

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.

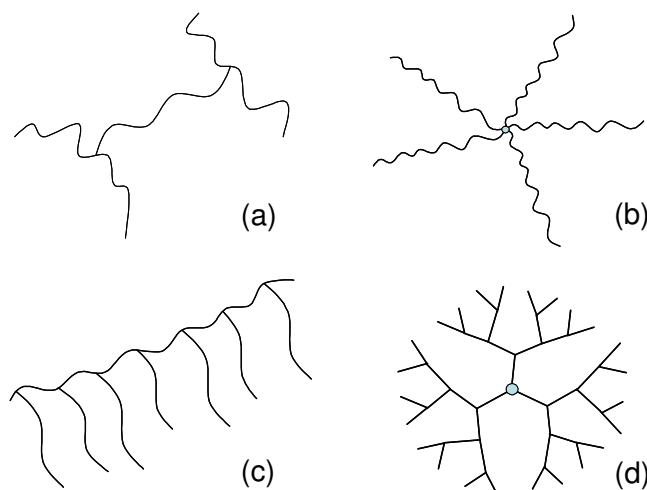


Figure 1.1. Configuration of different branched polymers. (a) Graft (b) Star (c) Comb and (d) Dendritic polymers.

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.

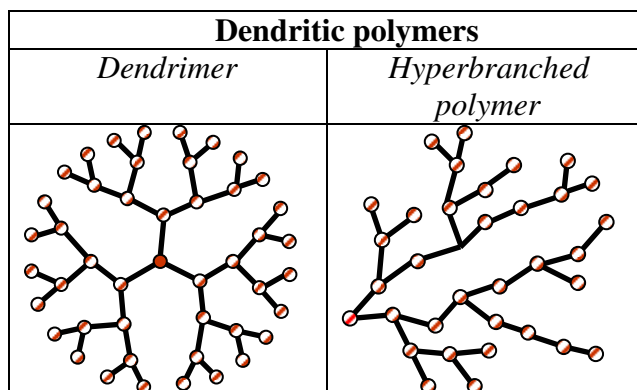


Figure 1.2. Comparison between the architecture of a dendrimer molecule and a randomly branched hyperbranched polymer molecule.

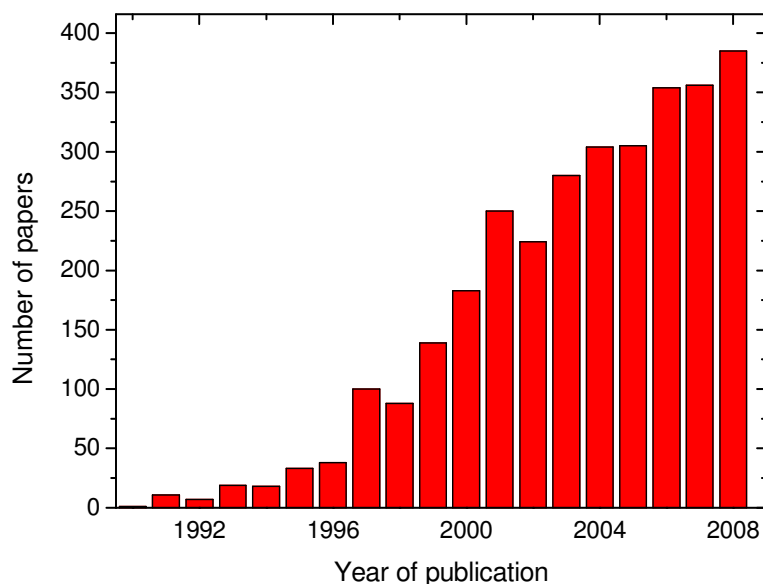


Figure 1.3. The number of scientific publications as a function of publication year based on a search by ISI web of science with hyperbranched polymers as the topic.

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.