Synthesis and Characterization of New Hyperbranched Poly(aryl ether oxadiazole)s

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ABSTRACT: A new AB2 monomer was synthesized for use in the preparation of a hyperbranched poly(aryl ether oxadiazole) with terminal phenol functionality. The AB2 monomer contains two phenolic groups and a single aryl fluoride group that is activated toward nucleophilic displacement by the attached oxadiazole ring. The nucleophilic substitution of the fluoride with the phenolate groups led to the formation of an ether linkage. Subsequently, a hyperbranched poly(aryl ether oxadiazole) having approximately a 44% degree of branching, as determined by a combination of model compound studies and 1H NMR, was obtained. The terminal phenolic groups underwent facile functionalization, furnishing hyperbranched polymers with a variety of functional chain ends. The nature of the chain-end groups had a significant influence on the physical properties of the polymers, such as the glass-transition temperature and their solubility. © 2001 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 39: 3851–3860, 2001

Keywords: hyperbranched; poly(aryl ether oxadiazole); AB2 monomer

INTRODUCTION

In view of their unique highly branched structure, which would be expected to confer some unusual properties, hyperbranched polymers have been the subject of considerable interest in recent years.1,2 Although such polymers can be conveniently prepared via the one-pot polymerization of ABn-type monomers, they maintain many of the architectural features and properties found in their more perfectly defined dendrimer counterparts3 that are built up via step-by-step synthetic sequences.4,5 The one-step synthesis allows hyperbranched polymers to be more readily available as well as their preparation on a large scale for potential applications. These attractive features have led to the development of novel synthetic routes for the preparation of such polymers.1,2

Poly(aryl ether)s represent a class of high-performance polymers that possess high thermal stability and good mechanical properties.6 It has been demonstrated that aromatic nucleophilic substitution reactions between activated aryl halide monomers and bisphenolates lead to the formation of linear poly(aryl ether)s.7 Electron-withdrawing groups such as ketones, sulfones, and some heterocycles, which can serve to stabilize the anionic intermediate, are frequently used as activating groups to facilitate the aromatic nucleophilic substitution in the synthesis of these types of polymers.7–11 Recently, these synthetic strategies have been extended to the preparation of hyperbranched poly(aryl ether)s in the one-step polymerization of AB2 monomers that contain activating moieties such as sulfone, ketone, and heterocyclic rings.12,13

It is well known that the high thermal stability and specific properties of aromatic poly(1,3,4-oxadiazole)s are largely due to the 1,3,4-oxadiazole ring.6(b) In this article, we report on a new AB2 monomer that can be used in the one-pot prepa-
EXPERIMENTAL

General Directions

Anhydrous K₂CO₃ was ground into fine powder and dried at 120 °C under vacuum. Anhydrous tetrahydrofuran (THF) was distilled from a sodium diphenyl ketone solution just prior to use. Diisopropyl azodicarboxylate (DIAD) and other starting materials and reagents were used as obtained from the suppliers. NMR spectra were recorded on a Varian Unity 300-MHz or a Bruker-DRX 300-MHz spectrometer, and the solvent peak served as the internal standard. DSC was performed on a Seiko SSC 5200 DSC unit using a heating/cooling rate of 10 °C min⁻¹. Samples were scanned from 25 to 330 °C and then cooled to 25 °C and again scanned for the second time from 25 to 330 °C. The glass-transition temperature was determined from the second heating scan. Thermogravimetric analyses (TGAs) were conducted on a Seiko TG/DTA 200 instrument. The thermal stabilities of the samples were 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 chromatograph, interfaced with 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 (105, 104, and 103 Å) were used with dimethylformamide (DMF)/0.05 M LiBr as the eluent, and poly(methyl methacrylate) standard samples were used for calibration. Mass spectra were obtained on a JEOL JMS-SX/SX 102A mass spectrometer.

3,5-Dimethoxyphenyltetrazole (1)

A mixture of 3,5-dimethoxybenzonitrile (4.60 g, 28.2 mmol), sodium azide (3.00 g, 46.2 mmol), and ammonium chloride (2.47 g, 46.2 mmol) in DMF (35 mL) was heated at 120 °C for 9 h. After cooling, the resulting mixture was poured into water (500 mL) and neutralized with 1 N HCl. The resulting precipitate was collected by filtration, washed with water, and dried to give 1 as a white solid (5.54 g, 95.3%).

³¹H NMR [dimethyl sulfoxide (DMSO-d₆)]: δ 3.82 (s, 6H), 6.70 (t, 1H, J = 2.4 Hz), 7.20 (d, 2H, J = 2.4 Hz). ¹³C NMR (DMSO-d₆): δ 55.5, 102.9, 104.8, 125.7, 155.2, 161.0. High-resolution mass spectrometry (HRMS) [M⁺]: 206.0811. Calcd. 206.0803 for C₉H₁₀O₂N₄.

2-(3,5-Dimethoxyphenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole (2)

To a solution of 1 (4.56 g, 22.1 mmol) in pyridine (10 mL), 4-fluorobenzoyl chloride (3.17 mL, 26.5 mmol) was added dropwise. The reaction mixture was refluxed for 1.5 h and then poured into water (500 mL). The precipitate was filtered off, washed with water, and dried in vacuo to give 2 as a white solid (6.21 g, 93.7%).

³¹H NMR (CDCl₃): δ 3.82 (s, 6H), 6.55 (t, 1H, J = 2.3 Hz), 7.16 (d, 2H, J = 8.9, 8.9 Hz), 7.17 (d, 2H, J = 2.3 Hz), 8.07 (dd, 2H, J = 8.9, 5.2 Hz). ¹³C NMR (CDCl₃): δ 55.7, 104.2, 104.7, 116.4 (d, J₆₋₇ = 22 Hz), 120.2 (d, J₇₋₈ = 3 Hz), 125.3, 129.2 (d, J₈₋₉ = 9 Hz), 161.2, 163.8, 164.6, 164.8 (d, J₉₋₁₀ = 252 Hz). HRMS [M⁺]: 300.0904. Calcd. 300.0910 for C₁₆H₁₃O₃N₂F₂.

5-[5-(4-Fluorophenyl)-1,3,4-oxadiazol-2-yl]-1,3-benzenediol (3)

A mixture of 2 (2.40 g, 8.0 mmol) and pyridine hydrochloride (6.5 g, 56 mmol) was heated at 205 °C for 1.5 h. After cooling to 80 °C, water (50 mL) was slowly added to the reaction mixture. The precipitate was collected by filtration, washed with water, and purified by column chromatography (hexane/EtOAc 3:1) to give 3 as a white solid (1.86 g, 85.7%).

³¹H NMR (DMSO-d₆): δ 6.45 (t, 1H, J = 2.2 Hz), 6.96 (d, 2H, J = 2.2 Hz), 7.46 (dd, 2H, J = 8.9, 8.9 Hz), 8.13 (dd, 2H, J = 8.9, 5.4 Hz). ¹³C NMR (DMSO-d₆): δ 104.6, 106.1, 116.7 (d, J₇₋₈ = 22 Hz), 120.1 (d, J₈₋₉ = 3 Hz), 124.5, 129.3 (d, J₉₋₁₀ = 9 Hz), 159.1, 163.1, 164.1 (d, J₆₋₇ = 250 Hz), 164.2. HRMS [M⁺]: 272.0594. Calcd. 272.0597 for C₁₄H₉O₃N₂F₂.
A mixture of 2 (1.50 g, 5.0 mmol), 3,5-di-tert-butyl phenol (1.55 g, 7.5 mmol), K$_2$CO$_3$ (0.69 g, 5.0 mmol), benzene (1.5 mL), and N-methylpyrrolidone (NMP) (4 mL) was heated at 120 °C. The water that was formed during the reaction was removed by azeotropic distillation and collected in a Dean–Stark trap. After 5 h, the remaining benzene in the reaction mixture was removed by distillation. The reaction mixture was then heated at 160 °C for 5 h, cooled, poured into water (200 mL), and extracted with EtOAc (3 × 100 mL). The combined extracts were dried over Na$_2$SO$_4$, and the solvent was removed in vacuo. The product was purified by column chromatography (hexane/EtOAc 2:1) to give 4 as a white solid (2.19 g, 90.1%).

$^1$H NMR (CDCl$_3$): δ 1.30 (s, 18H), 3.85 (s, 6H), 6.60 (t, 1H, J = 2.3 Hz), 6.92 (d, 2H, J = 1.7 Hz), 7.07 (d, 2H, J = 8.9 Hz), 7.23–7.24 (m, 3H), 8.06 (d, 2H, J = 8.9 Hz). $^{13}$C NMR (CDCl$_3$): δ 31.3, 53.0, 55.6, 104.1, 104.6, 114.4, 117.7, 117.8, 118.6, 125.4, 128.8, 153.1, 154.9, 161.1, 161.3, 164.2, 164. HRMS [M$^+$]: 486.2527. Calcd. 486.2518 for C$_{30}$H$_{34}$O$_4$N$_2$.

A mixture of 4 (1.00 g, 2.13 mmol) and pyridine hydrochloride (3.00 g, 25 mmol) was heated at 210 °C for 5 h. After cooling to 80 °C, water (50 mL) was slowly added to the reaction mixture, and the resulting mixture was extracted with EtOAc (3 × 40 mL). The combined extracts were dried over Na$_2$SO$_4$, and the solvent was removed in vacuo. The product was purified by column chromatography (hexane/EtOAc 2:1) to give 5 as a white solid (0.49 g, 51.9%).

$^1$H NMR (DMSO-d$_6$): δ 1.27 (s, 18H), 6.44 (t, 1H, J = 2.2 Hz), 6.94–6.95 (m, 4H), 7.14 (d, 2H, J = 8.8 Hz), 7.27 (t, 1H, J = 1.6 Hz), 8.06 (d, 2H, J = 8.8 Hz), 9.78 (s, 2H). $^{13}$C NMR (DMSO-d$_6$): δ 31.1, 34.7, 104.5, 106.0, 114.1, 117.6, 117.9, 118.3, 124.6, 128.8, 152.8, 154.5, 159.1, 160.4, 163.5, 163.9. HRMS [M$^+$ + H]: 459.2291. Calcd. 459.2283 for C$_{28}$H$_{31}$O$_4$N$_2$.

Synthesis of Model Compounds 6 and 7

A mixture of 5 (0.40 g, 0.87 mmol), 2 (0.26 g, 0.87 mmol), K$_2$CO$_3$ (0.12 g, 0.87 mmol), benzene (1 mL), and NMP (2 mL) was heated at 120 °C. The water that was formed during the reaction was removed by azeotropic distillation and collected in a Dean–Stark trap. After 5 h, the remaining benzene in the reaction mixture was removed by distillation. The reaction mixture was then heated at 155 °C for 6 h. The resulting mixture was poured into water (50 mL), neutralized with 1 N HCl, and extracted with EtOAc (3 × 30 mL). The combined extracts were dried over Na$_2$SO$_4$, and the solvent was removed in vacuo. The products were purified by column chromatography (CHCl$_3$).

Compound 6: $^1$H NMR (DMSO-d$_6$): δ 1.26 (s, 18H), 3.84 (s, 6H), 6.73–6.76 (m, 2H), 6.93 (d, 2H, J = 1.6 Hz), 7.11 (d, 2H, J = 8.8 Hz), 7.22 (d, 2H, J = 2.3 Hz), 7.24–7.26 (m, 2H), 7.29 (d, 2H, J = 8.9 Hz), 7.35 (t, 1H, J = 1.8 Hz), 8.08 (d, 2H, J = 8.8 Hz), 8.18 (d, 2H, J = 8.8 Hz), 10.35 (s, 1H). $^{13}$C NMR (DMSO-d$_6$): δ 31.0, 34.7, 55.6, 103.9, 104.4, 108.0, 109.5, 110.9, 111.3, 115.8, 118.3, 118.6, 124.9, 125.3, 128.9, 129.1, 152.8, 154.6, 157.2, 159.3, 159.7, 160.5, 161.0, 163.2, 163.6, 163.7, 163.8. HRMS [M$^+$ + H]: 739.3143. Calcd. 739.3131 for C$_{44}$H$_{43}$O$_7$N$_4$.

Compound 7: $^1$H NMR (DMSO-d$_6$): δ 1.26 (s, 18H), 3.84 (s, 12H), 6.73 (t, 2H, J = 2.3 Hz), 6.91 (d, 2H, J = 1.7 Hz), 7.05 (d, 2H, J = 8.9 Hz), 7.17 (t, 1H, J = 2.2 Hz), 7.18 (s, 4H, J = 8.8 Hz), 7.26 (d, 2H, J = 2.2 Hz), 8.08 (s, 2H, J = 8.9 Hz), 8.18 (d, 4H, J = 8.8 Hz). $^1$H NMR (CDCl$_3$): δ 1.30 (s, 18H), 3.86 (s, 12H), 6.62 (t, 2H, J = 2.3 Hz), 6.88 (d, 2H, J = 1.7 Hz), 6.96 (t, 1H, J = 2.2 Hz), 7.05 (d, 2H, J = 8.7 Hz), 7.20 (d, 4H, J = 8.8 Hz), 7.23–7.25 (m, 5H), 7.62 (d, 2H, J = 2.2 Hz), 8.02 (d, 2H, J = 8.9 Hz), 8.15 (d, 4H, J = 8.8 Hz). $^{13}$C NMR (DMSO-d$_6$): δ 31.1, 34.7, 55.6, 103.9, 104.5, 113.0, 114.0, 114.1, 117.2, 117.5, 118.3, 119.0, 119.3, 124.9, 126.6, 129.1, 129.2, 152.2, 154.4, 157.4, 159.0, 160.6, 161.0, 162.6, 163.6, 163.8, 164.2. HRMS [M$^+$ + H]: 1019.3967. Calcd. 1019.3979 for C$_{66}$H$_{55}$O$_{16}$N$_6$.

Synthesis of Model Compound 8

To a solution of 6 (52 mg, 135 μmol), PPh$_3$ (106 mg, 405 μmol), methanol (13 mg, 405 μmol) in anhydrous THF (1 mL), and DIAD (62 mg, 405 μmol) were added dropwise under nitrogen. The reaction mixture was stirred at 25 °C overnight, and the product was purified by preparative thin-layer chromatography (TLC) (EtOAc/CHCl$_3$ 1:4) to give 8 as a white solid.
1H NMR (CDCl₃): δ 1.29 (s, 18H), 3.86 (s, 6H), 3.88 (s, 3H), 6.61 (t, 1H, J = 2.3 Hz), 6.79 (t, 1H, J = 2.3 Hz), 6.90 (d, 2H, J = 1.6 Hz), 7.06 (d, 2H, J = 8.9 Hz), 7.17 (d, 2H, J = 8.9 Hz), 7.23–7.25 (m, 3H), 7.39 (dd, 1H, J = 2.4, 1.2 Hz), 7.49 (dd, 1H, J = 2.4, 1.2 Hz), 8.04 (d, 2H, J = 8.9 Hz), 8.12 (d, 2H, J = 8.8 Hz).

13C NMR (CDCl₃): δ 31.3, 35.0, 55.7, 55.9, 104.2, 104.7, 107.8, 109.3, 110.3, 114.4, 117.5, 117.7, 118.6, 118.8, 119.1, 125.4, 126.3, 128.8, 129.0, 153.1, 154.8, 157.5, 159.8, 161.2, 161.4, 161.5, 163.6, 164.1, 164.4, 164.6.

HRMS [M+H]: 753.3287. Calcd. 753.3288 for C₄₅H₄₅O₇N₄.

Preparation of Hyperbranched Poly(aryl ether oxadiazole) (P1)
A mixture of 3 (2.00 g, 7.35 mmol), K₂CO₃ (2.03 g, 14.7 mmol), benzene (4 mL), and NMP (11 mL) was heated at 120 °C. The water that was formed during the reaction was removed by azeotropic distillation and collected in a Dean–Stark trap. After 5 h, the remaining benzene in the reaction mixture was removed by distillation. The reaction mixture was then heated at 160 °C for 13 h. The resulting mixture was poured into a solution of water (200 mL) and methanol (200 mL) and neutralized with 1 N HCl. The polymer was collected by filtration and purified by precipitation from DMF into methanol to give P1 (1.56 g, 84.1%).

1H NMR (DMSO-d₆): δ 6.40–7.65 (m, 5H), 7.96 (br, 2H), 9.75 (br, 10.23 (br).

Preparation of Hyperbranched Poly(aryl ether oxadiazole) (P2)
To a solution of P1 (210 mg, 0.83 mmol), ethanol (81 mg, 2.5 mmol) and PPh₃ (656 mg, 2.5 mmol) in anhydrous DMF (4 mL) and DIAD (506 mg, 2.50 mmol) were added dropwise under nitrogen. The reaction mixture was stirred at 25 °C for 2 days and then added to a solution of water (25 mL) and methanol (20 mL). The collected polymer was purified by precipitation from CHCl₃ into methanol to give P2 (189 mg, 81.9%).

1H NMR (CDCl₃): δ 2.30 (br, 3H), 6.97 (br, 1H), 7.15 (br, 2H), 7.61 (br, 2H), 8.07 (br, 2H).

Preparation of Hyperbranched Poly(aryl ether oxadiazole) (P3)
P3 was prepared from P1 and 1-hexanol using the same procedure as was used for P2 (168 mg, 74.1%).

1H NMR (CDCl₃): δ 0.87 (br, 3H), 1.31–1.77 (m, 8H), 3.98 (br, 2H), 6.58–6.92 (m, 1H), 7.15 (br, 2H), 7.30–7.62 (m, 2H), 8.09 (br, 2H).

Preparation of Hyperbranched Poly(aryl ether oxadiazole) (P4)
To a solution of P1 (70 mg, 0.28 mmol) and Et₃N (113 mg, 1.12 mmol) in anhydrous DMF (4 mL), acetyl chloride (88 mg, 1.12 mmol) was added dropwise under nitrogen. The reaction mixture was stirred at 25 °C for 2 days and then added to a solution of water (20 mL) and methanol (20 mL). The collected polymer was purified by precipitation from CHCl₃ into methanol to give P4 (71 mg, 86.8%).

1H NMR (CDCl₃): δ 0.87 (br, 3H), 1.31–1.77 (m, 8H), 3.98 (br, 2H), 6.58–6.92 (m, 1H), 7.15 (br, 2H), 7.30–7.62 (m, 2H), 8.09 (br, 2H).

Preparation of Hyperbranched Poly(aryl ether oxadiazole) (P5)
To a solution of P1 (50 mg, 0.20 mmol), 4-(diethylamino)pyridine (97 mg, 0.80 mmol) in anhydrous DMF (3.0 mL) and hexanoic anhydride (171 mg, 0.80 mmol) were added dropwise under nitrogen. The mixture was stirred at 25 °C for 2 days and then added to a solution of water (20 mL) and methanol (20 mL). The collected polymer was purified by precipitation from CHCl₃ into methanol to give P5 (56 mg, 80.3%).

1H NMR (CDCl₃): δ 0.89 (br, 3H), 1.35 (br, 4H), 1.73 (br, 2H), 2.56 (br, 2H), 6.93–7.22 (m, 3H), 7.60–7.75 (m, 2H), 8.10 (br, 2H).

RESULTS AND DISCUSSION

Synthesis and Characterization of the AB₂ Monomer
The synthesis of the AB₂ oxadiazole monomer 3 is outlined in Scheme 1. The oxadiazole derivatives have usually been synthesized according to one of the following two synthetic routes: (1) by ring closure of dihydrazides with dehydrating agents such as phosphorous oxychloride14 and (2) from the reaction of tetrazole with an acid chloride followed by intramolecular ring transformation.15 The relatively high yields and facile workup procedures render the tetrazole route attractive for the preparation of pure oxadiazole derivatives.16 Commercially available 3,5-dimethoxybenzonic acid was treated with sodium azide to give tetra-
zole 1 that was transformed into oxadiazole derivative 2 by reaction with 4-fluorobenzoyl chloride. The subsequent demethylation of 2 with pyridine hydrochloride produced diol monomer 3 containing an activated aryl fluoride suitable for nucleophilic substitution. All compounds were characterized by $^1$H NMR, $^{13}$C NMR, and HRMS.

NMR has been used as an indicator for the ability of potential monomers to undergo nucleophilic displacement of the aryl fluoride. The $^{19}$F NMR chemical shift was 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). Figure 1 shows the $^{19}$F NMR of oxadiazole monomer 3 along with that of 4,4'-difluorophenyl sulfone and fluorobenzene. The $^{19}$F NMR chemical shift of 3 ($-107.20$ ppm) indicates a downfield shift that is closer to 4,4'-difluorophenyl sulfone than that of fluorobenzene. The magnitude of the downfield shift is comparable to other polymerizable fluoro-substituted monomers that are activated by heterocyclic rings. The $^{19}$F NMR data suggest that the fluoro group in monomer 3 is, in all likelihood, undergoing aromatic nucleophilic substitution.

**Model Reaction**

To demonstrate the feasibility of the oxadiazole-activated aryl ether synthesis, the reaction of potassium 3,5-di-tert-butylphenoxide with 2 in a solution of NMP and benzene was examined as a model reaction for the polymerization of monomer 3 (Scheme 2). Water, generated during phenoxide formation, was removed in the form of a benzene azeotrope during the initial stage of the reaction and, subsequently, the remaining benzene was removed from the system. The reaction mixture was then heated at 160 °C for 5 h, and the progress of the reaction was monitored by TLC. The crude product was purified by column chromatography to give compound 4 in quantitative yields. The model reaction reveals that the aryl fluoride at the 2-position of the oxadiazole ring is cleanly substituted by a phenoxide, and this transformation is suitable for use in a polymerization reaction.

**Synthesis and General Properties of Hyperbranched Poly(aryl ether oxazole) P1**

As shown in Scheme 3, the one-step polymerization of monomer 3 was carried out using a proce-
dure similar to that described for the model reaction. The nucleophilic substitution of the fluoride with the phenolic groups, activated by the oxadiazole moiety, led to the formation of an ether linkage and, subsequently, to the hyperbranched poly(aryl ether oxadiazole) $P_1$ with terminal phenolic groups. A high molecular weight polymer was produced within 12 h as judged by a pronounced increase in viscosity. The result of the one-step polymerization of monomer $3$ is summarized in Table I.

The molecular weight of $P_1$ was determined by SEC analysis in DMF solution calibrated against linear poly(methyl methacrylate) standards. Because of the highly irregular, branched nature of hyperbranched macromolecules, SEC analysis does not provide an accurate measurement of molecular weight and tends to underestimate the true molecular weight.\textsuperscript{18} Figure 2 shows the progression of molecular weight with reaction time for $P_1$. There is an increasing gap in the growth of number-average molecular weight ($M_n$) and weight-average molecular weight ($M_w$), leading to broad molecular weight distributions at higher conversions. This observation is consistent with previous reports of other hyperbranched polymers and is in agreement with Flory’s predictions on the molecular distribution behavior for highly branched systems.\textsuperscript{19} The glass-transition temperature ($T_g$) of the hyperbranched poly(aryl ether oxadiazole) was determined by DSC. The $T_g$ value for $P_1$ was observed at 286 °C. TGA was used to measure thermal stability. $P_1$ had a high thermal stability with a 5% weight loss observed at 419 °C, followed by an additional 5% weight loss at 456 °C.

### Table I. Data of the One-Step Polymerization of Monomer 3

<table>
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<th>Reaction Time (h)</th>
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<th>$M_w$ a</th>
<th>$M_w/M_n$</th>
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<td>11,000</td>
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</table>

a Determined by SEC on the basis of poly(methyl methacrylate) standards.

### Degree of Branching

The degree of branching (DB), defined as the sum of dendritic and terminal units versus total units (linear, dendritic, and terminal units), is a typical characteristic frequently used to evaluate the irregularity of the structure of hyperbranched polymers.\textsuperscript{20} A combination technique of model com-

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Reagents: (i) pyridine hydrochloride; (ii) $K_2$CO$_3$, 2, NMP/benzene; (iii) PPh$_3$, CH$_2$OH/THF, D1AD.
pound studies and NMR spectroscopy has been used to quantify the different subunits that appear in the hyperbranched polymer and subsequently to determine its DB. The model reaction performed to determine the DB of P1 is given in Scheme 4. An equimolar reaction of compounds 2 and 5, the demethylated form of 4, was conducted under experimental conditions that were similar to those used earlier for the polymerization of monomer 3. The model compounds were separated from the reaction mixture by preparative TLC and characterized by 1HNMR, 13CNMR, and HRMS. Figure 3 depicts the 1H NMR spectra of compounds 5, 6, and 7 that resemble the terminal unit, the linear unit, and the dendritic unit, respectively. The peaks that are associated with the aromatic protons of P1 are not well resolved, whereas resonances due to hydroxyl protons appear at significantly different positions, 9.75 and 10.23 ppm, respectively. A good correlation is observed in the comparison of the 1H NMR spectrum of P1 with that of model compounds 5 and 6. The resonance at 9.75 ppm is assigned to hydroxyl protons of the terminal subunits, whereas the resonance at 10.23 ppm is assigned to the hydroxyl proton of the linear subunits. The relative integrations of the resonances at 9.75 and 10.23 ppm are 100 and 79, respectively, allowing the relative percentage of each subunit to be determined. According to the theoretical prediction, the number of terminal units is equal to the number of dendritic units for an AB2-type hyperbranched polymer possessing high molecular weight. The DB is given by

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

where D, L, and T represent the fractions of dendritic, linear, and terminal units, respectively. On the basis of this formula, the DB of the hyperbranched poly(aryl ether oxadiazole) P1 was determined to be 44% based on the relative integration of the hydroxyl protons. The DB is lower than the statistical value of 50%, expected for a random AB2 polycondensation. The preference of linear product in the polycondensation reaction may result from steric hindrance because of the two hydroxyl groups of the AB2 monomer that are arranged in a metaorientation on the benzene ring.

By a similar rationale, the DB of the ether derivative P2 (vide infra) that had three well-resolved signals in the region of 6.45–6.98 ppm was also evaluated. Figure 4 represents the 1H NMR spectra of model compounds 4 (terminal), 8 (linear), and 7 (dendritic) as well as polymer P2. A comparison of the 1H NMR spectra of these model compounds with that of P2 allows the resonances corresponding to the dendritic, linear, and terminal subunits of the hyperbranched polymer to be identified. The resonances at 6.56, 6.72, and 6.90 ppm are assigned to the proton of the terminal, linear, and dendritic subunits of the hyperbranched polymer, respectively. The integration of the peak assigned to the terminal units is approximately equal to that of the peak assigned to the dendritic units. This result is consistent with the theoretical prediction that the number of terminal units should be equal to the number of dendritic units for a high molecular weight AB2-type hyperbranched polymer. On the basis of the integration ratio of these protons, the DB of P2 was determined to be 46%, which is in good agreement with the DB of P1.
Hyperbranched polymers are characterized by their large number of chain-end groups. As shown in Scheme 5, different functional groups could be introduced into P1 via reactions of the terminal phenolic groups. Using the Mitsunobu reaction, the phenolic groups of P1 were converted into ether groups to yield the ether derivatives P2 and P3. P1 could also be acrylated with an acid chloride or acid anhydride to give the corresponding ester derivatives P4 and P5. These derivatives contain alkyl chain ends exhibiting 1H NMR peaks that are well separated from the peaks associated with the aromatic units. The conversion of the 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 aforementioned modification reactions, the use of excess reagents resulted in a nearly complete (95–100%) functionalization, indicating that the hydroxyl groups at the chain ends are readily accessible to reagents in solution.

The nature of the end groups influences the physical and chemical properties of the hyperbranched polymers. Table II summarizes the $T_g$ and solubility of polymers P1–P5. It is known that, for hyperbranched polymers, the transition from the polar hydroxyl function to nonpolar aliphatic end groups results in a decrease in $T_g$ because of the reduction in the extent of intermolecular interactions in the polymeric molecules.

The different chain ends also lead to differences in solubility in polar and nonpolar solvents. The phenolic-terminated polymer P1 is soluble in a solution consisting of NaOH(aq)/CH$_3$OH and in polar solvents such as DMSO and DMF. In contrast, the ether-terminated polymers P2 and P3 are only partially soluble in DMF and insoluble in DMSO, and the ester-terminated polymers P4 and P5 are soluble in DMF and insoluble in DMSO. Conversely, polymers P2–P5 are extremely soluble in relatively nonpolar solvents such as CH$_2$Cl$_2$ and CHCl$_3$, whereas polymer P1 is insoluble. Polymers P3 and P5, with longer alkyl chain ends, are soluble in THF, and P3 is even soluble in toluene.

**SUMMARY**

The synthesis of hyperbranched poly(aryl ether oxadiazole)s on the basis of 2-(4-oxyphenyl)-5-
(3,5-dioxyphenyl)-1,3,4-oxadiazole as the repeating unit has been demonstrated. A new AB$_2$ monomer containing two phenolic hydroxyl groups and an oxadiazole ring-activated aryl fluoride was synthesized and used to prepare a phenolic-terminated hyperbranched poly(aryl ether oxadiazole). The $^{19}$F NMR data and the use of the model reaction clearly demonstrated the feasibility of the oxadiazole-activated aryl ether synthesis. Aromatic nucleophilic substitution of the aryl fluoride with the phenolates generated ether linkages and, subsequently, the hyperbranched poly(aryl ether oxadiazole) P1. As determined by a combination of model compound studies and $^1$H NMR integration data, the DB of P1 is approximately 44%. The terminal phenolic groups were readily functionalized, yielding hyperbranched polymers with a variety of functional chain ends. The nature of the chain ends was shown to have a significant effect on physical properties such as the $T_g$ and solubility of the hyperbranched poly(aryl ether oxadiazole)s.

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### Table II. Thermal and Solution Properties of the Hyperbranched Poly(aryl ether oxadiazole)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Toluene</td>
<td>CH$_2$Cl$_2$</td>
</tr>
<tr>
<td>P1</td>
<td>286</td>
<td>–</td>
</tr>
<tr>
<td>P2</td>
<td>183</td>
<td>–</td>
</tr>
<tr>
<td>P3</td>
<td>121</td>
<td>+</td>
</tr>
<tr>
<td>P4</td>
<td>220</td>
<td>–</td>
</tr>
<tr>
<td>P5</td>
<td>146</td>
<td>–</td>
</tr>
</tbody>
</table>

+ = Soluble; ± = partially soluble; – = insoluble.

### REFERENCES AND NOTES


5. (a) Hawk, C. J.; Fréchet, J. M. J. Am Chem Soc 1990, 112, 7638; (b) Miller, T. M.; Neenan, T. X.


