOGY OF HYPERBRANCHED POLYMER MELTS

Table 6.9. Linear fitting parameters for shear viscosity data dependence on hyperbranched polymer fraction for blends comprising type A polymers composed of 187 beads per molecule.

<table>
<thead>
<tr>
<th>Strain rate</th>
<th>a</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>61.59(2)</td>
<td>-0.239(3)</td>
</tr>
<tr>
<td>0.002</td>
<td>47.23(3)</td>
<td>-0.138(2)</td>
</tr>
<tr>
<td>0.005</td>
<td>26.01(4)</td>
<td>-0.002(1)</td>
</tr>
<tr>
<td>0.01</td>
<td>17.55(5)</td>
<td>0.0177(5)</td>
</tr>
<tr>
<td>0.02</td>
<td>8.52(3)</td>
<td>0.0567(2)</td>
</tr>
<tr>
<td>0.05</td>
<td>4.73(2)</td>
<td>0.0487(3)</td>
</tr>
</tbody>
</table>

Table 6.10. Linear fitting parameters for shear viscosity data dependence on hyperbranched polymer fraction for blends comprising the type D polymers composed of 187 beads per molecule.

<table>
<thead>
<tr>
<th>Strain rate</th>
<th>a</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>70.04(3)</td>
<td>-0.0683(6)</td>
</tr>
<tr>
<td>0.002</td>
<td>47.32(5)</td>
<td>-0.0575(2)</td>
</tr>
<tr>
<td>0.005</td>
<td>26.21(1)</td>
<td>0.0268(4)</td>
</tr>
<tr>
<td>0.01</td>
<td>17.77(2)</td>
<td>0.030(7)</td>
</tr>
<tr>
<td>0.02</td>
<td>8.57(4)</td>
<td>0.0508(3)</td>
</tr>
<tr>
<td>0.05</td>
<td>4.75(2)</td>
<td>0.035(1)</td>
</tr>
</tbody>
</table>

6.3. First and second normal stress coefficients

The first and second normal stress coefficients can be defined as $\psi_1 = \left( \langle P_{22} \rangle - \langle P_{11} \rangle \right) / \dot{\gamma}^2$ and $\psi_2 = \left( \langle P_{33} \rangle - \langle P_{22} \rangle \right) / \dot{\gamma}^2$, as presented in the first section of this Chapter. These values describe the effect of the normal stress differences exhibited by polymeric fluids. Unlike Newtonian fluids which have the normal stress differences exactly zero in shearing flow, polymeric fluids always have positive first normal stress coefficient which is
usually much larger than the magnitude of the negative second normal stress coefficient (Bird et al., 1987). An increase of these stress coefficients reflects a tendency of the fluid to deform in the normal directions under shear.

### 6.3.1. Normal stress coefficients for hyperbranched polymers of different molecular weights

Figure 6.13 shows the first and second normal stress coefficients for type A hyperbranched polymers of different molecular weights. For all polymer systems studied, the normal stress coefficients have a large power-law region in which it might decrease by as much as a factor of $10^6$ for a large molecular system. Furthermore, the rate of decline of the first and second normal stress coefficients with the strain rate is much greater than that of the shear viscosity. In the low shear rate region, the normal stress coefficients reach a plateau as the ratios of $P_{yy} - P_{xx}$ and $P_{zz} - P_{yy}$ are proportional to $\dot{\gamma}^2$ whereas at higher shear rates, the values of the normal stress coefficients rapidly decrease. This again indicates that the hyperbranched polymer fluid has a crossover from Newtonian to non-Newtonian behaviour. At the same strain rate, larger hyperbranched polymers have higher first and second normal stress coefficients as they tend to deform more in comparison with the small molecules. The second normal stress coefficient, which has been studied less extensively in experiments than the first coefficient, is negative and much smaller in magnitude than the first normal stress coefficient. In comparison with other simulation results (Bosko et al., 2004b), our normal stress coefficient values for hyperbranched polymers are larger than those for dendrimers but smaller than those for linear polymers.

Data for the first normal stress coefficient for hyperbranched polymers consisting of 19 and 43 beads were fitted using the Carreau-Yasuda model. The zero shear rate first normal stress coefficients $\psi_{1,0}$ for these systems were found to be 508(13) and 2430(45) respectively. From these values and zero shear rate viscosities $\eta_0$ obtained from the Carreau-Yasuda fit for shear viscosity, the viscous relaxation time $\tau_v$ can be computed. The viscous relaxation time, which is defined by

$$\tau_v = \frac{\int_0^\infty tG(t)dt}{\int_0^\infty G(t)dt}$$

where $G(t)$ is the stress relaxation modulus from the theory of linear viscoelasticity (Ferry, 1980), can be calculated by the expression $\tau_v = \psi_{1,0}/2\eta_0$. For hyperbranched polymers
comprising 19 and 43 beads, the values of $\tau_v$ were found to be 25(3) and 67(7) respectively. These values are in very good agreement with the time constants $K$ obtained from the Cross model which were found to be 24(9) and 60(10) for those hyperbranched polymer systems.

![Figure 6.13. First and second normal stress coefficients versus strain rate for type A hyperbranched polymers of different molecular weights.](image)

The normal stress coefficients for all hyperbranched polymers were fitted in the power-law region and the values of the exponents of the asymptotic dependences $\psi_1 \propto \dot{\gamma}^{-\alpha}$ and $\psi_2 \propto \dot{\gamma}^{-\beta}$.
\[ \dot{\psi}_2 \sim \dot{\psi}^\beta \]

are presented in Table 6.11. The values of these exponents are within the range of experimental values for polymer melts and concentrated solutions (Bird et al., 1987). Similar to NEMD simulation results for dendrimer melts (Bosko, 2005), the values of the \( \alpha \) and \( \beta \) exponents do not vary systematically with the size of the hyperbranched polymer molecules. This is in contrast with results for linear polymers (Bosko, 2005) which have the values of \( \alpha \) and \( \beta \) increasing with the chain lengths.

Table 6.11. Estimated values of the exponents in the power-law regions for the first and second normal stress coefficients of type A hyperbranched polymers.

<table>
<thead>
<tr>
<th>Number of beads</th>
<th>( \alpha )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>1.09(4)</td>
<td>0.96(2)</td>
</tr>
<tr>
<td>43</td>
<td>1.09(2)</td>
<td>1.0476(9)</td>
</tr>
<tr>
<td>91</td>
<td>1.05(3)</td>
<td>0.96(2)</td>
</tr>
<tr>
<td>187</td>
<td>1.00(2)</td>
<td>0.91(3)</td>
</tr>
</tbody>
</table>

Figure 6.14. Ratio of the second and first normal stress coefficients for type A hyperbranched polymers of different molecular weights.

The ratios of \( -\dot{\psi}_2/\dot{\psi}_1 \) are presented in Figure 6.14 which shows that the values of \( -\dot{\psi}_2/\dot{\psi}_1 \) are approximately 0.2 for type A all hyperbranched polymer systems. This is very similar to simulation results for dendrimers as they all have compact, highly
branched architectures with globular shape and internal bond constraints which prevent pronounced stretching of the molecules.

6.3.2. Normal stress coefficients of hyperbranched polymers with different numbers of spacers

Values of $\psi_1$ and $-\psi_2$ for 187 bead hyperbranched polymers with different numbers of spacers obtained from $NVT$ and $NpT$ simulations are shown in Figures 6.15 and 6.16. It can be seen that the first and second normal stress coefficients are always higher for systems with longer branches. However, the gap between the values of the normal stress coefficients of different hyperbranched polymers is more pronounced for $\psi_1$ than that for $-\psi_2$. The crossover from Newtonian to non-Newtonian behaviour cannot be captured due to the ‘noise’ of data in the low strain rate region. The normal stress coefficients for all simulated hyperbranched polymers in $NpT$ and $NVT$ simulations were fitted in the power-law region.

The exponents $\alpha$ and $\beta$ of the asymptotic dependences $\psi_1 \propto \dot{\gamma}^{-\alpha}$ and $|\psi_2| \propto \dot{\gamma}^{-\beta}$ are presented in Table 6.12. Similar to the behaviour of the shear viscosity, the decreasing rate of the normal stress coefficients is more pronounced for $NpT$ simulations, hence the exponents $\alpha$ and $\beta$ obtained from $NpT$ simulations have higher values than those from $NVT$ simulations. However, these values are still within the range of experimental values for polymer melts and concentrated solutions (Bird et al., 1987).

Table 6.12. Estimated values of the exponents in the power law regions for the first and second normal stress coefficients of 187 bead hyperbranched polymers with different numbers of spacers.

<table>
<thead>
<tr>
<th>Type of hyperbranched polymers</th>
<th>$NVT$</th>
<th>$NpT$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>Type A</td>
<td>1.0(2)</td>
<td>0.9(7)</td>
</tr>
<tr>
<td>Type B</td>
<td>1.1(1)</td>
<td>1.0(3)</td>
</tr>
<tr>
<td>Type C</td>
<td>1.0(9)</td>
<td>1.1(1)</td>
</tr>
<tr>
<td>Type D</td>
<td>1.1(5)</td>
<td>1.1(4)</td>
</tr>
</tbody>
</table>
Figure 6.15. First normal stress coefficient versus strain rate for 187 bead hyperbranched polymers (a) with different numbers of spacers in $NVT$ simulations, (b) with different numbers of spacers in $NpT$ simulation and (c) of type A in $NVT$ and $NpT$ simulations.
Figure 6.16. Second normal stress coefficient versus strain rate for 187 bead hyperbranched polymers (a) with different numbers of spacers in NVT simulations, (b) with different numbers of spacers in NpT simulation and (c) of type A in NVT and NpT simulations.
6.3.3. Normal stress coefficients of hyperbranched polymer blends

Figure 6.17 shows the first normal stress coefficients for blends of hyperbranched polymers and linear chains of the same molecular weight of 187 beads at different strain rates. As can be seen, there is no significant difference in the value of the normal stress coefficients between blends with different proportion of hyperbranched polymers. However it can still be observed that the pressure difference (between the $x$ and $y$ diagonal elements of the pressure tensor) is slightly stronger for blends with smaller hyperbranched polymer fraction at most of the considered strain rates. However, the difference between the first normal stress coefficients is typically about 5% for blends when the hyperbranched polymer ratios differ by 4%, as shown in the inset graph of Figure 6.17. This is similar to the behaviour of blends of dendrimers and linear polymers in NEMD simulations at constant pressure (Bosko, 2005).

Figure 6.18 presents the second normal stress coefficients for these simulated blends comprising hyperbranched polymers and linear analogues in the low strain rate region. Similar to the first normal stress coefficients, the pressure difference (between the $y$ and $z$ diagonal elements of the pressure tensor) does not change significantly with increasing proportion of hyperbranched polymers in the blends.

In comparison with pure hyperbranched polymers and pure linear analogues, the normal stress coefficient results for the blends of these polymers are always in between, as shown in Figure 6.19. However, the stress coefficients of the blends are closer to those of pure linear systems than to those of pure hyperbranched polymers because the proportion of hyperbranched polymers in the blends is small.
Figure 6.17. First normal stress coefficients of blends of hyperbranched and linear polymers composed of 187 beads per molecule at different strain rates.
(a) Hyperbranched polymer of type A with different blend proportions.
(b) Hyperbranched polymer of type D with different blend proportions.
(c) Hyperbranched polymers of type A and D with the blend proportion of 20%.
Figure 6.18. Second normal stress coefficients of blends of hyperbranched and linear polymers composed of 187 beads per molecule at different strain rates. (a) Hyperbranched polymer of type A with different blend proportions. (b) Hyperbranched polymer of type D with different blend proportions. (c) Hyperbranched polymers of type A and D with the blend proportion of 20%. 

6. RHEOLOGY OF HYPERBRANCHED POLYMER MELTS
6.4. Pressure and density

6.4.1. Pressure of hyperbranched polymers of different molecular weights

Figure 6.20 shows the isotropic pressure of the sheared hyperbranched polymer systems of type A in NVT simulations, which can be calculated as:

\[ p = \frac{1}{3} \text{Tr}(\mathbf{P}) = \frac{1}{3} \left( \langle P_{xx} \rangle + \langle P_{yy} \rangle + \langle P_{zz} \rangle \right) \]  

(6.9)

At low strain rates, the pressure of low molecular weight hyperbranched polymer fluids is higher than that of high molecular weight polymer fluids while at high strain rates, the pressure of the high molecular weight fluids increases earlier and more rapidly than that of the low molecular weight ones. This can be explained by the behaviour of different molecules under shear, as presented in the previous Chapter, namely that molecules of high molecular weight hyperbranched polymers become aspherical more quickly under shear than for low molecular weight polymers.
6. RHEOLOGY OF HYPERBRANCHED POLYMER MELTS

Figure 6.20. Dependence of the isotropic pressure on strain rate for type A hyperbranched polymers of different molecular weights (solid lines representing fitting with the Carreau-Yasuda model).

Fitting the pressure data using the Carreau-Yasuda model \( p = p_0 \left[ 1 + \left( \frac{\dot{\gamma}}{\lambda_p} \right)^2 \right]^{\nu} \), which has been applied for shear viscosity data, the zero shear pressure of hyperbranched polymers can be investigated. The values of the zero shear pressure \( p_0 \) are 5.540(3), 5.414(3), 5.349(6) and 5.299(8) for hyperbranched polymers composed of 19, 43, 91 and 187 monomers respectively. The critical strain rate at which the transition from Newtonian to non-Newtonian behaviour of the pressure occurs can be evaluated as the inverse of \( \lambda_p \) obtained from the Carreau-Yasuda model. The critical strain rate was found to have the value of 0.217(2), 0.126(5) and 0.06(2) for hyperbranched polymers comprising 43, 91 and 187 monomers respectively. For hyperbranched molecules composed of 19 monomers, the value of \( \lambda_p \) obtained is very small and the value of the standard error is large, hence the critical strain rate calculated is uncertain. In comparison to the critical strain rate for viscosity, the value of \( \dot{\gamma}_c \) for pressure is higher because a higher shear rate is required to distort the radial distribution function than that to distort the whole molecule. The trend of pressure changes due to strain rate observed here for hyperbranched polymer melts is similar to that seen previously in dendrimer melts and falls within the range between dendrimer and linear polymer melts (Bosko et al., 2004b). This is because dendrimers
have the most compact architecture, whereas hyperbranched polymers are less compact
and linear polymers have the largest spatial separation of monomers. This behaviour can
be found not only for dendritic polymer melts but also for solutions. It has been reported
by Lue (Lue, 2000) that dendritic polymers in low concentration solution have lower
pressure than linear polymers in \textit{NVT} simulations. In addition, it was found that
concentrated solutions of low-generation dendrimers show similar behaviour to linear
polymers and the pressure increases more rapidly with concentration for high-
generation dendrimers.

\textbf{6.4.2. Pressure and density of hyperbranched polymers with different numbers of
spacers}

Results of the isotropic pressure for hyperbranched polymers with the same molecular
weight of 187 beads per molecule but different numbers of spacers in \textit{NVT} simulations
are shown in Figure 6.21(a). It can be seen that at low strain rates, the pressure of all
systems is roughly constant while at high strain rates, the pressure increases rapidly.
This indicates that the behaviour of the isotropic pressure moves from the Newtonian to
non-Newtonian regime. In comparison to linear and other branched polymers, the
pressure for hyperbranched polymers shows a different trend due to the effect of the
shape and branching. It has been reported by several authors (Jabbarzadeh et al., 2003,
Kim et al., 2008) that before increasing rapidly, a drop can be observed in the plot of \( p \)
versus \( \dot{\gamma} \) for linear, star, H or comb-shaped polymer melts. We do not observe this
behaviour for hyperbranched polymers simulated to the same degree, the pressure only
slightly drops. The pressure data were fitted using the Carreau-Yasuda equation (Bird et
al., 1987)

\[
p = p_0 \left[ 1 + \left( \lambda_p \dot{\gamma} \right)^2 \right]^{m_p}
\]

where \( p_0 \) is the zero shear rate pressure, \( \lambda_p \) is a time constant and \( m_p \) is the power law exponent. Fitting parameters are shown in Table 6.13.

As can be seen from this Table, the zero shear rate isotropic pressure increases slightly
with increasing number of spacers due to the larger spatial separation of beads.
Furthermore, the critical strain rate \( \dot{\gamma}_c \) at which the transition from Newtonian to non-
Newtonian behaviour of the pressure occurs can be calculated as the inverse of \( \lambda_p \). The
values of \( \dot{\gamma}_c \) were found to be 0.06(2), 0.07(3), 0.09(2) and 0.09(2) for hyperbranched
polymers with the number of spacers of 2, 3, 4 and 5 respectively.
6. RHEOLOGY OF HYPERBRANCHED POLYMER MELTS

Figure 6.21. Dependence of the (a) isotropic pressure and (b) reduced bead density on strain rate of 187 bead hyperbrached polymers with different numbers of spacers in NVT and NpT simulations respectively (solid lines representing fitting with the Carreau-Yasuda model).
Table 6.13. Parameters of the Carreau-Yasuda model fitted to the isotropic pressure versus strain rate dependence for hyperbranched polymers with the same molecular weight of 187 beads but different numbers of spacers.

<table>
<thead>
<tr>
<th>Type of hyperbranched polymers</th>
<th>$\rho_0$</th>
<th>$\lambda_p$</th>
<th>$m_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5.295(6)</td>
<td>16.9(7)</td>
<td>-0.46(2)</td>
</tr>
<tr>
<td>B</td>
<td>5.334(4)</td>
<td>14.1(7)</td>
<td>-0.48(3)</td>
</tr>
<tr>
<td>C</td>
<td>5.336(9)</td>
<td>11(2)</td>
<td>-0.6(1)</td>
</tr>
<tr>
<td>D</td>
<td>5.34(1)</td>
<td>11(3)</td>
<td>-0.6(3)</td>
</tr>
</tbody>
</table>

As opposed to $NVT$ simulations with constant density and changing pressure, $NpT$ simulations have constant pressure and changing density. Figure 6.21(b) shows the reduced bead density profile in constant pressure simulations. It can be seen that the density remains constant at low strain rates while at high strain rates, the density falls rapidly. This phenomenon is called ‘shear dilatancy’ (Reynolds, 1885). Density data are fitted using Carreau-Yasuda equation $\rho = \rho_0 / \left[1 + \left(\frac{\dot{\gamma}}{\lambda_p}\right)^2\right]^{m_p}$ where $\rho_0$ is the zero shear rate density, $\lambda_p$ is a time constant from and $m_p$ is the power law exponent. Results of these parameters are presented in Table 6.14. The time constant for density $\lambda_p$ has lower values than those for isotropic pressure $\lambda_p$. Therefore the critical strain rates for the reduced bead density are higher than those for the pressure.

Table 6.14. Parameters of the Carreau-Yasuda model fitted to the reduced bead density versus strain rate dependence for hyperbranched polymers with the same molecular weight of 187 beads but different numbers of spacers.

<table>
<thead>
<tr>
<th>Type of hyperbranched polymers</th>
<th>$\rho_0$</th>
<th>$\lambda_p$</th>
<th>$m_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.8412(2)</td>
<td>12.6(5)</td>
<td>0.175(9)</td>
</tr>
<tr>
<td>B</td>
<td>0.8400(1)</td>
<td>11.1(3)</td>
<td>0.156(6)</td>
</tr>
<tr>
<td>C</td>
<td>0.8400(2)</td>
<td>9.4(8)</td>
<td>0.18(2)</td>
</tr>
<tr>
<td>D</td>
<td>0.8400(4)</td>
<td>9(2)</td>
<td>0.21(9)</td>
</tr>
</tbody>
</table>
6.4.3. Density of blends of hyperbranched and linear polymers

Densities of blends of linear polymer and different hyperbranched polymers in the melts in $NpT$ simulations are presented in Figure 6.22. As can be seen, at low strain rates, the densities of all systems simulated remain constant and these values for different blend compositions are very close. The zero shear rate density obtained from fitting the density data using the Carreau-Yasuda equation slightly increases with increasing proportion of hyperbranched polymers in the blends, as seen in Table 6.15. This can be explained by the difference in topologies of entangled, less compact linear chains and unentangled, more compact hyperbranched polymers, which lead to the increase in density when more hyperbranched polymers are added to the melts of linear analogues. In the linear regime with higher strain rates, the slope of the density vs. strain rate curve varies more when the hyperbranched polymer fraction rises. This is consistent with the behaviour of the shear viscosities as well as the normal stress coefficients of these blends. Furthermore the densities for blends composed of type A hyperbranched polymers are slightly higher than those for blends comprising type D polymers due to the shorter branches and more dense structure of type A molecules.

Table 6.15. Zero shear rate density for blends of 187 bead hyperbranched and 187 bead linear polymers with different hyperbranched polymer fractions.

<table>
<thead>
<tr>
<th>Type of hyperbranched polymers</th>
<th>4%</th>
<th>8%</th>
<th>12%</th>
<th>16%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.8370(2)</td>
<td>0.8370(1)</td>
<td>0.8372(1)</td>
<td>0.8373(1)</td>
<td>0.8375(2)</td>
</tr>
<tr>
<td>D</td>
<td>0.8364(1)</td>
<td>0.8365(1)</td>
<td>0.8366(2)</td>
<td>0.8370(2)</td>
<td>0.8372(1)</td>
</tr>
</tbody>
</table>
Figure 6.22. Density of blends of 187 bead linear polymers and 187 bead hyperbranched polymers of (a) type A and (b) type D with different hyperbranched polymer proportions.
6. RHEOLOGY OF HYPERBRANCHED POLYMER MELTS

6.5. Stress-optical rule

In order to characterize the relationship between macroscopic stress and the microscopic processes such as rotations and deformations of bonds (Wales, 1976), the stress-optical rule (SOR) can be tested from the bond alignment tensor and stress tensor. It states that the mechanical and optical tensors are coaxial and proportional to each other.

6.5.1. Stress-optical rule for hyperbranched polymers of different molecular weights

Figure 6.23 presents the ratio of \( (P_{xx} - P_{yy}) \) and \( (S_{xx} - S_{yy}) \) as well as that of \( (P_{yy} - P_{zz}) \) and \( (S_{yy} - S_{zz}) \) for type A hyperbranched polymers of different molecular weight. As can be seen, the components of the stress and alignment tensor are proportional at low strain rates. The proportionality constant, which is called the stress-optical coefficient, is independent of molecular weight. For all hyperbranched polymer systems, this coefficient has the value of approximately 3.3(3). The lack of dependence of the stress-optical coefficient on molecular weight for simulated hyperbranched polymers is in good agreement with experimental results which showed that the stress-optical coefficient is a function of the local condition such as the temperature, solvent or polymer concentration but does not depend on the features of molecular structure on a large length-scale such as molecular weight, molecular weight distribution, branching or degree of cross-linking (Doi and Edwards, 1986). At high strain rates, the SOR is invalid for all simulated hyperbranched polymers. The reason is that the micro structure of hyperbranched polymer melts is not included in the bond order tensor whereas the stress is determined by the alignment, deformation and micro structure of the systems. The SOR does not take into account the flow-induced changes of the radial distribution function which is distorted at high strain rates.
Figure 6.23. Deviations from the stress-optical rule \(-\frac{P_{xx} - P_{yy}}{(S_{xx} - S_{yy})}\) and \(-\frac{P_{yy} - P_{zz}}{(S_{yy} - S_{zz})}\) versus $\dot{\gamma}$ for type A hyperbranched polymers of different molecular weights.
It has been discussed elsewhere that the failure of the SOR could be due to the influence of the molecular weight distribution (van Meerveld, 2004), the chain conformation (Sridhar et al., 2000), or the role of the number of entanglements in the fluid (Rothstein and McKinley, 2002). There are also certain types of systems that do not follow the SOR at all such as rod-like polymers in the concentrated isotropic regime (Mead and Larson, 1990). In experiments, the experimental conditions can also lead to the failure of the SOR, such as performing experiments near the glass transition temperature (Kroger et al., 1997, Wales, 1976) or at a rate higher than the inverse of the Rouse time of the chain in an elongational experiment (Venerus et al., 1999). The SOR fails also because while birefringence saturates, the stress can continue to grow without limit (Wagner, 2006). These factors are not present in our study, hence we can deduce that the SOR is violated as flow-induced changes of the micro structure of hyperbranched polymers were not taken into account at high strain rates.

### 6.5.2. Stress-optical rule for hyperbranched polymers with different number of spacers

Figure 6.24 shows the deviations from the SOR for hyperbranched polymers with the same molecular weight of 187 beads but different number of spacers. As can be seen, components of the stress and alignment tensors are proportional, hence the SOR is valid, only in the low strain rate region. The proportionality constant – the stress-optical coefficient – is independent of the number of spacers and has the value of approximately 3.2(3) which is very close to the obtained stress optical coefficient for hyperbranched polymers of type A at different molecular weight. This is in agreement with experimental results which show that the stress optical coefficient does not depend on the molecular weight or branching of molecules (Doi and Edwards, 1986). As discussed in the previous section, the violation of the SOR in the high strain rate region is because it does not take into account the flow-induced changes of the radial distribution function of hyperbranched polymers that is distorted at high strain rates.
Figure 6.24. Deviations from the stress-optical rule – \( \frac{(P_{xx} - P_{yy})}{(S_{xx} - S_{yy})} \) and \( \frac{(P_{yy} - P_{zz})}{(S_{yy} - S_{zz})} \) versus \( \dot{\gamma} \) for hyperbranched polymers with the same molecular weight of 187 beads but different numbers of spacers.
7. CONCLUSIONS

7. Conclusions

This thesis has presented an extensive analysis of NEMD simulation results for hyperbranched polymers with different architectures and molecular weights. These imperfectly branched tree-like structures were shown to have special structural and rheological properties that might lead to potential applications in various areas such as rheology modifiers and drug delivery. A number of well-defined specific hyperbranched polymers were successfully modelled and their properties were compared to the behaviour of other polymers such as dendrimers, star polymers and linear chains to explain the relationship between molecular architecture and rheology. To the best of the author’s knowledge, this is the first NEMD study of hyperbranched polymers in the melt.

Hyperbranched polymers were simulated using the coarse-grained bead-spring model which have been widely used for polymers with different topologies. The molecular version of the SLLOD algorithm was employed effectively to simulate dense hyperbranched polymer melts under planar Couette flow in \( NVT \) and \( NpT \) ensembles.

Hyperbranched polymers with different sizes and architectures were studied. The structure of these polymers was fully characterized by the degree of branching together with the Wiener index. Results show that most of the microscopic structural properties have significant changes induced by the shear flow, which depend on the size and geometry of the molecules. These can be summarised as follows:

- Radius of gyration results indicate that molecules are stretched under shear and larger molecules have more flow-induced changes than the smaller ones. The radius of gyration for polymers with different number of spacers was found to be in accordance with the molecular architecture being less compact and more open with an increasing number of spacer units. Although the mean squared radius of gyration was found to scale with the Wiener index as \( \langle R^2 \rangle \propto W^{1.20(6)} \) for a fixed number of beads per molecule, more work is needed to clarify this relationship for varying chain length.

- Analysis of the tensor of gyration shows that hyperbranched polymer molecules have a prolate ellipsoid shape which is slightly flatter than the ellipsoid shape of
dendrimers. The conformational behaviour of large hyperbranched polymers is similar to that of linear polymers whereas for small hyperbranched polymers, the behaviour is similar to that of dendrimers.

- Having similar structures to dendrimers, simulated hyperbranched polymers show similar distribution of mass with terminal groups existing everywhere inside the molecules. The compact structure and the folded back branches are two factors that contribute to the suppression of entanglement between hyperbranched polymers.

- The interpenetration between molecules was found to decrease with the increase of molecular weight as the number of functional groups at the outer-most layer increases and the interior of molecules becomes less accessible. With fixed molecular weight, the interpenetration function is higher for polymers with larger number of spacer units due to less compact and more open topologies.

The flow birefringence of hyperbranched polymer melts was characterized by taking into account the calculation of the form and intrinsic birefringence:

- For all hyperbranched polymers, the flow alignment angle always converges to 45° in the Newtonian regime and decreases in the non-Newtonian regime. Furthermore the molecular alignment angle is found to be lower than the bond alignment angle for all molecular weights, architectures and shear rates.

- The order parameter remains constant in the low strain rate region and increases at high strain rates. The smaller value of the bond alignment parameter in comparison with the molecular alignment parameter indicates that the intrinsic birefringence is fairly small compared to the form birefringence.

- The SOR was shown to be valid only in the Newtonian regime as it does not take into account the flow-induced changes of the microstructure. The stress optical coefficient, which was found to be approximately 3.2 – 3.3, does not depend on the molecular weight or the topology of the polymers.

The melt rheology of hyperbranched polymers was also studied. Systems were simulated over a wide range of strain rates in order to capture the crossover behaviour from Newtonian to non-Newtonian regimes. Rheological properties obtained from $NpT$
7. CONCLUSIONS

Simulations were found to be the same as those from \textit{NVT} simulations except at high strain rates due to shear dilantancy:

- Computed shear viscosities of hyperbranched polymers are slightly higher than those for dendrimers and much lower than those for linear polymers of equivalent molecular weight in the Newtonian regime, but opposite in the non-Newtonian regime. This is in accordance with the molecular architecture being more open than that of dendrimers and much more compact than that of linear analogs. For fixed molecular weight, shear viscosities increase significantly with the increasing number of spacer units. Shear thinning is observed for all hyperbranched polymer fluids although it occurs at different strain rates for different systems. A linear dependence of zero strain rate viscosities on the number of spacer units as well as on the number of beads per molecule was found. Furthermore, the Weissenberg number and normalized viscosity can be used to establish a master curve for hyperbranched polymers of the same series but with different molecular weights. However, this method is not sufficient to eliminate differences between different architectures of hyperbranched molecules. Results for blends of hyperbranched and linear polymers show that a small proportion of hyperbranched molecules in the melt of linear chains can make the shear viscosity of the system drop. However there is no observed limit in the proportion of hyperbranched polymers in the blends above which the viscosity is stabilized. For simulated systems, the viscosity drops continuously, correlating with the amount of hyperbranched molecules present.

- Normal stress coefficients were also calculated and were shown to have very large power-law regions in all cases. The magnitude of the second normal stress coefficient is about 20\% of the first normal stress coefficients.

- In all \textit{NVT} simulations, the obtained pressure of the polymeric fluid remains constant at low strain rates and rapidly increases at very high strain rates, whereas in \textit{NpT} simulations, an opposite trend can be observed for the reduced bead density. The density of the fluids is constant in the low strain rate region and decreases at high strain rates.

This work only focuses on systems where the hyperbranched polymers are monodisperse. It has been found that all properties, especially the rheology, are affected by molecular weight, number of spacer units or the hyperbranched polymer proportion.
in blends with linear chains. This suggests the ability to tailor the rheology of polymer melts by controlling those parameters. A potential future study is to simulate polydisperse hyperbranched polymers as well as blends of polydisperse hyperbranched and linear polymers for application as rheology modifiers. Furthermore, instead of shear flow, simulating hyperbranched polymer systems under elongational flow should also be considered. Another valuable extension would be the simulation of dendronized polymer systems which have the highest level of structural complexity presently known for synthetic polymers with applications spanning from single molecule chemistry to surface patterning (Ding et al., 2007, Kroger et al., 2008). On the other hand, hyperbranched polymers simulated in this work were modelled using coarse-grained uniform beads which provide systems of flexible molecules. In order to compare these simulation results more quantitatively with those from experiments, the model needs further modification and fine-tuning to simulate semi-flexible polymers (Kroger, 2005).
References


BOSKO, J. T., TODD, B. D. & SADUS, R. J. (2005) Molecular simulation of dendrimers and their mixtures under shear: Comparison of isothermal-isobaric...
(NpT) and isothermal-isochoric (NVT) ensemble systems. *Journal of Chemical Physics*, 123, 034905.


FLORY, P. J. (1952) Molecular size distribution in three dimensional polymers VI. Branched polymers containing A-R-B_{f-1} type units. *Journal of the American Chemical Society*, 74, 2718-2723.


