Synthesis and Properties of Hyperbranched Aromatic Polyamide

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During the last decade, dendritic macromolecules (dendrimers and hyperbranched polymers) have attracted much attention due to their unique properties. Dendrimers have a well-defined structure and branching at each repeating unit. The structure of hyperbranched polymers is not as controlled as that of dendrimers with branching being random. It is reported that hyperbranched polymers have properties similar to those of dendrimers, such as low viscosity, good solubility.[1-3] The synthesis of dendrimers is often tedious as it often requires several protection and deprotection steps as well as extensive purification between successive generations. In contrast, hyperbranched polymers are readily synthesized by the direct polymerization of $AB_n(n \geq 2)$ monomers, which is advantageous over the multi-step synthesis of dendrimers because of the rapid production of large quantities.[3-4]

Aromatic polyamides (aramids) are well known as high performance polymers. They can be readily synthesized by the direct polycondensation of diacids and diamines,[5] and the low-temperature polycondensation of diacid chlorides and diamines.[6-7] However, these polymers dissolve only in highly polar solvents such as concentrated sulfuric acid. Kim reported the preparation of the hyperbranched aromatic polyamides from AB_2 monomers by the low temperature solution polycondensation,[8,9] which were soluble in DMF, DMSO.

It is very difficult to obtain aromatic polyamides having a high molecular weight by the thermal polycondensation method although aliphatic polyamides with a high molecular weight are readily synthesized by this method. This has been explained by the lower reactivity of aromatic amines compared to aliphatic amines. Amorphous morphology and high degree of branching for hyperbranched architecture generally result in lack of significant interchain entanglement, which give rise to a decreased melting viscosity as compared to the linear analogs of the same molar mass.

In this work, we report the synthesis of a novel hyperbranched aromatic polyamide prepared by the direct polycondensation of 3,5-bis(4-aminophenoxy)benzoic acid (monomer 1) in NMP solution. The thermal polymerization behaviors of monomer 1 and 3,5-bis(4-

aminophenoxy)benzoic acid methyl ester (monomer 2) are also presented.

The direct polycondensation of monomer 1 in NMP was carried out at 100 °C under nitrogen in the presence of triphenyl phosphite and pyridine as condensing agents, as shown in eq. 1.

The crude product was precipitated by pouring the reaction mixture into methanol. After purification by re-precipitated of the crude product from DMF solution into methanol containing 0.1% lithium chloride. A white polymer (polymer 1) was obtained. The results of the polycondensation were shown in Table 1. Structure of this polymer was confirmed by IR, ^{1}H-NMR, and ^{13}C-NMR measurements. A new carbonyl absorption corresponding to an amide bond was observed at 1655 cm^{-1} while an absorption for carboxylic acid at 1682 cm^{-1} observed in the monomer disappeared. The absorption at 3470 and 3380 cm^{-1} assigned as the amino groups of the monomer were also changed into a broad absorption at 3300 cm^{-1}. Furthermore, a peak attributed to the amide proton was observed at 10.30 ppm in ^{1}H-NMR spectrum of the polymer. These data indicate that an amide bond was formed through condensation reaction between the carboxylic acid and the amino functions in the AB$_2$ monomer during the reaction. The ^{1}H-NMR spectrum also showed a broad peak at 5.67 ppm, which was attributed to free amino groups in the resulting polyamide.
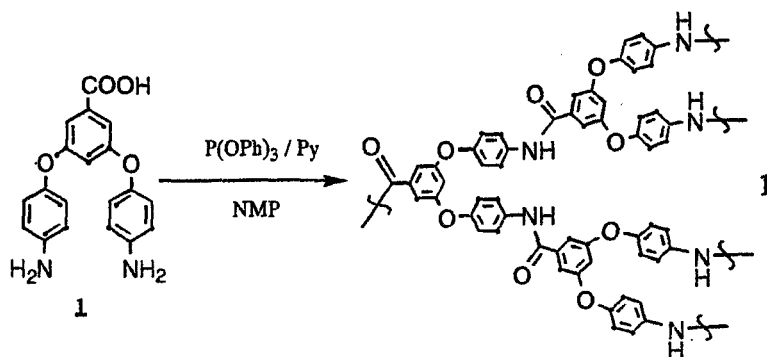
Hyperbranched polymers are composed of linear, dendritic and terminal units. Degree of branching (DB) of the hyperbranched polymers has been defined as follows:[10]

$$DB(\%) = \frac{\sum(\text{No. of Dendritic Units}) + \sum(\text{No. of Terminal Units})}{\sum(\text{No. of Total Units})} \times 100$$

Peaks in ^{13}C-NMR were assigned to the corresponding carbons for the resulting polymer. Some carbons arising from linear units were distinguished from those of terminal and dendritic units. For the polymer 1, degree of branching was determined as about 50% by the integration

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ratio in quantitative ^{13}C-NMR measurement.

Thermal polycondensations of monomer 1 and monomer 2 were conducted at 235 °C under reduced pressure for 1 h, forming Polymer 2 and Polymer 3, respectively, which were precipitated by pouring DMF solution of the crude products into methanol containing 0.1% lithium chloride. The results of the polymerizations are presented in Table 1.
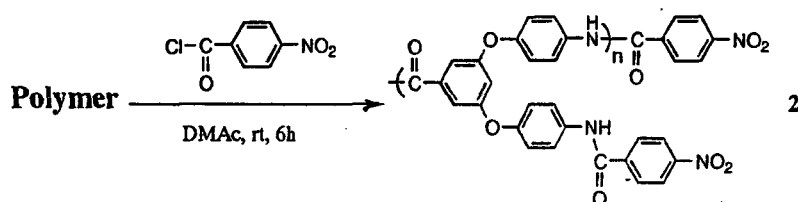
Table 1. Results of synthesis of AB$_2$ monomers

monomer	method	polymer	yield(%)	M$_w$(M$_w$/M$_n$)[a]	η_{inh}(dL/g)[b]
1	solution	1	92	64000(2.0)	0.19
1	thermal	2	75	70000(1.9)	0.19
2	thermal	3	77	58000(2.7)	0.17

[a] Measured by GPC in DMF containing lithium chloride (0.01 mol/L) as an eluent. [b] Measured in DMF at a concentration of 0.5 g/dL at 30 °C

For the polymer 2 and 3, the spectroscopic measurements indicate an identical structure compared to polymer 1. The degree of branching of polymer 2 was determined to be about 50%, which was the same as that of polymer 1.

The thermal polycondensation behaviors were investigated by microscopic study. Crystallization behavior was observed in the melt phase from the corresponding AB monomer, 3-(4-aminophenoxy)benzoic acid or the AA + BB monomers, which are isophtalic acid and p,p-oxydiaminodiphenyl ether, respectively. The melts advanced to solid quickly. On the other hand, no crystalline structure was observed in the melt from monomer 1 at 235 °C. Water formed in the reaction bubbled out from the melt and continued on for about 30 min, indicative of a relatively low viscous state. This is consistent with the characteristic of the hyperbranched polymer formed in the polymerization - no crystallization and lack of significant interchain entanglement.

For polymer 1, end-capping reactions of free amino groups in the polymers was conducted with 4-nitrobenzoyl chloride (eq 2). Theoretically, the resulting hyperbranched polymers contain an overall average composition of one nitrobenzoyl group per each monomeric repeat unit plus one additional nitrobenzoyl end-group. The end-capping reactions proceeded completely, which were

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confirmed by ^{1}H-NMR.

Solubility and thermal properties of the polymers were investigated. The results are shown in Table 2.

The polymer 1, 2 and 3 were soluble in organic solvents such as, dimethylformamide, N,N-dimethylacetamide, N-methyl-2-prrolidone, dimethylsulfoxide, m-cresol and 2-methoxyethanol. The end-capped polymer 1 became insoluble in 2-methoxyethanol, but partially soluble in THF. The glass transition temperature (T_g) was increased from 200 ℃ to 220 ℃ after the end-capping reacting.

Table 2. Properties of resulting polymers

polymer	T_g[a] (℃)	$T_0(T_{10})$[b] (℃)	Solubility[d]		
			DMF,DMAc,NMP DMSO,m-cresol	2-methoxyethanol	THF
1	200	310(530)	+	+	−
2	200	400(480)	+	+	−
3	180	400(475)	+	+	−
end-capped polymer 1	220	310(424)	+	−	±

[a] Measured by DSC using a heating rate of 20 Kmin[-1] under nitrogen atmosphere. [b] Performed by TGA with a heating rate of 10 Kmin[-1] under nitrogen atmosphere. [d] +: Soluble; −: insoluble; ±: partially soluble.

It is suggested that the difference in the thermal properties between polymer 1 and 2 is caused by some remaining impurities in polymer 1, which gave rise to a decrease in T_0 (from 400 ℃ to 310 ℃). In addition, the impurities may react with the amino end-groups and intermolecular cross-linking occurred under high temperatures, leading to a higher T_{10} (530 ℃).

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