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One-Pot Synthesis of Dendritic Poly(amide-urea)s via Curtius Rearrangement. 1. Monomer Syntheses and Model Reactions for the Dendritic Poly(amide-urea)s Synthesis

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ABSTRACT: The syntheses of two AB_2 monomers, aminodicarboxylic acid (**1**) and aminodicarbonyl azide (**2**), and their model reactions for the one-pot synthesis of dendritic aromatic poly(urea-amide)s using the two AB_2 monomers were carried out. The model reaction of **2** and *p*-tolyl isocyanate produced the target urea with two acyl azide groups in 93% yield at 25 °C for 30 min in tetrahydrofuran (THF). The Curtius rearrangement from an acyl azide to an isocyanate was completed at 140 °C for 30 min in THF. The isocyanate produced via the Curtius rearrangement readily reacted with aniline to give a urea compound in 93% yield. *p*-Tolyl isocyanate selectively reacted with an amine group of **1** to give a urea with end carboxylic acid groups. The end carboxylic acid groups of the urea could be activated with a condensing agent, diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP), and the condensation of the active amide with **2** provided an amide with acyl azide end groups.

Introduction

Dendrimers are highly branched macromolecules consisting of a multifunctional core from which successive branched repeating units extend radially outward. Moreover, the large numbers of reactive end groups existing at the periphery of dendrimer easily react with many reagents to give dendrimers with various functionalities at the periphery.[1] Therefore, they have received a great deal of attention as new polymeric materials for applications in molecular light harvesting, catalysts, chiral recognition, enantiomer separation, molecular electronics, and unimolecular micelles.[2]

The formation of dendrimer via a convergent or divergent route uses reiterative growth strategies that require a tedious multistep procedure involving repetitive protection−deprotection and purification processes in each generation. Quite recently, Rannard et al. reported new one-pot multiple-addition convergent polycarbonate dendrimers, where the second generation dendrimer was obtained by sequential activation of an alcohol unit with 1,1-carbonyl diimidazole and addition of an AB_2 triol.[3]

In contrast, hyperbranched polymers are easily prepared via a one-step polymerization method, where multifunctional AB_n ($n \geq 2$) monomers are allowed to react together in an uncontrolled manner, forming nonideally growth dendritic structures.[4] This leads to an extremely broad molecular weight distribution and a low degree of branching (DB) around 0.5. Several studies related to control of AB_2 polymerization have been reported; for example, a pseudo-one-step procedure,[5] utilization of specific AB_2 monomers,[6] and slow monomer addition method.[7]

Recently, we developed a one-pot synthesis of dendritic polyamides. This procedure consists of activation of end carboxyl groups with a condensing agent, diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP), followed by condensation of the active amide with aminodicarboxylic acid, 5-[3-(4-aminophenyl)propionylamino]isophthalic acid hydrochloride (**1**), as AB_2 monomer.[8−10] The obtained polymers had high DB (91%) and narrow molecular weight distribution (<1.1).

Various kinds of polymers have been prepared using azide chemistry; i.e., inert acyl azide groups can produce reactive isocyanate groups via the Curtius rearrangement.[11−15] Nishi and co-workers synthesized linear polyureas, polyurethanes, and polyamides by careful selection of the reaction substrate to acyl azide.[11] Quite recently, Kumar et al. have shown the efficiency of an acyl azide approach for the stepwise synthesis of dendritic polyureas.[13c] The versatility of the isocyanate chemistry has provided a basis for commercial utility of the isocyanate compounds.[16] We were interested in the Curtius rearrangement as a key reaction for the novel one-pot procedure of dendritic polymers.

In part 1, we will report the synthesis of novel AB_2 monomer, aminodicarbonyl azide, 5-[3-(4-aminophenyl)propionylamino]isophthaloyl azide hydrochloride (**2**),

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Scheme 1

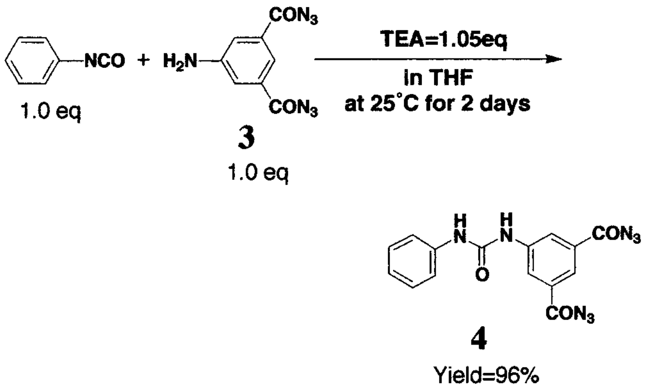


Table 1. Effect of Solvent and Reaction Temperature on the Condensation of 3 and Phenyl Isocyanate[a]

no.	solvent	ϵ	temp	reaction system	yield,[b] %
1	DMSO	47	*c*	homogeneous	22
2	DMF	37.8	*c*	homogeneous	54
3	NMP	32	75 °C	heterogeneous[d]	
4	NMP	32	*c*	homogeneous	64
5	NMP/dioxane = 1/2		*c*	homogeneous	73
6	NMP/THF = 1/2		*c*	homogeneous	93
7	THF	7.6	*c*	homogeneous	96
8	dioxane	2.2	*c*	heterogeneous[e]	95

[a] The reaction time was 2 days. [b] By HLPC. [c] Room temperature. [d] Obtained product was insoluble in any organic solvent due to gelation. [e] Obtained product (**4**) was soluble in THF, DMSO, NMP, and DMF.

and model reactions for the one-pot synthesis of dendritic aromatic poly(urea-amide)s with a very narrow molecular weight distribution (~1.1) and high DBs (≥90%). In addition, the detailed one-pot synthesis of dendritic aromatic poly(urea-amide)s from the two AB_2 monomers, **1** and **2** using condensation and the Curtius rearrangement will be discussed in part 2.

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), *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were distilled under reduced pressure before use. The condensing agent, DBOP, was prepared according to the reported procedure.[17] AB_2 monomer **1** was prepared by reported procedures.[8] The other reagents were obtained commercially and used as received.

Measurement. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer, PARAGON 1000. ^1H 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 $^1H\{^{13}C\}$-COSY, ^1H-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}. A time of fight (ESI-TOF) mass spectrometry (Applied Biosystems Marine) was used for molecular weight analysis with the mixture of methanol and LiI as a solvent.

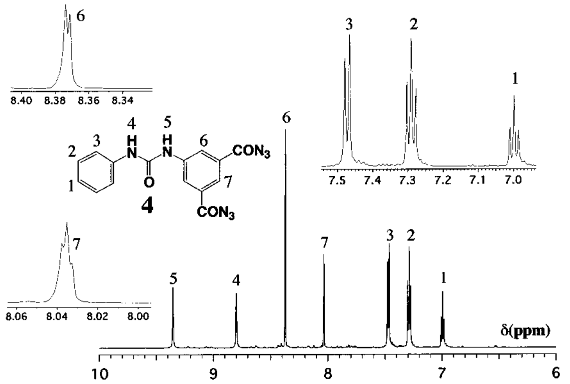


Figure 1. ^1H NMR spectra of **4**.

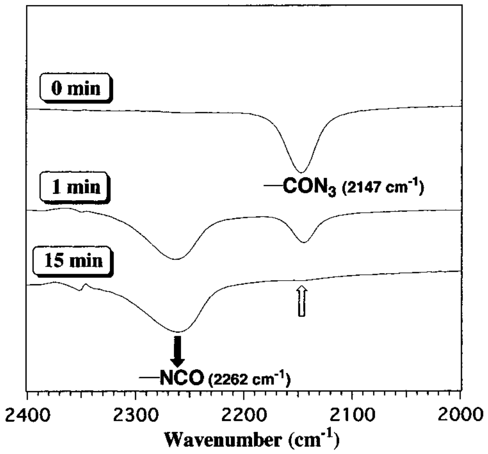
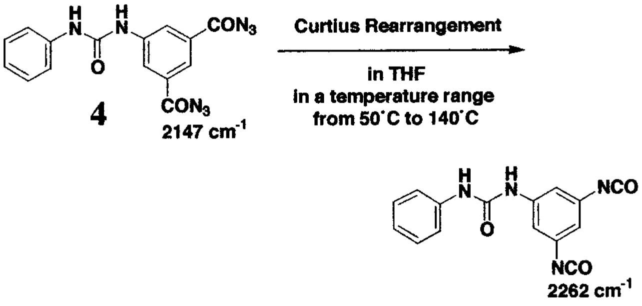


Figure 2. The change of IR spectra in the range from 2000 to 2400 cm^{-1} when **4** was heated at 140 °C.

Scheme 2



5-Amino Isophthaloyl Azide (3). Diphenylphosphonyl azide (DPA) (28.62 g, 104 mmol) and TEA (10.5 g, 104 mmol) were added to a solution of 5-amino isophthalic acid (7.246 g, 40 mmol) in NMP (200 mL) under dry argon at 25 °C. The solution was stirred at 25 °C for 12 h and poured into a 5% aqueous $NaHCO_3$ solution. The crude product was purified by dissolving in NMP and reprecipitating with a 5% aqueous $NaHCO_3$ solution to give **3** (73.4%) as a light yellow powder. **3** was dried in vacuo at 25 °C and stored at −20 °C. Decomposition temperature of the acyl azide group (Td$_{azide}$): 108 °C. IR (KBr), ν (cm^{-1}): 3471, 3386 ($-NH_2$), 2141 ($-CON_3$), 1689 (C=O), 1351, 1228, 1197 (C−N). Anal. Calcd for $C_8H_5N_7O_2$: C, 41.56; H, 2.18; N, 42.41. Found: C, 42.60; H, 1.95; N, 41.35.

5-(3-Phenylureido)isophthaloyl Azide (4). Phenyl isocyanate (47.7 mg, 0.4 mmol) was added to a solution of **3** (92.8 mg, 0.4 mmol) and TEA (42.5 mg, 0.42 mmol) in THF (2 mL) under dry argon at 25 °C. The reaction was performed at 25 °C for 2 days. The solution was poured into hexane and collected by filtration to give **4** as a pale yellow powder. Yield:

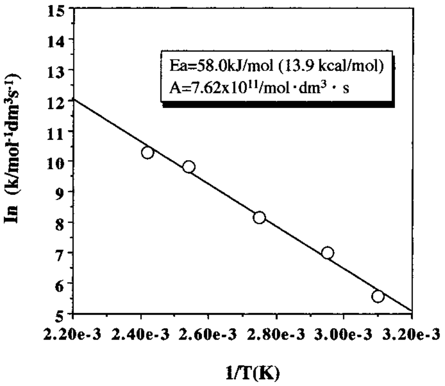


Figure 3. Arrhenius plot of the model Curtius rearrangement of **4**.

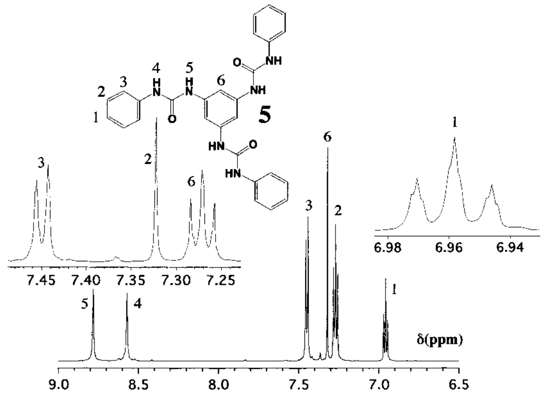


Figure 4. ^{1}H NMR spectra of the aromatic region of **5**.

135 mg (96%). The decomposition temperature of acyl azide group in air by TGA measurement (Td_{azide}): 106 °C. IR (KBr), ν (cm^{-1}): 3370 (−NH−), 2149 ($-CON_3$), 1697 (C=O), 1551 (−NH−), 1201 (C−N).

Model Curtius Rearrangement. Compound **4** (35.0 mg, 0.1 mmol) and THF (2.5 mL) were placed in a pressure resistant vessel equipped with a septum and metal cock under dry argon atmosphere. The solution was stirred and heated in a temperature range from 50 to 140 °C. The solution was cooled in a water−ice bath, and several drops were placed on a KBr pellet. After air-drying, IR analysis was immediately carried out. The activation energy of the Curtius rearrangement was calculated by the following equation.

$$\text{conversion of isocyanate compound from } \mathbf{4}\ (\%) = [\mathrm{NCO}]_t/([\mathbf{4}]_t + [\mathrm{NCO}]_t)$$

$$[\mathrm{NCO}]_t = D_{2262}/\epsilon(\mathrm{NCO}_{2262})$$

$$[\mathbf{4}]_t = (D_{2146} - D_{2262} \times \epsilon(\mathrm{NCO}_{2146})/\epsilon(\mathrm{NCO}_{2262}))/\epsilon(\mathbf{4}_{2262})$$

where $\epsilon(\mathbf{4}_{2146}) = 7.80 \times 10^{-2}$ (L/cm·mol), $\epsilon(\mathrm{NCO}_{2262}) = 8.24 \times 10^{-2}$ (L/ cm·mol), and $\epsilon(\mathrm{NCO}_{2146}) = 1.78 \times 10^{-2}$ (L/ cm·mol). ϵ and D are molar absorbance coefficient and absorbance at 2146 or 2262 cm^{-1}, respectively.

[3,5-Bis(3-phenylureido)phenyl]-3-phenylurea (5). Compound **4** (70.1 mg, 0.2 mmol), aniline (37.3 mg, 0.2 mmol), and THF (5 mL) were placed in a pressure resistant vessel under dry argon atmosphere. The reactor was sealed with a septum and metal cock. The solution was stirred at 140 °C for 30 min and poured into hexane. The product was collected by filtration to give **5** as a white powder. Yield: 89 mg (93%). IR (KBr) ν (cm^{-1}): 3383, 3311 (−NH−), 1547 (C=O), 1218 (C−N). Anal. Calcd for $C_{27}H_{24}N_6O_3{\cdot}1.4H_2O$: C, 64.12; H, 5.34; N, 16.62. Found: C, 64.18; H, 6.44; N, 16.35.

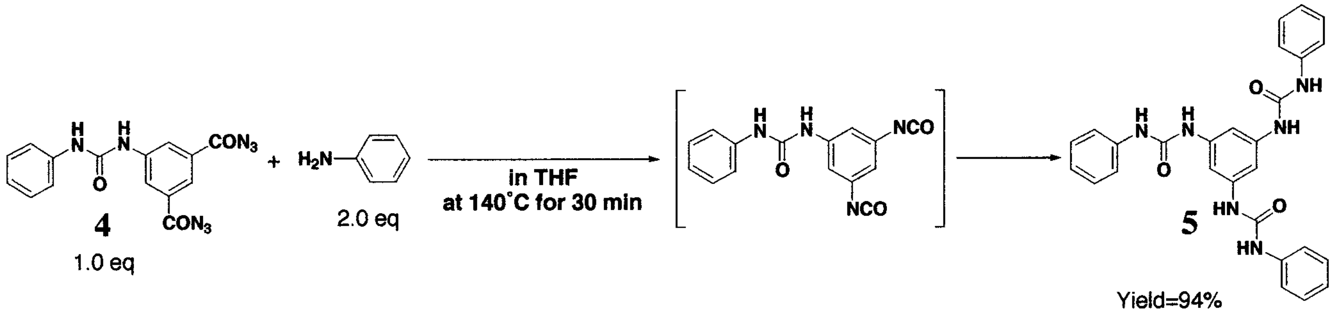
5-[3-(4-*tert*-Butoxycarbonylaminophenyl)propionylamino]isophthalic Acid (6). A mixture of **1** (9.25 g, 0.254 mmol), di-*tert*-butyl dicarbonate (6.09 g, 0.279 mmol), 0.5 N aqueous NaOH solution (95 mL), and NMP (95 mL) was stirred at 25 °C for 48 h under dry argon atmosphere. The crude product was obtained by pouring the mixture into a 5% aqueous HCl solution (500 mL) and collected by filtration. The crude product was purified by washing with ethyl acetate (200 mL) and collected by filtration to give **6** as a white powder. Yield: 7.45 g (69%). $Td_{t\text{-BOC}}$: 112 °C. IR (KBr) ν (cm^{-1}): 3341, 3301 (N−H), 2978 (CH_3), 2569 (COO−H), 1692 (PhCOOH), 1664 (O=CNH), 1396, 1367, 1249 (*tert*-butyl). Anal. Calcd for $C_{22}H_{24}N_2O_7{\cdot}0.4H_2O$: C, 60.65; H, 5.74; N, 6.43. Found: C, 60.60; H, 5.61; N, 6.57. m/z = 485 (M + Li$^+$ calcd = 485).

5-[3-(4-*tert*-Butoxycarbonylaminophenyl)propionylamino]isophthaloyl Azide (7). DPA (10.40 g, 37.8 mmol) and TEA (3.82 g, 37.8 mmol) were added to a solution of **6** (7.36 g, 17.2 mmol) in THF (74 mL) and NMP (5.2 mL) under dry argon atmosphere at 25 °C. The solution was stirred for 6 h, and poured into hexane (500 mL). The precipitate was collected by filtration to give **7** as a white powder. Yield = 6.66 g (81%). Td_{azide}: 188 °C. IR (KBr) ν (cm^{-1}): 3350, 3317 (N−H), 2979 (CH_3), 2153(CON_3), 1700 (O=C−Ph), 1675 (O=C−NH), 1564, 1539 (N−H), 1213 (N_3). Anal. Calcd for $C_{22}H_{22}N_8O_5{\cdot}0.1H_2O$; C, 55.02; H, 4.66; N, 23.33. Found: C, 55.04; H, 4.63; N, 22.57. m/z = 379 (M + Cl$^-$ calcd = 379).

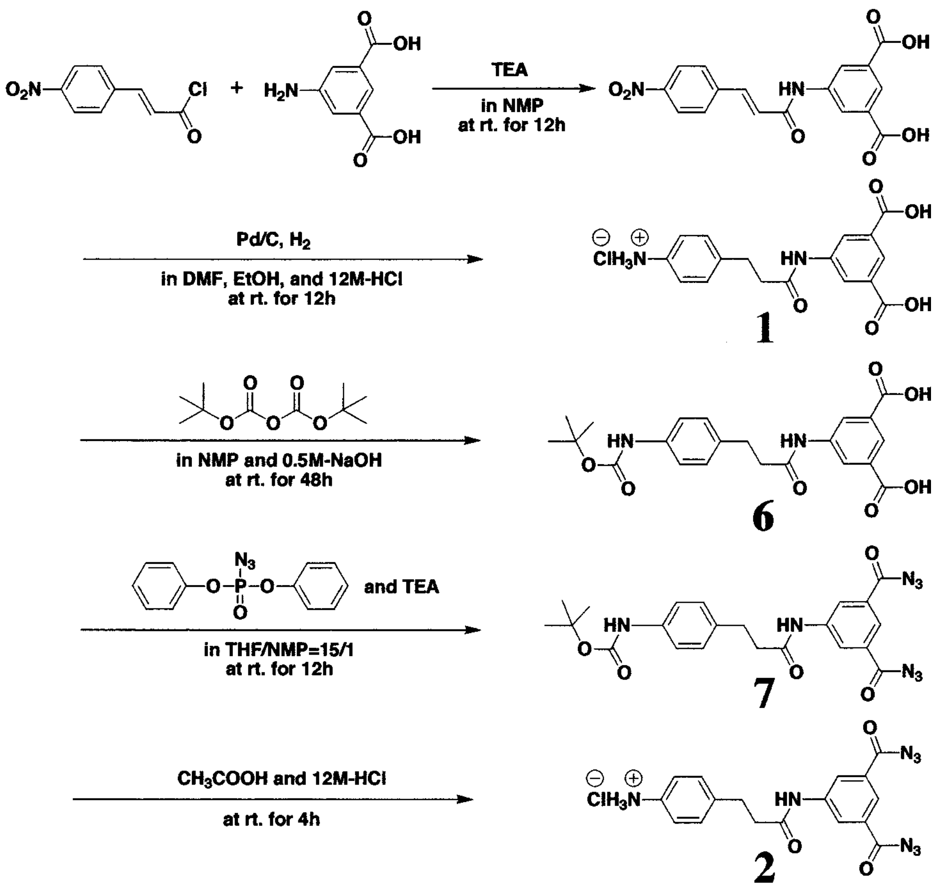
5-[3-(4-Aminophenyl)propionylamino]isophthaloyl Azide Hydrochloride (2). A mixture of **7** (3.00 g, 62.7 mmol), acetic acid (60 mL), and 36 wt % HCl (12 mL) was stirred under dry argon atmosphere at 25 °C for 6 h. The reaction solution was poured into a 5% aqueous HCl solution (300 mL), and the precipitate was collected by filtration, dried in vacuo to afford **2** as a pale yellow powder, and stored at −20 °C over calcium chloride. Yield = 1.77 g (68%). Td_{azide}: 123 °C. IR (KBr) ν (cm^{-1}): 2147 (CON_3), 1695 (O=CPh), 1661 (O=CNH), 1200 (N_3). Anal. Calcd for $C_{17}H_{15}N_8O_5{\cdot}1.1H_2O$: C, 46.98; H, 3.98; N, 25.89. Found: C, 47.13; H, 4.11; N, 23.69. Purity > 99% (by HPLC). m/z = 345 (M + Li$^+$ calcd = 345).

5-{3-[4-(3-*p*-Tolylureido)phenyl]propionylamino}isophthaloyl Azide (8). To a solution of **2** (41.5 mg, 0.1 mmol) in THF (0.5 mL), *p*-tolyl isocyanate (13.3 mg, 0.1 mmol) and TEA (10.6 mg, 0.105 mmol) were added, and the solution was stirred for 30 min at 25 °C. The solution was poured into a 5% aqueous $NaHCO_3$ solution, and the precipitate was collected by filtration and dried in vacuo at 25 °C to give **8** as a white powder. Yield = 44.6 mg (93%). IR (KBr) ν (cm^{-1}): 3287 (N−H), 2145 (CON_3), 1697 (N_3−O=C), 1528 (O=CNH), 1195 (N_3).

Scheme 3



Scheme 4



5-{3-[4-(3-*p*-Tolylureido)phenyl]propionylamino}isophthalic Acid (11). To a solution of **1** (36.5 mg, 0.1 mmol) and TEA (10.6 mg, 0.105 mmol) in NMP (0.5 mL), *p*-tolyl isocyanate (13.3 mg, 0.1 mmol) was added, and the condensation was performed for 30 min at 25 °C. The reaction solution was poured into a 5% aqueous HCl solution, and the precipitate was collected by filtration and dried in vacuo at 25 °C to give **11** as a white powder. Yield = 44.8 mg (97%). Td_{10}: 232 °C. IR(KBr) ν (cm^{-1}): 3296 (N−H), 2585 (COO−H), 1701 (PhC(=O)OH), 1665 (NHC(=O)NH), 1600 (Ph), 1545 (CON−H), 1514 (Ph), 1413 ($CO-CH_2$), 1315 (Ph-COOH). Anal. Calcd for $C_{25}H_{23}N_3O_6{\cdot}1.1H_2O$: C, 62.39; H, 5.28; N, 8.73. Found: C, 62.46; H, 5.00; N, 8.66.

Results and Discussion

AB$_2$ Monomer 3 Synthesis. 3 was prepared by the reaction of 5-aminoisophthalic acid with DPA in the presence of TEA.[18]

Reaction of 3 and Phenyl Isocyanate. To investigate the conditions for dendritic polymer synthesis, the reaction of **3** with phenyl isocyanate was carried out at 25 °C (Scheme 1). The results are summarized in Table 1.

The reaction was very slow and required about 2 days to obtain in essentially 100% yield of addition product acyl azide **(4)** even in the presence of 1.05 equivalent of TEA. The structure of **4** was confirmed by elemental analysis, and IR, ^1H, and ^{13}C NMR spectroscopies. The IR spectrum of **4** showed characteristic absorptions due to a urea group at 3370 cm^{-1} and acyl azide group at 2149 cm^{-1}. Figure 1 shows the ^1H NMR spectrum of **4** with the all peak assignments.

Characteristic two urea peaks (nos. 4 and 5), doublet (no. 6) and triplet peaks (no. 7) due to 1,3,5-trisubstituted aromatic protons, and monosubstituted aromatic peaks (nos. 1, 2, and 3) were observed. Solvents with a

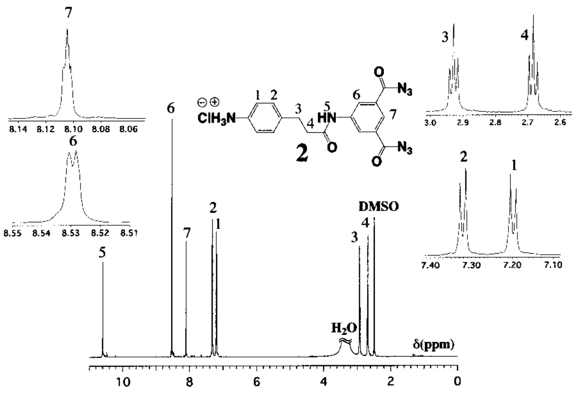


Figure 5. ^1H NMR spectra of **2**.

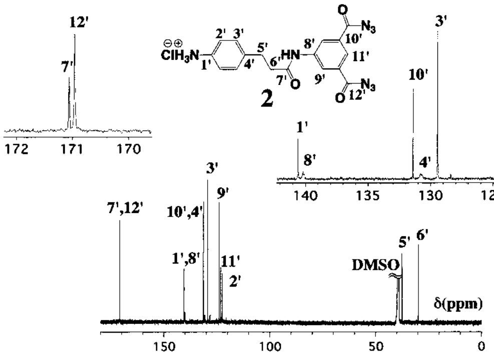
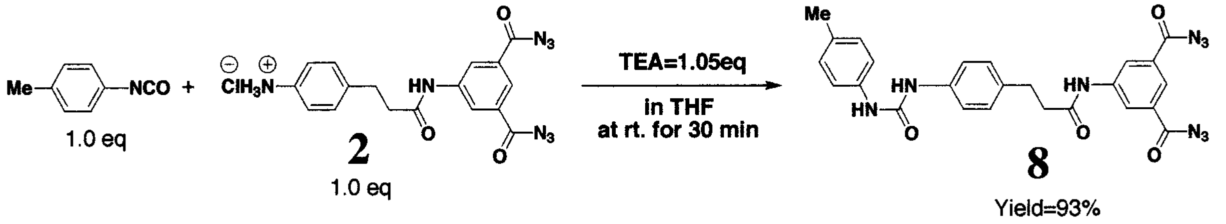
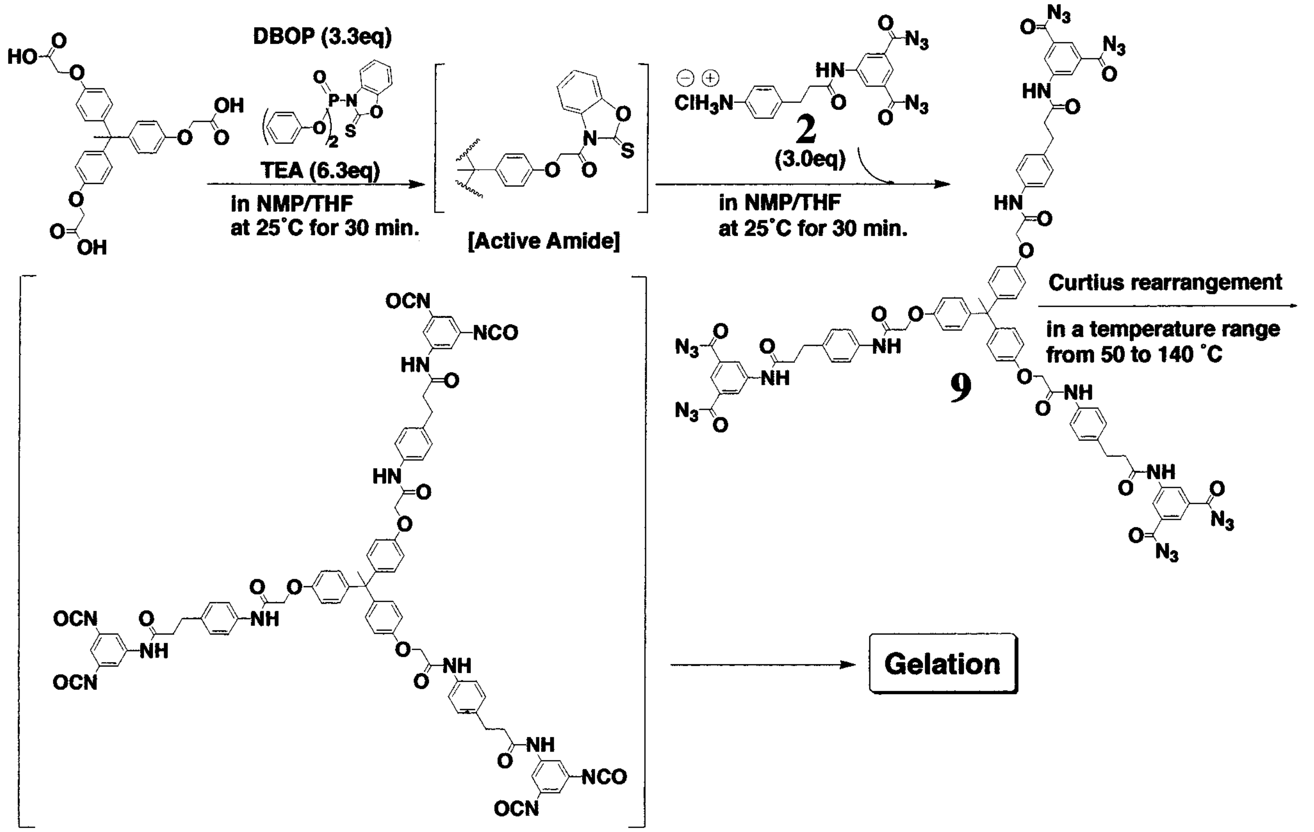


Figure 6. ^{13}C NMR spectra of **2**.

Scheme 5



Scheme 6



high dielectric constant (ε) such as DMSO, DMF, and NMP gave a poor yield of **4** because of a self-condensation reaction of **3**. In contrast, the target urea **4** was obtained in 95–96% yield in THF and dioxane. The reaction in dioxane, however, proceeded heterogeneously. Thus, a mixture of THF/NMP was chosen as a solvent for the dendritic polymer synthesis in part 2.

The Curtius Rearrangement of 4. To investigate the conversion of an acyl azide to an isocyanate in detail, the Curtius rearrangement using **4** was carried out in a temperature range from 50 to 140 °C in THF (Scheme 2).

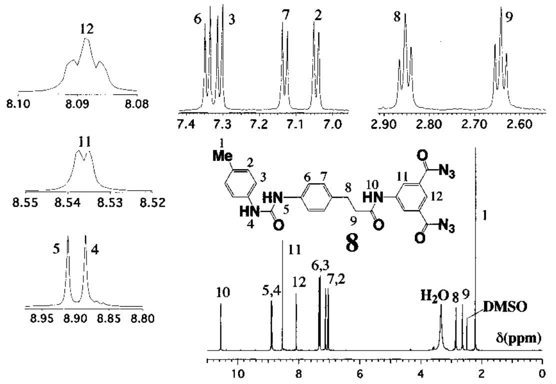


Figure 7. ^1H NMR spectra of **8**.

Figure 2 shows the change of IR spectra in the range from 2000 to 2400 cm^{-1} when **4** was heated at 140 °C. The characteristic acyl azide peak at 2147 cm^{-1} disappeared within 15 min, and the characteristic isocyanate peak appeared at 2262 cm^{-1}.

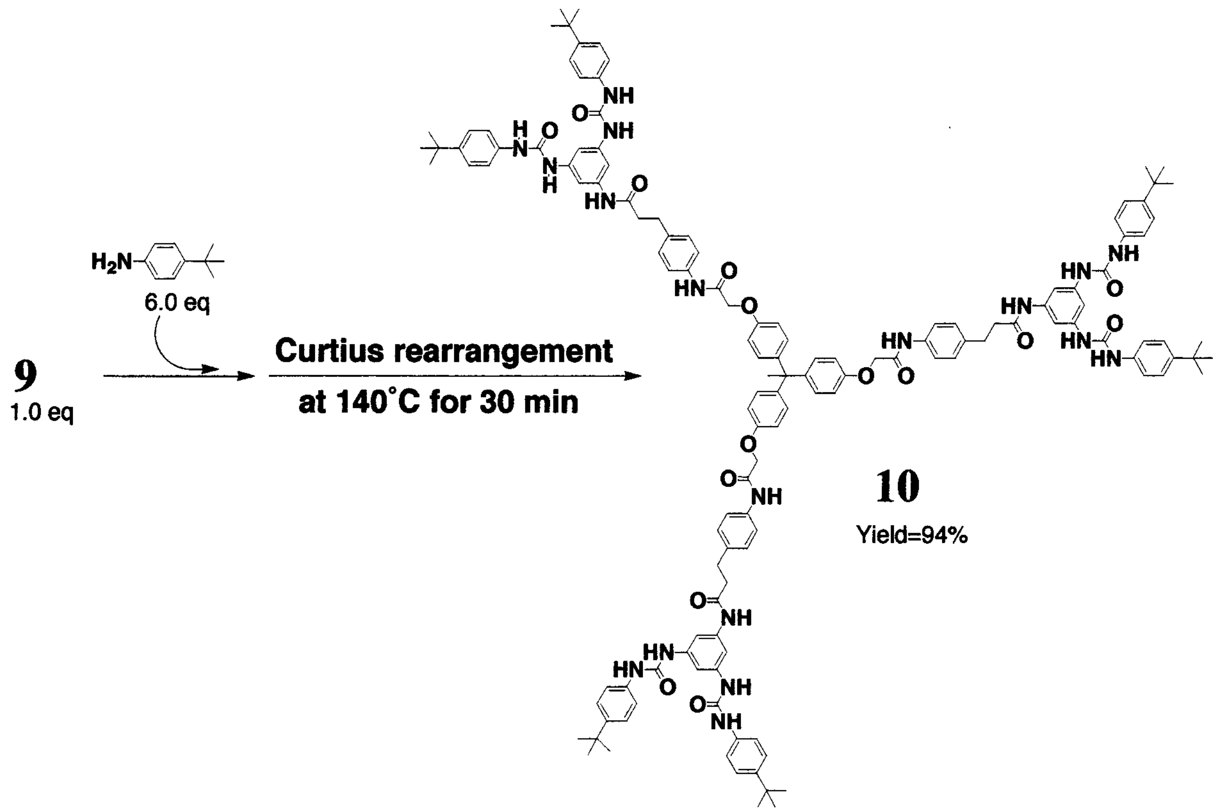
Figure 3 shows the Arrhenius plot of this reaction.

The rate of the Curtius rearrangement was inversely proportional to the reciprocal of the heating temperature. From this slope, the activation energy and the frequency factor were estimated to be 58 kJ/mol and 7.62 × 10 ^{11}/mol·dm^3·s, respectively. The activation energy was smaller than the value of mono-azide-substituted aromatic compounds previously reported.[19] The three electron-withdrawing groups of **4** appear to enhance the reactivity of the Curtius rearrangement.

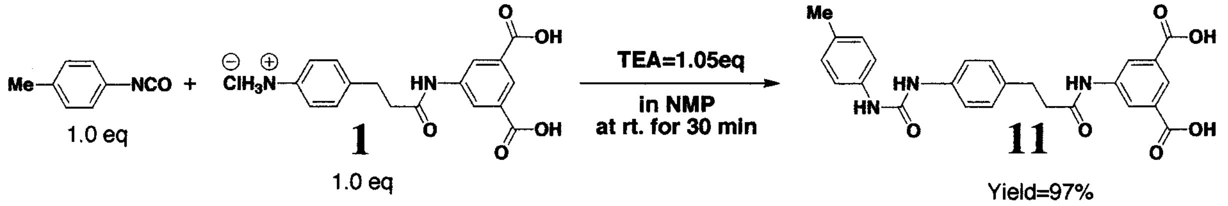
The Curtius rearrangement of **4** in the presence of 2 equiv of aniline was performed in THF at 140 °C for 30 min to examine whether a produced isocyanate reacts with aniline (Scheme 3).

Figure 4 shows ^1H NMR spectra of product **5** and peak assignment. Characteristic six urea protons of **5** (no. 5 and no. 4) were observed at 8.78 and 8.57 ppm. The small resonance peaks at 7.36–7.37 ppm may be as-

Scheme 7



Scheme 8



signed to protons of aromatic ring with at least one carboxylic acid group from the hydrolysis of acyl azide or one amide-linkage from the condensation between acyl azide and aniline.

AB$_2$ Monomer 2 Synthesis. AB$_2$ monomer **3** had some disadvantage, i.e., the low reactivity toward an isocyanate group and poor solubility of the obtained urea due to the rigid structure. Both problems provided long reaction in dilute monomer concentration and would inhibit the synthesis of high molecular weight polymers. To enhance both the solubility and nucleophilicity of AB$_2$ monomer **3** toward an isocyanate group, we designed a novel AB$_2$ monomer **2** having an amino group separated from acyl azide groups. Monomer **2** was synthesized according to Scheme 4.

The amino group of **1** was protected with *tert*-butyl carbamate group[20] (*t*-BOC) to **6**, which was then converted to **7** by the treatment with DPA.[18] Finally, the *t*-BOC group was readily cleaved with HCl and acetic acid to give the target AB$_2$ monomer **2**. Figures 5 and 6 show the ^{1}H and ^{13}C NMR spectra of **2** and the assignment of each peak, respectively. All signals were fully assigned to be **2**.

Reaction of 2 and *p*-Tolyl Isocyanate. To confirm the reactivity of **2** toward the isocyanate group, the reaction of **2** with *p*-tolyl isocyanate was carried out in THF at 25 °C for 30 min (Scheme 5). As soon as *p*-tolyl isocyanate was added to a solution of **2**, a white precipitate was produced. Figure 7 shows the ^{1}H NMR spectra of product and peak assignment. All peaks were fully assigned, and the signal intensity ratios were in very good agreement with the theoretical value of the target urea **8**. These results indicate that the nucleophilicity of **2** was enhanced remarkably in comparison with **3**.

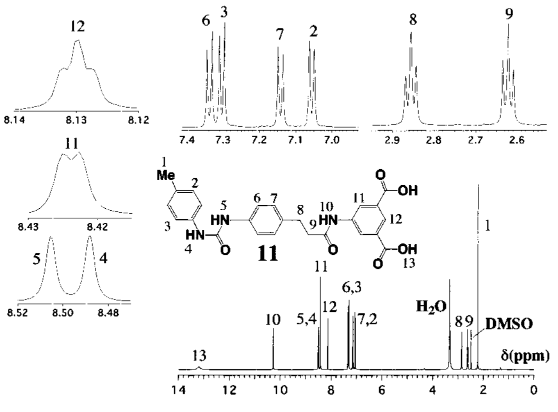


Figure 8. ^{1}H NMR spectra of **11**.

On the basis of these findings, the one-pot synthesis of dendritic polyurea was carried out according to the Scheme 6. However, the following problem was found. When the Curtius rearrangement of compound **9** was performed in a temperature range from 50 to 140 °C, gelation due to cross-linking through dimerization or trimerization of isocyanate groups[16] occurred. In contrast, the Curtius rearrangement of **9** in the presence of 6 equiv of *p*-*tert*-butylaniline suppressed the gelation, giving the soluble compound **10** (Scheme 7).

Kumar et al. also synthesized hyperbranched polyurethanes using 5-hydroxyisophthaloyl azide. They reported that a large number of terminal isocyanate groups of such hyperbranched macromolecules produced cross-linked polymers. However, the polymerization in the presence of a capping regent, such as an alcohol, resulted in formation of soluble polymers with carbamate chain ends.[10] These results indicate that the reactive isocyanate produced via the Curtius rearrangement exclusively reacts with nucleophiles such as *p*-*tert*-butylaniline and an alcohol. Thus, to depress the gelation and to get the high molecular weight dendritic polymers, the Curtius rearrangement in the presence of AB_2 monomer **1** was investigated. AB_2 monomer **1** has two carboxylic acid groups, which could be converted to an active amide with DBOP coupled with TEA.

Reaction of 1 and *p*-Tolyl Isocyanate. An isocyanate group reacts with various nucleophiles such as amine and carboxylic acid.[16,21] Thus, the model reaction of *p*-tolyl isocyanate and AB_2 monomer **1** was carried out at 25 °C to investigate whether the selective urea formation occurs or not (Scheme 8). A ^{1}H NMR spectrum of the obtained product is shown in Figure 8.

The two peaks due to the urea protons (no. 5 and no. 4) are clearly observed at 8.51 and 8.49 ppm, and all signals were assigned to **11**. Thus, *p*-tolyl isocyanate reacts selectively with the amine group of **1**.

On the basis of the above model reactions, the detailed one-pot synthesis of dendritic aromatic poly(urea-amide)s from two AB_2 monomers, **1** and **2,** using the condensation and the Curtius rearrangement will be discussed in part 2.

Conclusions

Aminodicarboxylic acid (**1**) and aminodicarbonyl azide (**2**) were synthesized, and model reactions for the one-pot synthesis of dendritic aromatic poly(urea-amide)s using the two AB_2 monomers were investigated in detail. The model reaction of **2** and *p*-tolyl isocyanate proceed in 93% yield for 30 min in THF to give the target urea with two acyl azide end groups. The Curtius rearrangement from an acyl azide to an isocyanate was completed in 30 min at 140 °C in THF. The isocyanate produced via the Curtius rearrangement readily reacted with aniline to give a urea compound in 93% yield. *p*-Tolyl isocyanate selectively reacted with an amine group of **1** to give a urea with two carboxylic acid end groups. These model reactions gave an important information for the preparation of dendritic poly(amide-urea)s with a very narrow molecular weight distribution high DB from 1,1,1-tris(4-carboxymethyloxyphenyl)-ethane as a core molecule, using **1** and **2** as two AB_2 monomers in a one-pot procedure that will be discussed in part 2. This procedure involves activation of end carboxyl groups with a condensing agent, DBOP, condensation of the active amide with **2**, the Curtius rearrangement in the presence of **1**, and, finally, capping of the end groups with *p*-*tert*-butylaniline without any purification step.

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Supporting Information Available: Detailed NMR data of the all compounds. ^{1}H NMR spectra of **1**, **3**, **6**, **7**, **9**, and **10**; ^{13}C NMR spectra of **1**, **3**, **6**, **7**, **9**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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