

Preparation of Dendritic Aromatic Polyamides

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It is well known that the shape of organic molecules is one of the important factors which determine their properties. During the last 15 years, scientists, especially polymer chemists, have introduced a new philosophy of "dendritic macromolecules" and prepared globular and spherical molecules in addition to the more conventional linear and crosslinked ones (Figure 1). Dendritic macromolecules are classified into dendrons, dendrimers and hyperbranched polymers, which are composed of successive branching units. Dendrons and dendrimers, having a well-controlled size and shape, are usually prepared by multi-step reactions, while hyperbranched polymers are prepared by a one-step self-polymerization of AB_x type multi-functional monomers. Although hyperbranched polymers contain unperfected branching units, the properties of hyperbranched polymers are similar to those of dendrimers and very different from their linear analogues. It has been reported that unique properties, such as good solubility, low viscosity, multi-functionality, and encapsulation effect, have been reported for many dendritic macromolecules, which is mainly caused by the branching and spherical architecture. This paper deals with the synthesis and properties of dendritic aromatic polyamides from synthetic view points. Linear aromatic polyamides (aramids) are known as one of the most important high performance polymers due to their exceptional chemical and thermal stability. The incorporation of dendritic branching units into main chains of aramids might produce new processable high performance materials. Polyamide dendrimers were first reported by Miller and Neenan in 1990¹⁾ and Kiim firstly reported the hyperbranched polyamides in 1992.²⁾ Recent progress, which contains the novel synthetic strategy, new monomers, investigation for the effect of branching structure on properties, will be discussed.

Multi-step reactions are required to prepare precisely controlled dendrimers. Divergent or convergent approach has been applied to prepare various dendrimers. Recently, we have reported the preparation of dendritic aromatic polyamides by an orthogonal and a double-stage convergent approach.³⁾ In the orthogonal approach, protection and deprotection reactions can be

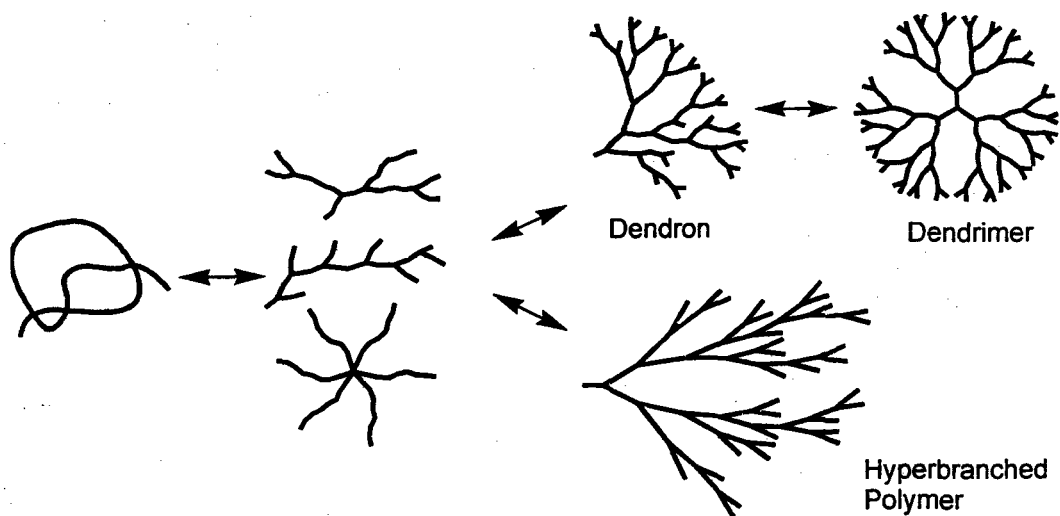
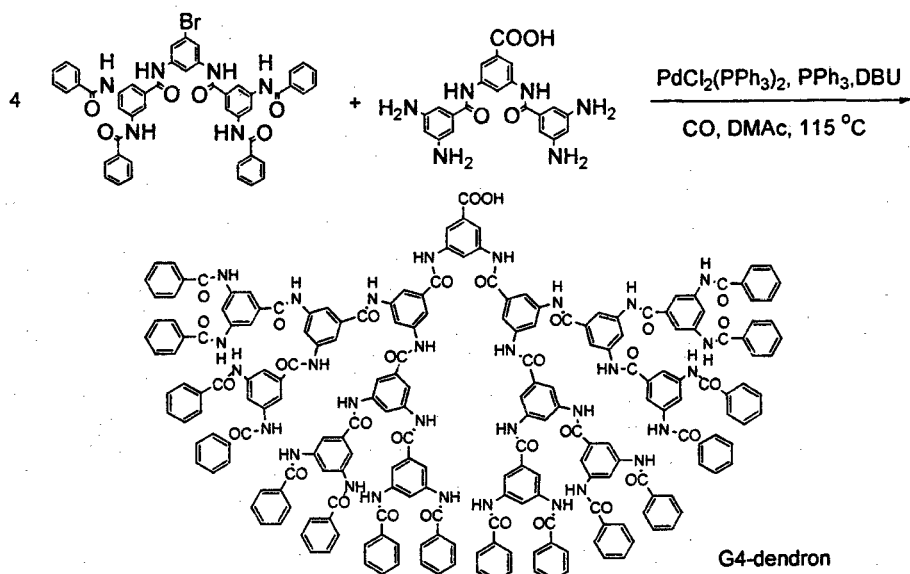
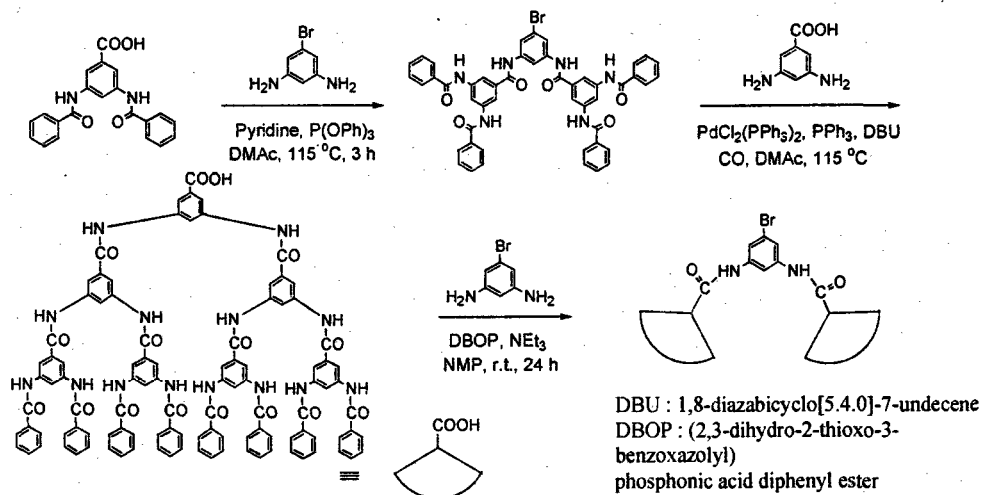


Figure 1 Architecture of branched macromolecules



Scheme 1 Orthogonal approach to form aromatic polyamide dendrimer

avoided by using two different building blocks. Low generation dendrons are used both as a core and a building block in the double-stage convergent approach. The synthetic strategy is potentially useful to prepare high generation dendrons and dendrimers because the number of reaction steps can be reduced in comparison with conventional methods. As shown in scheme 1, two different propagation reactions, direct condensation of carboxylic acid and aromatic amines and CO insertion reaction catalyzed by palladium complex, were applied in an alternating fashion for the orthogonal approach. Scheme 2



Scheme 2 Double-stage convergent approach to form aromatic polyamide dendron

describes the condensation of different dendrons to form a fourth generation dendron through the double-stage convergent approach. Application of the two approaches described above allows the preparation of fifth generation dendron in 6 steps. Since both of the dendrons can be purified by simple precipitation procedures, not column chromatography, the double-stage convergent approach potentially allows easy access for mass production of high-generation dendrimers.

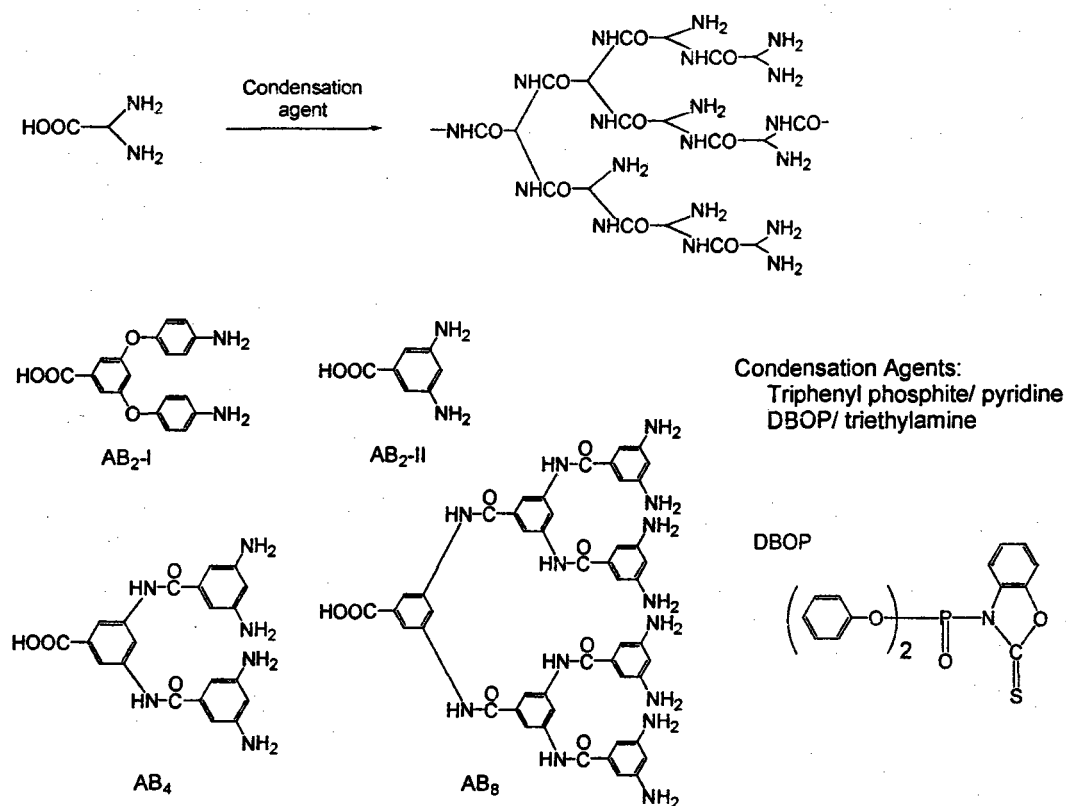
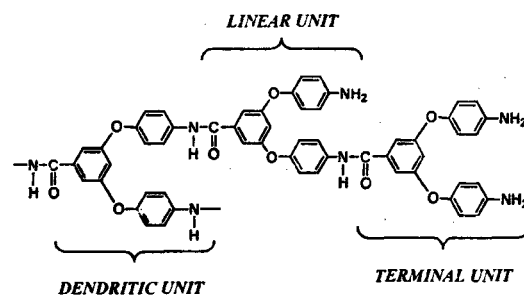


Figure 2 Direct polycondensation of AB_x monomers to prepare hyperbranched aromatic polyamides

Hyperbranched aromatic polyamides were prepared by one-step direct polycondensation of AB_x type monomers, as shown in Figure 2.^{4,5)} Triphenyl phosphate/pyridine and diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl) phosphonate (DBOP)/triethylamine were reported as efficient condensation agents for the polymerization. The hyperbranched aromatic polyamides were soluble in organic solvents, such as DMF and DMSO, in contrast with linear aramids. Inherent viscosity of resulting polymers was less than 0.3 dL/g even if the molecular weight was more than 10^4 . The low viscosity is one of the characteristic features for dendritic macromolecules. The resulting hyperbranched polyamides are composed of fully branched (dendritic), partially branched (linear) and terminal units. Degree of branching (DB) is one of the most important factors to explain the structure of hyperbranched polymers. It is known that the DB of the hyperbranched polymer prepared from an AB_2 monomer approaches 0.5 when the reactivity of 'B' function is equal during the polymerization. Degree of branching of the hyperbranched polyamide prepared from AB_2 -I, calculated by the ratio of the three repeating units, was 0.5 which is consistent with the statistical anticipation.



$$DB = \frac{\Sigma(\text{No. of Dendritic Units}) + \Sigma(\text{No. of Terminal units})}{\Sigma(\text{No. of Total Units})}$$

Structure of the starting AB_x monomer gives great influence on the DB of resulting

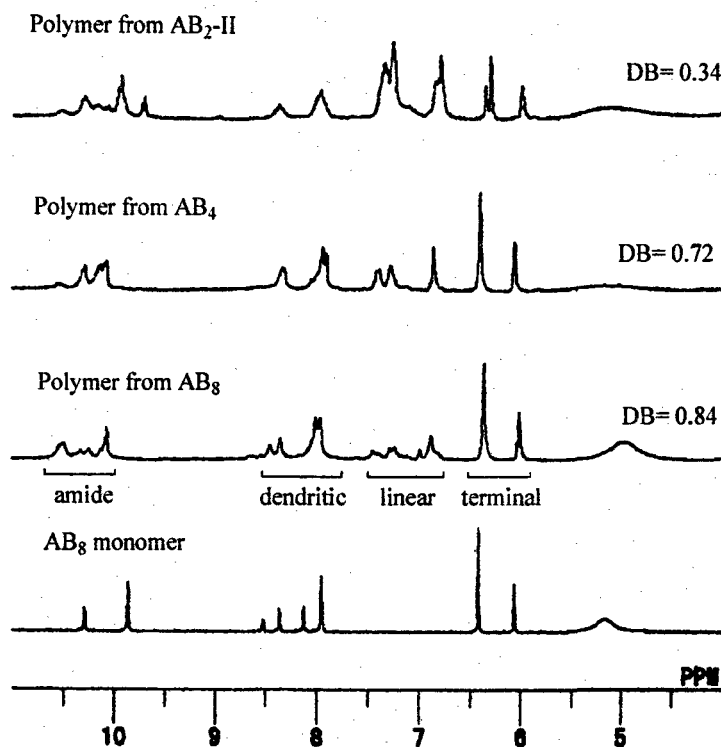


Figure 3 ^1H NMR spectra of dendritic aromatic polyamides

hyperbranched polymers, as shown in Figure 3. When 3,5-diaminobenzoic acid ($\text{AB}_2\text{-II}$) was used as an AB_2 monomer, DB of the polymer decreased to be about 0.3. AB_4 and AB_8 monomers were also polymerized to prepare high-DB polymers. ^1H NMR spectra (Figure 3) clearly showed the decrease of the peaks attributed to the linear unit. It should be pointed out that the increase in DB is attributed to prefabricated branching (dendritic) unit in the AB_4 and AB_8 monomers and does not imply the formation of perfectly branched dendrimers. Copolymerization of AB_2 and AB monomers allows the control of branching density of the resulting polymers. The effects of AB_2 type branching units on the properties of resulting polymers were quantitatively evaluated by the copolymerization.⁶⁾

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