Synthesis of Hyperbranched Aromatic Polyamides Starting from Dendrons as AB$_x$ Monomers: Effect of Monomer Multiplicity on the Degree of Branching

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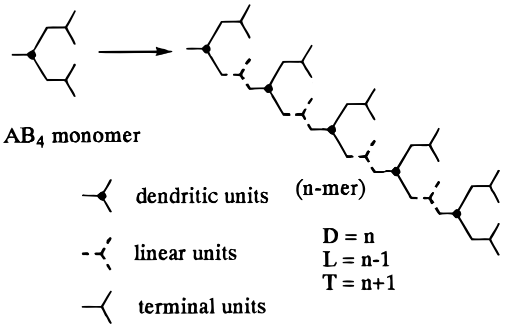
ABSTRACT: Three hyperbranched aromatic polyamides were synthesized by the direct polycondensation of 3,5-diaminobenzoic acid **2** (AB$_2$ monomer), G1 dendron **4** (AB$_4$ monomer), and G2 dendron **6** (AB$_8$ monomer). The weight-average molecular weights (M_w) of the resulting polymers were 100 000−200 000 with a polydispersity (PDI) of ca. 3. The degrees of branching (DB) of the polymers from **2**, **4**, and **6** were 0.32, 0.72, and 0.84, respectively, as determined by ^{1}H NMR spectroscopy. Thermal polymerization of **2** and **4** was also carried out to form hyperbranched polyamides without solvents and catalysts. The resulting polymers by the thermal polymerization had M_w's of around 20 000 with a PDI of around 2. DB of the hyperbranched polymers could be controlled within a range of 0.32−0.72 by the copolymerization of **2** and **4** in different molar ratios. DB had little influence on the T_g and solubility of the polymers.

Introduction

Dendritic macromolecules such as dendrimers and hyperbranched polymers have received considerable attention in recent years.[1−5] These polymers have unusual properties because of their unique molecular architecture. In addition, these molecules contain many terminal functional groups which can be modified with different functional groups in order to control the properties of the resulting polymers. Dendrimers, having perfect branching, have controllable size and structure. However, the synthesis of dendrimers is quite tedious because it requires multistep reactions with many protection and deprotection steps as well as purification at each generation. On the other hand, hyperbranched polymers can be synthesized by a one-step polymerization of AB$_n$-type monomers. It has been reported that hyperbranched polymers have properties similar to those of dendrimers, such as high solubility and low viscosity.[6,7] Therefore, in terms of industrial purposes, hyperbranched polymers are promising alternatives to dendrimers because of their capability to be produced on a large scale by a one-step process. Recently, the synthesis of various hyperbranched polymers, such as aromatic and aliphatic polyesters,[8−11] polyphenylenes,[12,13] polyethers,[14] poly(ether ketones),[15,16] polyamides,[17−20] polysiloxanes,[21] and poly(phenylene sulfides),[22] has been reported.

Hyperbranched polymers prepared from AB$_n$ monomers have highly, but not perfectly, branched structures. They are composed of terminal (T), linear (L), and dendritic (D) units, which are distinguished by the number of unreacted functional groups in the unit. The degree of branching (DB) is widely used as a parameter to indicate the architecture of hyperbranched polymers.[23] Frey reported that the one-pot polymerization of AB$_2$-type monomers statistically gives a DB of 0.5 when the reactivities of functional groups in each unit are identical.[24] Most hyperbranched polymers from AB$_2$ monomers actually have a DB close to 0.5. Enhancement and control of DB is one of the most interesting and important aspects of the synthesis of hyperbranched polymers. One proposed method for the enhancement of DB is to use AB$_x$-type dendrons, which contain prefabricated dendritic units, as macromonomers.[25] For example, the polymerization of the AB$_4$ dendron gives a higher DB compared with that of the corresponding AB$_2$ monomer because the AB$_4$ dendron composed of three AB$_2$ units contains one dendritic and two terminal units. If the propagation reaction of the AB$_4$ monomer gives all linear units at a certain degree of polymerization (n), the total numbers of D, L, and T are equal to n, $n - 1$, and $n + 1$, respectively, as shown in Figure 1. This implies that the minimum value of DB is 0.67 and a hyperbranched polymer having a DB higher than 0.67 can be prepared when an AB$_4$ monomer is used as a starting monomer. Hawker and Chu have synthesized hyperbranched poly(ether ketone) with a DB of 0.71 from an AB$_4$ monomer.[26]



$$DB = \frac{D + T}{D + L + T} = \frac{n + (n+1)}{n + (n-1) + (n+1)} = \frac{2n+1}{3n} \longrightarrow \frac{2}{3} \quad \text{from AB}_4\text{ monomer} \quad \text{min. DB} = 0.67$$

Figure 1. Minimum DB of the hyperbranched polymer from AB$_4$ monomers.

In this work, hyperbranched aromatic polyamides were prepared starting from AB$_x$ (x = 2, 4, and 8) monomers by direct polycondensation using a triphenyl phosphite (TPP)/pyridine system[27] and a (2,3-dihydro-

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2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP) system[28] to examine the effect of the monomer structure on DB. It was found that they were also prepared by thermal polymerization without catalysts. In addition, the copolymerization of the AB_2 and AB_4 monomers in different molar ratios was carried out in order to control the DB of the resulting polymer.

Experimental Section

Materials. 3,5-Diaminobenzoic acid (**2**) was purified by recrystallization from water. 3,5-Dinitrobenzoyl chloride (**1**) obtained from Tokyo Kasei, tetrahydrofuran (THF), ethanol, and 10% palladium on activated carbon (Pd−C) were used as received. TPP and DBOP were obtained from Tokyo Kasei and used as received. Triethylamine was purified by distillation over calcium hydride. *N*,*N*-Dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), and pyridine were purified by vacuum distillation over calcium hydride.

Preparation of 3. In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed **2** (6.09 g, 40 mmol) and DMAc (200 mL). The solution was cooled using a dry ice/acetone bath. After the solution was frozen, **1** (20.3 g, 88 mmol) was added. The dry ice/acetone bath was then replaced with an ice/water bath, and the solution was stirred for 15 h. The reaction mixture was then poured into dilute aqueous HCl. The crude product was filtered, washed with hot methanol, and recrystallized from THF. The product was filtered and dried at 80 °C in vacuo. The yield was 96%. IR (KBr): 1717 (carboxyl C═O), 1688, 1543 (amide C═O), 1624, 1449 cm^{-1} (aromatic). ^1H NMR (DMSO-d_6): δ 10.90 (s, CONH, 2H), 9.20 (d, 4H), 9.00 (t, 2H), 8.68 (t, 1H), 8.16 (d, 2H). ^{13}C NMR (DMSO-d_6): δ 166.51, 161.25, 148.18, 138.76, 137.30, 131.65, 127.88, 120.90, 117.46, 116.42.

Preparation of 4 (AB_4 Monomer). In a flask equipped with a magnetic stirrer and a hydrogen inlet were placed **3** (2.06 g, 4.0 mmol), THF (80 mL), ethanol (80 mL), and 10% Pd−C (0.851 g, 0.8 mmol/Pd). The flask was degassed and purged with hydrogen several times and then stirred at room temperature for 2 days. The mixture was filtered using Celite-545. The solution was concentrated using a rotary evaporator and poured into *n*-hexane. The product was filtered and dried at 80 °C in vacuo. The yield was 95%. IR (KBr): 1708 (carboxyl C═O), 1655, 1547 (amide C═O), 1601, 1451 cm^{-1} (aromatic). ^1H NMR (DMSO-d_6): δ 10.03 (s, CONH, 2H), 8.41 (t, 1H), 8.04 (d, 2H), 6.35 (d, 4H), 6.02 (t, 2H), 5.47 (br, NH_2). ^{13}C NMR (DMSO-d_6): δ 167.30, 167.29, 149.10, 139.74, 136.53, 131.26, 116.30, 102.43. Anal. Calcd for $C_{21}H_{20}N_6O_4$: C, 59.99; H, 4.79; N, 19.99. Found: C, 59.91; H, 5.14; N, 19.20.

Preparation of 5. In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed **4** (0.841 g, 2.0 mmol) and DMAc (20 mL). The solution was cooled using a dry ice/acetone bath. After the solution was frozen, **1** (2.306 g, 10 mmol) was added. The dry ice/acetone bath was replaced with an ice/water bath, and the solution was stirred for 15 h. The solution was then poured into dilute aqueous HCl. The crude product was filtered and dissolved in DMAc. The solution was poured into methanol. The product was filtered and dried at 80 °C in vacuo. The yield was 95%. IR (KBr): 1713 (carboxyl C═O), 1678, 1538 (amide C═O), 1605, 1451 cm^{-1} (aromatic). ^1H NMR (DMSO-d_6): δ 11.09 (s, CONH, 4H), 10.59 (s, CONH, 2H), 9.24 (d, 8H), 9.02 (t, 4H), 8.67 (t, 2H), 8.61 (t, 1H), 8.16 (d, 2H), 8.13 (d, 4H). ^{13}C NMR (DMSO-d_6): δ 165.45, 161.51, 148.29, 139.45, 138.69, 137.39, 136.13, 131.62, 127.91, 121.02, 117.10, 116.77, 116.53, 116.24.

Preparation of 6 (AB_8 Monomer). In a flask equipped with a magnetic stirrer and a hydrogen inlet were placed **5** (2.394 g, 2.0 mmol), DMAc (20 mL), and 10% Pd−C (0.851 g, 0.8 mmol/Pd). The flask was degassed and purged with hydrogen several times and then stirred at room temperature for 2 days. The mixture was filtered using Celite-545. The solution was poured into ethyl acetate. The product was filtered and dried at 80 °C in vacuo. The yield was 99%. IR (KBr): 1708 (carboxyl C═O), 1656, 1549 (amide C═O), 1601, 1451 cm^{-1} (aromatic). ^1H NMR (DMSO-d_6): δ 10.48 (s, CONH, 2H), 10.06 (s, CONH, 4H), 8.55 (t, 1H), 8.38 (t, 2H), 8.13 (d, 2H), 7.94 (d, 4H), 6.36 (d, 8H), 6.02 (t, 4H), 5.13 (br, NH_2). ^{13}C NMR (DMSO-d_6): δ 167.31, 167.16, 166.27, 149.13, 139.65, 139.62, 136.56, 135.71, 131.47, 116.49, 116.08, 115.52, 114.99, 102.38. Anal. Calcd for $C_{49}H_{44}N_{14}O_8$: C, 61.50; H, 4.63; N, 20.49. Found: C, 60.67; H, 4.94; N, 19.70.

Direct Polycondensation Using TPP/Pyridine. In a three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a reflux condenser were placed **2** (1.52 g, 10 mmol), NMP (10 mL), pyridine (2.5 mL), and TPP (2.6 mL, 10 mmol). The solution was stirred at 100 °C for 3 h. The solution was then poured into methanol. The crude product was filtered and dissolved in DMAc. The solution was poured into methanol containing 0.1% LiCl. The product was filtered and dried at room temperature in vacuo. The yield was 97%. IR (KBr): 1655, 1549 (amide C═O), 1603, 1443 (aromatic). ^1H NMR (DMSO-d_6): δ 10.58, 10.29, 10.17, 10.07, 9.96, 9.93, 9.73, 9.70 (m, CONH), 8.38, 7.97, 7.35, 7.26, 6.80, 6.35, 6.31, 5.99 (m, aromatic), 5.15 (br, NH_2). Anal. Calcd for $(C_7H_6N_2O)_n$: C, 62.68; H, 4.51; N, 20.88. Found: C, 60.90; H, 4.39; N, 19.04.

In the polymerization of the AB_4 monomer were used **4** (0.841 g, 2.0 mmol), NMP (5 mL), pyridine (1.25 mL), and TPP (0.53 mL, 2.0 mmol). The yield was 96%. IR (KBr): 1657, 1545 (amide C═O), 1601, 1445 cm^{-1} (aromatic). ^1H NMR (DMSO-d_6): δ 10.60, 10.38, 10.19, 10.12 (m, CONH), 8.36, 8.10, 7.99, 7.95, 7.45, 7.33, 6.91, 6.46, 6.12 (m, aromatic), 4.54 (br, NH_2). Anal. Calcd for $(C_7H_6N_2O)_n$: C, 62.68; H, 4.51; N, 20.88. Found: C, 59.19; H, 4.65; N, 18.89.

Direct Polycondensation Using DBOP. In a three-necked flask equipped with a magnetic stirrer and a nitrogen inlet were placed **4** (0.420 g, 1.0 mmol), NMP (2 mL), triethylamine (0.14 mL, 1.0 mmol), and DBOP (0.460 g, 1.2 mmol). The solution was stirred at room temperature for 24 h. The solution was then poured into methanol. The crude product was filtered and dissolved in DMAc. The solution was poured into methanol containing 0.1% LiCl. The product was filtered and dried at room temperature in vacuo. The yield was 97%. IR (KBr): 1647, 1539 (amide C═O), 1599, 1451 cm^{-1} (aromatic). ^1H NMR (DMSO-d_6): δ 10.56, 10.31, 10.16, 10.10 (m, CONH), 8.36, 7.97, 7.93, 7.43, 7.31, 7.27, 6.89, 6.41, 6.08 (m, aromatic), 5.30 (br, NH_2). Anal. Calcd for $(C_7H_6N_2O)_n$: C, 62.68; H, 4.51; N, 20.88. Found: C, 61.62; H, 4.61; N, 18.88.

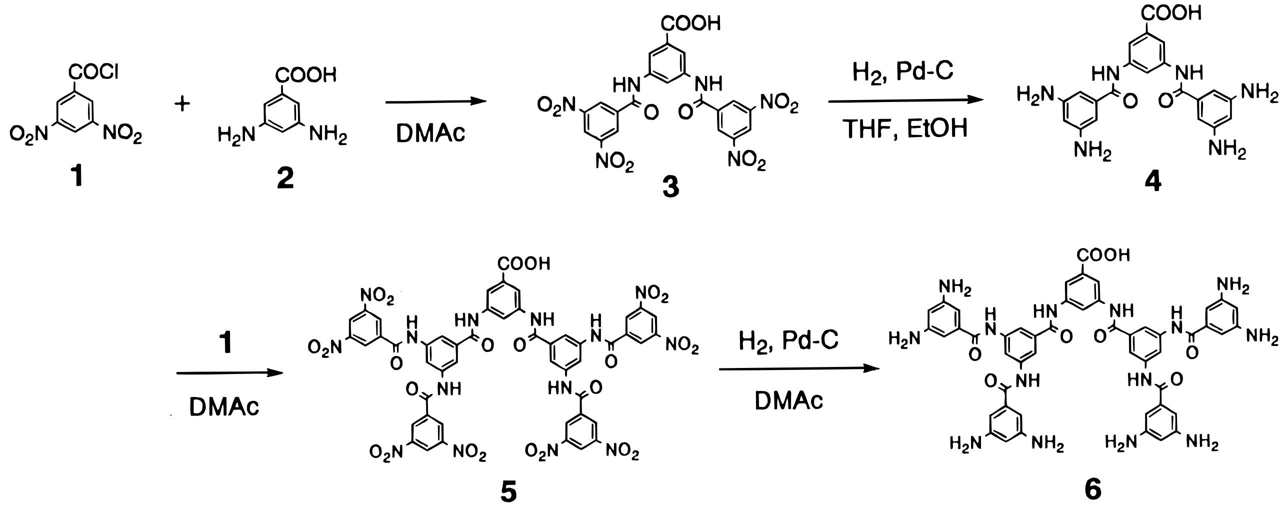
In the polymerization of the AB_8 monomer were used **6** (0.574 g, 0.6 mmol), NMP (3 mL), triethylamine (0.09 mL, 0.6 mmol), and DBOP (0.276 g, 0.72 mmol). The yield was 94%. IR (KBr): 1647, 1543 (amide C═O), 1601, 1450 cm^{-1} (aromatic). ^1H NMR (DMSO-d_6): δ 10.50, 10.33, 10.25, 10.08 (m, CONH), 8.47, 8.37, 8.02, 7.98, 7.46, 7.30, 7.25, 7.00, 6.90, 6.37, 6.02 (m, aromatic), 4.98 (br, NH_2). Anal. Calcd for $(C_7H_6N_2O)_n$: C, 62.68; H, 4.51; N, 20.88. Found: C, 61.21; H, 4.31; N, 19.05.

Thermal Polymerization. A flask containing **2** was flushed with nitrogen three times. The flask was heated at 240 °C under a nitrogen flow for 30 min in a glass tube oven. After the temperature was lowered to room temperature, the product was dissolved in DMAc. The solution was poured into methanol containing 0.1% LiCl. The product was filtered and dried at room temperature in vacuo. The yield was 87%. IR (KBr): 1650, 1536 (amide C═O), 1601, 1431 cm^{-1} (aromatic). ^1H NMR (DMSO-d_6): δ 10.33, 10.09, 9.97, 9.87, 9.73, 9.53, 9.51 (m, CONH), 8.37, 7.98, 7.38, 7.23, 6.88, 6.85, 6.43, 6.38, 6.05 (m, aromatic), 5.12 (br, NH_2). Anal. Calcd for $(C_7H_6N_2O)_n$: C, 62.68; H, 4.51; N, 20.88. Found: C, 61.37; H, 4.71; N, 20.33.

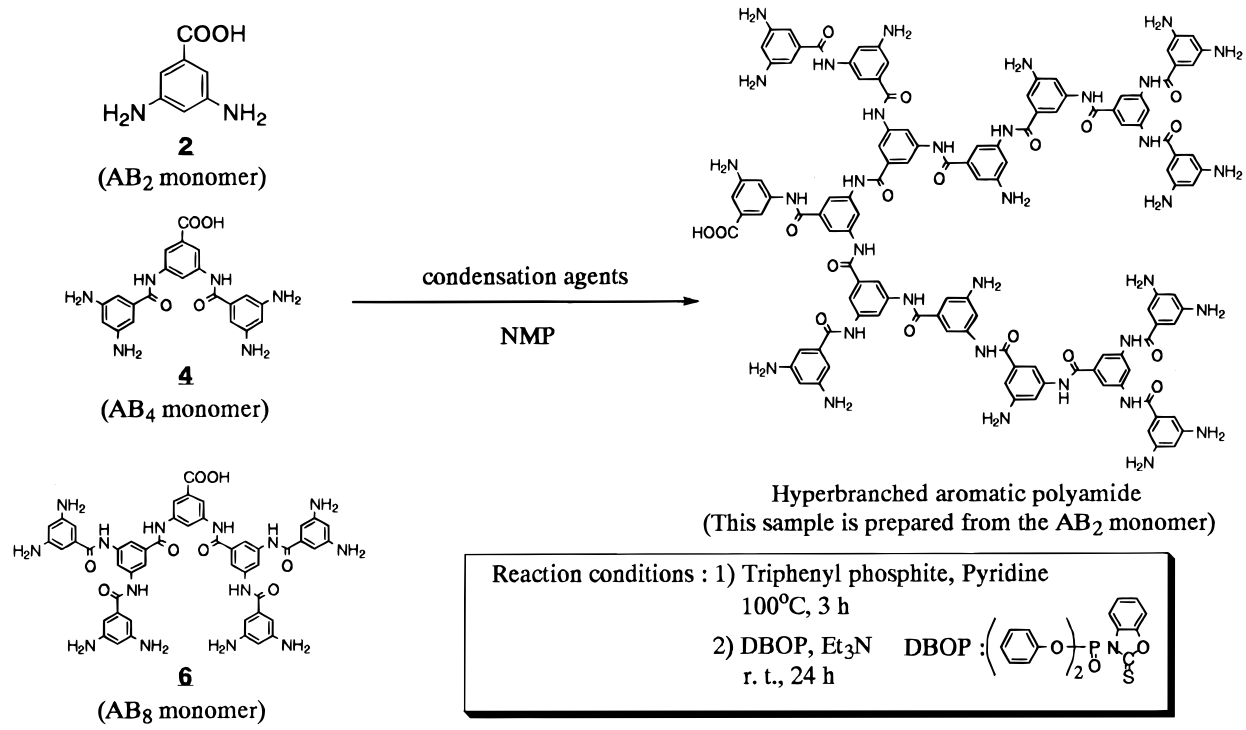
The thermal polymerization of the AB_4 monomer was carried out using the same procedures. Polymer from **4**. IR (KBr): 1653, 1543 (amide C═O), 1601, 1443 cm^{-1} (aromatic). ^1H NMR (DMSO-d_6): δ 10.28, 10.25, 10.13, 10.05 (m, CONH), 8.44, 8.33, 8.06, 8.03, 7.94, 7.91, 7.36, 7.31, 6.85, 6.35, 6.31, 6.00 (m, aromatic), 5.31 (br, NH_2). Anal. Calcd for $(C_7H_6N_2O)_n$: C, 62.68; H, 4.51; N, 20.88. Found: C, 61.84; H, 4.87; N, 20.30.

End-Capping Reaction with Benzoyl Chloride. In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed polymer from **2** (0.537 g, 4.0 mmol) and DMAc

Scheme 1. Synthesis of AB$_x$ (x = 2, 4, and 8) Monomers



Scheme 2. Direct Polycondensation of AB$_x$ (x = 2, 4, and 8) Monomers



(20 mL). The solution was cooled using a dry ice/acetone bath. After the solution was frozen, benzoyl chloride (2.3 mL, 20 mmol) was added. The dry ice/acetone bath was then replaced with an ice/water bath, and the solution was stirred for 15 h. The reaction mixture was then poured into methanol. The product was filtered and dried at room temperature in vacuo. The yield was 92%. IR (KBr): 1659, 1545 (amide C=O), 1601, 1449 cm^{-1} (aromatic). ^{1}H NMR (DMSO-d_6): δ 10.63, 10.50 (CONH), 8.55, 8.14, 8.02, 7.54 (aromatic).

Measurements. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100 Fourier transform infrared spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL JNM-AL 300 NMR spectrometer. Gel permeation chromatography (GPC) measurements using DMF containing 0.01 mol L^{-1} of lithium bromide as an eluent were carried out by using a Jasco HPLC 880PU, polystyrene–divinylbenzene columns (two Shodex KD-806M and KD-802), and a Shodex RI-71 refractive index detector. Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were carried out using a Seiko TGA 6200 TG/DTA analyzer at a heating rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) measurements were carried out using a Seiko DSC 6200 at a heating rate of 10 °C/min under nitrogen.

Results and Discussion

The AB$_4$ dendron, **4**, and AB$_8$ dendron, **6**, were prepared by the divergent method, as shown in Scheme 1. The dendron **3** was synthesized from 3,5-diaminobenzoic acid **2** and 3,5-dinitrobenzoyl chloride **1**. **3** was washed with hot methanol in order to remove excess **1** and its hydrate (generated by pouring the reaction mixture into dilute aqueous HCl) and then purified by recrystallization from THF. The AB$_4$ dendron **4** was prepared by the hydrogenation of **3**. The structures of **3** and **4** were confirmed by the ^{1}H and ^{13}C NMR spectra. The AB$_8$ dendron **6** was prepared by the hydrogenation of dendron **5**, which was synthesized from **4** and **1**. **5** was able to be isolated by reprecipitation into methanol because other compounds such as **1**, its hydrate, and **4** were soluble in methanol. The hydrogenation of **5**

Table 1. Synthesis of Hyperbranched Aromatic Polyamides by Direct Polycondensation

entry	monomer	condensing agents	equiv to COOH	yield (%)	η_{inh}[a] (dL/g)	M_w[b]	M_w/M_n[b]	DB[c]
1	**2**	TPP/Py	1.0	97	0.25	155 000	3.0	0.32
2	**2**	TPP/Py	2.0	100[d]				
3	**4**	TPP/Py	1.0	96	0.21	139 000	2.7	0.72
4	**4**	TPP/Py	2.0	*e*				
5	**4**	DBOP	1.2	99	0.25	193 000	3.3	0.67
6	**6**	TPP/Py	1.0	61				
7	**6**	DBOP	1.2	94	0.36	109 000	2.6	0.84

[a] Measured at a concentration of 0.5 g/dL in DMF containing 0.01 mol/L of LiBr at 30 °C. [b] Determined by GPC based on polystyrene standards. [c] Determined by ^{1}H NMR. [d] Precipitation occurred during the polymerization. [e] Gelation occurred during the polymerization.

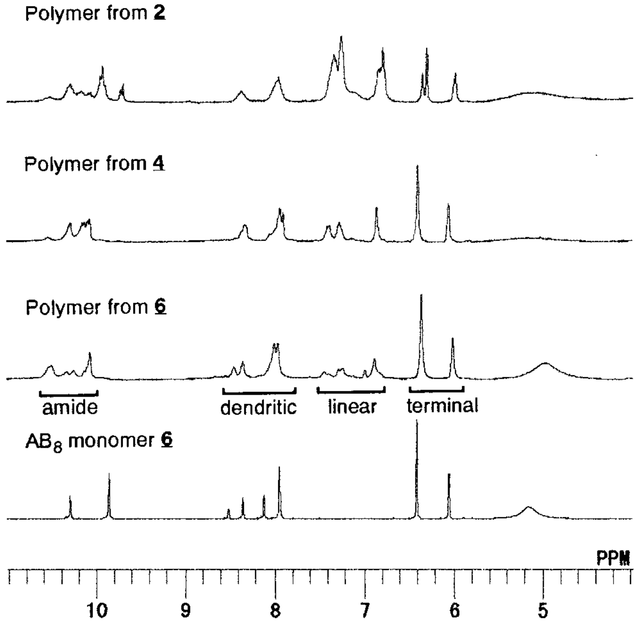


Figure 2. ^{1}H NMR spectra of the AB$_8$ monomer **6** and the hyperbranched aromatic polyamides prepared by direct polycondensation.

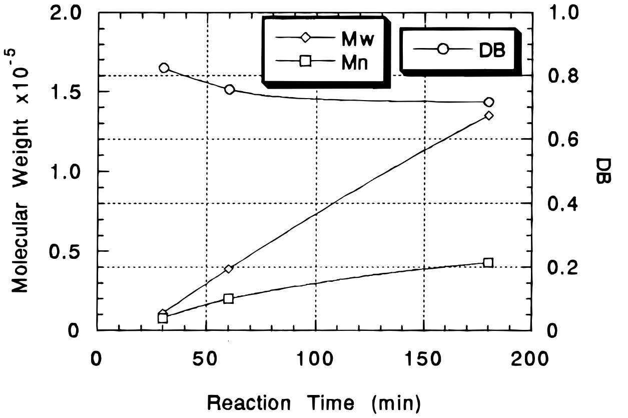


Figure 3. Effect of the reaction time on M_w (◇), M_n (□), and DB (○) of the resulting polymer from the AB$_4$ monomer **4** by the direct polycondensation in the presence of TPP/pyridine.

proceeded quantitatively, and **6** was isolated by pouring the reaction solution into ethyl acetate. The AB$_4$ and AB$_8$ dendrons, **3**−**6**, could be isolated by simple recrystallization and reprecipitation; thus, these dendrons can be synthesized easily on a large scale.

Direct polycondensation of the AB$_2$, AB$_4$, and AB$_8$ monomers—**2**, **4**, and **6**—was carried out in the presence of condensation agents, as shown in Scheme 2 and Table 1. The polymerization of both **2** and **4** using 1.0 equiv of TPP as compared to the carboxyl groups of the monomer proceeded efficiently in a homogeneous solution to form the polymers in high yield. For both resulting polymers, a carbonyl absorption corresponding to amide bonds was observed at 1655 cm^{-1} in the IR spectra, and signals attributed to the amide proton were observed at 10.58−9.70 ppm in the ^{1}H NMR spectra. The IR spectrum and chemical shifts in the ^{1}H NMR of the polymer from **2** were identical with those of the polymer from **4**, which indicated that the polymers from **2** and **4** have the same repeating units. When 2 equiv of TPP was used in the polymerization of **2**, precipitation occurred during the reaction. The IR spectrum of the resulting polymer showed the amide carbonyl absorption at 1655 cm^{-1}, but the polymer was insoluble even in aprotic polar solvents, which implies that an undesired side reaction occurred during the polymerization. In the case of **4** using 2 equiv of TPP, the polymer could not be isolated because the system gelated during polymerization. Direct polycondensation of the AB$_8$ monomer **6** was also carried out in the presence of 1.0 equiv of TPP. The yield was only 61%, and the ^{1}H NMR spectrum of the product was almost identical with that of the starting material, which implies that the polymerization had proceeded insufficiently. Increasing the amount of TPP to 1.2 equiv was ineffective in polymerizing **6**. Because the TPP/pyridine system could not polymerize **6**, DBOP was used as an alternative condensation agent to form the hyperbranched aromatic polyamide. The direct polycondensation for both **4** and **6** in the presence of DBOP proceeded in a homogeneous solution to form the corresponding polymer in high yield. The IR and ^{1}H NMR spectra of the resulting polymer from **6** were similar to those of **2** and **4**.

All hyperbranched aromatic polyamides prepared from the three different monomers by direct polymerization were soluble in DMF, DMAc, NMP, and DMSO. The weight-average molecular weights (M_w) of the resulting polymers measured by GPC based on polystyrene standards were in the range of 100 000−200 000. The M_w of the polymer prepared using TPP/pyridine was close to that of the polymer prepared using DBOP in the case of the AB$_4$ monomer **4**. The inherent viscosity of the polymers was relatively low, which is consistent with the characteristics of hyperbranched polymers.

^{1}H NMR spectra of the resulting polymers are shown in Figure 2. Peaks from the aromatic protons were observed at 8.3, 7.9, 7.3, 6.9, 6.4, and 6.0 ppm. By comparison of the spectra of the polymers from the AB$_8$ monomer **6**, the peaks at 8.3 and 7.9 ppm were attributed to the aromatic protons of the dendritic units and the peaks at 6.4 and 6.0 ppm were attributed to those of the terminal units. The DB of the polymer from the AB$_2$ monomer **2** was calculated to be 0.32 from the integration ratio of the peaks from ^{1}H NMR. The low DB is probably due to the steric hindrance and the lower

Table 2. Synthesis of Hyperbranched Aromatic Polyamides by Thermal Polymerization

entry	monomer	condition	temp (°C)	time (min)	yield[a] (%)	solubility in DMAc	M_w[b]	M_w/M_n[b]	DB[c]
1	**2**	N_2	240	30	87	+	26 100	1.9	0.43
2	**2**	N_2	270	6	25	+−	58 700	2.8	0.41
3	**2**	vacuum	240	30	*d*				
4	**4**	N_2	240	30	46	+−	24 300	2.0	0.71
5	**4**	N_2	270	15	40	swell			
6	**4**	vacuum	240	10	75	+	15 000	1.7	0.79
7	**4**	vacuum	270	5	73	+	16 500	2.0	0.76

[a] Soluble part in DMAc. [b] Determined by GPC based on polystyrene standards. [c] Determined by ^1H NMR. [d] Sublimation occurred.

Table 3. Copolymerization of the AB_2 and AB_4 Monomers Using the TPP/Pyridine System

molar ratio (**2**:**4**)	yield (%)	M_w[a]	M_w/M_n[a]	DB[b]
100:0	97	155 000	3.0	0.32
90:10	100	78 000	1.9	0.39
75:25	100	90 700	2.1	0.48
50:50	100	101 000	2.3	0.61
0:100	96	139 000	2.7	0.72

[a] Determined by GPC based on polystyrene standards. [b] Determined by ^1H NMR.

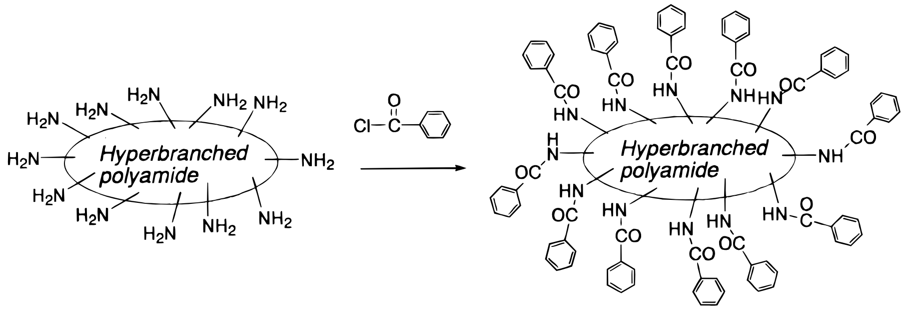
reactivity of amines in linear units relative to those in the terminal units. On the other hand, the DBs of the polymers from **4** and **6** were 0.72 and 0.84, respectively. Thus, the polymers having high DBs were obtained by using dendrons as starting materials.

The dependence of M_w, M_n, and DB on the reaction time in the direct polymerization of the AB_4 monomer **4** using TPP/pyridine is shown in Figure 3. M_w increased with increasing reaction time, while M_n increased slowly compared with the case of M_w. This resulted in a large polydispersity for the obtained polymers. The DB of the polymer decreased with increasing reaction time and leveled off at about 0.72. It is reported by statistical calculation that the DB of the polymer from AB_2 monomers decreased with increasing conversion and should approach 0.5.[29] In this work, the same trend was observed, but DB decreased toward 0.72 because the AB_4 monomer was used as a starting material.

Using another synthetic route, thermal polymerization of the AB_x monomers was carried out. Thermal polymerization is very suitable for industrial use, because neither solvents nor catalysts are used; thus, contamination from such impurities can be avoided. Although the thermal polymerization process is very useful for the synthesis of aliphatic polyamides with a high molecular weight, it is difficult to obtain aromatic polyamides having a high molecular weight by thermal polymerization. The reason has been explained by the low reactivity of aromatic amines due to the resonance effect of the phenyl groups. In a previous paper, we reported the successful thermal polycondensation of 3,5-bis(4-aminophenoxy) benzoic acid.[18,19] This was achieved by selecting a monomer that has an amorphous state during polymerization and an increased reactivity of the amines by the ether substitutions at the paraposition. In this work, the AB_x monomers in which the reactivity of the amines was not enhanced by substituents such as ether linkages afforded the hyperbranched aromatic polyamides by thermal polymerization as summarized in Table 2. A dark glassy product was obtained by the thermal polymerization of the AB_2 monomer **2** under a nitrogen gas flow at 240 °C. In the IR spectrum of the product, an amide carbonyl absorption was observed at 1650 cm^{-1}, and peaks attributed to the amide proton were observed at 10.33−9.51 ppm in the ^1H NMR spectrum. The spectroscopic data of the resulting polymer were almost identical with those of the polymers prepared by direct polycondensation. The resulting polymer was soluble in DMF, DMAc, NMP, and DMSO. Under reduced pressure, sublimation of **2** was observed and polymerization did not proceed efficiently. In the case of the AB_4 monomer **4**, the polymerization proceeded even under reduced pressure. The spectroscopic data of the hard foamlike products were almost identical with those of the polymers from **2**. High reaction temperature and longer reaction time gave polymers having poor solubility. The thermal polymerization of the AB_8 monomer **6** failed although a weight loss was observed at 260 °C in the TGA measurement of **6**. The product from **6** prepared at 260 °C was insoluble in DMSO and amide solvents, which implies that undesired side reactions occurred during the thermal polymerization. The molecular weights of the resulting polymers from **2** and **4** by the thermal polymerization were about 20 000, which were lower than those of the polymers prepared by the direct polycondensation. The reason for the lower molecular weight is probably due to the high T_g of the resulting polymer. The DBs of the polymers from **2** and **4** were 0.43 and 0.79, respectively.[30]

Next, copolymerization of **2** and **4** was carried out in the presence of TPP/pyridine, as shown in Table 3. The copolymers of **2** and **4** in different molar ratios were obtained in good yield. The DB of the copolymer

Scheme 3. End-Capping Reaction of the Hyperbranched Aromatic Polyamides with Benzoyl Chloride



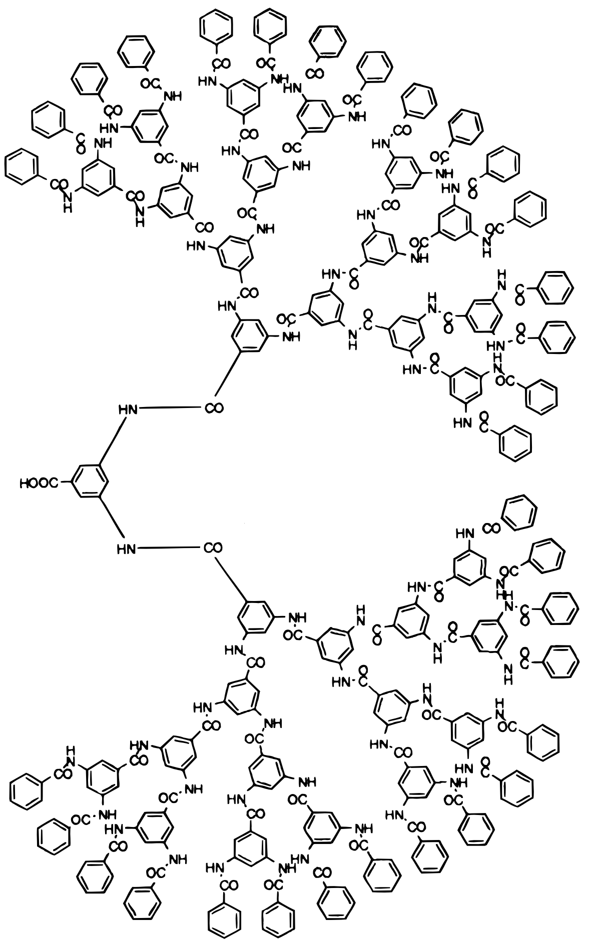


Figure 4. Structure of the aromatic polyamide G5 dendron.

Table 4. Properties of the End-Capped Polymers with Benzoyl Chloride

	DB	M_w	M_w/M_n	T_g[a] (°C)	solubility THF	solubility DMAc
PolyAB_2−EC[b]	0.34[c]	95 400[d]	2.5[d]	305	−	+
PolyAB_4−EC[b]	0.72[c]	160 000[d]	4.2[d]	309	−	+
G5 dendron	1.00	7 508[e]	1.0	275	+	+

[a] Measured by DSC at a heating rate of 10 °C/min under N_2. [b] Polymers end-capped with benzoyl chloride. [c] Determined by ^1H NMR before the end-capping reaction. [d] Determined by GPC based on polystyrene standards. [e] Formula weight.

increased with increasing amount of the AB_4 monomer **4**. In other words, DB could be controlled from 0.32 to 0.72 by changing the ratio of the monomers. Changes in DB were not observed to have any effect on the solubility in this range of DB.

It is known that hyperbranched polymers have a large number of unreacted end groups which affect the thermal properties and solubility of the polymers. In this work, the numerous amino end groups of the hyperbranched aromatic polyamides were modified by end-capping with benzoyl chloride (Scheme 3) in order to compare the properties of the polymers with the aromatic polyamide G5 dendron[31] composed of the same repeating units and end groups (Figure 4). The end-capping reaction proceeded quantitatively according to the ^1H NMR spectra. Thermal properties and solubilities of the end-capped polymers were summarized in Table 4. The T_g of the polymers before the end capping was not detected, whereas the end-capped polymers prepared from **2** and **4** had T_g's of 305 and 309 °C, respectively. Thus, it was found that DB had little influence on T_g of the polymers. The fact that the T_g of the end-capped polymers was higher than that of the G5 dendron is explained by the higher molecular weights of the polymers than that of the G5 dendron. The end-capped polymers were soluble in aprotic polar solvents such as DMF, DMAc, NMP, and DMSO. The G5 dendron was soluble in aprotic polar solvents and THF, whereas both the end-capped hyperbranched polyamides from **2** and **4** were insoluble in THF. We assume that the difference in solubility is caused by the difference in architecture of the molecule: random for the hyperbranched polymers and spherical for the G5 dendron.

Conclusions

Hyperbranched aromatic polyamides having high molecular weights were prepared by the direct polycondensation of AB_x monomers ($x = 2$, 4, and 8). The DB of the resulting polymers was increased to 0.84 by using dendron **6** as starting materials, whereas the direct polycondensation of the AB_2 monomer **2** gave a DB of 0.32. Hyperbranched aromatic polyamides were also prepared by thermal polymerization of the AB_2 and AB_4 monomers. It is notable that the thermal polymerization proceeded even if the amino groups of the monomer were not activated by substituents. The molecular weight of the polymer prepared by the thermal polymerization method was relatively low compared with that prepared by direct polymerization.

Copolymerization of the AB_2 and AB_4 monomers at different molar ratios allowed the control of DB of the resulting polymer. There was no detectable change in solubility of the polymers having DBs in the range of 0.32−0.72. T_g's of the polymers end-capped with benzoyl chloride were almost independent of the DB of the original polymers and higher than that of the G5 dendron composed of the same units. A difference in solubility in THF was observed between the end-capped polymers and the G5 dendron, which is probably due to differences in their architectures.

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