Rapid Synthesis of Aromatic Polyamide Dendrimers by an Orthogonal and a Double-Stage Convergent Approach

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ABSTRACT: Aromatic polyamide dendrons (HOOC-G1 (**6**), Br-G2 (**7**), HOOC-G3 (**8**), and Br-G4 (**9**)) were synthesized by an orthogonal approach, which utilizes the direct condensation reaction and palladium-catalyzed carbon monoxide insertion reaction in an alternating fashion to form amide linkages. G1, possessing four amino groups (HOOC-G1-4NH_2 (**12**)), and G2, possessing eight amino groups (HOOC-G2-8NH_2 (**14**)), were also prepared independently. HOOC-G4 (**15**) was synthesized from **12** and **7**, and HOOC-G5 (**16**) from **14** and **7** both with the double-stage convergent method. The aramid dendrons were soluble in amide solvents and THF. The coupling of dendrons with difunctional and trifunctional core molecules was attempted.

Introduction

Dendritic macromolecules such as dendrimers and hyperbranched polymers have received much attention in recent years.[1−5] Due to their unique architecture, these polymers have unique properties such as small radius of gyration, lack of entanglement, low viscosity, high solubility, and their amorphous nature. Dendritic macromolecules contain a lot of functional groups that can be efficiently modified to control the properties of the resulting polymers such as solubility and thermal properties. In particular, dendrimers have a well-controllable structure and size with perfect branching. Since the properties of polymers are related directly to structure and size, it is attractive to make and study well-defined macromolecules. The interests in dendrimers include also their unique properties which are not observed in other polymers. Usages of dendrimers include harvesting low-energy photons,[6] drug-delivery agents,[7] and molecular encapsulation.[8] Generally, dendrimers are synthesized by the divergent[9,10] and the convergent[11] strategies. These synthetic routes require a deprotection step in addition to the coupling step and purification at every step of the growth process. To synthesize the large generation dendrimers more easily, several successful attempts to shorten synthetic route, such as a double-stage convergent approach[12,13] and a double exponential growth approach,[14] have been studied. Recently, Zeng and Zimmerman have reported a synthesis of dendrimers by an orthogonal approach in which deprotection steps are not required by the sequential use of two different building blocks in two coupling reactions.[15] Although this approach halves the number of steps, the resulting dendrimer becomes an alternating copolymer because two different coupling reactions give different linkages. If two different reactions are selected to form the same linkage, homogeneous dendrimers could be obtained by the orthogonal approach. Yu et al. have reported the synthesis of poly(phenylenevinylene) dendrimers by this approach using the Heck and Horner−Wadsworth−Emmons reactions.[16]

Aromatic polyamides (aramids) are well-known as high-performance polymers because of their excellent thermal and mechanical properties.[17] These polymers, however, are only soluble in highly polar solvents. The poor processability could be improved by the introduction of dendritic structures. Feast et al. have already reported the synthesis of aramid dendrimers up to the second generation using 5-nitroisophthaloyl dichloride as a building block.[18] These dendrimers were soluble in amide solvents and THF, however, the second-generation dendrimer from G2 dendron and trimesoyl chloride was obtained in low yield.

Aramids have been prepared by the reactions as follows: (i) reaction of a diamine with a diacid chloride at low temperatures, (ii) direct condensation reaction of a diamine with a diacid using condensing agents such as triphenyl phosphite/pyridine[19] and (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP),[20] and (iii) carbon monoxide (CO) insertion reaction of a diamine and an aromatic dihalide using a palladium catalyst.[21,22] The aromatic bromide was stable in the direct condensation reaction, and the carboxyl group was stable in the CO insertion reaction, thus allowing the orthogonal approach to be applied. We now describe the synthesis of aromatic polyamide dendrons up to the fourth generation by an orthogonal approach in which the direct condensation reaction and palladium-catalyzed CO insertion reaction are used in an alternating fashion to form amide linkages. In addition, the fourth- and fifth-generation dendrons were synthesized by a double-stage convergent approach,[12,13] and the synthesis of dendrimers with difunctional and trifunctional cores was attempted.

Experimental Section

Materials. 3,5-Diaminobenzoic acid was purified by recrystallization from water. 2-Bromo-4,6-dinitroaniline and benzoyl chloride were used as received. Triphenyl phosphite, (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP), and bis(triphenylphosphine)palladium dichloride ($PdCl_2(PPh_3)_2$) were used as received. Triphenylphosphine (PPh_3) was purified by recrystallization from *n*-hexane. 1,8-Diazabicyclo[5.4.0]-7-undecene (DBU) was purified by vacuum distillation over sodium. Triethylamine was purified by distillation over calcium hydride. 3,5-Dinitrobenzoyl chloride, tetrahydrofuran (THF), ethanol, and 10% palladium on activated carbon (Pd−C) were used as received. *p*-Phenylenediamine was purified by sublimation. Trimesoyl chloride and 4-nitroaniline

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were used as received. *N*,*N*-Dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), and pyridine were purified by vacuum distillation over calcium hydride.

3,5-Dinitrobromobenzene (2). In a flask, glacial acetic acid (300 mL) and 2-bromo-4,6-dinitroaniline (**1**) (25.0 g, 95.4 mmol) were placed. A solution of sodium nitrite (9.87 g, 143 mmol) in H_2SO_4 (85 mL) was added into the mixture in an ice−water bath. After the mixture was stirred for 30 min, a suspension of cuprous oxide (2.05 g, 14.3 mmol) in ethanol (230 mL) was then added slowly into the mixture, and stirred overnight at room temperature. The mixture was quenched with water (100 mL). The organic layer was then extracted with ethyl acetate and washed with 10% NaOH(aq), saturated $NaHCO_3$(aq) and saturated NaCl(aq). The extract was dried with $MgSO_4$, and the solvent was removed by evaporation. The crude 3,5-dinitrobromobenzene was purified by vacuum distillation. The yield was 73%. ^{1}H NMR ($CDCl_3$): δ 8.98 (t, 1H), 8.69 (d, 2H).

3,5-Diaminobromobenzene (3). In a flask, 3,5-dinitrobromobenzene (**2**) (13.4 g, 54.0 mmol), stannous chloride dihydrate (125.4 g, 556 mmol) and ethanol (90 mL) were placed. The solution was stirred at 70 °C for 3 h under N_2 atmosphere. After cooling, the solution was concentrated by using a rotary evaporator and was diluted with excess 25% NaOH(aq). The organic layer was then extracted with ethyl acetate and washed with saturated NaCl(aq). The extract was dried with $MgSO_4$, and the solvent was removed by evaporation. The crude 3,5-diaminobromobenzene was purified by vacuum distillation. The yield was 68%. ^{1}H NMR (acetone-*d*$_6$): δ 6.11(d, 2H), 5.88 (t, 1H), 4.33 (br, NH_2).

HOOC-G1 (3,5-Bis(benzoylamino)benzoic Acid) (6). In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed 3,5-diaminobenzoic acid (**5**) (15.2 g, 100 mmol) and DMAc (100 mL). The solution was cooled using a dry ice−acetone bath. After the solution was frozen, benzoyl chloride (**4**) (25.3 mL, 220 mmol) was added. The dry ice−acetone bath was replaced with an ice−water bath and the solution was stirred at 0 °C for 3 h. The reaction mixture was then poured into dilute HCl water. The crude product was filtered, and washed with hot methanol. The product was filtered and dried at room temperature in vacuo. The yield was 98%. IR (KBr): 1701 cm^{-1} (carboxyl C═O), 1649, 1534 cm^{-1} (amide C═O), 1603, 1453 cm^{-1} (aromatic). ^{1}H NMR (DMSO-*d*$_6$): δ 12.9 (br, COOH), 10.4 (s, CONH 2H), 8.63 (t, 1H), 8.15 (d, 2H), 7.99 (q, 4H), 7.55 (m, 6H). ^{13}C NMR (DMSO-*d*$_6$): δ 167.01, 165.67, 139.49, 134.60, 131.56, 131.25, 128.26, 127.64, 116.75, 116.49. Anal. Calcd for $C_{21}H_{16}N_2O_4$: C, 69.99; H, 4.48; N, 7.77. Found: C, 70.21; H, 4.76; N, 7.82.

Br-G2 (7). In a three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a reflux condenser were placed 3,5-diaminobromobenzene (**3**) (1.50 g, 8 mmol), HOOC-G1 (**6**) (7.21 g, 20 mmol), DMAc (40 mL), pyridine (4 mL) and triphenyl phosphite (4.2 mL, 16 mmol). The solution was stirred at 115 °C for 3 h. The solution was then poured into dilute HCl water. The crude product was filtered, and dissolved in the mixture of THF/DMAc (9:1). The solution was poured into methanol. The product was filtered and dried at room temperature in vacuo. The yield was 89%. IR (KBr): 1657, 1539 cm^{-1} (amide C═O), 1599, 1451 cm^{-1} (aromatic). ^{1}H NMR (DMSO-*d*$_6$): δ 10.54 (s, CONH 2H), 10.49 (s, CONH 4H), 8.59 (t, 2H), 8.35 (t, 1H), 8.10−8.00 (m, 12H), 7.83 (d, 2H), 7.64−7.51 (m, 12H). ^{13}C NMR (DMSO-*d*$_6$): δ 166.03, 165.61, 140.78, 139.34, 135.69, 134.58, 131.60, 128.30, 127.62, 120.96, 117.91, 115.83, 115.46, 110.94. MALDI−TOF MS: *m*/*z* calcd for $C_{48}H_{35}BrN_6O_6$ 878.0 (M + K$^+$), found 878.0 (M + K$^+$). Anal. Calcd: C, 66.13; H, 4.05; Br, 9.17; N, 9.64. Found: C, 66.00; H, 4.31; Br, 9.50; N, 9.56.

HOOC-G3 (8). In a three-necked flask equipped with a magnetic stirrer, a carbon monoxide inlet, and a reflux condenser were placed 3,5-diaminobenzoic acid (**5**) (0.365 g, 2.4 mmol), Br-G2 (**7**) (5.231 g, 6 mmol), $PdCl_2(PPh_3)_2$ (0.202 g, 0.29 mmol), PPh_3 (0.293 g, 1.15 mmol), and DMAc (18 mL). The flask was degassed and purged with carbon monoxide several times, and then the solution was stirred and heated at 115 °C in an oil bath. To the solution was added DBU (1.73 mL, 11.5 mmol) using a syringe. The solution was stirred for 15 h at 115 °C. The solution was then poured into dilute HCl water. The crude product was filtered, and dissolved in the mixture of THF/DMAc (9:1). The solution was filtered and poured into ethyl acetate. The product was dissolved in THF and isolated using a preparative GPC. The isolated solution was concentrated using a rotary evaporator, and poured into *n*-hexane. The product was filtered and dried at room temperature in vacuo. The yield was 61%. IR (KBr): 1659, 1543 cm^{-1} (amide C═O), 1601, 1450 cm^{-1} (aromatic). ^{1}H NMR (DMSO-*d*$_6$): δ 10.60−10.48 (CONH 14H), 8.63−8.52 (7H), 8.10−8.00 (30H), 7.65−7.49 (24H). ^{13}C NMR (DMSO-*d*$_6$): δ 166.97, 165.95, 165.59, 139.55, 139.35, 139.31, 135.91, 135.81, 134.58, 131.58, 128.29, 127.60, 115.79, 115.50. MALDI−TOF MS: *m*/*z* calcd for $C_{105}H_{76}N_{14}O_{16}$ 1812.8 (M + Na$^+$), found 1812.7 (M + Na$^+$). Anal. Calcd: C, 70.46; H, 4.28; N, 10.96. Found: C, 68.76; H, 4.73; N, 10.69.

Br-G4 (9). In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed 3,5-diaminobromobenzene (**3**) (0.094 g, 0.5 mmol), HOOC-G3 (**8**) (2.24 g, 1.25 mmol), NMP (5 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 dilute HCl water. The crude product was filtered and dissolved in THF. The solution was poured into ethyl acetate. The product was dissolved in THF and isolated using a preparative GPC. The isolated solution was concentrated using a rotary evaporator, and poured into *n*-hexane. The product was filtered and dried at room temperature in vacuo. The yield was 54%. IR (KBr): 1663, 1553 cm^{-1} (amide C═O), 1601, 1451 cm^{-1} (aromatic). ^{1}H NMR (DMSO-*d*$_6$): δ 10.64−10.44 (CONH 30H), 8.60−8.50 (14H), 8.37 (1H), 8.17−7.97 (60H), 7.75 (2H), 7.63−7.49 (48H). ^{13}C NMR (DMSO-*d*$_6$): δ 165.97, 165.60, 139.38, 139.32, 135.94, 135.83, 134.59, 131.58, 128.30, 127.61, 115.79, 115.52. Anal. Calcd for $C_{216}H_{155}BrN_{30}O_{30}$: C, 69.54; H, 4.19; Br, 2.14; N, 11.26. Found: C, 67.92; H, 4.58; Br, 2.10; N, 10.69.

HOOC-G1-4NO$_2$ (3,5-Bis(3,5-dinitrobenzoylamino)benzoic Acid) (11). In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed 3,5-diaminobenzoic acid (**5**) (6.09 g, 40 mmol) and DMAc (200 mL). The solution was cooled using a dry ice−acetone bath. After the solution was frozen, 3,5-dinitrobenzoyl chloride (**10**) (20.3 g, 88 mmol) was added. The dry ice−acetone bath was replaced with an ice−water bath, and the solution was stirred for 15 h. The reaction mixture was then poured into dilute HCl water. The crude product was filtered and washed with hot methanol. The product was recrystallized from THF. The product was filtered and dried at 80 °C in vacuo. The yield was 96%. IR (KBr): 1717 cm^{-1} (carboxyl C═O), 1688, 1543 cm^{-1} (amide C═O), 1624, 1449 cm^{-1} (aromatic). ^{1}H 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.

HOOC-G1-4NH$_2$ (3,5-Bis(3,5-diaminobenzoylamino)benzoic Acid) (12). In a flask equipped with a magnetic stirrer and a hydrogen inlet were placed HOOC-G1-4NO$_2$ **(11)** (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 cm^{-1} (carboxyl C═O), 1655, 1547 cm^{-1} (amide C═O), 1601, 1451 cm^{-1} (aromatic). ^{1}H 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.

HOOC-G2-8NO$_2$ (13). In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed HOOC-G1-4NH$_2$ (**12**) (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, 3,5-dinitrobenzoyl chloride (**10**) (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 HCl water. 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 cm^{-1} (carboxyl C=O), 1678, 1538 cm^{-1} (amide C=O), 1605, 1451 cm^{-1} (aromatic). ^{1}H 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.

HOOC-G2-8NH$_2$ (14). In a flask equipped with a magnetic stirrer and a hydrogen inlet were placed HOOC-G2-8NO$_2$ (**13**) (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 cm^{-1} (carboxyl C=O), 1656, 1549 cm^{-1} (amide C=O), 1601, 1451 cm^{-1} (aromatic). ^{1}H 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.

HOOC-G4 (15) from Br-G2 and HOOC-G1-4NH$_2$. In a three-necked flask equipped with a magnetic stirrer, a carbon monoxide inlet, and a reflux condenser were placed HOOC-G1-4NH$_2$ (**12**) (0.541 g, 1.2 mmol), Br-G2 (**7**) (5.231 g, 6.0 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.202 g, 0.249 mmol), PPh$_3$ (0.293 g, 1.15 mmol), and DMAc (18 mL). The flask was degassed and purged with carbon monoxide several times, and then the solution was stirred and heated at 115 °C in an oil bath. To the solution was added DBU (1.44 mL, 9.6 mmol) using a syringe. The solution was stirred for 15 h at 115 °C. The solution was then poured into dilute HCl water. The product was isolated by the same procedure as HOOC-G3 (**8**). The yield was 63%. IR (KBr): 1663, 1553 cm^{-1} (amide C=O), 1601, 1451 cm^{-1} (aromatic). ^{1}H NMR (DMSO-d_6): δ 10.65−10.44 (CONH 30H), 8.59−8.48 (15H), 8.14−7.95 (60H), 7.63−7.48 (48H). ^{13}C NMR (DMSO-d_6): δ 166.05, 166.00, 165.63, 139.42, 139.35, 136.01, 135.86, 134.61, 131.60, 128.31, 127.63, 115.84, 115.55. MALDI−TOF MS: m/z calcd for $C_{217}H_{156}N_{30}O_{32}$ 3718.8 (M + Na$^+$), found 3719.3 (M + Na$^+$). Anal. Calcd: C, 70.52; H, 4.25; N, 11.37. Found: C, 68.29; H, 4.49; N, 10.98.

HOOC-G5 (16) from Br-G2 and HOOC-G2-8NH$_2$. In a three-necked flask equipped with a magnetic stirrer, a carbon monoxide inlet, and a reflux condenser were placed HOOC-G2-8NH$_2$ (**14**) (0.479 g, 0.5 mmol), Br-G2 (**7**) (4.359 g, 5.0 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.169 g, 0.24 mmol), PPh$_3$ (0.252 g, 0.96 mmol), and DMAc (15 mL). The flask was degassed and purged with carbon monoxide several times, and then the solution was stirred and heated at 115 °C in an oil bath. To the solution was added DBU (1.2 mL, 8.0 mmol) using a syringe. The solution was stirred for 15 h at 115 °C. The solution was then poured into dilute HCl water. The product was isolated by the same procedure as HOOC-G3 (**8**). The yield was 38%. IR (KBr): 1659, 1547 cm^{-1} (amide C=O), 1601, 1451 cm^{-1} (aromatic). ^{1}H NMR (DMSO-d_6): δ 10.69−10.42 (CONH 62H), 8.60−8.50 (30H), 8.15−7.93 (126H), 7.61−7.43 (96H). ^{13}C NMR (DMSO-d_6): δ 166.04, 165.98, 165.61, 139.39, 139.33, 135.99, 135.83, 134.59, 131.57, 128.27, 127.60, 115.80, 115.53. MALDI−TOF MS: m/z calcd for $C_{441}H_{316}N_{62}O_{64}$ 7530.7 (M + Na$^+$), 7640.7 (M + Cs$^+$), found 7531.7 (M + Na$^+$), 7641.5 (M + Cs$^+$). Anal. Calcd: C, 70.55; H, 4.24; N, 11.57. Found: C, 68.00; H, 4.54; N, 11.14.

HOOC-G2 (17). In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed HOOC-G1-4NH$_2$ (**12**) (0.420 g, 1.0 mmol) and DMAc (10 mL). The solution was cooled using a dry ice−acetone bath. After the solution was frozen, benzoyl chloride (**4**) (0.69 mL, 6.0 mmol) was added. The dry ice−acetone bath was replaced with an ice−water bath, and the solution was stirred at 0 °C for 6 h. The reaction mixture was then poured into dilute HCl water. The crude product was filtered and washed with hot methanol. The product was then filtered and dried at room temperature in vacuo. The yield was 83%. IR (KBr): 1708 cm^{-1} (carboxyl C=O), 1658, 1553 cm^{-1} (amide C=O), 1601, 1453 cm^{-1} (aromatic). ^{1}H NMR (DMSO-d_6): δ 12.9 (br, COOH), 10.55 (s, CONH 2H), 10.47 (s, CONH 4H), 8.60 (t, 1H), 8.57 (t, 2H), 8.17 (d, 2H), 8.10−8.00 (m, 12H), 7.64−7.50 (m, 12H). ^{13}C NMR (DMSO-d_6): δ 167.02, 165.95, 165.63, 139.57, 139.33, 135.82, 134.63, 131.61, 131.40, 128.32, 127.64, 116.67, 116.39, 115.84, 115.56. Anal. Calcd for $C_{49}H_{36}N_6O_8$: C, 70.33; H, 4.34; N, 10.04. Found: C, 69.36; H, 4.70; N, 9.87.

Br-G5 (18). In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed 3,5-diaminobromobenzene (**3**) (0.019 g, 0.1 mmol), HOOC-G4 (**15**) (0.739 g, 0.2 mmol), NMP (2 mL), triethylamine (0.03 mL, 0.2 mmol) and DBOP (0.092 g, 0.24 mmol). The solution was stirred at room temperature for 24 h. The solution was then poured into dilute HCl water. The product was isolated by the same procedure as Br-G4 (**9**). The yield was 43%. IR (KBr): 1663, 1553 cm^{-1} (amide C=O), 1601, 1451 cm^{-1} (aromatic). ^{1}H NMR (DMSO-d_6): δ 10.65−10.42 (CONH 62H), 8.57−8.50 (29H), 8.14−7.95 (124H), 7.62−7.45 (96H). ^{13}C NMR (DMSO-d_6): δ 165.98, 165.61, 139.39, 139.32, 135.99, 135.83, 134.58, 128.30, 127.61, 115.83, 115.53. Anal. Calcd for $C_{440}H_{315}BrN_{62}O_{62}$: C, 70.07; H, 4.21; Br, 1.06; N, 11.51. Found: C, 68.49; H, 4.65; Br, 1.28; N, 11.24.

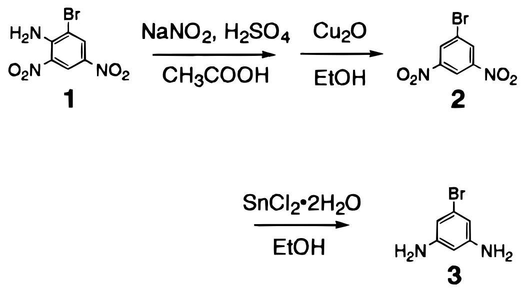
Coupling of HOOC-G3 to *p*-Phenylenediamine (20). In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed HOOC-G3 (**8**) (0.716 g, 0.4 mmol), *p*-phenylenediamine (**19**) (0.022 g, 0.2 mmol), NMP (2 mL), triethylamine (0.06 mL, 0.4 mmol), and DBOP (0.184 g, 0.48 mmol). The solution was stirred at room temperature for 24 h. The solution was then poured into dilute HCl water. The crude product was filtered and dissolved in THF. The solution was filtered and poured into ethyl acetate. The product was dissolved in THF and isolated using a preparative GPC. The isolated solution was concentrated using a rotary evaporator and poured into *n*-hexane. The product was filtered and dried at room temperature in vacuo. The yield was 36%. IR (KBr): 1663, 1553 cm^{-1} (amide C=O), 1601, 1451 cm^{-1} (aromatic). ^{1}H NMR (DMSO-d_6): δ 10.63−10.45 (CONH, 30H), 8.58−8.50 (14H), 8.15−7.97 (60H), 7.76 (4H), 7.63−7.48 (48H). Anal. Calcd for $C_{216}H_{156}N_{30}O_{30}$: C, 71.04; H, 4.31; N, 11.51. Found: C, 69.02; H, 4.79; N, 10.66.

Coupling of HOOC-G4 to *p*-phenylenediamine (**21**) and coupling of HOOC-G5 to *p*-phenylenediamine (**22**) were carried out by the same manner. The yield of **21** was 19%. IR (KBr): 1660, 1549 cm^{-1} (amide C=O), 1601, 1451 cm^{-1} (aromatic). ^{1}H NMR (DMSO-d_6): δ 10.65−10.43 (CONH, 62H), 8.57−8.49 (30H), 8.13−7.95 (124H), 7.74 (4H), 7.61−7.46 (96H). Anal. Calcd for $C_{440}H_{316}N_{62}O_{62}$: C, 70.81; H, 4.27; N, 11.64. Found: C, 69.45; H, 4.60; N, 11.24. The yield of **22** was 6.6%. IR (KBr): 1659, 1549 cm^{-1} (amide C=O), 1600, 1451 cm^{-1} (aromatic). ^{1}H NMR (DMSO-d_6): δ 10.65−10.40 (CONH, 126H), 8.57−8.48 (62H), 8.12−7.91 (252H), 7.73 (4H), 7.59−7.41 (192H). Anal. Calcd for $C_{888}H_{636}N_{126}O_{126}$: C, 70.69; H, 4.25; N, 11.70. Found: C, 69.67; H, 4.88; N, 11.52.

Core-3NO$_2$ (1,3,5-Tris(*N*-(4-nitrophenyl))benzenetricarboxamide) (25). In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed 4-nitroaniline (**24**) (9.12 g, 66 mmol) and DMAc (100 mL). The solution was cooled using a dry ice−acetone bath. After the solution was frozen, trimesoyl chloride (**23**) (5.31 g, 20 mmol) was added. The dry ice−acetone bath was replaced with an ice−water bath, and the solution was stirred for 3 h. The reaction mixture was then poured into dilute HCl water. The crude product was filtered and washed with hot methanol. The product was filtered and dried at room temperature in vacuo. The yield was 100%. IR (KBr): 1696, 1547 cm^{-1} (amide C=O), 1615, 1503 cm^{-1} (aromatic).

Core-3NH$_2$ (1,3,5-Tris(*N*-(4-aminophenyl))benzenetricarboxamide) (26). In a flask equipped with a magnetic stirrer and a hydrogen inlet were placed core-3NO$_2$ (**25**) (1.141 g, 2.0 mmol), DMAc (20 mL), and 10% Pd−C (0.319 g, 0.3 mmol/Pd). The flask was degassed and purged with hydrogen

Scheme 1. Synthesis of 3,5-Diaminobromobenzene



several times and then stirred at room temperature for 2 days. The mixture was filtered using Celite-545. The solution was poured into water. The product was filtered and dried at 80 °C in vacuo. The yield was 81%. IR (KBr): 1649, 1538 cm^{-1} (amide C=O), 1608, 1516 cm^{-1} (aromatic). ^{1}H NMR (DMSO-*d*$_6$): δ 10.09 (s, CONH 3H), 8.56 (s, 3H), 7.43, 7.40 (d, 6H), 6.59, 6.56 (d, 6H), 5.01 (br, NH$_2$).

Coupling of HOOC-G3 to Core-3NH$_2$ (27). In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed core-3NH$_2$ (0.096 g, 0.2 mmol), HOOC-G3 (1.342 g, 0.75 mmol), NMP (4 mL), triethylamine (0.09 mL, 0.6 mmol), and DBOP (0.278 g, 0.72 mmol). The solution was stirred at room temperature for 24 h. The solution was then poured into dilute HCl water. The product was isolated by the same procedure as HOOC-G3 (**8**).

Coupling of HOOC-G4 to core-3NH$_2$ (**28**) and coupling of HOOC-G5 to core-3NH$_2$ (**29**) were carried out by the same manner.

Measurements. Infrared (IR) spectra were recorded using a Shimadzu FTIR-8100 Fourier transform infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded using 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, three polystyrene−divinylbenzene columns (two Shodex KD-806 M and KD-802), and a Shodex RI-71 refractive index detector. GPC measurements using THF as an eluent were carried out by using a Shodex DS-4 pump, a polystyrene−divinylbenzene column (Shodex KF-802.5 or Shodex KF-806 M), and a Shodex RI SE−51 refractive index detector. Preparative GPC was carried out by using a Shodex DS-4 pump, a polystyrene−divinylbenzene column (Shodex KF-2003), a JASCO 875-UV UV/vis detector, and THF as an eluent. MALDI−TOF mass spectra were recorded on a Kratos Kompact MALDI III instrument operated in reflectron detection mode to generate positive ion spectra using 2-(4-hydroxyphenylazo)benzoic acid (HABA) as a matrix, THF as a solvent, and cesium iodide as an additive agent. Thermogravimetric analyses (TGA) were carried out using a Seiko TGA 6200 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} under nitrogen. Differential scanning calorimetry measurements (DSC) were carried out using a Seiko DSC 6200 at a heating rate of 10 °C min^{-1} under nitrogen. Static light scattering measurements (SLS) were carried out using an Otsuka SLS-6000 and THF as a solvent at 633 nm.

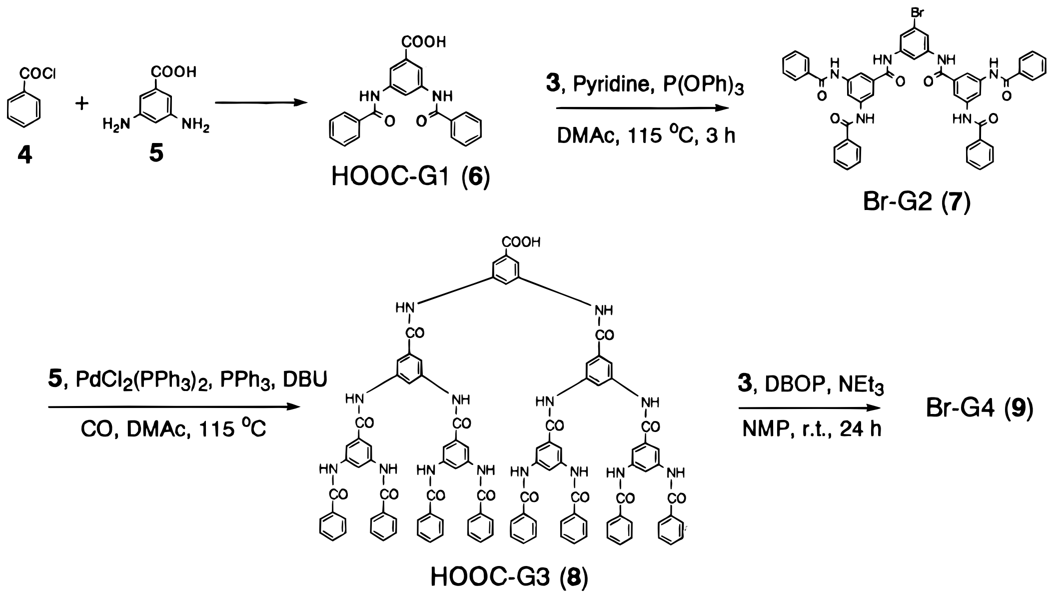
Results and Discussion

Synthesis of Aramid Dendrons by an Orthogonal Approach. 3,5-Diaminobenzoic acid and 3,5-diaminobromobenzene were selected as building blocks. 3,5-Diaminobromobenzene was prepared from 2-bromo-4,6-dinitroaniline in two steps, as shown in Scheme 1. Details for these preparations are provided in the Experimental Section. The synthetic route of the aromatic polyamide dendrons by the orthogonal approach is shown in Scheme 2. 3,5-Diaminobenzoic acid was reacted with benzoyl chloride in DMAc to obtain the first-generation dendron (HOOC-G1, **6**). Although precipitation was observed during the reaction, the reaction mixture was poured into dilute HCl water. The brownish product was washed with hot methanol in order to remove excess benzoyl chloride and its hydrate. Further purification of **6** was done by dissolving the product in THF and reprecipitation into hexane.

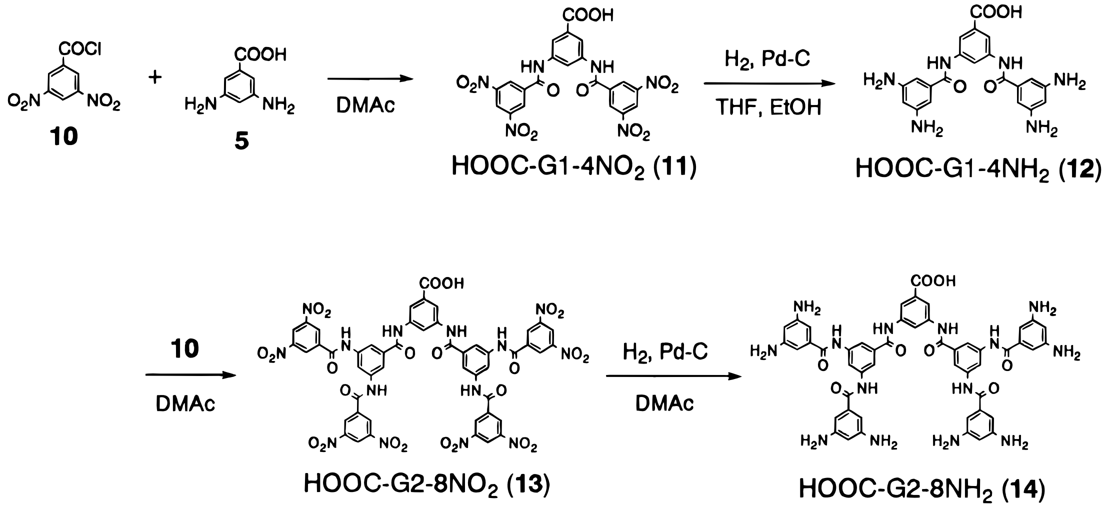
The second-generation dendron (Br-G2, **7**) was prepared from HOOC-G1 (**6**) and 3,5-diaminobromobenzene using the direct condensation reaction in the presence of triphenyl phosphite (TPP) and pyridine as condensing agents. The crude product was precipitated by pouring into dilute HCl water. Then the precipitate was dissolved in the mixture of THF/DMAc (9:1), followed by pouring it into methanol to reprecipitate **7**. The formation of **7** was confirmed by ^{1}H NMR, ^{13}C NMR, and MALDI−TOF mass spectroscopy.

The first- and second-generation dendrons, **6** and **7**, were able to be isolated by reprecipitation in hexane and methanol, respectively, without column chromatography. Thus, these dendrons can be synthesized easily on a large scale.

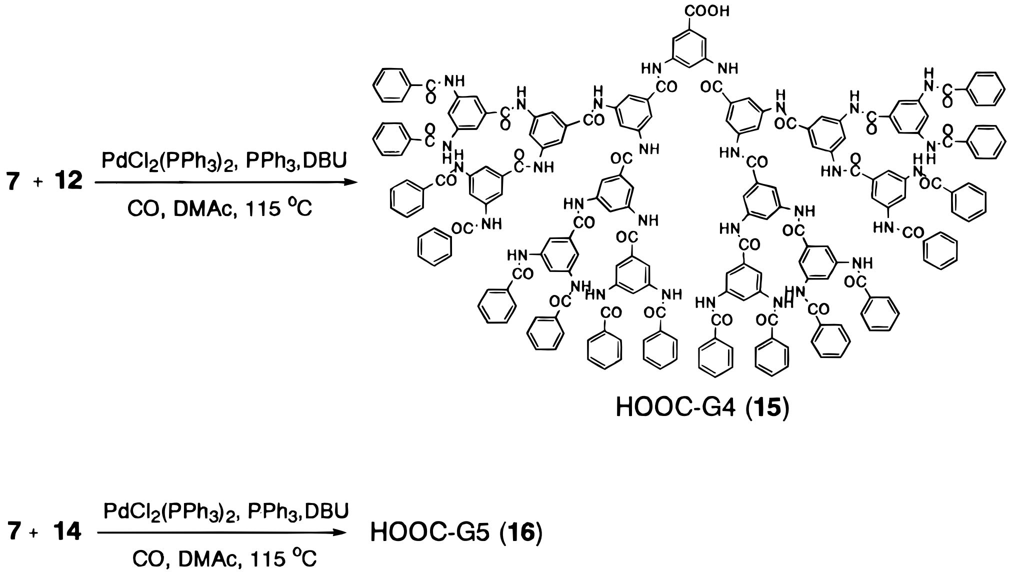
Scheme 2. Synthesis of Aromatic Polyamide Dendrons by an Orthogonal Approach



Scheme 3. Synthesis of HOOC-G1-4NH$_2$ (12) and HOOC-G2-8NH$_2$ (14)



Scheme 4. Synthesis of G4 and G5 Aramid Dendrons by a Double-Stage Convergent Approach



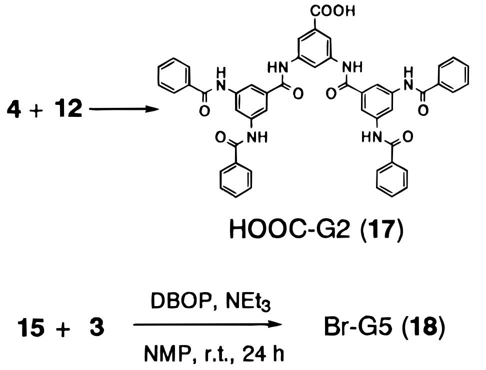
The third-generation dendron (HOOC-G3, **8**) was synthesized from Br-G2 (**7**) and 3,5-diaminobenzoic acid by the palladium-catalyzed CO insertion reaction. The reaction in the presence of 2.4 equiv of DBU based on 3,5-diaminobenzoic acid (1.2 equiv based on the amino group) did not proceed efficiently, because DBU was tied up with the acid group of 3,5-diaminobenzoic acid and became insufficient to neutralize the byproduct, hydrogen bromide. The reaction using 4.8 equiv of DBU based on the monomer (2.4 equiv based on the amino group) proceeded with high conversion. Since the starting materials, 3,5-diaminobenzoic acid and Br-G2 (**7**), were soluble in ethyl acetate, the crude product was reprecipitated by a THF/DMAc–ethyl acetate (9:1) system. However, the GPC curve of the product showed two peaks, which correspond to HOOC-G3 (**8**) and a one-substituted building block. Therefore, **8** was isolated by a preparative GPC using THF as an eluent.

HOOC-G3 (**8**) was reacted with 3,5-diaminobromobenzene by the direct condensation reaction to obtain the fourth-generation dendron (Br-G4, **9**). The reaction in the presence of TPP/pyridine proceeded inefficiently, as judged by ^{1}H NMR and GPC. Br-G4 (**9**) was then synthesized by the direct condensation reaction using DBOP as a condensing agent. The elution volume of the crude product shifted to higher molecular weight side than that of HOOC-G3 (**8**) in GPC. The product was isolated by the same procedure as **8** in 54% yield. It was found that DBOP was more suitable than TPP/pyridine for the synthesis of the higher generation dendrons.

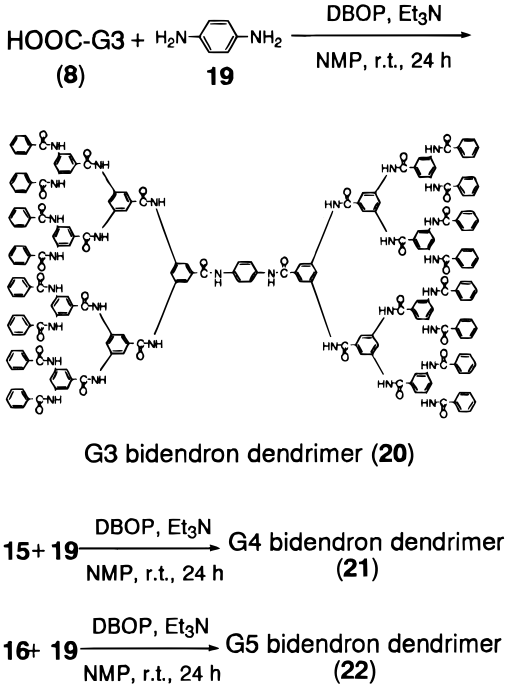
Synthesis of Aramid Dendrons by a Double-Stage Convergent Approach. Although the fourth-generation dendron (**9**) with only amide linkages was synthesized in four steps, dendrons higher than second generation could not be prepared on a large scale basis due to quantitative limitations of the preparative GPC used in the purification. The application of the double-stage convergent growth approach,[12,13] in which the preformed dendrons possessing functional groups are used as building blocks, allows for the synthesis of the fourth- and fifth-generation dendrons from the second-generation dendron in one step. Therefore, G1, possessing four amino groups (HOOC-G1-4NH$_2$ **12**), and G2, possessing eight amino groups (HOOC-G2-8NH$_2$ **14**), were synthesized by a divergent method independently (Scheme 3), and these dendrons were used in place of 3,5-diaminobenzoic acid.

HOOC-G1-4NH$_2$ (**12**) was prepared by the hydrogenation of HOOC-G1-4NO$_2$ (**11**), which was synthesized from 3,5-diaminobenzoic acid and 3,5-dinitrobenzoyl

Scheme 5. Synthesis of HOOC-G2 (17) and Br-G5 (18)



Scheme 6. Synthesis of Aramid Bidendron Dendrimers



chloride. The crude **11** was washed with hot methanol in order to remove excess 3,5-dinitrobenzoyl chloride and its hydrate and then purified by recrystallization from THF. The structure of **11** was confirmed by ^{1}H and ^{13}C NMR. The hydrogenation of **11** afforded the product **12**, as judged by ^{1}H and^{13}C NMR, and further purification was not necessary to use **12** as a building block. HOOC-G2-8NH$_2$ (**14**) was also prepared by the hydrogenation of HOOC-G2-8NO$_2$ (**13**), which was prepared from **12** and 3,5-dinitrobenzoyl chloride. **13** was able to be isolated by reprecipitation into methanol because other compounds such as **12**, 3,5-dinitrobenzoyl chloride, and its hydrate were soluble in methanol. Because **13** had poor solubility in THF and ethanol, DMAc was used as a solvent in the hydrogenation. The hydrogenation proceeded quantitatively, and **14** was isolated by pouring the reaction solution into ethyl acetate.

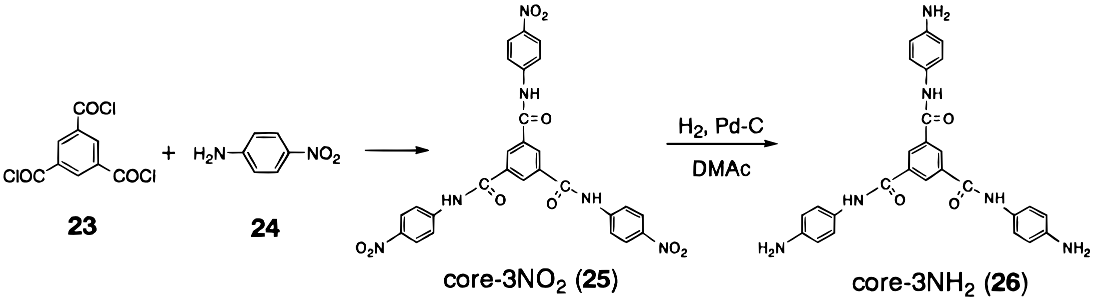
The fourth-generation dendron (HOOC-G4 **15**) was prepared from Br-G2 (**7**) and HOOC-G1-4NH$_2$ (**12**) by the CO insertion reaction (Scheme 4). GPC curve of the crude product showed two peaks. The strong peak with narrow distribution correspond to **15**, and the other low intensity peak correspond to excess **7**. The product was isolated by preparative GPC in 63% yield. The fifth-generation dendron (HOOC-G5 **16**) was synthesized from Br-G2 (**7**) and HOOC-G2-8NH$_2$ (**14**). **16** was isolated by the same procedure as **15** in 38% yield. Formation of **15** and **16** were confirmed by ^{1}H NMR and MALDI−TOF spectroscopies. Because the starting materials, **7**, **12**, and **14**, could be isolated without column chromatography, these dendrons can be synthesized readily on a large scale. Consequently, the synthesis of the fifth-generation dendron (**16**) benefited from the ease of synthesis of the starting materials.

To compare each generation dendron possessing a carboxylic acid at a focal point, HOOC-G2 (**17**) was synthesized from HOOC-G1-4NH$_2$ (**12**) and benzoyl chloride (Scheme 5). In addition, Br-G5 (**18**) was synthesized from HOOC-G4 (**15**) and 3,5-diaminobromobenzene by the direct condensation reaction using DBOP as a condensing agent. **18** was isolated by the same procedure as Br-G4 (**9**) in 43% yield.

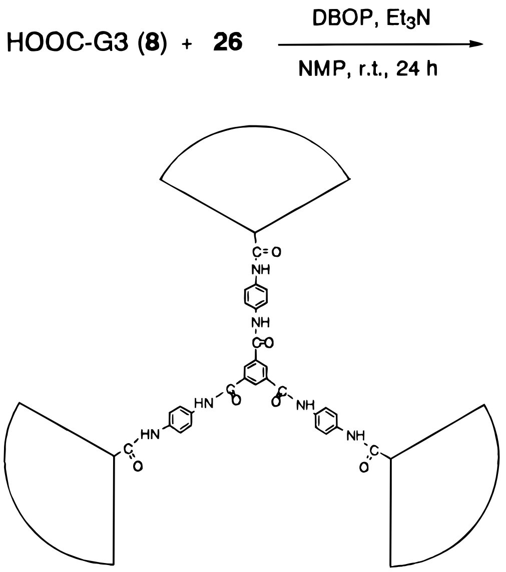
Coupling of Dendrons to Core Molecules. The bidendron dendrimer was synthesized from HOOC-G3 (**8**) and *p*-phenylenediamine, used as a difunctional core molecule (Scheme 6). The coupling reaction and purification were carried out by the same procedure as the synthesis of Br-G4 (**9**), and the isolated product was obtained in 36% yield. ^{1}H NMR spectrum of the product showed a signal at 7.76 ppm pertaining to protons of the core benzene ring in addition to **8**. The fourth- and fifth-generation dendrimers (**21** and **22**) were also synthesized in 19% and 6.6% yield, respectively. The low yield is possibly caused by increasing steric hindrance at a focal point with increasing the generation number.

The coupling of HOOC-G3 (**8**) to a trifunctional core was attempted. To reduce sterical hindrance around the core and to design dendrimers with only amide linkages, 1,3,5-tris(*N*-(4-aminophenyl))benzenetricarboxamide (core-3NH$_2$, **26**) was selected as a trifunctional core molecule. **26** was synthesized by the hydrogenation of 1,3,5-tris(*N*-(4-nitrophenyl))benzenetricarboxamide (core-3NO$_2$, **25**), which was prepared from trimesoyl chloride and 4-nitroaniline (Scheme 7). The direct condensation reaction of **8** with **26** was carried out using DBOP as a condensing agent (Scheme 8). GPC measurement of the

Scheme 7. Synthesis of the Trifunctional Core Molecule



Scheme 8. Attempted Synthesis of Aramid Tridendron Dendrimers



G3 tridendron dendrimer (**27**)

crude product in DMF revealed two peaks corresponding to the dendrimer (**27**) and **8**. The isolation of the dendrimer using preparative GPC failed because the product was only partially soluble in THF. The syntheses of the fourth- and fifth-generation tridendron dendrimers (**28** and **29**) were also attempted. GPC curves for the crude products suggest the formation of tridendron dendrimers since the peaks for the products were shifted forward high molecular weight in comparison with the bidendron dendrimers (**21** and **22**). However, the isolation of **28** and **29** was also unsuccessful due to the limited solubility in THF, similar to the case of **27**.

Characterization of Aramid Dendrons by ^{1}H NMR, ^{13}C NMR, and MALDI–TOF Mass Spectroscopies. The structures of the dendrons were confirmed by ^{1}H NMR (Figures 1–3) and ^{13}C NMR spectra. In ^{1}H NMR spectra, the assignment of the first- and second-generation dendrons was straightforward with amide and benzene ring proton signals. In all cases, the *m*- and *p*-position hydrogens located on the terminal benzene rings were observed as multiplets in the 7.45–7.65 ppm region. The signals at 8.45–8.65 and 7.95–8.20 ppm were assigned to *p*-position hydrogens, except for the hydrogens on the terminal benzene rings, and all *o*-position hydrogens, respectively. In the case of Br-G2 (**7**), *p*- and *o*-position hydrogens of the interior benzene ring were observed at 8.35 and 7.83 ppm respectively, but these signals have very low intensity in the case of Br-G4 (**9**) and Br-G5 (**18**). ^{13}C NMR spectra showed the chemical shift differences associated with the core, dendritic, and outer layers. However, elemental analyses for high-generation dendrons deviated slightly from calculated values. The deviation was probably caused by encapsulated solvents such as DMAc into dendrons. Actually, in some cases, DMAc was detected by ^{1}H NMR spectra for dendrons after isolation by preparative GPC using THF as an eluent.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI–TOF MS) was used for the analysis of the larger dendrons. All of the spectra confirmed that the dendrons were essentially pure and

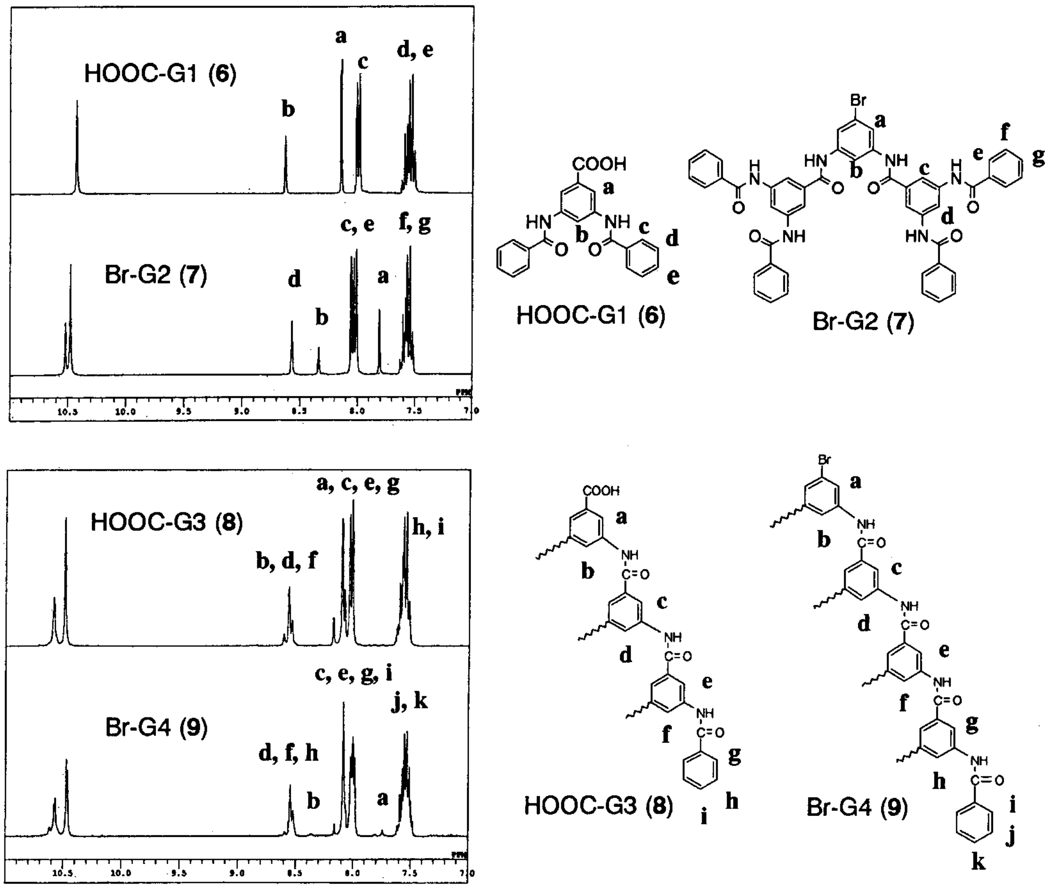


Figure 1. ^{1}H NMR spectra of aromatic polyamide dendrons.

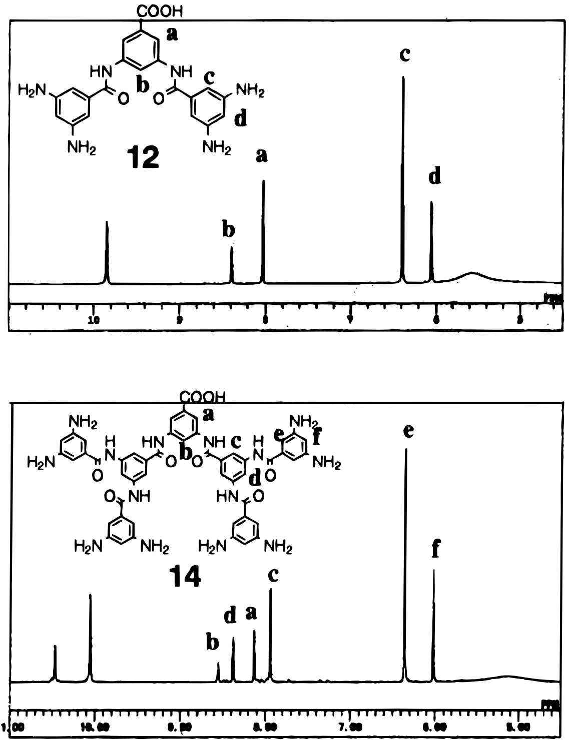


Figure 2. ^{1}H NMR spectra of HOOC-G1-4NH$_2$ (**12**) and HOOC-G2-8NH$_2$ (**14**).

Table 1. Solubility of Aramid Dendrons and Bidendron Dendrimers[a]

	1 M NaOH(aq)	MeOH	ace-tone	EtOAc	THF	DMAc
HOOC-G1 (**6**)	+	+−	+	+	+	+
HOOC-G2 (**17**)	−	+−	+	+	+	+
HOOC-G3 (**8**)	−	−	−	−	+	+
HOOC-G4 (**15**)	−	−	−	−	+	+
HOOC-G5 (**16**)	−	−	−	−	+	+
Br-G2 (**7**)	−	−	+	+	+	+
Br-G4 (**9**)	−	−	−	−	+	+
Br-G5 (**18**)	−	−	−	−	+	+
HOOC-G1-4NO$_2$ (**11**)	+	+−	+	+	+	+
HOOC-G1-4NH$_2$ (**12**)	+	+−	+	+	+	+
HOOC-G2-8NH$_2$ (**13**)	−	−	−	−	−	+
HOOC-G2-8NH$_2$ (**14**)	−	−	−	−	−	+
G3 dendrimer (**20**)	−	−	−	−	+	+
G4 dendrimer (**21**)	−	−	−	−	+	+
G5 dendrimer (**22**)	−	−	−	−	+	+

[a] Key: (+) soluble; (+−) partially soluble; (−) insoluble.

monodisperse. The spectrum of HOOC-G5 (**16**) showed the expected peaks at 7531.7 (M + Na$^+$) and 7641.5 (M + Cs$^+$), as shown in Figure 4. Although the dendron possessing eight functional groups was used as the building block, the peaks from incompletely substituted product were not detected.

Solubility and Thermal Properties of Aramid Dendrons. The series of aramid dendrons consisted of aromatic rings and amide linkages and were soluble in aprotic polar solvents such as DMF, DMAc, NMP, and DMSO (Table 1). Surprisingly, even HOOC-G5 (**16**) and Br-G5 (**18**) (63-mer, with molecular weights of 7508 and 7543) were also soluble in THF. HOOC-G1 (**6**) was soluble in 1 M NaOH(aq) and many organic solvents. Although the precipitation was not observed by pouring the HOOC-G1 (**6**) solution in THF or DMAc into methanol, **6** in the solid state was not very soluble in methanol. This behavior was also observed in HOOC-G2 (**17**), whereas Br-G2 (**7**) was insoluble in methanol both in solid state and in THF or DMAc solution. The solubility limit of **7** and **17** was higher than **6**.[17] The first- and second-generation dendrons (**6**, **7**, and **17**) were soluble in acetone and ethyl acetate in addition to amide solvent and THF. Although crude HOOC-G3, HOOC-G4, and HOOC-G5 (**8**, **15**, and **16**) were once dissolved in THF, slight precipitation occurred later after several hours. This may be due to the formation of salts between HOOC-dendrons and amino groups of partially substituted byproduct. The isolated HOOC-dendrons by the preparative GPC were quite soluble in THF. Solubility of HOOC-G1-4NO$_2$ (**11**) and HOOC-G1-4NH$_2$ (**12**) was similar to HOOC-G1 (**6**), while HOOC-G2-8NO$_2$ (**13**) and HOOC-G2-8NH$_2$ (**14**) were insoluble in acetone, ethyl acetate and THF. The bidendron dendrimers (**20**, **21**, and **22**) were soluble in THF just like the Br-dendrons (**7**, **9**, and **18**).

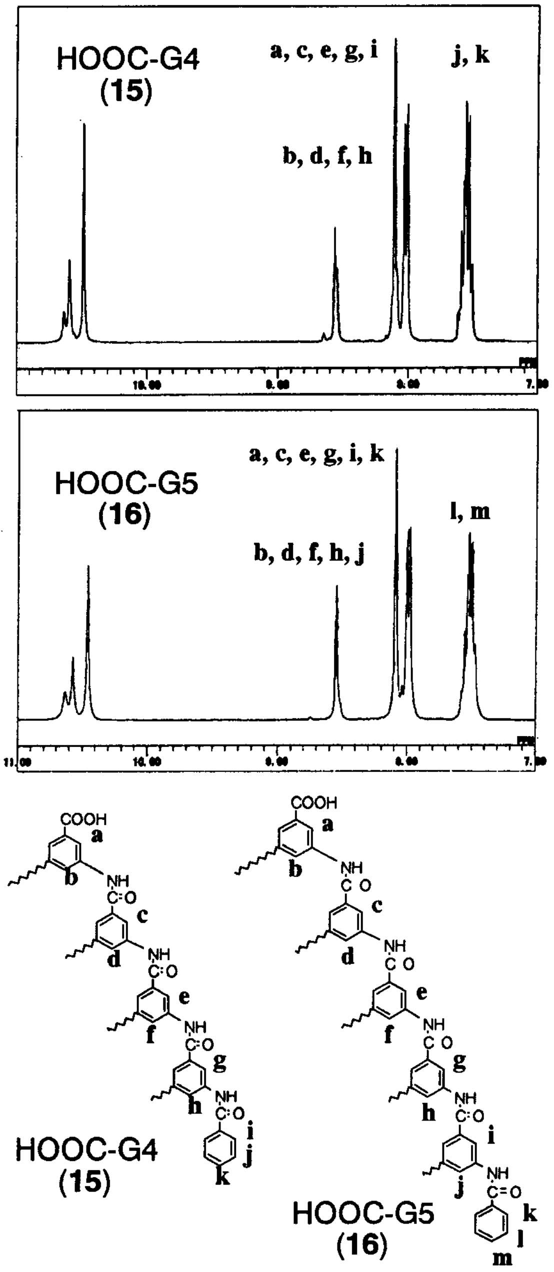


Figure 3. ^{1}H NMR spectra of HOOC-G4 (**15**) and HOOC-G5 (**16**).

Thermal properties of dendrons were examined by DSC and TGA (Table 2). Although the molecular weight

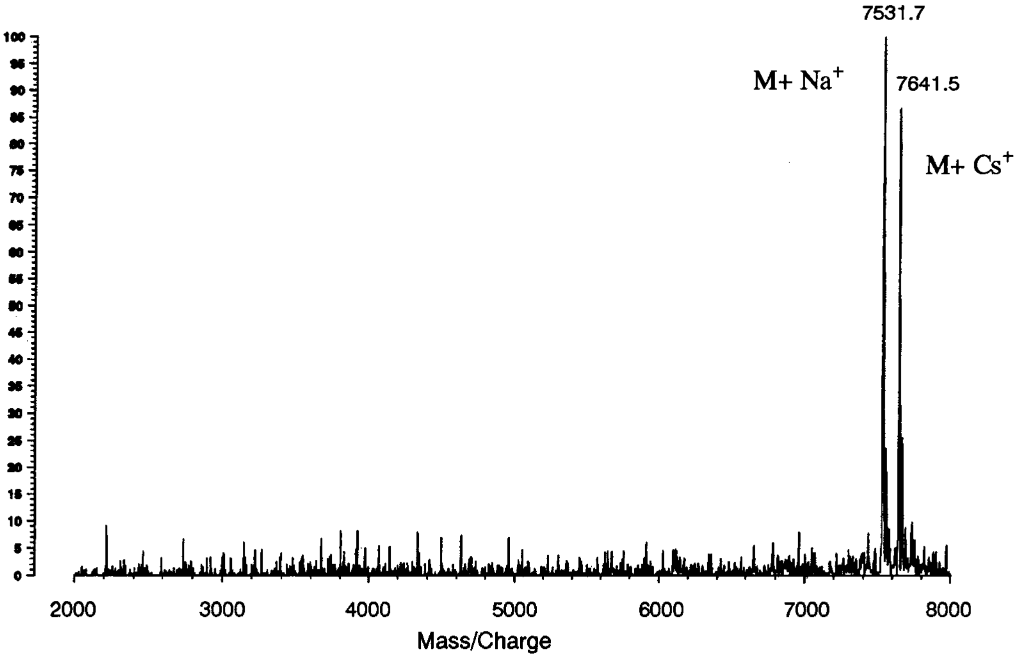


Figure 4. MALDI−TOF MS spectrum of HOOC-G5 (**16**).

Table 2. Thermal Analysis of Aramid Dendrons

dendron	formula weight	T_g[a] (°C)	T_d[b] (°C)
HOOC-G1 (**6**)	360		300
HOOC-G2 (**17**)	837		305
HOOC-G3 (**8**)	1790	245	315
HOOC-G4 (**15**)	3696	260	340
HOOC-G5 (**16**)	7508	275	375
Br-G2 (**7**)	872		350
Br-G4 (**9**)	3731	255	355
Br-G5 (**18**)	7543	270	345

[a] Determined by DSC at a heating rate of 10 K/min in N_2 (second scan). [b] Determined by TGA at a heating rate of 10 K/min in N_2.

of HOOC-G3 (**8**) (15-mer) was 1790 g mol^{-1}, it has a high glass transition temperature (T_g) of 245 °C. T_g was dependent on the generation number of dendrons and increased to 275 °C for HOOC-G5 (**16**). Thermal decomposition temperature (T_d) was more than 300 °C. The aramid dendrons exhibited high thermal stability though the T_g and T_d values were slightly lower than those of their linear analogues.

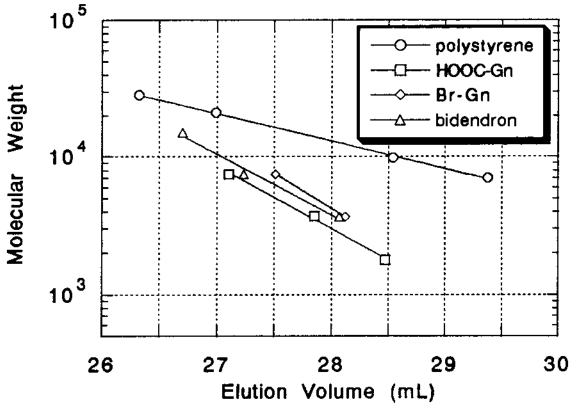


Figure 5. Elution volume (peak top) of aramid dendrimers in DMF containing 0.01 mol/L of LiBr.

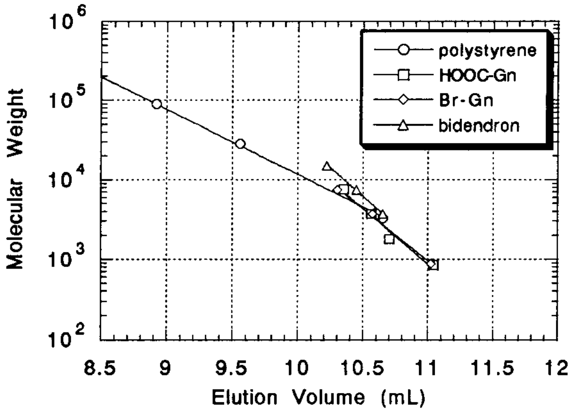


Figure 6. Elution volume (peak top) of aramid dendrimers in THF.

GPC Measurements of Aramid Dendrons and Dendrimers. GPC measurements were carried out in both THF and DMF containing 0.01 mol/L of LiBr. Polydispersity indices of all dendrons and dendrimers were lower than 1.10. The relationship between elution volume and molecular weight of dendrons and dendrimers was investigated, as shown in Figures 5 and 6. The difference in the elution volume between dendrons and bidendron dendrimers was not observed, when the molecular weights were close to each other. It suggests that molecular size was not so affected by the difference between *meta*-linked and *para*-linked aromatic rings at the most interior part. The plots of HOOC-dendrons, Br-dendrons, and bidendron dendrimers were found to be linear, and the slopes of the lines were steeper than that of polystyrene. This suggests that the tendency to increase in the molecular size of the dendritic molecules is weaker than that of polystyrene when the molecular weight of both molecules are increased equally. The molecular weight of dendrimers is often underestimated by GPC because the hydrodynamic volume of dendritic macromolecules is smaller than that of its linear isomer. In this work, however, the molecular weights of the aramid dendrons and dendrimers calculated by GPC based on polystyrene standards were much larger than their formula weights. We assume that the overestimation was caused by the rigid plane structure of the dendritic polyamides. The same overestimation by GPC has been reported in the case of poly(phenylenevinylene) dendrimers.[16] On the other hand, the molecular weights based on polystyrene standards were close to the theoretical values in THF. Since DMF was a better solvent for the aramid dendrons than THF, the structure of these molecules in DMF was probably more extensive than that in THF.

Static light scattering (SLS) measurements of HOOC-G3 (**8**) and HOOC-G5 (**16**) were carried out in THF. Zimm plots gave molecular weights of 187 000 and 842 000, respectively. These data correlate very well within the Zimm model, thus suggesting low polydispersity. The M_ws determined by SLS are a hundred times as much as the formula weights. It suggests that aggregation of dendrons occurred in THF. The aggregation probably occurs due to hydrogen bonds between amide bonds, but the reason for the narrow distribution is not understood. A similar problem was reported by Frey et al. on the aggregation of hyperbranched polycarbosilane coupled trifunctional ester−amide core molecule.[23] However, GPC measurements of **8** and **16** in THF yielded molecular weights of 2880 and 5690 respectively based on polystyrene standards. It is assumed that aggregates were broken up under the influence of strong shear forces in the GPC columns.

Conclusions

The orthogonal approach halves the number of steps by avoiding deprotection or activation steps. The homogeneous aromatic polyamide dendrons were obtained by the orthogonal approach, in which the direct condensation reaction and the CO insertion reaction were selected to form amide linkages. With this method, the fourth-generation aromatic polyamide dendron was synthesized in just four steps. The higher generation dendrons can also be synthesized rapidly by the double-stage convergent approach. The fifth-generation dendron, HOOC-G5 (**16**), could be synthesized in six steps only involving one purification by a preparative GPC. This approach can be utilized to allow rapid synthesis of various dendrimers.

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References and Notes

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