Articles

Hyperbranched Poly(aryl ether oxazole)s: Synthesis, Characterization, and Modification

Zhi-Hao Gong, Chi-Meng Leu, Fang-Iy Wu, and Ching-Fong Shu*

Department of Applied Chemistry, National Chiao Tung University, Hsin-Chu, Taiwan, 30035, R. O. C.

Received May 8, 2000; Revised Manuscript Received September 12, 2000

ABSTRACT: In this paper the synthesis and characterization of a hyperbranched poly(aryl ether oxazole) with terminal phenolic groups are described. An ABB′ monomer containing a pair of phenolic groups and an aryl fluoride which is activated toward displacement by the attached oxazole ring was prepared. The nucleophilic substitution of the fluoride with the phenolic group leads to the formation of ether linkage and subsequently the hyperbranched poly(aryl ether oxazole) **P1**. As determined by a combination of model compound studies and ^{1}H NMR integration experiments, the degree of branching of **P1** is approximately 50%. The polymer **P1** is thermally stable and readily soluble in polar organic solvents. The terminal phenolic groups in **P1** were easily functionalized, yielding hyperbranched polymers with a variety of functional chain ends. Physical properties, such as the glass transition temperature and the solubility of the hyperbranched poly(aryl ether oxazole)s, depended significantly on the nature of the chain ends.

Introduction

Recently, hyperbranched macromolecules have received considerable attention since their unique highly branched structure is expected to exhibit some unusual properties.[1−4] Such polymers are conveniently synthesized in a single step via random one-pot polymerization of AB_n-type monomers, yet they maintain many of the architectural features and properties found in their more perfectly defined dendrimer counterparts,[5] which are built up by step-by-step sequences requiring isolation and purification in each step.[6,7]

Poly(aryl ether)s are a class of thermoplastics possessing high thermal stability and good mechanical properties.[8] It has been shown that aromatic nucleophilic substitution reactions between activated aryl halide monomers and bisphenonates can lead to the formation of linear poly(aryl ether)s.[9] Electron-withdrawing groups like ketone, sulfone, and some heterocycles, which may stabilize the anionic intermediate, were utilized as activating groups to facilitate nucleophilic aromatic substitution in the synthesis of poly(aryl ether)s.[9−12] These synthetic strategies have been employed for the preparation of hyperbranched poly(aryl ether)s in one-step polymerization from AB_2 monomers containing a phenolic group and two aryl fluorides which were activated toward nucleophilic displacement by either a sulfone or carbonyl group.[13] Recently, Hedrick et al. have extended this synthetic strategy to heterocycle-activated systems in the synthesis of hyperbranched poly(aryl ether quinoxaline)s.[14]

This report concerns the synthesis of a hyperbranched poly(aryl ether oxazole) by the one-step polymerization of an ABB′ monomer which contains an aryl fluoride and two phenolic groups attached at C-2, C-4, and C-5 positions of an oxazole ring, respectively. The nucleophilic substitution of the fluoride with the pheonilic groups, activated by the oxazole moiety, leads to the formation of ether linkage and subsequently the poly(aryl ether oxazole). Furthermore, the modification of phenolic chain ends of the resulting polymers by reaction with several end-capping agents is described. The effects of the nature of the chain-end groups on the solubility and glass transition temperature of the hyperbranched polymers have also been investigated.

Experimental Section

General Directions. THF was distilled from a sodium diphenyl ketyl solution just prior to use. Benzene was distilled over sodium. Anhydrous K_2CO_3 was ground into fine powder and dried at 120 °C under vacuum. Other starting materials and reagents were used as obtained from the suppliers. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity 300 MHz or a Bruker-DRX 300 MHz spectrometer. Differential scanning calorimetry (DSC) was performed on a SEIKO SSC 5200 DSC using a heating/cooling rate of 10 °C min^{-1}. Samples were scanned from 30 to 300 °C and then cooled to 30 °C and scanned a second time from 30 to 300 °C. The glass transition temperature was determined from the second heating scan. Thermogravimetric analysis (TGA) was made on a SEIKO TG/DTA 200 instrument. The thermal stability of samples was determined in nitrogen by measuring weight loss while heating at a rate of 10 °C min^{-1}. Size exclusion chromatography (SEC) was carried out on a Waters chromatography connected to a Waters 410 differential refractometer. Three 5 μm Waters styragel columns (300 × 7.8 mm) connected in series in the decreasing order of pore size (10^5, 10^4, and 10^3 Å) were used with DMF/0.05 M LiBr as 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 TLC was performed on commercial Merck plated coated with silica gel

10.1021/ma000789y CCC: $19.00
Published on Web 10/21/2000

GF254. Silica gel for column chromatography was Merck Kieselgel 60 (70−230 mesh).

1,2-Di(4-methoxyphenyl)-2-oxyethyl-4-fluorobenzoate (2). A mixture containing 4,4′-dimethoxybenzil **1** (12.0 g, 44.0 mmol), 4-fluorobenzoic acid (6.17 g, 44.0 mmol), 4-(dimethylamino)pyridine (0.22 g), and dicyclohexylcarbodiimide (10.0 g) in dichloromethane (160 mL) was stirred at 25 °C under nitrogen for 15 h. The reaction mixture was filtered. The filtrate was concentrated under reduced pressure, and the resulting residue was purified by column chromatography (hexane/EtOAc 3:1) to give **2** (11.71 g, 67.4%). ^{1}H NMR (acetone-d_6): δ 3.80 (s, 3 H), 3.88 (s, 3 H), 7.00 (d, 2 H, J = 9.0 Hz), 7.01 (d, 2 H, J = 9.0 Hz), 7.17 (s, 1H), 7.30 (dd, 2 H, J = 8.7, 8.7 Hz), 7.60 (d, 2 H, J = 9.0 Hz), 8.08 (d, 2 H, J = 9.0 Hz), 8.13 (dd, 2H, J = 9.0, 5.7 Hz). ^{13}C NMR (acetone-d_6): δ 192.5, 166.6 (d, J_{C-F} = 253 Hz), 165.3, 164.7, 161.3, 133.2 (d, J_{C-F} = 9 Hz), 131.8, 131.1, 128.2, 127.2 (d, J_{C-F} = 2 Hz), 126.9, 116.4 (d, J_{C-F} = 22 Hz), 115.2, 114.7, 78.3, 55.9, 55.5. MS (*m*/*z*): 394.1215. Calcd. 394.1216 for $C_{23}H_{19}O_5F$.

2-(4-Fluorophenyl)-4,5-di(4-methoxyphenyl)-1,3-oxazole (3). A mixture of **2** (2.50 g, 6.34 mmol) and ammonium acetate (2.95 g, 38.3 mmol) in AcOH (27 mL) was heated at reflux under nitrogen for 8 h. The resulting mixture was poured into water (100 mL) and extracted with EtOAc (3 × 50 mL). The combined extracts were dried over $MgSO_4$, and the solvent was removed in vacuo. The crude product was purified by recrystallization from hexane/EtOAc to give **3** (1.44 g, 60.5%). ^{1}H NMR (acetone-d_6): δ 3.80 (s, 3 H), 3.88 (s, 3 H), 7.00 (d, 2 H, J = 9.0 Hz), 7.01 (d, 2 H, J = 9.0 Hz), 7.17 (s, 1H), 7.30 (dd, 2 H, J = 8.7, 8.7 Hz), 7.60 (d, 2 H, J = 9.0 Hz), 8.08 (d, 2 H, J = 9.0 Hz), 8.13 (dd, 2H, J = 9.0, 5.7 Hz). ^{13}C NMR (acetone-d_6): δ 192.5, 166.6 (d, J_{C-F} = 253 Hz), 165.3, 164.7, 161.3, 133.2(d, J_{C-F} = 9 Hz), 131.8, 131.1, 128.2, 127.2 (d, J_{C-F} = 2 Hz), 126.9, 116.4(d, J_{C-F} = 22 Hz), 115.2, 114.7, 78.3, 55.9, 55.5. MS (*m*/*z*): 394.1215. Calcd. 394.1216 for $C_{23}H_{19}O_5F$.

2-(4-Fluorophenyl)-4,5-di(4-hydroxyphenyl)-1,3-oxazole (4). A suspension of **3** (4.00 g, 10.7 mmol) in AcOH (40 mL) and 48% aqueous HBr (125 mL) was heated at reflux for 48 h. The reaction mixture was cooled, and the precipitate was collected by filtration. The solid was then dissolved in 1.0 N NaOH solution, and the pH was adjusted to neutral using concentrated HCl. The resulting precipitate was filtered, washed with water, and dried to give **4** (3.54 g, 95,6%). ^{1}H NMR (DMSO-d_6): δ 6.80 (d, 2 H, J = 8.7 Hz), 6.83 (d, 2 H, J = 8.4 Hz), 7.38 (dd, 2 H, J = 8.7, 8.7 Hz), 7.44 (d, 2 H, J = 8.7 Hz), 7.46 (d, 2 H, J = 8.4 Hz), 8.09 (dd, 2 H, J = 8.7, 5.4 Hz), 9.67 (s, 1H), 9.88 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 163.4 (d, J_{C-F} = 248 Hz), 158.1, 157.7, 157.5, 144.8, 134.7, 129.0, 128.3 (d, J_{C-F} = 9 Hz), 128.1, 123.7 (d, J_{C-F} = 2 Hz), 123.0, 119.5, 116.2 (d, J_{C-F} = 22 Hz), 115.8, 115.6. MS (*m*/*z*): 347.0963. Calcd. 347.0957 for $C_{21}H_{14}O_3NF$.

2-{4-[3,5-Di(*tert*-butyl)phenoxy]phenyl}-4,5-di(4-methoxyphenyl)-1,3-oxazole (5). A mixture of **3** (0.20 g, 0.53 mmol), 3.5-di-*tert*-butylphenol (216 mg, 1.06 mmol), anhydrous K_2CO_3 (150 mg, 1.07 mmol), benzene (4 mL), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (0.8 mL) was heated at 110 °C. The water formed during the reaction was removed through an azeotropic distillation and collected in a Dean-Stark trap. After 4 h, the benzene was collected and removed from the system. The reaction mixture was then heated at 180 °C for 3 h. The resulting mixture was cooled, poured into water (10 mL), and extracted with EtOAc (3 × 20 mL). The combined extracts were dried over Na_2SO_4, and the solvent was removed in vacuo. The product was purified by column chromatography (hexane/EtOAc 3:2) to give **5** (0,28 g, 93,4%). ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 18 H), 3.83 (s, 6 H), 6.85−6.97 (m, 6 H), 7.05 (d, 2 H, J = 9 Hz), 7.21 (t, 1 H, J = 1.5 Hz), 7.57 (d, 2 H, J = 9.3 Hz), 7.62 (d, 2 H, J = 8.7 Hz), 8.07 (d, 2 H, J = 9 Hz). ^{13}C NMR ($CDCl_3$): δ 159.7, 159.6, 159.4, 155.5, 152.9, 144.6, 135.2, 129.2, 128.0, 127.9, 125.1, 121.9, 121.8, 118.0, 117.9, 114.1, 113.99, 113.96, 113.8, 55.22, 55.19, 35.0, 31.3. MS (*m*/*z*): 561.2885. Calcd. 561.2879 for $C_{37}H_{39}O_4N$.

2-{4-[3,5-Di(*tert*-butyl)phenoxy]phenyl}-4,5-di(4-hydroxyphenyl)-1,3-oxazole (6). A suspension of **5** (1.20 g) in AcOH (8 mL) and 48% aqueous HBr (25 mL) was heated at reflux for 48 h. The reaction mixture was cooled, and the precipitate was collected by filtration. The solid was then dissolved in 1.0 N NaOH solution and filtered. The filtrate was acidified with 1 N HCl, and the pH was adjusted to 7−8 using $NaHCO_3$. The resulting precipitate was filtered, washed with water, and dried to give **6** (0.95 g, 83%). ^{1}H NMR (DMSO-d_6): δ 1.27 (s, 18 H), 6.80 (d, 2 H, J = 9.0 Hz), 6.83 (d, 2 H, J = 9.0 Hz), 6.92 (s, 2 H), 7.09 (d, 2 H, J = 9.0 Hz), 7.25 (s, 1 H), 7.44 (d, 2 H, J = 9.0 Hz), 7.45 (d, 2 H, J = 9.0 Hz), 8.03 (d, 2 H, J = 9.0 Hz), 9.63 (s, 1 H), 9.83 (s, 1 H). ^{13}C NMR (DMSO-d_6): δ 159.1, 158.1, 157.9, 157.3, 155.0, 152.6, 144.3, 134.5, 128.8, 128.0, 127.8, 122.9, 121.5, 119.4, 117.9, 117.8, 115.7, 115.4, 113.7, 34.6, 31.0. MS (*m*/*z*): 533.2560. Calcd. 533.2569 for $C_{35}H_{35}O_4N$.

Preparation of Hyperbranched Poly(aryl ether oxazole) (P1). A mixture of **4** (0.7 g, 2.01 mmol), anhydrous K_2CO_3 (1.12 g, 8 mmol), benzene (5 mL), and DMPU (2.8 mL) was heated at 120 °C for 5 h. The water formed during the reaction was removed through an azeotropic distillation and was collected in a Dean-Stark trap. The reaction mixture was then heated to 180 °C while the benzene was removed through the Dean-Stark trap. After 10 h, the resulting mixture was poured into methanol (50 mL) and neutralized with 1 N HCl. The polymer was collected by filtration and purified by precipitating from DMF into methanol to give **P1** (0.56 g, 85.2%). Anal. Calcd for $(C_{21}H_{13}NO_3)_n$: C, 77.06; H, 4.00; N, 4.28. Found: C, 77.47; H, 4.29; N, 4.19.

Preparation of Hyperbranched Poly(aryl ether oxazole) (P2). To a solution of **P1** (0.30 g) and 4-(dimethylamino)-pyridine (0.17 g) in THF (7.0 mL) was added dropwise acetyl chloride (91 μL) under nitrogen. The reaction mixture was stirred at 25 °C for 48 h, later heated at reflux for 2 h, and then added to methanol. The collected polymer was purified by precipitating from $CHCl_3$ into methanol to give **P2** (0.28 g, 82%). Anal. Calcd for $(C_{23}H_{15}NO_4)_n$: C, 74.79; H, 4.09; N, 3.79. Found: C, 74.24; H, 4.19; N, 3.37.

Preparation of Hyperbranched Poly(aryl ether oxazole) (P3). To a solution of **P1** (0.20 g) and 4-(dimethylamino)-pyridine (113 mg) in THF (3.0 mL) was added dropwise hexanoic anhydride (190 μL) under nitrogen. The reaction mixture was stirred at 25 °C for 24 h and then added to methanol. The collected polymer was purified by precipitating from $CHCl_3$ into methanol to give **P3** (0.21 g, 81%). Anal. Calcd for $(C_{27}H_{23}NO_4)_n$: C, 76.22; H, 5.54; N, 3.29. Found: C, 76.51; H, 5.96; N, 3.51.

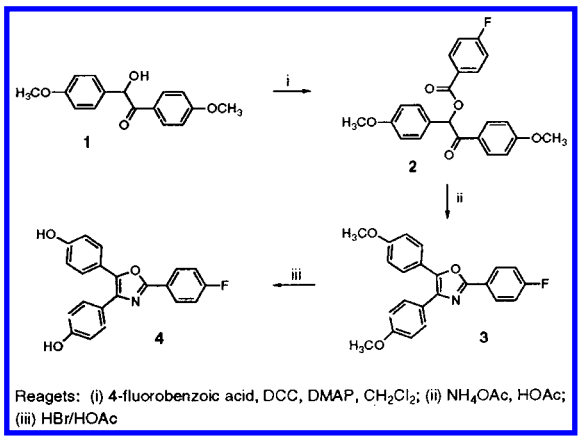
Preparation of Hyperbranched Poly(aryl ether oxazole) (P4). To a solution of **P1** (0.20 g), PPh_3 (0.488 g), and ethanol (103 μL) in THF (15 mL) was added dropwise diisopropyl azodicarboxylate (0.36 mL) under nitrogen. The reaction mixture was stirred at 25 °C for 24 h and then added to methanol. The collected polymer was purified by precipitating from $CHCl_3$ into methanol to give **P4** (0.209 g, 96%). Anal. Calcd for $(C_{23}H_{17}NO_3)_n$: C, 77.73; H, 4.82; N, 3.94. Found: C, 77.15; H, 4.65; N, 4.40.

Preparation of Hyperbranched Poly(aryl ether oxazole) (P5). P5 was prepared from **P1** and 1-hexanol using the same procedure as for **P4** (0.215 g, 95%). Anal. Calcd for $(C_{27}H_{25}NO_3)_n$: C, 78.81; H, 6.12; N, 3.40. Found: C, 78.49; H, 5.90; N, 3.67.

Results and Discussion

Synthesis and Characterization of the ABB′ Monomer. The ABB′ oxazole monomer **4** was synthesized by the cyclocondensation reaction, similar to the method described by Moylan and co-workers[15] (Scheme 1). The 4-(dimethylamino)pyridine (DMAP) catalyzed the dicyclohexylcarbodiimide (DCC) coupling of the substituted benzoin **1** with 4-fluorobenzoic acid and gave the benzoin benzoate **2**. Ring closure of the benzoin benzoate **2** with ammonium acetate in AcOH yielded the 2,4,5-triphenyloxazole **3** which was subsequently demethylated with HBr to afford the ABB′ monomer **4.**

Scheme 1



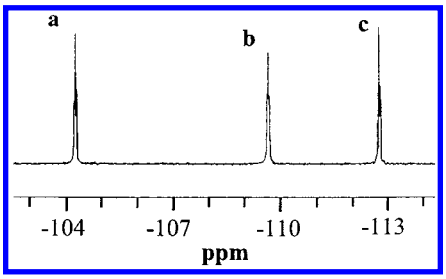


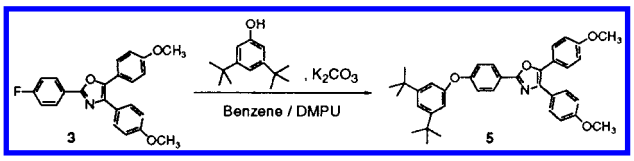
Figure 1. ^{19}F NMR spectra in DMSO-d_6 of a mixture of (a) 4,4′-difluorophenyl sulfone, (b) monomer **4**, and (c) fluorobenzene.

The monomer **4** contains an aryl fluoride and two phenolic groups.

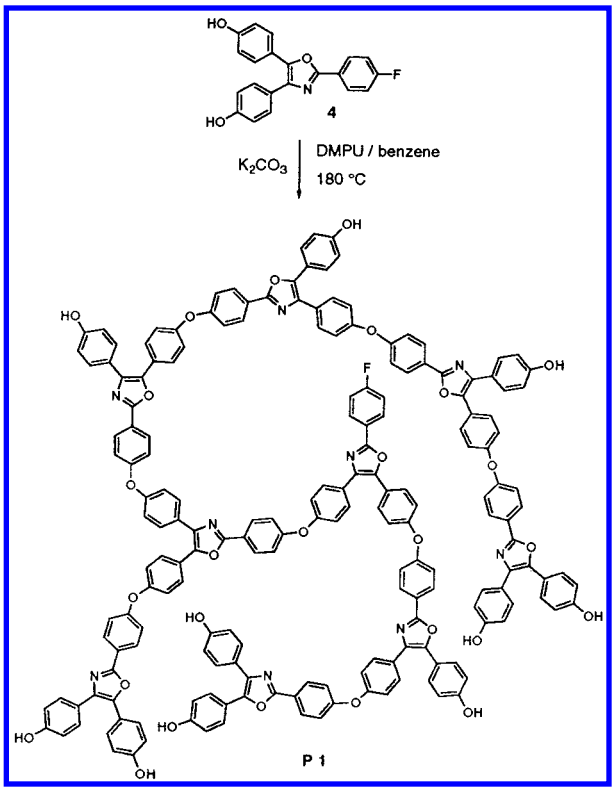
All compounds were characterized by ^1H NMR, ^{13}C NMR, and high-resolution mass spectroscopy. The 4- and 5-positions in the oxazole ring are not identical due to the nonsymmetrical nature of this heterocycle, and therefore the chemical shift of the two hydroxyphenyl groups in **4** are not equal. The ^1H NMR (DMSO-d_6) resonances for the aromatic protons of the two hydroxyphenyl groups overlap somewhat and appear at 7.46, 6.83 ppm and 7.44, 6.80 ppm, respectively, while resonances for the proton of the hydroxyl groups are well-resolved and observed at 9.88 and 9.67 ppm, respectively. Though the two phenolic groups are chemically nonequivalent, their corresponding phenolate anions have similar reactivity undergoing nucleophilic attack under the reaction conditions.

NMR has been used as an indicator for the ability of potential monomers to undergo nucleophilic displacement of the fluorine atom.[16] Both ^{13}C and ^{19}F NMR spectrocopy were used to probe the electron density at the actual site of nucleophilic reaction, i.e., the C−F bond of aryl fluorides. ^{19}F NMR chemical shifts were the most sensitive probe for the reactivity of nucleophilic substitution of aryl fluorides, with a span of 9 ppm between the most activated monomer, 4,4′-difluorophenyl sulfone (−104.28 ppm), and nonactivated fluorobenzene (−112.77 ppm).[16] The ^{19}F NMR of the oxazole monomer **4** is shown in Figure 1 together with that of 4,4-difluorophenyl sulfone and fluorobenzene. The ^{19}F NMR chemical shift of **4** (−109.68 ppm) indicates a downfield shift similar to that of 4,4-difluorophenyl sulfone. The magnitude of the downfield shift is comparable to other polymerizable fluoromonomers activated by heterocyclic rings.[16] The ^{19}F NMR data suggest that the fluorophenyl group in monomer **4** is likely to undergo nucleophilic aromatic substitution.

Scheme 2



Scheme 3



Model Compound Synthesis. To demonstrate the feasibility of the oxazole activated aryl ether synthesis, the reaction of potassium 3,5-di-*tert*-butylphenoxide with **3** was investigated as the model reaction for the polymerization of monomer **4**. As shown in Scheme 2, l equiv of **3** and l equiv of 3,5-di-*tert*-butylphenol were reacted in the presence of anhydrous K_2CO_3 in a solvent mix of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) and benzene under the conditions used for polymerization of **4**. DMPU was chosen as the solvent for polymerization because it has been shown to be an excellent solvent for polyether synthesis.[17] Benzene was used to remove water generated by phenoxide formation during the initial stage through the Dean-Stark trap. Upon completion of phenoxide formation and dehydration, benzene was removed from the system, and the reaction mixture was then heated to 180 °C to effect the displacement reaction. After 3 h, TLC analysis indicated the complete conversion of **3** to **5**, which was in high yield (93%) after column chromatography. The model reaction reveals that the aryl fluoride at the 2-position of the oxazole ring is cleanly substituted by a phenoxide, and this transformation is suitable for a polymer formation reaction.

Synthesis and General Properties of Hyperbranched Poly(aryl ether oxazole) P1. The one-step polymerization of **4** was performed under similar conditions used in the model reaction to give the corresponding hyperbranched poly(aryl ether oxazole) **P1**. High molecular polymer was attained within 10 h as judged by a pronounced increase in viscosity. A schematic

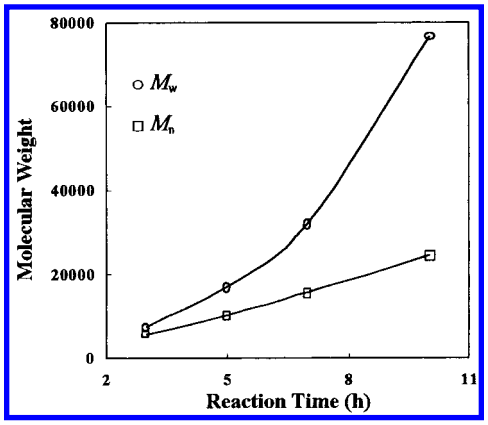
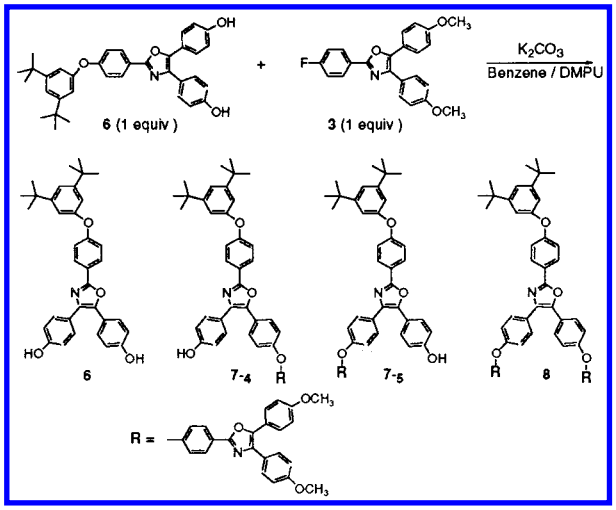


Figure 2. Molecular weight as determined by SEC analysis vs reaction time plot for the polymerization reaction of monomer **4** at 180 °C.

structure of **P1** and the general reaction are shown in Scheme 3. The molecular weight of **P1** was determined by SEC analysis in DMF solution calibrated against linear poly(methyl methacrylate) standards and used only for a rough estimate. Because of the highly branched nature of hyperbranched macromolecules, SEC measurements tend to underestimate the true molecular weight.[18] Figure 2 shows the progression of molecular weight with reaction time for **P1**. There is an increasing gap in the growth of M_n and M_w that leads to broad molecular weight distributions at higher conversions. This observation resembles previous reports of other hyperbranched polymers and is consistent with Flory's predictions on molecular distribution behavior for highly branched system.[19] The glass transition temperature (T_g) of the hyperbranched poly(aryl ether oxazole) was determined by DSC. T_g of **P1** was observed to increase modestly with molecular weight, ranging from 213 to 247 °C with M_w changing from 5600 to 76 500. Thermogravimetric analysis (TGA) was used to measure the thermal stability of **P1**, and because of its high aromaticity, **P1** had high thermal stability. For a sample with M_w = 76 500 and M_w/M_n = 3.1, **P1** lost 5 wt % at 392 °C and an additional 5 wt % at 458 °C.

Degree of Branching. Hyperbranched polymer **P1** was formed by a sequence of condensation of ABB′ monomer, resulting in an irregular dendritic structure. The degree of branching (DB) is an important characteristic often used to reveal the structure of hyperbranched polymers. A combination technique of model compound studies and NMR spectroscopy has been used to quantify the different subunits appearing in the hyperbranched polymer and subsequently determine its DB.[20] Scheme 4 shows the model reaction performed to determine the DB of **P1**. Samples of 1 equiv of compound **6** and 1 equiv of compound **3** were reacted under the same conditions used for polymerization of monomer **4**. After the reaction, TLC analysis indicated that complete conversion of **3** occurred. The model compounds were separated from the reaction mixture by preparative TLC, eluting with CH_2Cl_2/ethyl acetate 20:1. Figure 3 shows the ^{1}H NMR spectra of **6**, which resembles the terminal unit, monoarylated products **7**$_{-4}$ and **7**$_{-5}$, which resemble the linear units, and diarylated product **8**, which resembles the dendritic unit. The peak assignments are based on the peak positions of compounds **3** and **6** as well as the auxiliary of 2D (H,H)-COSY spectra. Because of the nonsymmetrical nature

Scheme 4



of the oxazole ring, there were two different monoarylated products, **7**$_{-4}$ and **7**$_{-5}$. Individual resonances associated with the aromatic protons of **7**$_{-4}$ and **7**$_{-5}$ are indistinguishable, whereas resonances due to the protons of the phenolic groups of **7**$_{-4}$ and **7**$_{-5}$ occur at significantly different positions, 9.92 and 9.72 ppm, respectively. It was reported that in the oxazole ring the charge density at C-5 is more negative than that at C-4.[21] On the basis of the inductive effect, we tentatively assume that the resonance for the proton of the hydroxyl group of **7**$_{-5}$ might appear at upfield 9.72 ppm and that of **7**$_{-4}$ might occur downfield 9.92 ppm. The resonances of two hydroxyl protons of compound **6** are well-resolved and appear at 9.84 and 9.63 ppm. Figure 3 also includes ^{1}H NMR spectra of the reaction mixture obtained directly from the model reaction without further separation and the hyperbranched poly(aryl ether oxazole) **P1**. For the reaction mixture, the relative integration of the peaks for the signal at 9.92, 9.84, 9.72, and 9.63 ppm are 102, 100, 95, and 102 respectively, which indicates the abundance of compounds **6**, **7**$_{-4}$, and **7**$_{-5}$ in the reaction mixture. The fact that almost the same quantity of the two monoarylated products **7**$_{-4}$ and **7**$_{-5}$ were produced in the reaction mixture reveals that the two phenoxide groups attached to the C-5 and C-2 positions of the oxazole ring of compound **6** have almost the same reactivity for undergoing nucleophilic attack under the reaction conditions. Additional comparison of the integration values for the peaks in the regions of 8.4−8.0 and 7.8−7.6 ppm allows the ratio of compounds **6** and **8** in the reaction mix to be obtained, which is 1:1. On the basis of these data, the percentage of compounds **6**, **7**$_{-4}$, **7**$_{-5}$, and **8** in the reaction mixture was calculated as approximately 25% for each compound. Good correlation is observed in the comparison of the ^{1}H NMR spectra of these model compounds with that of the hyperbranched poly(aryl ether oxazole) **P1**. The resonances at 9.92 and 9.71 ppm are attributed to the phenol protons of the two different linear subunits, whereas the resonances at 9.84 and 9.64 ppm are due to the two phenol protons of the terminal subunit. Integration of these resonances allows the relative percentage of each subunit to be determined. The total percentage estimated for the two linear subunits is approximately twice the percentage of the terminal subunit. According to the theoretical prediction, the number of terminal units is equal to the number of dendritic units for an AB_2-type hyperbranched polymer possessing high molecular

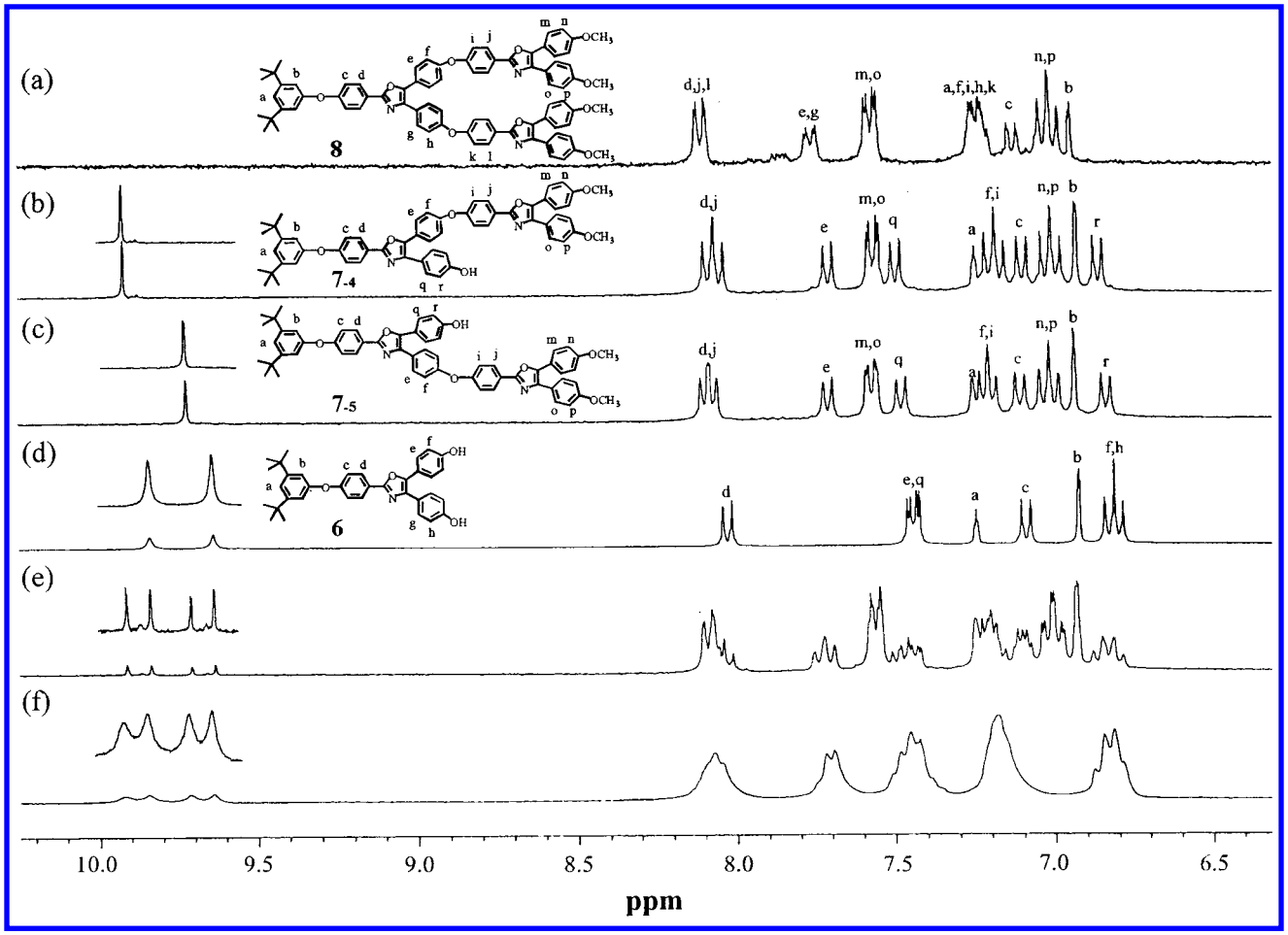


Figure 3. ^{1}H NMR spectra in DMSO-d_6 of model compounds (a) **8**, (b) **7**$_{-4}$, (c) **7**$_{-5}$, (d) **6**, and (e) the reaction mixture obtained directly from the model reaction without further separation, compared with (f) the hyperbranched poly(aryl ether oxazole) **P1**.

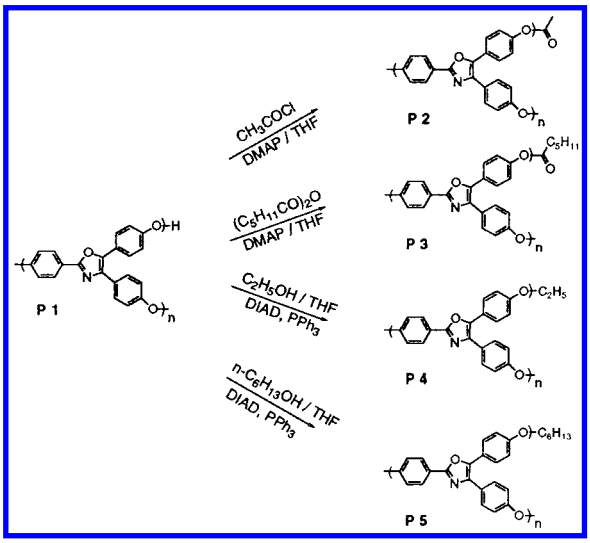
weight.[19,22] The DB is given by[22]

$$\mathrm{DB} = \frac{D + T}{D + L + T} \cong \frac{2T}{2T + L}$$

where D, L, and T represent the fractions of dendritic, linear, and terminal units, respectively. On the basis of this formula, the calculated DB of the hyperbranched poly(aryl ether oxazole) is approximately 50%, which is the statistical value expected for a random AB_2 polycondensation.[22] This value is also in agreement with the ratio of the abundance of the model compounds obtained from the model reaction, which indicates that the reactivity of the nucleophilic substitution for ether linkage formation in the polymerization reaction is independent of molecular size.

Chemical Modification of Hyperbranched Poly(aryl ether oxazole) P1. Unlike linear poly(aryl ether oxazole)s,[12a,d] the hyperbranched polymer **P1** is characterized by a large number of chain end groups. The terminal 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. As shown in Scheme 5, different functional groups could be introduced into **P1** by reactions of the phenolic end groups. For the sake of simplicity, Scheme 5 only shows the overall compositional repeat units, even though each polymer contains a combination of linear units, which could be in the 4- or 5-positions of the oxazole ring, dendritic units, and

Scheme 5



terminal units. The phenolic groups of **P1** were acylated with acid chloride or acid anhydride to give corresponding ester derivatives **P2** and **P3**, respectively. Via the Mitsunobu reactions,[23] the phenolic groups of **P1** were converted to ether groups to yield the ether derivatives **P4** and **P5**. Successful modification of end groups of **P1** could be confirmed by the ^{1}H NMR spectra of the derivatives, which contain alkyl chain ends that exhibit ^{1}H NMR peaks well separated from the peaks associated with aromatic units. Figure 4 shows the ^{1}H NMR

Table 1. Effect of the Functionality of the Chain Ends on the Thermal and Solution Properties of the Hyperbranched Poly(aryl ether oxazole)s

		solubility[a] in					
polymer	T_g (°C)	CH_2Cl_2	$CHCl_3$	THF	DMF	DMSO	CH_3OH/[b] 1 N $NaOH_{(aq)}$[b]
P1[c]	247	−	−	+	+	+	+
P2	197	+	+	+	+ −	−	−
P3	124	+	+	+	+ −	−	−
P4	154	+	+	+	−	−	−
P5	119	+	+	+	−	−	−

[a] Solubility: +, soluble; + −, partially soluble; −, insoluble. [b] Volume ratio 1:1. [c] M_w = 76 500.

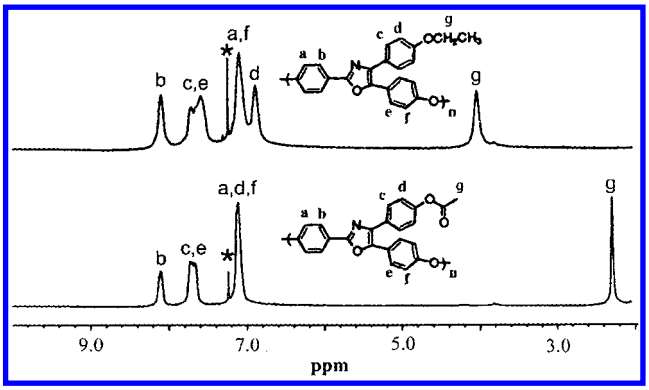


Figure 4. ^{1}H NMR spectra in $CDCl_3$ of the hyperbranched poly(aryl ether oxazole)s **P2** and **P4**. Asterisk: signal due to $CDCl_3$.

spectra of **P2** and **P4**. The conversion of end-capping reaction was calculated by comparing the integration ratio of the protons attributed to the alkyl end groups versus those from the aromatic units. For all the modification reactions above, the use of excess reagents resulted in almost complete (95−100%) functionalization, indicating that the hydroxyl groups at the chain ends are readily accessible to reagents in solution.

The glass transition temperature (T_g) and the solubility of polymers **P1**−**P5** are summarized in Table 1. The T_g values determined by differential scanning calorimetry (DSC) of these polymers are very dependent on the nature of chain ends, which increases with increasing chain-end polarities. The T_g of **P1**, which has polar hydroxyl terminal groups, is 274 °C. The T_g values of **P2** and **P4**, which have less polar terminal groups such as ester and ether groups, are 197 and 154 °C, respectively. A further decrease in T_g to 124 and 119 °C is observed for **P3** and **P5**, respectively, due to increasing length of the alkoxyl chain of the terminal ester or ether groups.

The different chain ends also lead to differences in solubility. The phenolic-terminated polymer **P1** is soluble in a solvent mixture consisting of $NaOH_{(aq)}/CH_3OH$ and in polar solvents such as DMSO and DMF, whereas the ester-terminated polymers **P2** and **P3** are only partially soluble in DMF and insoluble in DMSO, and the ether-terminated polymers **P4** and **P5** are totally insoluble in both polar solvents. Conversely, in relatively nonpolar solvents such as CH_2Cl_2 and $CHCl_3$ polymers **P2**−**P5** are extremely soluble, whereas polymer **P1** is insoluble.

Summary

A hyperbranched poly(aryl ether oxazole) with terminal phenolic groups was prepared by the one-step polymerization of an ABB′ monomer containing an aryl fluoride and two phenolic groups. Though the two phenolic groups are nonequivalent, the reactivity of their phenolates undergoing nucleophilic attack is similar under the applied reaction conditions. The nucleophilic substitution of the fluoride with the phenolate groups, which is activated by the oxazole moiety, resulted in the formation of ether linkage and subsequently the hyperbranched poly(aryl ether oxazole) **P1**. The degree of branching of **P1** as characterized by ^{1}H NMR spectroscopy is approximately 50%. The phenolic groups at the chain ends were readily accessible to reagents in solution and were converted to a variety of functional groups. The nature of the end groups could highly affect the physical properties of the hyperbranched macromolecule.

Acknowledgment. We thank the National Science Council (ROC) (NSC 89-2113-M009-001) for financial support.

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MA000789Y