Preparation and Properties of Hyperbranched Poly(ether ketones) with a Various Number of Phenylene Units

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ABSTRACT: New AB_2 type monomers, with a various number of phenylene units, were prepared and converted to hyperbranched poly(ether ketones) by polymerization. Four kinds of AB_2 type monomers, 4-hydroxy-3′,5′-bis(4-fluorobenzoyl)-biphenyl, **1**, 4-hydroxy-3″,5″-bis(4-fluorobenzoyl)-*p*-terphenyl, **2**, 4-hydroxy-3‴,5‴-bis(4-fluorobenzoyl)-*p*-quarterphenyl, **3**, and 4-hydroxy-3⁗,5⁗-bis(4-fluorobenzoyl)-*p*-quinquephenyl, **4**, were synthesized in a stepwise manner starting from 3,5-bis(4-fluorobenzoyl)phenol, **5**, repeating a series of conversions of the hydroxy group to the triflate, cross-coupling reaction of the triflate with (*p*-methoxyphenyl)boronic acid, and cleavage of the methyl ether. Four kinds of hyperbranched poly(ether ketones) were prepared by the polymerization of the four AB_2 type monomers. Obtained hyperbranched poly(ether ketones) from **1** and **2** were soluble in various organic solvents including *N*-methyl-2-pyrrolidone, *m*-cresol, chloroform, and tetrahydrofuran, but those from **3** and **4** were insoluble in organic solvents. The thermal properties of these hyperbranched poly(ether ketones) depended on the number of the phenylene units. The values of the glass transition temperature increased with increasing number of the phenylene units, and only hyperbranched poly(ether ketone) from **5** showed crystalline character. The thermal properties of these hyperbranched poly(ether ketones) were compared with those of hyperbranched poly(ether ketones) having various numbers of phenylene units in the chain ends.

Introduction

Hyperbranched polymers are generally prepared by one-step synthesis of AB_2 type monomers and have received considerable attention recently.[1] The characteristics of these polymers are a branched structure with a large number of chain end groups as dendrimers.[2] However, there is distinct difference between hyperbranched polymers and dendrimers, since the synthetic approach of hyperbranched polymers is different from that of dendrimers. Dendrimers have a perfectly branched and monodispersed structure based on the stepwise synthesis,[3] but hyperbranched polymers are irregular and polydispersed structure due to one-step synthesis. Because of the easy one-step synthesis, hyperbranched polymers are more available at lower costs than dendrimers.

In the course of examining properties of dendrimers and hyperbranched polymers, interesting physical properties of these polymers have been observed, for example, low melting temperature,[4] and low intrinsic viscosity[5] despite their high molecular weight, which is generally ascribed to low ability of forming intermolecular entanglements. To confirm this point, it is interesting to prepare hyperbranched polymers with very rigid structures in the backbone and to examine the properties of these polymers. Moreover, it is interesting to compare the properties of these polymers with those of hyperbranched polymers having very rigid structure in the chain ends, as the properties of the hyperbranched polymer have been reported to be heavily dependent on the nature of the chain end groups.[6]

In this paper, we prepared a series of hyperbranched poly(ether ketones) having various numbers of phenylene units in the backbone. Miller[7] and Hawker[6] have first prepared this kind of polymer. Miller prepared hyperbranched poly(ether ketone) from 3,5-bis(4-fluorobenzoyl)phenol, **5**, as starting molecules. On applying their synthetic methods to a series of new AB_2 type monomers derived from **5**, we obtained hyperbranched poly(ether ketones) with rigid phenylene units in the backbone. The characteristics of the hyperbranched poly(ether ketones) such as solubility and thermal properties were discussed on the basis of phenylene chain length and compared with those of hyperbranched poly(ether ketones) having various numbers of phenylene units in the chain ends.

Experimental Section

^{1}H- and ^{13}C-NMR spectra 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 MIXED-C, and tetrahydrofuran (THF) as eluent. X-ray diffraction and differential scanning calorimetry (DSC) were performed with a Rigaku RAD-B System and 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, and the sample weights used for the measurement were 5.0 mg.

3,5-Bis(4-fluorobenzoyl)phenol, **5**,[6] and (4-methoxyphenyl)-boronic acid[8] were prepared according to the literature methods.

3,5-Bis(4-fluorobenzoyl)phenyl Triflate, 6. A solution of trifluoromethanesulfonyl anhydride (15.99 g, 57 mmol) in dichloromethane (50 mL) was added dropwise to a mixture of 3,5-bis(4-fluorobenzoyl)phenol (16.92 g, 50 mmol) and pyridine (10 mL) in dichloromethane (200 mL) at 0 °C. After being stirred at 20 °C for 2 h, the mixture was poured into ice−water. The organic layer was collected, and the aqueous layer was extracted twice with 50 mL of dichloromethane. The combined extract was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was dried in vacuo and recrystallized from methanol to give white crystalline solids. Yield: 20.23 g (86%). Mp: 100−101 °C. IR(KBr): 3040, 1660 (C═O), 1595, 1500, 1420 (S═O), 1415, 1320, 1295, 1265, 1250,

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1230, 1165 (Ar−F), 1140, 1120, 1005, 985, 880, 855, 760 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): 7.23 (m, 4H, aromatic ortho to fluoro groups), 7.86 (m, 4H, aromatic meta to fluoro groups), 7.89 (d, 2H, J = 1.5 Hz, aromatic ortho to TfO group), 8.16 (t, 1H, J = 1.5 Hz, aromatic para to TfO group). ^{13}C-NMR ($CDCl_3$, ppm): 116.1 (d, J = 22 Hz), 118.7 (q, J = 320 Hz), 125.9, 130.1, 132.2 (d, J = 3 Hz), 132.8 (d, J = 10 Hz), 140.1, 149.1, 166.0 (d, J = 256 Hz), 191.8. Anal. Calcd for $C_{21}H_{11}O_5F_5S$: C, 53.63; H, 2.36. Found: C, 53.56; H, 2.34.

4-Methoxy-3′,5′-bis(4-fluorobenzoyl)biphenyl, 7. (4-Methoxyphenyl)boronic acid (9.12 g, 60 mmol), **6** (18.82 g, 40 mmol), potassium carbonate (16.58 g, 120 mmol), and deoxygenated toluene (150 mL) were added to a flask equipped with a reflux condenser. The flask was flushed with nitrogen, and tetrakis(triphenlyphosphine)paladium ($Pd(PPh_3)_4$) (0.3 g) was added to the reaction mixture. After the mixture was stirred at 90 °C for 8 h, salts were removed by filtration, and the solvent was evaporated. The residue was dissolved in hot ethanol with activated charcoal and recrystallized to give a white crystalline product. Yield: 14.39 g (84%). Mp: 134−135 °C. IR (KBr): 3040, 2920 (CH_3), 1670 (C═O), 1595, 1515, 1505, 1460, 1445, 1410, 1330, 1265, 1230, 1180, 1165 (Ar−F), 1125, 1095, 1035, 1010, 845, 830, 750 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): 3.86 (s, 3H, OCH_3), 7.01 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.19 (m, 4H, aromatic ortho to fluoro groups), 7.58 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.90 (m, 4H, aromatic meta to fluoro groups), 8.00 (t, 1H, J = 1.5 Hz, aromatic at position 4′), 8.16 (d, 2H, J = 1.5 Hz, aromatic at positions 2′ and 6′). ^{13}C-NMR ($CDCl_3$, ppm): 55.4, 114.6, 115.8 (d, J = 22 Hz), 128.3, 128.8, 131.2, 131.3, 132.7 (d, J = 10 Hz), 133.2 (d, J = 3 Hz), 138.3, 141.6, 160.0, 165.7 (d, J = 254 Hz), 194.4. Anal. Calcd for $C_{27}H_{18}O_3F_2$: C, 75.69; H, 4.23. Found: C, 75.50; H, 4.10.

4-Hydroxy-3′,5′-bis(4-fluorobenzoyl)biphenyl, 1. **7** (14.14 g, 33 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). The precipitated solid was collected by filtration, washed thoroughly with water, dried under vacuum, and distilled under reduced pressure (glass tube oven) to give **1**. Yield: 12.99 g (95%). Bp: 320 °C (1 Torr). Mp: 205.5−206.5. IR(KBr): 3400−3300 (OH), 3040, 1670 (C═O), 1595, 1515, 1505, 1445, 1430, 1405, 1345, 1270, 1235, 1210, 1180, 1165 (Ar−F), 1100, 1005, 860, 840, 750 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 100, ppm): 6.90 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.43 (m, 4H, aromatic ortho to fluoro groups), 7.61 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.85 (t, 1H, J = 1.5 Hz, aromatic at position 4′), 7.95 (m, 4H, aromatic meta to fluoro groups), 8.16 (d, 2H, J = 1.5 Hz, aromatic at positions 2′ and 6′), 9.75 (s, 1H, OH). ^{13}C-NMR (DMSO-d_6, 100, ppm): 115.2 (d, J = 22 Hz), 115.7, 127.2, 127.6, 128.7, 129.5, 132.0 (d, J = 10 Hz), 132.9 (d, J = 3 Hz), 137.6, 140.7, 157.6, 164.5 (d, J = 250 Hz), 193.2. Anal. Calcd for $C_{26}H_{16}O_3F_2$: C, 75.36; H, 3.89. Found: C, 75.15; H, 3.62.

3′,5′-Bis(4-fluorobenzoyl)biphenyltriflate, 8. **8** was prepared by the same procedure as that for the synthesis of **6** using **1** (12.43 g, 30 mmol), trifluoromethanesulfonyl anhydride (9.65 g, 34 mmol), pyridine (10 mL), and dichloromethane (150 mL). Pure **8** was obtained by silica gel chromatography eluted by dichloromethane. Yield: 13.77 g (84%). Mp: 105.5−107 °C. IR (KBr): 3040, 1660 (C═O), 1595, 1500, 1435, 1425 (S═O), 1410, 1335, 1290, 1275, 1250, 1235, 1210, 1165 (Ar−F), 1140, 1020, 1000, 940, 880, 845, 765 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): 7.21 (m, 4H, aromatic ortho to fluoro groups), 7.41 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.73 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.92 (m, 4H, aromatic meta to fluoro groups), 8.09 (t, 1H, J = 1.5 Hz, aromatic at position 4′), 8.18 (d, 2H, J = 1.5 Hz, aromatic at positions 2′ and 6′). ^{13}C-NMR ($CDCl_3$, ppm): 115.9 (d, J = 22 Hz), 118.7 (q, J = 320 Hz), 122.1, 129.2, 130.1, 131.7, 132.7 (d, J = 10 Hz), 133.0 (d, J = 3 Hz), 138.7, 139.4, 140.2, 149.6, 165.8 (d, J = 256 Hz), 193.9. Anal. Calcd for $C_{27}H_{15}O_5F_5S$: C, 59.35; H, 2.77. Found: C, 59.15; H, 2.75.

4-Methoxy-3″,5″-bis(4-fluorobenzoyl)-*p*-terphenyl, 9. **9** was prepared by the same procedure as that for the synthesis of **7** using **8** (13.66 g, 25 mmol), (4-methoxyphenyl)boronic acid (5.77 g, 38 mmol), potassium carbonate (10.50 g, 76 mmol), deoxygenated toluene (150 mL), and $Pd(PPh_3)_4$ (0.19 g). Pure **9** was obtained by distillation under reduced pressure (glass tube oven). Yield: 10.34 g (82%). Bp: 320 °C (1 Torr). Mp: 200−201 °C. IR (KBr): 3040, 2920 (CH_3), 1665 (C═O), 1590, 1490, 1430, 1405, 1340, 1250, 1235, 1175, 1165 (Ar−F), 1090, 1050, 1000, 855, 825, 765 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): 3.86 (s, 3H, OCH_3), 7.00 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.20 (m, 4H, aromatic ortho to fluoro groups), 7.57 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.67 (d, 2H, J = 8.8 Hz, aromatic at positions 2′ and 6′), 7.69 (d, 2H, J = 8.8 Hz, aromatic at positions 3′ and 5′), 7.92 (m, 4H, aromatic meta to fluoro groups), 8.06 (t, 1H, J = 1.5 Hz, aromatic at position 4″), 8.24 (d, 2H, J = 1.5 Hz, aromatic at positions 2″ and 6″). ^{13}C-NMR ($CDCl_3$, ppm): 55.4, 114.4, 115.8 (d, J = 21 Hz), 127.4, 127.6, 128.1, 129.4, 131.5, 132.8 (d, J = 10 Hz), 132.7, 133.2 (d, J = 3 Hz), 137.1, 138.5, 141.0, 141.6, 159.5, 165.7 (d, J = 254 Hz), 194.3. Anal. Calcd for $C_{33}H_{22}O_3F_2$: C, 78.56; H, 4.39. Found: C, 78.40; H, 4.28.

4-Hydroxy-3″,5″-bis(4-fluorobenzoyl)-*p*-terphenyl, 2. **2** was prepared by the same procedure as that for the synthesis of **1** using **9** (10.09 g, 20 mmol) and pyridine hydrochloride (40 g). Pure **2** was obtained by distillation under reduced pressure (glass tube oven). Yield: 9.03 g (92%). Bp: 330 °C (1 Torr). Mp: 247−248 °C. IR (KBr): 3400−3000 (OH), 3040, 1665 (C═O), 1590, 1495, 1430, 1405, 1340, 1250, 1235, 1190, 1175, 1165 (Ar−F), 1090, 1000, 855, 825, 765 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 100, ppm): 6.87 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.42 (m, 4H, aromatic ortho to fluoro groups), 7.55 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.71 (d, 2H, J = 8.8 Hz, aromatic at positions 2′ and 6′), 7.81 (d, 2 H, J = 8.8 Hz, aromatic at positions 3′ and 5′), 7.92 (t, 1H, J = 1.5 Hz, aromatic at position 4″), 7.95 (m, 4H, aromatic meta to fluoro groups), 8.25 (d, 2H, J = 1.5 Hz, aromatic at positions 2″ and 6″). ^{13}C-NMR (DMSO-d_6, 100, ppm): 115.2 (d, J = 22 Hz), 115.5, 126.2, 126.8, 127.2, 128.2, 129.8, 130.1, 132.1 (d, J = 10 Hz), 132.9 (d, J = 3 Hz), 135.7, 137.7, 139.9, 140.3, 157.0, 164,6 (d, J = 250 Hz), 193.2. Anal. Calcd for $C_{32}H_{20}O_3F_2$: C, 78.36; H, 4.11. Found: C, 78.16; H, 3.99.

3″,5″-Bis(4-fluorobenzoyl)-*p*-terphenyl triflate, 10. **10** was prepared by the same procedure as that for the synthesis of **6** using **2** (8.83 g, 18 mmol), trifluoromethanesulfonyl anhydride (5.79 g, 21 mmol), pyridine (10 mL), and dichloromethane (100 mL). Pure **10** was obtained by silica gel chromatography eluted by dichloromethane. Yield: 9.08 g (81%). Mp: 107−108.5 °C. IR (KBr): 3040, 1660 (C═O), 1595, 1495, 1425 (S═O), 1410, 1330, 1250, 1235, 1225, 1200, 1165 (Ar−F), 1150, 1100, 1000, 940, 875, 855, 825, 765 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): 7.21 (m, 4H, aromatic ortho to fluoro groups), 7.38 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.69 (d, 2H, J = 8.8 Hz, aromatic at positions 2′ and 6′), 7.70 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.75 (d, 2H, J = 8.8 Hz, aromatic at positions 3′ and 5′), 7.92 (m, 4H, aromatic meta to fluoro groups), 8.07 (t, 1H, J = 1.5 Hz, aromatic at position 4″), 8.25 (d, 2H, J = 1.5 Hz, aromatic at positions 2″ and 6″). ^{13}C-NMR ($CDCl_3$, ppm): 115.9 (d, J = 22 Hz), 118.8 (q, J = 320 Hz), 121.8, 127.8, 127.9, 128.8, 129.7, 131.6, 132.8 (d, J = 10 Hz), 133.1 (d, J = 3 Hz), 138.5, 138.6, 139.4, 140.7, 141.3, 149.2, 165.8 (d, J = 256 Hz), 194.2. Anal. Calcd for $C_{33}H_{19}O_5F_5S$: C, 63.67; H, 3.08. Found: C, 63.49; H, 3.00.

4-Methoxy-3‴,5‴-bis(4-fluorobenzoyl)-*p*-quarterphenyl, 11. **11** was prepared by the same procedure as that for the synthesis of **7** using **10** (8.72 g, 14 mmol), (4-methoxyphenyl)boronic acid (3.19 g, 21 mmol), potassium carbonate (5.80 g, 42 mmol), deoxygenated toluene (100 mL), and $Pd(PPh_3)_4$ (0.11 g). After the reaction mixture was stirred for 8 h, it was cooled to room temperature. The precipitated product was collected by filtration, washed with water to remove salts, dried under vacuum, and twice recrystallized from toluene to give pure **11**. Yield: 6.34 g (78%). Mp: 221−222 °C. IR (KBr): 3040, 2920 (CH_3), 1670 (C═O), 1595, 1500, 1490, 1430, 1400, 1335, 1250, 1220, 1165 (Ar−F), 1045, 995, 850, 820, 760 cm^{-1}.

^{1}H-NMR ($CDCl_3$, ppm): 3.86 (s, 3H, OCH_3), 7.00 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.20 (m, 4H, aromatic ortho to fluoro groups), 7.58 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.65 (d, 2H, J = 8.8 Hz, aromatic at positions 2′ and 6′), 7.69 (d, 2H, J = 8.8 Hz, aromatic at positions 3′ and 5′), 7.72 (d, 2H, J = 8.8 Hz, aromatic at positions 2″ and 6″), 7.76 (d, 2H, J = 8.8 Hz, aromatic at positions 3″ and 5″), 7.92 (m, 4H, aromatic meta to fluoro groups), 8.07 (t, 1H, J = 1.5 Hz, aromatic at position 4‴), 8.25 (d, 2H, J = 1.5 Hz, aromatic at positions 2‴ and 6‴). ^{13}C-NMR ($CDCl_3$, ppm): 55.3, 114.3, 115.8 (d, J = 21 Hz), 127.2, 127.4, 127.6, 128.0, 129.5, 131.6, 132.8 (d, J = 10 Hz), 133.0, 133.2 (d, J = 3 Hz), 137.7, 138.4, 138.5, 140.2, 140.9, 141.5, 159.3, 165.7 (d, J = 254 Hz), 194.2. Anal. Calcd for $C_{39}H_{26}O_3F_2$: C, 80.68; H, 4.51. Found: C, 80.49; H, 4.48.

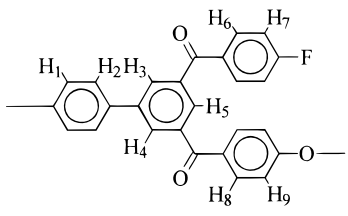
4-Hydroxy-3‴,5‴-bis(4-fluorobenzoyl)-*p*-quarterphenyl, 3. **3** was prepared by the same procedure as that for the synthesis of **1** using **11** (5.81 g, 10 mmol) and pyridine hydrochloride (50 g). Pure **3** was obtained by recrystallization from diphenyl ether. Yield: 4.82 g (85%). Mp: 243−244 °C. IR (KBr): 3400−3000 (OH), 3040, 1665 (C═O), 1595, 1500, 1490, 1430, 1400, 1340, 1250, 1220, 1165 (Ar−F), 995, 850, 820, 760 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 100, ppm): 6.89 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.44 (m, 4H, aromatic ortho to fluoro groups), 7.57 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.70 (d, 2H, J = 8.8 Hz, aromatic at positions 2′ and 6′), 7.78 (d, 2H, J = 8.8 Hz, aromatic at positions 3′ and 5′), 7.85 (d, 2H, J = 8.8 Hz, aromatic at positions 2″ and 6″), 7.89 (d, 2H, J = 8.8 Hz, aromatic at positions 3″ and 5″), 7.95 (t, 1H, J = 1.5 Hz, aromatic at position 4‴), 7.98 (m, 4H, aromatic meta to fluoro groups), 8.29 (d, 2H, J = 1.5 Hz, aromatic at positions 2‴ and 6‴), 9.58 (s, 1H, OH). ^{13}C-NMR (DMSO-d_6, 100, ppm): 115.2 (d, J = 22 Hz), 115.3, 125.9, 126.5, 126.7, 127.0, 128.3, 129.4, 130.1, 130.2, 132.1 (d, J = 10 Hz), 132.9 (d, J = 3 Hz), 136.7, 136.9, 137.8, 139.3, 139.5, 140.2, 156.8, 164.6 (d, J = 250 Hz), 192.9. Anal. Calcd for $C_{38}H_{24}O_3F_2$: C, 80.55; H, 4.27. Found: C, 80.33; H, 4.20.

3‴,5‴-Bis(4-fluorobenzoyl)-*p*-quarterphenyl triflate, 12. **12** was prepared by the same procedure as that for the synthesis of **6** using **3** (2.83 g, 5 mmol), trifluoromethanesulfonyl anhydride (1.69 g, 6 mmol), pyridine (5 mL), and dichloromethane (70 mL). Pure **12** was obtained by silica gel chromatography eluted by dichloromethane. Yield: 2.90 g (83%). Mp: 167−168.5 °C. IR (KBr): 3040, 1660 (C═O), 1595, 1500, 1485, 1425 (S═O), 1410, 1335, 1235, 1215, 1165 (Ar−F), 1145, 1100, 1000, 940, 875, 855, 825, 765 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): 7.20 (m, 4H, aromatic ortho to fluoro groups), 7.37 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.67 (d, 2H, J = 8.8 Hz, aromatic at positions 2′ and 6′), 7.70 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.72 (d, 2H, J = 8.8 Hz, aromatic at positions 3′ and 5′), 7.74 (d, 2H, J = 8.8 Hz, aromatic at positions 2″ and 6″), 7.76 (d, 2H, J = 8.8 Hz, aromatic at positions 3″ and 5″), 7.92 (m, 4H, aromatic meta to fluoro groups), 8.07 (t, 1H, J = 1.5 Hz, aromatic at position 4‴), 8.27 (d, 2H, J = 1.5 Hz, aromatic at positions 2‴ and 6‴). ^{13}C-NMR ($CDCl_3$, ppm): 115.8 (d, J = 22 Hz), 118.8 (q, J = 320 Hz), 121.7, 127.6, 127.69, 127.71, 127.74, 128.8, 129.5, 131.5, 132.7 (d, J = 10 Hz), 133.3 (d, J = 3 Hz), 138.1, 138.59, 138.62, 140.0, 140.5, 141.1, 141.5, 149.1, 165.8 (d, J = 256 Hz), 194.1. Anal. Calcd for $C_{39}H_{23}O_5F_5S$: C, 67.05; H, 3.32. Found: C, 69.89; H, 3.26.

4-Methoxy-3⁗,5⁗-bis(4-fluorobenzoyl)-*p*-quinquephenyl, 13. **13** was prepared by the same procedure as that for the synthesis of **7** using **12** (2.79 g, 4 mmol), (4-methoxyphenyl)boronic acid (0.92 g, 6 mmol), potassium carbonate (1.66 g, 12 mmol), deoxygenated toluene (80 mL), and $Pd(PPh_3)_4$ (0.03 g). After the reaction mixture was stirred for 8 h, it was cooled to room temperature. The precipitated product was collected by filtration, washed with water to remove salts, dried under vacuum, and twice recrystallized from *N*,*N*-dimethylacetamide to give pure **13**. Yield: 2.12 g (79%). Mp: 303.5−305 °C. IR (KBr): 3040, 2920 (CH_3), 1665 (C═O), 1600, 1510, 1490, 1435, 1400, 1330, 1250, 1220, 1165 (Ar−F), 1040, 995, 855, 820, 760 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm): 3.86 (s, 3H, OCH_3), 7.00 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.20 (m, 4H, aromatic ortho to fluoro groups), 7.58 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.65 (d, 2H, J = 8.4 Hz, aromatic at positions 2′ and 6′), 7.70 (d, 2H, J = 8.4 Hz, aromatic at positions 3′ and 5′), 7.73 (m, 4H, aromatic at positions 2″, 6″, 2‴ and 6‴), 7.74 (d, 2H, J = 4.0 Hz, aromatic at positions 3″ and 5″), 7.77 (d, 2H, J = 8.4 Hz, aromatic at positions 3‴ and 5‴), 7.92 (m, 4H, aromatic meta to fluoro groups), 8.07 (t, 1H, J = 1.5 Hz, aromatic at position 4⁗), 8.25 (d, 2H, J = 1.5 Hz, aromatic at positions 2⁗ and 6⁗). ^{13}C-NMR ($CDCl_3$, ppm): 55.3, 114.3, 115.7 (d, J = 22 Hz), 127.0, 127.2, 127.4, 127.58, 127.63, 128.0, 129.3, 131.4, 132.6 (d, J = 10 Hz), 133.3 (d, J = 3 Hz), 133.9, 135.9, 136.6, 137.8, 138.5, 139.0, 139.1, 140.0, 141.1, 141.6, 159.4, 165.7 (d, J = 254 Hz), 194.0. Anal. Calcd for $C_{45}H_{30}O_3F_2$: C, 82.30; H, 4.60. Found: C, 82.11; H, 4.52.

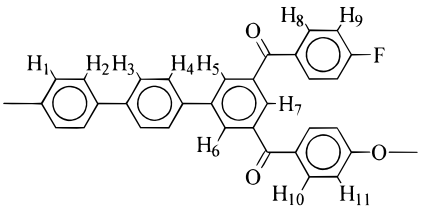
4-Hydroxy-3⁗,5⁗-bis(4-fluorobenzoyl)-*p*-quinquephenyl, 4. **13** (2.02 g, 3.1 mmol) was heated together with pyridine hydrochloride (150 g) at reflux temperature for about 5 h. After the reaction mixture was homogeneous, it was poured into water (1000 mL). The precipitated solid was collected by filtration, washed thoroughly with water, and dried under vacuum, and pure **4** was obtained by recrystallization from diphenyl ether. Yield: 1.43 g (74%). Mp: 313−314 °C. IR (KBr): 3400−3000 (OH), 3040, 1660 (C═O), 1600, 1510, 1490, 1435, 1400, 1335, 1250, 1220, 1165 (Ar−F), 995, 855, 820, 760 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 140, ppm): 6.88 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.34 (m, 4H, aromatic ortho to fluoro groups), 7.51 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.65 (d, 2H, J = 8.8 Hz, aromatic at positions 2′ and 6′), 7.73 (d, 2H, J = 8.8 Hz, aromatic at positions 3′ and 5′), 7.78 (broad s, 4H, aromatic at positions 2″, 3″, 5″, and 6″), 7.82 (broad s, 4H, aromatic at positions 2‴, 3‴, 5‴, and 6‴), 7.90 (t, 1H, J = 1.5 Hz, aromatic at position 4⁗), 7.93 (m, 4H, aromatic meta to fluoro groups), 8.24 (d, 2H, J = 1.5 Hz, aromatic at positions 2⁗ and 6⁗), 8.98 (s, 1H, OH). ^{13}C-NMR (DMSO-d_6, 140, ppm): 114.9 (d, J = 22 Hz), 115.3, 125.7, 126.1, 126.2, 126.4, 126.5, 126.8, 127.9, 129.1, 129.8, 130.1, 131.7 (d, J = 10 Hz), 132.9 (d, J = 3 Hz), 136.8, 137.0, 137.7, 137.8, 138.7, 139.0, 139.3, 140.1, 156.7, 164.3 (d, J = 251 Hz), 192.7. Anal. Calcd for $C_{44}H_{28}O_3F_2$: C, 82.23; H, 4.39. Found: C, 81.15; H, 4.21.

Hyperbranched Poly(ether ketone), 14. A mixture of **1** (1.24 g, 3 mmol), potassium carbonate (0.214 g, 1.55 mmol), toluene (10 mL), and *N*,*N*-dimethylacetamide (10 mL) was stirred in a flask at 120 °C. The temperature was then raised from 120 to 165 °C, to remove water formed during the reaction as an azeotrope with toluene by the use of a Dean−Stark trap. The reaction mixture was stirred at this temperature for 3 h. The polymerization proceeded homogeneously. After the reaction was complete, the mixture was cooled to room temperature and poured into 300 mL of methanol. The precipitated polymer was collected by filtration, washed thoroughly with water and methanol, and dried under vacuum. Yield: 1.09 g (92%). IR (KBr): 3040, 1665 (C═O), 1590, 1490, 1425, 1400, 1330, 1235, 1175, 1160 (Ar−F), 990, 860, 830, 765 cm^{-1}.



^{1}H-NMR ($CDCl_3$, ppm): 7.10 (2H, H1), 7.19 (4H, H7 and H9), 7.67 (2H, H2), 7.89 (4H, H6, and H8), 8.03 (1H, H5), 8.18 (2H, H3, and H4). ^{13}C-NMR ($CDCl_3$, ppm): 115.7, 115.9, 117.7, 118.0, 119.4, 120.1, 120.6, 128.5, 129.0, 129.4, 130.8, 131.2, 131.4, 131.8, 132.6, 132.66, 132.74, 133.3, 135.6, 137.6, 138.5, 138.6, 138.9, 139.0, 141.1, 156.0, 161.6, 164.5, 167.0, 194.1. Anal. Calcd for $(C_{26}H_{15}O_3F)_n$: C, 79.18; H, 3.83. Found: C, 79.00; H, 3.79.

Hyperbranched Poly(ether ketone), 15. Hyperbranched poly(ether ketone), **15**, was prepared by the same procedure as that for the synthesis of **14** using **2** (1.47 g, 3 mmol), potassium carbonate (0.214 g, 1.55 mmol), toluene (10 mL), and *N*,*N*-dimethylacetamide (10 mL). The polymerization proceeded homogeneously, as well as that of **14**. Yield: 1.31 g (93%). IR (KBr): 3040, 1665 (C═O), 1590, 1490, 1425, 1400, 1330, 1240, 1175, 1160 (Ar−F), 990, 860, 845, 825, 765 cm^{-1}.



^{1}H-NMR ($CDCl_3$, ppm): 7.11 (2H, H1), 7.18 (4H, H9 and H11), 7.68 (6H, H2, H3, and H4), 7.90 (4H, H8, and H10), 8.06 (1H, H7), 8.25 (2H, H5, and H6). ^{13}C-NMR ($CDCl_3$, ppm): 115.7, 115.9, 117.4, 119.5, 120.3, 120.6, 127.6, 127.7, 128.7, 129.6, 131.3, 131.4, 131.5, 132.6, 132.7, 132.8, 133.2, 136.8, 137.8, 137.9, 138.3, 138.4, 138.7, 138.9, 140.2, 141.4, 155.1, 161.9, 164.4, 167.0, 194.3. Anal. Calcd for $(C_{32}H_{19}O_3F)_n$: C, 81.69; H, 4.07. Found: C, 81.49; H, 3.91.

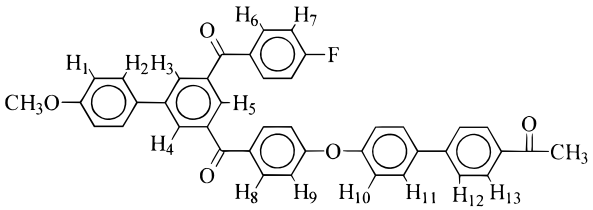
Hyperbranched Poly(ether ketone), 16. Hyperbranched poly(ether ketone), **16**, was prepared by the same procedure as that for the synthesis of **14** using **3** (1.13 g, 2 mmol), potassium carbonate (0.142 g, 1.03 mmol), toluene (10 mL), and *N*,*N*-dimethylacetamide (10 mL). However, during the polymerization at 165 °C, the generated polymer, **16**, was precipitated due to the low solubility. After the reaction mixture was stirred for 3 h, cooled to room temperature, and poured into 300 mL of methanol, the precipitated polymer was collected by filtration, washed thoroughly with water and methanol, and dried under vacuum. Yield: 1.02 g (93%). IR (KBr): 3040, 1665 (C═O), 1590, 1485, 1425, 1400, 1330, 1240, 1175, 1160 (Ar−F), 990, 860, 845, 825, 765 cm^{-1}. ^{1}H-NMR and ^{13}C-NMR could not be measured because **16** was insoluble in organic solvents. Anal. Calcd for $(C_{38}H_{23}O_3F)_n$: C, 83.50; H, 4.24. Found: C, 83.36; H, 4.14.

Hyperbranched Poly(ether ketone), 17. Hyperbranched poly(ether ketone), **17**, was prepared by the same procedure as that for the synthesis of **14** using **4** (1.29 g, 2 mmol), potassium carbonate (0.142 g 1.03 mmol), toluene (10 mL), and *N*,*N*-dimethylacetamide (10 mL). During the polymerization at 165 °C, the generated polymer, **17**, was precipitated due to the low solubility, as well as **16**. After the reaction mixture was stirred for 3 h, cooled to room temperature, and poured into 300 mL of methanol, the precipitated polymer was collected by filtration, washed thoroughly with water and methanol, and dried under vacuum. Yield: 1.21 g (94%). IR (KBr): 3040, 1665 (C═O), 1590, 1480, 1425, 1400, 1330, 1240, 1175, 1160 (Ar−F), 990, 860, 845, 825, 765 cm^{-1}. ^{1}H-NMR and ^{13}C-NMR could not be measured because **17** was insoluble in organic solvents. Anal. Calcd for $(C_{26}H_{15}O_3F)_n$: C, 84.87; H, 4.37. Found: C, 84.59; H, 4.18.

4-Hydroxy-4′-acetylbiphenyl, 18. A solution of acetyl chloride (3.92 g, 50 mmol) in dichloromethane (20 mL) was added dropwise to a mixture of 4-methoxybiphenyl (9.21 g, 50 mmol), aluminum chloride (7.33 g, 55 mmol), and dichloromethane (50 mL) at 0 °C. After being stirred 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 dichloromethane. The combined organic layer was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was recrystallized from ethanol to give 4-methoxy-4′-acetylbiphenyl (7.47 g, 33 mmol). The biphenyl compound was converted to 4-hydroxy-4′-acetylbiphenyl by the same procedure as that for the synthesis of **1** using pyridine hydrochloride (50 g). Pure **18** was obtained by recrystallization from toluene. Yield: 5.31 g (50%). Mp: 205−206 °C. IR (KBr): 3400−3000 (OH), 3040, 2920 (CH_3), 1670 (C═O), 1595, 1580, 1490, 1445, 1370, 1290, 1270, 1200, 820 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 50, ppm): 2.64 (s, 3H, CH3), 6.89 (d, 2H, J = 8.1 Hz, aromatic at positions 3, and 5), 7.59 (d, 2H, J = 8.1 Hz, aromatic at positions 2, and 6), 7.73 (d, 2H, J = 8.1 Hz, aromatic at positions 2′, and 6′), 7.98 (d, 2H, J = 8.1 Hz, aromatic at positions 3′, and 5′), 9.60 (s, 1H, OH). ^{13}C-NMR (DMSO-d_6, 50, ppm): 26.4, 115.7, 125.7, 127.9, 128.6, 129.4, 134.6, 144.4, 157.8, 197.0. Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.11; H, 5.61.

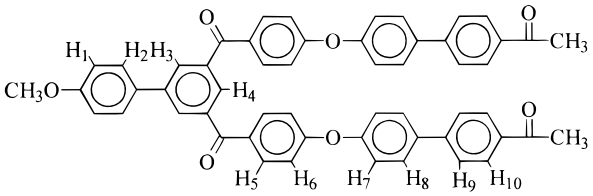
Linear Model Compound, 19, and Dendric Model Compound, 20. A mixture of **18** (2.12 g, 10 mmol), **7** (4.28 g, 10 mmol), potassium carbonate (0.69 g, 5 mmol), toluene (20 mL), and *N*,*N*-dimethylacetamide (20 mL) was stirred in a flask at 120 °C. The temperature was then raised from 120 to 165 °C, to remove water formed during the reaction as an azeotrope with toluene by the use of a Dean−Stark trap. The reaction mixture was stirred at this temperature for 3 h and cooled to 80 °C, and the solvent was evaporated under the reduced pressure of 15−20 Torr. The residue was washed with 200 mL of water and extracted twice with 200 mL of dichloromethane. The combined organic layer was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the mixture of **19** and **20** was obtained. The pure **19** and **20** were obtained by silica gel column chromatography eluted by dichloromethane as a colorless oils.

Linear Model Compound 19. Yield: 2.79 g. IR (KBr): 3040, 2920 (CH_3), 1685 (C═O), 1655, 1595, 1520, 1490, 1425, 1350, 1335, 1300, 1255, 1185, 1170, 1160 (Ar−F), 1025, 1000, 965, 880, 825, 770 cm^{-1}.



^{1}H-NMR ($CDCl_3$, ppm): 2.65 (s, 3H, $COCH_3$), 3.86 (s, 3H, OCH_3), 7.01 (d, 2H, J = 8.8 Hz, H1), 7.11 (d, 2H, J = 8.8 Hz, H10), 7.19 (m, 2H, H7), 7.20 (d, 2H, J = 8.8 Hz, H9), 7.58 (d, 2H, J = 8.8 Hz, H2), 7.67 (d, 2H, J = 8.8 Hz, H11), 7.68 (d, 2H, J = 8.8 Hz, H12), 7.90 (d, 2H, J = 8.8 Hz, H8), 7.91 (m, 2H, H6), 8.02 (m, 1H, H5), 8.04 (d, 2H, J = 8.8 Hz, H13), 8.14 (m, 1H, H3), 8.18 (m, 1H, H4). ^{13}C-NMR ($CDCl_3$, ppm): 26.6, 55.4, 114.6, 115.7 (d, J = 22 Hz), 117.6, 120.5, 127.0, 128.3, 128.86, 128.96, 128.99, 131.0, 131.2, 131.4, 131.6, 132.6, 132.7 (d, J = 10 Hz), 133.3 (d, J = 3 Hz), 135.9, 136.3, 138.2, 138.7, 141.6, 144.7, 155.7, 160.0, 161.7, 165.6 (d, J = 256 Hz), 194.4, 194.5, 197.6. Anal. Calcd for $C_{41}H_{29}O_5F$: C, 79.34; H, 4.71. Found: C, 79.18; H, 4.69.

Dendritic Model Compound, 20. Yield: 2.28 g. IR (KBr): 3040, 2920 (CH_3), 1680 (C═O), 1660, 1610, 1590, 1520, 1490, 1425, 1400, 1355, 1335, 1300, 1275, 1255, 1185, 1110, 1075, 1035, 1005, 965, 880, 825, 770 cm^{-1}.



^{1}H-NMR ($CDCl_3$, ppm): 2.64 (s, 6H, $COCH_3$), 3.87 (s, 3H, OCH_3), 7.01 (d, 2H, J = 8.8 Hz, H1), 7.12 (d, 4H, J = 8.8 Hz, H7), 7.20 (d, 4H, J = 8.8 Hz, H6), 7.60 (d, 2H, J = 8.8 Hz, H2), 7.67 (d, 4H, J = 8.8 Hz, H8), 7.68 (d, 4H, J = 8.8 Hz, H9), 7.91 (d, 4H, J = 8.8 Hz, H5), 8.04 (d, 4H, J = 8.8 Hz, H10), 8.04 (t, 1H, J = 1.5 Hz, H4), 8.17 (d, 2H, J = 1.5 Hz, H3). ^{13}C-NMR ($CDCl_3$, ppm): 26.6, 55.4, 114.5, 117.6, 120.5, 127.0, 128.4, 128.93, 128.96, 128.99, 131.0, 131.5, 131.7, 132.6, 135.9, 136.3, 138.6, 141.5, 144.7, 155.7, 159.9, 161.6, 194.6,

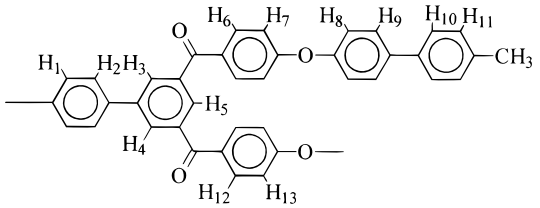
197.6. Anal. Calcd for $C_{55}H_{40}O_7$: C, 81.26; H, 4.96. Found: C, 81.01; H, 4.85.

4-Hydroxy-4′-methylbiphenyl, 21. (4-Methoxyphenyl)-boronic acid (9.12 g, 60 mmol), 4-bromotoluene (8.55 g, 50 mmol), potassium carbonate (16.58 g, 120 mmol), and deoxygenated toluene (150 mL) were added to a flask equipped with a reflux condenser. The flask was flushed with nitrogen, and $Pd(PPh_3)_4$ (0.38 g) was added to the reaction mixture. After the mixture was stirred at 90 °C for 8 h, salts were removed by filtration, and the solvent was evaporated. The residue was recrystallized from ethanol to give pure 4-methoxy-4′-methylbiphenyl (8.13 g, 41 mmol). The biphenyl compound was converted to 4-hydroxy-4′-methylbiphenyl, **21**, by the same procedure as that for the synthesis of **1** using pyridine hydrochloride (40 g). Pure **21** was obtained by recrystallization from toluene. Yield: 6.45 g (65%). Mp: 146−147 °C. IR (KBr): 3400−3000 (OH), 3040, 2920 (CH_3), 1610, 1600, 1500, 1470, 1270, 820 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 50, ppm): 2.32 (s, 3H, CH_3), 6.84 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.43 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.20 (d, 2H, J = 8.4 Hz, aromatic at positions 3′ and 5′), 7.45 (d, 2H, J = 8.4 Hz, aromatic at positions 2′ and 6′), 9.36 (s, 1H, OH). ^{13}C-NMR (DMSO-d_6, 50, ppm): 20.4, 115.5, 125.6, 127.2, 129.2, 130.8, 135.2, 137.3, 156.7. Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.61; H, 6.50.

4-Hydroxy-4″-methyl-*p*-terphenyl, 22. A mixture of 4-hydroxy-4′-bromobiphenyl (24.90 g, 0.1 mol), dimethyl sulfate (6.94 g, 55 mmol), and potassium carbonate (8.29 g, 60 mmol) in ethanol (200 mL) was refluxed for 8 h and then poured into water (1000 mL). The aqueous layer was extracted twice with 150 mL of toluene. The combined extract was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was recrystallized from ethanol to give 4-methoxy-4′-bromobiphenyl (21.57 g, 82 mmol). The 4-methoxy-4′-bromobiphenyl was reacted with (*p*-methoxyphenyl)-boronic acid (14.95 g, 98 mmol) by the same procedure as that for the synthesis of 4-methoxy-4′-methylbiphenyl using Pd-$(PPh_3)_4$ (0.45 g), potassium carbonate (27.09 g, 19.6 mmol), and deoxygenated toluene (200 mL). After the reaction mixture was stirred for 8 h, salts were removed by filtration, and the solvent was evaporated. The residue was recrystallized from toluene to give pure 4-methoxy-4″-methyl-*p*-terphenyl (18.11 g, 66 mmol). It was converted to 4-hydroxy-4″-methyl-*p*-terphenyl, **22**, by the same procedure as that for the synthesis of **1** using pyridine hydrochloride (50 g). Pure **22** was obtained by distillation under reduced pressure (glass tube oven). Yield: 15.10 g (58%). Bp: 280 °C (1 Torr). Mp: 265−266 °C. IR (KBr): 3400−3000 (OH), 3040, 2920 (CH_3), 1615, 1595, 1490, 1455, 1375, 1265, 805 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 50, ppm): 2.35 (s, 3H, CH_3), 6.88 (d, 2H, J = 8.1 Hz, aromatic at positions 3 and 5), 7.27 (d, 2H, J = 8.1 Hz, aromatic at positions 3″ and 5″), 7.53 (d, 2H, J = 8.1 Hz, aromatic at positions 2 and 6), 7.58 (d, 2H, J = 8.1 Hz, aromatic at positions 2″ and 6″), 7.64 (d, 2H, J = 8.1 Hz, aromatic at positions 2′ and 6′) 7.67 (d, 2H, J = 8.8 Hz, aromatic at positions 3′ and 5′), 9.45 (s, 1H, OH). ^{13}C-NMR (DMSO-d_6, 50, ppm): 20.4, 115.6, 126.1, 126.2, 126.6, 127.4, 129.3, 130.3, 136.4, 136.7, 137.8, 138.8, 157.0. Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.51; H, 6.02.

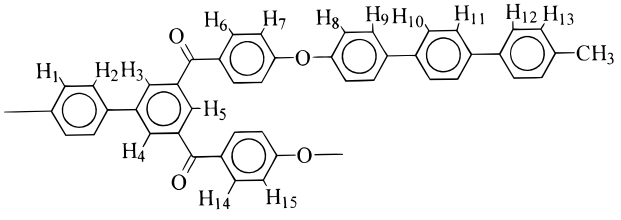
4-Hydroxy-4‴-methyl-*p*-quarterphenyl, 23. 4″-Methyl-*p*-terphenyltriflate was prepared by the same procedure as that for the synthesis of **6** using **22** (10.41 g, 40 mmol), trifluoromethanesulfonyl anhydride (12.70 g, 45 mmol), pyridine (15 mL), and dichloromethane (200 mL). The pure 4″-methyl-*p*-terphenyltriflate (13.34 g, 34 mmol) obtained by recrystallization from toluene was reacted with (*p*-methoxyphenyl)boronic acid (6.20 g, 40.8 mmol) by the same procedure as that for the synthesis of **7** using $Pd(PPh_3)_4$ (0.2 g), potassium carbonate (11.28 g, 81.6 mmol), and deoxygenated toluene (100 mL). After being stirred for 8 h, the reaction mixture was cooled to room temperature. The precipitated product was collected by filtration, washed with water to remove salts, dried under vacuum, and sublimated under reduced pressure (glass tube oven, 330 (1 Torr)) to give pure 4-methoxy-4‴-methyl-*p*-quarterphenyl (7.01 g, 20 mmol). It was converted to 4-hydroxy-4‴-methyl-*p*-quarterphenyl, **23**, by the same procedure as that for the synthesis of **4** using pyridine hydrochloride (100 g). Pure **23** was obtained by sublimation under reduced pressure (glass tube oven, 330 (1 Torr)). Yield: 5.05 g (37.5%). Mp > 350 °C. IR (KBr): 3400−3000 (OH), 3040, 2920 (CH_3), 1610, 1590, 1485, 1450, 1380, 1255, 805 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 140, ppm): 2.38 (s, 3H, CH_3), 6.90 (d, 2H, J = 8.8 Hz, aromatic at positions 3 and 5), 7.29 (d, 2H, J = 8.8 Hz, aromatic at positions 3‴ and 5‴), 7.53 (d, 2H, J = 8.8 Hz, aromatic at positions 2 and 6), 7.60 (d, 2H, J = 8.8 Hz, aromatic at positions 2‴ and 6‴), 7.67 (d, 2H, J = 8.8 Hz, aromatic at positions 3′ and 5′), 7.71 (d, 2H, J = 8.8 Hz, aromatic at positions 2″ and 6″), 7.74 (d, 2H, J = 8.4 Hz, aromatic at positions 3′ and 5′), 7.76 (d, 2H, J = 8.8 Hz, aromatic at positions 3″ and 5″), 9.00 (s, 1H, OH). ^{13}C-NMR (DMSO-d_6, 140, ppm): 19.8, 115.2, 125.6, 125.7, 126.06, 126.13, 126.78, 126.82, 128.7, 130.1, 136.0, 136.4, 137.2, 138.0, 138.6, 138.9, 156.6. Anal. Calcd for $C_{25}H_{20}O$: C, 89.25; H, 5.99. Found: C, 89.11; H, 5.79.

Biphenyl Oxy-Terminated Hyperbranched Poly(ether ketone), 24. A mixture of **1** (1.24 g, 3 mmol), potassium carbonate (0.214 g, 1.55 mmol), toluene (10 mL), and *N*,*N*-dimethylacetamide (10 mL), was stirred in a flask at 120 °C. The temperature was then raised from 120 to 165 °C, to remove water formed during reaction as an azeotrope with toluene by the use of a Dean−Stark trap. The reaction mixture was stirred at this temperature for 3 h, and **21** (0.55 g, 3 mmol), potassium carbonate (0.214 g, 1.55 mmol), toluene (10 mL), and *N*,*N*-dimethylacetamide (10 mL) were added. The mixture was stirred at 165 °C for another 3 h, cooled to room temperature, and poured into 300 mL of methanol. The precipitated polymer was collected by filtration, washed thoroughly with water and methanol, and dried under vacuum. Yield: 1.56 g (93%). IR (KBr): 3040, 2920 (CH_3), 1665 (C=O), 1590, 1490, 1435, 1410, 1335, 1300, 1250, 1110, 1005, 945, 870, 835, 810, 760 cm^{-1}.



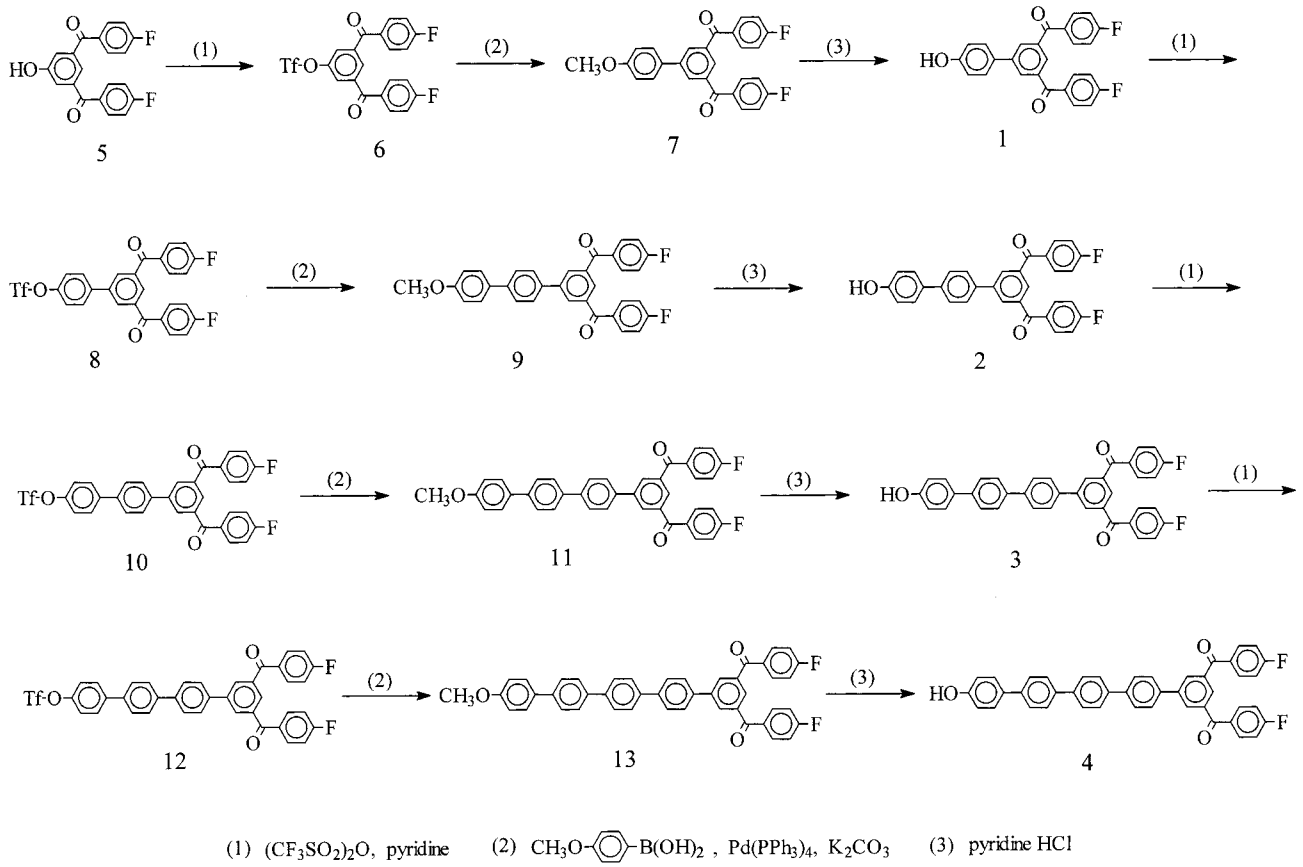
^{1}H-NMR ($CDCl_3$, ppm): 2.39 (3H, CH_3), 7.09 (6H, H1, H8, and H11), 7.21 (4H, H7, and H13), 7.46 (2H, H2), 7.58 (2H, H9), 7.67 (2H, H10), 7.87 (4H, H6 and H 12), 8.06 (1H, H5), 8.19 (2H, H3, and H4). Anal. Calcd for $(C_{39}H_{26}O_4)_n$: C, 83.85; H, 4.69. Found: C, 83.64; H, 4.57.

Terphenyl Oxy-Terminated Hyperbranched Poly-(ether ketone), 25. Terphenyl oxy-terminated hyperbranched poly(ether ketone), **25**, was prepared by the same procedure as that for the synthesis of **24** using **1** (1.24 g, 3 mmol), **22** (0.78 g, 3 mmol), potassium carbonate (0.428 g, 3.1 mmol), toluene (20 mL), and *N*,*N*-dimethylacetamide (20 mL). Yield: 1.75 g (92%). IR (KBr): 3040, 2920 (CH_3), 1665 (C=O), 1590, 1500, 1485, 1435, 1410, 1335, 1300, 1250, 1110, 1005, 945, 870, 835, 810, 760 cm^{-1}.



^{1}H-NMR ($CDCl_3$, ppm): 2.38 (3H, CH_3), 7.01−7.29 (10H, H1, H7, H8, H13, and H15), 7.51 (2H, H2), 7.62 (8H, H9, H10, H11, and H12), 7.88 (4H, H6 and H14), 8.05 (1H, H5), 8.19 (2H,

Scheme 1



H3, and H4). Anal. Calcd for $(C_{45}H_{30}O_4)_n$: C, 85.15; H, 4.76. Found: C, 84.88; H, 4.51.

Quarterphenyl Oxy-Terminated Hyperbranched Poly(ether ketone), 26. Quarterphenyl oxy-terminated hyperbranched poly(ether ketone), **26**, was prepared by the same procedure as that for the synthesis of **24** using **1** (1.24 g, 3 mmol), **23** (1.01 g, 3 mmol), potassium carbonate (0.428 g, 3.1 mmol), toluene (20 mL), and *N*,*N*-dimethylacetamide (20 mL). During the reaction of the polymer prepared from **1** with **23,** the generated quarterphenyl oxy-terminated polymer, **26**, was precipitated due to the low solubility. After the reaction mixture was stirred for 3 h, cooled to room temperature, and poured into 300 mL of methanol, the precipitated polymer was collected by filtration, washed thoroughly with water and methanol, and dried under vacuum. Yield: 2.00 g (94%). IR (KBr): 3040, 2920 (CH_3), 1660 (C=O), 1585, 1495, 1480, 1435, 1410, 1335, 1300, 1250, 1110, 1005, 945, 870, 835, 810, 760 cm^{-1}. ^{1}H-NMR could not be measured because **26** was insoluble in organic solvents. Anal. Calcd for $(C_{51}H_{34}O_4)_n$: C, 86.18; H, 4.82. Found: C, 85.85; H, 4.60.

Results and Discussion

Monomer Synthesis. The key step for the preparation of rigid AB_2 type monomers used in this study is the stepwise extension of phenylene units. For this purpose, a series of reaction containing cross-coupling[9] of *p*-methoxyphenylboronic acid and triflate was selected. Namely, the synthetic approach for the rigid AB_2 type monomers is as follows (Scheme 1). 3,5-Bis(4-fluorobenzoyl)phenol, **5**, was selected as the starting molecule. First, after **5** was converted to the triflate, **6**, by using tifluoromethanesulfonic anhydride, the cross-coupling of **6** with (*p*-methoxyphenyl)boronic acid, using tetrakis(triphenlyphosphine)paladium ($Pd(PPh_3)_4$) as catalyst, gave 4-methoxy-3,5-bis(4-fluorobenzoyl)-biphenyl, **7**. Next, the methyl ether was cleaved with pyridine hydrochloride to give 4-hydroxy-3′,5′-bis(4-fluorobenzoyl)biphenyl, **1**, which was the desired AB_2 monomer with biphenyl structure. Further, 4-hydroxy-3″,5″-bis(4-fluorobenzoyl)-p-terphenyl, **2**, the monomer with *p*-terphenyl structure, could be obtained in a similar manner as the conversion of the hydroxy group of **1** to the triflate, **8**, the cross-coupling of the triflate, **8**, with (*p*-methoxyphenyl)boronic acid, and cleavage of the methyl ether. When the procedure is repeated, 4-hydroxy-3‴,5‴-bis(4-fluorobenzoyl)-*p*-quarterphenyl, **3**, and 4-hydroxy-3⁗,5⁗-bis(4-fluorobenzoyl)-*p*-quinquephenl, **4**, which has *p*-quarterphenyl and *p*-quinquephenyl structure, were prepared, respectively. The structural characterization of these compounds was made by elemental analysis and IR, ^{1}H, and ^{13}C NMR spectrometry. As these compounds had one hydroxy group and two aromatic fluorides activated by a carbonyl group in the para position, the hyperbranched poly(ether ketones) were expected to be prepared by the polymerization of them.

Polymer Synthesis. The polymerization conditions used for the synthesis of hyperbranched poly(ether ketones) were similar to those reported by Viswanathan for the preparation of linear poly(ether ketones)[10] and by Hawker for the preparation of hyperbranched poly(ether ketones).[7] In these cases, the polymer linkages are formed by aromatic nucleophilic substitution of activated aromatic fluoride with a phenol group in the presence of a suitable base such as potassium carbonate. The polymerization was proceeded at 120−165 °C using a mixture of *N*,*N*-dimethylacetamide and toluene as a solvent. The water formed during the reaction was removed as an azeotrope to promote the polymerization. In the case of **1** and **2**, the polymerization proceeded

Table 1. Synthesis of Hyperbranched Poly(ether ketones)

polymer	yield (%)	M_n[a]	M_w/M_n	remarks[b]
14	92	17,700	6.42	S
15	93	26,000	8.82	S
16	93	*c*	–	P
17	94	–	–	P

[a] Determined by GPC based on standard polystyrene using THF as eluents. [b] Appearance of the polymerization mixture: S, homogeneous solution; P, precipitation during the reaction. [c] Insoluble.

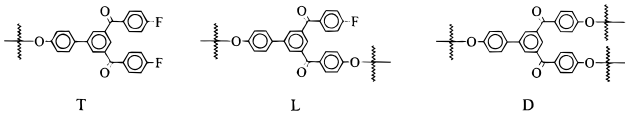


Figure 1. Structure of repeat units in hyperbranched poly(ether ketone), **14**.

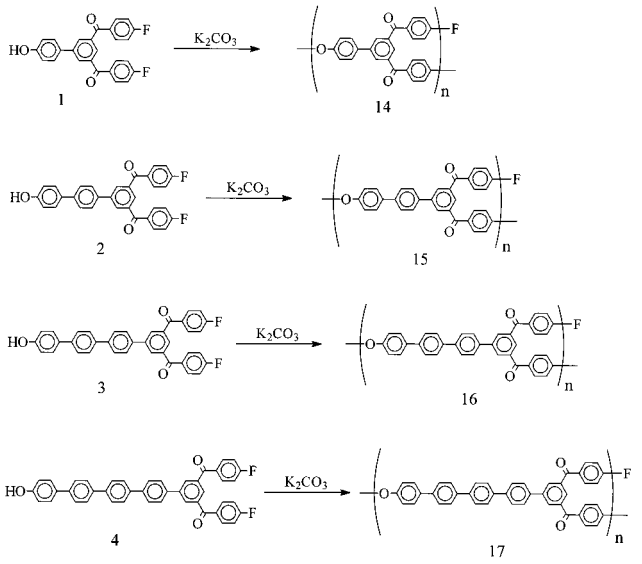
homogeneously, but the generated polymer, **16** and **17**, from **3** and **4**, respectively, was precipitated during polymerization due to their low solubility (Scheme 2). The results of the polymerization are summarized in Table 1. All the hyperbranched poly(ether ketones) were obtained in high yields (90−100%). GPC measurements of the hyperbranched poly(ether ketones), **14** and **15**, indicated that the M_n values were 18 000 and 26 000 relative to standard polystyrene, and M_w/M_n values, the measure of molecular weight distributions, were 6.4 and 8.8, respectively. M_n and M_w/M_n of the hyperbranched poly(ether ketones), **16** and **17**, could not be measured due to the low solubilities. Both the M_n and M_w/M_n values of hyperbranched poly(ether ketone) **15** were higher than those of hyperbranched poly(ether ketone) **14**. Higher molecular weight and broader molecular weight distribution of **15** may be attributed to the larger repeating unit and the higher reactivity of the hydroxy group, since the hydroxy group of starting monomer **2** was away from the aromatic ring connected with the electron-withdrawing carbonyl group in comparison with that of **1**.

The degree of branching of these hyperbranched poly(ether ketones) could be evaluated by means of NMR spectra. Dendritic macromolecules are perfectly branched and have a degree of branching of 100%, while hyperbranched polymers have a much more irregular structure due to the one-step synthesis. Although it is difficult to define unequivocally the irregular structure, the degree of branching (DB) was used as a measure of irregularity, which was defined in the following equation.[11]

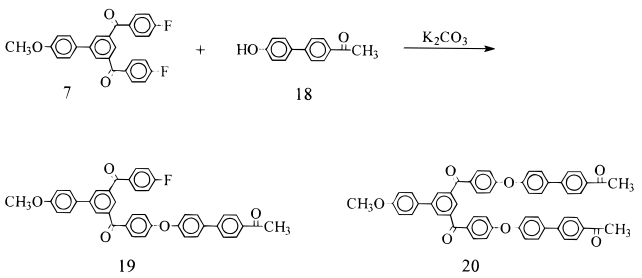
DB = (number of dendritic units + number of terminal units)/number of total units.

For hyperbranched poly(ether ketones), the overall structure reveals three different types of subunits. These include "dendritic", **D**, which has no fluoro group;"linear", **L**, which has one fluoro group; and "terminal", **T**, which has two fluoro groups (Figure 1). Since the chemical environment of the trisubstituted aromatic ring of **D**, **L**, and **T** will be substantially different, the relative percentage of **D**, **L**, and **T** can be evaluated by NMR spectroscopy. To discriminate the three subunits of the polymer backbone, model compounds **19** and **20** were synthesized (Scheme 3). **19**, **20**, and **7** were used as the model compound for linear, dendritic, and terminal subunits, respectively. Comparison of the ^{1}H-NMR spectra of these model compounds with ^{1}H-NMR spectra of the hyperbranched

Scheme 2



Scheme 3



poly(ether ketones) allowed the resonance of linear, dendritic, and terminal subunits to be identified. Figure 2 shows the ^{1}H-NMR spectra of **19**, **20**, **7**, and the hyperbranched poly(ether ketone), **14**. Distinct resonances for the linear model compounds, **19**, were observed at 8.14 and 8.18 ppm (Ha and Hb) while the corresponding protons for the dendritic model compound, **20**, and terminal model compound, **7**, appeared at 8.17 and 8.16 ppm, respectively. In the spectrum of the hyperbranched poly(ether ketone), **14**, the corresponding protons were observed at 8.13−8.23 ppm. These resonances were overlapped, but four peaks (8.16, 8.18, 8.19, and 8.20 ppm) could be identified. As compared with the ^{1}H-NMR spectra of the model compounds, the resonances at 8.16 and 8.20 ppm could be assigned to the linear subunits, while the resonances at 8.18 and 8.19 ppm could be assigned to the terminal and dendritic subunits, respectively. Peak separation of the resonances allowed the relative percentage of the three subunits in the hyperbranched poly(ether ketone), **14**, and the degree of branching of **14** was evaluated to be 0.63. The degree of branching of the hyperbranched poly(ether ketone), **15**, was evaluated to be 0.65 by the same method. However, the degree of branching of hyperbranched poly(ether ketones) **16** and **17** could not be evaluated as these polymers were insoluble in organic solvents.

Alternatively, the degree of branching of these hyperbranched poly(ether ketones), **14** and **15**, could be also evaluated by means of ^{13}C NMR spectra (Figure 3). Distinct resonances of carbons (a and b) connected with carbonyl group were observed at 138.2 and 138.7 ppm in the linear model compound, **19**, while the corresponding resonances for the dendritic model com-

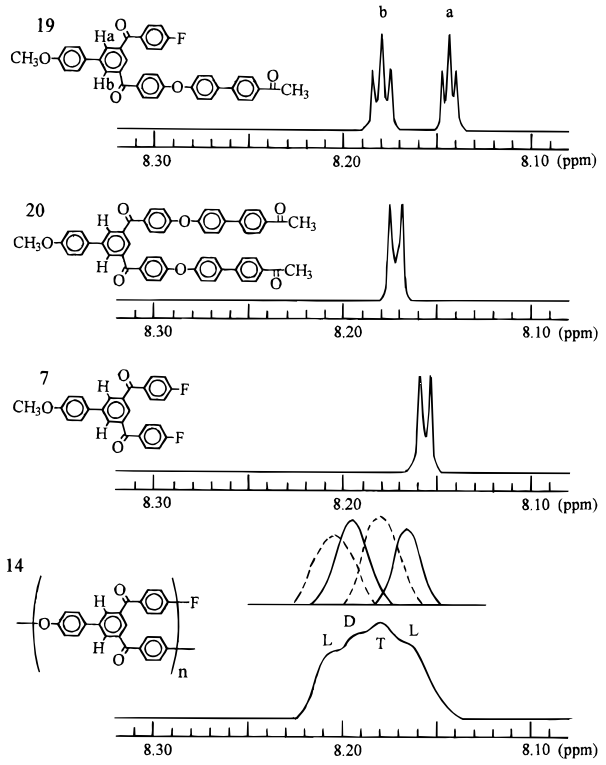


Figure 2. Comparison of the 400-MHz ^{1}H-NMR spectra for the linear, dendritic, and terminal model compounds, **19**, **20**, and **7**, respectively, with the hyperbranched poly(ether ketone), **14**.

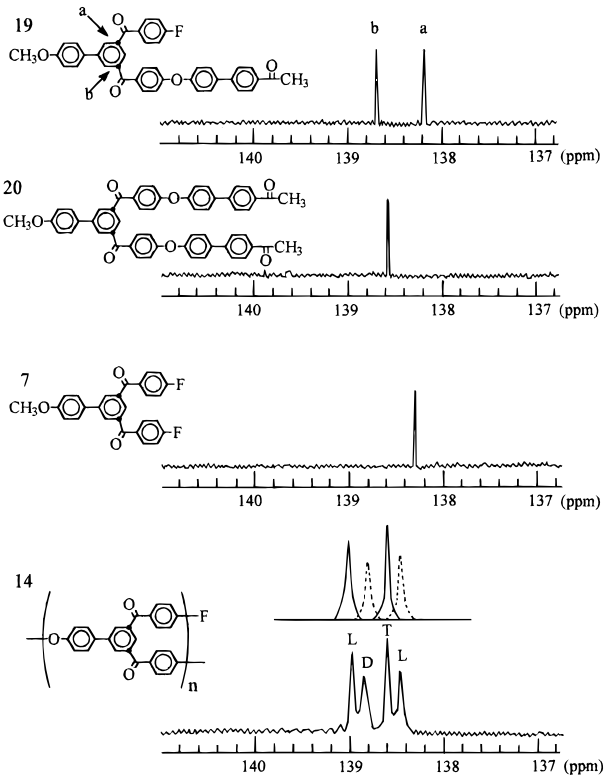


Figure 3. Comparison of the 100-MHz ^{13}C-NMR spectra for the linear, dendritic, and terminal model compounds, **19**, **20**, and **7**, respectively, with the hyperbranched poly(ether ketone), **14**.

pound, **20**, and terminal model compound, **7**, appeared at 138.6 and 138.3 ppm, respectively. In the spectrum of hyperbranched poly(ether ketone), **14**, four resonances (139.0, 138.9, 138.6, and 138.5 ppm) were

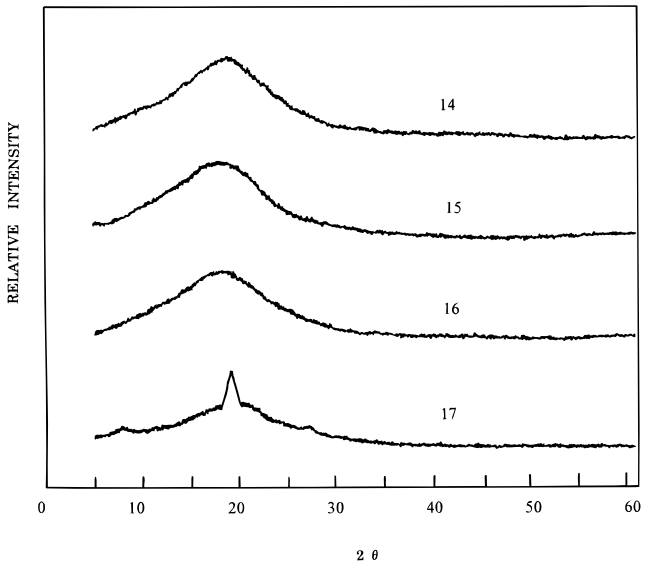


Figure 4. X-ray diffraction patterns of hyperbranched poly(ether ketones), **14**, **15**, **16**, and **17**.

observed at the corresponding region. When compared with the ^{13}C-NMR spectra of the model compounds, the resonances at 139.0 and 138.5 ppm could be assigned to the linear subunits, while the resonances at 138.9 and 138.6 ppm were due to the dendritic and terminal subunits, respectively. Peak separation of the resonances allowed the relative percentage of the three subunits in the hyperbranched poly(ether ketone), **14**, and the degree of branching of **14** was evaluated to be 0.57. The degree of branching of the hyperbranched poly(ether ketone), **15**, was evaluated to be 0.60 by the same method. These values are consistent with those obtained from ^{1}H-NMR, indicating the validity of the assigment.

Properties of Hyperbranched Poly(ether ketones). In the X-ray diffraction studies, the hyperbranched poly(ether ketones), **14**, **15**, and **16**, were amorphous despite their rigid structure, whereas the only hyperbranched poly(ether ketone), **17**, was crystalline (Figure 4). As hyperbranched polymers generally are known not to crystallize, this fact is very interesting. However, the fact that all of the other hyperbranched poly(ether ketones), even **16**, having quarterphenyl structure, were amorphous suggested that the branched structure hindered the crystallization.

Thermal behaviors of these hyperbranched poly(ether ketones) were evaluated by means of DSC. The DSC curves of these hyperbranched poly(ether ketones) are given in Figure 5. The glass transition temperature (T_g) was observed in **14**, **15**, and **16**, while only melting point (T_m) was obseved in **17**. The T_g of **17** was obtained by quenching from 400 °C (above the T_m). The T_gs of these polymers were much higher than the polymer obtained from **5** (140 °C, Miller[7]) and were in the range of 190−240 °C. Though the T_gs increased with increasing number of phenylene units in the polymer backbone, the increment per single phenylene unit was only 10−20 °C, and the increase of phenylene units affected less dramatically the T_gs than the modification of the end groups in the hyperbranched poly(ether ketones), which had been reported by Hawker et al.[6] On the other hand, T_m was observed in the range of 275−315 °C in **17** and reflected the crystalline nature as confirmed in X-ray diffraction. However, the value of the T_m was not

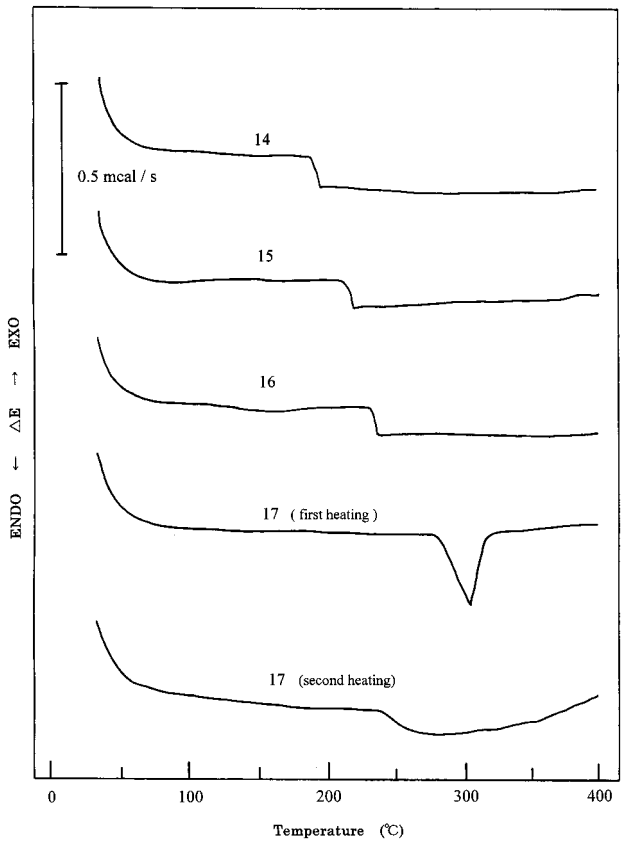


Figure 5. DSC curves of hyperbranched poly(ether ketones), **14**, **15**, **16**, and **17**.

seemed to be so high considering the *p*-quinquephenyl structure since the melting point of linear poly(ether ether ketone), which was prepared from 4-fluoro-4′-hydroxybenzophenone, was reported to be about 360 °C.[12] These results suggest that the branched structure caused higher disorder in the molecular chains and therefore less chain packing.

Though the linear poly(ether ketones) were soluble in only limited solvents, the hyperbranched poly(ether ketones) **14** and **15** were highly soluble in polar solvents such as *N*-methyl-2-pyrrolidone, *o*-chlorophenol, and *m*-cresol, and even in the less polar chloroform and tetrahydrofuran. However, **16** and **17** barely swelled on heating in polar solvents such as *N*,*N*-dimethylacetamide and *N*-methyl-2-pyrrolidone and were insoluble in usual the organic solvents. The effects of the introduction of rigid structure in the backbone were strongly reflected in solubility rather than in the thermal properties.

Introduction of Phenylene Units to the Chain Ends Group of the Hyperbranched Poly(ether ketone), 14. In this series of hyperbranched poly(ether ketones), a dramatic change of thermal properties was observed by increasing the number of phenylene units in the backbone from 3 to 4. However, it has been reported that hyperbranched polymers are characterized by the large number of chain end groups and that these groups play an important role in determining the final properties of the polymer.[6] Thus it will be interesting to introduce the same phenylene units into the chain end using a substitution reaction. Fortunately, the introduction of phenylene units could be easily accomplished, since the chain end of the hyperbranched poly(ether ketones) is the active 4-fluorobenzoyl group.

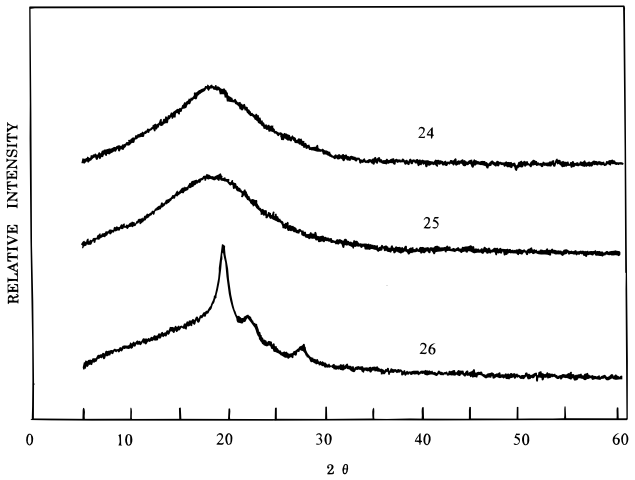
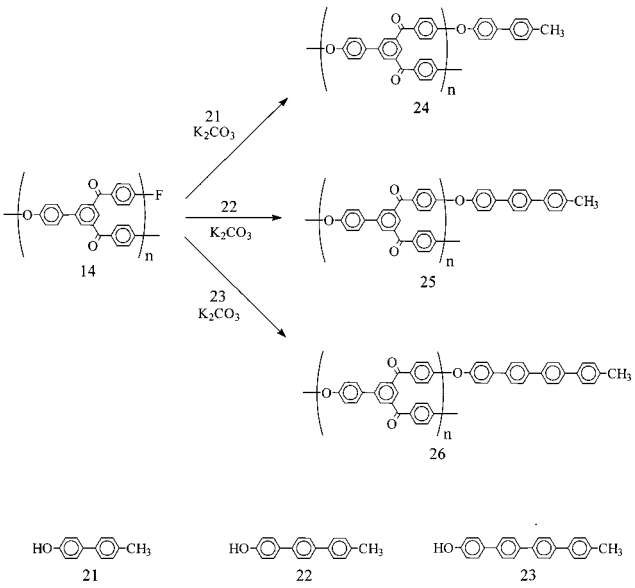


Figure 6. X-ray diffraction patterns of hyperbranched poly(ether ketones), **24**, **25**, and **26**.

Scheme 4



Hyperbranched poly(ether ketone) **14** with the least phenylene units, was selected for the introduction of phenylene units, and the introduction of these units to the chain ends was accomplished by nucleophilic displacement of the activated fluoro groups. The hyperbranched poly(ether ketones) **24**, **25**, and **26**, with biphenyloxy, *p*-terphenyloxy, and quarterphenyloxy end groups, could be prepared by the addition of the phenol derivatives, 4-hydroxy-4′-methylbiphenyl, **21**, 4-hydroxy-4″-methyl-*p*-terphenyl, **22**, and 4-hydroxy-4‴-methyl-*p*-quarterphenyl, **23**, to the reaction mixture at the end of the polymerization of **14**, respectively (Scheme 4).

In the X-ray diffraction studies, the hyperbranched poly(ether ketones) **24** and **25**, with biphenyloxy and *p*-terphenyloxy end groups, were amorphous, respectively, whereas the only hyperbranched poly(ether ketone), **26**, was crystalline with *p*-quarterphenyloxy end groups (Figure 6). These results suggested that the properties of chain end substituted hyperbranched poly(ether ketones) depended primarily on the nature of the substituent.

In the measurement of DSC, the only T_g was observed in **24** and **25**, and both the T_g and the T_m were observed

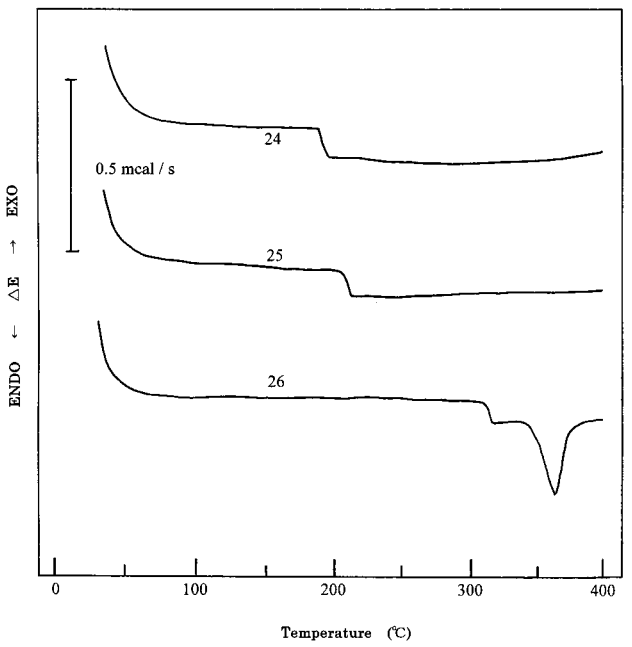


Figure 7. DSC curves of hyperbranched poly(ether ketones), **24**, **25**, and **26**.

in **26** (Figure 7). The T_g of **24** was 190 °C, the same as that of the unmodified hyperbranched poly(ether ketone), **14**, with 4-fluorobenzoyl end groups. The T_g of **25**, was slightly higher (205 °C) than that of **14**, but dramatically high T_g (315 °C) and T_m (345−385 °C) in **26** was observed. The T_g was much higher than that (218 °C) of the unmodified hyperbranched poly(ether ketone), **16**, with the same *p*-quarterphenyl structure in the backbone, and the T_m was much higher than that (275−315 °C) of the unmodified hyperbranched poly(ether ketone), **17**, with the *p*-quinquephenyl structure in the backbone. Moreover, by comparing the X-ray diffraction pattern of **17** and that of **26**, the latter showed more distinct pattern indicating the presence of the more ordered crystalline structure. It should be noted that a drastic change of thermal properties was again observed by increasing the number of phenylene unit of the chain end groups from 3 to 4 and that the change was more distinct as compared with that for the backbone chain. It is not clear at present why the larger effect of phenylene chain length was observed for the substitution of chain ends than main chain. The great increase of the intermolecular chain packing expected for the chain ends with long phenylene groups may be a reason for the drastic increase of the T_g and the T_m.

Conclusion

The stepwise synthesis of new AB_2 type monomers, with various numbers of phenylene units, and the preparation of the hyperbranched poly(ether ketones) from these monomers have been demonstrated. Obtained hyperbranched poly(ether ketones) from 4-hydroxy-3′,5′-bis(4-fluorobenzoyl)biphenyl, **1**, 4-hydroxy-3″,5″-bis(4-fluorobenzoyl)-*p*-terphenyl, **2**, and 4-hydroxy-3‴,5‴-bis(4-fluorobenzoyl)-*p*-quarterphenyl, **3**, were amorphous, the values of the glass transition temperatures were 188, 208, and 218 °C, respectively, and slightly increased with increasing number of the phenylene units. On the other hand, the only hyperbranched poly(ether ketone) from 4-hydroxy-3⁗,5⁗-bis(4-fluorobenzoyl)-*p*-quinquephenyl, **4**, was crystalline and the value of the melting point was 275−315 °C. The degree of branching of the hyperbranched poly(ether ketones) **14** and **15**, were evaluated to be about 60% from NMR spectroscopy. The introduction of phenol derivatives with various phenylene units, 4-hydroxy-4′-methylbiphenyl, **21**, 4-hydroxy-4″-methyl-p-terphenyl, **22**, and 4-hydroxy-4‴-methyl-p-quarterphenyl, **23**, on the chain ends of the hyperbranched poly(ether ketone), **14**, has been also carried out. The hyperbranched poly(ether ketone), **26**, connected with 4‴-methyl-*p*-quarterphenyloxy group showed dramatically high T_g (315 °C) and T_m (345−385 °C), and it was suggested that the structure of chain end groups had a stronger influence upon the thermal properties of hyperbranched polymers than the structure of polymer backbone.

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