Rheology and Structural Properties of Hyperbranched Polymers: a Non-Equilibrium Molecular Dynamics Study

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Abstract. Hyperbranched polymers are imperfectly branched or irregular tree-like structures that have special properties and potential applications in various areas such as thermoset resins, toughening agents and drug delivery. They can be synthesized economically by one-pot reaction which adapts well to large-scale production but provides a polydisperse mixture of randomly branched polymers with different size and topology. This leads to difficulties in experiments and gives simulation a valuable opportunity to gain further insight in understanding the structure and rheology of hyperbranched structures. They have been simulated using bead-rod models together with Monte Carlo and Brownian dynamics techniques. In this research, hyperbranched polymers were simulated using coarse-grained uniform beads and non-equilibrium molecular dynamics (NEMD) methods. Polymeric chains are composed of interconnected beads interacting via finitely extensible nonlinear elastic (FENE) and Weeks-Chandler-Anderson (WCA) potentials. Viscoelastic properties and structural changes of trifunctional hyperbranched polymers in the melt undergoing planar shear are investigated. Our results are in the range between those of dendrimers and linear analogues of equivalent molecular mass.

Keywords: Hyperbranched polymers, Non-Equilibrium Molecular Dynamics, Coarse-grained model
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INTRODUCTION

Dendritic polymers have received considerable interest over the last twenty years due to their unusual properties in comparison with linear polymers. They are tree-like structures usually built from AB\textsubscript{2} monomers of which B reacts with A of another monomer. Completely branched star-like topologies are referred to as dendrimers whereas imperfectly branched or irregular structures are referred to as hyperbranched polymers, as shown in figure 1. For a given number of monomers, there is only one dendrimer structure but a large number of hyperbranched structures can be formed because of different ways in distributing the branched and unbranched monomers.

\begin{table}[h]
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Dendritic polymers & \\
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Dendrimer & Hyperbranched polymer \\
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\caption{Comparison between dendrimer and hyperbranched polymer architecture}
\end{table}

One of the interesting properties of the dendritics is that a peak is observed in plots of intrinsic viscosity as a function of molecular weight in contrast to linear analogues which show a steady increase of intrinsic viscosity with increasing molecular weight. Therefore, they have potential applications in various areas such as viscosity modifiers, toughening agents, thermoset resins and drug delivery\textsuperscript{1}. The synthesis of dendrimers is time-consuming and expensive due to the number of protection and deprotection steps while hyperbranched polymers can be synthesized...
economically in a one-pot reaction which adapts well to large-scale production but provides a polydisperse mixture of randomly branched polymers with different size and topology. This leads to difficulties in experiments and gives simulation a valuable opportunity to shed light on the geometry and rheology of hyperbranched structures. Hyperbranched polymer solutions have been simulated using Monte Carlo and Brownian dynamics methods\textsuperscript{2,3}. To the best of our knowledge, this is the first reported NEMD study of hyperbranched polymer melts.

METHODS

Hyperbranched polymers are simulated using coarse-grained uniform beads. These basic units correspond to the parts of the molecule like linear units or branching points 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 position in the molecule. Polymeric chains are composed of 19, 43, 91 and 187 interconnected beads interacting via FENE and WCA potentials\textsuperscript{4}.

Physical properties of the hyperbranched polymer systems shown in figure 2 were studied using NEMD methods. To simulate fluids under shear, the molecular SLLOD algorithm\textsuperscript{5} was applied. To maintain constant temperature, the kinetic energy of the system has been constrained using the molecular version of the Gaussian isokinetic thermostat. All simulations were performed at constant volume at a reduced temperature of 1.25. The equations of motion of atoms were integrated with time step $\Delta t = 0.001$ (reduced units) using a fifth-order Gear predictor corrector differential equation solver.

RESULTS AND DISCUSSION

In contrast to previous studies which simulated hyperbranched polymers in solution, our work focuses on properties of these macromolecules in the melt away from equilibrium. Viscoelastic properties and structural changes of hyperbranched materials have been analyzed.

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<th>19-monomers</th>
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**FIGURE 2.** Configuration of simulated hyperbranched polymers in comparison with dendrimers and linear polymers

Figure 3 shows that shear viscosities of hyperbranched polymeric fluids exhibit a transition from Newtonian to non-Newtonian behavior. At low strain rates, the viscosity is independent of strain rate, whereas at higher strain rates shear thinning is observed (the viscosity decreases as a function of strain rate). At the same strain rate, shear viscosities increase with the molecular weight of hyperbranched polymers.

Radii of gyration which indicate the extension of a molecule are shown in figure 4. For small strain rates, the size of the polymer remains constant and unchanged from its equilibrium value. But for large values of strain rate, there is a noticeable increase in the value of $<R_g^2>$ which indicates that shear-induced stretching of the molecules has occurred. For a given value of strain rate, the extent of shear induced stretching increases with the number of beads.
CONCLUSIONS

The shearing behaviour of hyperbranched polymers in the melt has been reported by NEMD simulations. All structural and viscoelastic properties of these macromolecules are in the range between those of dendrimers and linear polymers. Shear viscosity results of hyperbranched materials are in good agreement with other simulation results. Most of the microscopic properties have significant changes due to shear flow, the size and geometry of molecules.

REFERENCES

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