

# Synthesis and Properties of Aromatic Hyperbranched polymers

Masa-aki Kakimoto

Department of Organic and Polymeric Materials,  
Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

Much attention has been focused on dendritic polymers because of their unique characteristics such as considerably low viscosity, amorphous nature, and high solubility in organic solvents. The dendritic polymers are classified into dendrimers and hyperbranched polymers. (Fig. 1) The formers have the precise chemical structure and molecular weights, however complicated stepwise synthetic reactions are usually required like the case of

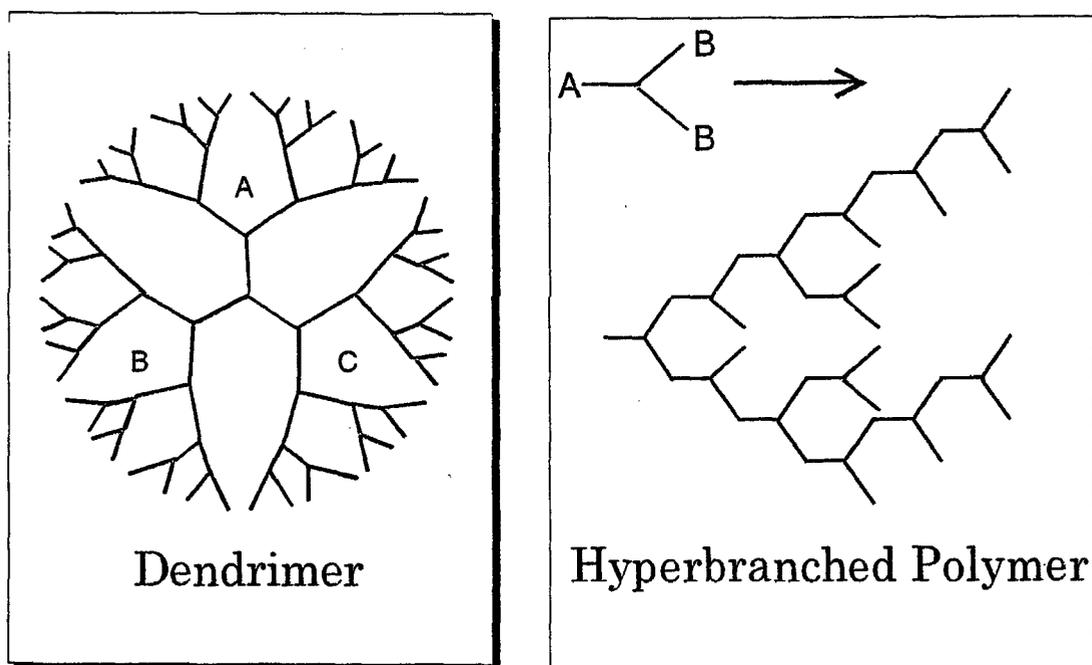


Fig. 1. Dendritic macromolecules

polypeptide synthesis. On the other hand, the hyperbranched polymers are readily prepared by the self-polycondensation of  $AB_2$  type monomers. Although they have some defects and average molecular weights, it was reported that the physical properties of the hyperbranched polymers are not so far from the dendrimers possessing the same chemical structure.

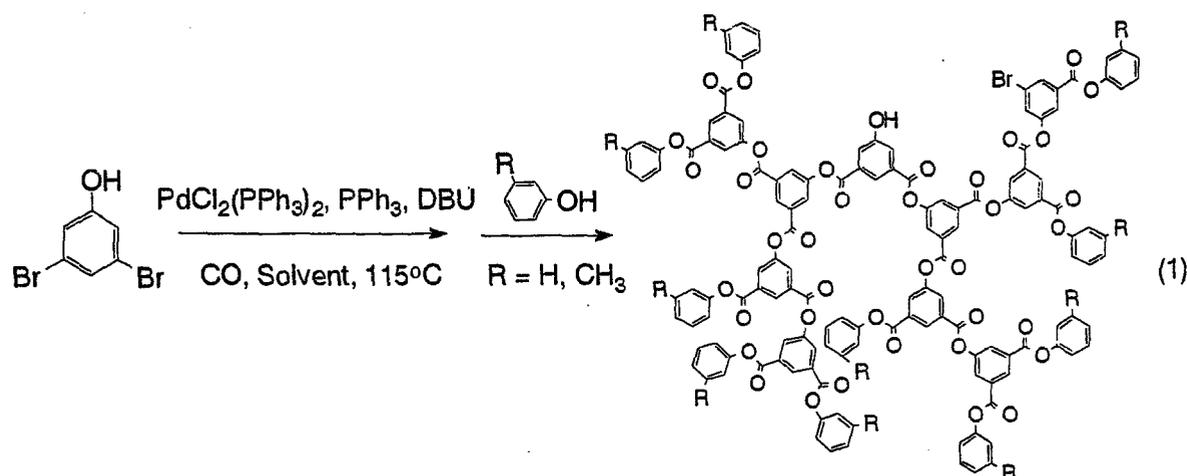
In this paper, synthesis of aromatic hyperbranched polyesters (polyarylates) and polyamides (aramids) are described. Especially, in the case of aramids, not only usual  $AB_2$  strategy but also  $A_2$  plus  $B_3$  method are attempted.

### Polyarylates Hyperbranched Polymers<sup>1)</sup>

Polyarylates are, in principle, crystalline polymers, and applied to liquid crystalline polymers. Some amorphous polyarylates, which are accepted as the high temperature polymers, include flexible, unsymmetrical, and copolymer structure. Hyperbranched polyarylates have been synthesized from the  $AB_2$  type monomer possessing one acid chloride and two silylether functions. The obtained polymers were amorphous and soluble in organic solvents.

We have developed synthesis of the linear polyarylates using palladium catalyzed carbon monoxide insertion reaction starting from aromatic dibromides and dioles.<sup>2)</sup> This reaction was extended to the synthesis of hyperbranched polyarylates.  $AB_2$  type new monomer, 3,5-dibromophenol was synthesized starting from pentabromophenol as described in the literature.<sup>3)</sup> The polymerization was carried out under carbon monoxide atmosphere (1 atm) in the presence of palladium chloride, triphenylphosphine, and 1,8-diazabicyclo[5,4,0]-7-undecene (DBU). Alternatively, end-capping agents such as phenol and cresol were added at the end of the polymerization as shown in Eq. 1. The obtained hyperbranched polymers had molecular weights of several thousands, and soluble in DMF, NMP, DMSO, and m-cresol. The polymer end capped with phenol showed the glass transition temperature ( $T_g$ ) and the decomposition temperature ( $T_d$ ) as 109°C and 200°C, respectively. Unexpected low  $T_d$  was explained by the inclusion of low molecular weight chemicals such as

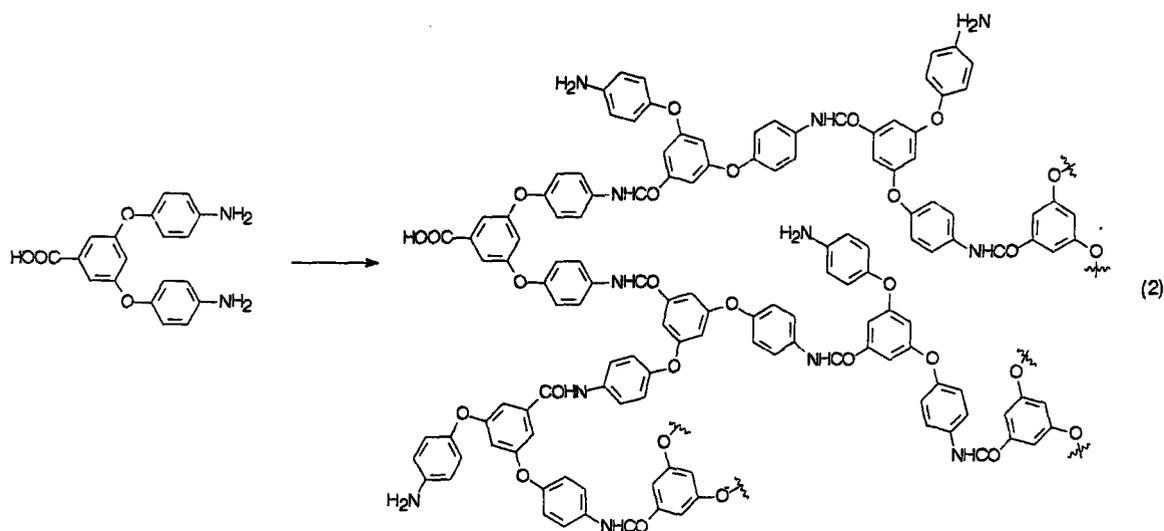
solvent and condensation reagents. This was supported by observation of the impurity signals in  $^1\text{H-NMR}$  spectra.



### Aramids Hyperbranched Polymers

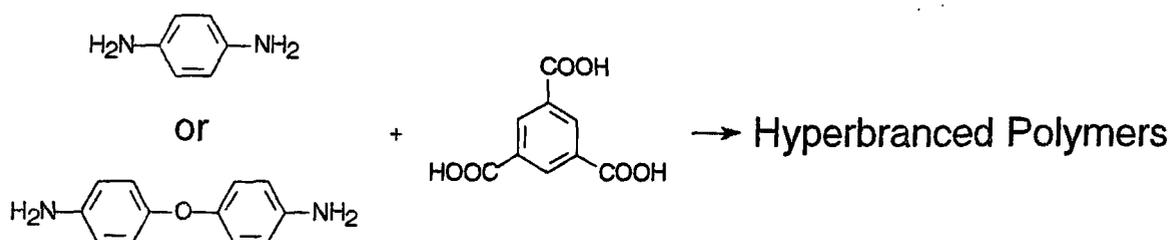
Aramids are well known as super strong fibers such as Kevlar and Nomex. They have strong hydrogen bond between amide function to cause high crystallinity. We prepared aramids hyperbranched polymers by two methods that are self-polycondensation of an  $\text{AB}_2$  type monomer and polycondensation of  $\text{A}_2$  and  $\text{B}_3$  monomers.

The  $\text{AB}_2$  monomer we used in this study has one carboxylic acid and two amines as shown in Eq. 2. The self-polycondensation of the monomer was carried out as well as thermal polymerization and the direct polycondensation in the presence of triphenyl phosphite and pyridine. It was remarkable that the simple thermal polymerization was successful in the present aramids preparation. In fact, the corresponding AB type monomer, 3-(4-aminophenoxy)benzoic acid, afforded a low molecular weight polyamide by heating at  $230^\circ\text{C}$ . This is because the molten AB monomer afforded solid crystalline oligomers, and the further polycondensation was prevented. On the other hand, the hyperbranched polymer (oligomer) prepared from  $\text{AB}_2$  monomer had amorphous and low viscous nature. Inherent viscosity of the hyperbranched aramids was only  $0.19 \text{ dL/g}$  even though the molecular weight was  $60\text{-}70 \times 10^3$ . The hyperbranched aramids



dissolved in polar solvents such as DMF, NMP, DMSO, m-cresol, and 2-methoxyethanol. They had Tg's around 200°C. The aramid prepared by the thermal polymerization and the direct polycondensation had Td's at 400°C and 310°C, respectively. The latter seemed to remain impurities, which were hardly removed by washing with methanol.

In general, hyperbranched polymers are synthesized by the self-polycondensation of AB<sub>2</sub> type monomers, whose preparation, in turn, takes a long time rather than the following polymerization. On the other hand, many chemicals containing two same functional groups (A<sub>2</sub>) are commercially available as monomers for linear condensation polymers. Furthermore, some reagents with three same functional groups (B<sub>3</sub>) are also found as crosslinking agents. We, next, investigated a polymerization of diamine and triacid for the new route to synthesize hyperbranched polymers from A<sub>2</sub> and B<sub>3</sub> monomers, as shown in the following scheme. In most cases, when three-dimensional structure is developed, the polymer becomes a gel or highly crosslinked material, which is insoluble in organic solvents. If the first



condensation of  $A_2$  and  $B_3$  molecules were faster than the following propagation,  $AB_2$  type molecule would be formed and accumulated in solution. Therefore, hyperbranched polymers might be prepared through intermediate  $AB_2$  molecules formed from  $A_2$  and  $B_3$  monomers.

Equimolar amounts of p-phenylene diamine (PD) and trimesic acid (TMA) were allowed to polymerize in the presence of triphenyl phosphite and pyridine as condensation agents. Polymerization proceeded in homogeneous solution and no gelation occurred when the total concentration of monomers was 0.25 mol/L (ca. 4 wt%), as shown in Table 1. Powdery polymer was isolated quantitatively after precipitation in methanol. The resulting polymer was soluble in aprotic polar solvents, such as DMF, DMAc, NMP, and DMSO, which is completely different from gel and highly crosslinked materials. In the IR spectrum of the resulting polymer, a broad absorption band from 3,400 to 3,200  $\text{cm}^{-1}$  and strong carbonyl absorption at 1653  $\text{cm}^{-1}$  with a shoulder peak at 1707  $\text{cm}^{-1}$  are observed. These data suggest the formation of the amide and the existence of carboxyl group in the polymer. The proton of the carboxyl group was also observed as a broad peak at 13.47 ppm in the  $^1\text{H}$  NMR spectrum. Integration ratio for the peaks attributed to aromatic protons of PD unit and of TMA unit was 3 : 4.5, which indicates that the PD unit was incorporated 1.1 times more than the TMA unit. GPC measurement was carried out in DMF with lithium bromide (LiBr) (0.01 mol/L) after the carboxylic acid group of the polymer was reacted with p-methoxyaniline (end-capping reaction). The weight average molecular weight of the end-capped polymer was  $3.43 \times 10^5$ . Gelation occurred when polymerization was carried out at a total concentration of 0.40 mol/L of monomers under the same reaction condition (Table 1, run 2). Three equivalent of triphenyl phosphite was required to achieve a high inherent viscosity when the polymerization was carried out without lithium chloride (LiCl). Addition of LiCl accelerated the polymerization, as reported in literature.<sup>4)</sup> The polymer having a high viscosity was obtained from the polymerization with two equivalents of triphenyl phosphite in the presence of LiCl (Table 1, run 5).

4,4'-Oxyphenylene diamine (ODA) was also used as an  $A_2$  monomer

for the direct polycondensation. Powdery polymer was formed by the direct polymerization with TMA in the presence of three equivalent of triphenyl phosphite. IR and  $^1\text{H}$  NMR spectroscopic data indicate the formation of amide bond and the existence of carboxylic acid. From the integration ratio of aromatic peaks in  $^1\text{H}$  NMR, ODA unit was incorporated more than TMA unit, similar to the polymerization of PD and TMA. Gelation occurred when the polymerization was carried out with LiCl.

Table 1 Polycondensation of diamines and trimesic acid

Run	diamine	Conc. (mol/L)	P(OPh) <sub>3</sub> (eq) <sup>a)</sup>	LiCl (g)	Y(%)	$\eta_{inh}$ (dL/g)
1	PD	0.13	3.0	0	92	0.96
2		0.20	3.0	0	gel	
3		0.13	2.0	0	74	0.31
4		0.13	2.5	0	72	0.29
5		0.13	2.0	1	93	0.72
6	ODA	0.13	3.0	0	88	0.49
7		0.13	2.0	1	gel	
8		0.10	2.0	1	gel	

a) Molar ratio of triphenyl phosphite against diamine.

#### References

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