Macromolecules **1993**, *26*, 6324–6329

Convergent Synthesis of Starburst Poly(ether ketone) Dendrons

Atsushi Morikawa, Masa-aki Kakimoto,* and Yoshio Imai

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

Received May 27, 1993; Revised Manuscript Received August 16, 1993⊗

ABSTRACT: New highly branched Starburst poly(ether ketone) dendrons were synthesized by the convergent approach through aromatic nucleophilic substitution reactions. 3,5-Bis(4-fluorobenzoyl)anisole was used as the building block, where the methoxy group was a protected form of the hydroxy group. The reaction of the building block with phenol gave the first-generation dendron (**G1**). Next, after the methoxy group was converted to a hydroxy group by reaction with aluminum chloride, the resulting phenol functionality of **G1-OH** was allowed to react with the building block to yield the second-generation dendron (**G2**). By repeating these procedures **G3** and **G4** generation dendrons possessing 8 and 16 phenoxy groups, respectively, at the periphery position were obtained. The ^{1}H- and ^{13}C-NMR spectra were consistent with the structure of these dendrons. The molecular weight and molecular weight distribution determined by gel permeation chromatography indicated that after purification by silica gel column chromatography the dendrons possessed remarkably narrow molecular distribution.

Introduction

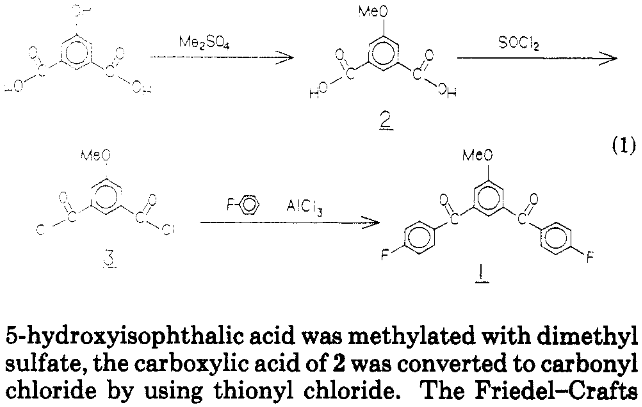
Starburst dendrimers[1,2] are highly branched regular molecules, whose geometrical structure is usually prepared by repeating stepwise reactions. Their size is accurately controlled and expected to be a monosphere consisting of one molecule. Furthermore, by introduction of functional groups into the periphery, properties of the molecules such as the solubility and affinity with other molecules can be controlled.[3] Unimolecular micelles have been prepared by the introduction of electric charges on the periphery.[4]

The divergent and convergent methods have been developed for the synthesis of Starburst dendrimers. In the divergent approach, the preparation of the Starburst dendrimers starts from a core molecule, which possesses two or more reactive groups. A building block containing one functional group to connect with reactive groups of the core and two or more protected reactive groups, which are usually the same as those on the core, is applied to propagate the dendrimers. On the other hand, in the divergent method there is only one reactive group in the starting molecule, and the building block possesses two or more connecting points and one protected reactive group. In both cases, after the reactive points on the core and the building block are connected, the protected reactive points are released on the newly obtained molecule. Connection of building blocks followed by deprotection are repeated until the Starburst dendrimers have grown to the desired size.

By the divergent approach, Starburst dendrimers such as poly(amido–amine),[5] polyether,[6] and polysiloxane[7] have been prepared, while the convergent approach has been applied to the synthesis of 1,3,5-trisubstituted phenylene-based hydrocarbon dendrimers[8] and polyesters,[9] polyether,[10] polyamides,[11] polysiloxane,[12] and poly(arylacetylene).[13] These polymers were usually prepared by nucleophilic substitution reactions, that included, for example, the reactions of amines and phenols with acid chlorides, alcohols with alkyl halides, and silanols with silylamines. Only one example was reported using the aromatic nucleophilic substitution reaction between activated aromatic halide and aromatic amine for a wholly aromatic Starburst dendrimer.[14] Another applicable candidate of the aromatic nucleophilic substitution reactions is the formation of aromatic ether ketone by the reaction of phenol with aromatic fluoride activated by a carbonyl greoup. Recently, Miller et al. reported the preparation of dendritic poly(aryl ethers) by the one-step method, which consisted of uncontrolled reaction of AB_2 monomers.[15] In this paper, we describe the convergent stepwise synthesis of Starburst poly(ether ketone) dendrons possessing monodispersed molecular weight, where the methoxy group was employed as a synthon for a phenol group.

Results and Discussion

The key steps in the synthesis of Starburst dendrons are the formation of covalent bonds for the extension to polymers and deprotection to release reactive points. In this study, the former step was the formation of aromatic ether by the reaction of phenol with aromatic fluoride activated by an electron-withdrawing carbonyl group. Second, the phenol was protected by a methyl group, which can be cleaved by reaction with Lewis acids such as aluminum chloride.[16] As the building block for the present Starburst dendrons, 3,5-bis(4-fluorobenzoyl)anisole (**1**) was employed, that possessed one methoxy group and two aromatic fluorides activated by carbonyl groups in the para position. The building block **1** was synthesized starting from commercially available 5-hydroxyisophthalic acid as shown in eq 1. After the hydroxy group of 5-hydroxyisophthalic acid was methylated with dimethyl sulfate, the carboxylic acid of **2** was converted to carbonyl chloride by using thionyl chloride. The Friedel–Crafts reaction of **3** with fluorobenzene afforded the building block **1**. The overall yield of the three-step sequence was 62%.



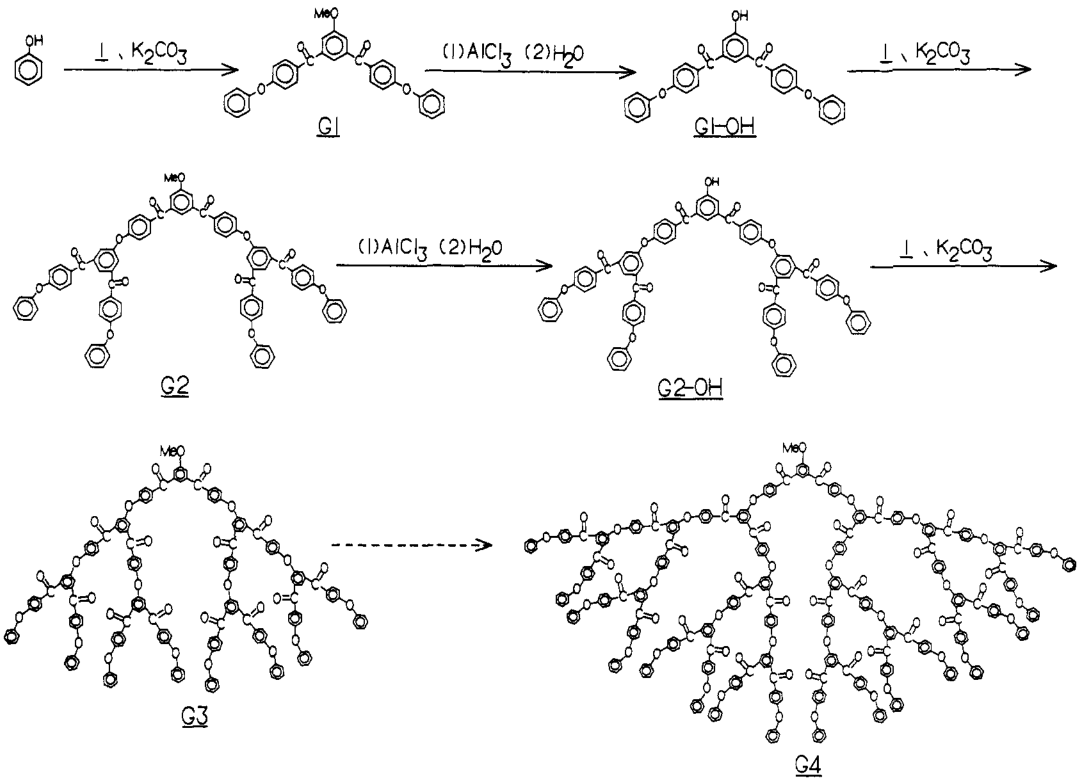
(1)

A general synthetic procedure for the Starburst dendrons is shown in eq 2. First, reaction of the building block **1** with phenol in the presence of potassium carbonate yielded 3,5-bis(4-phenoxybenzoyl)anisole **G1**. Next, the methyl

---

⊗ Abstract published in *Advance ACS Abstracts*, October 15, 1993.

0024-9297/93/2226-6324$04.00/0

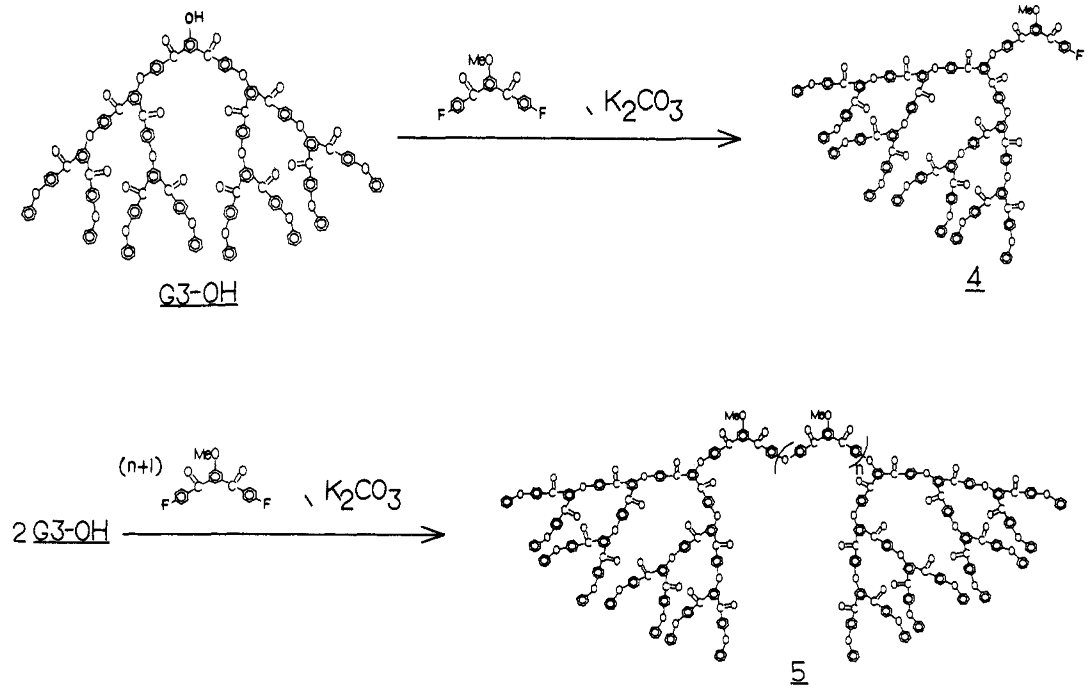


(2)

ether was cleaved with aluminum chloride in benzene to form **G1-OH**.[16] Further reaction of **G1-OH** with the building block yielded **G2** under the similar conditions for the preparation of **G1**. Thus, the further generations up to **G4** were prepared by repeating the formation of aromatic ethers and cleavage of the methyl protecting group. These dendrons **G1**, **G2**, **G3**, and **G4** obtained were colorless powders, which were purified by silica gel column chromatography with final isolated yields of 84, 83, 55, and 30%, respectively.

As shown in Figure 1A, the crude higher generation dendrons, especially **G4**, showed relatively broad molecular weight distribution due to the presence of small amounts of impurities. As shown in eq 3, the lower molecular weight impurities in the crude products might be compound **4**, which was caused by the one to one reaction between **G3-OH** and the building block, while it could be possible that the reaction of **G3-OH** with an excess amount of the building block forms the higher molecular weight impurities **5**. The latter reaction has been reported in the synthesis of linear poly(ether ketone)s.[17] As indicated in Parts B and C of Figure 1, the molecular weights of the purified dendrons increased with increasing generation, where the molecular weight distributions of these dendrons were remarkably narrow.

Typical carbonyl and ether absorptions were observed at 1654 and 1200 cm^{-1}, respectively, in the IR spectra of all the dendrons. The elemental analyses were also in good agreement those for the proposed structures in all cases.



(3)

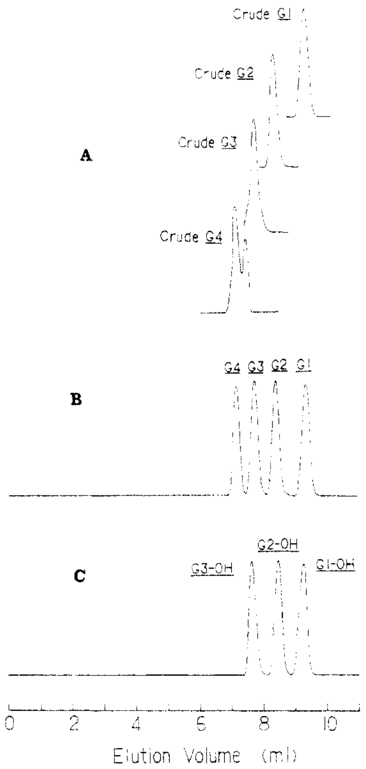


Figure 1. GPC curves of Starburst dendrons: (A) crude products; (B and C) after purification by using silica gel column chromatography.

The ^{1}H-NMR spectra of these dendrons are shown in Figure 2. These molecules contained four kinds of benzene ring systems. The terminal positions comprised two of them, which were trisubstituted benzene with methoxy and two carbonyl functions and the phenoxy groups. The other two benzene ring systems were trisubstituted branching points and 1,4-disubstituted benzene with carbonyl and aryloxy groups. The ^{1}H-NMR signals of the benzene rings were well-resolved in **G1** and **G2**, whereas those in **G3** and **G4** overlapped with each other. The generation number of a dendron could be estimated from the number of signals appearing around 7.85 ppm, which were the low-field signals of the A_2B_2 quartet pattern due to the 1,4-disubstituted phenyl rings and corresponded to protons meta to ether oxygen atoms. The ratio of integration of the aromatic protons to that of methyl protons shown in Table I was additional evidence of the formation of dendrons.

In the ^{13}C-NMR spectra shown in Figure 3, the signals of carbons could be classified into four groups, i.e., the signals of the carbonyl carbons around 193 ppm, the carbons bonded to oxygen atoms on the 1,4-disubstituted phenyl rings around 160–163 ppm, the carbons bonded to oxygen atoms on the 1,3,5-trisubstituted phenyl rings around 156–160 ppm, and the carbons bonded with carbonyl groups on the 1,3,5-trisubstituted phenyl rings around 140 ppm. These peaks were clearly separated from each other, and the chemical structure of the dendrons was obviously elucidated as the expected structure.

These dendrons were soluble in various organic solvents such as amide solvents, dimethyl sulfoxide, tetrahydrofuran, methylene chloride, chloroform, and benzene. The solubility behavior differed markedly from that of linear poly(ether ketone)s, whose solvents are only amide solvents and sulfuric acid.

According to differential scanning calorimetry (DSC), **G1** showed a sharp melting point at 161 °C. On the other hand, glass transition temperatures (T_g) of dendrons **G2**, **G3**, and **G4** were observed at 89, 108, and 123 °C, respectively, where clear melting points were not observed. The T_g's of the dendrons were rather lower compared with that of 144 °C of poly(ether ether ketone) (PEEK) because of the low molecular weight.

PEEK is known as a high crystalline polymer. It is interesting that the present dendrons exhibited noncrystalline nature in spite of possessing similar chemical structure. This phenomenon must arise from their highly branched structure, which also contributed to the high solubility of the dendrons.

Experimental Section

^{1}H- and ^{13}C-NMR spectra and IR spectra were recorded on a JEOL GX-270 FT-NMR spectrometer and a Nicolet 60SX spectrophotometer, respectively. Gel permeation chromatography (GPC) was performed with an apparatus using a Shodex analytical column KF8025 and tetrahydrofuran (THF) as the eluent. Differential scanning calorimetry (DSC) was performed with a Shimadzu thermal analyzer DSC-41M.

5-Methoxyisophthalic Acid (2). In a flask, 18.21 g (0.1 mol) of 5-hydroxyisophthalic acid was dissolved in 150 mL of a 2 M aqueous sodium hydroxide solution, and to the solution was added dropwise 12.61 g (0.10 mol) of dimethyl sulfate. After the solution was stirred at 80 °C for 30 min, it was acidified by 1 M hydrochloric acid. The precipitated 5-methoxyisophthalic acid (**2**) was collected and dried *in vacuo*. This compound was used without purification for the further reaction. Yield: 19.01 g (97%). ^{1}H-NMR (DMSO-d_6, ppm): δ 9.65 (br s, 2H), 8.15 (t, 1H), 7.70 (d, 2H), 3.90 (s, 3H).

5-Methoxyisophthaloyl Chloride (3). A mixture of 19.00 g (96.9 mmol) of **2**, 40 mL of thionyl chloride, and a small amount of dimethylformamide (DMF) was stirred at reflux temperature until the solution became homogeneous. The excess amount of thionyl chloride was distilled off, and the residue was distilled under reduced pressure to afford pure 5-methoxyisophthaloyl chloride (**3**). Yield: 16.94 g (75%). Bp: 85–90 °C (0.5 mmHg). ^{1}H-NMR ($CDCl_3$, ppm): δ 8.48 (t, 1H), 7.90 (d, 2H), 3.98 (s, 3H). ^{13}C-NMR ($CDCl_3$, ppm): δ 167.2, 160.5, 135.4, 126.3, 122.2, 56.5.

Building Block, 3,5-Bis(4-fluorobenzoyl)anisole (1). To a suspension of 20.00 g (0.15 mol) of aluminum chloride in 100 mL of fluorobenzene was added dropwise a solution of 16.31 g (0.07 mol) of **3** in 50 mL of fluorobenzene at 0 °C. After stirring at 20 °C for 3 h, the mixture was poured into ice water. The organic layer was collected, and the aqueous layer was extracted twice with 100 mL of methylene chloride. The combined extract was dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was distilled under reduced pressure (Kugelrohr) to afford 3,5-bis(4-fluorobenzoyl)anisole (**1**). Yield: 20.96 g (85%). Bp: 260 °C (0.5 mmHg). IR (liquid film): 3079, 1655, 1597, 1228, 1145 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): δ 7.88 (m, 4H), 7.65 (t, 1H), 7.54 (d, 2H), 7.17 (m, 4H), 3.92 (s, 3H). ^{13}C-NMR ($CDCl_3$, ppm): δ 194.0, 160.5 (d, J = 142.4 Hz), 159.9, 139.2, 133.1, 132.5, 123.7, 118.8, 115.8 (d, J = 38.6 Hz), 56.0.

First-Generation Dendron (G1). In a flask, a mixture of 10.57 g (0.03 mol) of **1**, 6.21 g (0.066 mol) of phenol, 12.44 g (0.09 mol) of potassium carbonate, 30 mL of toluene, and 60 mL of DMSO was stirred at 130 °C for 1 h. The water formed during the reaction was removed by azeotropic distillation using toluene. Next, the reaction temperature was raised to 150 °C, and the mixture was stirred at this temperature for 1.5 h. The reaction mixture was cooled to about 80 °C, and the solvent was evaporated under a reduced pressure of 15–25 mmHg. The residue was washed with 200 mL of water and extracted twice with 200 mL of methylene chloride. The combined extract was dried over anhydrous sodium sulfate. The crude first-generation dendron (**G1**) was obtained by evaporation of the solvent and purified by silica gel column chromatography eluted by methylene chloride. Yield: 12.65 g (84%). IR (KBr): 3078, 1652, 1585, 1236 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): δ 7.84 (m, 4H), 7.66 (t, 1H), 7.52 (d, 2H), 7.41 (m, 4H), 7.23 (m, 2H), 7.09 (m, 4H), 7.02 (m, 4H), 3.92 (s, 3H). ^{13}C-NMR ($CDCl_3$, ppm): δ 194.0, 162.0, 159.6, 155.4, 139.2, 132.3, 131.5, 130.2, 124.6, 123.7, 120.0, 117.8, 116.7, 55.8. Anal. Calcd for $C_{33}H_{24}O_5$: C, 79.19; H, 4.83. Found: C, 78.95; H, 4.89.

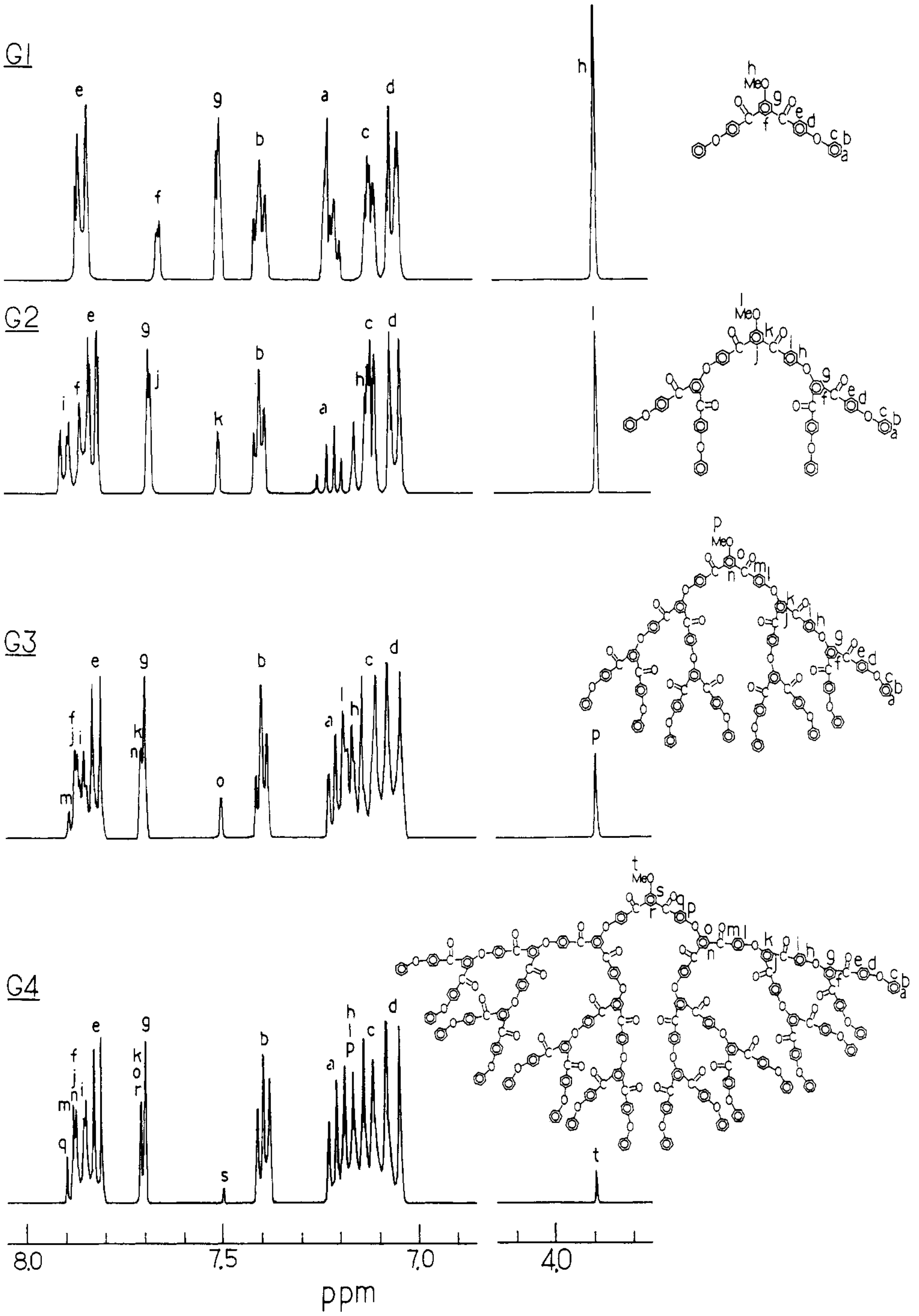


Figure 2. ^{1}H-NMR spectra of G1, G2, G3, and G4 measured in $CDCl_3$.

Table I. Ratio of Integration of Aromatic Protons to Methyl Protons of Starburst Dendrons in ^{1}H-NMR Spectra

	aromatic protons/ methyl protons			aromatic protons/ methyl protons	
	calcd	found		calcd	found
G1	7.00	6.97	G3	39.0	40.0
G2	17.7	17.6	G4	81.7	83.1

G1-OH. A mixture of 12.51 g (0.025 mol) of G1, 33.34 g (0.24 mol) of aluminum chloride, and 100 mL of benzene was stirred at reflux temperature for 1 h. The demethylation reaction was monitored by thin layer chromatography (TLC). After the mixture was poured into ice water, the organic layer was collected, and the aqueous layer was extracted twice with 100 mL of methylene chloride. The combined extract was dried over anhydrous sodium sulfate. G1-OH obtained by evaporation of the solvent was used for the next reaction without further purification. Yield: 11.80 g (97%). IR (KBr): 3200, 3079, 1645, 1584, 1249 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): δ 7.84 (m, 5H), 7.58 (d, 2H), 7.41 (m, 4H), 7.22 (m, 2H), 7.08 (m, 4H), 7.00 (m, 4H). ^{13}C-NMR ($CDCl_3$, ppm): δ 194.8, 162.2, 157.0, 155.3, 139.2, 132.4, 131.5, 130.2, 124.4, 123.0, 120.2, 117.1. Anal. Calcd for $C_{32}H_{22}O_5$: C, 79.00; H, 4.56. Found: C, 78.82; H, 4.63.

Second-Generation Dendron (G2). G2 was prepared by the same procedure as that for the synthesis of G1 starting from 11.68 g (0.024 mol) of G1-OH. Pure G2 was obtained by silica gel column chromatography eluted by methylene chloride. Yield: 12.80 g (83%). IR (KBr): 3078, 1655, 1584, 1240 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): 7.96–7.80 (m, 14H), 7.70 (m, 5H), 7.52 (d, 2H), 77.38 (m, 8H), 7.20 (m, 4H), 7.17–6.96 (m, 16H), 3.92 (s, 3H). ^{13}C-NMR ($CDCl_3$, ppm): δ 194.0, 193.3, 162.3, 160.7, 159.6, 155.8, 155.2, 140.3, 139.2, 132.5, 132.4, 130.7, 130.2, 127.2, 126.4, 124.7, 123.8, 120.9, 120.4, 117.7, 117.2, 55.8. Anal. Calcd for $C_{85}H_{55}O_{13}$: C, 79.43; H, 4.39. Found: C, 79.31; H, 4.44.

G2-OH. G2-OH was prepared by the same procedure as that for the synthesis of G1-OH starting from 11.57 g (9 mmol) of G2. It was used for the next reaction without further purification. Yield: 10.87 g (95%). IR (KBr) 3200, 3078, 1654, 1584, 1241 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): δ 7.96–7.76 (m, 15H), 7.66 (d,

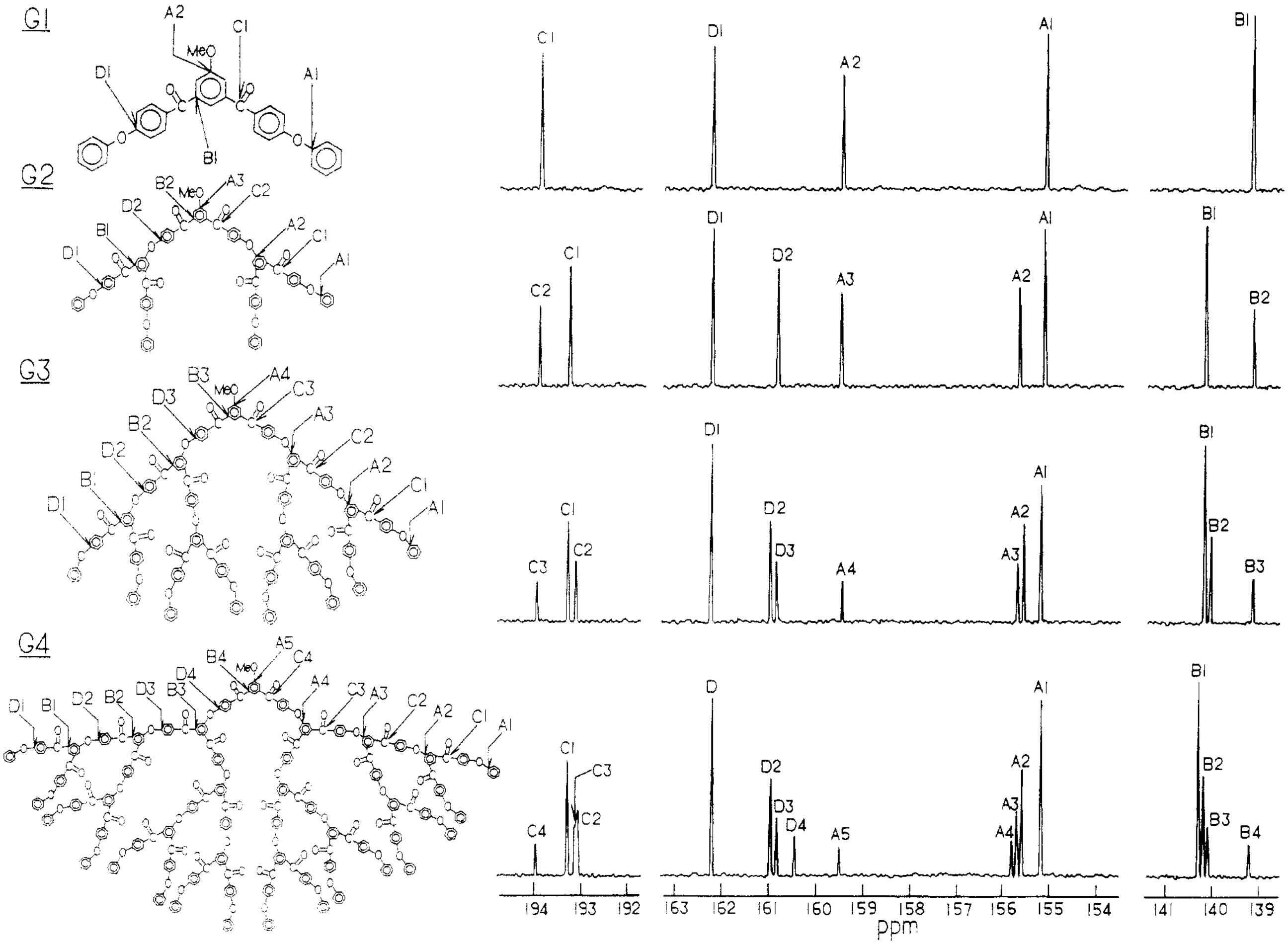


Figure 3. ^{13}C-NMR spectra of **G1**, **G2**, **G3**, and **G4** measured in $CDCl_3$.

4H), 7.48 (d, 2H), 7.38 (m, 8H), 7.19 (m, 4H), 7.14–6.90 (m, 16H), 3.92 (s, 3H). ^{13}C-NMR ($CDCl_3$, ppm): δ 194.2, 193.7, 162.3, 160.7, 156.5, 155.8, 155.1, 140.1, 139.1, 132.5, 132.3, 130.5, 130.2, 126.5, 124.9, 123.8, 122.7, 120.3, 117.8, 117.1. Anal. Calcd for $C_{84}H_{54}O_{13}$: C, 79.36; H, 4.28. Found: C, 79.11; H, 4.42.

Third-Generation Dendron (G3). Third-generation dendron **G3** was prepared by the same procedure as that for the synthesis of **G1** starting from 10.17 g (8 mmol) of **G2-OH**. Pure **G3** was obtained by silica gel column chromatography eluted by a mixture of methylene chloride and ethyl acetate (50:1). Yield: 6.28 g (55%). IR (KBr): 3078, 1654, 1584, 1240 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): δ 8.00–7.76 (m, 34H), 7.72 (m, 13H), 7.50 (d, 2H), 7.38 (m, 16H), 7.24–6.92 (m, 52H), 3.92 (s, 3H). ^{13}C-NMR ($CDCl_3$, ppm): δ 194.0, 193.2, 193.0, 162.3, 160.9, 160.7, 159.5, 155.8, 155.7, 155.2, 140.2, 140.0, 139.1, 132.5, 132.3, 132.2, 131.8, 130.7, 130.3, 130.2, 126.6, 126.5, 124.7, 123.8, 122.8, 120.4, 120.3, 118.8, 117.8, 117.5, 117.3, 55.8. Anal. Calcd for $C_{189}H_{120}O_{29}$: C, 79.51; H, 4.24. Found: C, 79.42; H, 4.38.

G3-OH. **G3-OH** was prepared by the same procedure as that for the synthesis of **G1-OH** starting from 5.71 g (2 mmol) of **G3**. It was used for the next reaction without further purification. Yield: 5.45 g (97%). IR (KBr): 3200, 3078, 1654, 1584, 1240 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): δ 8.00–7.75 (m, 35H), 7.68 (m, 12H), 7.43 (d, 2H), 7.36 (m, 16H), 7.26–6.92 (m, 52H). ^{13}C-NMR ($CDCl_3$, ppm): δ 194.0, 193.3, 193.1, 162.3, 160.8, 160.6, 156.6, 155.9, 155.7, 155.1, 140.2, 140.0, 139.2, 132.8, 132.6, 132.5, 131.7, 130.6, 130.2, 127.0, 126.9, 125.3, 124.7, 123.8, 120.2, 117.8, 117.7, 117.2, 117.0. Anal. Calcd for $C_{188}H_{118}O_{29}$: C, 79.48; H, 4.19. Found: C, 79.22; H, 4.35.

Fourth-Generation Dendron (G4). **G4** was prepared by the same procedure as that for the synthesis of **G1** starting from 2.27 g (0.8 mmol) of **G3-OH**. Pure **G4** was obtained by silica gel column chromatography eluted by a mixture of methylene chloride and ethyl acetate (30:1). Yield: 0.72 g (30%). IR (KBr): 3079, 1654, 1583, 1240 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): δ 7.98–7.76 (m, 74H), 7.68 (m, 29H), 7.47 (d, 2H), 7.38 (m, 32H), 7.24–6.94 (m, 108H), 3.92 (s, 3H). ^{13}C-NMR ($CDCl_3$, ppm): δ 194.0, 193.3, 193.1, 163.4, 161.0, 160.9, 160.7, 159.5, 155.8, 155.7, 155.6, 155.3, 140.3, 140.2, 140.1, 139.2, 132.7, 132.5, 132.4, 131.8, 131.7, 130.7, 130.2, 126.7, 126.6, 126.5, 124.8, 123.9, 123.8, 120.2, 118.5, 117.9, 117.8, 117.3, 117.2, 55.8. Anal. Calcd for $C_{397}H_{248}O_{61}$: C, 79.55; H, 4.17. Found: C, 79.45; H, 4.25.

References and Notes

(1) Starburst is a registered trademark of the Michigan Molecular Institute.

(2) For a review of Starburst dendrimers, see: (a) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138. (b) Tomalia, D. A.; Durst, H. D. In *Supramolecular Chemistry I—Directed Synthesis and Molecular Recognition*; Weber, E., Ed.; Topics in Current Chemistry Vol. 165; Springer-Verlag: Berlin, Heidelberg, 1993; pp 193–313.

(3) (a) Constable, E. C.; Thompson, A. M. W. C. *J. Chem. Soc., Chem. Commun.* **1992**, 617. (b) Nagasaki, T.; Arimori, S.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1992**, 608.

(4) (a) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Saunders, M. J.; Grossman, S. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1178. (b) Gopidas, K. R.; Leheny, A. R.; Caminati, G.; Turro, N. J.; Tomalia, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 7335. (c) Turro, N. J.; Barton, J. K.; Tomalia, D. A. *Acc. Chem. Res.* **1991**, *24*, 332. (d) Morikawa, A.; Kakimoto, M.; Imai, Y. *Polym. J.* **1992**, *24*, 573.

(5) (a) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1989**, *17*, 117. (b) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466. (c) Tomalia, D. A.; Hall, M.; Hedstrand, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 1601. (d) Tomalia, D. A.; Berry, V.; Hall, M.; Hedstrand, D. M. *Macromolecules* **1987**, *20*, 1164. (e) Naylor, A. M.; Goddard, W. A., III; Keifer, G. E.; Tomalia, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2339. (f) Moreno-Bundi, M. C.; Orellana, G.; Turro, N. J.; Tomalia, D. A. *Macromolecules* **1990**, *23*, 910.

(6) Padia, A. B.; Hall, H. K., Jr.; Tomalia, D. A. *Macromolecules* **1990**, *23*, 910.

(7) (a) Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 7077. (b) Morikawa, A.; Kakimoto, M.; Imai, Y. *Macromolecules* **1991**, *24*, 3469.

(8) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018.

(9) Miller, T. M.; Kwock, E. W.; Neenan, T. X. *Macromolecules* **1992**, *25*, 3143.

(10) (a) Hawker, C. J.; Frechet, J. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1010. (b) Hawker, C. J.; Frechet, J. M. J. *Macromolecules* **1990**, *23*, 4726. (c) Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (d) Wooley, K. L.; Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4252.

(11) Bayliff, P. M.; Feast, W. J.; Parker, D. *Polym. Bull.* **1992**, *29*, 265.

(12) Morikawa, A.; Kakimoto, M.; Imai, Y. *Macromolecules* **1992**, *25*, 3247.

(13) Moore, J. S.; Xu, Z. *Macromolecules* **1991**, *24*, 5893.

(14) Hall, H. K., Jr.; Polis, D. W. *Polym. Bull.* **1987**, *17*, 409.

(15) Millar, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M. *J. Am. Chem. Soc.* **1993**, *115*, 356.

(16) Prager, H. R.; Tan, Y. T. *Tetrahedron Lett.* **1967**, 3661.

(17) (a) Fukawa, I.; Tanabe, T.; Dozono, T. *J. Chem. Soc., Perkin Trans. 2* **1992**, 377. (b) Fukawa, I.; Tanabe, T.; Dozono, T. *Macromolecules* **1991**, *24*, 3838.