ORIGINAL ARTICLE

Hyperbranched poly(ether ether ketone)s: preparation and comparison of properties with the corresponding dendrimers

Atsushi Morikawa and Minoru Akagi

Hyperbranched poly(ether ether ketone)s with hydroxyl terminal groups are prepared by a one-step polycondensation of 3,5-dihydroxy-4'-(4-fluorobenzoyl)diphenylether (AB₂-type monomer) through an aromatic nucleophilic substitution reaction. With the help of model compounds, ¹H-NMR studies reveal that the degree of branching of the poly(ether ether ketone)s is about 52%. The possibility of entanglement among the hyperbranched polymer molecules is suggested from comparison of their glass transition temperatures with the corresponding dendrimers and the optimized structure of the hyperbranched polymers. The terminal hydroxyl groups were readily functionalized, yielding hyperbranched polymers with a variety of different functional chain ends. The nature of the chain end is shown to dramatically affect the properties of the hyperbranched polymers.

Polymer Journal (2013) 45, 614–621; doi:10.1038/pj.2012.188; published online 14 November 2012

Keywords: dendrimers; entanglement; hyperbranched poly(ether ether ketone)s; optimized structure; 3, 5-dihydroxy-4'-(4-fluorobenzoyl)diphenylether

INTRODUCTION

Compared with linear polymers, dendritic macromolecules are more amorphous, and are usually soluble in organic solvents because of their branched structures. Dendritic macromolecules can be classified as dendrimers or hyperbranched polymers. Dendrimers are well-defined macromolecules exhibiting precise tree-like structures, and consist of dendritic units and terminal units, whereas hyperbranched polymers consist of dendritic units, linear units and terminal units. Hyperbranched polymers possess numerous branching points and end groups, and their properties, such as high solubility, low solution viscosity and absence of entanglement, are similar to those of dendrimers. Thus, hyperbranched polymers have received considerable attention due to the expectation that their unique highly branched structures will impart unusual properties. Although dendrimers are constructed via step-by-step sequences, requiring isolation and purification after each step, hyperbranched polymers can be prepared by one-step polymerization of AB_x-type monomers. As hyperbranched polymers are thought to possess similar properties to those of dendrimers and are easily prepared, many varieties of hyperbranched polymers, such as polyesters,^{1–4} polyamides,^{5–7} poly(ether ketone)s,^{8–11} polyphenylene,¹² polyurethanes,¹³ polyimides,^{14–16} polycarbonates,¹⁷ polysiloxanes,^{18,19} poly(benzoxazole)s,^{20,21} poly(triphenylamine)s²² and poly(ether sulfone)s²³ have been prepared from AB_x-type monomers and their properties have been investigated. Moreover, hyperbranched polymers were prepared from A₂-type and B₃-type monomers,^{24,25} and

hyperbranched polymers with controlled degrees of branching were also prepared.^{26,27} Hyperbranched polymers and dendrimers have been modified by introduction of functional groups to the chain end or chain backbone, and a variety of applications, such as encapsulators,^{11–19,28} composite materials,^{29–31} ion-exchange membranes,³² photoresistors,³³ nonlinear optical devices,³⁴ diodes³⁵ and cross-linkers,^{36,37} have been investigated. Therefore, it is thought to be important to compare the properties of hyperbranched polymers with those of the corresponding dendrimers.

In our previous paper, we synthesized poly(ether ether ketone) dendrimers by the divergent approach through an aromatic nucleophilic substitution reaction using 3,5-dimethoxy-4'-(4-fluorobenzoyl)diphenyl ether and 1,3,5-tris(p-(3,5-dihydroxyphenoxy)phenyl)benzene as a building block and a starting core, respectively.³⁸ **Den G3-OMe** and **Den G3-OH** possessing 48 methoxy groups and hydroxyl groups on the periphery were obtained, and the periphery groups had great influence on the properties of the resulting dendrimers.

In this study, hyperbranched poly(ether ether ketone)s with hydroxyl terminal groups were prepared by a one-step polycondensation of 3,5-dihydroxy-4'-(4-fluorobenzoyl)diphenylether through an aromatic nucleophilic substitution reaction, and the properties were compared with those of the dendrimers. The hydroxyl groups at the chain end were converted to various functional groups, and the properties of the hyperbranched polymers were found to be dependent on the functional groups.

EXPERIMENTAL PROCEDURE

^1H - and ^{13}C - NMR spectra were recorded on a JNM-GSX400 FT-NMR spectrometer (JEOL, Tokyo, Japan) and IR spectra were recorded on a Shimadzu spectrophotometer IR 435 (Shimadzu Corporation, Kyoto, Japan). Gel permeation chromatography was carried out on a Polymer Laboratories analytical column, PL gel 5 μ MIXED-C (Polymer Laboratories LTD, Tokyo, Japan), with tetrahydrofuran as the eluent. Reduced viscosity was measured at various concentrations using an Ubbelohde-type capillary viscometer (Shibata Corporation, Sohka, Japan) in tetrahydrofuran at 30 °C. Differential scanning calorimetry was performed with a Shimadzu DSC-60 instruct (Shimadzu Corporation) and measurements were made at a heating rate of 10 °C min⁻¹ in air or nitrogen from room temperature to 280 °C. Thermogravimetry (TG) was performed with a Rigaku thermal analysis station TG8110 (Rigaku Corporation, Tokyo, Japan), and measurements were made at a heating rate of 10 °C min⁻¹ in air from room temperature to 800 °C.

Preparation of 3,5-dihydroxy-4'-(4-fluorobenzoyl)diphenylether 1

A mixture of 4,4'-difluorobenzophenone (10.91 g, 0.05 mol), 3,5-dimethoxyphenol (7.71 g, 0.05 mol), potassium carbonate (6.91 g, 0.05 mol), toluene (25 ml) and *N,N*-dimethylacetamide (DMAc) (45 ml) was stirred at 130 °C for 1 h.^{38,39} 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 100 ml of dichloromethane. 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 pure 3,5-dimethoxy-4'-(4-fluorobenzoyl)diphenylether.³⁸ Yield: 8.82 g (50%). Mp: 53–54 °C. Bp: 260 °C (1 torr).

3,5-dimethoxy-4'-(4-fluorobenzoyl)diphenylether (5.29 g, 15 mmol) was heated together with pyridine hydrochloride (30 g) at reflux temperature (240 °C) for about 30 min. After the reaction mixture was homogeneous, it was poured into water (500 ml), and extracted twice with 100 ml of ethyl acetate. The combined extract was dried over anhydrous magnesium sulfate. After the solvent was evaporated, pure 1 was obtained by silica gel column eluted by dichloromethane and ethyl acetate (2: 1).³⁹ Yield: 4.23 g (87%). Mp: 137–138 °C.

The IR spectrum exhibited absorption bands at 3400–3000 cm⁻¹ (OH), 1640 cm⁻¹ (C=O), and 1240 cm⁻¹ (Ar-O-Ar).

The ^1H NMR spectrum (δ in CDCl_3) showed signals at 5.40 (s, 2H, OH), 6.15 (d, 2H, $J=2.2$ Hz, H5), 6.19 (t, 1H, $J=2.2$ Hz, H6), 7.06 (d, 2H, $J=8.8$ Hz, H4), 7.16 (m, 2H, H1), 7.77 (d, 2H, $J=8.8$ Hz, H3) and 7.81 (m, 2H, H2). The ^{13}C NMR spectrum (δ in CDCl_3) showed signals at 99.28, 99.88, 115.53 (d, $J=22.3$ Hz), 117.92, 132.09, 132.31, 132.55 (d, $J=9.5$ Hz), 133.89 (d, $J=3.2$ Hz), 157.66, 157.88, 160.99, 165.37 (d, $J=234.3$ Hz) and 194.61.

Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{FO}_4$: C, 70.37%; H, 4.04%. Found: C, 70.48%; H, 4.15%.

Preparation of hyperbranched poly(ether ether ketone) P1

A mixture of 1 (1.62 g, 5 mmol), potassium carbonate (0.373 g, 2.7 mmol), toluene (10 ml) and DMAc (20 ml) was stirred in a flask at 120 °C. The temperature was then raised from 120 °C to 165 °C, to remove water formed during the reaction as an azeotrope with toluene. The reaction mixture was stirred at this temperature for 6 h. The polymerization proceeded homogeneously. After the reaction was completed, 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: 1.34 g (88%).

The IR spectrum exhibited absorption bands at 3400–3000 cm⁻¹ (OH), 1650 cm⁻¹ (C=O) and 1240 cm⁻¹ (Ar-O-Ar).

The ^1H NMR spectrum [δ in $\text{DMSO}-d_6$] showed signals at 5.90–5.96 (0.64H, H5 terminal unit), 6.04–6.08 (0.32H, H5 terminal unit), 6.24–6.31 (0.51H, H5 linear unit), 6.31–6.36 (1.03H, H5 linear unit), 6.64–6.72 (0.51H, H5 dendritic unit), 7.00–7.30 (4H, H1 and H4), and 7.58–7.86 (4H, H2 and H3) p.p.m.

Anal. Calcd for $\text{C}_{19}\text{H}_{12}\text{O}_4$: C, 74.99%; H, 3.97%. Found: C, 74.52%; H, 3.64%.

Preparation of the model compound

4-benzoyl-3, 5-dimethoxy-diphenylether 2. A mixture of 4-fluorobenzophenone (5.00 g, 25 mmol), 3,5-dimethoxyphenol (3.85 g, 25 mmol), potassium carbonate (1.93 g, 14 mmol), toluene (30 ml) and DMAc (60 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. The reaction mixture was stirred at this temperature for 6 h, and cooled to 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 100 ml of dichloromethane. The combined organic layer was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was distilled under reduced (ceramic heater) pressure to give pure 2. Yield: 6.02 g (72%). Bp. 240 °C (1 torr). Mp. 62–64 °C.

The IR spectrum exhibited absorption bands at 2940 cm⁻¹ (CH_3), 1650 cm⁻¹ (C=O) and 1240 cm⁻¹ (Ar-O-Ar).

The ^1H NMR spectrum (δ in $\text{DMSO}-d_6$) showed signals at 3.77 (s, 6H, $-\text{CH}_3$), 5.94 (d, 2H, $J=2.2$ Hz, H6), 6.09 (t, 1H, $J=2.2$ Hz, H7), 7.10 (d, 2H, $J=8.8$ Hz, H5), 7.52–7.58 (m, 2H, H2), 7.64–7.69 (m, 1H, H1), 7.72–7.73 (m, 2H, H3) and 7.79 (d, 2H, $J=8.8$ Hz, H4) p.p.m. The ^{13}C NMR spectrum (δ in $\text{DMSO}-d_6$) showed signals at 55.6, 97.8, 98.8, 117.4, 128.1, 128.8, 131.5, 131.7, 131.9, 137.2, 156.9, 159.5, 160.7 and 194.3.

Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_2$: C, 75.43%; H, 5.43%. Found: C, 75.23%; H, 5.24%.

3(4-benzoylphenoxy) resorcinol 3. 2 (6.02 g, 18 mmol) was heated together with pyridine hydrochloride (40 g) at reflux temperature (240 °C) for about 30 min. After the reaction mixture was homogeneous, it was poured into water (400 ml) and extracted twice with 100 ml of ethyl acetate. The combined organic layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated. Pure 3 was obtained by silica gel column chromatography with dichloromethane and ethyl acetate (10:1). Yield: 4.68 g (85%). Mp. 52–53 °C.

The IR spectrum exhibited absorption bands at 3400–3000 cm⁻¹ (OH), 1650 cm⁻¹ (C=O) and 1240 cm⁻¹ (Ar-O-Ar).

The ^1H NMR spectrum (δ in $\text{DMSO}-d_6$) showed signals at 5.95 (d, 2H, $J=2.2$ Hz, H6), 6.10 (t, 1H, $J=2.2$ Hz, H7), 7.10 (d, 2H, $J=8.8$ Hz, H5), 7.53–7.58 (m, 2H, H2), 7.64–7.68 (m, 1H, H1), 7.72–7.73 (m, 2H, H3), 7.77 (d, 2H, $J=8.8$ Hz, H4) and 9.38 (s, 2H OH) p.p.m. The ^{13}C NMR spectrum (δ in $\text{DMSO}-d_6$) showed signals at 97.5, 98.8, 117.2, 127.9, 128.8, 131.3, 131.5, 131.7, 137.2, 156.6, 159.3, 160.7 and 194.1.

Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{O}_4$: C, 74.50%; H, 4.61%. Found: C, 74.36%; H, 4.43%.

3,5-bis(4-benzoylphenoxy)phenol **4** and 1,3,5-tris(benzoylphenoxy)benzene **5**. A mixture of 4-fluorobenzophenone (3.00 g, 15 mmol), **3** (4.59 g, 15 mmol), potassium carbonate (1.24 g, 9 mmol), toluene (30 ml) and DMAc (60 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. The reaction mixture was stirred at this temperature for 6 h, then cooled to 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 100 ml of dichloromethane. The combined organic layer was dried over anhydrous magnesium sulfate. After evaporation of the solvent, a mixture of **4** and **5** was obtained. Pure **4** and **5** were obtained by silica gel column chromatography with dichloromethane and ethylacetate (40:1).

3,5-bis(4-benzoylphenoxy)phenol (**4**). Yield: 1.92 g. Mp. 82–84 °C.

The IR spectrum exhibited absorption bands at 3400–3000 cm⁻¹ (OH), 1650 cm⁻¹ (C=O) and 1240 cm⁻¹ (Ar-O-Ar).

The ¹H NMR spectrum (δ in DMSO-*d*₆) showed signals at 6.30 (t, 1H, *J* = 2.2 Hz, H7), 6.37 (d, 2H, *J* = 2.2 Hz, H6), 7.18 (d, 2H, *J* = 8.8 Hz, H5), 7.53–7.58 (m, 2H, H2), 7.66–7.69 (m, 1H, H1), 7.69–7.73 (m, 1H, H3), 7.81 (d, 2H, *J* = 8.8 Hz, H4) and 9.95 (s, 1H, OH) p.p.m. The ¹³C NMR spectrum (δ in DMSO-*d*₆) showed signals at 101.2, 102.5, 116.0, 117.8, 128.0, 128.8, 131.7, 131.8, 132.2, 137.2, 157.3, 160.0 and 194.1.

Anal. Calcd for C₃₂H₂₂O₅: C, 79.00%; H, 4.56%. Found: C, 79.02%; H, 4.54%.

1,3,5-tris(benzoylphenoxy)benzene (**5**). Yield: 1.92 g. Mp. 95–96 °C.

The IR spectrum exhibited absorption bands at 1650 cm⁻¹ (C=O) and 1240 cm⁻¹ (Ar-O-Ar).

The ¹H NMR spectrum (δ in DMSO-*d*₆) showed signals at 6.73 (s, 3H, H6), 7.23 (d, 6H, *J* = 2.2 Hz, H6), 7.49–7.54 (m, 6H, H2), 7.63–7.66 (m, 3H, H1), 7.68–7.71 (m, 6H, H3) and 7.88 (d, 2H, *J* = 8.8 Hz, H4) p.p.m. The ¹³C NMR spectrum (δ in DMSO-*d*₆) showed signals at 106.2, 117.8, 128.1, 129.0, 131.6, 132.0, 132.3, 137.0, 157.6 and 194.2.

Anal. Calcd for C₄₅H₃₀O₆: C, 81.70%; H, 4.54%; N, 5.38%. Found: C, 81.41%; H, 4.38%.

Preparation of hyperbranched poly(ether ether ketone) P2.

A mixture of **1** (1.62 g, 5 mmol), potassium carbonate (0.373 g, 2.7 mmol), toluene (10 ml) and DMAc (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, and the reaction mixture was stirred at this temperature for 6 h. After the reaction mixture was cooled to room temperature, methyl sulfate (0.38 g, 3 mmol) and potassium carbonate (0.42 g, 3 mmol) were added. The mixture was stirred at 80 °C for another 6 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: 1.35 g (85%).

The IR spectrum exhibited absorption bands at 2945 cm⁻¹ (CH₃), 1650 cm⁻¹ (C=O) and 1240 cm⁻¹ (Ar-O-Ar).

The ¹H NMR spectrum (δ in DMSO-*d*₆) showed signals at 3.75–3.81 (3H, CH₃), 5.93–6.00 (0.65H, H5 terminal unit), 6.07–6.011 (0.33H, H5 terminal

unit), 6.24–6.31 (0.50H, H5 linear unit), 6.31–6.36 (1.00H, H5 linear unit), 6.64–6.72 (0.52H, H5 dendritic unit), 7.00–7.30 (4H, H1 and H4) and 7.58–7.86 (4H, H2 and H3) p.p.m.

Anal. Calcd for C₂₀H₁₄O₄: C, 75.46%; H, 4.43%. Found: C, 75.05%; H, 4.23%.

Preparation of hyperbranched poly(ether ether ketone) P3

A mixture of **1** (1.62 g, 5 mmol), potassium carbonate (0.373 g, 2.7 mmol), toluene (10 ml) and DMAc (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, and the reaction mixture was stirred at this temperature for 6 h. After the reaction mixture was cooled to room temperature, 1-bromohexane (0.50 g, 3 mmol) and potassium carbonate (0.42 g, 3 mmol) were added. The mixture was stirred at 80 °C for another 6 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: 1.47 g (76%).

The IR spectrum exhibited absorption bands at 2940–2960 cm⁻¹ (C₆H₁₃), 1650 cm⁻¹ (C=O) and 1240 cm⁻¹ (Ar-O-Ar).

The ¹H NMR spectrum (δ in DMSO-*d*₆) showed signals at 0.82–1.23 (9H, -CH₂CH₂CH₂CH₂CH₂CH₃), 1.80–1.83 (2H, -CH₂CH₂CH₂CH₂CH₂CH₃), 3.70–3.79 (3H, -CH₂CH₂CH₂CH₂CH₂CH₃), 5.93–6.01 (0.65H, H5 terminal unit), 6.07–6.11 (0.33H, H5 terminal unit), 6.24–6.32 (0.50H, H5 linear unit), 6.31–6.36 (1.00H, H5 linear unit), 6.64–6.72 (0.52H, H5 dendritic unit), 7.00–7.30 (4H, H1 and H4) and 7.58–7.86 (4H, H2 and H3) p.p.m.

Anal. Calcd for C₂₅H₂₄O₄: C, 77.30%; H, 6.23%. Found: C, 77.10%; H, 5.98%.

Preparation of hyperbranched poly(ether ether ketone) P4

A mixture of **1** (1.62 g, 5 mmol), potassium carbonate (0.373 g, 2.7 mmol), toluene (10 ml) and DMAc (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, and the reaction mixture was stirred at this temperature for 6 h. After the reaction mixture was cooled to room temperature, benzoyl chloride (0.42 g, 3 mmol) and triethylamine (0.30 g, 3 mmol) were added. The mixture was stirred at room temperature for another 6 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: 1.85 g (91%).

The IR spectrum exhibited absorption bands at 1720 cm⁻¹ (C=O), 1650 cm⁻¹ (C=O) and 1240 cm⁻¹ (Ar-O-Ar).

The ¹H NMR spectrum (δ in DMSO-*d*₆) showed signals at 5.94–6.01 (0.64H, H5 terminal unit), 6.09–6.13 (0.32H, H5 terminal unit), 6.23–6.33 (0.51H, H5 linear unit), 6.33–6.38 (1.03H, H5 linear unit), 6.65–6.73 (0.51H, H5 dendritic unit), 7.00–7.88 (9H, H1, H2, H3, H4, H6, H7 and H8) p.p.m.

Anal. Calcd for C₂₆H₁₆O₅: C, 76.46%; H, 3.95%. Found: C, 76.05%; H, 3.72%.

RESULTS AND DISCUSSION

Polymer synthesis

The AB₂-type monomer, 3,5-dihydroxy-4'-(4-fluorobenzoyl)diphenylether **1**, was synthesized according to the previous method.^{38,39}

3,5-dimethoxy-4'-(4-fluorobenzoyl)diphenylether was synthesized by the reaction between 4,4'-difluorobenzophenone and 3,5-dimethoxyphenol, and the 3,5-methoxy-4'-(4-fluorobenzoyl)diphenylether was treated with pyridine hydrochloride to give **1**. Poly((ether)-(ether ether ketone))dendrimers were also prepared using **1** as a building block.³⁹

Hyperbranched polymers were synthesized by the method similar to that of poly(ether ether ketone) dendrimers.³⁹ The polymer linkages are formed by aromatic nucleophilic substitution of an activated aromatic fluoride with a phenol group in the presence of a suitable base such as potassium carbonate (Figure 1). Polymerization proceeded at 120–165 °C using a mixture of DMAc and toluene as the solvent. The water formed during the reaction was removed as an azeotrope to promote the polymerization. The polymerization proceeded homogeneously, and the corresponding hydroxyl terminated hyperbranched poly(ether ether ketone), **P1**, was generated in 88% yield. Gel permeation chromatography analysis of **P1** gave a *M_n* of 5200 and a *M_w* of 20 300 (*M_w*/*M_n* = 3.9) (Figure 2). Those of the corresponding dendrimers are also shown in Figure 2 for comparison. The molecular weight of the polymer was calibrated against polystyrene. The polymerization was also carried out at 120–200 °C using a mixture of NMP (*N*-methyl-2-pyrrolidinone) and toluene as a solvent. *M_n* and *M_w* of the obtained polymer were 4800 and 20 600, respectively, and not very dependent on the solvent or the reaction temperature.

Degree of branching

Hyperbranched polymer **P1** was formed by a sequence of condensations of the AB₂-type monomers resulting in an irregular dendritic structure. This structure included terminal units, **T**, which have two hydroxyl groups, linear units, **L**, which have one hydroxyl group, and

dendritic units, **D**, which have no hydroxyl groups. The degree of branching (DB) of hyperbranched polymers is given by

$$DB = [(\text{number of dendritic units}) + (\text{number of terminal units})] / (\text{number of total units})$$

As the chemical environment of the trisubstituted aromatic ring of **T**, **L** and **D** will be substantially different, the relative percentage of **T**, **L** and **D** can be evaluated by ¹H-NMR spectroscopy. To discriminate the three subunits of the polymer backbone, model compounds **3**, **4** and **5** were synthesized (Figure 3). The ¹H-NMR spectra for model compounds **3**, **4**, **5** and **P1** are shown in Figure 4. That of the corresponding dendrimer **DenG3-OH** is also shown in Figure 4 for comparison. Distinct resonances for the terminal model compound **3** appeared at 5.95 p.p.m. (H6) and 6.10 p.p.m. (H7), whereas the corresponding resonances for the linear model compound **4** appeared at 6.37 p.p.m. (H6) and 6.30 p.p.m. (H7). H6 protons of the dendritic model compound **5** were observed at 6.73 p.p.m. In the ¹H-NMR spectrum of **DenG3-OH**, the corresponding protons for the terminal units were observed at 5.93 p.p.m. and 6.08 p.p.m. and those for the dendritic units were observed at 6.55, 6.61 and 6.63 p.p.m.³⁸ Good correlation was observed in the comparison of the ¹H-NMR spectra of these model compounds with that of the hyperbranched polymer **P1**. The resonances at 5.90–5.96 p.p.m. and 6.04–6.08 p.p.m. are attributed to protons of the terminal subunit, those of

Figure 1 Synthesis of hyperbranched poly(ether ether ketone) and structures of the corresponding dendrimers.

Figure 2 Gel permeation chromatography chromatograms of **P1** and the corresponding dendrimers.

Figure 3 Model compounds **3**, **4** and **5**, and the synthetic procedures.

Figure 4 Comparison of ^1H -NMR spectrum for the hyperbranched polymer **P1** with those of the terminal, linear and dendritic model compounds, **3**, **4** and **5**, respectively.

6.24–6.31 p.p.m. and 6.31–6.36 p.p.m. are attributed to protons of the linear subunit, and that of 6.64–6.72 p.p.m. is attributed to protons of the dendritic subunit. Integration of the resonances provided the relative percentage of the three subunits in the hyperbranched polymer of **P1**, and the DB of **P1** was evaluated to be 0.52.

When the ^1H -NMR spectrum for **P1** is compared with that of **DenG3-OH**, the signals for the terminal units have nearly the same chemical shift, but the signals for dendritic units in **P1** appear downfield from those in **DenG3-OH**. The environment of dendritic units in **P1** could be evaluated by the ^1H -NMR spectrum for dendritic units in **P1** compared with those of the corresponding dendrimers **DenG1-OH**, **DenG2-OH** and **DenG3-OH** (Figure 5). The signals for Ha in **DenG1-OH**, **DenG2-OH** and **DenG3-OH** appear at 6.63 p.p.m., 6.59 p.p.m. and 6.55 p.p.m., respectively, and those for Hb in **DenG2-OH** and **DenG3-OH** appear at 6.66 p.p.m. and 6.61 p.p.m., respectively. The signals of higher generation dendrimers appear at higher field, and the protons in the interior of the molecule are thought to feel the shielding effect of the π electrons in other aromatic rings. As the signals in **P1** appear downfield from those in **DenG1-OH**, the protons in **P1** are barely shielded by the π electrons in other aromatic rings, which exist in the surroundings. Therefore, almost all the dendritic units in **P1** are thought to be near chain ends, and the hyperbranched polymer shown in Figure 1 is proposed as that with such a structure, of which the DB is about 50%.

The present DB value (0.52) was higher than those of the hyperbranched polymers prepared by self-condensation of AB_2 monomers, which had one aromatic fluoride and two hydroxyl groups, in the presence of potassium carbonate. The DB values

Figure 5 Comparison of ^1H -NMR spectra for dendritic units in the hyperbranched polymer **P1** with those for **DenG1-OH**, **DenG2-OH** and **DenG3-OH**.

were 0.15 and 0.17 in the preparation of the hyperbranched poly(ether ketone)⁹ from 3,5-dihydroxy-4'-fluorobenzophenone and hyperbranched poly(ether sulfone)⁴¹ from 4-(3,5-dihydroxyphenoxy)-4'-fluorodiphenylsulfone, respectively. In the preparation of hyperbranched poly(ether sulfone), 4-fluorophenylsulfonyl groups reacted with potassium phenolates *in situ*. The formation of linear units by the reaction with the monophenolates was suggested to be advantageous due to low solubility of diphenolates, which formed dendritic units. In the present preparation of **P1**, 4-fluorobenzoyl groups reacted with potassium phenolates *in situ*, and reactivity of 4-fluorobenzoyl groups was lower than 4-fluorophenylsulfonyl groups due to weak electron-withdrawing of the carbonyl groups. The 4-fluorobenzoyl groups did not react with monophenolate completely in the reaction condition (160 °C), and the rest of them were thought to be able to react with the phenolate derived from the hydroxyl group in the linear units. Consequently, the DB value of **P1** was thought to be higher than that of poly(ether sulfone) prepared in the presence of potassium carbonate. In the preparation of the hyperbranched poly(ether ketone)⁹ from 3,5-dihydroxy-4'-fluorobenzophenone, the polymerization was performed at higher temperature (200 °C), and the 4-fluorobenzoyl groups were thought to react with the monophenolate almost completely. The hyperbranched polymer with low DB value was generated as a result. The reactivity of aromatic fluorides might affect DB values.

Properties of hyperbranched polymers

Hyperbranched polymers resemble dendrimers in many physical properties, such as high solubility, low solution viscosity and absence of entanglement.⁴⁰ The reduced viscosity of the hyperbranched polymer **P1** was compared with that of the corresponding dendrimer **DenG3-OH** (Figure 6). Though neither viscosity was dependent on the concentration, the viscosity of **P1** was 0.15, and higher than that (0.10) (Morikawa *et al.*³⁸) of **DenG3-OH**. The Gel permeation chromatography chromatogram shows that the size of **P1** in tetrahydrofuran is smaller than that of **DenG3-OH** (Figure 2). The viscosity of **P1** was higher in spite of its smaller size. The higher

Figure 6 Reduced viscosities of the hyperbranched polymer **P1** and **DenG3-OH**.

viscosity of **P1** suggested a higher degree of interaction with the solvents, and the molecular structure in the solution was thought to be affected by the viscosities.

The thermal behavior of **P1** was evaluated by differential scanning calorimetry, and **P1** showed a glass transition (T_g) at 190 °C (Figure 9). The T_g value was higher than that of **DenG3-OH** (140 °C) (Morikawa *et al.*³⁸), and suggested a higher degree of interaction among molecules. As T_g values were greatly dependent on the molecular structure, density functional theory (DFT) calculations were carried out as implemented in the Gaussian09W package of quantum chemical programs. The optimized structure of the hyperbranched polymer, which was proposed on the basis of ¹H-NMR chemical shifts of the dendritic unit, was obtained by the RHF/6-31G method in the gas phase (Figure 7). Long side-chains exist in the molecule, and the possibility of entanglement among the molecules was suggested. The comparison between hyperbranched polymers and the corresponding dendrimers can be also performed in polyesters from 3,5-dihydroxybenzoic acid, poly(ether ketone)s from 3,5-bis(4-fluorophenyl)phenol and polyamides from 3,5-diaminobenzoic acid. The T_g value of hyperbranched polyester¹ was 197 °C, and almost the same as that (201 °C) of the corresponding dendrimer⁴² possessing 48 hydroxyl groups. The T_g value of hyperbranched poly(ether ketone)⁸ was 144 °C, and higher than that (123 °C) of the corresponding dendron⁴³ possessing 16 phenoxy groups. The T_g value of hyperbranched polyamide⁷ was 305 °C, and higher than that (275 °C) of the corresponding dendron^{7,44} possessing 32 benzamide groups. Most of the hyperbranched polymers had higher T_g values than the corresponding dendrimers or dendrons, and the difference in T_g value between the present **P1** and **DenG3-OH** was the largest. 4,4'-benzophenone units may contribute to the formation of the long side chains.

The solubility of **P1** was compared with that of **DenG3-OH** (Table 1). **P1** was insoluble in non-polar solvents, such as chloroform and toluene, and soluble in amide solvents, pyridine and tetrahydrofuran, and showed similar solubility as **DenG3-OH**. However, **DenG3-OH** was soluble in methanol and aqueous NaOH solution at room temperature, whereas **P1** was insoluble in methanol and soluble in aqueous NaOH solution upon heating.

Chemical modification of hyperbranched polymer

Hyperbranched polymers based on AB_n monomers are characterized by a large number of chain end groups, and the chain end groups have an important role in determining the final properties of the

Figure 7 Optimized structure of the hyperbranched polymer.

Table 1 Solubility of hyperbranched polymers **P1**, **P2**, **P3** and **P4** and dendrimer **DenG3-OH**

	NMP	DMAc	CHCl ₃	pyridine	THF	toluene	CH ₃ OH	NaOH aqueous
P1	++	++	--	++	++	--	--	+
DenG3-OH	++	++	--	++	++	--	++	++
P2	++	++	++	++	++	++	--	--
P3	+	+	++	++	++	++	--	--
P4	++	++	++	++	++	++	--	--

Abbreviations: DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidinone; THF, tetrahydrofuran.

Solubility: ++, soluble at room temperature; +, soluble on heating, --, insoluble.

polymers. As shown in Figure 8, a variety of different functional groups were introduced into **P1**. Hyperbranched polymers **P2**, **P3** and **P4**, with methoxy groups, *n*-hexyloxy groups and benzoyloxy groups, could be prepared by the addition of methyl sulfate, 1-bromohexane and benzoyl chloride, respectively, to the reaction mixture at the end of the polymerization of **1**. ¹H-NMR analysis confirmed that the hydroxyl groups were quantitatively converted.

Properties of hyperbranched polymers are affected by the functionality of the terminal groups. The T_g values determined by differential scanning calorimetry of these hyperbranched polymers were dependent on the chain ends, and decreased as chain end polarity became lower. The T_g of **P1**, which had hydroxyl groups, was 190 °C, whereas the T_g values of **P2**, **P3** and **P4**, which had less polar terminal groups such as methoxy groups, *n*-hexyloxy groups and benzoyloxy groups, were 160, 100 and 165 °C, respectively (Figure 9). The T_g value of **P2**, as well as **P1**, was higher than that (101 °C)³⁸ of the corresponding dendrimer **DenG3-OMe**.

Figure 8 Chemical modification of hyperbranched polymer.

Figure 9 Differential scanning calorimetry curves of hyperbranched polymer P1, P2, P3 and P4.

The chain end groups had influence on the solubility of the hyperbranched polymers (Table 1). P1 was insoluble in non-polar solvents such as chloroform and toluene, whereas P2, P3 and P4 were soluble. P2 and P4, as well as P1, were soluble in polar solvents, NMP and DMAc, whereas P3 was soluble in NMP and DMAc upon heating above $100^\circ C$, and precipitated upon cooling.

Thermal stabilities of hyperbranched polymers

The thermal stabilities of P1 and P2 were compared with the corresponding dendrimers, DenG3-OH and DenG3-OMe by TG, respectively (Figure 10). P1 initiated to lost weight at $315^\circ C$, and completed thermal decomposition at $578^\circ C$. P2 initiated to lost weight at $355^\circ C$, and completed thermal decomposition at $628^\circ C$. Though the hyperbranched polymer P1 and P2 initiated thermal decomposition at lower temperature than the corresponding dendrimers, the thermal decomposition proceeded more slowly.

CONCLUSION

Hyperbranched poly(ether ether ketone)s with hydroxyl terminal groups were prepared by a one-step synthesis of an AB₂-type monomer 3,5-dihydroxy-4'-(4-fluorobenzoyl)diphenylether through

Figure 10 Comparison of TG curves between hyperbranched polymers and dendrimers. (a) P1 and DenG3-OH and (b) P2 and DenG3-OMe.

an aromatic nucleophilic substitution reaction. The degree of branching determined by 1H -NMR analysis was about 52%. The glass transition temperatures of the hyperbranched polymers were higher than those of the dendrimers and the possibility of entanglement among the hyperbranched polymer molecules was suggested. The optimized structure of the hyperbranched polymers, which was proposed on the basis of the 1H -NMR chemical shifts of the dendritic units, supported this hypothesis. The hydroxyl groups at the chain ends were converted into a variety of functional groups. The nature of the chain end was shown to affect the glass transition temperatures and solubilities of the hyperbranched polymers.

- Hawker, C. J., Lee, R. & Frechet, J. M. J. One-pot synthesis of hyperbranched polyester. *J. Am. Chem. Soc.* **113**, 4583–4588 (1991).
- Turner, S. R., Viot, B. I. & Mourey, T. H. All-aromatic hyperbranched polyesters with phenol and acetate end groups: Synthesis and characterization. *Macromolecules* **26**, 4617–4623 (1993).
- Malmstrom, E., Johansson, M. & Hult, A. Hyperbranched aliphatic polyester. *Macromolecules* **28**, 1698–1703 (1995).
- Ishida, Y., Jikei, M. & Kakimoto, M. Synthesis of hyperbranched aromatic polyester by carbon monoxide insertion reaction using palladium catalyst. *Poly. Adv. Technol* **11**, 684–704 (2000).
- Yang, G., Jikei, M. & Kakimoto, M. Successful terminal self-condensation of AB₂ monomer to form hyperbranched aromatic polyamide. *Macromolecules* **31**, 5964–5966 (1998).
- Yang, G., Jikei, M. & Kakimoto, M. Synthesis and properties of hyperbranched aromatic polyamide. *Macromolecules* **32**, 2215–2220 (1999).
- Ishida, Y., Sun, A. C. F., Jikei, M. & Kakimoto, M. Synthesis of hyperbranched aromatic polyamides starting from dendrons as AB_x monomers: effect of monomer multiplicity on the degree of branching. *Macromolecules* **33**, 2832–2838 (2000).

- 8 Miller, T. M., Neenan, T. X., Kwok, E. W. & Stein, S. M. Dendritic analogs of engineering plastics: A general one-step synthesis of dendritic polyaryl ethers. *J. Am. Chem. Soc.* **115**, 356–357 (1993).
- 9 Hawker, C. J. & Chu, F. Hyperbranched poly(ether ketone)s: manipulation of structure and physical properties. *Macromolecules* **29**, 4370–4380 (1996).
- 10 Morikawa, A. Preparation and properties of hyperbranched poly(ether ketone)s with a various number of phenylene units. *Macromolecules* **31**, 5999–6009 (1998).
- 11 Shu, C. F. & Leu, C. M. Hyperbranched poly(ether ketone) with carboxylic acid terminal groups: synthesis, characterization, and derivation. *Macromolecules* **32**, 100–105 (1999).
- 12 Kim, Y. H. & Webster, O. W. Hyperbranched polyphenylenes. *Macromolecules* **25**, 5561–5572 (1992).
- 13 Spindler, R. & Frechet, J. M. J. Synthesis and characterization of hyperbranched polyurethanes from blocked isocyanate monomers by step-growth polymerization. *Macromolecules* **26**, 4809–4813 (1993).
- 14 Yamanaka, K., Jikei, M. & Kakimoto, M. Preparation and properties of hyperbranched aromatic polyimides via polyamic acid methyl ester precursor. *Macromolecules* **33**, 6937–6944 (2000).
- 15 Yamanaka, K., Jikei, M. & Kakimoto, M. Synthesis of hyperbranched aromatic polyimides via polyamic acid methyl ester precursor. *Macromolecules* **33**, 1111–1114 (2000).
- 16 Yamanaka, K., Jikei, M. & Kakimoto, M. Preparation of hyperbranched aromatic polyimides without linear units by end capping reaction. *Macromolecules* **34**, 3910–3915 (2001).
- 17 Bolton, D. H. & Wooley, K. L. Synthesis and characterization of hyperbranched polycarbonates. *Macromolecules* **30**, 1890–1896 (1997).
- 18 Kim, K., Jikei, M. & Kakimoto, M. Preparation and properties of novel hyperbranched poly(dimethylsiloxane). *Polym. J.* **34**, 275–279 (2002).
- 19 Kim, K., Jikei, M. & Kakimoto, M. Synthesis and properties of amphiphilic hyperbranched poly(dimethylsiloxane) possessing hydrophilic and terminal group. *Polym. J.* **34**, 755–760 (2002).
- 20 Hong, C., Jikei, M. & Kakimoto, M. Synthesis and characterization of hyperbranched polybenzoxazoles. *J. Photopolym. Sci. Technol.* **15**, 219–222 (2002).
- 21 Hong, C. S., Jikei, M., Kikuchi, R. & Kakimoto, M. Chemically amplified photosensitive polybenzoxazoles based on tert-butoxycarbonyl protected hyperbranched poly(o-hydroxyamide)s. *Macromolecules* **36**, 3174–3179 (2003).
- 22 Jikei, M., Mori, R., Kawauchi, S. & Kakimoto, M. Synthesis and properties of hyperbranched poly(triphenylamine)s prepared by palladium catalyzed C–N coupling reaction. *Polym. J.* **34**, 550–557 (2002).
- 23 Takeuchi, M., Jikei, M. & Kakimoto, M. Preparation of hyperbranched aromatic poly(ether sulfone)s possessing sulfonic acid terminal groups for polymer electrolyte. *Chem. Lett.* **32**, 242–243 (2003).
- 24 Jikei, M., Chon, S.-H., Kakimoto, M., Kawauchi, S., Imase, T. & Watanabe, J. Synthesis of hyperbranched aromatic polyamides from aromatic diamines and trimellitic acid. *Macromolecules* **32**, 2061–2064 (1999).
- 25 Hao, J., Jikei, M. & Kakimoto, M. Synthesis and comparison of hyperbranched aromatic polyimides having the same repeating unit by AB₂ self-polycondensation and A₂ + B₃ polycondensation. *Macromolecules* **36**, 3519–3528 (2003).
- 26 Sinanwanich, W., Higashihara, T. & Ueda, M. Synthesis of a hyperbranched polymer with perfect branching based on piperidine-4-one. *Macromolecules* **42**, 994–1001 (2009).
- 27 Sagawa, Y., Higashihara, T. & Ueda, M. Hyperbranched polymers with controlled degree of branching 0 to 100%. *J. Am. Chem. Soc.* **132**, 11000–11001 (2010).
- 28 Tian, W., Fan, X., Kong, J., Liu, Y. & Hung, Y. Novel supramolecular system of amphiphilic hyperbranched polymer with β -cyclodextrine and hyperbranched topography cavities: Synthesis and selective encapsulation. *Polymer (Guildf)* **51**, 2556–2564 (2010).
- 29 Kaneko, R., Jikei, M. & Kakimoto, M. Preparation and properties of composite materials composed aromatic polyamides and vinyl polymers. *High Perform. Polym.* **14**, 41–51 (2002).
- 30 Kaneko, R., Suzuki, E., Jikei, M. & Kakimoto, M. Preparation and properties of hyperbranched aromatic polyamide-silica composites by sol-gel method. *High Perform. Polym.* **14**, 105–114 (2002).
- 31 Gao, H., Yorifuji, D., Wakita, J., Jiang, Z. H. & Ando, S. In situ preparation of nano ZnO/hyperbranched polyimide hybrid film and their optical properties. *Polymer (Guildf)* **51**, 3173–3180 (2010).
- 32 Kakimoto, M., Grunzinger, S. J. & Hayakawa, T. Hyperbranched poly(ether sulfone)s: preparation and application to ion-exchange membranes. *Polym. J.* **42**, 697–705 (2010).
- 33 Kaneko, R., Jikei, M. & Kakimoto, M. Preparation and properties of photosensitive polymers based on hyperbranched aromatic polyamides. *High Perform. Polym.* **14**, 53–62 (2002).
- 34 Xie, J., Deng, X., Cao, Z., Shen, Q., Zhang, W. & Shi, W. Synthesis and second-order nonlinear optical properties of hyperbranched polymers containing pendant azobenzene chromophores. *Polymer (Guildf)* **48**, 5988–5993 (2007).
- 35 Wen, G. A., Xin, Y., Zhu, X. R., Zeng, W. J., Zhu, R., Feng, J. C., Cao, Y., Zhao, L., Wang, L. H., Wei, W., Peng, B. & Hung, W. Hyperbranched triazine-containing polyfluorene: Efficient blue emitters for polymer light-emitting diodes (PLEDs). *Polymer (Guildf)* **48**, 1824–1829 (2007).
- 36 Taniguchi, Y., Shirai, K., Saitoh, H., Yamaguchi, T. & Tubokawa, N. Postgrafting of vinyl polymers onto hyperbranched poly(amino-amido)-grafted nano-sized silica surface. *Polymer (Guildf)* **46**, 2541–2547 (2005).
- 37 Oh, J. H., Jang, J. & Lee, S. H. Curing behavior of tetrafunctional epoxy resin/hyperbranched polymer system. *Polymer (Guildf)* **42**, 8339–8347 (2001).
- 38 Morikawa, A. & Ono, K. Preparation of poly(ether ether ketone) dendrimers by the divergent Method. *Polym. J.* **32**, 234–242 (2000).
- 39 Morikawa, A. & Ono, K. Preparation of poly(ether)-(ether ether ketone)dendrimers by the convergent method. *Polym. J.* **32**, 255–262 (2000).
- 40 Ishizu, K., Shibuya, T. & Mori, A. Synthesis and characterization of hyperbranched poly(ethyl methacrylate) by quasi-living radical polymerization of photofunctional inimer. *Polym. Int.* **51**, 424–428 (2002).
- 41 Jikei, M., Uchida, D., Haruta, Y., Takahashi, Y. & Matsumoto, K. Synthesis and properties of hyperbranched poly(ether sulfone)s prepared by self-polycondensation of novel AB₂ monomer. *J. Polym. Sci. Part A, Polym. Chem.* **50**, 3830–3839 (2012).
- 42 Hawker, C. J. & Frechet, J. M. Monodispersed dendritic polyesters with removable chain ends; a versatile approach to globular macromolecules with chemically reversible polarities. *J. Chem. Soc. Perkin. Trans. 1*, 2459–2469 (1992).
- 43 Morikawa, A., Kakimoto, M. & Imai, Y. Convergent synthesis of starburst poly(ether ketone) dendrons. *Macromolecules* **26**, 6324–6329 (1993).
- 44 Ishida, Y., Jikei, M. & Kakimoto, M. Rapid synthesis of aromatic polyamide dendrimers by orthogonal and a double-stage convergent approach. *Macromolecules* **33**, 3202–3211 (2000).