

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.

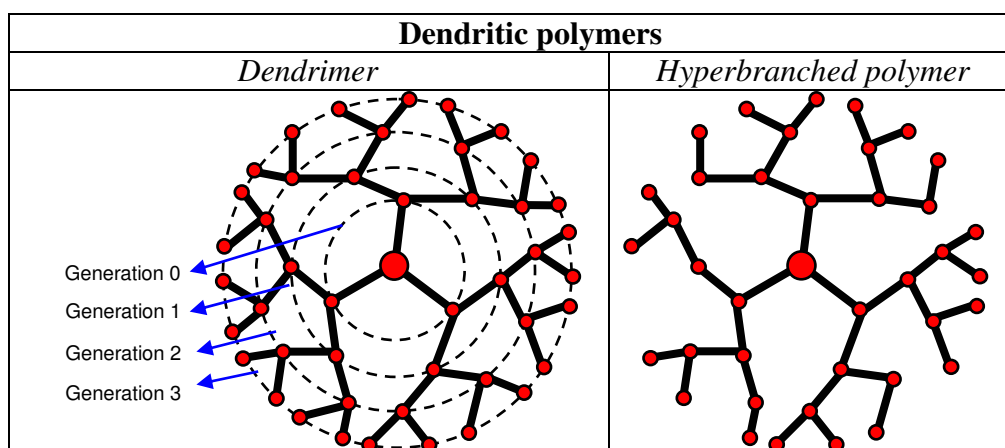


Figure 2.1. Schematic configuration of a tri-functional dendrimer of generation 3 and an example of a hyperbranched polymer molecule.

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 $B = 2D/(2D + L)$ 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 $W = \frac{1}{2} \sum_{j=1}^{N_s} \sum_{i=1}^{N_s} d_{ij}$ 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_2B_2 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 (O dian, 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 ($n \geq 2$) 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).

- ‘A₂ + B₃’ 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 ‘A₂ + B₃’, 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 AB_2 monomer units to a B_3 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.

Hyperbranched polymers and their substitutes can be used as nanomaterials for host-guest encapsulation (Stiriba et al., 2002, Slagt et al., 2002, Mecking et al., 2000, Yang et al., 2001), fabrication of organic-inorganic hybrids (Hedrick et al., 1997, Sun et al., 2000, Sun et al., 2001, Nguyen et al., 2000) and nanoreactors (Gao and Yan, 2004, Lebib et al., 2001, Lebib et al., 2002, Maier and Griebel, 2000).

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).