Successful Thermal Self-Polycondensation of AB_2 Monomer to Form Hyperbranched Aromatic Polyamide

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Introduction. Aromatic polyamides are well-known as high performance polymers due to their excellent thermal, mechanical and chemical properties.[1−6] There are two conventional methods for the synthesis of aromatic polyamides. One is a low-temperature solution polymerization, where diacid chlorides are reacted with aromatic diamines to form polyamides.[3,7] The other is a direct polycondensation of aromatic diacids and diamines in the presence of condensing agents.[8−10] Although thermal polymerization is a well-known industrial process for aliphatic polyamides with a high molecular weight,[11] it is very difficult to obtain aromatic polyamides having a high molecular weight by the molten polycondensation method.[1,6] This has been mainly explained by the lower reactivity of aromatic amines compared with that of aliphatic amines because of the resonance effect of phenyl groups. The high reaction temperatures usually result in extensive side reactions that restrict polymer molecular weight. Morgan[7] reported a synthesis of an aromatic polyamide by thermal polymerization of 4-aminobenzoyl chloride hydrochloride, which is highly activated as compared to the corresponding carboxylic acid. Fedotova et al.[12] reported the synthesis of a series of aromatic polyamides via ester aminolysis of aromatic diester with aromatic diamines by heating. However, the molecular weights of resulting polyamides were below 15 000, which might be caused by a high melting point of the resulting polymers. There have not been any reports about synthesis of the aromatic polyamides having a high molecular weight by the direct thermal polycondensation of not only the pairs of aromatic diacids and aromatic diamines but also aromatic amino acids.

In recent years, synthesis and characterization of hyperbranched condensation polymers from AB_2 type monomers have received considerable attention since some properties of hyperbranched polymers are similar to those of the corresponding dendrimers.[13,14] In general, the hyperbranched architecture has the characteristic of amorphous morphology, and its high degree of branching results in lack of significant interchain entanglement, which gives rise to a decreased melt viscosity as compared to the linear analogues of the same molar mass.[15−17] Kim[18,19] reported the preparation of the hyperbranched aromatic polyamides from AB_2 type monomers by the Morgan's aramid synthesis.

In this paper, we report the successful thermal self-polycondensation of 3,5-bis(4-aminophenoxy)benzoic acid as an AB_2 monomer, forming the novel aromatic hyperbranched polyamide.

Results and Discussion. 3,5-Bis(4-aminophenoxy)benzoic acid was prepared through reduction of 3,5-bis(4-nitrophenoxy)benzoic acid, which was obtained by condensation of 3,5-dihydroxybenzoic acid and 4-fluoronitrobenzene in the presence of sodium carbonate.[20] Direct thermal self-polycondensation of 3,5-bis(4-aminophenoxy)benzoic acid was carried out under the reduced pressure at 235 °C for 1 h as shown in eq 1 in Scheme 1,[21] to obtain a transparent glasslike product. A white polymer was precipitated by pouring the dimethylformamide solution of the crude product into methanol containing 0.1% lithium chloride.

The structure of the polymer was confirmed by IR, ^{1}H NMR, and ^{13}C NMR measurements. In the IR spectrum of the resulting polymer, 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 thermal polymerization. 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. Degree of branching was determined as 50% by the integration ratio of quarternary carbons in the quantitative ^{13}C NMR measurement.[22]

The polymer was soluble in organic solvents such as dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), *m*-cresol, and 2-methoxyethanol. The molecular weight (M_w) and the molecular weight distribution (M_w/M_n) of the resulting polymer were determined as 74600 and 2.6, respectively.[23] The glass transition temperature (T_g) was observed at 200 °C by the differential scanning calorimetry (DSC).

Thermal polymerization of the corresponding AB monomer, 3-(4-aminophenoxy)benzoic acid, was carried out at 235 °C under argon,[24,25] as shown in eq 2 in Scheme 1). The melt phase advanced to a nontransparent solid quickly. Amine and carboxylic acid groups which are the end groups of the resulting product were observed in IR and ^{1}H NMR spectra. This linear product was soluble in NMP, partially soluble in DMAc and DMSO, but insoluble in DMF, *m*-cresol, and 2-methoxyethanol. It is clear that the corresponding hyperbranched polymer described above has a better solubility, which should be attributed to a highly branched structure.

The polycondensation of the AA + BB was conducted at 260 °C in argon because isophthalic acid (AA) could not be well dissolved in the melt of *p,p′*-oxydiaminodiphenyl ether (BB) below this temperature[26] (eq 3 in Scheme 1). The melt phase advanced to a solid in a short period. The product was found to be black in color and insoluble in any organic solvents. Some side reactions may occur during the thermal reaction.

The results of the thermal polycondensation are summarized in Table 1. It is clear that the AB_2 type monomer gave rise to a much higher number average molecular weight (M_n) than the corresponding AB monomer. This indicates that the polymerization of the

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Scheme 1

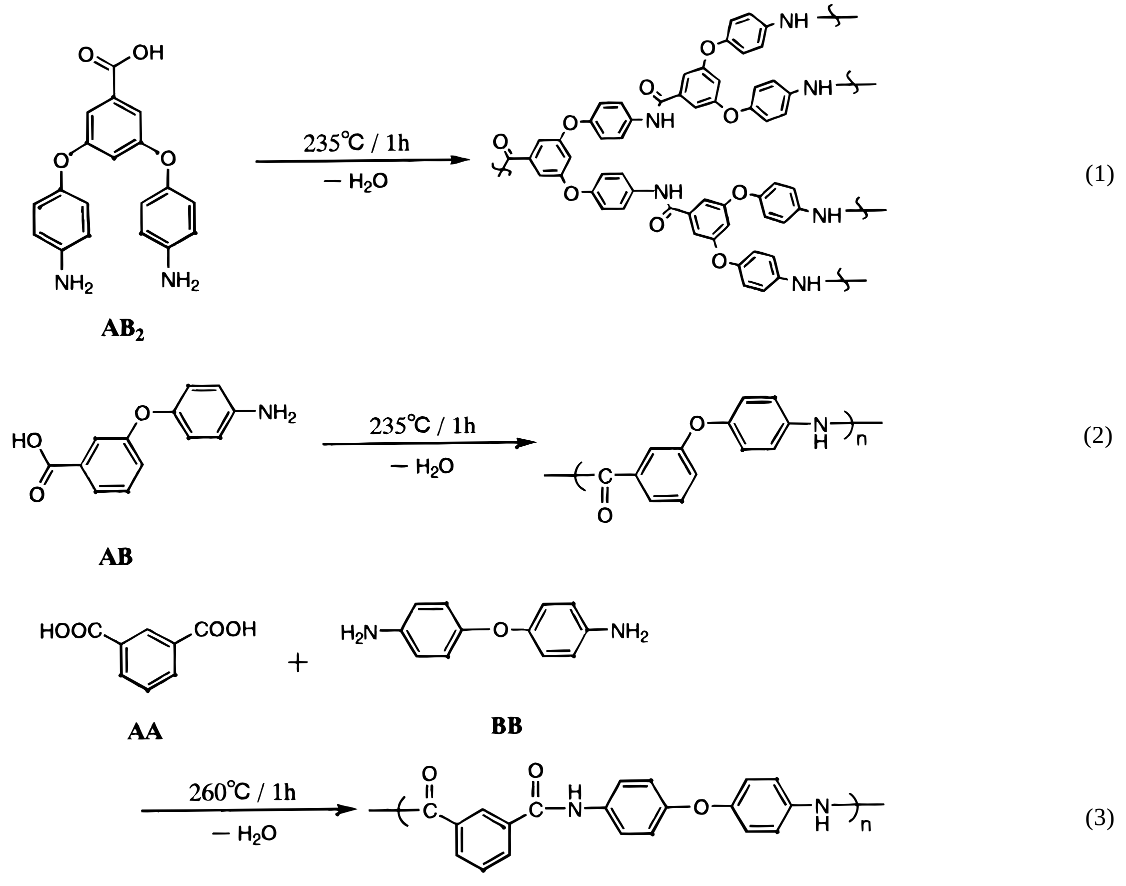

Table 1. Results of Thermal Polymerization

monomer	condition	yield, %	η_{inh},[f] dL/g	M_w	M_n	T_g,[h] °C
AB_2[a]	vacuum	75	0.25	74 600	29 000	200
AB[b]	argon	38	0.13		2 800[g]	
AA[c] + BB[d]	argon	68[e]	0.20			

[a] AB_2: 3,5-bis(4-aminophenoxy)benzoic acid. [b] AB: 3-(4-aminophenoxy)benzoic acid. [c] AA: isophthalic acid. [d] BB: *p,p*′-oxydiaminodiphenyl ether. [e] Crude yield. [f] Inherent viscosity measured in concentrated sulfuric acid at a concentration of 0.5 g/dL at 30. [g] Number average molecular weight for the sample from AB was determined by ^{1}H NMR. [h] Measured by DSC using a heating rate of 20 K min^{-1} under nitrogen atmosphere.

AB_2 monomer proceeded much more efficiently. The hyperbranched polymer showed a obviously low inherent viscosity compared to its molecular weight, which was caused by the highly branched structure.

Thermal polycondensation behaviors were investigated by microscopic study. In the micrograph of the melt phase from the AB monomer, crystal morphology was clearly observed in 5 min after the temperature was increased up to 235 °C. Because the functional end groups of the crystallized oligomers formed in the reaction should be no longer accessible to each other, it must be difficult to achieve the further growth to obtain the high molecular weight polymer under such reaction conditions. The differential thermal analysis (DTA) of the resulting crude polymer showed no melting point below 350 °C, implying that it is difficult to improve molecular weight by raising reaction temperature. In the comparative experiment, crystallization behavior was also observed in the morphology study of the melt phase from the AA + BB monomers.

On the other hand, no crystalline structure was observed in the micrograph in the case of the present AB_2 monomer at 235 °C. The water formed in the reaction bubbled out through the melt and continued on for about 30 min. The glass transition temperature for the crude product was determined as 172 °C by DSC,[27] noticeably lower than the reaction temperature (235 °C). These results suggest that the polycondensation of the AB_2 monomer proceed in a relatively lower viscous state, and evolved water can be easily removed under the reduced pressure. This is consistent with the characteristics of the hyperbranched polymer formed in the polymerization: no crystallization and lack of significant interchain entanglement.

Conclusion. The novel hyperbranched aromatic polymer was obtained by thermal self-polycondensation of 3,5-bis(4-aminophenoxy)benzoic acid as an aromatic AB_2 type monomer. The amorphous state and low viscosity due to high degree of branching of the hyperbranched polymer formed in the reaction gave rise to the different thermal polymerization behavior of the AB_2 type monomer from those of the AB and AA + BB monomers.

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(20) Yield: 63%. Mp: 228−235 °C. IR (KBr): 3470, 3380, 1682, 1622, 1213, 1003 cm^{-1}. ^{1}H NMR (DMSO-d_6, ppm): 6.93 (s, 2H), 6.80 (d, 4H), 6.64 (s, 1H), 6.61 (d, 4H). ^{13}C NMR (DMSO-d_6, ppm): 166.72, 160.72, 146.23, 144.85, 133.33, 121.58, 115.17, 109.18, 109.17. Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33. Found: C, 67.78; H, 4.70; N, 8.20.
(21) Into a glass reaction tube was charged 0.50 g of AB_2 monomer, 3,5-bis(4-aminophenoxy)benzoic acid. After the reaction tube was flushed with nitrogen and evacuated three times, the tube was heated at 235 °C under reduced pressure with the use of a rotary pump for 1 h. The crude product was dissolved in DMF, and then the solution was poured into methanol containing 0.1% lithium chloride. The precipitation was filtered, washed with methanol, and dried in vacuo at 90 °C to constant weight. Yield: 0.36 g (75%). Anal. Calcd for $C_{19}H_{14}N_2O_3$: C, 71.69; H, 4.43; N, 8.80. Found: C, 70.49; H, 4.44; N, 8.59.
(22) Since the spin−lattice relaxation time (T_1) for the quarternary carbons and carbonyl carbons of the polymer was measured in advance to be approximately 2.5 s, the sum of the acquisition and delay time for the measurement was set to 15 s.
(23) Gel permeation chromatography (GPC) was performed in DMF containing 0.01 mol L^{-1} of lithium bromide as an eluent. The absolute molecular weight was calculated by GPC with a light scattering detector. The specific refractive index increment of the resulting polymer was determined to be 0.216 mL g^{-1}.
(24) The AB monomer, 3-(4-aminophenoxy)benzoic acid, was prepared through reduction of 3-(4-nitrophenoxy)benzoic acid, which was obtained by condensation of 3-hydroxybenzoic acid and 4-fluoronitrobenzene in the presence of sodium carbonate. Yield: 54%. Mp: 194−198 °C. IR (KBr): 3401, 3322, 1690, 1609, 1233, 1001 cm^{-1}. ^{1}H NMR (DMSO-d_6, ppm): 7.58 (d, 1H), 7.42 (tr, 1H), 7.29 (s, 1H), 7.15 (d, 1H), 6.79 (d, 2H), 6.61 (d, 2H). ^{13}C NMR (DMSO-d_6, ppm): 166.77, 159.18, 145.84, 144.67, 132.17, 129.91, 122.47, 121.16, 120.94, 115.90, 114.81. Anal. Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.43; H, 4.97; N, 6.01.
(25) Polymerization of the AB monomer, 3-(4-aminophenoxy)benzoic acid, was carried out under argon gas at 235 °C for 1 h. The crude product was purified by precipitation from NMP solution into methanol, refluxed with methanol, and dried in vacuo at 80 °C overnight. Yield: 38%. IR (KBr): 3350, 1690, 1659, 1210, 1005 cm^{-1}. Anal. Calcd for $C_{13}H_9NO_2$: C, 73.92; H, 4.29; N, 6.63. Found: C, 72.93; H, 4.55; N, 6.47.
(26) Commercially available AA monomer (isophthalic acid) and BB monomer (*p*,*p*′-oxydiaminodiphenyl ether) were used after sublimation.
(27) T_g for the crude product was lower than that for the purified product (200 °C). This is because that the crude contained low molecular weight components which were removed by reprecipitation.

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