# Synthesis and Properties of Hyperbranched Aromatic Polyamide

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ABSTRACT: Previous experiments from our group [*Macromolecules* **1998**, *31*, 5964] have established that thermal polymerization of 3,5-bis(4-aminophenoxy)benzoic acid (monomer **1**) gave a hyperbranched aromatic polyamide (polymer **1**). Here we show that thermal polymerization of methyl 3,5-bis(4-aminophenoxy)benzoate (monomer **2**), having the same reaction behavior as that of monomer **1**, gives a hyperbranched aromatic polyamide (polymer **2**). In addition, the direct polycondensation of monomer **1** was conducted in the presence of triphenyl phosphite and pyridine as condensing agents in NMP to give a hyperbranched aromatic polyamide (polymer **3**). The structures of the resulting polymers were confirmed to be identical by IR, $^1$H NMR, and $^{13}$C NMR. All three polymers were soluble in DMF, DMAc, NMP, DMSO, and 2-methoxyethanol. The inherent viscosity of the polymers in DMF ranged from 0.17 to 0.19 dL/g. Absolute molecular weights ($M_w$) determined by laser light scattering for polymers 1, 2, and 3 were 74 600, 47 800 and 36 800, respectively, and the corresponding polydispersities were 2.6, 3.2, and 1.8. The glass transition temperatures ($T_g$) of polymers **1**, **2**, and **3** were 200, 180, and 200 °C, respectively. End-capping reactions of the terminal amino groups in polymer **3** was easily accomplished with several kinds of acid chlorides. Thermal properties and solubility of the polymers changed after end-capping reactions.

## Introduction

Dendritic macromolecules have received considerable attention due to their unique chemical and physical properties. These macromolecules are classified into dendrimers and hyperbranched polymers, where the former have a more defined structure. It was reported that hyperbranched polymers show similar properties to those of dendrimers, such as low viscosity, high solubility in organic solvents, and lack of significant entanglement in the solid state.[1−12] The synthesis of dendrimers often requires several protection and deprotection steps as well as purification at each synthetic step. In contrast, hyperbranched polymers are readily synthesized by one-step polymerization of $AB_n$ ($n \geq 2$) monomers. This is advantageous over the multistep synthesis of dendrimers because of the rapid production of large quantities.[12,13]

Aromatic polyamides (aramids), such as poly(*p*-phenyleneterephthalamide), are well-known as high-performance polymers due to their excellent thermal, mechanical, and chemical properties. Aramid fibers, prepared by liquid crystal spinning, and films have a large number of applications in modern industries.[14−25] Aromatic polyamides can be readily synthesized by low-temperature polycondensation of diacid chlorides and diamines[16,26] and, alternatively, by direct polycondensation of diacids and diamines in the presence of condensing agents such as triphenyl phosphite and pyridine.[27] These polymers, however, are only soluble in highly polar solvents such as concentrated sulfuric acid. A dendritic structure generally gives rise to better solubility than the corresponding linear one. For example, aromatic polyamide dendrimers and hyperbranched aromatic polyamides are soluble in amide type solvents, even in tetrahydrofuran.[28−32]

In the previous communication, we reported that the direct thermal polycondensation of $AB_2$ type monomer (3,5-bis(4-aminophenoxy)benzoic acid) successfully gave a hyperbranched aromatic polyamide,[33] although thermal polymerization of aromatic diacids and aromatic diamines generally does not give high-molecular-weight linear aromatic polyamides because of low reactivity of aromatic amines.[34,35] In this paper, hyperbranched aromatic polyamides are prepared not only by thermal polymerization but also by direct polycondensation using the condensing agents. Furthermore, the modification of amino groups in the resulting polymers by reaction with several acid chlorides as end-capping agents is also described.

## Experimental Section

**Measurements**. Infrared (IR) spectra were recorded using a JASCO FTIR-8100 Fourier transform infrared spectrophotometer. $^1$H and $^{13}$C NMR spectra were recorded using a JEOL JNM-AL 300. Thermogravimetric analysis (TGA) was carried out with a Shimazhu TGA-40 using a heating rate of 10 K min$^{-1}$ in nitrogen. DSC was carried out on a Shimadzu DSC-41 and a Seiko DSC 6200 using a heating rate of 20 K min$^{-1}$ in nitrogen. Inherent viscosity was measured in DMF (0.5 g/dL) at 30 °C. Gel permeation chromatography (GPC) was performed on a JASCO HPLC 880PU fitted with polystyrene−divinylbenzene columns (two Shodex KD806M and KD802) and a Shodex RI-71 refractive index detector in DMF containing 0.01 mol L$^{-1}$ of lithium bromide as an eluent. The molecular weights were determined by laser light scattering measurement using a miniDAWN apparatus (Wyatt Technology Co.) and a Shimadzu RID-6A refractive index detector. A specific refractive index increment (d*n*/d*c*) of the polymer in DMF at 690 nm was determined to be 0.216 mL g$^{-1}$ by using an Optilab 903 apparatus (Wyatt Technology Co.). Wide-angle X-ray diffraction curves were recorded with a Rigaku RU-200 diffractometer using Ni-filtered Cu Kα radiation (50 V, 180 mA, $\lambda = 0.154$ nm). A polarized microscope (Olympus BH-2) equipped with an Olympas PM-20 exposure control unit was used to observe morphology at 235 °C for the melts from monomers **1** and **2** and to measure the melting points of the monomers using a heating rate of 1 K min$^{-1}$ under nitrogen.

**Materials**. Commercially available 3,5-dihydroxybenzoic acid was used after recrystallization from water and dried at 110 °C for 12 h. 3,5-Bis(4-aminophenoxy)benzoic acid (monomer **1**) was prepared from 4-fluoronitrobenzene and 3,5-

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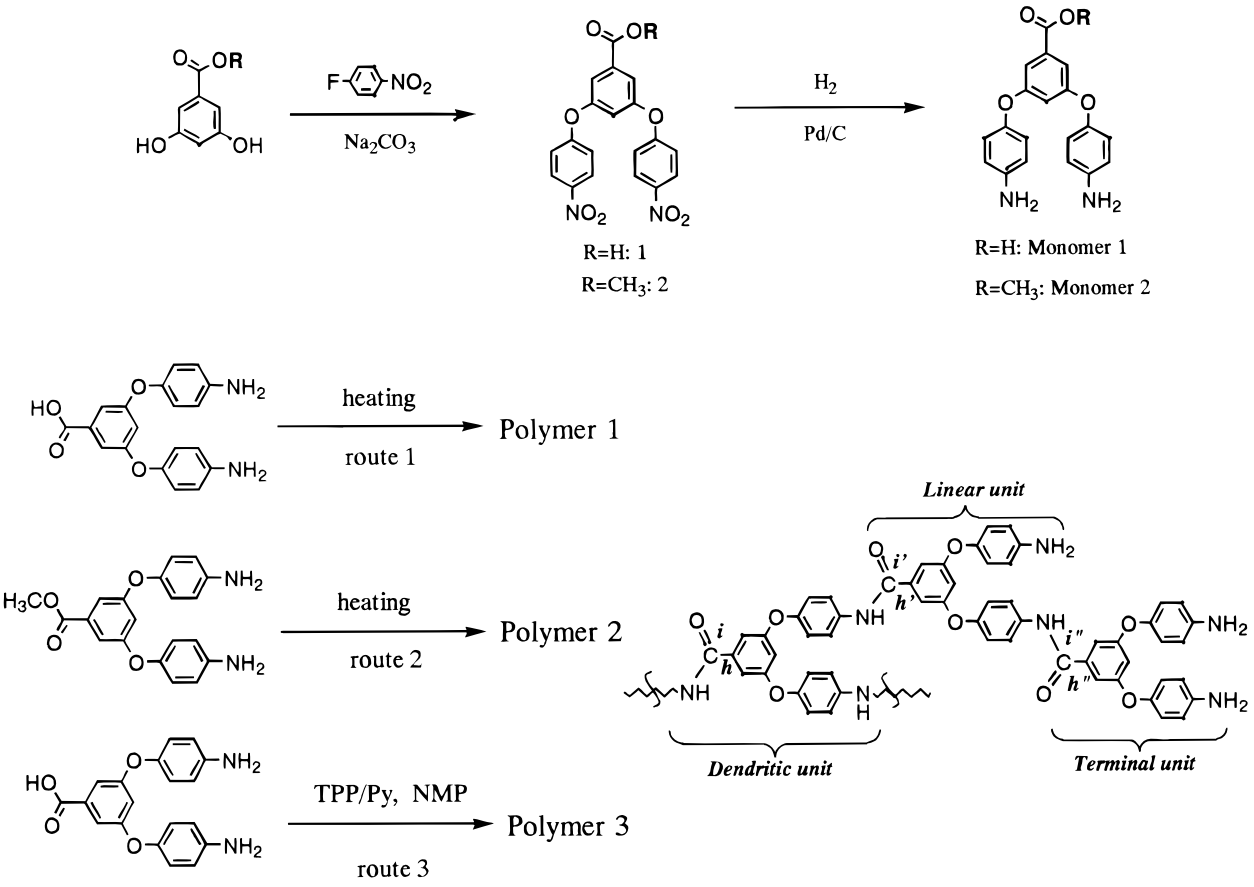
**Scheme 1**




dihydroxybenzoic acid, as described in the literature.[33] *N*,*N*-Dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) were used after distillation under reduced pressure from calcium hydride. Pyridine was dried with calcium hydride, followed by fractional distillation before use. Lithium chloride was dried at 230 °C overnight before use. Other solvents and reagents were used without further purification.

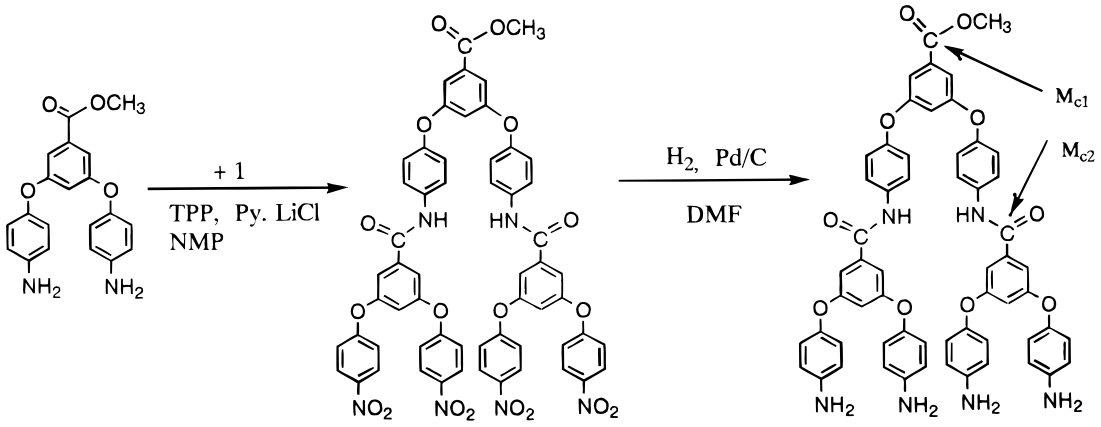
**Synthesis of Methyl 3,5-Bis(4-aminophenoxy)benzoate (Monomer 2).** Monomer **2** was synthesized by reduction of methyl 3,5-bis(4-nitrophenoxy)benzoate, which was obtained by reaction of 3,5-dihydroxybenzoic acid methyl ester and 4-fluoronitrobenzene in the presence of sodium carbonate. The synthesis procedure for monomer **2** is similar to that for monomer **1**, as shown in Scheme 1. Yield: 55%. Melting point: 165−167 °C. IR (KBr): 3440, 3339, 1719, 1609, 1211, 1009 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$, ppm): 6.93 (s, 2H), 6.79 (d, 4H), 6.70 (s, 1H), 6.61 (d, 4H), 5.06 (b, $NH_2$), 3.75 (s, $CH_3$). Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.62; H, 5.27; N, 8.02.

**Synthesis of Model Compound (I).** In a flask, 0.3 g (0.7 mmol) of monomer **2** and 0.56 g (1.4 mmol) of 3,5-bis(4-nitrophenoxy)benzoic acid (**1**) were dissolved in 5 mL of NMP. Condensing agents, 0.43 mL of pyridine, 0.45 mL of triphenyl phosphite, and 0.087 g of lithium chloride, were added into the flask. The reaction mixture was heated to 100 °C and stirred under nitrogen for 3 h. After the temperature was lowered to room temperature, the crude product was precipitated by pouring the reaction mixture into water containing 5% sodium chloride and then collected by filtration. The product was purified by reprecipitation from acetone solution into water containing 5% sodium chloride, refluxed with methanol containing 1% lithium chloride, washed with methanol, and dried in vacuo at 80 °C overnight. Yield: 0.68 g (87%). The product (0.3 g, 0.27 mmol) was reduced under hydrogen in the presence of palladium−charcoal catalyst (10%, 0.045 g) in dimethylformamide (DMF) at room temperature for 48 h. After palladium−charcoal catalyst was removed by filtration through Celite, the product was precipitated from the filtrate into 100 mL of water containing 5% sodium chloride, washed with water, collected by filtration, and dried in vacuo at 115 °C overnight. Yield: 0.20 g (74%). IR (KBr): 3366, 1719, 1660, 1590, 1210, 1005 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$, ppm): 10.29 (d, CONH), 7.77 (d, 4H), 7.14 (d, 4H), 7.09 (d, 6H), 6.96 (tr, 1H), 6.81 (d, 8H), 6.58 (d, 8H), 6.49 (tr, 2H), 5.05 (br, $NH_2$), 3.77 (s, $CH_3$). $^{13}C$ NMR (DMSO-$d_6$, ppm): 164.65, 164.06, 159.45, 158.56, 151.02, 145.30, 144.95, 137.11, 135.05, 132.22, 122.03, 120.03, 119.12, 114.65, 11.81, 11.74, 109.30, 107.71.

**Thermal Polymerization of Monomer 2.** A glass reaction tube with 0.50 g of monomer **2** 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. After the temperature was lowered down to room temperature, a transparent glasslike product was obtained. A white powdery polymer (polymer **2**) was precipitated from DMF solution of the product into methanol containing 0.1% lithium chloride, collected by filtration, washed with methanol, and dried in a vacuum at 90 °C to constant weight. Yield: 0.35 g (77%). $^{13}C$ NMR (DMF-$d_7$, ppm): 165.33, 165.06, 164.81, 161.12, 160.91, 159.58, 159.35, 153.11, 147.19, 147.07, 146.28, 146.16, 138.89, 138.71, 138.51, 136.08, 122.88, 121.08, 119.67, 115.88, 113.33, 112.62, 111.62, 110.51, 109.40. Weight-average molecular weight ($M_w$): 47 800. Anal. Calcd for $C_{19}H_{14}N_2O_3$: C, 71.69; H, 4.43; N, 8.80. Found: C, 71.33; H, 4.58; N, 8.43.

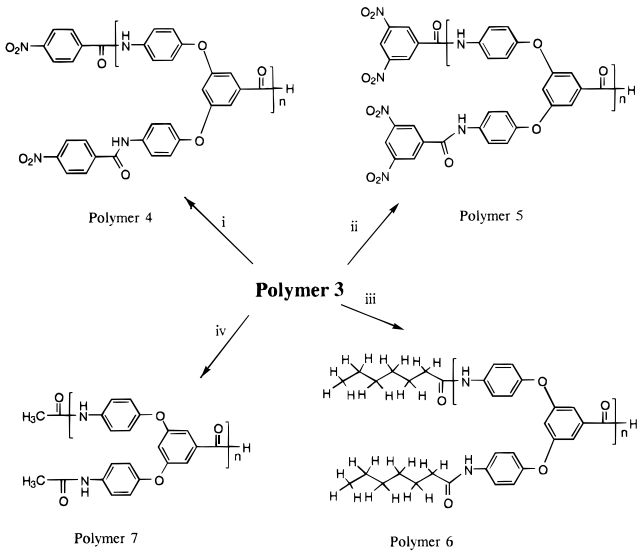
**Direct Polycondensation of Monomer 1.** In a flask, 0.84 g (2.5 mmol) of monomer **1** was dissolved in 5 mL of NMP, then 1.25 mL of pyridine and 1.3 mL (5.0 mmol) of triphenyl phosphite were charged into the flask. The solution was heated to 100 °C and stirred under nitrogen for 3 h. After the temperature was decreased to room temperature, the solution was poured into 300 mL of methanol to precipitate the polymer. The polymer was collected by filtration and purified by reprecipitation from DMF solution into methanol containing 0.1% lithium chloride. The product was finally filtered and washed with cold methanol and dried in a vacuum at 90 °C to

**Scheme 2**




3 Model Compound (I)

**Scheme 3**




i) 4 -nitrobenzoyl chloride (5 equiv.), DMAc, 8h;
ii) 3,5 - dinitrobenzoyl chloride (5 equiv.), DMAc, 8h;
iii) enanthyl chloride (5 equiv.), DMAc, 8h;
iv) acetyl chloride (5 equiv.), DMAc, 8h.

constant weight. Yield: 0.74 g (92.4%). $^{13}$C NMR (DMF-$d_7$, ppm): 165.33, 165.07, 164.83, 161.10, 160.89, 159.56, 159.33, 153.09, 147.17, 147.05, 146.28, 146.16, 138.89, 138.70, 138.50, 136.10, 129.60, 122.91, 121.06, 119.64, 115.88, 113.33, 112.65, 111.65, 110.53, 109.36. Weight-average molecular weight ($M_w$) and polydispersity index ($M_w/M_n$) were determined as 36 800 and 1.8, respectively. Anal. Calcd for $C_{19}H_{14}N_2O_3$: C, 71.69; H, 4.43; N, 8.80. Found: C, 67.96; H, 4.45; N, 8.16.

**End-Capping Reaction.** A typical experiment is shown in Scheme 3 and as follows. In a 50 mL three-neck flask, 0.60 g of polymer **3** was dissolved in 20 mL of DMAc. The flask was frozen using a dry ice acetone bath, and then 1.83 g (9.33 mmol) of 4-nitrobenzoyl chloride was added to the reaction mixture. The reaction was conducted at 0 °C for 2 h and then stirred at room temperature for 6 h. After the reaction mixture was poured into methanol, the precipitate was collected by filtration. The crude product was purified by reflux with methanol containing 0.1% lithium chloride, filtered, washed with cold methanol, and dried in a vacuum at about 130 °C overnight to give polymer **4**. Yield: 0.81 g (93.5%); $T_g$ = 220 °C. Conversion of amino groups was determined as 97% by $^1$H NMR. $^1$H NMR (DMSO-$d_6$, ppm): 10.60 (s, CONH), 10.30 (s, CONH), 8.33 (s, 2H), 8.16 (s, 2H), 7.79 (s, 4H), 7.33 (s, 2H), 7.12 (s, 4H), 6.76 (s, 1H).

Polymer **5** was prepared from polymer **3** (0.60 g) and 3,5-dinitrobenzoyl chloride (2.20 g, 9.33 mmol) by the same procedure as for the preparation of polymer **4**. Yield: 0.92 g (95%); $T_g$ = 238 °C. Conversion of amino groups was determined as 98% by $^1$H NMR. $^1$H NMR (DMSO-$d_6$, ppm): 10.84 (s, CONH), 10.30 (s, CONH), 9.12 (s, 2H), 8.94 (s, 1H), 7.77 (s, 4H), 7.55 (s, 2H), 7.10 (s, 4H), 6.80 (s, 1H).

Polymer **6** was prepared from polymer **3** (0.60 g) and heptanoyl chloride (1.40 g, 9.33 mmol) by the same procedure as for the preparation of polymer **4**. Yield: 0.78 g (92%); $T_g$ = 164 °C. Conversion of amino groups was determined as 95% by $^1$H NMR. $^1$H NMR (DMSO-$d_6$, ppm): 10.30 (s, CONH), 9.90 (s, CONH), 7.75 (s, 2H), 7.62 (s, 2H), 7.30 (s, 2H), 7.06 (s, 4H), 6.70 (s, 1H), 2.51 (s, $CH_2$), 1.56 (s, $CH_2$), 1.25 (s, 6H, $CH_2$), 0.83 (s, $CH_3$).

Polymer 7 was prepared from polymer **3** (0.60 g) and acetyl chloride (0.66 mL, 9.33 mmol) by the same procedure as for the preparation of polymer **4**. Yield: 0.63 g (93%); $T_g$ = 203 °C. Conversion of amino groups was determined as 98% by $^1$H NMR. $^1$H NMR (DMSO-$d_6$,ppm): 10.30 (s, CONH), 9.96 (s, CONH), 7.74 (s, 2H), 7.620(s, 2H), 7.30 (s, 2H), 7.06 (s, 4H), 6.70 (s, 1H), 2.01 (s, $CH_3$).

## Results and Discussion

Two kinds of $AB_2$ type monomers, monomers **1** and **2**, were prepared as shown in Scheme 1. Monomer **1** has one carboxyl and two amino groups, while monomer **2** has one methyl ester and two amino groups. Using monomers **1** and **2**, hyperbranched polymers **1**, **2**, and **3** were synthesized by both thermal polymerization and direct polycondensation in the presence of the condensing agents.

**Thermal Polymerization.** We have reported that hyperbranched polyamide polymer **1** was synthesized by thermal polymerization starting from monomer **1**.[33] Thermal polymerization of monomer **2** to form polymer **2** was carried out under the same conditions as that of monomer **1**, shown as route 2 in Scheme 1. The structure of polymer **2** was confirmed by IR, $^1$H NMR, and $^{13}$C NMR measurements. In the IR spectrum of polymer **2**, a new carbonyl absorption band appeared at 1655 cm$^{-1}$ while an absorption band attributed to methyl ester at 1719 cm$^{-1}$ in monomer **2** disappeared. The absorptions at 3400 and 3339 cm$^{-1}$ assigned to amino groups of monomer **2** were replaced by a broad absorption band at 3300 cm$^{-1}$ in polymer **2**. In the $^1$H NMR spectrum of polymer **2**, the peak for the hydrogen of the amide bond was observed at 10.30 ppm, and a broad peak at 5.67 ppm attributed to free amino groups

**Table 1. Data of Thermal Polymerizations**

| monomer | time, min | yield, % | $M_w$[a] | $M_w/M_n$ | $\eta_{inh}$,[b] dL/g |
|---|---|---|---|---|---|
| **1** | 35 | 61 | 27 500 | 1.8 | 0.15 |
| | 45 | 64 | 40 300 | 1.9 | 0.16 |
| | 60 | 75 | 74 600 | 2.6 | 0.19 |
| **2** | 35 | 53 | 20 500 | 2.2 | 0.13 |
| | 45 | 69 | 37 900 | 1.8 | 0.16 |
| | 60 | 77 | 47 800 | 3.2 | 0.17 |

[a] Absolute molecular weight. [b] Measured in DMF at a concentration of 0.5 g/dL at 30 °C.

was also observed. These data indicate that an amide bond was formed via aminolysis of the methyl carboxylate with amino groups in the monomer **2**. Furthermore, the peak at 3.75 ppm arising from the methyl group in monomer **2** disappeared after thermal polymerization.

The hyperbranched polymer **2** is composed of linear, dendritic, and terminal units, as shown in Scheme 1. Fréchet has described the degree of branching (DB) for hyperbranched polymers as the ratio of the sum of dendritic and terminal units versus the total units (linear, dendritic, and terminal units).[36] It is difficult to determine the DB by using $^1$H NMR spectrum for polymer **2** because the peaks attributed to each unit were overlapped. On the other hand, the DB was quantitatively measured by $^{13}$C NMR in DMF. Since the spin−lattice relaxation time ($T_1$) for the carbonyl carbons and quaternary carbons was measured to be approximately 2.5 s, the sum of the acquisition and delay time for the measurement was set to 15 s. Three kinds of peaks from the carbonyl carbons were observed at 164.58, 164.30, and 164.04 ppm. By comparison with the peaks ($M_{c1}$, 164.77 ppm; $M_{c2}$, 164.09 ppm) of the model compound (**I**) (Scheme 2), the central peak (164.30 ppm) was assigned to the carbonyl carbon of the linear unit (i′), and the peaks at 164.58 and 164.04 ppm were attributed to the carbonyl carbons of the dendritic (i) and terminal (i″) units. Alternatively, the peak (137.89 ppm) arising from the carbon h′ was distinguished from the peaks (138.06, 137.69 ppm) of the carbons h and h″ having the same intensity of resonance. Thus, the average DB was calculated to be 46% by the integration ratios of the peaks (45% from the peaks of the carbons i, i′, and i″ and 47% from the peaks of carbons h, h′, and h″). The DB of polymer **2** is similar to that of polymer **1** (50%) reported in our previous communication.[33]

The results of thermal polymerizations are summarized in Table 1. The data indicate that the thermal polymerization of monomer **2** led to similar results to those of monomer **1**. No acceleration effect was observed in the case of the thermal polymerization of monomer **2**, even though methyl ester group is expected to show higher reactivity in aminolysis by heating than that of carboxyl group.

The inherent viscosity for the resulting polymers **1** and **2** did not change drastically with increasing molecular weight. The relationship between intrinsic viscosity ([$\eta$]) and molecular weight can be described by the Mark−Houwink equation ($[\eta] = KM^{\alpha}$). The shape factor, $\alpha$, was calculated to be 0.35 from the slope of the dotted straight line drawn by a least-squares fit, shown in Figure 1. The value, noticeably lower than 0.5, is consistent with a highly branched structure. However, the curve of [$\eta$] versus log $M_w$ deviates from a fully linear behavior. This might be caused by a more compact structure with increasing molecular weight.

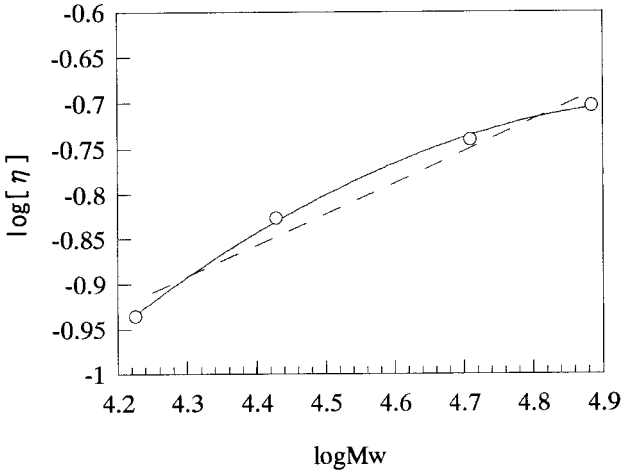



**Figure 1.** Relationship between log[$\eta$] and log $M_w$ for polymer **1**. The dotted line is drawn by a least-squares fit. The continuous line is the curve of log[$\eta$] versus log $M_w$.

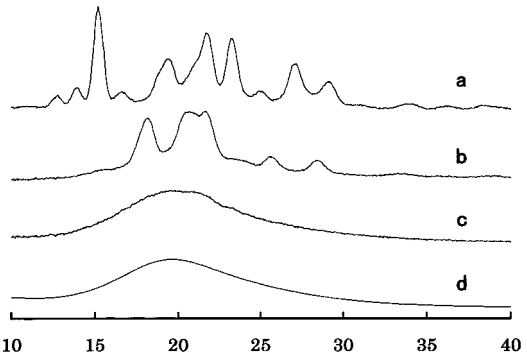



**Figure 2.** Wide-angle X-ray powder diffraction curves of (a) AB monomer, (b) the crude from AB monomer, (c) the crude from $AB_2$ monomer **1**, and (d) the crude from $AB_2$ monomer **2**.

Despite the low basicity of the aromatic amine, the thermal polymerization of monomer **1** proceeded efficiently due to the amorphous state and low viscosity of the melt.[33] Similar to the thermal polymerization of monomer **1**, no crystallization was observed in the case of the thermal polymerization of monomer **2**. Methanol formed during the reaction bubbled out through the melt for about 30 min. This indicates that thermal polymerization of monomer **2** had the same reaction behavior as that of monomer **1**. The crude products from monomers **1** and **2** and AB monomer (3-(4-aminophenoxy)benzoic acid) were investigated by wide-angle X-ray diffraction, as shown in Figure 2. The amorphous characteristic of the products from $AB_2$ type monomers **1** and **2** can be clearly observed, whereas the product from the AB monomer shows a high degree of crystallinity. It is clear that the hyperbranched structure prevented the crystallization and gave a low melt viscosity during the polymerizations, leading to high molecular weight polymers.

**Direct Polycondensation.** The direct polycondensation of monomer **1** in NMP was conducted at 100 °C under nitrogen in the presence of triphenyl phosphite (TPP) and pyridine as condensing agents, giving a white powdery polymer (polymer **3**), shown as route 3 in Scheme 1.

The structure of polymer 3 was determined to be identical with that of polymers **1** and **2** by IR, $^1$H, and $^{13}$C NMR. The DB of polymer **3** was determined by the same manner as that of polymer **2** and calculated to be

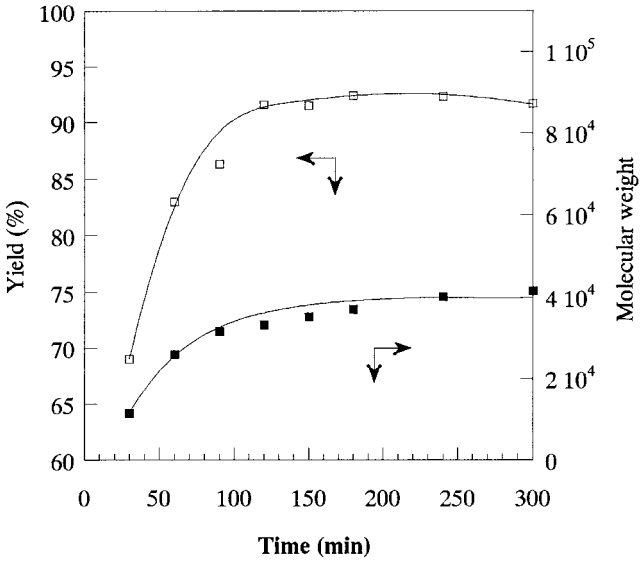



**Figure 3.** Time dependence of weight-average molecular weight ($M_w$) and yield of polymer **3**.

48% by the integration ratios of the peaks in $^{13}C$ NMR spectrum (47% from the peaks of the carbons i, i′, and i″ and 48% from the peaks of carbons h, h′, and h″).

When the molar feed ratio of TPP to carboxyl group of monomer **1** was one, the polymerization did not proceed sufficiently. After the polycondensation was proceeded for 3 h, pouring the reaction mixture into methanol gave an emulsion. On the other hand, a high molecular weight polymer was obtained when the feed molar ratio of TPP/COOH was two. The dependence of the yield and the molar mass on the reaction time is shown in Figure 3. It was found that both yield and weight-average molecular weight ($M_w$) of polymer **3** increased continuously for 150 min. However, not much change was observed after that. The inherent viscosity of the polymer increased slowly from 0.16 dL/g at 30 min up to 0.18 dL/g at 150 min and did not change after 180 min (0.19 dL/g). The inherent viscosity is obviously low compared to the molecular weight. This is consistent with a highly branched structure. The polydispersity index ($M_w/M_n$) increased from 1.3 at 30 min up to 1.8 at 180 min. No great change in $M_w/M_n$ was observed in the present study. The theoretical aspects of hyperbranched polymers were first studied by Flory[37] and later by Burchard.[38−40] The uncontrolled growth lead to broad molar mass distributions for hyperbranched polymers. In the present study, the relatively low $M_w/M_n$ may be cause by the fact that the low molecular weight components were difficult to precipitate during purification.

Thermogravimetric analysis (TGA) was used to measure the thermal stability of the samples, as shown in Figure 4. A weight loss for polymer **3** was observed at 310 °C, while the decomposition temperature ($T_0$) of both polymers **1** and **2** was determined as 400 °C. In contrast, 10% weight loss temperature ($T_{10}$) of polymer **3** was observed at 530 °C, which is higher than those of polymers **1** and **2** (480 and 475 °C). After thermal treatment of polymer **3** up to 350 °C in nitrogen, it became insoluble in any organic solvents. The difference in TGA traces may be caused by the residual TPP in polymer **3** that could not be removed from the hyperbranched structure. In fact, the small peak at 129.60 ppm arising from TPP was observed in the $^{13}C$ NMR spectrum of polymer **3**, even though purification had been repeated five times by reprecipitation of polymer **3** from DMF solution into methanol.

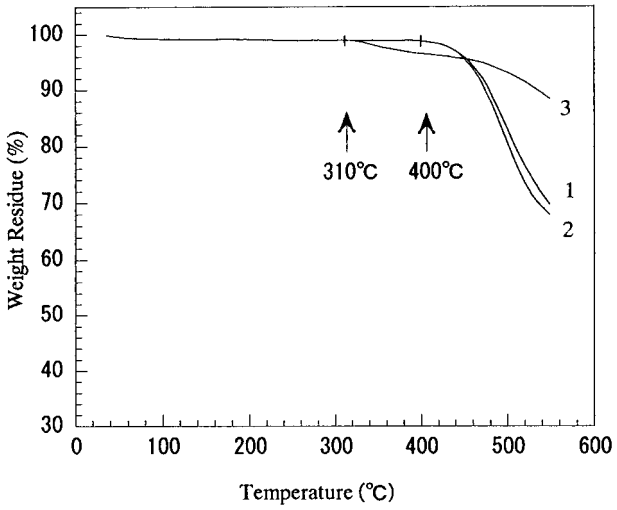



**Figure 4.** TGA (10 °C/min) traces of polymers **1**, **2**, and **3** under nitrogen.

**Modification of Properties.** Hyperbranched polymers from $AB_2$ type monomers have a large number of end groups (B). The nature of the end groups influences the physical and chemical properties of the hyperbranched polymers.[41−46] In this study, the end groups in the resulting polymers are amines, and they were used as reactive sites for modification. The end-capping reactions of polymer **3** were carried out with different kinds of acid chlorides, as shown in Scheme 3. The overall compositional repeat units are shown in Scheme 3, even though each of the polymers contains a combination of linear, dendritic, and terminal units.

The hyperbranched polymer **4** was synthesized by the reaction of polymer **3** with 4-nitrobenzoyl chloride. When 3 equiv of 4-nitrobenzoyl chloride was used, only about 70% of the amino terminal groups were substituted. On the other hand, complete substitution required 5 equiv of 4-nitrobenzoyl chloride. In $^1H$ NMR of polymer **4**, the peak at 10.60 ppm corresponding to the hydrogen of the amide bond formed by end-capping reaction was observed, while the broad peak at 5.67 ppm of the amino protons in polymer **3** disappeared. It was found that integration intensity of the peak at 10.30 ppm, due to the $AB_2$ units as formed in the synthesis of polymer **3**, was equal to that of the peak of the new amide proton formed in the end-capping reaction. The conversion of end-capping reaction was also calculated to be 97% by the integration ratio of the protons attributed to the end-group aromatics (8.33, 8.16 ppm) versus those from the $AB_2$ units (7.79, 7.33, 7.12, 6.76 ppm).

The 3,5-dinitrobenzoyl-substituted polymer **5**, heptanoyl-substituted polymer **6**, and acetyl-substituted polymer **7** were synthesized in the same manner as for polymer **4** and resulted in 95−100% conversions of the amino end groups.

Solubility and thermal properties of polymers **1**−**7** are summarized in Table 2. Polymers **4**−**7**, obtained by the end-capping reactions, were insoluble in 2-methoxyethanol, whereas they were partially soluble in THF. The glass transition temperature ($T_g$) was increased from 200 °C to 220 and 238 °C after the end-capping reactions of polymer **3** with 4-nitrobenzoyl chloride and 3,5-dinitrobenzoyl chloride, respectively. On the other

**Table 2. Properties of Resulting Polymers**

| polymer | $T_g$[e] (°C) | $T_0$[f] (°C) | $T_{10}$ (°C) | solubility[g] DMF, DMAc, NMP, DMSO | 2-methoxy-ethanol | THF |
|---|---|---|---|---|---|---|
| **1** | 200 | 400 | 480 | + | + | − |
| **2** | 180 | 400 | 475 | + | + | − |
| **3** | 200 | 310 | 530 | + | + | − |
| **4**[a] | 220 | 310 | 424 | + | − | ± |
| **5**[b] | 238 | 309 | 406 | + | − | ± |
| **6**[c] | 164 | 308 | 427 | + | − | ± |
| **7**[d] | 203 | 304 | 444 | + | − | ± |

[a−d] End-capped polymers from polymer **1** with the use of 4-nitrobenzoyl chloride, 3,5-dinitrobenzoyl chloride, heptanoyl chloride, and acetyl chloride as end-capping agents, respectively. [e] Measured by DSC using a heating rate of 20 K $min^{-1}$ under nitrogen atmosphere. [f] Performed by TGA with a heating rate of 10 K $min^{-1}$ under nitrogen atmosphere. [g] +, Soluble; −, insoluble; ±, partially soluble.

hand, $T_g$ was decreased to 164 °C when the polymer **3** was end-capped by a longer alkyl group (heptanoyl), even though the acetylation did not give rise to a noticeable change in $T_g$. Thus, the changes in properties between the polymers **3**−**7** were due to the nature of the different end groups.

## Conclusions

Using three different synthetic routes, a hyperbranched aromatic polyamide was successfully prepared. The thermal polycondensation of the $AB_2$ monomer **2** (route 2) showed the same polymerization behavior as that of the $AB_2$ monomer **1** (route 1). Although the direct polycondensation of the $AB_2$ monomer **1** (route 3) gave polymer **3**, TPP could not be completely removed from the hyperbranched structure. The degree of branching was determined to be approximately 50% in all cases. Modification of polymer **3** was successfully achieved by end-capping reactions with several acid chlorides. Solubility in organic solvents and glass transition temperatures were highly dependent on the nature of the end groups.

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