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Synthesis and Properties of Hyperbranched Poly(ether sulfone)s Prepared by Self-Polycondensation of Novel AB_2 Monomer

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ABSTRACT: Hyperbranched poly(ether sulfone)s were prepared by the self-polycondensation of the novel AB_2 monomer, 4-(3,5-hydroxyphenoxy)-4′-fluorodiphenylsulfone. The high-molecular-weight polymers were isolated in good yields. The degree of branching (DB) of the resulting polymers was investigated by the preparation of dendritic and linear model compounds. The DB determined by gated decoupling ^{13}C NMR measurements was in the range 0.17–0.41 and was dependent on the base used for the self-polycondensation. It was found that cesium fluoride was an effective base to form the polymer having the DB of 0.41. The resulting hyperbranched poly(ether sulfone)s showed good solubility in organic solvents. The solubility and the glass transition temperature of the polymers were influenced by the terminal functional groups. The unique thermal crosslinking phenomenon was observed during the DSC measurements of the hydroxyl-terminated hyperbranched poly(ether sulfone) under air condition. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: crosslinking; degree of branching; hyperbranched; poly(ether sulfones); polycondensation; thermal crosslinking

INTRODUCTION Hyperbranched polymers are unique branched macromolecules, which have consecutive branching points in their repeating units and many terminal functional groups.[1–4] As analog to dendrimers, hyperbranched polymers have a three-dimensional architecture in contrast to linear polymers. Many functional groups present in the hyperbranched polymers could allow fine-tuning of the material properties, such as solubility and thermal properties. The viscosity of hyperbranched polymers is generally low even if the molecular weight is high enough due to the lack of chain entanglements. One of the potential advantages of the hyperbranched polymers lies in its production process. Hyperbranched polymers can be prepared by the one-step polymerization of the designed monomers. Therefore, mass production of hyperbranched polymers can be easily achieved in contrast to dendrimers. It should be mentioned that hyperbranched polymers contain an irregular structure as the linear units, which is different from the perfect-branched dendrimers.

There are several articles describing the preparation of hyperbranched engineering plastics. Miller and Neenan first reported the preparation of hyperbranched poly(aryl ether)s by a nucleophilic aromatic substitution.[5] Hyperbranched poly(ether ketone)s,[6–8] polyamides,[9–15] polyimides,[16–21] poly(phenylene oxide)s,[22,23] poly(phenylene sulfide)s,[24,25] and poly(ether sulfone)s[26–28] have already been reported in the literature. It is reported that the introduction of branching points to the rigid aromatic polymers results in an improved solubility, low viscosity, and low crystallinity. As the chain entanglements are reduced, the mechanical properties of the hyperbranched polymers become lower than the corresponding linear polymers. Therefore, the application of the hyperbranched engineering plastics as bulk materials seems to be limited. On the other hand, it has been observed for the copolymers of hyperbranched aromatic polyamides[29] and polyimides[30] that the small number of the branching components dramatically changes the properties. The fact suggests that the hyperbranched polymers have the potential as additives, such as a viscosity modifier, crystallization inhibitor, solubility controller, and compatibilizer.

There are only a few papers describing the study of hyperbranched poly(ether sulfone)s. Hay and coworker reported the hyperbranched poly(ether sulfone)s prepared from AB_2 and A_2B monomers.[26] Fossum and coworker reported the hyperbranched poly(ether sulfone) from the self-polycondensation of 3,5-difluuoro-4′-hydroxydiphenyl sulfone as an AB_2 monomer.[27] In this study, we report the synthesis and properties of hyperbranched poly(ether sulfone)s through the nucleophilic aromatic substitution of the novel AB_2 monomer. The simple AB_2 monomer was prepared from bis(*p*-fluorophenyl) sulfone and 3,5-dimethoxyphenol as the starting materials. The hyperbranched poly(ether sulfone)s were prepared by the self-polycondensation of the AB_2 monomer. It was found that the reaction condition affected the degree of branching (DB) of the resulting polymer. A unique thermal crosslinking was also observed during the DSC measurements.

EXPERIMENTAL

Materials

Bis(*p*-fluorophenyl) sulfone and phloroglucinol were purchased from Wako Pure Chemical Industry and used without further purification. 3,5-Dimethoxyphenol was purchased from Tokyo Chemical Industry and used without further purification. Cesium fluoride was purchased from Sigma-Aldrich, and dried under vacuum at 150 °C for 2 h before use. *N*,*N*-Dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP; Sigma-Aldrich) were purified by distillation before use. Boron tribromide was purchased from Nacalai Tesque, and used without further purification. 5-Benzyloxyresorcinol was prepared by a procedure reported in literature.[31] All other reagents and solvents were purchased from Kanto Chemical, and used without further purification.

Preparation of 4-(3,5-Dimethoxyphenoxy)-4′-fluorodiphenylsulfone (AB_2' Monomer)

In a three-necked flask equipped with a Dean-Stark trap, a condenser, and a nitrogen inlet, difluorodiphenylsulfone (6.55 g, 25.6 mmol), 3,5-dimethoxyphenol (3.97 g, 25.6 mmol), potassium carbonate (4.58 g, 33.1 mmol), toluene (20 mL), and NMP (100 mL) were charged under nitrogen. The flask was heated at 160 °C for 90 min under nitrogen flow. The azeotrope of toluene and water was removed from the Dean-Stark trap. The flask was subsequently heated at 160 °C for an additional 4 h under nitrogen. After cooling to room temperature, the NMP was removed by reduced distillation (ca. 1 mmHg). A small amount of chloroform was added to the flask and the insoluble inorganic salts were removed by filtration. The filtrate was evaporated to remove the chloroform and the crude product was dried under vacuum at room temperature. The dried crude product was purified by flash column chromatography in chloroform/hexane (2/1, v/v). After removing the solvents, the white powder was isolated in 49% yield.

^{1}H NMR (DMSO, ppm): 8.1 (2H, m, aromatic), 7.9 (2H, d, aromatic), 7.5 (2H, t, aromatic), 7.1 (2H, d, aromatic), 6.4 (1H, t, aromatic), 6.3 (2H, d, aromatic), 3.7 (6H, s, methyl). ^{13}C NMR (DMSO, ppm): 168.6, 163.8, 162.2, 156.1, 138.5, 135.0, 131.0, 130.8, 118.5, 117.8, 100.0, 97.9, 57.2.

Preparation of 4-(3,5-Hydroxyphenoxy)-4′-fluorodiphenylsulfone (AB_2 Monomer)

In a three-necked flask equipped with a nitrogen inlet and a dropping funnel, the AB_2' monomer (10.00 g, 25.8 mmol) was dissolved in dichloromethane (140 mL) under nitrogen. After cooling the flask in an ice-bath, boron tribromide (14.7 mL, 0.156 mol) was dropwise added to the flask through the dropping funnel. After stirring at 0 °C for 20 h, the solution was slowly poured into ice water (700 mL). The mixture was stirred and warmed to remove the dichloromethane. The precipitate was recovered by filtration, washed with water, and dried under vacuum at 100 °C for 5 h. The isolated yield was 89%.

^{1}H NMR (DMSO, ppm): 9.6 (2H, br, OH), 8.0 (2H, m, aromatic), 7.9 (2H, d, aromatic), 7.5 (2H, t, aromatic), 7.1 (2H, d, aromatic), 6.1 (1H, t, aromatic), 5.9 (2H, d, aromatic). ^{13}C NMR (DMSO, ppm): 167.2, 163.9, 162.0, 160.1, 156.9, 138.5, 135.3, 131.1, 130.9, 118.9, 117.9, 100.2, 98.9. Anal. Cald for $C_{20}H_{17}F_7O_5S$: C, 59.99; H, 3.64. Found: C, 59.44; H, 3.74. mp = 161.5–162.5 °C.

Self-Polycondensation of the AB_2 Monomer Using Potassium Carbonate

In a three-necked flask equipped with a nitrogen inlet, a Dean-Stark trap, and a condenser, the AB_2 monomer (0.48 g, 1.33 mmol), potassium carbonate (0.46 g, 3.3 mmol), DMAc (5 mL), and toluene (5 mL) were charged under nitrogen. The mixture was stirred at 160 °C for 90 min under flowing nitrogen. The azeotrope of toluene and water was removed from the Dean-Stark trap. The flask was subsequently heated at 160 °C for an additional 10 h under nitrogen. After cooling, the mixture was poured into an aqueous HCl solution (0.1 mol/L). The precipitate was recovered by filtration and dried under vacuum at 100 °C for 5 h. The polymer was isolated as a brown powder in 91% yield.

^{1}H NMR (DMSO, ppm): 10.6, 10.3, 10.1, 8.0–7.7, 7.3–7.0, 7.0–6.8, 6.6, 6.4–6.2, 6.1, 5.9, 5.8, 5.7. ^{13}C NMR (DMSO, ppm): 162.5, 162.0, 161.3, 160.9, 157.6, 157.4, 156.5, 156.0, 137.0, 136.5, 136.0, 135.9, 131.7, 130.5, 119.0, 117.5, 116.8, 110.9, 109.6, 106.5, 104.4, 103.4, 101.0, 100.2, 98.9, 97.7.

Self-Polycondensation of the AB_2 Monomer Using Cesium Fluoride

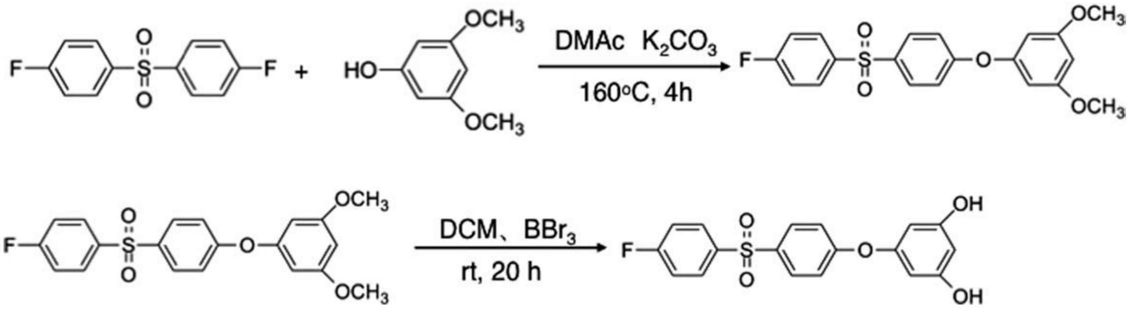
In a three-necked flask equipped with a nitrogen inlet and a condenser, the AB_2 monomer (0.48 g, 1.33 mmol), cesium fluoride (0.47 g, 3.1 mmol), and DMAc (5 mL) were charged under nitrogen. The mixture was stirred at 160 °C for 10 h under nitrogen. After cooling, the mixture was poured into an aqueous HCl solution (0.1 mol/L). The precipitate was recovered by filtration and dried under vacuum at 100 °C for 5 h. The polymer was isolated as a brown powder in 94% yield.

Self-Polycondensation of the AB_2 Monomer Under Diluted Conditions

The polymerization was carried out using the same procedure as described above. The AB_2 monomer (0.188 g, 0.5 mmol) was dissolved in DMAc (5 mL) to achieve an approximately five times diluted solution.

Preparation of the Dendritic Model Compound

In a three-necked flask equipped with a nitrogen inlet, phloroglucinol (63.1 mg, 0.50 mmol), the AB_2' monomer (0.583 g, 1.5 mmol), cesium fluoride (0.273 g, 1.8 mmol), and DMAc (5 mL) were charged under nitrogen. The mixture was stirred at 160 °C for 10 h. After cooling to room temperature, the mixture was poured into an aqueous HCl solution (0.1 mol/L). The precipitate was recovered by filtration and dried under vacuum at 100 °C. The crude product was purified by flash column chromatography in



SCHEME 1 Preparation of the AB_2 monomer.

chloroform/hexane (13/1, v/v). After removing the solvents, a yellow powdery product was isolated in 97% yield.

^1H NMR (DMSO, ppm): 7.9 (m, aromatic), 7.2 (d, aromatic), 7.1 (d, aromatic), 6.9 (s, aromatic), 6.4 (m, aromatic), 6.4 (m, aromatic), 6.3 (m, aromatic), 3.7 (s, methyl). ^{13}C NMR (DMSO, ppm): 162.1, 162.0, 161.0, 157.9, 156.6, 136.4, 135.8, 130.4, 119.2, 118.4, 109.6, 103.5, 99.6, 98.0, 56.1.

Preparation of the Linear Model Compound

In a three-necked flask equipped with a nitrogen inlet, 5-benzyloxyresorcinol (0.123 g, 0.50 mmol), the AB_2' monomer (0.388 g, 1.0 mmol), cesium fluoride (0.182 g, 1.2 mmol), and DMAc (5 mL) were charged under nitrogen. The mixture was stirred at 160 °C for 10 h. After cooling to room temperature, the mixture was poured into an aqueous HCl solution (0.1 mol/L). The precipitate was recovered by filtration and dried under vacuum at 100 °C. The crude product was purified by flash column chromatography in chloroform/hexane (13/1, v/v). After removing the solvents, a yellow powdery product was isolated in 17% yield.

^1H NMR (DMSO, ppm): 10.1 (s, OH), 7.9 (d, aromatic), 7.2 (m, aromatic), 6.4_0 (s, aromatic), 6.3_8 (d, aromatic), 6.3_1 (d, aromatic), 6.3_0 (d, aromatic), 3.7 (s, methyl). ^{13}C NMR (DMSO, ppm): 162.1, 162.0, 161.5, 160.9, 157.8, 157.4, 136.2, 135.8, 130.4, 119.2, 118.4, 104.4, 103.4, 99.6, 98.0, 56.1.

Preparation of the Nitrobenzene-Terminated Polymer

In a two-necked flask equipped with a nitrogen inlet, the resulting polymer (56 mg), potassium carbonate (50 mg, 0.4 mmol), and DMAc (2 mL) were charged under nitrogen. *p*-Fluoronitorobenzene (0.02 mL, 0.2 mmol) was added dropwise to the flask, and the mixture was stirred at 120 °C for 24 h. After cooling, any unreacted *p*-fluoronitrobenzene was removed by precipitation in methanol. The formed precipitate was recovered by filtration and dried under vacuum at 100 °C for 10 h. A brown powder (46 mg, 61%) was isolated.

^1H NMR (DMSO, ppm): 8.2 (br, aromatic), 7.9 (br, aromatic), 7.3 (br, aromatic), 6.8 (br, aromatic). ^{13}C NMR (DMSO, ppm): 162.0, 161.5, 160.0, 158.0, 156.9, 143.0, 136.1, 130.8, 126.2, 119.0, 109.1.

Measurements

The ^1H and ^{13}C NMR spectra were recorded using a JEOL JNM-ECX 500 NMR spectrometer. The inherent viscosity was measured in NMP at 30 °C at a concentration of 0.5 g/dL. The gel permeation chromatography (GPC) measurements with NMP containing lithium bromide (0.01 mol/L) as the eluent were carried out using a Wyatt DAWN HELEOSII 8+, a Wyatt Optilab rEX differential refractometer, and three polystyrene-divinylbenzene columns (three Shodex LF-804 columns). The specific refractive index increment (d*n*/d*c*) at 658 nm was measured using a Wyatt Optilab rEX differential refractometer. The d*n*/d*c* of the hyperbranched poly(ether sulfone) in NMP containing lithium bromide (0.01 mol/L) was determined to be 0.1499. The DSC measurements were carried out by a Rigaku Thermo plus DSC 8230. The heating rate was set at 10 °C/min. The TG/DTA measurements were carried out by a Rigaku Thermo plus TG 8230 at a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

The AB_2 monomer, 4-(3,5-hydroxyphenoxy)-4′-fluorodiphenylsulfone, was prepared from difluorodiphenylsulfone and 3,5-dimethoxyphenol as the starting materials. As shown in Scheme 1, difluorodiphenylsulfone was reacted with 3,5-dimethoxyphenol via nucleophilic aromatic substitution to form 4-(3,5-methoxyphenoxy)-4′-fluorodiphenylsulfone. The crude product contained monosubstituted and disubstituted compounds and unreacted difluorodiphenylsulfone. The monosubstituted compound, 4-(3,5-methoxyphenoxy)-4′-fluorodiphenylsulfone, was isolated by flash column chromatography. As the methoxy groups can be converted to hydroxyl groups, 4-(3,5-methoxyphenoxy)-4′-fluorodiphenylsulfone is recognized as an AB_2' monomer. The reaction of the AB_2' monomer and boron tribromide efficiently proceeded to form 4-(3,5-hydroxyphenoxy)-4′-fluorodiphenylsulfone (AB_2 monomer). The structure of the AB_2 monomer was confirmed by NMR and elemental analysis. Figure 1 shows the ^1H NMR spectra of the AB_2' and AB_2 monomers. The peak at 3.7 ppm, attributed to the methoxy group of the AB_2' monomer, disappeared from the spectrum of the AB_2 monomer. Moreover, a broad peak at 9.6 ppm in the AB_2 monomer spectrum was attributed to the hydroxyl groups. The peaks at 6.4 and 6.3 ppm in the spectrum of the AB_2' monomer were clearly shifted to a higher magnetic field in the

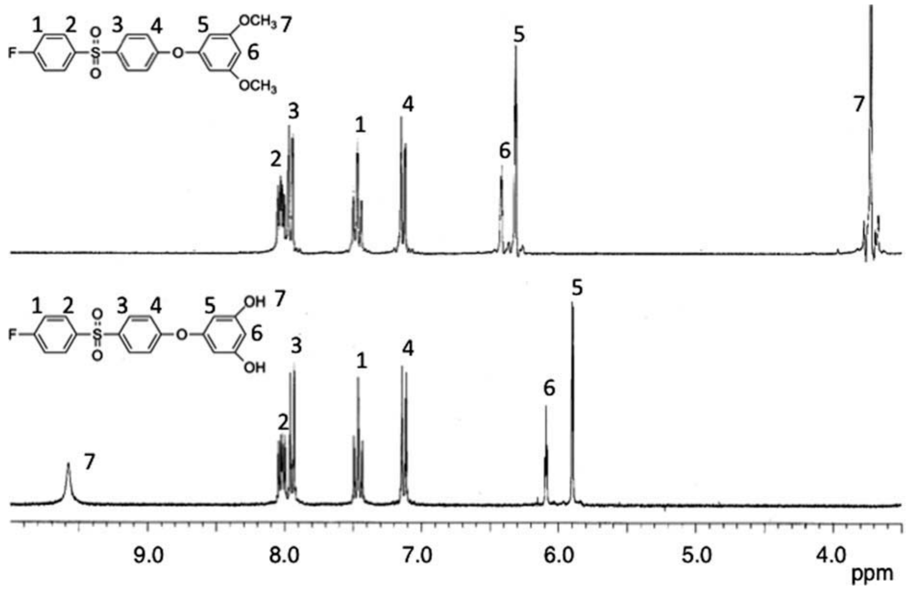


FIGURE 1 ^{1}H NMR spectra of the AB$_2'$ and AB$_2$ monomers (DMSO-d_6).

spectrum of the AB$_2$ monomer. All the other peaks were reasonably assigned to the proposed structure and the integration ratio of the peaks supported the assignment. Figure 2 shows the ^{13}C NMR spectra of the AB$_2'$ and AB$_2$ monomers. The peak at 57 ppm, attributed to methoxy carbon of the AB$_2'$ monomer, disappeared in the spectrum of the AB$_2$ monomer. All the other peaks were assigned to the proposed structures. It should be noted that the peaks attributed to the aromatic ring connected to the fluoro group were split due to the ^{19}F nuclear resonance effect.

The self-polycondensation of the AB$_2$ monomer was carried out in the presence of a base at 160 °C in DMAc (Scheme 2). When potassium carbonate was used as a base, water generated by the formation of potassium phenolate was removed by azeotropic distillation with toluene. The results of the self-polycondensation are summarized in Table 1. The hyperbranched poly(ether sulfone)s were isolated in good yield in all experiments. The absolute molecular weights determined by GPC with a laser light scattering detector indicated the formation of high-molecular-weight polymers. The GPC

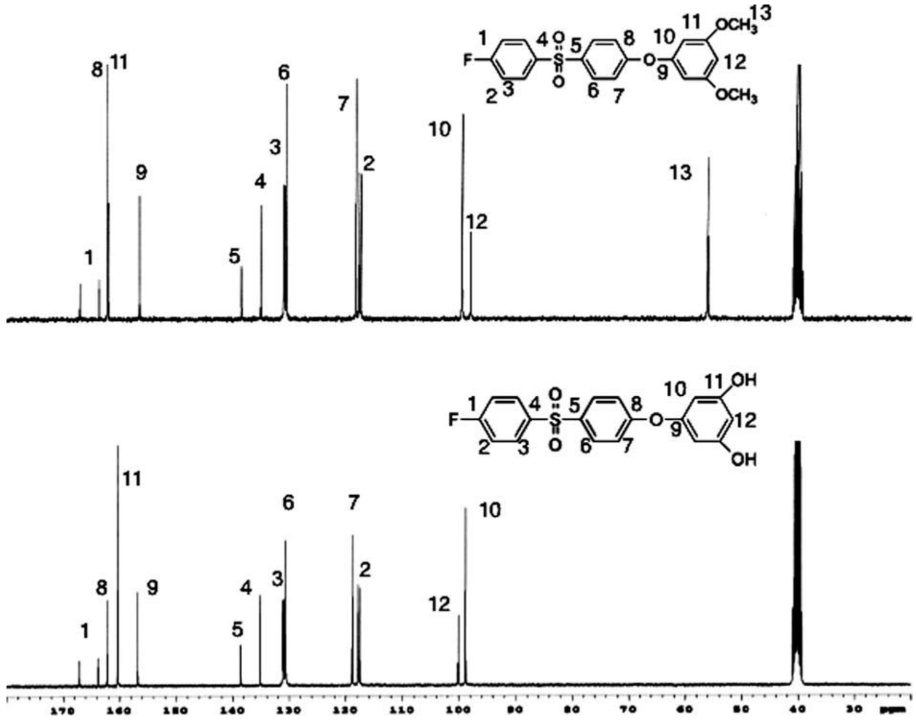
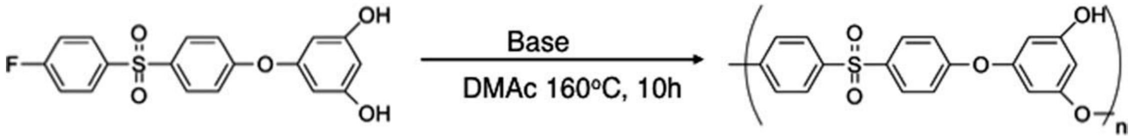


FIGURE 2 ^{13}C NMR spectra of the AB$_2'$ and AB$_2$ monomers (DMSO-d_6).



SCHEME 2 Self-polycondensation of the AB_2 monomer.

curves of the samples prepared at 160 °C are shown in Figure 3. It is clear that the polymer prepared in the presence of potassium carbonate showed a large shoulder peak in the high-molecular-weight region. The shoulder peak was not observed for the polymers prepared in the presence of cesium fluoride. The shoulder peak might be caused by the undesired side reactions. The fluoride anions generated during the self-polycondensation might cause the side reactions.[32] As a result, the molecular weight distribution (M_w/M_n) of the polymer prepared in the presence of potassium carbonate was much higher than the polymer prepared with cesium fluoride. The high-molecular-weight polymer was also isolated by the polymerization at 120 °C for 40 h. The inherent viscosity of the polymer prepared with potassium carbonate was clearly higher than the polymer prepared with cesium fluoride.

DB is one of the key factors to define the molecular structure of hyperbranched polymers. To determine the DB, the dendritic and the linear model compounds were prepared as shown in Scheme 3. The dendritic model contains the trisubstituted phloroglucinol unit and no hydroxyl groups. The linear model contains the disubstituted phloroglucinol unit and one hydroxyl group. Figure 4 shows the ^{1}H NMR spectra of the resulting polymer, the dendritic model and the linear model. In the spectrum of the dendritic model, the peak at 6.9 ppm is attributed to the aromatic proton of the tri-substituted phloroglucinol unit (peak D_H). The peaks at 6.4 and 6.3 ppm in the spectrum of the linear model were attributed to the aromatic protons of the disubstituted phloroglucinol (peaks L_{1H} and L_{2H}). The peaks labeled ***a*** and ***b*** were attributed to the aromatic protons of the dimethoxy-substituted phloroglucinol unit. According to the ^{1}H NMR spectra, the resulting polymer apparently contained the dendritic and linear units. Unfortunately, these peaks were broad and some undefined peaks were also observed. Therefore, it is difficult to determine the DB from these ^{1}H NMR spectra. Figure 5 shows the gated decoupling ^{13}C NMR spectra of the resulting polymer and the model compounds. The dendritic model showed one peak at 109.7 ppm attributed to the tri-substituted phloroglucinol unit (peak D_C). The linear model showed two peaks at 104.4 and 103.4 ppm attributed to the disubstituted phloroglucinol unit (peaks L_{2C} and L_{1C}). The resulting polymer contained peaks attributed to the dendritic and linear units. The peaks that originated from the terminal unit were assigned by the peaks of the AB_2 monomer. The DBs of the resulting polymers were calculated on the basis of the integration ratio of these peaks and listed in Table 1. It is clear that the DB of the polymer prepared with cesium fluoride is higher than the polymer prepared with potassium carbonate. The difference in DBs could give influence on the solution viscosity. The polymer prepared with cesium fluoride had a lower inherent viscosity and larger DB. It is well known that hyperbranched polymers show low solution viscosity in comparison with linear polymers even the molecular weight is high enough.

Generally, the DB of hyperbranched polymers prepared by the self-polycondensation of the AB_2 monomers statistically approaches 0.5. Most DBs reported in the literature are in the range of 0.4–0.6. Therefore, the polymer prepared with potassium carbonate has a noticeably low DB. The low DB (0.15) was also reported in the case of the hyperbranched poly(ether ketone) prepared from 3,5-dihydroxy-4′-fluorobenzophenone.[6] When the conventional nucleophilic aromatic substitution was carried out, the hydroxyl groups are converted to the corresponding phenolate anions which act as strong nucleophiles. On the other hand, potassium phenolates formed *in situ* have a limited solubility in organic solvents. In this study, the AB_2 monomer contains the dihydroxyphenyl unit as a B_2 function. When both of the hydroxyl groups are converted to the corresponding phenolates, the solubility of the diphenolates might be very low. Therefore, the concentration of the diphenolates in the polymerization mixture could be much lower than the corresponding monophenolate. Consequently, the formation of the linear units

TABLE 1 Self-Polycondensation of the AB_2 Monomer to Form Hyperbranched Poly(ether sulfone)s

No	Base	Temperature (°C)	Yield (%)	M_w[a]	M_w/M_n	η_{inh} (dL/g)[b]	DB[c]
1	K_2CO_3	160	91	2.7×10^5	5.7	0.32	0.17
2	CsF	160	94	5.6×10^4	1.8	0.19	0.39
3	CsF	120	89	2.7×10^4	2.0	0.17	0.41

[a] Absolute molecular weight determined by GPC-MALLS in NMP.
[b] Measured in NMP at a concentration of 0.5 g/dL at 30 °C.
[c] Degree of branching determined by gated decoupling ^{13}C NMR measurements.

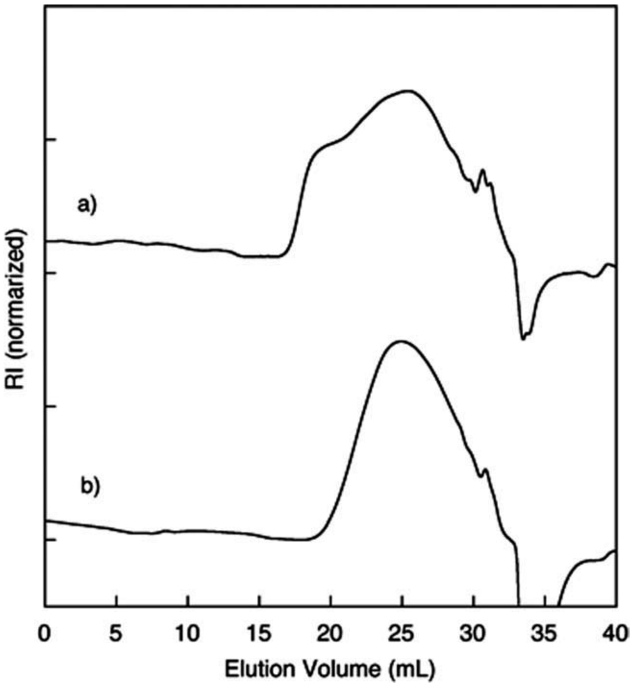
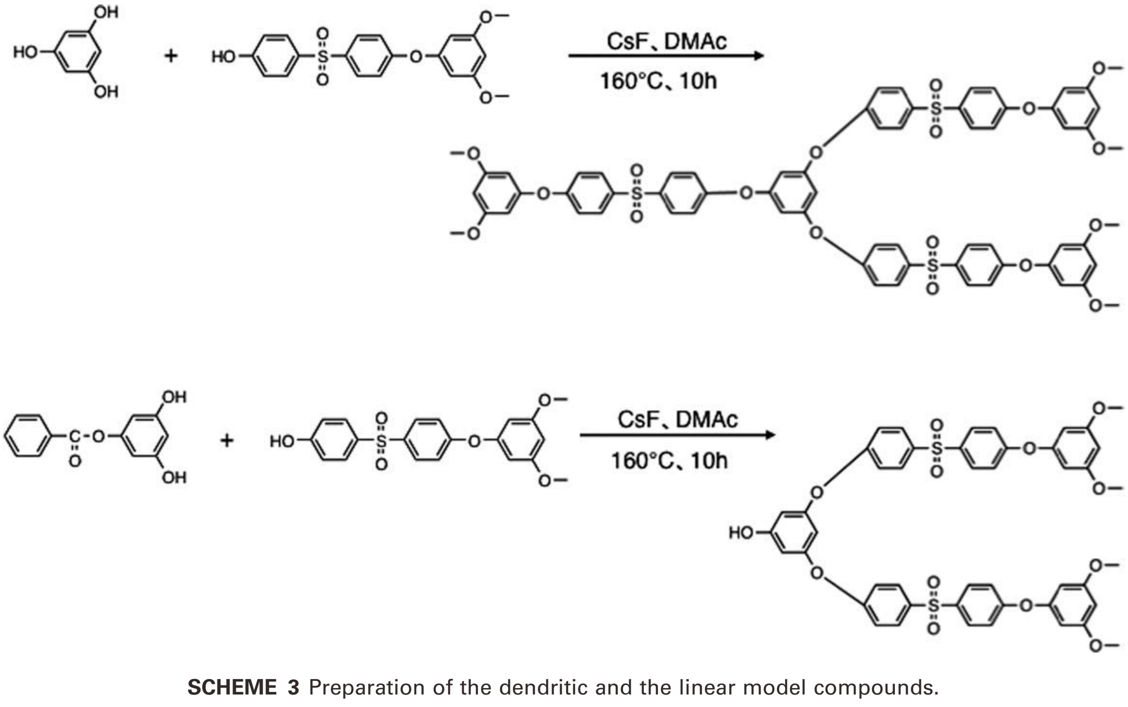


FIGURE 3 GPC curves of the resulting polymers prepared at 160 °C in the presence of potassium carbonate (a) and cesium fluoride (b).

might be preferred by the reaction of the monophenolate with the AB_2 monomer, especially in the early stage of the polymerization. On the other hand, it is reported that the nucleophilic aromatic substitution mediated by cesium fluoride proceeds through the formation of phenolate-ion-like intermediates.[33] In other words, completely dissociated phenolate anions could not be formed during the reaction. The phenolate-ion-like intermediates show a better solubility in organic solvents, which eventually results in the formation of the higher DB polymer. The solubility difference between the dissociated phenolate and the phenolate-ion-like intermediate was also observed for the preparation of the dendritic model compound. Only the cesium fluoride-mediated coupling of phloroglucinol with the AB_2' monomer produced a high yield of the dendritic model.

It should be mentioned that there are several unknown peaks in the ^1H and ^{13}C NMR spectra of the resulting polymers. Ether exchange reactions and intramolecular cyclizations are two possible reasons for the structural defects. The ^1H and ^{13}C NMR spectra of the polymer prepared at 120 °C were almost consistent with the ones of the polymer prepared at 160 °C. This fact suggests that the ether exchange reactions are not the main reason for the unknown peaks. The polymerization under diluted conditions was carried out in order to investigate the contribution of the intramolecular cyclization. ^1H NMR spectra of the polymers prepared at normal or diluted conditions are shown in Figure 6. Several unknown peaks in the range of 7.2–6.2 ppm, which are marked by the arrows in Figure 6(b), became stronger than those of the polymer prepared under normal concentrations. Therefore, these peaks could be attributed to the intramolecular cyclized products. Fossum and coworker have already pointed out that the cyclization reaction was accompanied by the propagation reaction for the self-polycondensation of 3,5-difluoro-4′-hydroxydiphenyl sulfone to form the hyperbranched poly(ether sulfone).[27] We assume that the unknown peaks mainly originated from the structural defects formed by the cyclization reactions.



SCHEME 3 Preparation of the dendritic and the linear model compounds.

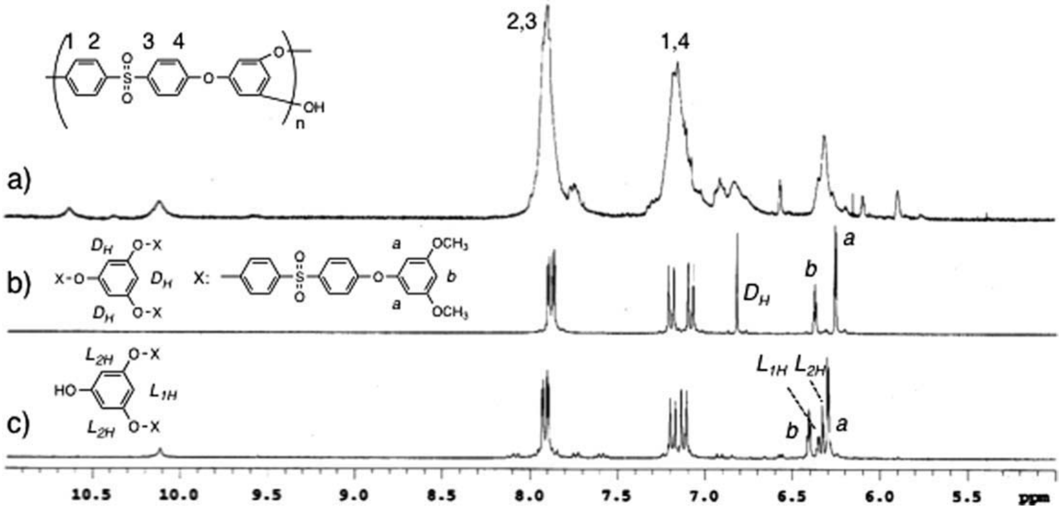


FIGURE 4 ^{1}H NMR spectra of the resulting polymer (a), the dendritic model (b), and the linear model (c) (DMSO-d_6).

The hyperbranched poly(ether sulfone) is soluble in organic solvents, such as DMF, DMAc, NMP, DMSO, tetrahydrofuran, and acetone and insoluble in chloroform. The 5% weight-loss temperature of the hyperbranched poly(ether sulfone) determined by TG/DTA measurements was 385 °C. The glass transition temperature (T_g) determined by the DSC measurements under nitrogen was 217 °C. It is well known that the solubility and glass transition temperature are influenced by the terminal function of the hyperbranched polymer. The hydroxyl groups in the hyperbranched poly(ether sulfone) were chemically modified to the nitrophenyl ether by the reaction with *p*-fluoronitrobenzene. The nitrobenzene-terminated polymer became soluble in chloroform but insoluble in acetone. The T_g of the nitrobenzene-terminated polymer was 183 °C which is noticeably lower than the original hydroxyl-terminated polymer. The hydroxyl groups may play an important role in the strong intra-and intermolecular interactions.

When the DSC measurements of the hydroxyl-terminated polymer prepared with cesium fluoride were carried out in air, the T_g gradually increased with the measurement times. Figure 7 shows the DSC curves of the hydroxyl-terminated polymer. When the DSC measurements were carried out under nitrogen, the reproducible T_g at 217 °C was observed. On the other hand, the T_g increased with the measurement times when the measurements were carried out in air. Figure 8 shows the plots of the T_g s of the hyperbranched

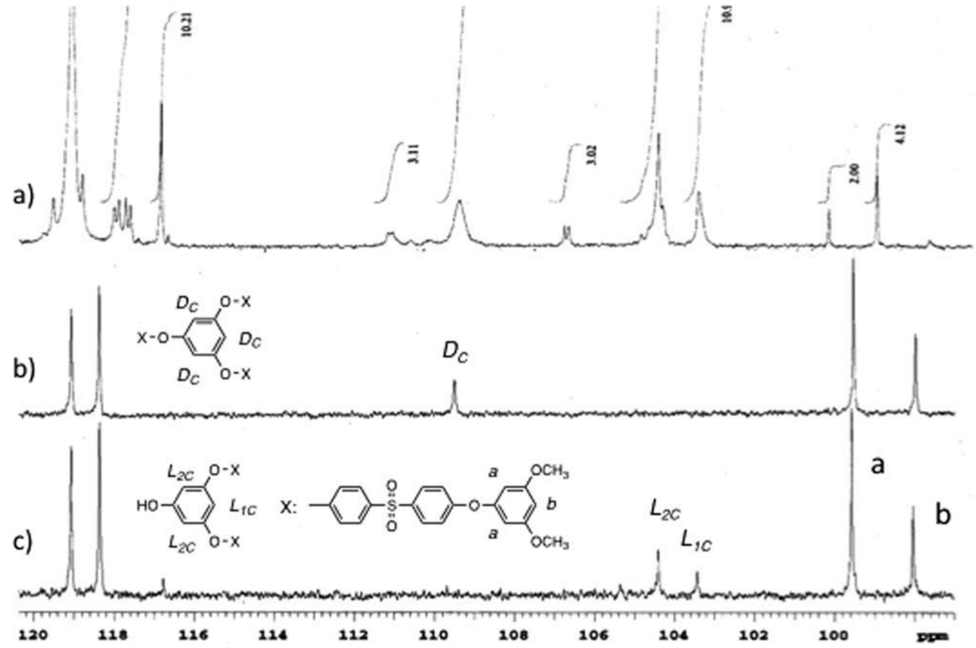


FIGURE 5 Gated decoupling ^{13}C NMR spectra of the resulting polymer (a), the dendritic model (b), and the linear model (c).

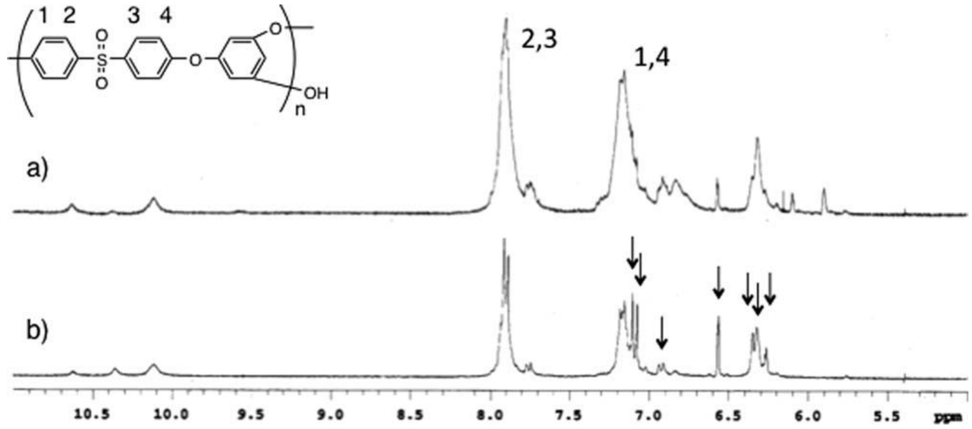


FIGURE 6 ^{1}H NMR spectra of the resulting polymers prepared under the normal (a) and the diluted (b) conditions (DMSO-d_6).

poly(ether sulfone) determined by the DSC measurements in air. When the heating-cooling scan in air from 50 to 300 °C was carried out five times, the T_g increased to 236 °C. The sample having the T_g at 236 °C became insoluble in all of the organic solvents. It is clear that thermal crosslinking reactions occur during the heating–cooling scan in air. Figure 8 also shows the effect of the DB on the thermal crosslinking reaction. The polymer prepared with potassium carbonate also showed an increase in the T_g but the trend was weak. The location or geometry of the hydroxyl groups may influence the crosslinking reaction. It should be pointed out that the nitrobenzene-terminated polymer did not show the T_g increase after the heating–cooling scans from 50 to 260 °C for five times in air. Figure 9 shows the TGA curves of the polymer before and after heating at 300 °C for 30 min. The hydroxyl-terminated polymer prepared with cesium fluoride showed the gradual weight loss from 150 to 350 °C. The 5 and 10% weight loss temperature were 339 and 404 °C, respectively. The curve (b) in Figure 9 represents the weight loss of the polymer after the heating at 300 °C for 30 min. The gradual weight loss observed before the heating was not observed. The 5 and 10% weight loss were 406 and 424 °C, respectively. It is clear that the thermal stability of the hydroxyl-terminated hyperbranched poly(ether sulfone) is improved by the heating at 300 °C. IR spectra of the hydroxyl-terminated hyperbranched poly(ether sulfone)s before and after the heating–cooling scans in air are shown in Figure 10. Some of the peaks in the IR spectrum of the sample after the heating scans became broad. It is difficult to assign the each change in the spectra to the certain functional group. The broad peaks from 1100 to 1200 /cm might suggest the formation of aromatic ether linkages.

CONCLUSIONS

Hyperbranched poly(ether sulfone)s were prepared by the self-polycondensation of 4-(3,5-hydroxyphenoxy)-4′-fluorodiphenylsulfone as an AB_2 monomer. The high-molecular-weight polymers were isolated in good yields. DB of the

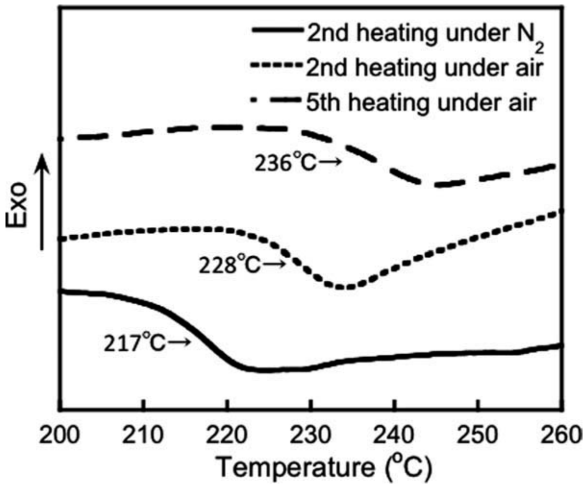


FIGURE 7 DSC curves of the hyperbranched poly(ether sulfone) (OH terminal) at a heating rate of 10 °C/min.

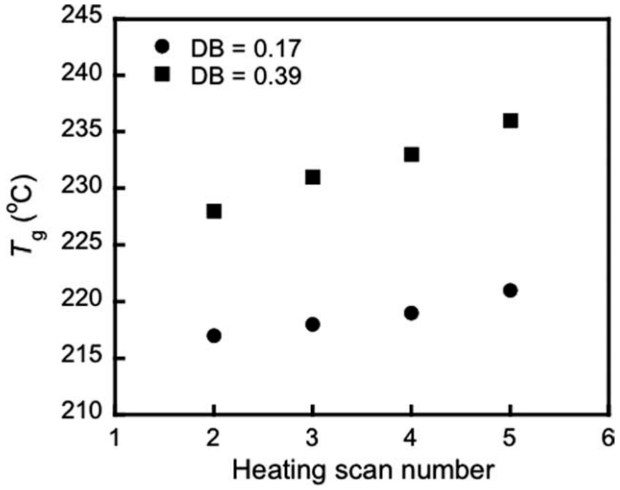


FIGURE 8 The T_g increase of the hydroxyl-terminated hyperbranched poly(ether sulfone) by the heating-cooling scans in air from 30 to 300 °C.

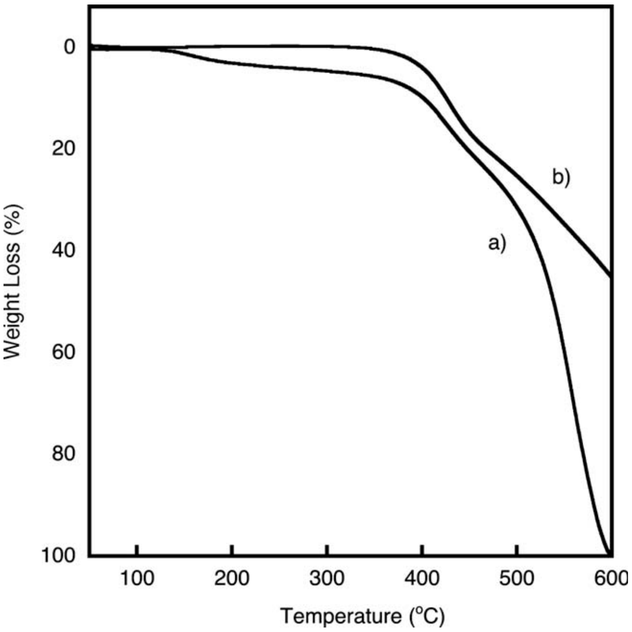


FIGURE 9 TGA curves of hydroxyl-terminated hyperbranched poly(ether sulfone) prepared with cesium fluoride before (a) and after (b) heating at 300 °C for 30 min.

resulting polymers was determined by gated decoupling ^{13}C NMR measurements. The DB of the polymer prepared with potassium carbonate was lower than that prepared with cesium fluoride. The low DB might be caused by the poor solubility of the phenolate anions formed *in situ* during the polymerization. The resulting hyperbranched poly(ether sulfone)s showed good solubilities in organic solvents, and the solubility was influenced by the terminal functional groups. The unique thermal crosslinking phenomenon was observed during the DSC measurements of the hydroxyl-terminated hyperbranched poly(ether sulfone) in air. The crosslinking behavior was also influenced by the DB. The thermal crosslinking may be useful for application in solvent-less coatings.

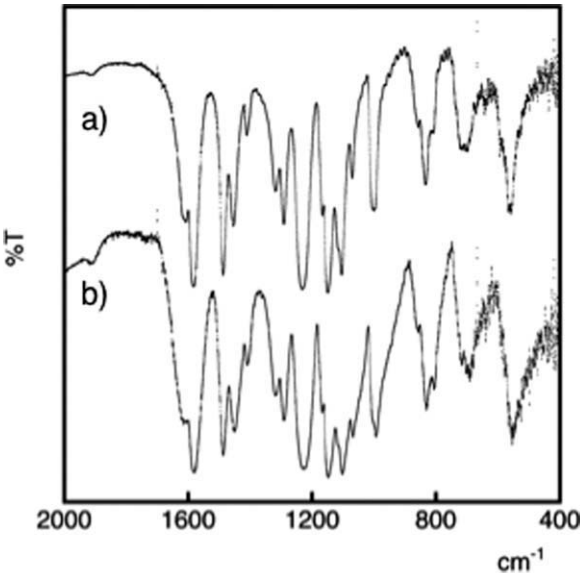


FIGURE 10 IR spectra of the hydroxyl-terminated hyperbranched poly(ether sulfone)s before (a) and after (b) the five heating–cooling scans from 30 to 300 °C.

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