

PART TWO

MODIFICATIONS OF EPOXY RESINS WITH FUNCTIONAL HYPERBRANCHED POLY(ARYLENE ESTER)S

Chapter 7

Literature Review of Hyperbranched Polymers

7.1 Introduction

Molecular architecture has become an important tool to improve material properties, which depend on the structure and organization of molecules. Organic macromolecules having novel molecular architectures have received great interest in recent years. One example is dendritic polymers,¹ including hyperbranched polymers and dendrimers. These polymers have highly branched structures and numerous reactive groups. Both dendrimers and hyperbranched polymers are based on AB_x ($x \geq 2$) monomers with two different functional groups. They are considered to be somewhat spherical in shape above a certain size; as a consequence, these polymers behave as non-entangled polymers.²

7.2 Dendrimers

Dendrimers are highly and regularly branched, fractal-like structures whose arms emanate from a central core. They are essentially monodisperse and defect free. They exhibit unique properties such as globular shapes, lack of entanglement, extremely low viscosity, high solubility and high degree of surface functionality. The first dendrimer precursors (dendrons)

¹Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules* VCH Publishers: Weinheim, Germany, **1996**.

²Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem. Int. Ed. Engl.*, **1990**, 29, 138.

were reported in 1978 by Vögtle as “cascade” molecules.³ More extensive pioneering work on the synthesis and characterization of dendrimers has been presented by Denkewalter,⁴ Tomalia,⁵ Newkome,⁶ Meijer,⁷ Fréchet⁸ and their co-workers.

Dendrimers are prepared in discrete stepwise procedures, which often involves protection deprotection in each generation. To generate defect-free structures, purification is required in each step to remove incomplete coupling products. They are prepared through either divergent^{4,5,6,7} (from core outward) or convergent⁹ (from the periphery inward) synthetic methods. Each synthetic method has its advantages and disadvantages. Due to the nature of stepwise synthesis, construction of dendrimers are usually costly and time consuming. They are difficult to obtain in large quantity.

Well designed dendrimers have demonstrated potential applications as unimolecular micelles,¹⁰ host-guest molecules,¹¹ catalysts,¹² chromatography¹³ and controlled release agents,¹⁴ etc.

³ (a) Buhleier, E.; Wehner, W.; Vögtle, F. *Synthesis*, **1978**, 155. (b) Vögtle, F.; Weber, E. *Angew. Chem., Int. Ed. Engl.*, **1979**, *18*, 753.

⁴ Denkewalter, R. G.; Kolc, J. F.; Lukasavage, W. J. US Patent 4,410,688 (**1983**).

⁵ (a) Tomalia, D. A.; Dewald, J. R. World Patent PCT W084/02705 (**1984**). (b) Tomalia, D. A.; Baker, H.; Dewald, J. R.; Hall, M.; Kallas, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polymer J.*, **1985**, *17*, 117.

⁶ Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.*, **1985**, *50*, 2003.

⁷ (a) de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Angew. Chem. Int. Ed. Engl.*, **1993**, *32*, 1308. (b) van Hest, J. C. M.; Delnoye, D. A. P.; Baars, M. W. P. L.; Elissen-Roman, C. E.; van Genderen, M. H. P.; Meijer, E. W. *Chem. Eur. J.*, **1996**, 1616.

⁸ Fréchet, J. M. J. *Science*, **1994**, *263*, 1710.

⁹ (a) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.*, **1990**, *112*, 7638. (b) Hawker, C. J.; Fréchet, J. M. J. *Macromolecules*, **1990**, *23*, 4726.

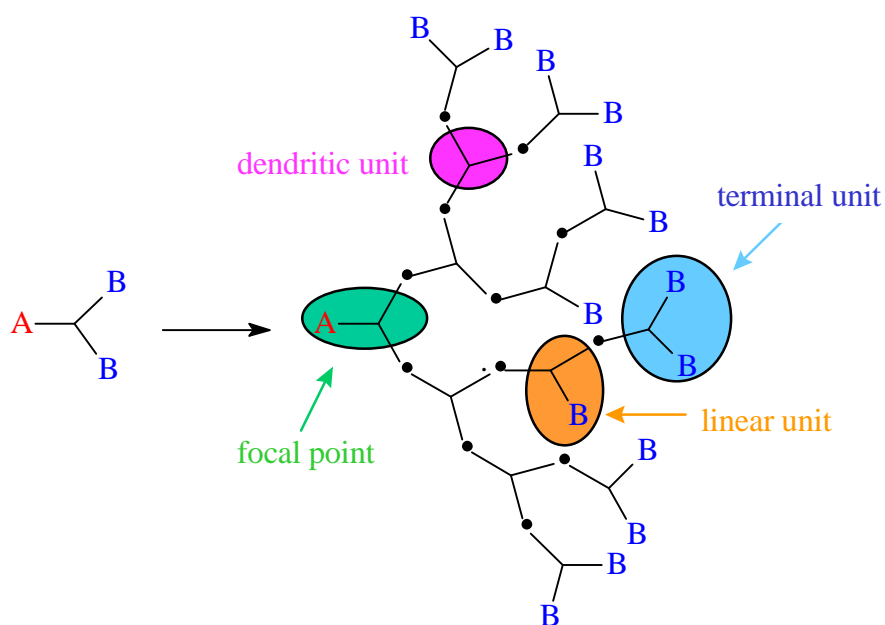
¹⁰ Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Am. Chem. Soc., Perkin Trans. Part I* **1993**, 1287.

¹¹ (a) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science*, **1994**, *266*, 1226. (b) Jansen, J. F. G. A.; Meijer, E. W. *J. Am. Chem. Soc.*, **1995**, *117*, 4417.

7.3 Hyperbranched Polymers

Hyperbranched polymers are highly branched polymers prepared by one-step direct polymerization of an AB_x ($x \geq 2$) monomer (Scheme 7.1). The A and B functional groups must be able to react with each other upon addition of a catalyst or by the application of heat to form a highly branched, globular, three dimensional structure with numerous functional groups (B groups). Due to the lack of chain entanglement and globular in shape, these polymers exhibit unusual properties compared with their linear analogues, such as high polydispersity, low viscosity and high solubility in various organic solvents.

Scheme 7.1



¹² Newkome, G. R.; Moorefield, C. N.; Keith, J. M.; Baker, G. R.; Escamilla, G. H. *Angew. Chem., Int. Ed. Engl.*, **1994**, 33, 666.

¹³ Kuzdzal, S.; Monning, C. A.; Newkome, G. R.; Moorefield, C. N. *J. Chem. Soc., Chem. Commun.*, **1994**, 2139.

¹⁴ Jansen, J. F. G. A.; Meijer, E. W. *J. Am. Chem. Soc.*, **1995**, 117, 4417.

Hyperbranched polymers can be considered to be imperfect analogs of dendrimers. There are four different types of subunits present in the hyperbranched polymer structure: the unique focal point in the green box, which has one A group for each molecule unless cyclization has occurred; the dendritic unit in the pink box, which has no B group; the linear unit in the orange box, which has only one B group; and the terminal unit in the blue box, which has two B groups (Scheme 7.1). The degree of branching¹⁵ (DB) is defined as

$$\text{DB (\%)} = \frac{(\text{no. of dendritic units}) + (\text{no. of terminal units})}{(\text{total number of units})} \times 100$$

If the molecular weight of the hyperbranched polymer is high enough, the focal point can be neglected, and the degree of branching can be estimated as

$$\text{DB (\%)} = \left[1 - \frac{(\text{no. of linear units})}{(\text{total number of units})} \right] \times 100$$

For a perfect linear molecule, the degree of branching would be 0; and for a perfect dendritic molecule, the degree of branching would be 100%. In all cases, DB is between 0 and 100%.

Although hyperbranched polymers based on AB_x monomers were theoretically described by Flory in 1952,¹⁶ they did not receive much attention until recently due to the poor mechanical properties resulting from the lack of entanglement and amorphous morphology. The recent interest in hyperbranched polymers is stimulated by the rapidly growing interest in the dendrimers. In the early 1990s, after Kim and Webster¹⁷ reported hyperbranched polyphenylenes with unique properties, a wide variety of hyperbranched

¹⁵ Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, 113, 4583.

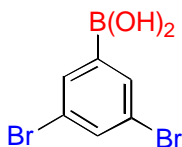
¹⁶ (a) Flory, P. J. *J. Am. Chem. Soc.*, **1952**, 74, 2718. (b) Flory, P. J. *Principles of Polymer Chemistry*, Cornell University Press: Ithaca, NY, **1953**.

¹⁷ Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, 112, 4592.

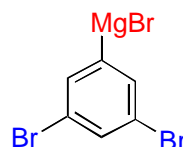
polymers have been reported in the literature. Reviews are available.^{1,18} The majority of these hyperbranched polymers were prepared by condensation reactions of AB₂ monomers.

7.3.1 Polyphenylenes

Kim and Webster^{17,19} reported the first synthesis of hyperbranched polyphenylenes by one step polymerization of 3,5-dibromophenylboronic acid (**7.1**) in the presence of tetrakis(triphenylphosphine)palladium (0) as a catalyst, or 3,5-dibromophenyl Grignard reagent (**7.2**) and bis(triphenylphosphine)nickel chloride. The molecular weight of bromo terminated hyperbranched polyphenylenes was found to be a function of the organic solvent employed. The number average molecular weights of polymers synthesized from **7.2** were higher than those of polymers synthesized from **7.1**, often with greater polydispersity. The molecular weight limitations may result from the steric hindrance at the catalytic center or intramolecular cyclization. The degree of branching was estimated to be about 70%. When they used bromo terminated hyperbranched polyphenylene as a rheology modifier, it was found that a large decrease in the melt viscosity of polystyrene was induced.



7.1



7.2

¹⁸ Bochkarev, M. N.; Katkova, M. A. *Russ. Chem. Rev.* **1995**, 95, 2725.

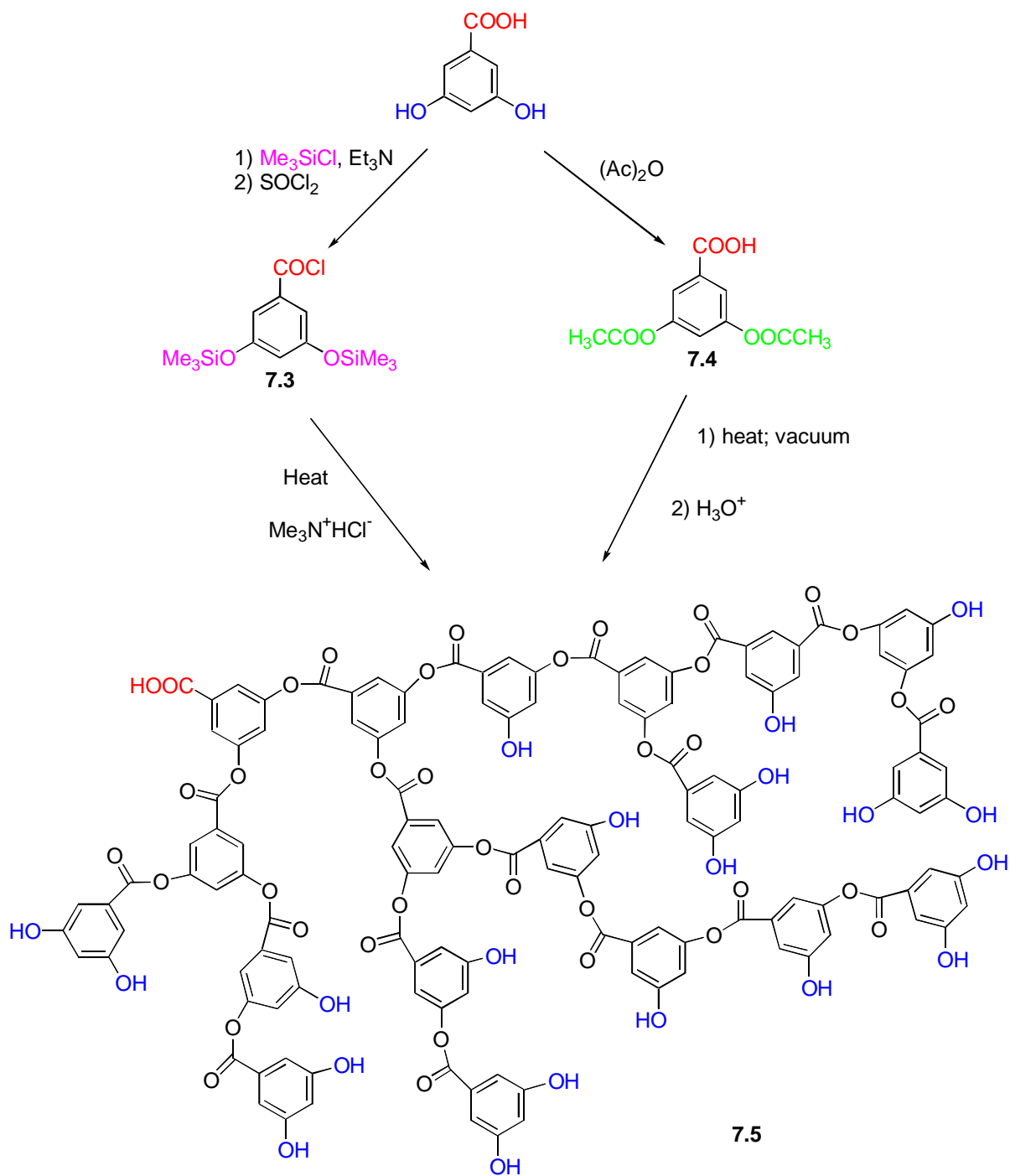
¹⁹ Kim, Y. H.; Webster, O. W. *Macromolecules* **1992**, 26, 5561.

7.3.2 Hyperbranched Poly(arylene ester)s

Hyperbranched poly(arylene ester)s are synthesized from AB₂ monomers derived from 3,5-dihydroxybenzoic acid or 5-hydroxyisophthalic acid since direct esterification of these two monomers at high temperature is not possible due to the decomposition of the monomers before polymerization occurs. Fréchet and Hawker²⁰ reported the first synthesis of a hyperbranched poly(arylene ester) (**7.5**) by self-condensation of 3,5-bis(trimethylsiloxy)-benzoyl chloride (**7.3**), which was synthesized from 3,5-dihydroxybenzoic acid by silylation with Me₃SiCl and subsequent treatment with thionyl chloride and a catalytic amount of Me₄N⁺Cl⁻ (scheme 7.2). Thermal polymerization of **7.3** at 200 °C with catalytic amounts of DMF or trimethylamine hydrochloride yielded hyperbranched polyester **7.5** with weight average molecular weight (polystyrene standards) up to 184 kg/mol. The degree of branching of this phenolic terminated hyperbranched polyester was determined to be about 55%. Compared to their linear analogues, the solubility in organic solvents was found to be enhanced and the thermal stability was about the same.

²⁰ Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, 113, 4583.

Scheme 7.2



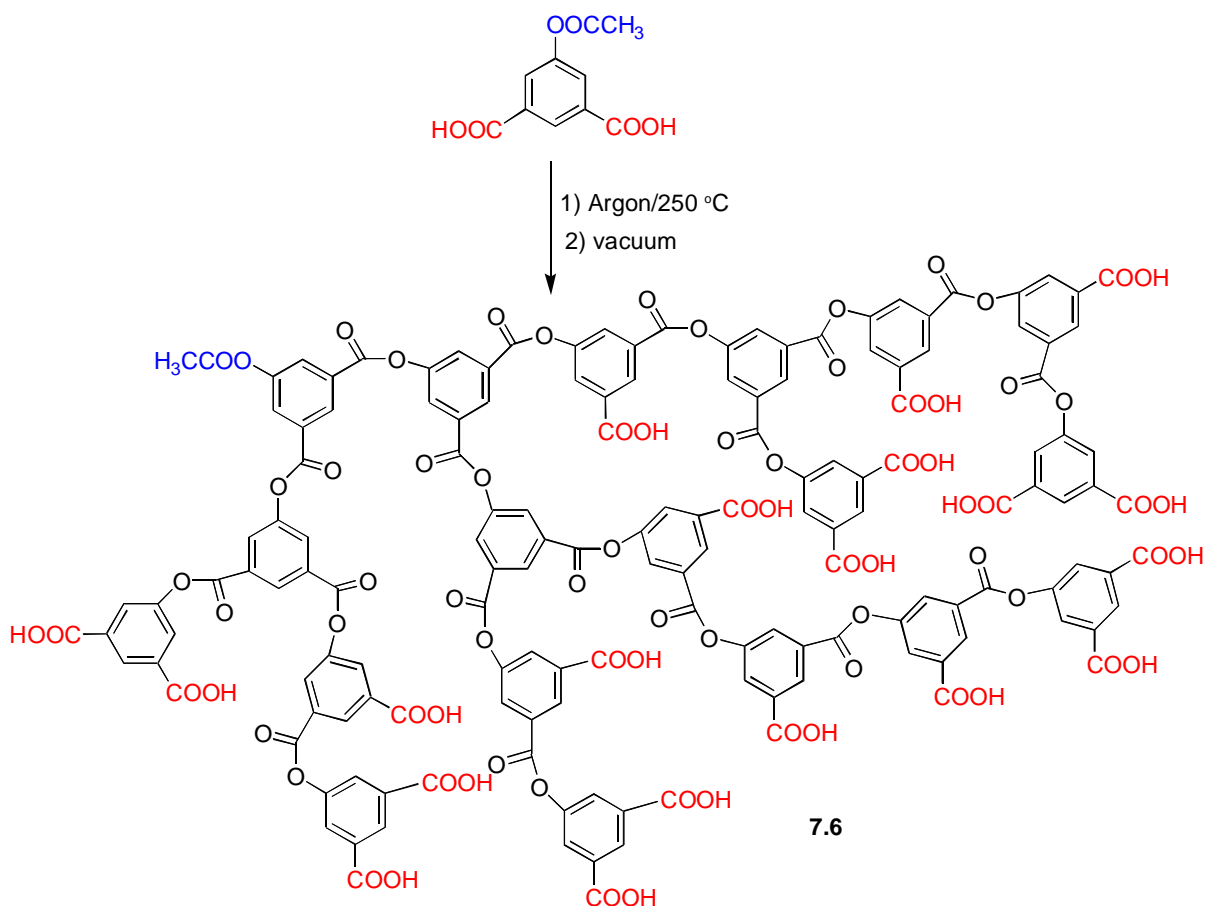
Thermal polymerization of 3,5-diacetoxybenzoic acid (**7.4**) was reported by Turner *et al.*²¹ to produce analogous hyperbranched polyester **7.5** with very high molecular weight ($M_w > 1,000$ kg/mol). The weight average molecular weights were measured by GPC using a low-angle laser light scattering (LALLS) detector. Molecular weight distributions were calculated from GPC measurements using differential viscometry (DV) and differential refractive index (ΔRI) data and the universal calibration concept. The molecular weights obtained from LALLS and DV/ ΔRI detectors were in excellent agreement. The molecular weight of polymer **7.5** depended on the reaction temperature, reaction time and duration under vacuum. Compared to polymers synthesized from monomer **7.3**, the molecular weight of polymers synthesized from this transesterification approach were much less sensitive to the purity of the starting monomer. The degree of branching for polymer **7.5** measured by 1H NMR was about 57% and was found to be independent of molecular weight.

Turner *et al.*²² produced high molecular weight carboxylic acid terminated hyperbranched polyester **7.6** by one-step bulk polymerization of 5-acetoxyisophthalic acid (Scheme 7.3). The polymerization was carried out at 250 °C (about the melting point of the monomer) under argon and then vacuum was applied to remove acetic acid. It is necessary to reflux the resultant polymers in THF and water to cleave the crosslinked anhydride linkages formed during high temperature polymerization. The molecular weight of the carboxylic acid terminated hyperbranched polymer **7.6** was indirectly measured from the corresponding ethyl esters, which were obtained by reaction of polymer **7.6** with thionyl chloride and then ethanol.

²¹ Turner, S. R.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1993**, 26, 4617.

²² Turner, S. R.; Walter, F.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1994**, 27, 1611.

Scheme 7.3



7.3.3 Aliphatic Polyesters and Aromatic/Aliphatic polyesters

As predicted by Flory,¹⁶ hyperbranched polymers prepared directly from AB_x monomers have broad molecular weight distributions, especially at high conversion. The degree of branching ranges from 40% to 70%. To obtain polymers with a high degree of branching, Hult²³ reported a pseudo one-step procedure for the preparation of hyperbranched aliphatic hyperbranched polyesters. An AB_2 monomer, 2,2-bis(hydroxymethyl)propionic acid

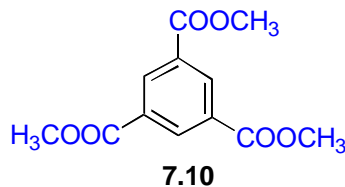
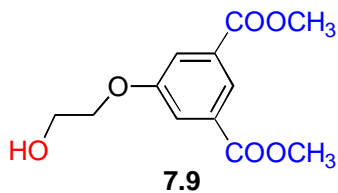
(**7.7**) was added consecutively in stoichiometric amounts after completion of each preceding generation to a reaction vessel which contained a core molecule, 2-ethyl-2-hydroxymethyl-1,3-propanediol (**7.8**). This *p*-tolenesulfonic acid catalyzed melt polyesterification was carried out at a reaction temperature (140°C) below the melting point of the starting monomer **7.7** (190 °C). It was proposed that the reaction mixture was initially a two-phase system containing the core molecule **7.8** in the melt and monomer **7.7** slowly dissolved to allow the carboxylic acid groups to react with the hydroxyl groups of the core molecule or polymer. This stepwise melt polymerization and the use of the core molecule yielded polyester with higher degree of branching (~80%) than those of hyperbranched polymers made by statistical polymerization of AB₂ monomers.



Feast and Stainton²⁴ described a one-pot synthesis of mixed aliphatic/aromatic hyperbranched polyesters using an AB₂ monomer, dimethyl 5-(2-hydroxyethoxy)isophthalate (**7.9**), in the presence of a B₃ core molecule, trimethyl 1,3,5-benzenetricarboxylate (**7.10**). This approach allows control of molecular weights and molecular weight distribution by varying the ratio of AB₂/B₃.

²³ Malmström, E.; Johansson, M.; Hult, A. *Macromolecules* **1995**, 28, 1698.

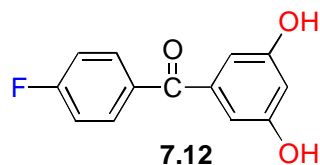
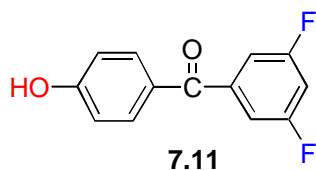
²⁴ Feast, W. J.; Stainton, N. M. *J. Mater. Chem.* **1995**, 5, 405.



7.3.4 Poly(ether ketone)s

As discussed in Chapter 1, poly(arylene ether ketone)s are an important class of high performance engineering thermoplastics. They are difficult to synthesize due to their crystallinity and the resultant low solubility in common organic solvents. Chu and Hawker²⁵ prepared hyperbranched poly(ether ether ketone)s by aromatic nucleophilic substitution reaction of two different AB₂ monomers, 3,5-difluoro-4'-hydroxybenzophenone (**7.11**) and 3,5-dihydroxy-4'-fluorobenzophenone (**7.12**). Polymerization of these two monomers gave the same internal linkages but with different terminal groups. High molecular weight polymers were obtained when polymerization was carried out at 200 °C in an NMP/toluene solvent mixture using sodium carbonate as base. Higher molecular weight polymer ($M_n = 95$ kg/mol) was obtained from **7.12** than from **7.11** ($M_n = 20$ kg/mol) due to the different reactivities of these two monomers. The degree of branching was also different for these two hyperbranched poly(ether ether ketone) analogues. They ranged from 14% for the phenolic terminated polymer to 49% for the fluoro terminated polymer.

²⁵ (a) Chu, F.; Hawker, C. J. *Polym. Bull.* **1993**, 30, 265; (b) Chu, F.; Hawker, C. *Macromolecules* **1996**, 29, 4370.



Other hyperbranched poly(arylene ether ketone)s and hyperbranched poly(arylene ether sulfone)s were also reported by Miller *et al.*^{26,27}

7.3.5 Polyethers

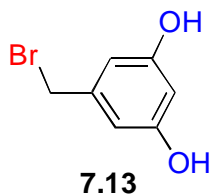
The synthesis of hyperbranched polyether was reported by Uhrich and Fréchet²⁸ in 1991. The monomer 3,5-dihydroxybenzyl bromide (**7.13**) was prepared from 3,5-dihydroxybenzyl alcohol and carbon tetrabromide in the presence of triphenylphosphine. Polymerization of monomer **7.13** in a suspension of potassium carbonate in acetone and 18-crown-6 yielded a phenolic terminated hyperbranched polyether whose weight average molecular weight exceeded 100 kg/mol measured GPC by using a LALLS detector. The addition rate of the monomer did not significantly affect the molecular weight of the polymer.²⁹ However, the molecular weight of the polymer was found to be dependent on the solvent employed.

²⁶ Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M. *J. Am. Chem. Soc.* **1993**, 115, 356.

²⁷ Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M. *Polym. Preprints* **1993**, 34 (1), 58.

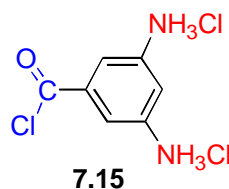
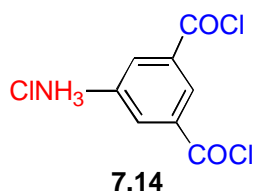
²⁸ Uhrich, K. E.; Hawker, C. J.; Fréchet, J. M. J. *Polym. Mater. Sci. Eng.* **1991**, 64, 237.

²⁹ Uhrich, K. E.; Hawker, C. J.; Fréchet, J. M. J. *Macromolecules* **1992**, 25, 4583.



7.3.6 Polyamides

Kim^{30,31} reported the synthesis of hyperbranched aromatic polyamides using masked aromatic amino acid chlorides **7.14** and **7.15**. Neutralization of these two monomers produced carboxylic acid and amine terminated hyperbranched polyamides, respectively. The carboxylic acid terminated hyperbranched polyamide exhibited lyotropic liquid crystalline behavior in DMF. Formation of aggregates in DMF and the absence of complexing ions was observed by gel permeation chromatography. The number average molecular weights ranged from 24 kg/mol to 46 kg/mol (polystyrene standards) when the eluent was NMP/LiBr/H₃PO₄/THF; however, the number average molecular weight ranged from 700 kg/mol to 1000 kg/mol (polystyrene standards) when the eluent was pure DMF.



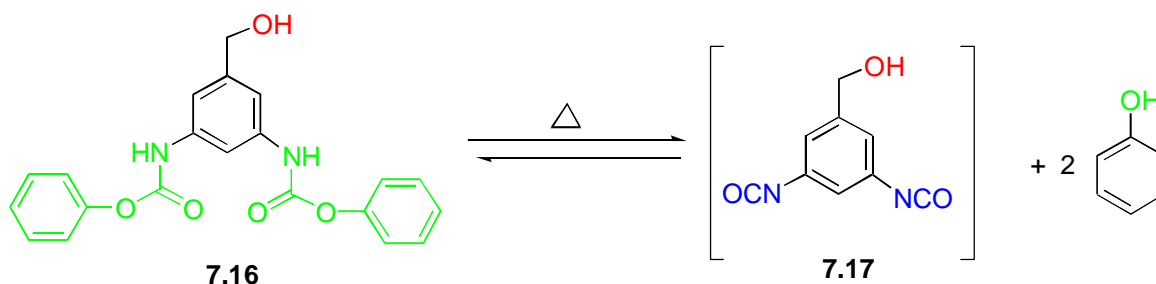
³⁰ Kim, Y. H. *J. Am. Chem. Soc.* **1992**, 114,4947.

³¹ Kim, Y. H. *Makromol. Chem., Macromol. Symp.* **1994**, 77,21.

7.3.7 Polyurethanes

Hyperbranched polyurethanes were prepared by Spindler and Fréchet³² using a protected isocyanate AB₂ monomer, 3,5-bis[(phenoxy-carbonyl)imino]benzyl alcohol (**7.16**). The corresponding diisocyanate monomer **7.17** was generated by thermal decomposition of **7.16** (scheme 7.4). Self-condensation of this AB₂ monomer yielded hyperbranched polyurethane with an M_w of 34 kg/mol. To reduce the amount of side reactions that are characteristic of systems involving isocyanates, the polymerization was carried out with addition of an alcohol at an early stage of the reaction or at low monomer concentration.

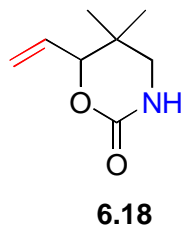
Scheme 7.4



7.3.8 Polyamines

Only one example of hyperbranched polyamine synthesis was reported by Suzuki *et al.*³³ using a cyclic monomer, 5,5-dimethyl-6-ethenylperhydro-1,3-oxazin-2-one (**7.18**). Platinum-catalyzed ring-opening polymerization of this monomer at room temperature in THF afforded a hyperbranched polyamine. The process involved the evolution of carbon dioxide and the high yield conversion of the monomer was confirmed by NMR spectroscopy. The degree of branching ranged from 44%-52%.

³² Spindler, R.; Fréchet, J. M. J. *Macromolecules* **1993**, 26, 4809.

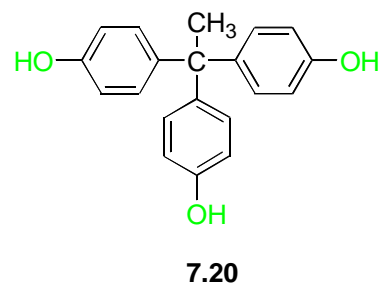
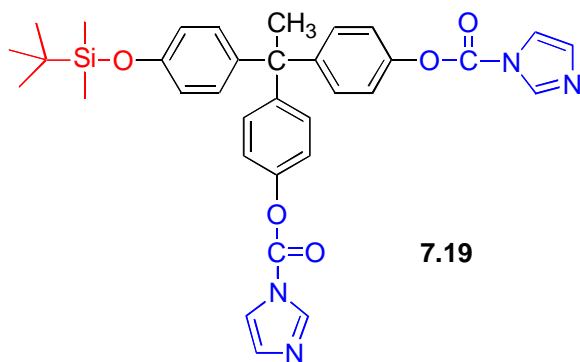


7.3.9 Polycarbonates

Very recently, Bolton and Wooley³⁴ reported the synthesis of hyperbranched aromatic polycarbonates by polymerization of an AB₂ monomer **7.19** derived from 1,1,1-tris(4'-hydroxyphenyl)ethane (**7.20**). Polymerization was accomplished by removal of the silicon protecting group and subsequent reaction of the phenoxide with carbonylimidazolide moiety to give a hyperbranched carbonate. Cleavage of the protecting groups yield the phenolic terminated hyperbranched polycarbonate. The weight average molecular weights of these polycarbonates ranged from 16 to 180 kg/mol as determined by GPC using polystyrene standards, universal calibration and LALLS detectors. The degree of branching was determined as 53% based on a technique using protection, degradation, and followed by HPLC analysis of the degradation products.

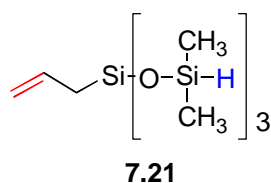
³³ Suzuki, M.; Ii, A.; Saegusa, T. *Macromolecules* **1992**, 25, 7071.

³⁴ Bolton, D. H.; Wooley, K. L. *Macromolecules* **1997**, 30, 1890.



7.3.10 Polysiloxysilanes

Mathias and Carothers³⁵ prepared hyperbranched polysiloxysilanes by platinum catalyzed alkene hydrosilylation of a silicon based AB₃ monomer (**7.21**). The polymers were obtained with a number average molecular weight of about 19 kg/mol as determined by GPC using polystyrene standards. The physical and chemical properties of the resultant polymers can be altered by chemical modification of the surface functionality (Si-H bonds).



Similarly, a family of hyperbranched polycarbosilanes was prepared by Muzafarov³⁶ using vinylmethylsilane, vinylmethylsilane and triallylmethylsilane as monomers.

³⁵ Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, 113, 4043.

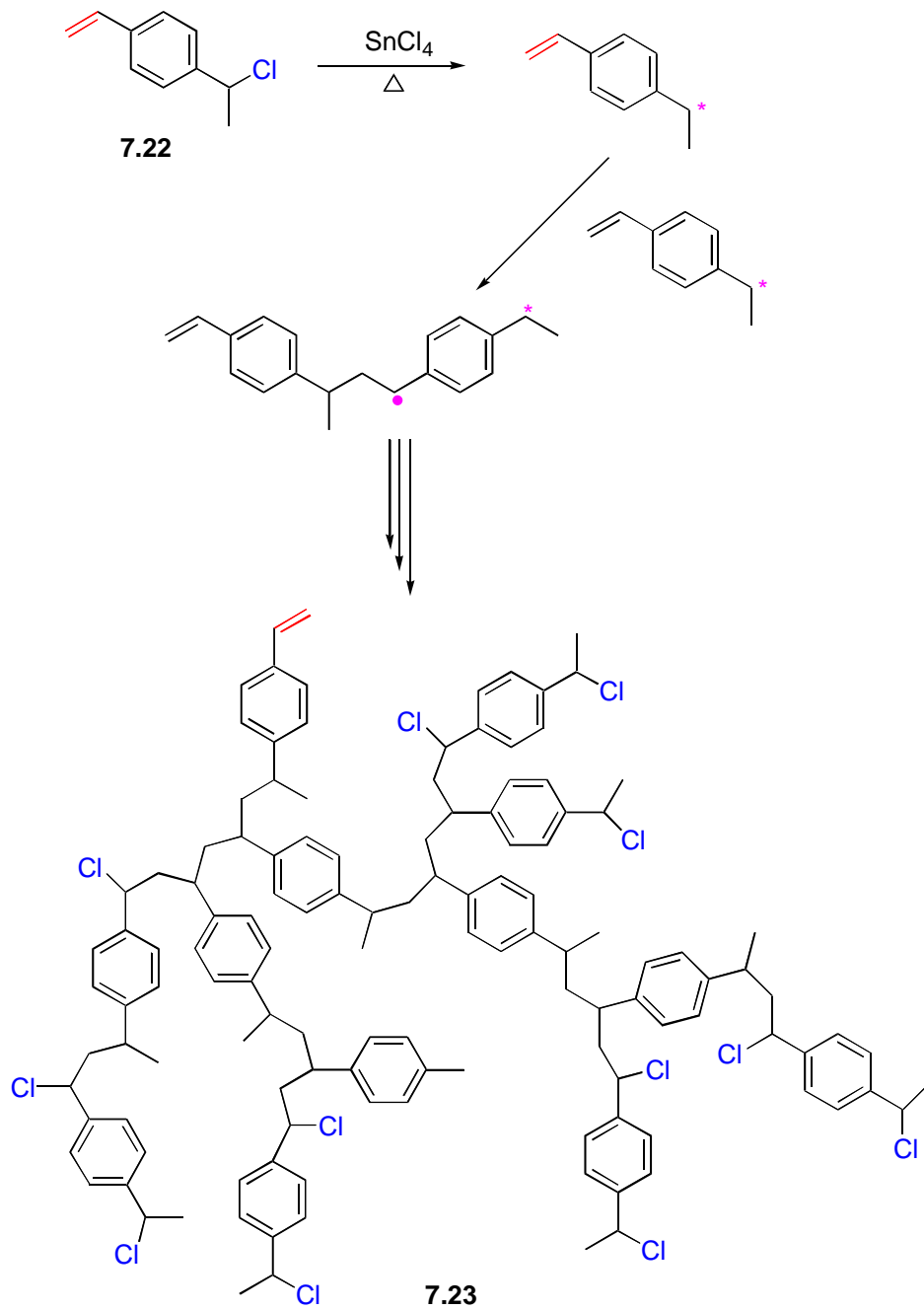
³⁶ Muzafarov, A. M.; Gorbatshevich, O. B.; Rebrov, E. A.; Ignateve, G. M.; Chenskaya, T. B.; Makushev, V. D.; Bulkin, A. F.; Papkov, V.S. *Polym. Sci. (USSR) Engl. Tr.* **1993**, 35,1575.

7.3.11 Hyperbranched vinyl Polymers

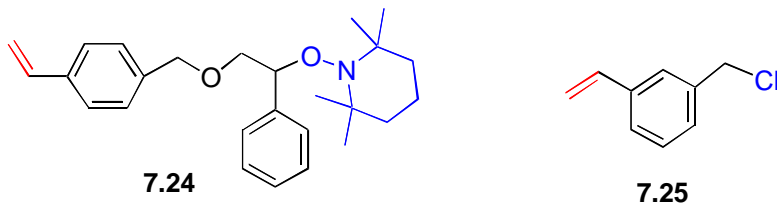
Fréchet *et al.*³⁷ reported the preparation of a hyperbranched vinyl polymer using the concept of self-condensing vinyl polymerization. This method for the preparation of hyperbranched polymers is a combination of classical living polymerization and step-growth polymerization. The vinyl monomer, 3-(α -chloroethyl)-styrene (**7.22**), was activated by SnCl₄ to give an activated AB* monomer, which was able to react with another activated AB* monomer to generate a dimer containing an initiating center and a propagating center. The reactant functionality increased with the monomer conversion from a single double bond to very large numbers of activated growing sites. Further propagation produced hyperbranched polystyrenes **7.23** with number average molecular weights higher than 100 kg/mol as determined by GPC using universal calibration (Scheme 7.5).

³⁷ Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Groubbs, R. B. *Science* **1995**, 269, 1080.

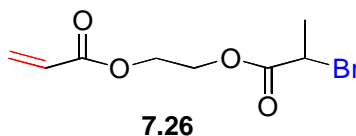
Scheme 7.5



Another AB* vinyl monomer analog **7.24** containing a nitroxide initiator was reported by Fréchet³⁸ to produce hyperbranched polymers by “living” radical polymerization. Similarly, hyperbranched polystyrenes with weight average molecular weights up to 150 kg/mol have been reported by an atom transfer radical polymerization of 4-chloromethylstyrene (**7.25**) in the presence of Cu(I) and 2,2’bipyridyl.^{39,40}



Very recently, hyperbranched polyacrylates formed by atom transfer “living” radical polymerization of acrylic AB* monomer (**7.26**) have also been reported.⁴¹ This monomer was polymerized in bulk using a Cu(I)Br/Cu(II)Br catalyst system to give a hyperbranched polyester with an M_n of 8.3 kg/mol as determined by GPC using linear PMMA standards. The degree of branching based on proton NMR spectrum was about 44%.



³⁸ Hawker, C. J.; Fréchet, J. M. J.; Groubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, 117, 10763.

³⁹ Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, 29, 1079.

⁴⁰ Fréchet, J. M. J.; Leduce, M. R.; Weimer, M.; Groubbs, R. B.; Liu, M.; Hawker, C. J.; *Polym. Preprints* **1997**, 38 (1), 756.

⁴¹ Matyjaszewski, K.; Gaynor, S. G.; Kulfan, A.; Podwika, M. *Macromolecules* **1997**, 30, 5192.

7.4 Properties and Applications of Hyperbranched Polymers

The properties of dendrimers are easier to understand due to their regular structure. Hyperbranched polymers are considered to be imperfect structures of their dendritic analogs. Their properties are not fully understood at the moment since they are a relatively new class of materials. Generally speaking, hyperbranched polymers are considered to be somewhat in globular in shape and they do not have good entanglement between macromolecules. Compared to their linear analogs, they have high solubility and low viscosity. To investigate the differences in properties related to variation of molecular architecture, Wooley *et al.*⁴² compared the properties of linear, hyperbranched and dendritic aromatic polyesters. For this particular case, the glass transition temperatures for these phenolic terminated polymers were found to be approximately 200 °C, and not affected by the variation of the architecture. For some properties, such as solubility and viscosity, hyperbranched polymers resembled dendrimers. Acetoxy terminated hyperbranched poly(aryl ester)s reported by Turner²¹ exhibited very low intrinsic viscosities, e.g., $[\eta] = 0.34$ dL/g for an Mw of 1000 kg/mol.

Compared to linear polymers, hyperbranched polymers have large numbers of surface functionalities. The properties of hyperbranched polymers vary with the structure of the terminal groups. The solubility of hyperbranched poly(aryl ester)s^{21,22} **7.5** and **7.6** is largely dependent on the polarity of the terminal groups. The carboxylic acid salts of polymer **7.6** was soluble in water. The glass transition temperatures of these hyperbranched polyesters were found to be highly dependent on the terminal groups. The T_g of the carboxylic acid terminated polymer is about 100 °C higher than that of the acetoxy terminated polymer.

Hyperbranched polymers have been generally considered to be amorphous polymers unless the polymeric backbone structures were built specifically with mesogenic units to form liquid crystalline materials, as demonstrated by Percec⁴³ and Ringsdorf⁴⁴.

Potential applications of hyperbranched polymers have been demonstrated or suggested to take advantage of their special properties, such as low viscosity, high solubility and high degree of surface functionality. Because hyperbranched polymers are usually non-entangled, amorphous polymers, they are mainly considered to be used as blends, additives and thermosets.

Kim and Webster¹⁷ used hyperbranched polyphenylenes as rheology modifiers for polystyrene. A significant decrease in the melt viscosity of polystyrene and an increase in the modulus of resultant materials were observed. Similarly, Massa and Turner reported that the immiscible blends of a linear polycarbonate and hyperbranched poly(arylene ester)s **7.6** resulted in an increase in tensile strength and compressive moduli, and a decrease in strength-to-break and toughness.

Another application for hyperbranched polymers is in thermoset resins. It has been reported that epoxy functionalized aliphatic dendrimers were used as tougheners for a DGEBA commercially available epoxy resin (LY5082, CIBA-GEIGY).⁴⁵ A blend with 5% of the modifiers was cured isothermally with an isophorone diamine hardener. The initial viscosities of the uncured epoxy resin blends were about the same as that of the neat resin.

⁴² Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *Polymer* **1994**, 35, 4489.

⁴³ Percec, V.; Kawasumi, M. *Macromolecules* **1992**, 25, 3843.

⁴⁴ Bauer, S.; Fischer, H.; Ringsdorf, H. *Angew. Chem., Intt. Ed. Engl.* **1993**, 32, 1589.

⁴⁵ Boogh, L.; Pettersson, B.; Japon, S.; Manson, J.-A. *Proced. Tenth Intern. Conf. Composite Mater.*, **1995**, vol. 4, pp. 389-396.

Compared to the cured neat resin, a 2.5 fold increase in the K_{IC} (plane strain critical stress intensity factor) was observed for the modified epoxy resins. Allyl carbosilane hyperbranched polymers (1-2 weight %) were also reported by Russian workers as silicone rubber modifiers to give a 20% increase in the tensile strength and a two fold increase in the tear strength of the resultant materials.⁴⁶

7.5 Summary and Conclusions

The field of hyperbranched polymers has expanded rapidly in recent years. Compared to dendrimers, the major value of hyperbranched polymers is their relatively easy synthesis. They have properties resembling those of dendrimers and can be produced on a large scale at low cost using simple chemical reaction conditions. The high degree of surface functionality allows one to modify the functional groups and vary the properties of the materials. A wide variety of potential applications has been demonstrated or suggested to take advantage of the special properties of hyperbranched polymers. However, the molecular weight, the polydispersity and the degree of branching are difficult to control because they are mainly decided by statistics and the accessibility of functional groups.

⁴⁶ Muzafarov, A. M.; Gorbatshevich, O. B.; Rebrov, E. A.; Ignateva, G. M.; Chenskaya, T. B.; Myakushev, V. D.; Bulkin, A. F.; Papkov, V. S. *Polym. Sci. (USR) Engl. Tr.*, **1993**, 35, 1575.