Hyperbranched Aromatic Poly(ether imide)s: Synthesis, Characterization, and Modification

FANG-IY WU, CHING-FONG SHU

Department of Applied Chemistry, National Chiao Tung University, Hsin-Chu, Taiwan, 30035, Republic of China

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ABSTRACT: The synthesis and characterization of hyperbranched aromatic poly(ether imide)s are described. An AB_2 monomer, which contained a pair of phenolic groups and an aryl fluoro moiety activated toward displacement by the attached imide heterocyclic ring, was prepared. The nucleophilic substitution of the fluoride with the phenolate groups led to the formation of an ether linkage and, subsequently, to the hyperbranched poly(ether imide), which contained terminal phenolic groups. A similar one-step polymerization involving a monomer that contained silyl-protected phenols yielded a hyperbranched poly(ether imide) with terminal silylated phenols. The degree of branching of these hyperbranched polymers was approximately 55%, as determined by a combination of model compound studies and ^{1}H NMR integration experiments. End-capping reactions of the terminal phenolic groups were readily accomplished with a variety of acid chlorides and acid anhydrides. The nature of the chain-end groups significantly influenced physical properties, such as the glass-transition temperature and the solubility of the hyperbranched poly(ether imide)s. As the length of the acyl chain of the terminal ester groups increased, the glass-transition temperature value for the polymer decreased, and the solubility of the polymer in polar solvents was reduced, becoming more soluble in nonpolar solvents. © 2001 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 39: 2536–2546, 2001

Keywords: hyperbranched; poly(ether imide)s; AR_2 monomer; degree of branching

INTRODUCTION

Hyperbranched polymers have been the subject of considerable interest in recent years because their unique highly branched structures can be predicted to exhibit some unusual properties.[1,2] Such polymers are prepared in a single step via a random one-pot polymerization of AB_n-type monomers. As predicted theoretically by Flory,[3] the direct polymerization of AB_n-type monomers is expected to give rise to a highly branched, irregular structure that contains a large number of terminal functional groups. Hyperbranched polymers are generally composed of three parts, dendritic, linear, and terminal units, and may be considered to be irregular analogues of dendritic macromolecules,[4] which are built up by step-by-step synthetic sequences.[5,6] Nevertheless, they still maintain many of the properties found in their more perfectly defined dendrimer counterparts.

One-step synthesis allows hyperbranched polymers to be more readily available (as well as large-scale preparation) for potential applications. This significant feature has led to the development of novel synthetic routes for the preparation of such polymers.[1,2] Aromatic poly(ether imide)s represent a class of polymers that have gained technical interest because of their excellent electrical, thermal, and mechanical proper-

Correspondence to: C.-F. Shu (E-mail: shu@cc.nctu.edu.tw)

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ties.[7] Two typical synthetic methods have been employed for their preparation. The first involves the condensation of dianhydride and diamine monomers, thus generating a poly(amic acid), followed by cyclodehydration to form the imide ring.[8] The second method involves aromatic nucleophilic substitution reactions of phenoxide nucleophiles with nitro- or fluoro-substituted phthalimides to form the ether linkage.[9,10] Because of the high reactivity of amine and anhydride groups, no stable AB_2-type monomer that contains one amino group and two anhydride groups (or one anhydride group and two amino groups) appears to be available for the preparation of hyperbranched poly(ether imide)s. To solve this problem, Kakimoto et al.[11] recently reported the synthesis of a hyperbranched poly(ether imide) derived from a monomer composed of an amino group and a phthalic acid monomethyl ester. Moore et al. reported a modification of the nucleophilic displacement method for the preparation of hyperbranched poly(ether imide)s with a Kricheldorf-type reaction involving *tert*-butyldimethylsilyl (TBDMS) protected benzenediol groups and an activated fluoride in the presence of a catalytic amount of CsF.[12,13]

In a previous study, we reported the synthesis of dendritic poly(ether imide)s from the building block 1-(4-aminophenyl)-1,1-bis(4-hydroxyphenyl)ethane (**1**),[14] in which two hydroxy groups are attached to two separated benzene rings, to prevent the formation of complex products due to electron-transfer redox reactions between the electron-deficient nitrophthalimide and electron-rich benzenediol dianion.[15] In this article, we report the synthesis and characterization of hyperbranched poly(ether imide)s containing terminal phenolic groups. The polymers were prepared directly via aromatic nucleophilic substitution from an AB_2 monomer, which contained a fluoro-substituted phthalimide, derived from compound **1**. Even though the nitro group was readily displaced, the resulting nitrite ion was reactive and could participate in side reactions during the polymerization at a high temperature.[16] Because of this, the fluoride was the more desirable leaving group. The phenolic terminal units of the resulting polymers were modified by reaction with several end-capping agents. The influence of the chain-end groups on the solubility and glass-transition temperature (T_g) of the hyperbranched polymers was also investigated.

EXPERIMENTAL

General Directions

Anhydrous tetrahydrofuran (THF) was distilled from a sodium diphenyl ketyl solution just prior to use. Other starting materials and reagents were used as obtained from the suppliers. NMR spectra were recorded on a Varian Unity 300-MHz spectrometer or a Bruker-DRX 300-MHz spectrometer. Differential scanning calorimetry (DSC) was performed on a Seiko SSC 5200 DSC with a heating/cooling rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was performed on a Seiko TG/DTA 200 instrument. The thermal stability of samples was determined in nitrogen on the basis of the weight loss at a heating rate of 10 °C min^{-1}. Size exclusion chromatography (SEC) was carried out on a Waters chromatography unit interfaced with a Waters 410 differential refractometer. Three 5-μm Waters styragel columns (300 × 7.8 mm) connected in series in decreasing order of pore size (10^5, 10^4, and 10^3 Å) were used with dimethylformamide (DMF)/0.05 M LiBr as an eluent, and poly(methyl methacrylate) standard samples were used for calibration. Mass spectra were obtained on a JEOL JMS-SX/SX 102A mass spectrometer. Analytical thin-layer chromatography (TLC) was performed on silica gel GF254 plates. The silica gel used for column chromatography was Merck Kieselgel 60 (70–230 mesh). **1**[14] and *N*-phenyl-4-fluorophthalimide (**5**)[9] were prepared according to literature methods.

N-{4-[1,1-Di(4-hydroxyphenyl)ethyl]phenyl}-4-fluorophthalimide (2)

A mixture of **1** (1.01 g, 3.30 mmol) and 4-fluorophthalic anhydride (0.55 g, 3.31 mmol) in 1,2-dichlorobenzene (5.0 mL) was heated at reflux with stirring under nitrogen for 2 h. The resulting mixture was added to hexane (150 mL). The resulting precipitate was collected and dried at 60 °C *in vacuo* to give **2** (1.27g, 84.9%).

^{1}H NMR [dimethyl sulfoxide (DMSO)-d_6, δ]: 9.29 (s, 2 H) 8.02 (dd, 1 H, J = 4.6, 8.2 Hz), 7.86 (dd, 1 H, J = 2.2, 7.4 Hz), 7.74–7.67 (m, 1 H), 7.32 (d, 2 H, J = 8.4 Hz), 7.15 (d, 2 H, J = 8.4 Hz), 6.85 (d, 4 H, J = 8.6 Hz), 6.67 (d, 4 H, J = 8.6 Hz), 2.05 (s, 3 H). ^{13}C NMR (DMSO-d_6, δ): 166.1, 165.9 (d, $J_{C—F}$ = 252 Hz), 165.8 (d, $J_{C—F}$ = 3 Hz), 155.3, 149.9, 139.2, 134.6 (d, $J_{C—F}$ = 10 Hz), 129.3, 129.2, 128.7, 127.7 (d, $J_{C—F}$ = 3 Hz), 126.4, 126.2

(d, $J_{C—F}$ = 10 Hz), 121.5 (d, $J_{C—F}$ = 24 Hz), 114.6, 111.2 (d, $J_{C—F}$ = 25 Hz), 50.6, 30.3. High-resolution mass spectrometry (HRMS) [M^+]: 453.1373. Calcd. for $C_{28}H_{20}FNO_4$: 453.1376.

N-{4-[1,1-Di(4-*tert*-butyldimethylsilyloxyphenyl)ethyl]phenyl}-4-fluorophthalimide (3)

A mixture of **2** (1.28 g, 2.81 mmol), *tert*-butyldimethylsilyl chloride (1.01 g, 6.70 mmol), and imidazole (0.46 g, 6.76 mmol) in CH_2Cl_2 (8.0 mL) was stirred under nitrogen at 25 °C for 7 h. The imidazole salts were removed by filtration, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (CH_2Cl_2) to give **3** (1.64 g, 85.8%).

^{1}H NMR ($CDCl_3$, δ): 7.94 (dd, 1 H, J = 4.4, 8.2 Hz), 7.61 (dd, 1 H, J = 2.1, 7.0 Hz), 7.46–7.40 (m, 1 H), 7.29 (d, 2 H, J = 8.7 Hz), 7.19 (d, 2 H, J = 8.7 Hz), 6.94 (d, 4 H, J = 8.7 Hz), 6.72 (d, 4 H, J = 8.7 Hz), 2.13 (s, 3 H), 0.97 (s, 18 H), 0.19 (s, 12 H). ^{13}C NMR ($CDCl_3$, δ): 166.6 (d, $J_{C—F}$ = 256 Hz), 166.3, 166.0 (d, $J_{C—F}$ = 3 Hz), 153.7, 150.0, 141.5, 134.5 (d, $J_{C—F}$ = 9 Hz), 129.6, 129.4, 129.1, 127.5 (d, $J_{C—F}$ = 3 Hz), 126.1 (d, $J_{C—F}$ = 9 Hz), 121.5, 121.4 (d, $J_{C—F}$ = 24 Hz), 119.2, 111.4 (d, $J_{C—F}$ = 25 Hz), 51.2, 30.7, 25.7, 18.2, −4.4. HRMS [M^+]: 681.3097. Calcd. for $C_{40}H_{48}FNO_4Si_2$: 681.3106.

N-{4-[1,1-Di(4-hydroxyphenyl)ethyl]phenyl}phthalimide (4)

A mixture of **1** (0.52 g, 1.69 mmol) and phthalic anhydride (0.25 g, 1.69 mmol) in 1,2-dichlorobenzene (1.2 mL) was heated at reflux with stirring under nitrogen for 1.5 h. The resulting mixture was added to hexane (100 mL). The precipitate was collected and dried at 60 °C *in vacuo* to give **4** (0.606 g, 82.3%).

^{1}H NMR (DMSO-d_6, δ): 9.28 (s,2 H), 7.97–7.93 (m, 2 H), 7.91–7.87 (m, 2 H), 7.33 (d, 2 H, J = 8.6 Hz), 7.15 (d, 2 H, J = 8.6 Hz), 6.86 (d, 4 H, J = 8.7 Hz), 6.66 (d, 4 H, J = 8.7 Hz), 2.06 (s,3 H). ^{13}C NMR (DMSO-d_6, δ): 167.1, 155.3, 149.8, 139.2, 134.7, 131.5, 129.4, 129.2, 128.6, 126.4, 123.4, 114.6, 50.6, 30.3. HRMS [M^+]: 435.1463. Calcd. for $C_{28}H_{21}NO_4$: 435.1470.

Synthesis of Model Compounds 6 and 7

A mixture of **4** (40 mg, 90 μmol), **5** (21 mg, 90 μmol), CsF (13 mg, 90 μmol), and diphenylsulfone (DPS; 0.50 g) was heated under nitrogen at 235 °C for 15 min. The model compounds were isolated from the reaction mixture by preparative TLC (1/2/2 hexane/EtOAc, ethyl acetate/CH_2Cl_2).

Compound 6

^{1}H NMR (DMSO-d_6, δ): 9.37 (s, 1 H), 7.97–7.95 (m, 3 H), 7.89–7.87 (m, 2 H), 7.54–7.37 (m, 9 H), 7.22 (d, 2 H, J = 8.6 Hz), 7.20 (d, 2 H, J = 8.9 Hz), 7.13 (d, 2 H, J = 8.9 Hz), 6.92 (d, 2 H, J = 8.7 Hz), 6.73 (d, 2 H, J = 8.7 Hz), 2.15 (s, 3 H). ^{13}C NMR (DMSO-d_6, δ): 167.0, 166.4, 166.2, 162.7, 155.6, 152.7, 149.0, 146.0, 138.4, 134.7, 134.2, 131.9, 131.5, 130.3, 129.6, 129.3, 128.8, 128.7, 128.0, 127.3, 126.6, 125.9, 125.3, 123.4, 122.9, 119.5, 114.8, 111.8, 51.1, 30.3. HRMS [M^+ + H]: 657.2017. Calcd. for $C_{42}H_{29}FN_2O_6$: 657.2025.

Compound 7

^{1}H NMR (DMSO-d_6, δ): 7.97–7.94 (m, 4 H), 7.92–7.87 (m, 2 H), 7.54–7.39 (m, 16 H), 7.30 (d, 2 H, J = 8.7 Hz), 7.26 (d, 4 H, J = 8.9 Hz), 7.17 (d, 4 H, J = 8.9 Hz), 2.25 (s, 3 H). ^{13}C NMR (DMSO-d_6, δ): 167.0 166.3, 166.2, 162.5, 153.0, 148.2, 145.2, 134.7, 134.2, 131.9, 131.5, 130.4, 130.0, 128.8, 128.7, 128.0, 127.3, 126.8, 125.9, 125.4, 123.4, 123.0, 119.6, 111.9, 51.5, 30.2. HRMS [M^+ + H]: 878.2501. Calcd. for $C_{56}H_{36}N_3O_8$: 878.2502.

N-{4-[1,1-Di(4-*tert*-butyldimethylsilyloxyphenyl)ethyl]phenyl}-4-fluorophthalimide (8)

A mixture of **4** (0.62 g, 1.41 mmol), *tert*-butyldimethylsilyl chloride (0.43 g, 2.83 mmol), and imidazole (0.19 g, 2.82 mmol) in CH_2Cl_2 (5.0 mL) was stirred under nitrogen at 25 °C for 12 h. The imidazole salts were removed by filtration, and the solvent evaporated *in vacuo*. The crude product was purified by column chromatography (CH_2Cl_2) to give **8** (0.48 g, 51.3%).

^{1}H NMR ($CDCl_3$, δ): 7.95–7.92 (m, 2 H), 7.79–7.75 (m, 2 H), 7.31 (d, 2 H, J = 8.9 Hz), 7.20 (d, 2 H, J = 8.9 Hz), 6.95 (d, 4 H, J = 8.8 Hz), 6.73 (d, 4 H, J = 8.8 Hz), 2.13 (s, 3 H), 0.97 (s, 18 H), 0.18 (s, 12 H). ^{13}C NMR ($CDCl_3$, δ): 167.4, 153.7, 149.7, 141.6, 134.3, 131.8, 129.7, 129.4, 129.3, 125.6, 123.7, 119.2, 51.2, 30.7, 25.7, 18.2, −4.4. HRMS [M^+ CH_3]: 648.2953. Calcd. for $C_{39}H_{46}NO_4Si_2$: 648.2965.

Synthesis of Model Compound 9

A mixture of **8** (60 mg, 90 μmol), **5** (23 mg, 90 μmol), CsF (1.4 mg, 9 μmol), and DPS (0.60 g) was

heated under nitrogen at 210 °C for 10 min. The model compound **9** was isolated from the reaction mixture by preparative TLC (5/1/2 hexane/EtOAc/CH_2Cl_2).

^{1}H NMR ($CDCl_3$, δ): 7.95–7.93 (m, 2 H), 7.88 (d, 1 H, J = 8.2 Hz), 7.79–7.76 (m, 2 H), 7.51–7.32 (m, 9 H), 7.24 (d, 2 H, J = 8.6 Hz), 7.18 (d, 2 H, J = 8.7 Hz), 7.01–6.98 (m, 4 H), 6.77 (d, 2 H, J = 8.6 Hz), 2.20 (s, 3 H), 0.96 (s, 9 H), 0.20 (s, 6 H). ^{13}C NMR ($CDCl_3$, δ): 167.3, 166.8, 166.7, 163.6, 153.9, 152.9, 148.9, 146.3, 140.8, 134.4, 134.2, 131.7, 130.7, 129.6, 129.5, 129.3, 129.1, 128.0, 126.5, 125.8, 125.7, 125.1, 123.7, 123.0, 119.6, 119.4, 112.1, 51.6, 30.7, 25.6, 18.2, −4.4. HRMS [M^+ + H]: 771.2893. Calcd. for $C_{48}H_{43}N_2O_6Si$: 771.2890.

Preparation of Hyperbranched Poly(ether imide) P1

A mixture of **2** (0.15 g, 0.33 mmol), CsF (40 mg, 0.26 mmol), and DPS (0.45 g) was heated at 235 °C with stirring under nitrogen for 15 min. The mixture was then dissolved in DMF (3.0 mL) and precipitated into methanol (40 mL). The resulting polymer was collected and purified by precipitation from DMF into methanol two times to give **P1** (0.123 g, 85.5%).

Preparation of Hyperbranched Poly(ether imide) P2

A mixture of **3** (3.00 g, 4.40 mmol), CsF (6.67 mg, 44 μmol), and DPS (4.50 g) was heated at 210 °C with stirring under nitrogen for 10 min. The reaction mixture was dissolved in THF (30 mL) and precipitated into a mixture of hexane (50 mL) and methanol (150 mL). The resulting polymer was collected and purified by precipitation from THF into a mixture of hexane, acetone, and methanol (1/1/3 v/v/v) two times to give **P2** (2.19 g, 91.0%).

Preparation of Hyperbranched Poly(ether imide) P3

To a solution of **P1** (60 mg, 0.14 mmol) and triethylamine (Et_3N) (73 mg, 0.72 mmol) in anhydrous THF (6.0 mL), acetyl chloride (57 mg, 0.73 mmol) was added dropwise under nitrogen. The mixture was stirred at 25 °C for 24 h and then added to a mixture of water (10 mL) and methanol (10 mL). The resulting polymer was collected and purified by precipitation from $CHCl_3$ into methanol to give **P3** (50 mg, 76%).

Preparation of Hyperbranched Poly(ether imide) P4

To a solution of **P1** (60 mg, 0.14 mmol) and 4-(dimethylamino)pyridine (DMAP) (91 mg, 0.74 mmol) in anhydrous THF (3.0 mL), hexanoic anhydride (154 mg, 0.72 mmol) was added dropwise under nitrogen. The mixture was stirred at 25 °C for 24 h and then added to a mixture of water (10 mL) and methanol (10 mL). The resulting polymer was collected and purified by precipitation from $CHCl_3$ into methanol to give **P4** (61 mg, 83%).

Preparation of Hyperbranched Poly(ether imide) P5

To a solution of **P1** (60 mg, 0.14 mmol) and DMAP (88 mg, 0.72 mmol) in anhydrous THF (3.0 mL), lauric anhydride (275 mg, 0.72 mmol) was added dropwise under nitrogen. The mixture was stirred at 25 °C for 24 h and then added to a mixture of water (10 mL) and methanol (10 mL). The resulting polymer was collected and purified by precipitation from $CHCl_3$ into methanol to give **P5** (70 mg, 83%).

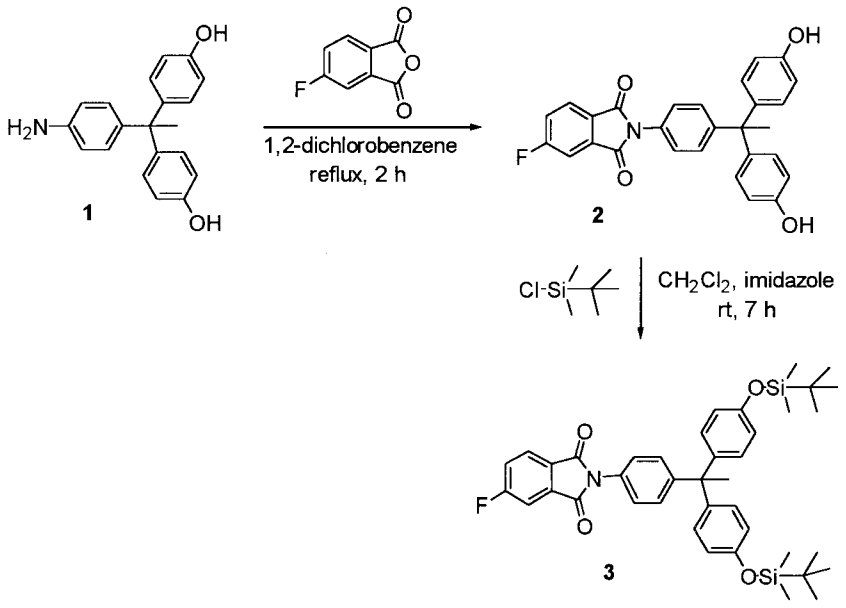
Preparation of Hyperbranched Poly(ether imide) P6

A mixture of stearic acid (204 mg, 0.72 mmol) and thionyl chloride (0.8 mL) was heated at reflux with stirring under nitrogen for 2.5 h. The excess thionyl chloride was then removed *in vacuo*. To the acid chloride was added a solution of **P1** (50 mg, 0.12 mmol) and Et_3N (73 mg, 0.72 mmol) in anhydrous THF (6.0 mL). The mixture was stirred at 25 °C for 15 h and then poured into a mixture of water (10 mL) and methanol (10 mL). The collected polymer was purified by precipitation from $CHCl_3$ in methanol and then precipitated from $CHCl_3$ into a solvent mixture of hexane and methanol (1/2 v/v) to give **P6** (49 mg, 61%).

RESULTS AND DISCUSSION

Synthesis and Characterization

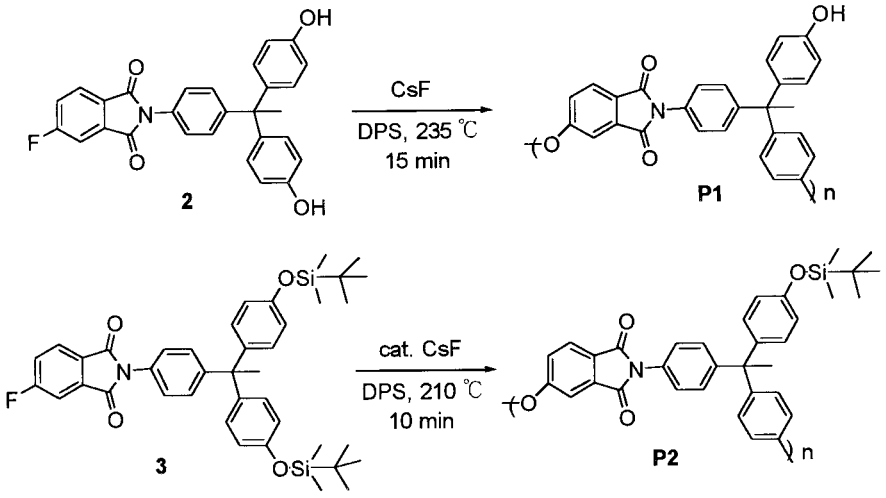
Two types of AB_2-type monomers, **2** and **3**, were prepared as shown in Scheme 1. The condensation of the amino group of compound **1** with 4-fluorophthalic anhydride followed by cyclodehydration gave monomer **2**, which contained an activated aryl fluoride and two phenolic groups. The



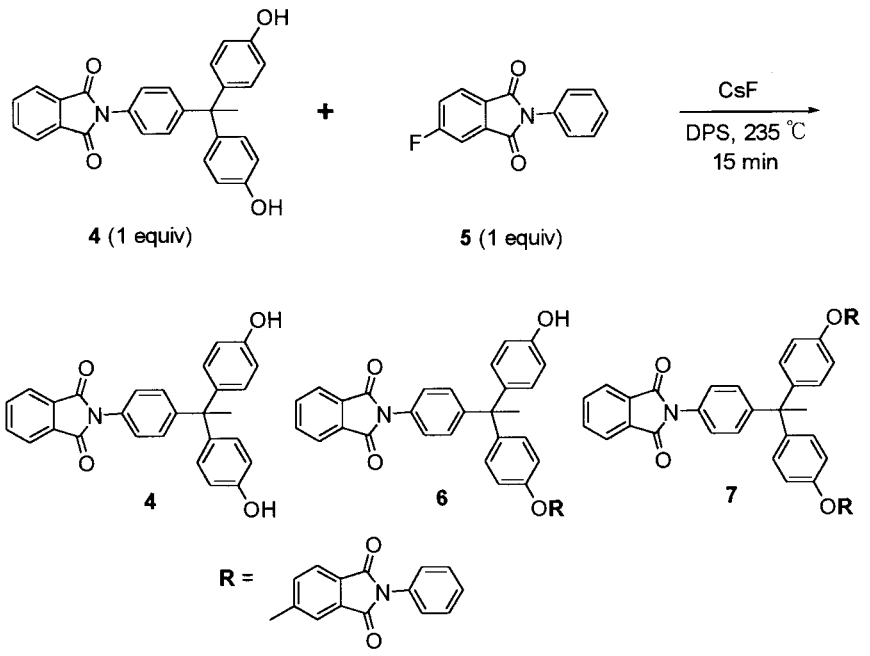
Scheme 1

phenolic groups of **2** were then converted into *t*-butyldimethylsilyl ether by stirring with TBDMS chloride in methylene chloride in the presence of imidazole to yield monomer **3**.

The polymerization of monomer **2** was performed in DPS at 235 °C in the presence of CsF (0.8 equiv), as shown in Scheme 2. The nucleophilic substitution of the fluoride with the phenolic groups,[9] activated by the imide moiety, led to the formation of an ether linkage and, subsequently, to the hyperbranched poly(ether imide) **P1** with terminal phenolic groups. For the sake of simplicity, Scheme 2 only shows the overall compositional repeat units, even though the hyperbranched polymer contained a combination of dendritic, linear, and terminal units. For the polycondensation of monomer **3**, reaction conditions similar to those reported by Moore et al.[13] were employed to give the corresponding hyperbranched poly(ether imide) **P2**, which contained terminal silylated phenol units. The TBDMS end groups in **P2** remained fully intact, as indicated by the ^{1}H NMR integration ratio of the protons attributed to the methyl (or *t*-butyl) groups in silyl ether group versus the methyl (or phenyl) protons of the AB_2 unit. Both hyperbranched



Scheme 2



Scheme 3

poly(ether imide)s were obtained in good yields (85–90%).

The molecular weight of **P1** and **P2** was determined by SEC analysis in a DMF solution calibrated against linear poly(methyl methacrylate) standards. SEC measurements of **P1** and **P3** indicated that the weight-average molecular weights were 34,500 and 74,900, respectively, relative to standard poly(methyl methacrylate), and the polydispersity values (weight-average molecular weight/number-average molecular weight) were determined to be 3.9 and 3.4, respectively. Because of the highly branched nature of the hyperbranched macromolecules, the result from SEC measurements was used only for a rough estimate. The structures of the polymers were characterized by infrared spectroscopy. A Fourier transform infrared spectrum of **P1** showed characteristic absorptions corresponding to imide at 1778 (C═O asymmetric stretching), 1718 (C═O symmetric stretching), and 1375 cm^{-1} (C—N stretching). The corresponding imide bands of the **P2** polymer appeared at 1779, 1727, and 1374 cm^{-1}. For **P1**, an additional broad band appeared at 3470 cm^{-1} and was assigned to the O—H stretching of the terminal phenolic groups. T_g of the hyperbranched poly(ether imide)s was determined by DSC. T_g of **P1**, which had polar hydroxyl terminal groups, was observed at 270 °C. T_g of **P2**, which had silyl-protected terminal phenols, decreased to 223 °C. TGA was used to examine the thermal stability of these polymers. A 5% weight loss for **P1** was observed at 376 °C, followed by an additional 5% weight loss at 402 °C. **P2**, in which the terminal phenols were protected by TBDMS groups, showed better thermal stability, with a 5 wt % loss at 467 °C followed by a 10 wt % loss at 480 °C.

Degree of Branching (DB)

The DB, which is a typical characteristic often used to evaluate the irregularity of the structure of hyperbranched polymers, was defined as the sum of dendritic and terminal units versus total units (linear, dendritic, and terminal units).[17] A combination technique of model compound studies and NMR spectroscopy was used to quantify the different subunits that were present in the hyperbranched polymer and, subsequently, to determine its DB.[17] Scheme 3 shows the model reaction used in determining the DB of **P1**. An equimolar mixture of compounds **4** and **5** was reacted under conditions that were similar to those used for the polymerization of monomer **2**. The model compounds were separated from the reaction mixture by preparative TLC. Figure 1 shows the ^1H NMR spectra of **4**, which resembles the terminal unit, the monosubstituted product **6**, which resembles the linear unit, and the disubstituted product **7**, which resembles the dendritic

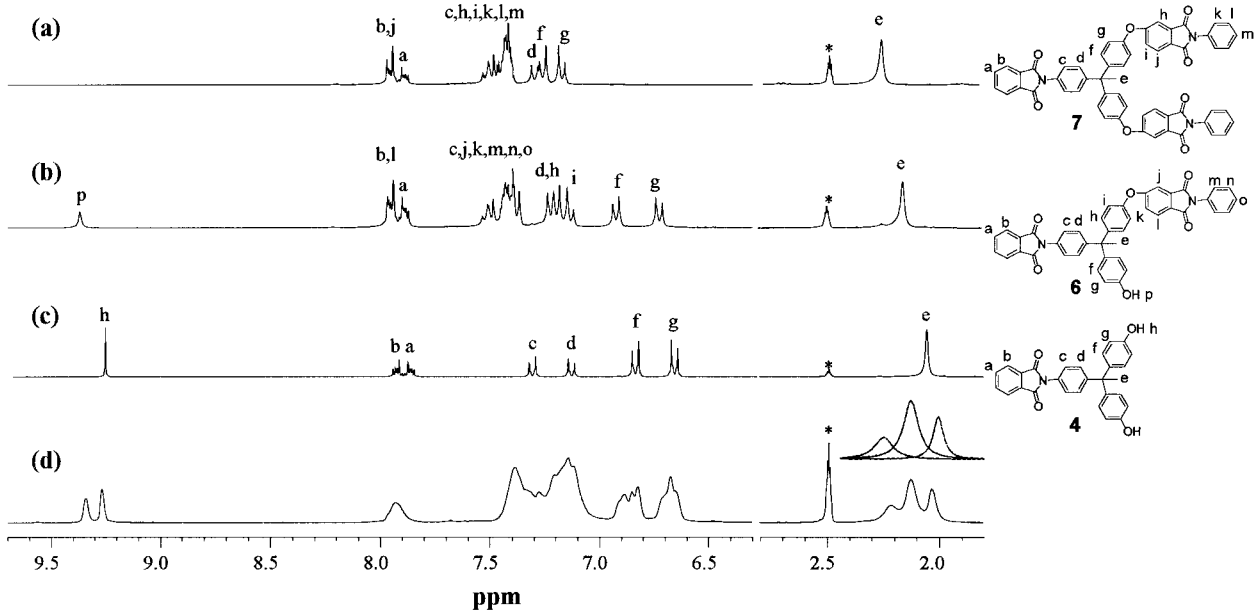


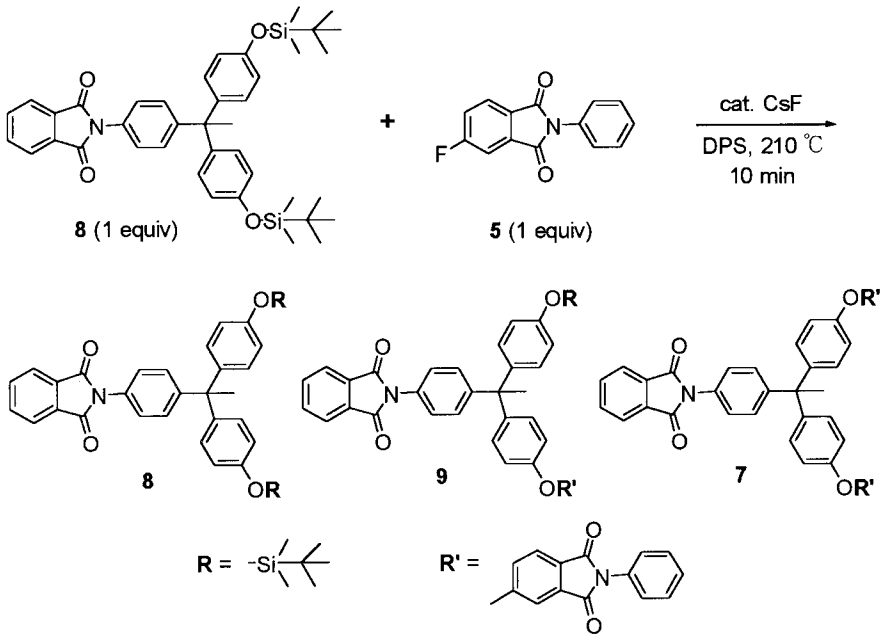
Figure 1. ^{1}H NMR spectra in DMSO-d_6 of model compounds (a) **7**, (b) **6**, and (c) **4** compared with (d) **P1**. * indicates a signal arising from DMSO.

unit. The peak assignments were based on the peak positions of compounds **4** and **5** as well as the auxiliary of two-dimensional (H, H) and (C, H) correlation NMR spectroscopy. Distinct resonances for the terminal model compound **4** appeared at 9.28 and 2.06 ppm, respectively, and were assigned to the protons of the phenolic groups and the methyl group, whereas the corresponding protons for the linear model compound **6** were observed at 9.37 and 2.15 ppm, respectively. The resonance for the methyl protons of the dendritic model compound **7** appeared at 2.25 ppm. Figure 1 also shows the ^{1}H NMR spectrum of the hyperbranched poly(ether imide) **P1**. A good correlation can be seen in a comparison of the ^{1}H NMR spectra of these model compounds with that of **P1**. The resonances at 9.33 and 9.25 ppm were assigned to the phenol protons of the linear and terminal subunits, respectively, whereas the resonances at 2.21, 2.15, and 2.03 ppm were assigned to the methyl protons of the dendritic, linear, and terminal subunits, respectively.[18] The integration of these resonances allowed the relative percentage of each subunit to be determined. The DB of **P1** was determined to be 52% on the basis of the relative integration of the phenolic protons. By calculating the integration ratio of the methyl protons, we also estimated the DB of **P1** to be 55%,[18] which is in good agreement with the value determined from the phenolic protons. The DB values calculated for **P1** are close to the statistical value of 50%, which would be expected for a random AB_2 polycondensation.[19]

The DB of the hyperbranched poly(ether imide) **P2** was also evaluated with a similar rationale. The synthesis of the model compounds is detailed in Scheme 4. Figure 2 shows the ^{1}H NMR spectra of model compounds **7**, **8**, and **9** and the polymer **P2**. A comparison of the ^{1}H NMR spectra of these model compounds with that of **P2** allowed the resonances corresponding to the dendritic, linear, and terminal subunits of the hyperbranched polymer to be identified. The resonances of the AB spin system at 6.75 and 6.70 ppm were assigned to the protons in the ortho position of the silylether of the linear and terminal subunits, respectively, whereas the resonances at 2.25, 2.18, and 2.11 ppm correspond to the methyl protons of the dendritic, linear, and terminal units, respectively.[20] Based on the integration ratio of the ortho protons of the silylether and that of the methyl protons, the DB values of **P2** were determined to be 57% and 54%,[20] values which are in reasonable agreement with each other and approach the expected statistical value 50%.[19]

Chemical Modification of Hyperbranched Poly(ether imide) P1

Hyperbranched polymers are characterized by a large number of chain-end groups. The terminal



Scheme 4

phenolic groups in **P1** could be easily functionalized to yield hyperbranched polymers with a variety of functional chain ends. The nature of the end groups influences the physical and chemical properties of the hyperbranched polymers.[21] In this study, the terminal phenolic groups of **P1** were acylated with acid chlorides or anhydrides to give the corresponding ester derivatives, as shown in Scheme 5. The degree of modification could be estimated from the ^{1}H NMR integration ratio of proton signals attributed to the methylene group in the α position of the ester group

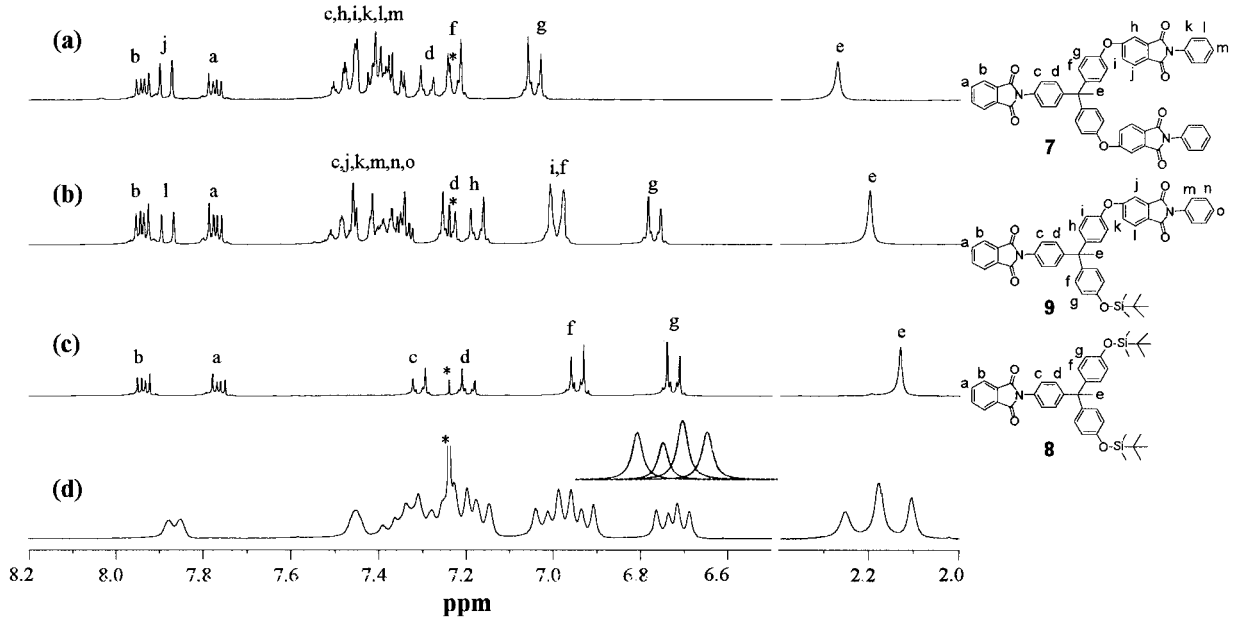
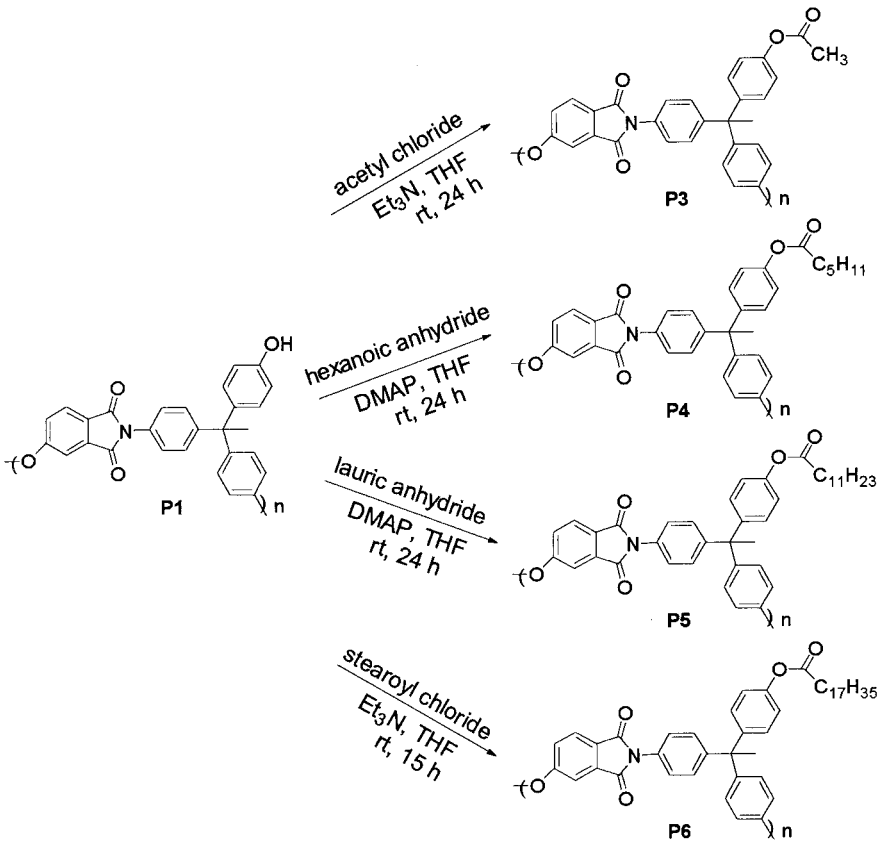


Figure 2. ^{1}H NMR spectra in $CDCl_3$ of model compounds (a) **7**, (b) **9**, and (c) **8** compared with (d) **P2**. * indicates a signal arising from $CHCl_3$.



Scheme 5

versus the methyl protons of the AB_2 unit. For all the modification reactions, the use of excess reagents resulted in almost complete (95–100%) functionalization.

The T_g and solubility of the hyperbranched poly(ether imide)s **P1**–**P6** are summarized in Table I. The influence of T_g through variation of the end groups could be assigned to the translational motion and an intermolecular effect.[22,23] It is known that for hyperbranched polymers, the transition from the polar hydroxy function to nonpolar aliphatic end groups results in a decrease in T_g due to the reduction in the extent of intermolecular interactions in the polymer molecules.[23] T_g of **P1**, which had polar hydroxyl terminal groups, was 270 °C, whereas the T_g values of **P2** and **P3**, which had fewer polar terminal groups, namely, silylether and ester groups, were 223 and

Table I. Thermal and Solution Properties of Hyperbranched Poly(ether imide)s

		Solubility[a]					
Polymer	T_g (°C)	Toluene	CH_2Cl_2	$CHCl_3$	THF	DMF	DMSO
P1	270	−	−	−	+	+	+
P2	223	+	+	+	+	+	−
P3	227	−	+	+	+	+	+
P4	163	+	+	+	+	+	−
P5	43	+	+	+	+	+	−
P6	−41	+	+	+	+	−	−

[a] + = soluble; − = insoluble.

227 °C, respectively. The reduction in T_g was caused by a reduction in the extent of hydrogen bonding. The polar hydrogen-bonding interactions were replaced by nonpolar hydrophobic interactions as the result of esterification with fatty acids. Therefore, the intermolecular interaction was lower, and the mobility was increased. A further decrease in T_g to 163, 43, and −41 °C was observed for **P3**, **P4**, and **P5**, respectively, because of the increasing length of the alkoxyl chain of the terminal ester groups. Hult et al.[24] investigated the alkyl modification of hyperbranched polyesters based on 2,2-bis(hydroxymethyl)propionic acid. They reported that, when a sufficiently long alkyl chain (12–16 carbons) was introduced, the side chain of the polymers tended to crystallize, so an increase in the polyester T_g was observed. However, the same phenomenon was not observed for the hyperbranched poly(ether imide)s, which contained rigid aromatic imide units and could exhibit a lower tendency for side-chain crystallization.

Because of their highly branched structures, these hyperbranched poly(ether imide)s possessed good solubility in organic solvents. However, the different chain ends resulted in differences of solubility in polar vis-à-vis nonpolar solvents. **P1**, which had polar phenolic terminal groups, was soluble in polar solvents such as DMSO, DMF, and THF. **P2**, which contained fewer polar silylether terminal groups, was insoluble in DMSO but soluble in relatively nonpolar solvents such as toluene, CH_2Cl_2, and $CHCl_3$, in which **P1** was insoluble. The length of the acyl chain of the terminal ester groups also had an influence on the solubility of the hyperbranched poly(ether imide)s. **P3**, which contained acetyl terminal groups, was soluble in DMSO and insoluble in toluene, whereas the **P4**–**P6** polymers, which contained longer acyl chains (6–18 carbons), were soluble in toluene and insoluble in DMSO.

SUMMARY

A hyperbranched poly(ether imide) that contained terminal phenolic groups was prepared by the one-step polymerization of an AB_2 monomer containing a pair of phenolic groups and an aryl fluoride. The nucleophilic substitution of the fluoride by the phenolate groups, which was activated by the imide ring, resulted in the formation of an ether linkage and, subsequently, the hyperbranched poly(ether imide) **P1**. A Kricheldorf-type polymerization reaction involving TBDMS protected groups and catalyzed by CsF was also carried out to give the corresponding hyperbranched poly(ether imide) **P2**, which contained terminal silylated phenols. As determined by a combination of model compound studies and ^{1}H NMR integration data, the DB of both **P1** and **P2** was approximately 55%. The terminal phenolic groups in **P1** were easily modified, yielding hyperbranched polymers that contained a variety of functional chain ends. Physical properties, such as the T_g and solubility of the hyperbranched poly(ether imide)s, were dependent on the nature of the chain ends.

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