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Preparation of Poly(ether ketone) Dendrons with Graded Structures

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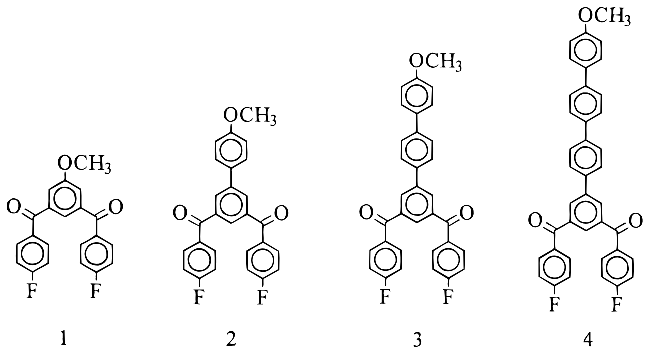
ABSTRACT: New highly branched poly(ether ketone) dendrons, with graded structures, were synthesized by the convergent approach using aromatic nucleophilic substitution reactions. Four kinds of compounds—3,5-bis(4-fluorobenzoyl)anisole, **1**; 4-methoxy-3′,5′-bis(4-fluorobenzoyl)-biphenyl, **2**; 4-methoxy-3″,5″-bis-(4-fluorobenzoyl)-*p*-terphenyl, **3**; and 4-methoxy-3‴,5‴-bis(4-fluorobenzoyl)-*p*-quaterphenyl, **4**—(numberedin the order of the phenylene length) were used as the building blocks, where the methoxy groups were the protected form of hydroxy groups. The reactions of **1** with phenol gave the first generation dendron, **G1**. Next, after the methoxy group of **G1** was converted to the hydroxy derivative, **G1−OH** by the reaction with aluminum chloride, the resultant phenol functionality of **G1−OH** was allowed to react with **2** to yield the second generation dendron: **G2**. By repeating the procedure, further generations **G3** and **G4**, were prepared using **3** and **4** as the building block, respectively. 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 the dendron posessed remarkably narrow molecular weight distribution after purification by silica gel chromatography. The analysis of these structurally unambiguous dendrons by matrix-assisted laser desorption ionization time of flight is described. The structure of the dendrons were demonstrated with a gradient of phenylene chain lengths from the periphery to the core.

Introduction

Dendrimers[1−4] are highly branched regular molecules, whose geometrical structure is usually prepared by repeating stepwise reaction. There have been divergent[5] and convergent[6] methods for the synthesis of dendrimers. In the divergent method, the preparation 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 the same as those of the core. In the convergent method, a compound possessing only one reactive group is used as 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 starting molecule and the building block are connected, the protected reactive points are released. Connection of building blocks followed by deprotection is repeated until the molecules have grown to the desired size. In the convergent method, the resulting molecule, which is called a dendron, is finally reacted with a core molecule which possesses two or more reactive groups to give a dendrimer. By the divergent method, dendrimers such as poly(amido−amine),[5,7−11] polyamine,[12] polyether,[13] polysiloxane,[14,15] polyamide[16−19] poly(carbosilane),[20] and poy(alkyl hydrocarbon)[21] have been synthesized. The convergent method has been used to synthesize polyether[6,22−25], polyester,[26,27] polyamide,[28] polysiloxane,[29] poly(phenylene),[30] poly(ether ketone),[31] and poly(arylacetylene).[32−36] The size of these products could be accurately controlled,[37,38] and functional groups could be introduced into the periphery using such a stepwise reaction.[39−47] Therefore, the dendrimers are considered to be promising as functional supramolecules with controlled structures. For example, amphiphilic dendrimers, with relatively nonpolar cores and hydrophilic outer surfaces, have been applied as micelles.[48−52]

Almost all of the dendrimers and dendrons were prepared using only one kind of building block. Only a few examples—poly(arylacetylene) dendrimers,[33,53−55] isocianate-based dendrimers[56,57] arboral,[58] and orthogonal dendrimers[59]—have been reported using different kinds of building blocks. In this study, poly(ether ketone) dendrons with graded structures were synthesized by the convergent approach, using four kinds of building blocks, which were synthesized by us in a stepwise manner,[60] in preparing each generation. The building blocks, with different phenylene chain lengths, were used in the order of increasing of phenylene numbers. Thus, the resultant dendrons are expected to have a graded structure of phenylene chain length from the periphery to the core. The properties of obtained dendrons were compared with those of poly(ether ketone) dendrons,[31] which was prepared by using only 3,5-bis(4-fluorobenzoyl)anisole, **1**, as the building block.

Chart 1



Results and Discussion

In this study, the key step of the synthesis of dendrons with graded structures is the same as that of poly(ether ketone) dendrons,[31] which we have synthesized using only **1** as the building block. The aromatic ether was formed by the reaction of aromatic fluoride, which was activated by a carbonyl group with a phenol group, whereas a phenol group was protected by a methyl

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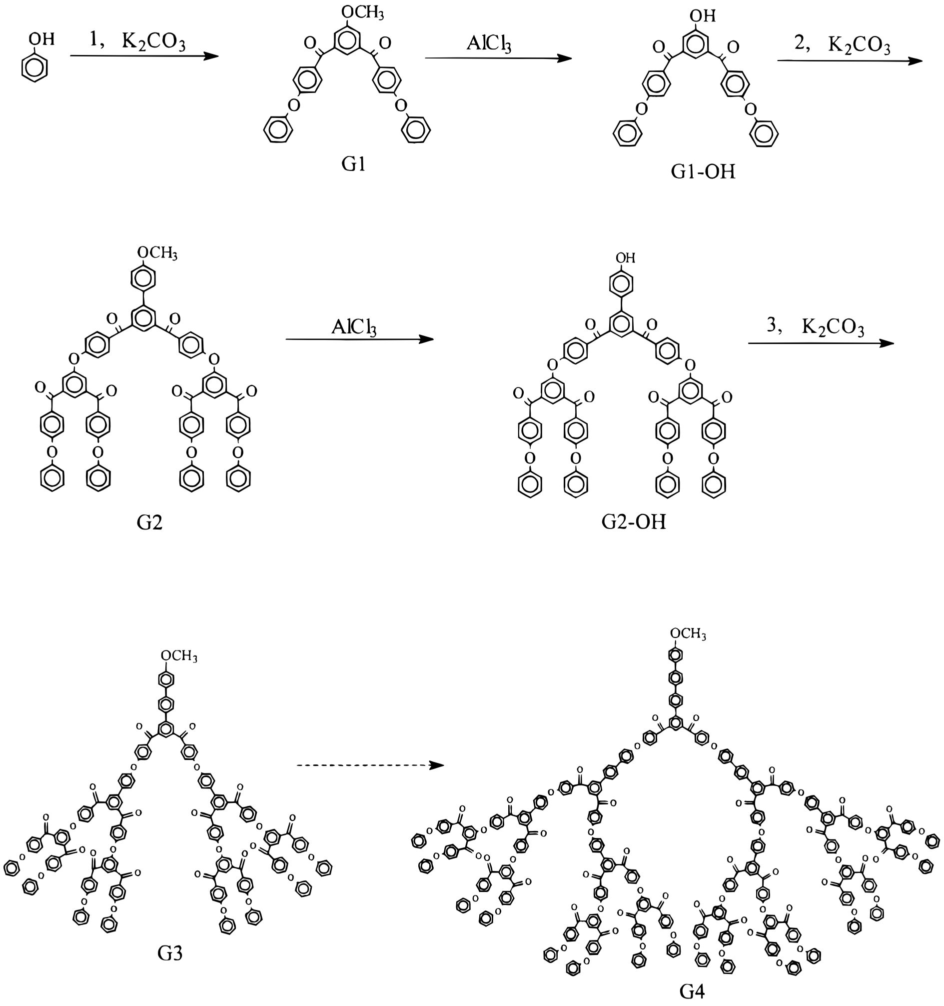
Scheme 1



group, which could be cleaved by the reaction with Lewis acids such as aluminum chloride. The four kinds of building blocks—**1**; 4-methoxy-3′,5′-bis(4-fluorobenzoyl)-biphenyl, **2**; 4-methoxy-3″,5″-bis(4-fluorobenzoyl)-*p*-terphenyl, **3**; and 4-methoxy-3‴,5‴-bis(4-fluorobenzoyl)-*p*-quaterphenyl, **4**—possessed one methoxy group and two aromatic fluorides activated by carbonyl groups in the para position (Chart 1) and have been synthesized using 3,5-bis(4-fluorobenzoyl)-phenol as starting molecule, in a stepwise manner, repeating a series of conversions of the hydroxy group to the triflate, cross-coupling the triflate with (*p*-methoxyphenyl)boronic acid, and cleaving the methyl ether.[60]

A general synthetic procedure for the poly(ether ketone) dendrons is shown in Scheme 1. First, reaction of **1** with phenol in the presence of potassium carbonate yielded first the generation dendron, **G1**. Next, the methoxy group of **G1** was cleaved with aluminum chloride in benzene to form **G1−OH** with **2**, which was one phenylene unit longer than **1**, yielded the second generation dendron, **G2**, under conditions similar to the preparation of **G1**. **G3** was prepared by the cleavage of the methoxy group of **G2** and the reaction of the resultant **G2−OH** with **3**, which was one phenylene unit longer than **2**, and similarly, **G4** was prepared by the cleavage of the methoxy group of **G3** and the reaction of the resultant **G3−OH** with **4**, which was one phenylene unit longer than **3**. The series of dendrons **G1−4** were obtained as colorless powders, which were purified by silica gel chromatography with final isolated yields of 85, 84 65, and 43% respectively. The yields of higher generations of this series were somewhat higher than those of poly(ether ketone) dendrons[31] prepared by using only **1** as the building blocks. The higher yields may be attributed to the lower degree of steric hindrance to the hydroxy group and accordingly the higher reactivity of the hydroxy group, because the hydroxy group of the higher generation, **G−OH**, was separated by phenylene units from the aromatic ring connected with the electron-withdrawing carbonyl group in comparison with those in the case of poly(ether ketone) dendrons[31] prepared from only **1**.

As shown in part A of Figure 1, the crude higher generation dendrons, especially **G4**, showed relatively broad molecular weight distribution because of the presence of small amounts of impurities. As has been reported in the synthesis of poly(ether ketone) dendrons[31] prepared by using only **1** as the building block, the lower molecular weight impurities in the crude products were regarded to be a compound which was caused by the one-to-one reaction between **G−OH** and the building block, whereas the higher molecular weight impurities were formed by the reaction of **G−OH** with an excess amount of the building block and potassium carbonate. The latter reaction has been reported in the synthesis of linear poly(ether ketones).[61,62] The relative ratio of these impurities was less than those of poly(ether ketone) dendrons[31] prepared by using only **1** as the building block. The higher selectivity of the coupling reaction of the higher generation, **G−OH**, may be also

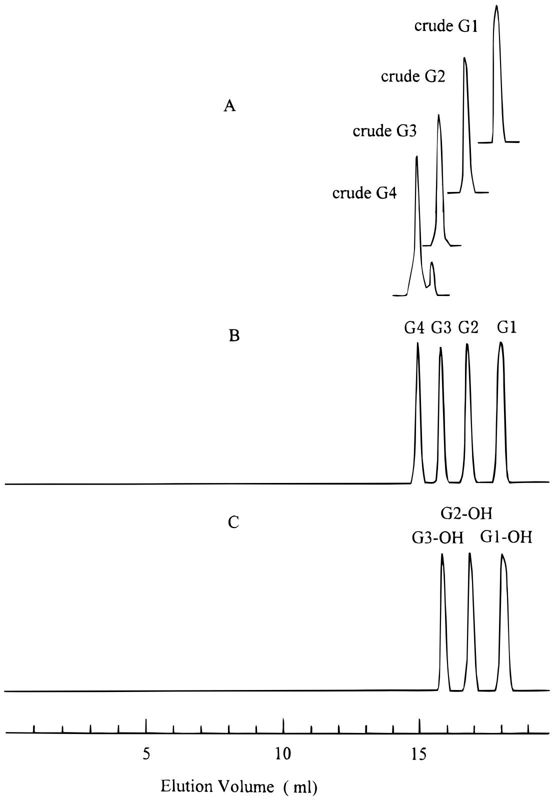


Figure 1. GPC curves of poly(ether ketone) dendrons: (A) crude products; (B) and (C) after purification with silica gel column chromatography.

ascribed to the lower steric hindrance of the hydroxy group. As indicated in parts B and C of Figure 1, the molecular weights of the purified dendrons and their hydroxy derivatives increased with increasing generation, and the molecular weight distributions of these dendrons were remarkably narrow. The reaction volumes were smaller than those of poly(ether ketone) dendrons[31] prepared by using only **1** as the building block, indicating that the sizes of the present dendrons were larger due to the large size of their building blocks.

Typical carbonyl and ether adsorptions were observed at 1665 and 1165 cm^{-1}, respectively, in the IR spectra of all of the dendrons. Elemental analyses were also in good agreement with the calculated value for the proposed structures in all cases.

The ^1H NMR spectra and the assignments of **G2−4** are shown in Figure 2. The NMR of **G1** is not shown because **G1** is the same compound as that of poly(ether ketone) dendrons[31] prepared by using only **1** as the building block. These molecules contained seven kinds of aromatic ring systems. The terminal and the branching points comprised the first two of them. The former were phenoxy groups, and the latter were trisubstituted aromatic rings with aryl oxy and two carbonyl groups and phenylene and two carbonyl groups. The other aromatic ring systems were four kinds of 1,4-disubstituted aromatic rings with methoxy and phenylene groups, aryl oxy and phenylene groups, two phenylene groups, and aryl oxy and carbonyl groups. The ^1H NMR signals of the aromatic rings were well-resolved in **G2**, whereas those in **G3** and **G4** overlapped each other. The generation number of a dendron could be estimated from the number of the triplet and doublet signals appearing around 8.07−8.14 and 8.17−8.27 ppm, which corresponded to protons para (*j*, *p*, and *v*) and meta (*k*, *q*, and *w*) to phenylene substituent in trisubstituted aro-

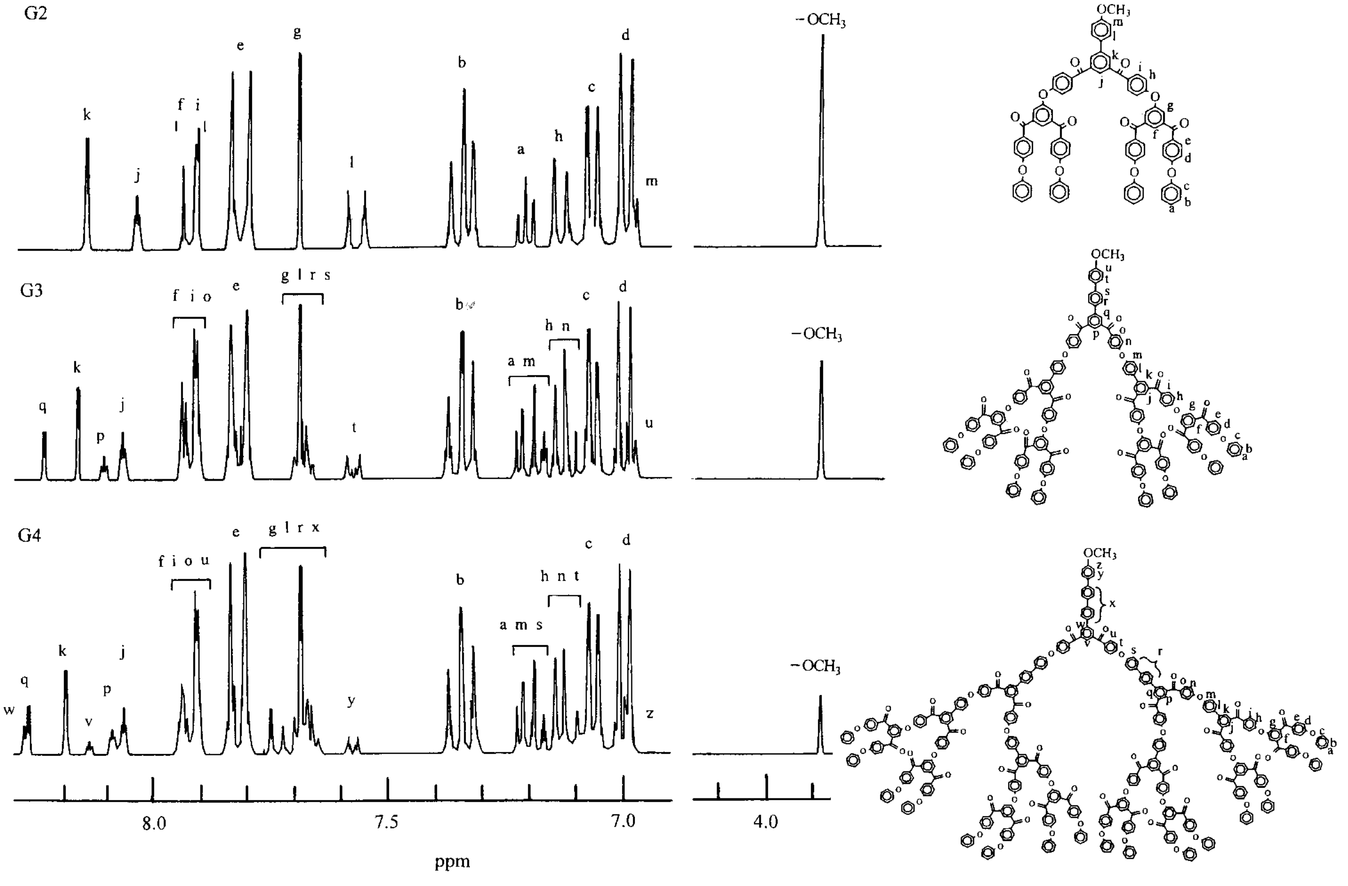


Figure 2. ^1H NMR spectra of **G2−4** measured in $CDCl_3$.

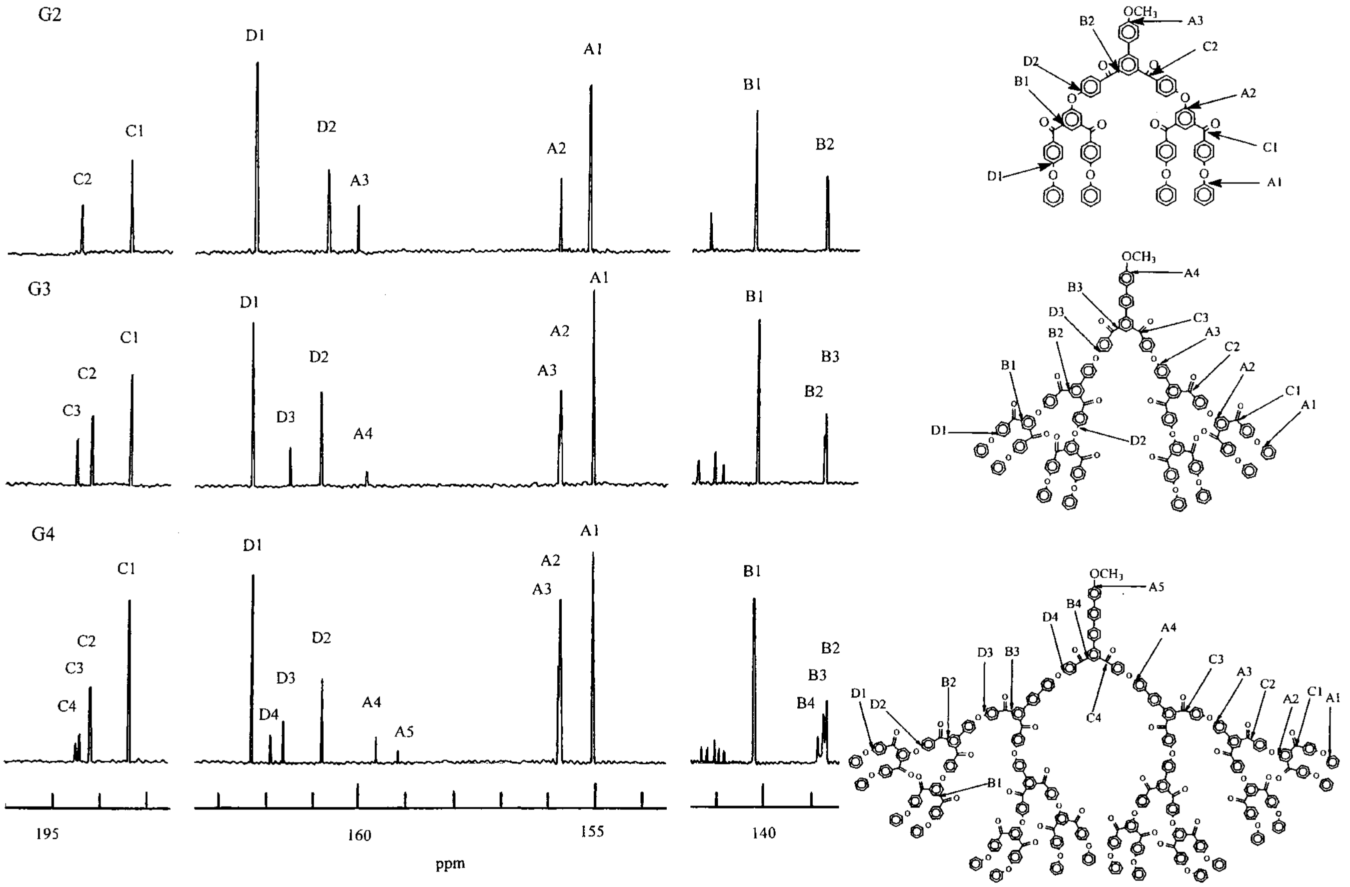


Figure 3. ^{13}C NMR spectra **G2**−**4** measured in $CDCl_3$.

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

	ratio	
	calcd	found
G1	7.00	6.97
G2	19.0	18.9
G3	44.3	44.1
G4	96.3	96.8

matic rings with phenylene and two carbonyl groups, respectively. The ratio of integration of aromatic protons to that of methyl protons (shown in Table 1) provided additional evidence for the formation of dendrons.

^{13}C NMR spectra of **G2**−**4** were complicated because of the presence of many signals, but four kinds of characteristic signals, which corresponded to the carbonyl carbons (C type, around 194 ppm), the carbons bonded to oxygen atoms on the 1,4-disubstituted aromatic rings with aryl oxy and carbonyl groups (D type, around 160−163 ppm), the other carbons bonded to the oxygen atoms (A type, around 155−160 ppm), which were present on the opposite side of D type carbons, and the carbons bonded to carbonyl group on the trisubstituted aromatic rings (B type, around 138−140 ppm) could clearly be assigned (Figure 3). These peaks clearly were separated from one another, and the chemical structure of the dendrons obviously was elucidated as the expected structure.

Although NMR spectroscopy is a valuable tool for monitoring growth of the dendrimers, the sensitivity of the integration was not sufficient for an assessment of the structural perfection of dendrimers. For this purpose, the matrix-assisted laser desorption ionization time of flight (MALDI-TOF) technique was employed in order to obtain definite evidence for the structure of the present poly(ether ketone) dendrons. This method can provide highly accurate mass determinations for nonvolatile intact molecular ions and was used in recent investigations of dendrimers with excellent results.[20,34,52,63−68] Figure 4shows the MALDI-TOF spectra of **G2**−**4**. The molecular ion peaks occurred at m/z values which agree very closely with calculated values (Table 2), and all of the spectra confirm that the products are of very high purity and monodispersed. Besides the molecular ion species, sodium adducts, potassium adducts, and matrix adducts were observed, and the relative ratio of the adducts to the molecular ion species increased with increasing number of generation.

These dendrons were soluble in various organic solvents such as amide solvents, dimethyl sulfoxide, tetrahydrofuran (THF)methylene chloride, chloroform, and benzene, as well as the dendrons[31] prepared by using only **1** as the building block.

According to differential scanning calorimetry (DSC), glass transition temperatures (T_g) of **G2**−**4** were observed at 89, 123, and 132 °C, respectively. The T_g's of these dendrons were slightly higher than those of the dendrons[31] prepared by using only **1** as the building block. The presence of rigid structures, for example, the biphenyl, terphenyl, and quarterphenyl structures in the present dendrons, may affect the higher T_g's.

Experimental Section

^{1}H and ^{13}C NMR and IR spectra were recorded on a JNM-GSX-400 FT-NMR spectrometer and a Shimadzu IR 435 spectrophotometer, respectively. Gel permeation chromatography (GPC) was performed with an apparatus using a Polymer Laboratories analytical column, PL gel 5 μm MIXED-

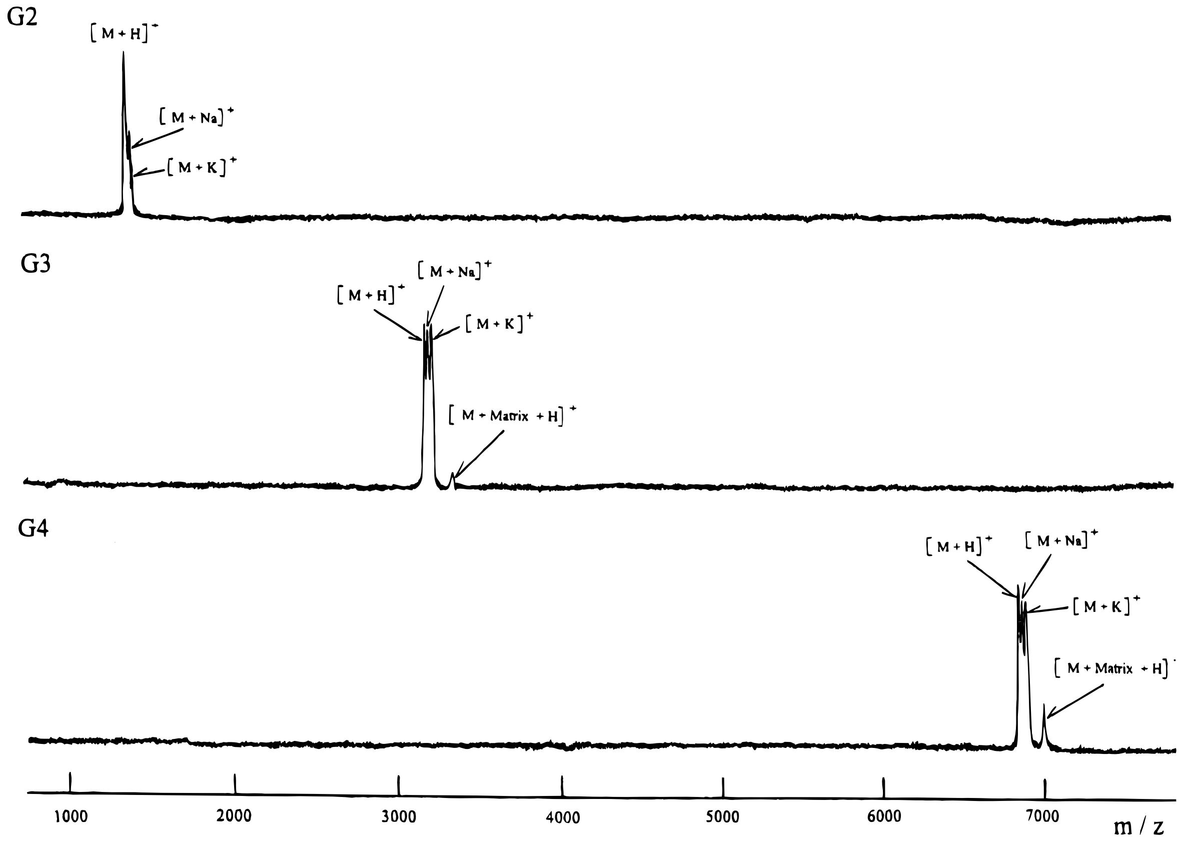


Figure 4. MALDI-TOF mass spectra of **G2**−**4**.

Table 2. Results of MALDI-TOF Mass Spectrometry of Dendrons

	calcd mass[a]	measured mass
G1	501.55	501.58
G2	1362.46	1362.75
G3	3160.40	3161.22
G4	6832.37	6833.45

C, and THF as eluent. DSC was performed with a Rigaku Thermal Analysis Station TAS 100, respectively. The measurements of DSC were made at a heating rate of 10 °C min^{-1} in nitrogen. MALDI-TOF spectra were recorded on a Shimadz/Kratos Kompact MALDI II equipped with a 337 nm nitrogen laser. The sample preparation was as follows. The solution of analyte (5 mg) and matrix (20 mg) in THF (1 mL) was prepared and 1 μl of this matrix/analyte solution was transferred to a stainless steel sample plate via automatic pipette. The measurement was performed in positive ion mode using 2,5-dihydroxybenzoic acid as the matrix.

Four kinds of building block, **1**−**4**, were synthesized according to the method reported previously.[51]

First-Generation Dendron (G1). In a flask, a mixture of 17.62 g (0.05 mol) of **1**, 10.35 g (0.11 mol) of phenol, 13.82 g (0.10 mol) of potassium carbonate, 50 mL of toluene, and 90 mL of *N*,*N*-dimethylacetamide was stirred at 130 °C for 1 h. Then the temperature was raised to 160 °C, and water formed during the reaction was removed as an azeotrope with toluene. The reaction mixture was stirred at this temperature for 1.5 h. After the reaction was complete, the mixture was cooled to about 80 °C, and the solvent was evaporated under a reduced pressure of 15−20 torr. The residue was washed with 300 mL of water and extracted with 200 mL of methylene chloride. The combined extract was dried over anhydrous magnesium sulfate. The crude **G1** was obtained by evaporation of the solvent and purified by recrystallization from acetic acid. Yield: 21.29 g (85%). IR (KBr): 3040, 2920, 1665, 1585, 1490, 1320, 1240, 1165 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): δ 3.92 (s, 3H), 7.02 (d, 4H, J = 8.8 Hz), 7.05−7.14 (m, 4H), 7.18−7.24 (m, 2H), 7.35−7.48 (m, 4H), 7.52 (d, 2H, J = 1.5 Hz), 7.66 (t, 1H, J = 1.5 Hz), 7.84 (d, 4H, J = 8.8 Hz). ^{13}C NMR (CDCl$_3$, ppm): δ 55.81, 116.72, 117.83, 120.02, 123.75, 124.63, 130.19, 131.48, 132.32, 139.19, 155.44, 159.61, 162.03, 194.2. Anal. Calcd for $C_{33}H_{24}O_5$: C, 79.19; H, 4.83. Found: C, 78.95; H, 4.89.

G1−OH. A mixture of 20.04 g (0.04 mol) of **G1**, 8.00 g (0.06 mol) of aluminum chloride, and 150 mL of benzene was stirred at reflux temperature for 2 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 magnesium sulfate. The crude **G1−OH** was obtained by evaporation of the solvent and purification by recrystallization from toluene. Yield: 18.22 g (94%). IR (KBr): 3400−3000, 3040, 1665, 1585, 1490, 1320, 1240, 1165 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): δ 7.00 (d, 4H, J = 8.8 Hz), 7.04−7.14 (m, 4H), 7.16−7.28 (m, 2H), 7.32−7.46 (m, 4H), 7.58 (d, 2H, J = 1.5 Hz), 7.72−7.92 (m, 5H). ^{13}C NMR (CDCl$_3$, ppm): δ 116.52, 117.13, 120.22, 123.01, 124.44, 130.19, 131.52, 132.39, 139.18, 155.31, 156.98, 162.23, 194.83. 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** but using 17.05 g (0.035 mol) of **G1−OH**, 7.28 g (0.017 mol) of 2, 4.70 g (0.034 mol) of potassium carbonate, 40 mL of toluene, and 80 mL of *N*,*N*-dimethylacetamide. Pure **G2** was obtained by silica gel column chromatography beginning with methylene chloride as the eluent and gradually changing to 2% ethyl acetate in methylene chloride. Yield: 19.43 g (84%). IR (KBr): 3040, 2920, 1665, 1585, 1490, 1320, 1165 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): δ 3.85 (s, 3H), 6.97−7.05 (m, 10H), 7.07−7.11 (m, 8H), 7.13 (d, 4H, J = 8.8 Hz), 7.18−7.24 (m, 4H), 7.37−7.43 (m, 8H), 7.58 (d, 2H, J = 8.8 Hz), 7.70 (d, 4H, J = 1.5 Hz), 7.83 (d, 8H, J = 8.8 Hz), 7.89−7.94 (m, 6H), 8.05 (t, 1H, J = 1.5 Hz), 8.14 (d, 2H, J = 1.5 Hz). ^{13}C NMR (CDCl$_3$, ppm): δ 55.40, 114.58, 117.21, 117.92, 120.34, 123.88, 124.86, 126.57, 128.37, 128.69, 130.13, 130.76, 131.03, 131.46, 132.39, 132.51, 132.75, 138.60, 140.20, 141.46, 155.19, 155.82, 159.96, 160.72, 162.34, 193.42, 194.43. Anal. Calcd for $C_{91}H_{60}O_{13}$: C, 80.28; H, 4.44. Found: C, 80.01; H, 4.52.

G2−OH. G2−OH was prepared by the same procedure as that for the synthesis of **G1−OH** but using 19.05 g (0.014 mol) of **G2**, 2.80 g (0.021 mol) of aluminum chloride, and 120 mL of benzene, and the reaction mixture was stirred at reflux temperature for 10 h. Pure **G2−OH** was obtained by silica gel column chromatography beginning with methylene chloride as the eluent and gradually changing to 10% ethyl acetate in methylene chloride. Yield: 15.46 g (82%). IR (KBr): 3400−3000, 3040, 1665, 1585, 1490, 1325, 1240, 1165 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): δ 6.94 (d, 2H, $J = 8.8$ Hz), 7.02 (d, 8H, $J = 8.8$ Hz), 7.06−7.10 (m, 8H), 7.12 (d, 4H, $J = 8.8$ Hz), 7.18−7.23 (m, 4H), 7.34−7.43 (m, 8H), 7.50 (d, 2H, $J = 8.8$ Hz), 7.69 (d, 4H, $J = 1.5$ Hz), 7.82 (d, 8H $J = 8.8$ Hz), 7.88−7.93 (m, 6H), 8.03 (t, 1H, $J = 1.5$ Hz), 8.12 (d, 2H, $J = 1.5$ Hz). ^{13}C NMR (CDCl$_3$, ppm): δ 116.09, 117.19, 117.90, 120.32, 123.88, 124.85, 126.57, 128.55, 128.69, 130.11, 130.71, 130.98, 131.31, 132.33, 132.51, 132.75, 138.52, 140.17, 141.48, 155.16, 155.79, 156.47, 160.71, 162.34, 193.47, 194.48. Anal. Calcd for $C_{90}H_{58}O_{13}$: C, 80.23; H, 4.34. Found: C, 79.97; H, 4.45.

Third-Generation Dendron (G3). G3 was prepared by the same procedure as that for the synthesis of **G1** buC using 14.82 g (0.011 mol) of **G2−OH**, 2.67 g (5.3 mmol) of **3**, 1.46 g (10.6 mmol) of potassium carbonate, 25 mL of toluene, and 60 mL of *N*,*N*-dimethylacetamide. Pure **G3** was obtained by silica gel column chromatography beginning with methylene chloride as the eluent and gradually changing to 5% ethyl acetate in methylene chloride. Yield: 10.88 g (65%). IR (KBr): 3040, 2920, 1665, 1580, 1490, 1325, 1240, 1165 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): δ 3.85 (s, 3H), 6.97−7.04 (m, 18H), 7.05−7.10 (m, 16H), 7.10−7.16 (m, 12H), 7.18−7.24 (m, 12H), 7.36−7.42 (m, 16H), 7.57 (d, 2H, $J = 8.8$ Hz), 7.64−7.71 (m, 16H), 7.82 (d, 16H, $J = 8.8$ Hz), 7.89−7.94 (m, 16H), 8.09 (t, 2H, $J = 1.5$ Hz), 8.11 (t, 1H, $J = 1.5$ Hz), 8.18 (d, 4H, $J = 1.5$ Hz), 8.23 (d, 2H, $J = 1.5$ Hz). ^{13}C NMR (CDCl$_3$, ppm): δ 55.34, 114.32, 117.16, 117.59, 117.92, 120.34, 120.69, 123.87, 124.85, 126.60, 127.28, 127.60, 128.71, 129.20, 129.27, 129.38, 130.11, 130.68, 130.98, 131.25, 131.30, 131.68, 132.20, 132.48, 132.63, 132.74, 135.49, 137.29, 138.70, 138.73, 140.15, 140.83, 140.96, 141.37, 155.11, 155.76, 155.79, 159.43, 160.77, 161.54, 162.30, 193.39, 194.23, 194.48. Anal. Calcd for $C_{213}H_{136}O_{29}$: C, 80.98; H, 4.34. Found: C, 80.71; H, 4.42.

G3−OH. G3−OH was prepared by the same procedure as that for the synthesis of **G1−OH** but using 10.42 g (3.3 mmol) of **G3**, 0.67 g (5.0 mmol) of aluminum chloride, and 60 mL of benzene. The reaction mixture was stirred at reflux temperature for 10 h as was done for **G2−OH**. Pure **G3−OH** was obtained by silica gel column chromatography beginning with methylene chloride as the eluent and gradually changing to 10% ethyl acetate in methylene chloride. Yield: 7.89 g (76%). IR (KBr): 3400−3000, 3040, 1665, 1585, 1490, 1320, 1165 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): δ 6.93 (d, 2H, $J = 8.8$ Hz), 7.01 (d, 16H, $J = 8.8$ Hz), 7.05−7.11 (m, 16H), 7.11−7.16 (m, 12 H), 7.17−7.24 (m, 12H), 7.36−7.43 (m, 16 H), 7.48 (d, 2H, $J = 8.8$ Hz), 7.60−7.71 (m, 16H), 7.82 (d, 16H, $J = 8.8$ Hz), 7.88−7.95 (m, 16H), 8.09 (t, 2H, $J = 1.5$ Hz), 8.13 (t, 1H, $J = 1.5$ Hz), 8.18 (d, 4H, $J = 1.5$ Hz), 8.21 (d, 2H, $J = 1.5$ Hz). ^{13}C NMR (CDCl$_3$, ppm): δ 115.85, 117.16, 117.59, 117.95, 120.32, 120.69, 123.87, 124.86, 126.62, 127.23, 127.58, 128.21, 129.00, 129.27, 129.40, 130.11, 130.65, 131.25, 131.30, 131.34, 131.65, 132.20, 132.51, 132.64, 132.75, 135.46, 137.24, 138.70, 138.73, 140.14, 140.85, 140.93, 141.29, 155.09, 155.11, 155.77, 155.90, 160.75, 161.56, 162.34, 193.45, 194.26, 194.50. Anal. Calcd for $C_{212}H_{134}O_{29}$: C, 80.95; H, 4.29. Found: C, 80.76; H, 4.41.

Fourth-Generation Dendron (G4). G4 was prepared by the same procedure as that for the synthesis of **G1** but using 7.55 g (2.4 mmol) of **G3−OH**, 0.67 g (1.15 mmol) of **4**, 0.32 g (2.3 mmol) of potassium carbonate, 15 mL of toluene, and 40 mL of *N*,*N*-dimethylacetamide. Pure **G4** was obtained by silica gel column chromatography beginning with methylene chloride as the eluent and gradually changing to 10% ethyl acetate in methylene chloride. Yield: 3.38 g (43%). IR (KBr): 3040, 2920, 1665, 1585, 1485, 1320, 1235, 1165 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): δ 3.85 (s, 3H), 6.98−7.04 (m, 34H), 7.05−7.10 (m, 32H), 7.10−7.16 (m, 28H), 7.17−7.23 (m, 28H), 7.36−7.42 (m, 32H), 7.58 (d, 2H, $J = 8.8$ Hz), 7.63−7.76 (m, 44H), 7.81 (d, 32H, $J = 8.8$ Hz), 7.88−7.95 (m, 36H), 8.08 (t, 4H, $J = 1.5$ Hz), 8.10 (t, 2H, $J = 1.5$ Hz), 8.13 (t, 1H, $J = 1.5$ Hz), 8.18 (d, 8H, $J = 1.5$ Hz), 8.25 (d, 4H, $J = 1.5$ Hz), 8.26 (t, 2H, $J = 1.5$ Hz). ^{13}C NMR (CDCl$_3$, ppm): δ 55.37, 114.30, 117.20, 117.48, 117.62, 117.95, 120.34, 120.61, 120.71, 123.90, 124.88, 126.63, 127.16, 127.38, 127.63, 127.71, 127.74, 127.76, 128.06, 128.74, 129.05, 129.31, 129.51, 129.58, 130.13, 130.71, 131.22, 131.27, 131.32, 131.52, 131.66, 131.87, 132.22, 132.52, 132.64, 132.66, 132.77, 135.54, 136.83, 137.24, 138.04, 138.73, 138.76, 138.84, 140.19, 140.77, 140.93, 140.98, 141.17, 141.26, 141.29, 141.37, 155.14, 155.79, 155.81, 158.43, 159.32, 160.80, 161.63, 161.89, 162.34, 193.39, 194.23, 194.43, 194.53. Anal. Calcd for $C_{463}H_{292}O_{61}$: C, 81.41; H, 4.31. Found: C, 81.22; H, 4.50.

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