

Preparation of Poly(ether ether ketone) Dendrimers by the Divergent Method

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ABSTRACT: New highly branched poly(ether ether ketone) dendrimers were synthesized by the divergent approach through aromatic nucleophilic substitution reactions. 3,5-Dimethoxy-4'-(4-fluorobenzoyl)diphenylether, **1**, and 1,3,5-tris[*p*-(3,5-dihydroxyphenoxy)phenyl]benzene, **G0-OH**, were used as a building block and starting core, respectively. The reaction of **1** with **G0-OH** gave the first-generation dendrimer (**G1-OMe**), which possessed 12 methoxy groups on the periphery. After the methoxy groups were converted to hydroxy groups by treatment with pyridine hydrochloride, the resultant phenol functionality (**G1-OH**) was allowed to react with **1** to yield the second-generation dendrimer (**G2-OMe**) which possessed 24 methoxy groups. By repeating these procedures **G3-OMe** dendrimer and **G3-OH** dendrimer possessing 48 methoxy and hydroxy groups, respectively, on the periphery were obtained. ¹H and ¹³C NMR spectra were consistent with the structures of these dendrimers. Molecular weights and molecular weight distribution determined by gel permeation chromatography indicated that the dendrimers possessed remarkably narrow molecular weight distribution. Analysis was made of these structurally unambiguous dendrimers by matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectroscopy. The characteristics of these dendrimers, **Gn-OMe** and **Gn-OH**, such as solubility and thermal properties were compared.

KEY WORDS Poly(ether ether ketone) Dendrimers / Divergent Method / 3,5-Dimethoxy-4'-(4-fluorobenzoyl)diphenylether / 1,3,5-Tris[*p*-(3,5-dihydroxyphenoxy)phenyl]benzene / Aromatic Nucleophilic Substitution Reactions /

Dendrimers^{1–4} are highly branched regular molecules, whose geometrical structures are usually prepared by repeating stepwise reaction. There have been divergent⁵ and convergent⁶ 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 contains one functional group to connect with reactive groups of the core and two or more protected reactive group, 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 building block are connected, the protected reactive points are released. Connection of building blocks followed by deprotection are repeated until the molecules have grown to desired size. By the divergent method, dendrimers such as poly(amido-amine),^{5,7–11} polyamine,¹² polyether,^{13,14} polysiloxane,^{15,16} polyamide,^{17–20} poly(carbosilane),^{21–23} poly(carbosilazane)²⁴ and poly(alkyl hydrocarbon)²⁵ have been synthesized. The convergent method has been used to synthesize polyether,^{6,26–29} polyester,^{30–32} polyamide,³³ polysiloxane,³⁴ poly(phenylene),³⁵ poly(ether ketone),^{36,37} poly(arylacetylene),^{38–42} poly(arylamine)⁴³ and aliphatic polyether.⁴⁴ The orthogonal approach,^{45–47} wherein the protection or deprotection steps are eliminated by use of two different building blocks, was demonstrated in the convergent method. Their size could be accurately controlled^{48,49} and functional groups could be introduced into the periphery using such a stepwise reaction.^{50–58} Dendrimers with well-defined controlled structure are considered promising as functional supramolecules. Am-

phiphilic dendrimers, with relatively nonpolar cores and hydrophilic outer surfaces, have been applied as micelles.^{59–63}

However, the divergent method appears more advantageous to introduce functional groups into the periphery than the convergent method because it allows exterior functionalization of the dendrimers subsequent to dendrimer synthesis. One more step for the introduction of the functional groups is required after dendrimer synthesis in the convergent method. A new process, the conversion of the benzyl ester groups to the carboxyl groups, was required in the convergent synthesis of polyester.³⁰ It was thought to be impossible to introduce functional groups into the periphery in author's convergent synthesis of poly(ether ketone) because highly reactive aluminum chloride was used in the conversion of the protected methoxy group to the reactive hydroxy group.^{36,37}

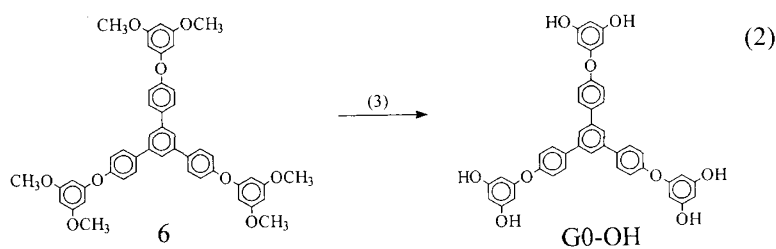
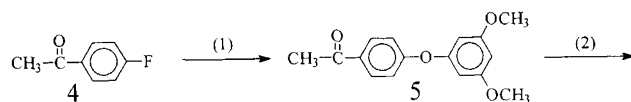
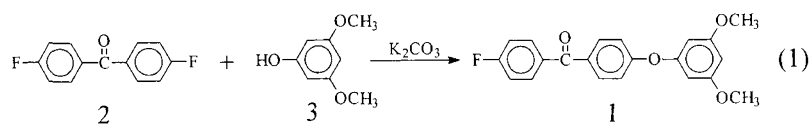
This study describes a divergent synthetic route to dendritic poly(ether ether ketone)s possessing methoxy or hydroxy groups at the periphery, where methoxy groups are used as protective form for hydroxy groups, and dendritic molecules are grown by a reaction between the hydroxy groups and aromatic fluorides activated by carbonyl groups in the para position. All dendrimers prepared are characterized with respect to molecular weight using MALDI-TOF. The characteristics of the dendrimers such as solubility and thermal properties are discussed on the basis of the contribution of the end methoxy or hydroxy groups, on the periphery.

RESULTS AND DISCUSSION

The key steps in the synthesis of poly(ether ether ketone) dendrimers are the formation of covalent bonds for extension to dendrimers and deprotection to release reactive points. These steps are similar to those of poly-

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(1) 3, K₂CO₃ (2) CF₃SO₃H (3) pyridine HCl

(ether ketone) dendrons,^{36,37} as reported, and the former step is the formation of aromatic ether by reaction between phenol and aromatic fluoride activated by carbonyl group. Secondly, phenol is protected by the methyl group, which can be cleaved by the treatment with pyridine hydrochloride.^{64,65} Thus, 3,5-dimethoxy-4'-(4-fluorobenzoyl)diphenylether, **1**, was used as the building block for the present dendrimer, which possessed two methoxy groups and one aromatic fluoride activated by carbonyl group. Building block, **1**, was synthesized by the reaction between 4,4'-difluorobenzophenone, **2**, and 3,5-dimethoxyphenol, **3**, as shown in eq 1, and was purified by fractional distillation.

As the starting core, 1,3,5-tris(*p*-(3,5-dihydroxyphenoxy)phenyl)benzene, **G0-OH**, was used. **G0-OH** was synthesized in three steps starting from 4-fluoroacetophenone, **4**, and **3** as shown in eq 2. After the reaction of **4** with **3**, the acetyl group of the resultant compound, **5**, was condensed to 1,3,5-trisphenylbenzene derivative, **6**, by acid catalysis.⁶⁶ The cleavage of methoxy group in **6** afforded the starting core, **G0-OH**. The overall yield of the three steps was 58%.

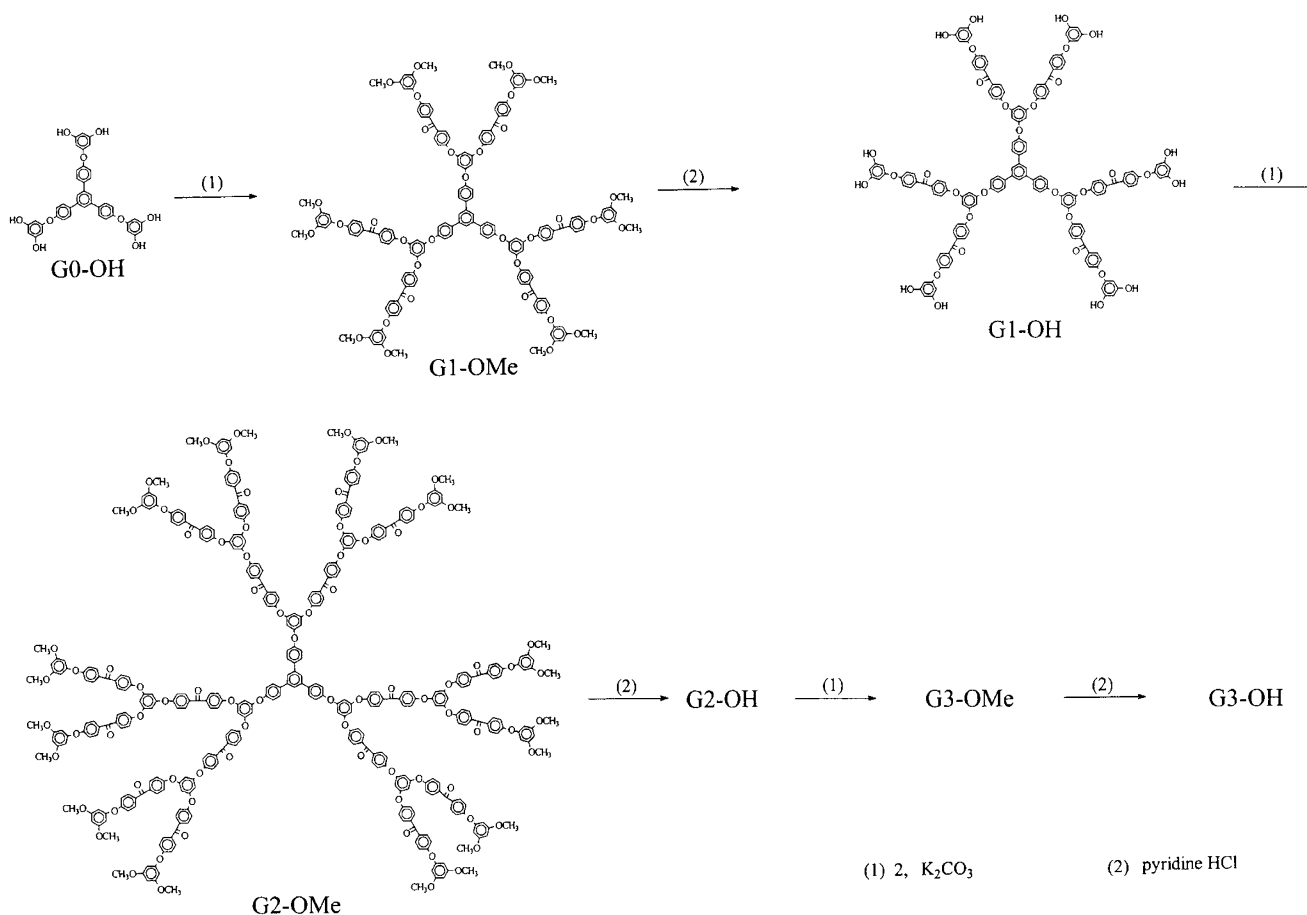
A general synthetic procedure for the poly(ether ether ketone) dendrimers is shown in Scheme 1. First, reaction of **G0-OH** with **1** in the presence of potassium carbonate yielded the first-generation dendrimer, **G1-OMe**. The methoxy group of **G1-OMe** was cleaved by the treatment with pyridine hydrochloride at 240°C to give **G1-OH**. Further reaction of **G1-OH** with **1** yielded the second-generation dendrimers, **G2-OMe**, under similar conditions for the preparation of **G1-OMe**. After conversion of **G2-OMe** to **G2-OH**, one more repeat of these procedures afforded **G3-OMe** and **G3-OH** possessing 48 methoxy and hydroxy groups, respectively, on the pe-

riphery were prepared. The obtained dendrimers were colorless powders, which were purified by silica gel column chromatography. The final isolated yields of **G1-OMe**, **G2-OMe**, and **G3-OMe** were 92%, 83%, and 62%, respectively, and those of **G1-OH**, **G2-OH**, and **G3-OH** were 95%, 91%, and 87%, respectively.

The growth and purity of these dendrimers were confirmed by GPC (Figure 1) and MALDI-TOF (Figure 2). MALDI-TOF was used to obtain definite evidence for the structure of the present poly(ether ether ketone) dendrimers. This method provides highly accurate mass determinations for nonvolatile intact molecular ions, and has been demonstrated by recent investigation of dendrimers with excellent results.^{21,40,63,66-71}

In GPC curves, the crude higher generation dendrimers (**G2-OMe** and **G3-OMe**) showed relatively broad molecular weight distribution because of the presence of the lower molecular weight impurities. In the MALDI-TOF mass spectra of the crude **G3-OMe**, signals for the lower molecular weight impurities were observed besides abundant peaks for the dendrimers, and as differences between these observed signals were 332 aum, which corresponded to the $-C_6H_4COC_6H_4OC_6H_3(OMe)_2$ unit, the formation of these low molecular weight impurities were regarded to due to incomplete reaction between **G-OH** and **1**. In the MALDI-TOF mass spectra of the purified dendrimers, molecular ion peaks occurred at *m/z* which agreed very closely with calculated values, and all spectra confirmed that the products were of very high purity and monodispersed. That no signals for impurities were observed in the spectra of **Gn-OH** suggests that no side reaction occurs even during deprotective treatment at high temperatures.

Figure 3 shows the ¹H NMR spectra of the dendrimers.



Scheme 1.

In the 1H NMR spectra of **Gn-OH**, signals of the methoxy protons being present in **Gn-OMe** disappeared, while signals of the hydroxy group appeared. The signals of aromatic protons could be classified as signals of protons on the exterior 1,3,5-trisubstituted aromatic rings with two methoxy groups or two hydroxy groups (a), protons on the 1,3,5-trisubstituted aromatic rings with three phenoxy groups in the interior of the molecules (b), protons on the meta-position of the carbonyl groups (c), protons on the ortho-position of the carbonyl groups (d), and protons on 1,3,5-trisphenylbenzene ring ascribed to the starting core, **G0-OH** (e). The obtained ratios of these protons agreed with calculated values.

^{13}C NMR spectra of these dendrimers were complicated due to the presence of many signals. Thus, only the regions 195–190 ppm and 110–95 ppm of **Gn-OH**, the most distinctive, are shown in Figure 4. Resonance for the carbonyl carbons is seen in the former region. Resonance for the carbons bonded to hydrogen atoms on the 1,3,5-trisubstituted aromatic rings is seen in the latter region. Resonance attributed to the trisubstituted aromatic rings originated in the starting core, **G0-OH**, near 105 ppm, those attributed to the trisubstituted aromatic rings located at the exterior near 99 and 98 ppm, and those attributed to the other trisubstituted aromatic rings located at the interior near 106 ppm. As generation number increased, the signals for the units originated in the starting core, **Gn-OH**, decreased in the intensity compared to the corresponding resonance for other units.

The solubility of these dendrimers was remarkably in-

fluenced by groups at the periphery. Dendrimers possessing the methoxy groups at the periphery, **Gn-OMe**, were soluble in various organic solvents such as amide solvents, dimethyl sulfoxide, tetrahydrofuran, methylene chloride, chloroform and benzene. Dendrimers possessing the hydroxy groups at the periphery, **Gn-OH**, insoluble in non-polar solvents such as methylene chloride, chloroform and benzene, and soluble in amides solvent, dimethyl sulfoxide, tetrahydrofuran, methanol, and surprisingly, aqueous KOH or NaOH solution. The solubility of **G1-OH**, **G2-OH**, and **G3-OH**, in 1.0 g of 1 M aqueous NaOH solution were 90 mg, 70 mg, and 25 mg, respectively. Therefore, the solubility of the higher generation dendrimer was lower. These dendrimers, **Gn-OH**, were not soluble in water.

The viscosity of these dendrimers was measured. Figures 5 and 6 show the relationships between reduced viscosity η_{sp}/C and concentration C in tetrahydrofuran and 1 M aqueous NaOH solution, respectively. **Gn-OMe** could not be measured in 1 M aqueous NaOH solution due to the insolubility. The reduced viscosity of these dendrimers was independent on concentration, and that of higher generation dendrimers was higher. These dendrimers were thus not associated one another in solution. The viscosity of **Gn-OH** in tetrahydrofuran was higher than that of **Gn-OMe** in the same solvent and that of **Gn-OH** in 1 M aqueous NaOH solution. This higher viscosity of **Gn-OH** in tetrahydrofuran may be due to solvation of tetrahydrofuran to hydroxy groups, leading extension of the molecule.

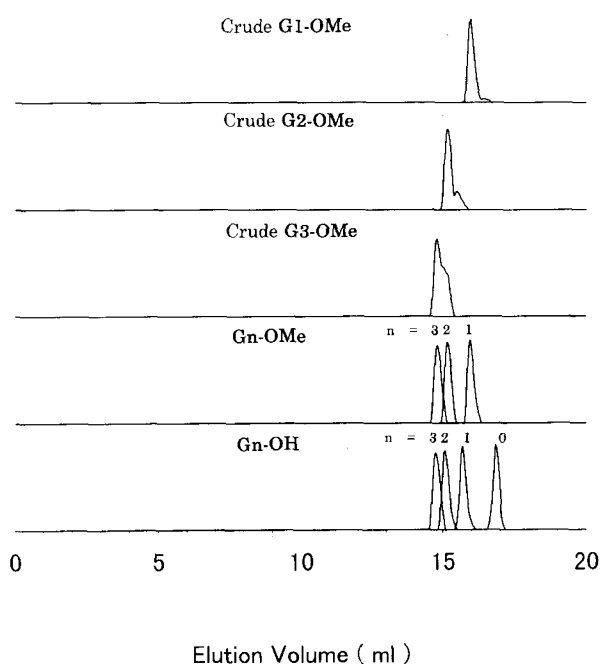


Figure 1. GPC curves of crude and purified poly(ether ether ketone) dendrimers.

Thermal behavior of these dendrimers was evaluated by differential scanning calorimetry (DSC). These dendrimers seemed to be non-crystalline and only glass transition temperature (T_g) was observed. T_g s of **G1-OMe**, **G2-OMe**, and **G3-OMe** were 75, 95 and 101°C, respectively, and higher generation dendrimers showed higher T_g s. **G1-OH**, **G2-OH**, and **G3-OH** appeared at 143, 145, and 144°C, respectively, and much higher T_g s than those of **Gn-OMe**, which were thought to be due to interactions such as hydrogen-bonding. In the case of **Gn-OH** T_g s were independent of generation in contrast to the case of **Gn-OMe**. This suggests that interactions between the peripheral groups affect T_g s of dendrimers more dramatically than the movement of chains. Such interactions seemed negligible in the case of **Gn-OMe**. T_g s of the present dendrimers, **Gn-OH**, were more independent of generation in comparison with the previous polyether⁷² and poly(carbosilazane)²⁴ dendrimers which had the same hydroxy groups at the periphery. The formation of a network structure may thus occur among dendrimers, **Gn-OH**, by the hydrogen-bonding between not only the hydroxy groups but also the hydroxy groups and the carbonyl groups, not present in previous dendrimers. Such hydrogen-bonding was confirmed in the IR spectra of **Gn-OH**. In the IR spectra of **Gn-OH**, two carbonyl absorption bands at 1650 and 1630 cm^{-1} , assigned to the free carbonyl groups and the hydrogen-bonding carbonyl groups, respectively, were observed, but in those of **Gn-OMe**, only one carbonyl band was observed at 1650 cm^{-1} .

EXPERIMENTAL

^1H and ^{13}C NMR spectra and IR spectra were recorded on a JNM-GSX-400 FT-NMR spectrometer and Shimadzu IR 435 spectro-photometer, respectively. Gel permeation chromatography (GPC) was performed using a

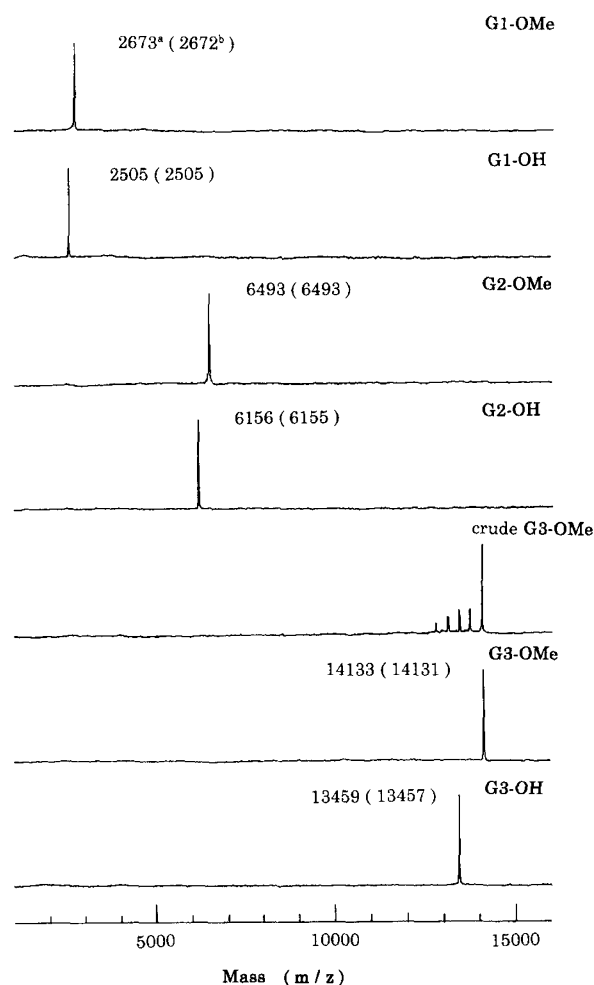


Figure 2. MALDI-TOF mass spectra and molecular mass data of poly(ether ether ketone) dendrimers: **Gn-OMe**, **Gn-OH** ($n=1, 2, 3$), and crude **G3-OMe**. ^a Measured mass. ^b Calculated mass.

Polymer Laboratories analytical column, PL gel 5 μ MIXED-C, and tetrahydrofuran as eluent. Specific viscosity η_{sp} was measured at various concentrations using Ubbelohde-type capillary viscometer in tetrahydrofuran and 1 M aqueous NaOH solution at 30°C. Differential scanning calorimetry (DSC) was performed with a Shimadzu DSC-60. Measurements of DSC were made at a heating rate of 10°C min^{-1} in nitrogen. MALDI-TOF spectra were recorded on a Shimadzu/Kratos Kompact MALDI II equipped with a 337 nm nitrogen laser. For dendrimers except **G3-OMe**, sample preparation was as follows. The solution of the analyte (5 mg), the matrix (20 mg), and trifluoroacetic acid (one drop) in tetrahydrofuran (THF) (1 mL) was prepared and a 1 μl of this matrix/sample solution was transferred to a stainless steel sample plate *via* an automatic pipette. The measurement was performed in positive ion mode using 2,5-dihydroxybenzoic acid as the matrix. In the case of **G3-OMe** after the solution of the matrix and trifluoroacetic acid in THF was transferred to the stainless steel sample plate, the solution of **G3-OMe** in THF was transferred to the same position in the plate. *o*-[(*p*-Hydroxyphenyl)azo]-benzoic acid was used as the matrix.

3,5-Dimethoxy-4'-(4-fluorobenzoyl)diphenylether (1). In a flask, a mixture of 21.82 g (0.1 mol) of 4,4'-difluoro-

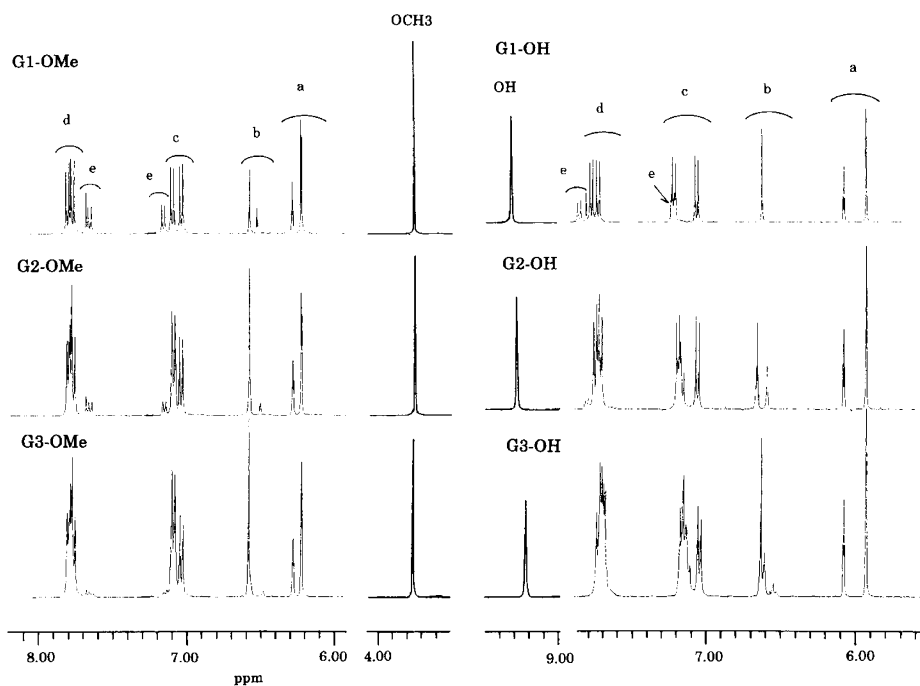


Figure 3. ^1H NMR spectra of $G_n\text{-OMe}$ and $G_n\text{-OH}$ ($n=1, 2, 3$).

benzophenone, 15.42 g (0.1 mol) of 3,5-dimethoxyphenol, 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. 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 reduced pressure of 15–20 torr. The residue was washed with 300 mL of water and extracted twice with 200 mL of methylene chloride. After the combined extract was dried over anhydrous magnesium sulfate, the solvent was evaporated. The residue was distilled three times under reduced pressure (Glass tube oven) by fractional distillation to give pure **1**. Yield: 18.52 g (53%). Mp: 53–54°C. Bp: 260°C (1 torr). IR (KBr): 2940, 1640, 1600, 1230, 1160 cm^{-1} . ^1H NMR (CDCl_3 , ppm): δ 3.77 (s, 6H), 6.25 (d, 2H, $J=2.2$ Hz), 6.31 (t, 1H, $d=2.2$ Hz), 7.07 (d, 2H, $J=8.8$ Hz), 7.15 (m, 2H), 7.79 (d, 2H, $J=8.8$ Hz), 7.82 (m, 2H). ^{13}C NMR (CDCl_3 , ppm): δ 55.46, 96.72, 98.52, 115.37 (d, $J=22.3$ Hz), 117.49, 131.95, 132.21, 132.37 (d, $J=8.0$ Hz), 134.06 (d, $J=3.2$ Hz), 157.32, 161.21, 161.78, 165.18 (d, $J=234.3$ Hz), 193.96. Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{O}_4\text{F}$: C, 71.58; H, 4.86. Found: C, 71.43; H, 4.88.

3,5-Dimethoxy-4'-acetyl-diphenylether (5). In a flask, a mixture of 13.81 g (0.1 mol) of 4-fluoroacetophenone, 15.42 g (0.1 mol) of 3,5-dimethoxyphenol, 13.82 g (0.10 mol) of potassium carbonate, 30 mL of toluene, and 60 mL of *N,N*-dimethylacetamide was stirred at 130°C for 1 h. 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 reduced pressure of 15–20 torr. The residue was washed with 300 mL of water and ex-

tracted twice with 200 mL of methylene chloride. After the combined extract was dried over anhydrous magnesium sulfate, the solvent was evaporated. The residue was distilled under reduced pressure to give pure **5**. Yield: 23.5 g (86%). Bp: 168–170°C (1 torr). Mp: 79–80°C. IR (KBr): 2940, 1675, 1590, 1235, 1155 cm^{-1} . ^1H NMR (CDCl_3 , ppm): δ 2.55 (s, 3H), 3.76 (s, 6H), 6.40 (d, 2H, $J=2.2$ Hz), 6.55 (t, ^1H , $d=2.2$ Hz), 7.05 (d, 2H, $J=8.8$ Hz), 7.94 (d, 2H, $J=8.8$ Hz). ^{13}C NMR (CDCl_3 , ppm): δ 26.43, 55.48, 96.78, 98.50, 117.60, 130.54, 132.14, 154.31, 157.05, 161.78, 196.80. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4$: C, 70.58; H, 5.92. Found: C, 70.62; H, 5.99.

1,3,5-Tris(*p*-3,5-dimethoxyphenoxy)phenyl)benzene (6).

A mixture of 21.8 g (0.08 mol) of **5** and 0.3 mL of trifluoromethanesulfonic acid in 200 mL of toluene was refluxed with removal of water through a Dean-Stark trap for about 8 h. After the generation of water stopped, the reaction mixture was cooled to room temperature. The precipitated product was collected by filtration, washed with methanol to remove the trifluoromethanesulfonic acid, dried under vacuum, and twice recrystallized from toluene to give pure **6**. Yield: 14.3 g (70%). Mp: 224–225°C. IR(KBr): 2940, 1605, 1225, 1155, 1130 cm^{-1} . ^1H NMR (CDCl_3 , ppm): δ 3.76 (s, 18H), 6.23 (d, 6H, $J=2.2$ Hz), 6.25 (t, 3H, $d=2.2$ Hz), 7.13 (d, 6H, $J=8.8$ Hz), 7.66 (d, 6H, $J=8.8$ Hz), 7.72 (s, 3H). ^{13}C NMR (CDCl_3 , ppm): δ 55.47, 95.69, 97.43, 119.49, 124.53, 128.63, 136.40, 141.73, 156.58, 159.09, 161.69. Anal. Calcd for $\text{C}_{48}\text{H}_{42}\text{O}_9$: C, 75.58; H, 5.55. Found: C, 75.73; H, 5.69.

1,3,5-Tris(*p*-3,5-dihydroxyphenoxy)phenyl)benzene (G0-OH). **6** (11.4 g, 15 mmol) was heated together with pyridine hydrochloride (50 g) at reflux temperature (240°C) for about 30 min. After the reaction mixture was homogeneous, it was poured into water (1000 mL), and extracted twice with 100 mL of ethyl acetate. The combined extract was dried over anhydrous magnesium sul-

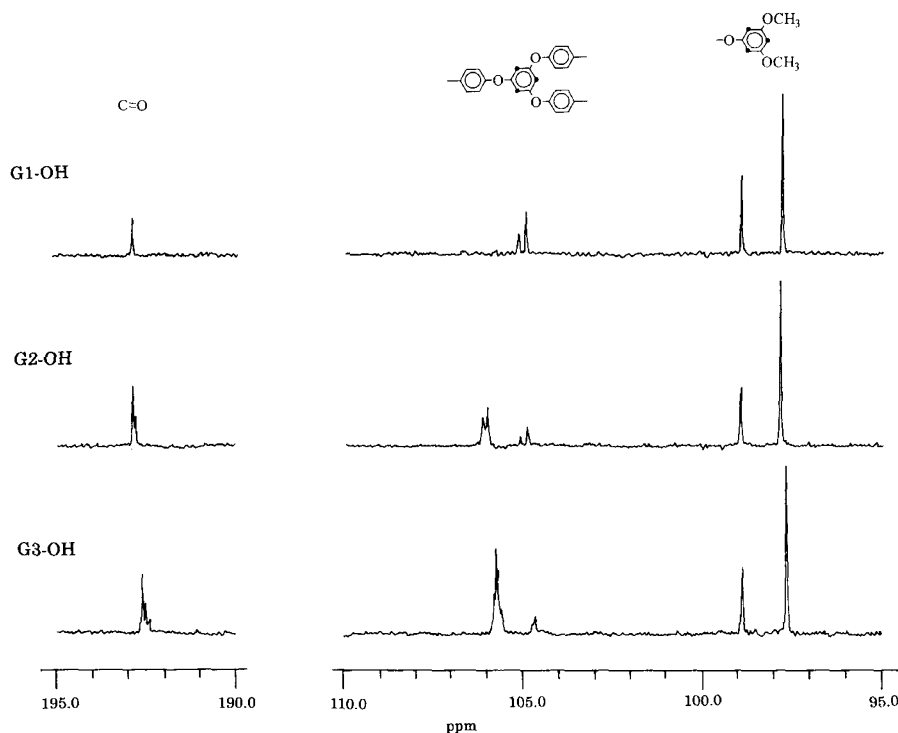


Figure 4. ^{13}C NMR spectra of $\text{G}_n\text{-OH}$ ($n = 1, 2, 3$).

fate. After evaporation of the solvent, pure 2 was obtained as amorphous solid by silica gel column eluted by methylene chloride and ethyl acetate (1 : 1). Yield : 9.8 g (96%). IR (KBr) : 3400–3000, 1600, 1500, 1220, 1150, 1000 cm^{-1} . ^1H NMR (dimethyl sulfoxide (DMSO)- d_6 , ppm) : δ 5.91 (d, 6H, $J=2.2$ Hz), 6.02 (t, 3H, $d=2.2$ Hz), 7.12 (d, 6H, $J=8.8$ Hz), 7.82 (s, 3H), 7.86 (d, 6H, $J=8.8$ Hz), 9.30 (s, 3H). ^{13}C NMR ($\text{DMSO}-d_6$, ppm) : δ 96.85, 97.97, 119.06, 123.35, 128.31, 135.05, 140.74, 156.17, 158.21, 159.15. Anal. Calcd for $\text{C}_{42}\text{H}_{30}\text{O}_9$: C, 74.33 ; H, 4.46. Found : C, 74.31 ; H, 4.44.

First-Generation Dendrimer (G1-OMe). In a flask, a mixture of 7.05 g (20 mmol) of 1, 1.70 g (2.5 mmol) of 2, 2.76 g (20 mmol) of potassium carbonate, 30 mL of toluene, and 60 mL of *N,N*-dimethylacetamide was stirred at 130°C for 1 h. 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 reduced pressure of 15–20 torr. The residue was washed with 300 mL of water and extracted twice with 200 mL of methylene chloride. After the combined extract was dried over anhydrous magnesium sulfate, the solvent was evaporated. Pure **G1-OMe** was obtained by silica gel column chromatography beginning with methylene chloride as the eluent and gradually changing to methylene chloride and ethyl acetate (20 : 1). Yield : 6.1 g (92%). IR (KBr) : 2940, 1650, 1590, 1225, 1160 cm^{-1} . ^1H NMR (CDCl_3 , ppm) : δ 3.76 (s, 36H), 6.23 (d, 12H, $J=2.2$ Hz), 6.29 (t, 6H, $d=2.2$ Hz), 6.53 (t, 3H, $d=2.2$ Hz), 6.59 (d, 6H, $J=2.2$ Hz), 7.05 (d, 12H, $J=8.8$ Hz), 7.11 (d, 12H, $J=8.8$ Hz), 7.17 (d, 6H, $J=8.8$ Hz), 7.66 (d, 6H, $J=8.8$ Hz), 7.69 (s, 3H), 7.78 (d, 12H, $J=8.8$ Hz), 7.81 (d, 12H, $J=8.8$ Hz). ^{13}C NMR

(CDCl_3 , ppm) : δ 55.47, 96.67, 98.46, 105.35, 105.37, 117.53, 117.95, 119.96, 124.74, 128.86, 132.18, 132.23, 133.16, 133.18, 137.15, 141.54, 155.54, 157.40, 158.18, 158.19, 159.98, 161.05, 161.77, 194.12. Anal. Calcd for $\text{C}_{168}\text{H}_{126}\text{O}_{33}$: C, 75.50 ; H, 4.75. Found : C, 75.61 ; H, 4.79.

G1-OH. G1-OMe (5.35 g, 2 mmol) was heated together with pyridine hydrochloride (50 g) at reflux temperature for about 30 min. After the reaction mixture was homogeneous, it was poured into water (1000 mL), and extracted twice with 100 mL of ethyl acetate. The combined extract was dried over anhydrous magnesium sulfate. After evaporation of the solvent, pure **G1-OH** was obtained by silica gel column chromatography eluted by methylene chloride and ethyl acetate (1 : 1). Yield : 4.76 g (95%). IR (KBr) : 3400–3000, 1650, 1590, 1225, 1160 cm^{-1} . ^1H NMR ($\text{DMSO}-d_6$, ppm) : δ 5.93 (d, 12H, $J=2.2$ Hz), 6.08 (t, 6H, $d=2.2$ Hz), 6.63 (m, 9H), 7.07 (d, 12H, $J=8.8$ Hz), 7.22 (d, 12H, $J=8.8$ Hz), 7.23 (d, 6H, $J=8.8$ Hz), 7.74 (d, 12H, $J=8.8$ Hz), 7.78 (d, 12H, $J=8.8$ Hz), 7.82 (s, 3H), 7.86 (d, 6H, $J=8.8$ Hz), 9.34 (s, 12H). ^{13}C NMR ($\text{DMSO}-d_6$, ppm) : δ 97.77, 98.90, 104.96, 105.09, 117.34, 117.86, 119.48, 123.73, 128.65, 131.51, 131.62, 131.71, 132.63, 136.05, 140.54, 155.02, 156.70, 157.66, 158.94, 159.18, 159.29, 160.36, 192.87. Anal. Calcd for $\text{C}_{156}\text{H}_{102}\text{O}_{33}$: C, 74.81 ; H, 4.10. Found : C, 75.00 ; H, 4.15.

Second-Generation Dendrimer (G2-OMe). **G2-OMe** was prepared by the same procedure as that for the synthesis of **G1-OMe** using 2.50 g (1 mmol) of **G1-OH**, 6.34 g (18 mmol) of 1, 2.49 g (18 mmol) of potassium carbonate, 23 mL of toluene, and 60 mL of *N,N*-dimethylacetamide. Pure **G2-OMe** was obtained by silica gel column chromatography beginning with methylene chloride and ethyl acetate (25 : 1) as the eluent and gradually changing to methylene chloride and ethyl ace-

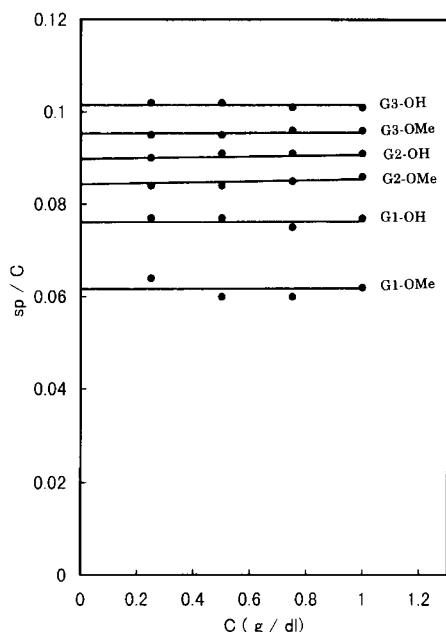


Figure 5. Plots of reduced viscosity η_{sp}/C vs. concentration C of **Gn-OMe** and **Gn-OH** ($n = 1, 2, 3$) in tetrahydrofuran.

tate (15 : 1). Yield : 5.39 g (83%). IR (KBr) : 2940, 1650, 1590, 1225, 1160 cm^{-1} . ^1H NMR (CDCl_3 , ppm) : δ 3.75 (s, 72H), 6.23 (d, 24H, $J = 2.2$ Hz), 6.29 (t, 12H, $d = 2.2$ Hz), 6.51 (t, 3H, $d = 2.2$ Hz), 6.58 (m, 24H), 7.05 (d, 24H, $J = 8.8$ Hz), 7.10 (m, 48H), 7.16 (d, 6H, $J = 8.8$ Hz), 7.66 (d, 6H, $J = 8.8$ Hz), 7.69 (s, 3H), 7.75—7.83 (m, 72H). ^{13}C NMR (CDCl_3 , ppm) : δ 55.47, 96.69, 98.47, 105.32, 105.38, 106.06, 106.22, 117.51, 117.81, 117.98, 118.11, 120.01, 124.72, 128.86, 132.09, 132.20, 132.26, 132.29, 132.89, 133.08, 133.35, 133.37, 137.13, 141.54, 155.49, 157.35, 158.11, 158.33, 158.43, 159.71, 159.87, 160.01, 160.11, 161.10, 161.77, 193.94, 194.67. *Anal.* Calcd for $\text{C}_{408}\text{H}_{294}\text{O}_{81}$: C, 75.48 ; H, 4.56. Found : C, 75.43 ; H, 4.48.

G2-OH. **G2-OH** was prepared by the same procedure as that for the synthesis of **G1-OH** using 4.54 g (0.7 mmol) of **G2-OMe**, and 60 g of pyridine hydrochloride. Pure **G2-OH** was obtained by silica gel column chromatography by methylene chloride and ethyl acetate (3 : 7). Yield : 4.31 g (91%). IR (KBr) : 3400—3000, 1650, 1590, 1227, 1160 cm^{-1} . ^1H NMR ($\text{DMSO}-d_6$, ppm) : δ 5.93 (d, 24H, $J = 2.2$ Hz), 6.08 (t, 12H, $d = 2.2$ Hz), 6.59 (m, 9H), 6.66 (m, 18H), 7.06 (d, 24H, $J = 8.8$ Hz), 7.15—7.22 (m, 54H), 7.69—7.78 (m, 72H), 7.81 (d, 6H, $J = 8.8$ Hz). ^{13}C NMR ($\text{DMSO}-d_6$, ppm) : δ 97.81, 98.94, 104.88, 105.02, 106.05, 106.08, 117.26, 117.34, 117.85, 117.94, 119.43, 123.68, 128.57, 131.48, 131.59, 131.67, 131.73, 131.76, 132.29, 132.42, 132.49, 132.66, 136.01, 140.54, 155.02, 156.68, 157.66, 157.75, 157.77, 158.96, 159.10, 159.16, 159.26, 159.30, 160.40, 192.81, 192.84. *Anal.* Calcd for $\text{C}_{384}\text{H}_{246}\text{O}_{81}$: C, 74.92 ; H, 4.03. Found : C, 74.81 ; H, 3.99.

Third-Generation Dendrimer (G3-OMe). **G3-OMe** was prepared by the same procedure as that for the synthesis of **G1-OMe** using 1.85 g (0.3 mmol) of **G2-OH**, 3.81 g (10.8 mmol) of **1**, 1.49 g (10.8 mmol) of potassium carbonate, 15 mL of toluene and 30 mL of *N,N*-dimethylacetamide. Pure **G3-OMe** was obtained by silica gel column chromatography beginning with methylene chlo-

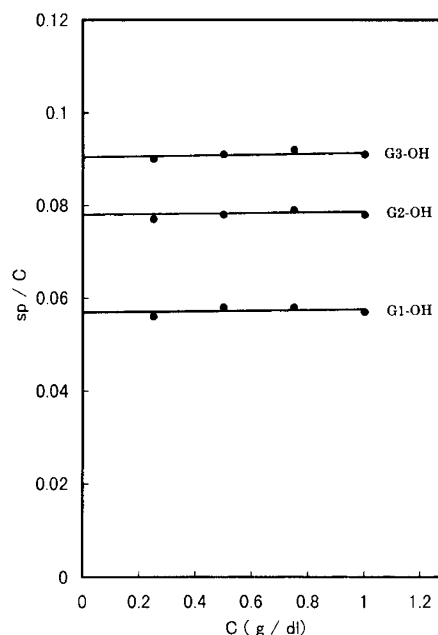


Figure 6. Plots of reduced viscosity η_{sp}/C vs. concentration C of **Gn-OH** ($n = 1, 2, 3$) in 1 M NaOH aqueous solution.

ride and ethyl acetate (20 : 1) as eluent and gradually changing to methylene chloride and ethyl acetate (13 : 1). Yield : 2.63 g (62%). IR (KBr) : 2940, 1655, 1590, 1225, 1160 cm^{-1} . ^1H NMR (CDCl_3 , ppm) : δ 3.75 (s, 144H), 6.22 (d, 48H, $J = 2.2$ Hz), 6.28 (t, 24H, $d = 2.2$ Hz), 6.48 (t, 3H, $d = 2.2$ Hz), 6.58 (m, 60H), 7.04 (d, 48H, $J = 8.8$ Hz), 7.06—7.10 (m, 120H), 7.15 (d, 6H, $J = 8.8$ Hz), 7.65 (d, 6H, $J = 8.8$ Hz), 7.68 (s, 3H), 7.74—7.83 (m, 168H). ^{13}C NMR (CDCl_3 , ppm) : δ 55.48, 96.83, 98.60, 105.32, 105.49, 106.22, 106.27, 106.30, 117.60, 118.05, 118.16, 118.46, 119.98, 124.70, 128.88, 131.85, 132.09, 132.17, 132.23, 132.29, 133.02, 133.18, 133.24, 133.27, 133.53, 137.19, 141.59, 155.63, 157.51, 158.22, 158.45, 158.48, 158.51, 158.54, 159.76, 159.87, 159.90, 159.98, 160.06, 160.14, 161.13, 161.89, 193.75, 193.86, 193.93. *Anal.* Calcd for $\text{C}_{888}\text{H}_{630}\text{O}_{177}$: C, 75.47 ; H, 4.49. Found : C, 75.35 ; H, 4.41.

G3-OH. **G3-OH** was prepared by the same procedure as that for the synthesis of **G1-OH** using 2.11 g (0.15 mmol) of **G3-OMe** and 80 g of pyridine hydrochloride. Pure **G3-OH** was obtained by silica gel column chromatography by methylene chloride and ethyl acetate (3 : 7). Yield : 1.76 g (87%). IR (KBr) : 3400—3000, 1650, 1590, 1227, 1162 cm^{-1} . ^1H NMR ($\text{DMSO}-d_6$, ppm) : δ 5.93 (d, 48H, $J = 2.2$ Hz), 6.08 (t, 24H, $d = 2.2$ Hz), 6.55 (m, 9H), 6.61 (m, 18H), 6.63 (m, 36H), 7.05 (d, 48H, $J = 8.8$ Hz), 7.09—7.20 (m, 126H), 7.65—7.77 (m, 177H), 9.20 (s, 48H). ^{13}C NMR ($\text{DMSO}-d_6$, ppm) : δ 97.67, 98.86, 104.49, 104.69, 105.61, 105.67, 105.74, 105.77, 117.13, 117.21, 117.67, 117.78, 119.19, 123.96, 128.30, 131.22, 131.35, 131.43, 132.01, 132.35, 132.42, 132.65, 135.81, 140.35, 154.88, 156.60, 157.50, 157.53, 157.63, 157.66, 157.68, 158.69, 158.86, 158.91, 158.96, 159.00, 159.10, 159.40, 160.19, 192.45, 192.52, 192.60. *Anal.* Calcd for $\text{C}_{840}\text{H}_{534}\text{O}_{177}$: C, 74.96 ; H, 4.00. Found : C, 75.01 ; H, 4.03.

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