One-Pot Synthesis of Dendritic Poly(amide-urea)s via Curtius Rearrangement. 2. Synthesis and Characterization of Dendritic Poly(amide-urea)s

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ABSTRACT: Dendritic poly(amide-urea)s from the first to fourth generations with a very narrow molecular weight distribution were prepared from 1,1,1-tris(4-carboxymethyloxyphenyl)ethane as a core molecule, using aminodicarboxylic acid and aminodicarbonyl azide as two AB_2 monomers in a one-pot procedure. This procedure involves activation of end carboxyl groups with a condensing agent, diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate, condensation of the active amide with aminodicarbonyl azide, the Curtius rearrangement in the presence of aminodicarboxylic acid, and, finally, capping of the end groups with *p-tert*-butylaniline. All dendritic polymers were obtained quantitatively and fully characterized by elemental analysis and IR and NMR spectroscopies. Number average molecular weights (M_n) of dendritic poly(amide-urea)s were estimated by end group analysis, and each dendritic poly(amide-urea) had M_n close to the calculated value. Degrees of branching for the second and third generation dendritic polymers were found to be 0.93 and 0.90, respectively by ^{1}H NMR spectroscopy.

Introduction

The well-characterized perfect structures of dendrimers are constructed by discrete stepwise procedures that consist of a tedious repetitive protection−deprotection and purification process in each generation.[1,2] On the other hand, hyperbranched polymers can be prepared easily by one-step polycondensation of multifunctional AB_n ($n \geq 2$) monomers, but which are not as faultless as the stepwise constructed dendrimers, such as a low degree of branching (DB) and a broad molecular weight distribution.[3] Thus, it is important to develop an efficient method to prepare dendritic polymers with a high DB (>0.9) and a very narrow molecular weight distribution.

In a preceding paper, we reported the syntheses of monomers, the aminodicarboxylic acid, 5-[3-(4-aminophenyl)propionylamino]isophthalic acid hydrochloride (**1**), aminodicarbonyl azide, 5-[3-(4-aminophenyl)propionylamino]isophthaloyl azide hydrochloride (**2**), and model reactions for the one-pot synthesis of dendritic aromatic poly(urea-amide)s. On the basis of the detailed model reactions, this article reports the successful one-pot synthesis of dendritic aromatic poly(urea-amide)s with a high DB and very narrow molecular weight distribution from AB_2 monomers, **1** and **2** using condensation and the Curtius rearrangement

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Experimental Section

Materials. Tetrahydrofuran (THF) was freshly distilled before use. Triethylamine (TEA) was dried over anhydrous 3 Å molecular sieves and freshly distilled before use. *p-tert*-Butylaniline, 1-methyl-2-pyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) were distilled under reduced pressure before use. The condensing agent, diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP), was prepared according to the reported procedure.[4] The other reagents were obtained commercially and used as received.

Measurement. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer PARAGON 1000. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL JNM-LA600 in DMSO-d_6 as a solvent. All NMR spectra of the products were assigned with the aid of the ^{1}H{^{13}C}-COSY, ^{1}H-homodecoupling, and the ^{13}C DEPT techniques. In the chemical structure, plane and prime numbers show numbering of proton and carbon, respectively. Gel permeation chromatography (GPC) was performed in THF as an eluent using a TOSHO 8020 HPLC apparatus equipped with four TSKgel columns (GMH_{HR}-M, GMH-N, GMH_{HR}-H(S), G1000H) using a RI detector and polystyrene calibration. High-performance liquid chromatography (HPLC) was performed in acetonitrile/water 2:1 mixture containing 0.1% phosphoric acid using a TOSHO 8020 HPLC apparatus with ODS-80Ts columns equipped with a UV detector using nitrobenzene as an internal standard. Elemental analysis was performed on a CE INSRTUMENTS EA 1110. Thermal analysis was performed on a MAC Science DSC 3200 at a heating rate of 10 K min^{-1}.

1,1,1-Tris(4-carboxymethyloxyphenyl)ethane (3). The core molecule **3** was prepared as reported.[5a]

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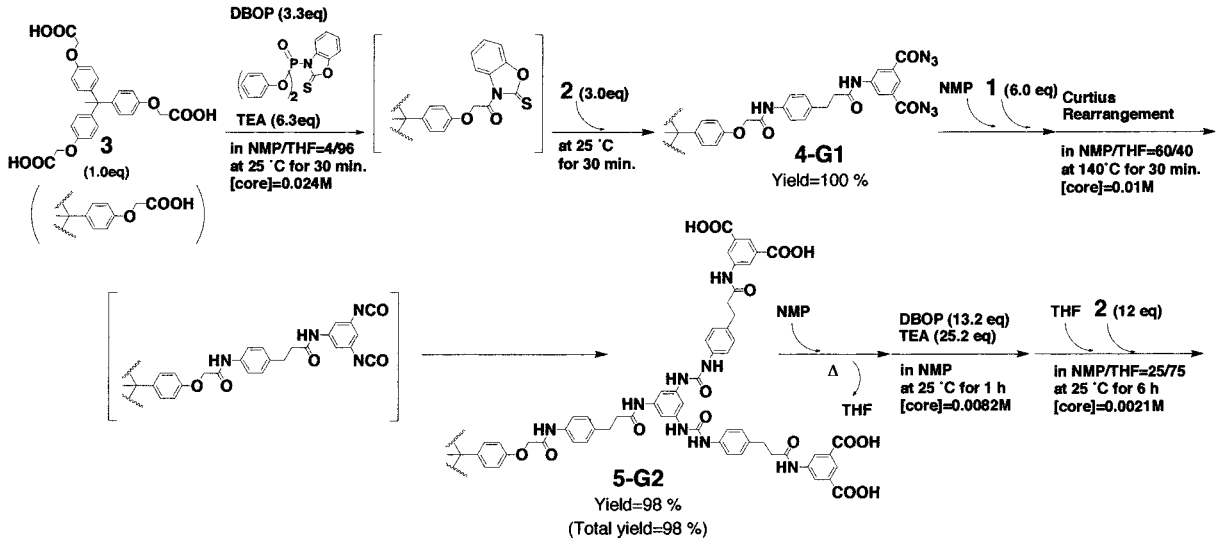
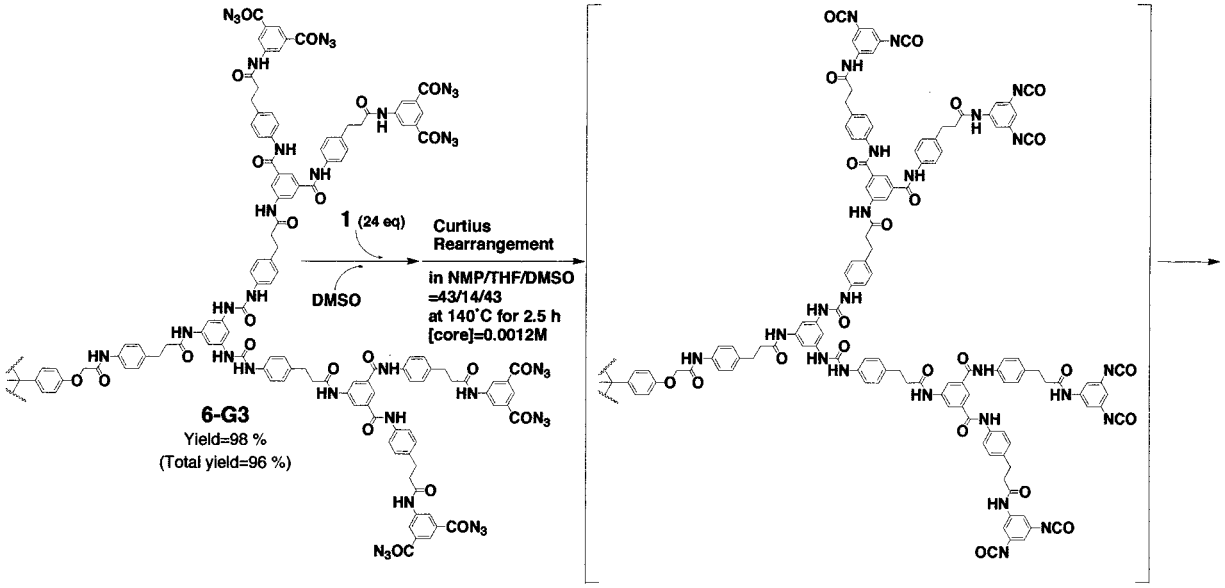
Scheme 1



Scheme 2

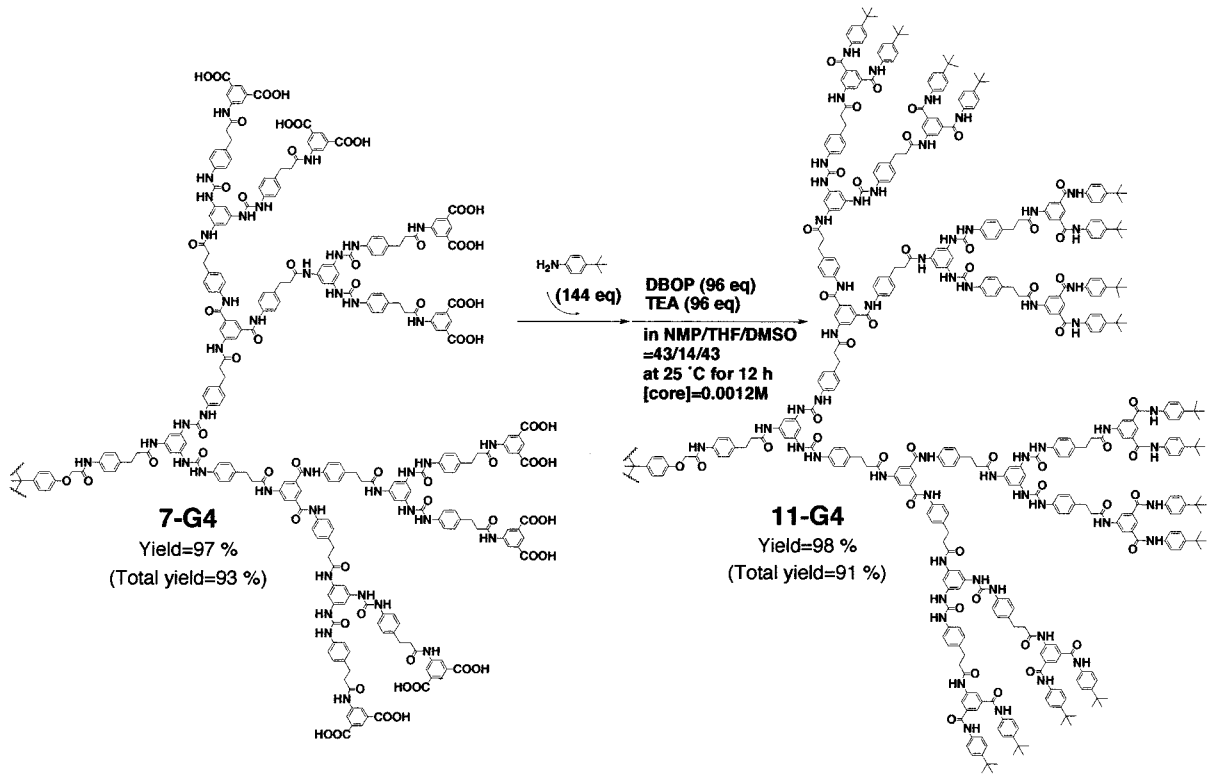


General Synthetic Procedure of the Fourth Generation Dendritic Poly(amide-urea) (11-G4). A pressure resistant vessel equipped with a septum seal and metal cock was used as a reactor for this reaction. To a solution of **3** (4.80 mg, 0.01 mmol) and DBOP (12.65 g, 0.033 mmol) in THF (0.4 mL)/NMP (0.015 mL), TEA (6.38 mg, 63 mmol) was added under a dry argon atmosphere. The solution was stirred at 25 °C for 30 min, then 3 equiv of **2** (12.44 mg, 0.03 mmol) was added to the solution and condensation was performed at 25 °C for 30 min (**4-G1**). To this solution, NMP (0.6 mL) and 6 equiv of **1** (21.89 mg, 0.06 mmol) were added, the solution was stirred to dissolve **1**, and then TEA (6.38 mg, 0.063 mmol) was added. The reactor was sealed with a septum and metal cock under dry argon atmosphere, and the solution was stirred at 140 °C for 30 min (**5-G2**). A septum seal and metal cock was removed from the vessel under dry argon atmosphere, and NMP (0.6 mL) was added to the solution. The solution was heated gradually at 100 °C for 1 h to evaporate THF and cooled to 25 °C. DBOP (50.6 mg, 0.132 mmol) and TEA (25.5 mg, 0.252 mmol) were added to the solution, and the reaction continued for 1 h. THF (3.6 mL) and 12 equiv of **2** (49.8 mg, 0.12 mmol) were added into the solution and stirred for 12 h at 25 °C (**6-G3**). To the solution, 24 equiv of **1** (87.6 mg, 0.24 mmol) and DMSO (3.6 mL) were added. The reactor was then sealed with a septum and metal cock under dry argon atmosphere and heated at 140 °C for 2.5 h (**7-G4**). Finally, *p*-*tert*-butylaniline (214.9 mg, 1.44 mmol) was added to the solution, followed by dropwise addition of DBOP (368 mg, 0.96 mmol) and TEA (16.2 mg, 0.96 mg), and the condensation was performed at 25 °C for 12 h. The solution was poured into a 5% $NaHCO_3$ solution, and the precipitate was collected by filtration, washed with methanol, and dried in vacuo at 25 °C to give **11-G4** as a white powder. The addition of DMSO in the end capping reaction was not carried out except for **11-G4**. Yield = 197.1 mg (93%). The 10% weight loss temperature in air by thermal gravimetric analysis (TGA) measurement (Td_{10}): 371 °C. IR (KBr) ν (cm^{-1}): 3311 (N−H), 2962, 2868 (CH_3), 1665 (O═CNH), 1598 (Ar), 1518 (O═CNH), 1364, 1249, 1213 ($C(CH_3)_3$). Anal. Calcd for $C_{1271}H_{1308}N_{168}O_{141}\cdot 33.5H_2O$: C, 70.04; H, 6.36; N, 10.80. Found: C, 70.18; H, 6.41; N, 10.64. M_n by ^1H NMR analysis (M_n(found)): 20750 (calcd, 21193). M_w/M_n by GPC analysis in THF as an eluent: 1.15.

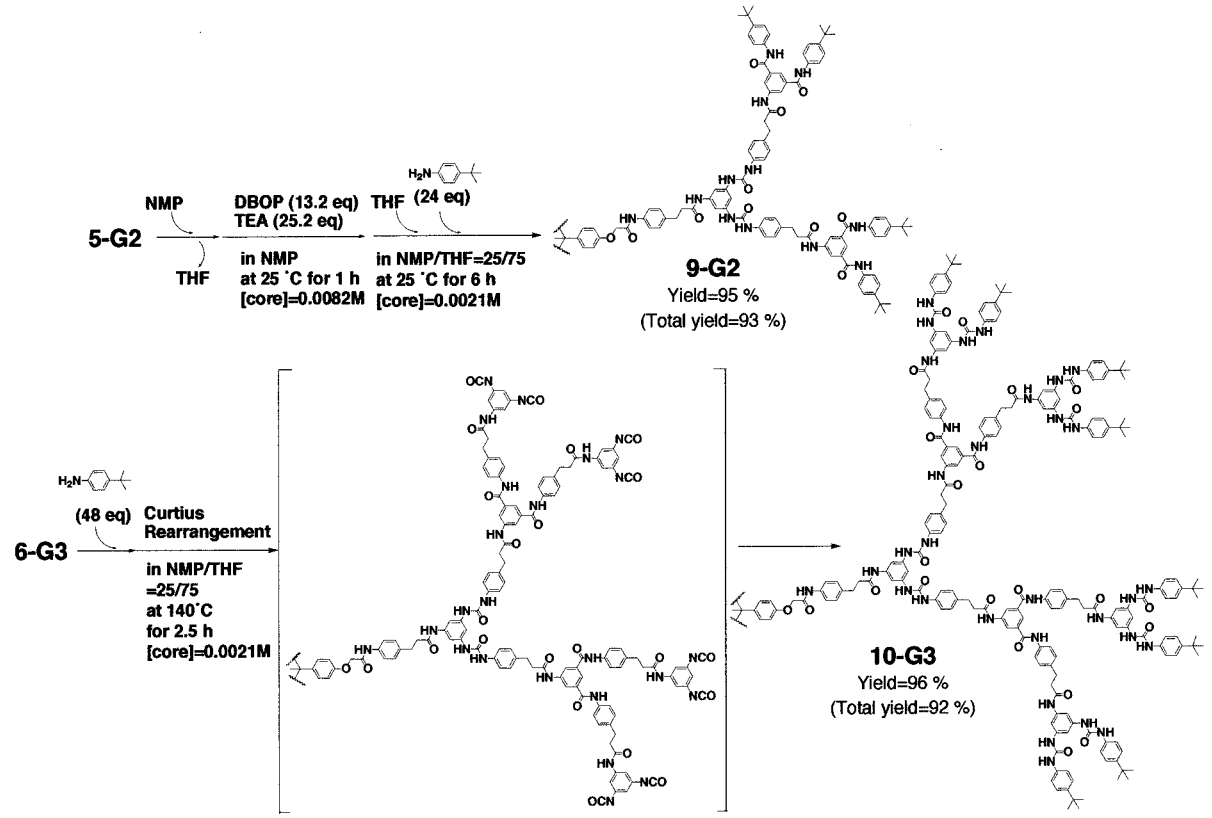
4-G1. White powder. Yield = 15.8 mg (100%). Decomposition temperature of the acyl azide group (Td_{azide}): 108 °C. IR (KBr) ν (cm^{-1}): 3384 (N−H), 2147 (CON_3), 1695 (O═CPh), 1537, 1532 (O═CNH), 1416 (O═C−CH_2), 1198 (N_3). Anal. Calcd for $C_{137}H_{150}N_{18}O_{15}\cdot 0.7H_2O$: C, 58.92; H, 4.15; N, 21.14. Found: C, 58.90; H, 3.97; N, 19.03.

5-G2. White powder. Yield = 33.0 mg (98%). Td_{10}: 239 °C. IR (KBr) ν (cm^{-1}): 3330 (N−H), 2610 (COO−H), 1682 (C═O),

Scheme 3



Scheme 4



1605 (Ph), 1539, 1520 (CON−H), 1451 (Ph), 1416 (COC−H_2), 1220 (Ar−COOH). Anal. Calcd for $C_{179}H_{156}N_{24}O_{45}$·15.2$H_2O$: C, 59.11; H, 5.17; N, 9.24. Found: C, 59.10; H, 5.13; N, 9.31.

6-G3. White powder. Yield = 73.1 mg (96%). Td_{azide}: 119 °C. IR (KBr) ν (cm^{-1}): 3306 (N−H), 2147 (CON_3), 1690 (O=C), 1599 (Ph), 1530, 1516 (CON−H), 1412 (COC−H_2), 1198 (N_3). Anal. Calcd for $C_{382}H_{300}N_{117}O_{68}$·18.7$H_2O$: C, 57.68; H, 4.28; N, 20.6. Found: C, 57.69; H, 4.64; N, 17.45.

7-G4. White powder. Yield = 137.0 mg (92%). IR (KBr) ν (cm^{-1}): 3314 (N−H), 2614 (COOH), 1670 (O=CNH), 1603 (Ar), 1539 (O=CNH), 1413 (CH_2−CO), 1220 (Ph−COOH). Anal. Calcd for $C_{791}H_{684}N_{120}O_{189}$·54.5$H_2O$: C, 59.84; H, 5.03; N, 10.59. Found: C, 59.84; H, 4.94; N, 10.62.

8-G1. White powder. Yield = 22.2 mg (97%). Td_{10}: 246 °C. IR (KBr) ν (cm^{-1}): 3320 (N−H), 2961, 2868 (CH_3), 1674 (O=CNH), 1606, 1519 (Ph), 1414 (O=C−CH_2), 1363, 1244, 1214

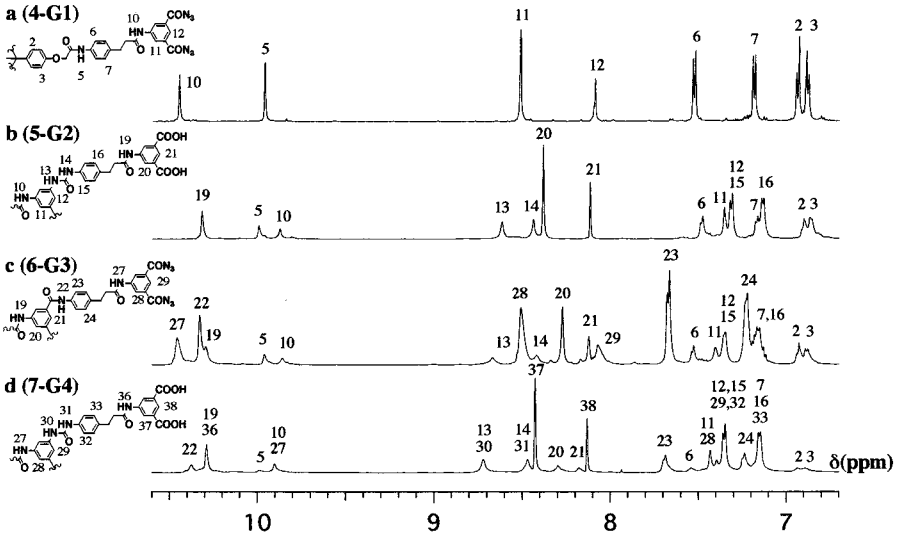


Figure 1. ^{1}H NMR spectra of the aromatic region of **4-G1**, **5-G2**, **6-G3**, and **7-G4**.

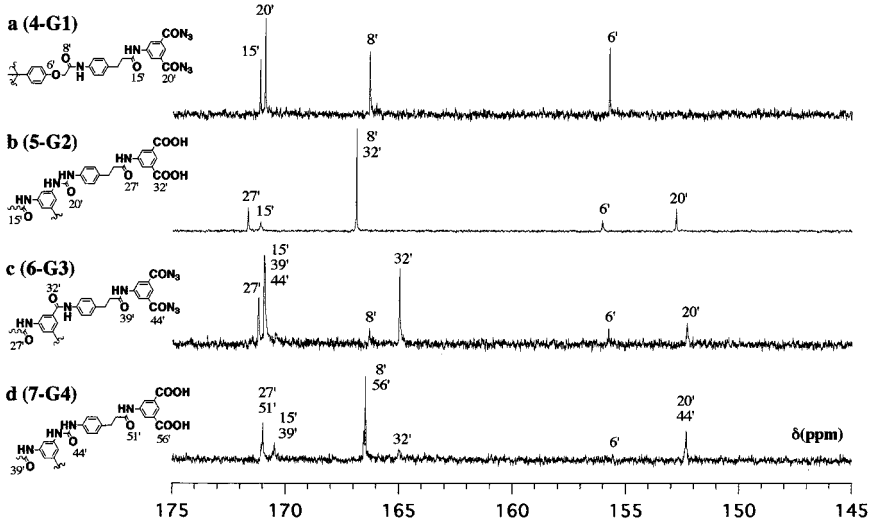


Figure 2. ^{13}C NMR spectra in the range from 175 to 145 ppm of **4-G1**, **5-G2**, **6-G3**, and **7-G4**.

($C(CH_3)_3$). Anal. Calcd for $C_{137}H_{150}N_{18}O_{15}\cdot 8.2H_2O$: C, 67.53; H, 6.88; N, 10.35. Found: C, 67.53; H, 6.61; N, 10.15. M_n(found): 2290 (calcd, 2287). M_w/M_n: 1.08.

9-G2. Yield = 45.9 mg (93%). Td_{10}: 272 °C. IR (KBr) ν (cm^{-1}): 3301 (N−H), 2960 (CH_3), 1668 (O=CNH), 1597, 1518 (Ph), 1408 (O=C−CH_2), 1363, 1246 ($C(CH_3)_3$). Anal. Calcd for $C_{299}H_{312}N_{36}O_{33}\cdot 11.8H_2O$: C, 69.73; H, 6.75; N, 10.68. Found: C, 69.84; H, 6.40; N, 9.44. M_n(found): 4990 (calcd, 4938). M_w/M_n: 1.09.

10-G3. White powder. Yield = 97.8 mg (92%). Td_{10}: 250 °C. IR (KBr) ν (cm^{-1}): 3316 (N−H), 2960, 2867 (C−H_3), 1668 (O=CNH), 1600 (Ar), 1538, 1517 (O=CNH), 1363, 1247, 1213 ($C(CH_3)_3$). Anal. Calcd for $C_{625}H_{668}N_{96}O_{69}\cdot 36.7H_2O$: C, 69.49; H, 6.62; N, 11.91. Found: C, 69.49; H, 6.38; N, 11.50. M_n(found): 10800 (calcd, 10629). M_w/M_n: 1.09.

12-G1. Pale brown powder. Yield = 22.8 mg (91%). Td_{10}: 253 °C. IR (KBr) ν (cm^{-1}): 2954 (CH_3), 2928, 2857 (CH_2), 1651 (O=CNH), 1612 (Ph), 1537 (CON−H), 1376 (C−CH_3), 1202, 1183, 831 (Ph). Anal. Calcd for $C_{149}H_{222}N_{18}O_{15}\cdot 1.5H_2O$: C, 70.69; H, 8.95; N, 9.96. Found: C, 70.68; H, 8.77; N, 9.63.

13-G1. White powder.

14-G2. Pale brown powder. Yield = 49.9 mg (93%). IR (KBr) ν (cm^{-1}): 3298 (N−H), 2955 (CH_3), 2929, 2857 (CH_2), 1696 (O=CNH), 1668 (NHC=ONH), 1613 (Ph), 1537 (O=CNH), 1439 ((CH_2), 1376 ($C(CH_3)_3$), 1198 (Ph). Anal. Calcd for $C_{323}H_{456}N_{36}O_{33}\cdot 5.7H_2O$: C, 70.87; H, 8.61; N, 9.21. Found: C, 70.88; H, 8.43; N, 8.98.

15-G3. Pale brown powder. Yield = 102.1 mg (92%). Td_{10}: 289 °C. IR (KBr) ν (cm^{-1}): 3289 (N−H), 2954 (CH_3), 2928, 2856 (CH_2), 1690 (O=CNH), 1672 (NHC=ONH), 1597 (Ph), 1515 (O=CNH), 1440 ((CH_2), 1376 ($C(CH_3)_3$), 1201 (Ph). Anal. Calcd for $C_{671}H_{924}N_{72}O_{68}\cdot 8.5H_2O$: C, 71.31; H, 8.44; N, 8.92. Found: C, 71.31; H, 8.38; N, 9.13.

Results and Discussion

One-Pot Synthesis of Dendritic Poly(amide-urea)s from the First to Fourth Generation. The design of the core molecule is one of the most important factors for dendrimer synthesis.[1] For instance, we demonstrated that in the synthesis of dendritic polyamides, trimesic acid as a core molecule is so small that steric hindrance interferes with coupling of dendrons and end groups of dendrimer. However, a large core **3** gave the desired dendritic polyamides with a very narrow molecular weight distribution.[5a] Therefore, compound **3** was selected as the core in this study. Schemes 1−4 show a synthetic route of dendritic polymers from the first to fourth generation. The structures of dendritic polymers from the first to fourth generation were confirmed by ^{1}H (Figure 1), ^{13}C NMR (Figure 2), and elemental analyses (Table 1).

The three carboxyl groups of **3** were activated with DBOP in the presence of TEA at 25 °C for 30 min in

Table 1. Characterizations of Dendritic Poly(urea-amide)s Capped with *p-tert*-Butylaniline

generation	structure	% yield	molecular weight calcd[a]	molecular weight found[b]	M_w/M_n[c]	elemental analysis, C/H/N calcd[d]	elemental analysis, C/H/N found	degree of branching[b]
first	8-G1	100	2289	2290	1.08	67.53/6.88/10.36[e]	67.53/6.61/10.15	
second	9-G2	96	4938	4990	1.09	69.73/6.75/10.68[f]	69.84/6.40/9.44	0.93
third	10-G3	92	10629	10800	1.09	69.49/6.62/11.91[g]	69.49/6.38/11.50	0.90
fourth	11-G4	93	21193	20750	1.15	70.04/6.36/10.80[h]	70.18/6.41/10.64	

[a] Calculated molecular weight. [b] Measured by ^{1}H NMR spectroscopy. [c] Measured by GPC using THF as eluents. [d] Calculated elemental analysis. [e] $C_{137}H_{150}N_{18}O_{15}\cdot 8.2H_2O$. [f] $C_{299}H_{312}N_{36}O_{33}\cdot 11.8H_2O$. [g] $C_{625}H_{668}N_{96}O_{69}\cdot 36.7H_2O$. [h] $C_{1271}H_{1308}N_{168}O_{141}\cdot 33.5H_2O$.

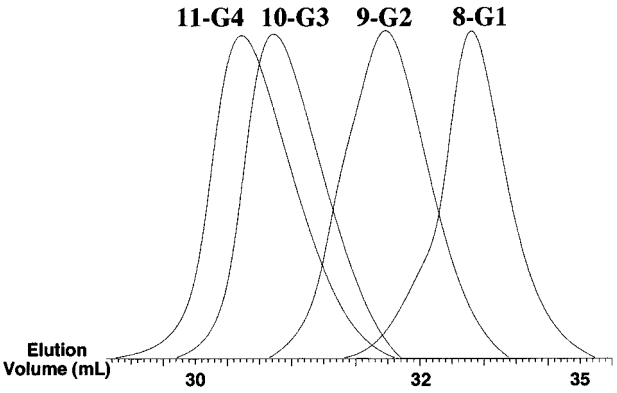


Figure 3. GPC traces of **8-G1**, **9-G2**, **10-G3**, and **11-G4**.

THF/NMP, followed by condensation of active amide and 3 equiv of AB_2 monomer **2** to give the first generation dendritic polyamide with six azide terminal groups (**4-G1**) in 100% yield. In both ^{1}H and ^{13}C NMR spectra of **4-G1**, all signals were fully assigned to **4-G1**.

The Curtius rearrangement of **4-G1** in the presence of 6 equiv of AB_2 monomer **1** was carried out to give a soluble second generation dendritic poly(amide-urea) (**5-G2**) having 12 carboxylic acid end groups in 98% yield. In the ^{1}H NMR spectra (Figure 1b), **5-G2** clearly shows a peak at 7.35 ppm (no.11) due to dendritic protons, and 12 urea protons (no.13 and 14) were also observed at 8.62 and 8.44 ppm. The new amide protons (no.19), which connect with the end phenyl groups substituted by carboxylic acid moieties, also appeared at 10.32 ppm. In the ^{13}C NMR spectra, no. **20′** carbonyl carbons indicate the change from the end acyl azide carbons of **4-G1** at 171 ppm to the urea carbonyl carbons of **5-G2** at 152 ppm as shown in Figure 2. Before the active amide formation of **5-G2**, NMP was added and THF evaporated from the reaction system by heating because the active amide is insoluble in THF. The end carboxyl groups of **5-G2** were activated with DBOP and TEA at 25 °C for 1 h. Then, THF and 12 equiv of AB_2 monomer **2** were added into the stirred solution (NMP/THF = 25/75), and the condensation reaction was performed at 25 °C for 6 h to give the third generation dendritic poly(amide-urea) with 24 azide terminal groups (**6-G3**). In the ^{1}H NMR spectra, incorporation of azide groups into the polymer end was conformed by appearance of amide protons at 10.46 ppm (no. 27), and dendritic benzene protons substituted by three amide groups at 8.51 (no. 20) and 8.07 ppm (no. 21) were observed. In the ^{13}C NMR spectra, disappearance of no. **32′** end carbonyl carbons of **5-G2** at 167 ppm was clearly observed. The dendritic polymer of **7-G4** with 48 end carboxylic acid groups shows characteristic urea protons at 8.72 (no. 13 and no. 30) and 8.47 ppm (no. 14 and 31) as shown in Figure 1d. In IR analysis, appearance and disappearance of characteristic acyl azide and carboxylic acid peaks were observed around 2150 and 2600 cm^{-1}, respectively, through the sequential dendritic polymer synthesis. The dendritic poly(amide-urea) of each generation was obtained essentially in 100% yield. Elemental analysis in each generation was in very good agreement with the theoretical value (Table 1).

Molecular Weight and Polydispersity. Molecular weight distribution is also important to evaluate the regularity of dendritic polymers. Dendritic polymers from the first to fourth generations were capped with *p-tert*-butylaniline. The M_w/M_n was measured by GPC

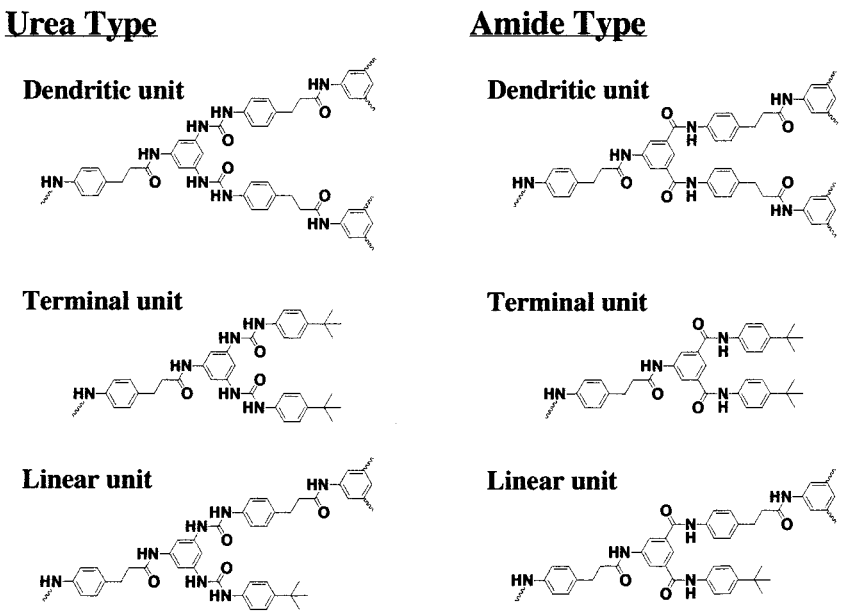
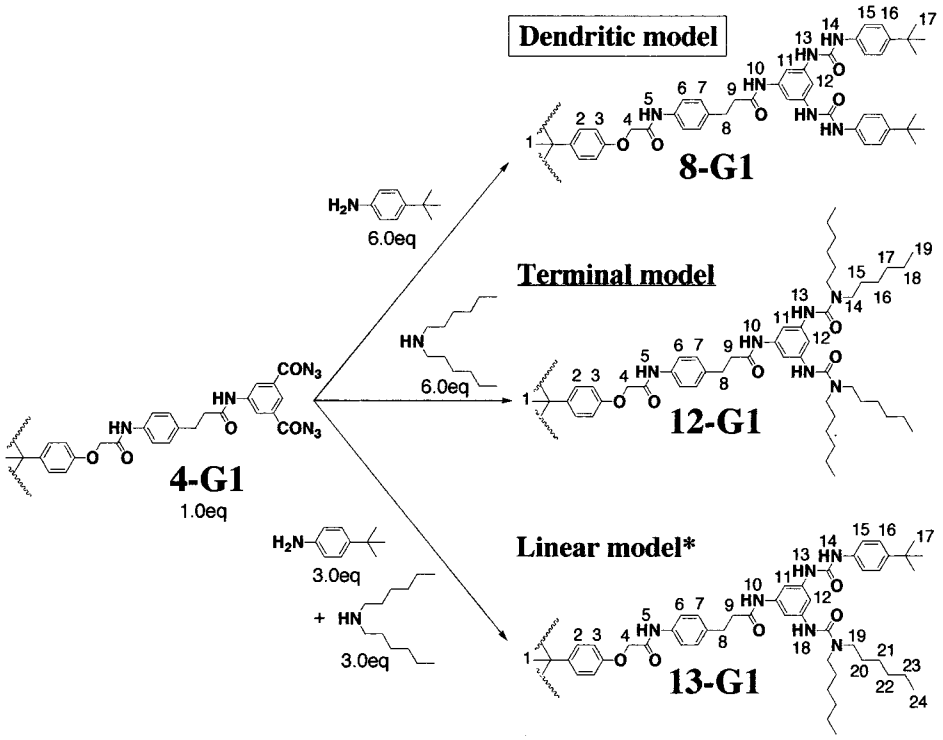


Figure 4. Structures of repeat unit in the dendritic poly(amide-urea).

Scheme 5



in THF as an eluent. GPC traces of first (**8-G1**), second (**9-G2**), third (**10-G3**), and fourth generation polymers (**11-G4**) are shown in Figure 3.

The M_w/M_n values were very narrow in the range of 1.08−1.15 (Table 1). The molecular weight distribution (MWD) of each generation was nearly monodisperse and clearly shifted to the higher molecular weight region with their increasing generation. The correct molecular weight of polymers was not determined by GPC measurement using polystyrene as a standard. Therefore, number-average molecular weight (M_n) of dendritic polymers was estimated by the end group analysis. The integrated intensity of methylene protons of the core molecule with terminal *tert*-butyl protons was used for this purpose. The M_n value in each generation was found to be close to the calculated value as shown in Table 1.

Degree of Branching. An important characteristic of dendritic polymer is degree of branching (DB). Obtained dendritic polymers involve urea branching units and amide branching unit, among which the dendritic, terminal, and linear units exist as shown in Figure 4.

DB of dendritic polymers capped by *p-tert*-butylaniline was difficult to estimate using ^{1}H NMR signals of these units because they overlapped with each other. Therefore, a secondary aliphatic amine, i.e., dihexylamine, was selected as the end-capping agent. DB of the polyamide unit could be determined by ^{1}H NMR of model compound studies and integration of each unit as we described previously.[5b]

To determine DB of the polyurea unit, three urea model compounds, **8-G1**, **12-G1,** and **13-G1**, were synthesized via the Curtius rearrangement of **4-G1** in the presence of 6 equiv of the amine(s) as shown in Scheme 5. Their ^{1}H NMR spectra are shown in Figure 5.

Dendritic urea model **8-G1** shows characteristic five dendritic peaks (square) at 9.88 ppm (no. 10) due to end-amide protons, at 8.66 ppm (no. 13) and 8.41 ppm (no. 14) corresponding to urea protons, and at 7.43 ppm (no. 11) and 7.37 ppm (no. 12) due to trisubstituted phenyl ring. The corresponding signals of the terminal model (underline, **12-G1**) were shifted to a higher magnetic field by incorporation of aliphatic groups into phenyl rings. They show four characteristic peaks at 9.71 (no. 10), 8.02 (no. 13), 7.34 (no. 11), and 7.22 ppm (no. 12). Six peaks* of linear model **13-G1**, that were not observed in either **8-G1** or **12-G1**, could be assigned to aromatic protons in the linear structure.

Figure 6 shows the ^{1}H NMR spectra of the second (**14-G2**) and third generation dendritic poly(amide-urea)s (**15-G3**) capped with dihexylamine.

In **14-G2,** the signals corresponding to the dendritic peaks [7.38 ppm (no. 11)] and aromatic protons in the terminal structure [7.61 (no. 20), 6.81 ppm(no. 21)] were observed. However, no aromatic protons at 7.3 ppm and aromatic NH protons in the range of 8.4−9.0 ppm in the linear structure were observed because of overlapping with other peaks. In contrast, aliphatic urea protons* in the linear structure at 8.05 ppm were observed. DB of **14-G2** was calculated by the signal

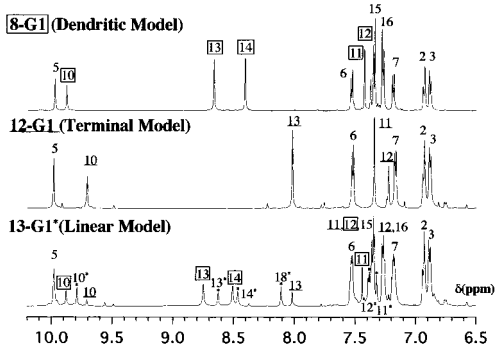


Figure 5. ^{1}H NMR spectra of the aromatic region of **8-G1** (dendritic model), **12-G1**(terminal model), and **13-G1** (linear model).

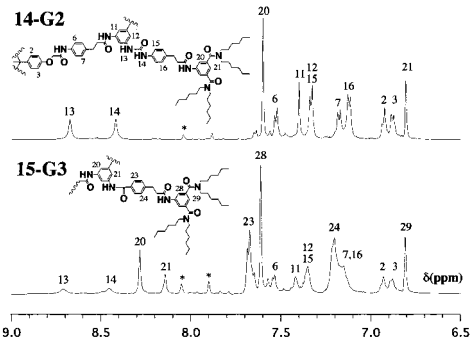


Figure 6. ^{1}H NMR spectra of the aromatic region of **14-G2** and **15-G3**.

intensity ratio of the dendritic urea protons at 8.69 ppm (no. 13) to aliphatic urea NH protons* in the linear structure at 8.05 ppm according to the following Freys definition:[6] DB = (2 × number of dendritic unit)/(2 × number of dendritic unit + number of linear units). Estimated DB of **14-G2** was 0.93.

In the synthesis of **15-G3**, the Curtius rearrangement of **10-G3** in the excess feed amount of dihexylamine gave not only urea formation but also amide linkage due to a strong nucleophilicity of dihexylamine compared with *p-tert*-butylaniline. Nishi and co-workers also reported the same results in the synthesis of polyureas and polyamides by copolymerization of diacyl azides and diamines.[7] The reaction, therefore, was carried out at 25 °C to give amide linkage of **15-G3**. In **15-G3**, the signals corresponding to the dendritic [8.28 (no. 20), 8.14 ppm (no. 21)] and terminal units [7.61 (no. 28), 6.81 ppm (no. 29)] were clearly observed. Peaks at 8.05 and 7.90 ppm are attributed to the corresponding aromatic protons in the linear structure of amide unit.[5] They overlapped with aromatic protons in the linear structure of the urea units. Overall DB of **15-G3** involving the first and second generation was estimated by the signal intensity ratio of the dendritic phenyl protons at 8.28 ppm (no. 20) to aliphatic protons in the linear structure at 8.14 ppm in a fashion similar to that for **14-G2**. Estimated DB of **15-G3** was 0.90.

Conclusions

A novel one-pot procedure for the synthesis of dendritic poly(amide-urea)s with a very narrow molecular weight distribution and high DB via the Curtius rearrangement was developed. This procedure involves activation of end carboxyl groups with the condensing agent, DBOP, condensation of the active amide with aminodicarbonyl azide, the Curtius rearrangement, subsequent addition with aminodicarboxylic acid, and, finally, capping of the end groups with *p-tert*-butylaniline. Estimated M_n of dendritic poly(amide-urea)s was close to the calculated value. Degree of branching of the second and third generation dendritic polymers was found to be 0.93 and 0.91 by ^{1}H NMR studies of model compounds. We believe that this novel procedure using isocyanate chemistry can be widely applied to synthesis of various dendritic polymers such as polyurethane, polyimides, and polyamides as well as polyureas.

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Supporting Information Available: Detailed NMR data of all compounds. IR spectra of **3**, **4-G1**, **5-G2**, **6-G3**, and **7-G4**; ^{13}C NMR spectra of **4-G1**, **5-G2**, **6-G3**, and **7-G4** at 140−130 ppm; ^{13}C NMR spectra of **4-G1**, **5-G2**, **6-G3**, and **7-G4** at 130−110 ppm; ^{13}C NMR spectra **4-G1**, **5-G2**, **6-G3**, and **7-G4** at 110−25 ppm; Synthetic routes of all dendritic polymers and their numbering of H and C. This material is available free of charge via the Internet at http://pubs.acs.org.

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