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

FANG-IY WU, CHING-FONG SHU

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

Received 10 June 2001; accepted 20 August 2001

ABSTRACT: A new AB_2 monomer was synthesized for use in the preparation of a hyperbranched poly(aryl ether oxadiazole) with terminal phenol functionality. The AB_2 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 ^{1}H 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); AB_2 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 AB_n-type monomers, they maintain many of the architectural features and properties found in their more perfectly defined dendrimer counterparts[3] 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 AB_2 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 AB_2 monomer that can be used in the one-pot prepa-

Correspondence to: C.-F. Shu (E-mail: shu@cc.nctu.edu.tw)
Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 39, 3851–3860 (2001)

ration of a hyperbranched poly(aryl ether oxadiazole) with terminal phenolic groups. The AB_2 monomer contains an aryl fluoride and two phenolic groups connected by a 1,3,4-oxadiazole ring. Activated by the oxadiazole moiety, the nucleophilic substitution of the fluoride with a phenolic group results in ether linkage, subsequently leading to the formation of the corresponding hyperbranched poly(aryl ether oxadiazole). The phenolic terminal units of this polymer were modified by reaction with several end-capping agents. The effect of the nature of the chain-end groups on the solubility and glass-transition temperature of the hyperbranched polymers was also examined.

EXPERIMENTAL

General Directions

Anhydrous K_2CO_3 was ground into fine powder and dried at 120 °C under vacuum. Anhydrous tetrahydrofuran (THF) was distilled from a sodium diphenyl ketyl 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 chromatographer, 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%).

^{1}H NMR [dimethyl sulfoxide (DMSO-d_6)]: δ 3.82 (s, 6H), 6.70 (t, 1H, J = 2.4 Hz), 7.20 (d, 2H, J = 2.4 Hz). ^{13}C NMR (DMSO-d_6): 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 $C_9H_{10}O_2N_4$.

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%).

^{1}H NMR ($CDCl_3$): δ 3.82 (s, 6H), 6.55 (t, 1H, J = 2.3 Hz), 7.16 (dd, 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). ^{13}C NMR ($CDCl_3$): δ 55.7, 104.2, 104.7, 116.4 (d, $J_{C—F}$ = 22 Hz), 120.2 (d, $J_{C—F}$ = 3 Hz), 125.3, 129.2 (d, $J_{C—F}$ = 9 Hz), 161.2, 163.8, 164.6, 164.8 (d, $J_{C—F}$ = 252 Hz). HRMS [M^+]: 300.0904. Calcd. 300.0910 for $C_{16}H_{13}O_3N_2F$.

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%).

^{1}H NMR (DMSO-d_6): 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). ^{13}C NMR (DMSO-d_6): δ 104.6, 106.1, 116.7 (d, $J_{C—F}$ = 22 Hz), 120.1 (d, $J_{C—F}$ = 3 Hz), 124.5, 129.3 (d, $J_{C—F}$ = 9 Hz), 159.1, 163.1, 164.1 (d, $J_{C—F}$ = 250 Hz), 164.2. HRMS [M^+]: 272.0594. Calcd. 272.0597 for $C_{14}H_9O_3N_2F$.

2-4-[3,5-Di(*tert*-butyl)phenoxy]phenyl-5-(3,5-dimethoxyphenyl)-1,3,4-oxadiazole (4)

A mixture of **2** (1.50 g, 5.0 mmol), 3,5-di-*tert*-butyl phenol (1.55 g, 7.5 mmol), K_2CO_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_2SO_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 $C_{30}H_{34}O_4N_2$.

5-(5-4-[3,5-Di(*tert*-butyl)phenoxy]phenyl-1,3,4-oxadiazol-2-yl)-1,3-benzenediol (5)

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_2SO_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 $C_{28}H_{31}O_4N_2$.

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_2CO_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_2SO_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, 109.8, 114.1, 117.4, 117.8, 118.3, 118.6, 119.1, 124.9, 125.7, 128.9, 129.1, 152.8, 154.5, 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 $C_{44}H_{43}O_7N_4$. 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), 7.08 (d, 2H, *J* = 8.9 Hz), 7.17 (t, 1H, *J* = 2.2 Hz), 7.19 (d, 4H, *J* = 2.3 Hz), 7.24 (t, 1H, *J* = 1.7 Hz), 7.36 (d, 4H, *J* = 8.8 Hz), 7.63 (d, 2H, *J* = 2.2 Hz), 8.08 (d, 2H, *J* = 8.9 Hz), 8.18 (d, 4H, *J* = 8.8 Hz). ^{1}H NMR ($CDCl_3$): δ 1.29 (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, 117.8, 118.3, 119.0, 119.3, 124.9, 126.6, 129.1, 129.2, 152.8, 154.4, 157.7, 159.0, 160.6, 161.0, 162.6, 163.6, 163.8, 164.2. HRMS [M^+ + H]: 1019.3967. Calcd. 1019.3979 for $C_{60}H_{55}O_{10}N_6$.

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.

^{1}H NMR ($CDCl_3$): 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 = 2.1, 1.4 Hz), 7.49 (dd, 1H, J = 2.2, 1.3 Hz), 8.04 (d, 2H, J = 8.9 Hz), 8.12 (d, 2H, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$): 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 $C_{45}H_{45}O_7N_4$.

Preparation of Hyperbranched Poly(aryl ether oxadiazole) (P1)

A mixture of **3** (2.00 g, 7.35 mmol), K_2CO_3 (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%).

^{1}H NMR (DMSO-d_6): 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 PPh_3 (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 (25 mL). The collected polymer was purified by precipitation from $CHCl_3$ into methanol to give **P2** (189 mg, 81.9%).

^{1}H NMR ($CDCl_3$): δ 1.25 (br, 3H), 4.05 (br, 2H), 6.56–6.90 (m, 1H), 7.13 (br, 2H), 7.34–7.56 (m, 2H), 8.06 (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%).

^{1}H NMR ($CDCl_3$): 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 Et_3N (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 $CHCl_3$ into methanol to give **P4** (71 mg, 86.8%).

^{1}H NMR ($CDCl_3$): 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) (P5)

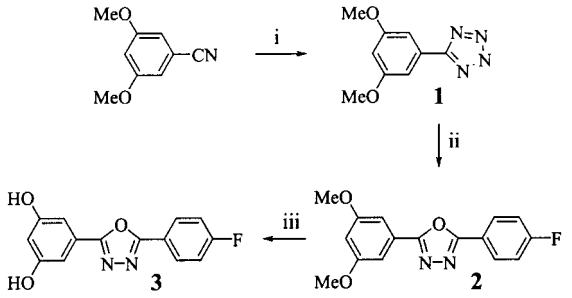
To a solution of **P1** (50 mg, 0.20 mmol), 4-(dimethylamino)pyridine (97 mg, 0.80 mmol) in anhydrous DMF (3.0 mL) and hexanoic anhydride (171 mg, 0.80 mmol) were added dropwise under nitrogen. The mixture was stirred at 25 °C for 2 days and then added to a solution of water (20 mL) and methanol (20 mL). The collected polymer was purified by precipitation from $CHCl_3$ into methanol to give **P5** (56 mg, 80.3%).

^{1}H NMR ($CDCl_3$): 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 AB_2 Monomer

The synthesis of the AB_2 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 oxychloride[14] 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-dimethoxybenzonitrile was treated with sodium azide to give tetra-



Reagents: (i) NaN_3, NH_4Cl/DMF; (ii) 4-fluorobenzoyl chloride/pyridine; (iii) pyridine hydrochloride.

Scheme 1

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.[17] 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,′-difluorophenyl sulfone (−104.28 ppm), and nonactivated fluorobenzene (−112.77 ppm).[17] 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

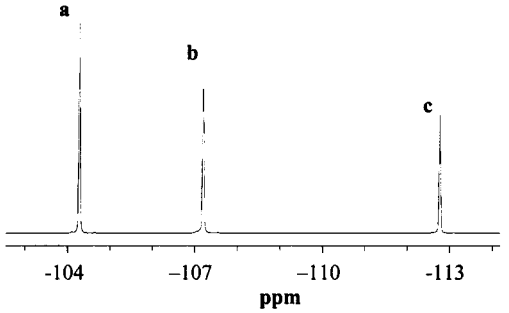
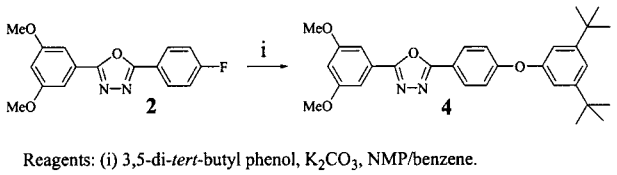


Figure 1. ^{19}F NMR spectra in DMSO-d_6 of a mixture of (a) 4,4′-difluorophenyl sulfone, (b) monomer **3**, and (c) fluorobenzene.



Reagents: (i) 3,5-di-*tert*-butyl phenol, K_2CO_3, NMP/benzene.

Scheme 2

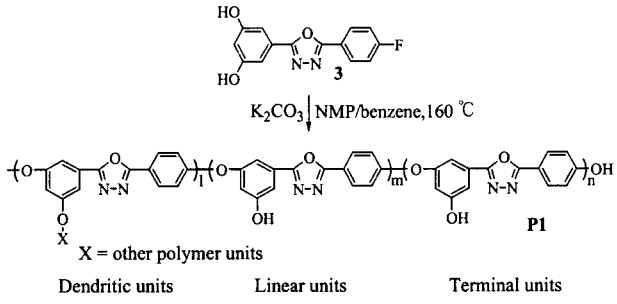
monomers that are activated by heterocyclic rings.[17] The ^{19}F NMR data suggest that the fluoro group in monomer **3** is, in all likelihood, undergoing aromatic nucleophilic substitution.

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-



Scheme 3

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

Reaction Time (h)	M_n[a]	M_w[a]	M_w/M_n
2.5	3,200	3,400	1.06
4.0	3,600	3,900	1.08
5.5	4,200	4,900	1.17
7.0	4,600	5,600	1.22
8.5	5,800	8,400	1.45
10.0	7,000	11,500	1.64
11.5	7,900	14,600	1.85
13.0	8,800	19,800	2.25
14.5	11,000	39,400	3.58

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

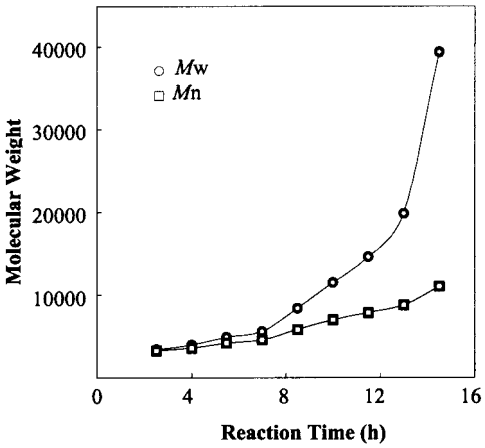
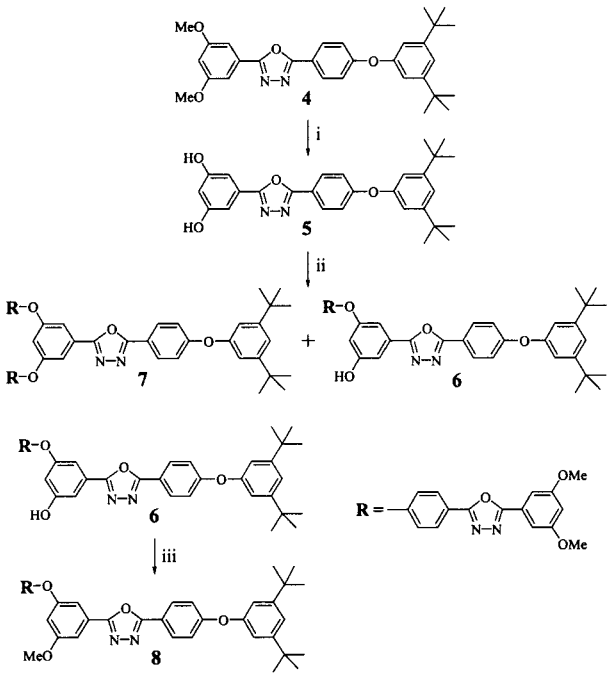


Figure 2. Molecular weight as determined by SEC analysis versus reaction time plot for the polymerization reaction of monomer **3** at 160 °C.

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) **P1** 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 **P1** 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.[18] Figure 2 shows the progression of molecular weight with reaction time for **P1**. 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.[19] The glass-transition temperature (T_g) of the hyperbranched poly(aryl ether oxadiazole) was determined by DSC. The T_g value for **P1** was observed at 286 °C. TGA was used to measure thermal stability. **P1** had a high thermal stability with a 5% weight loss observed at 419 °C, followed by an additional 5% weight loss at 456 °C.

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.[20] A combination technique of model com-



Reagents: (i) pyridine hydrochloride; (ii) K_2CO_3, **2**, NMP/benzene; (iii) PPh_3, CH_3OH/THF, DIAD.

Scheme 4

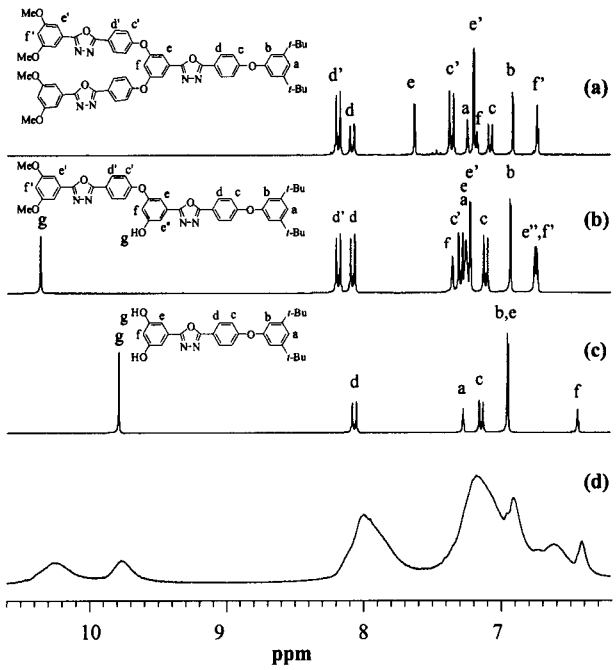


Figure 3. ^{1}H NMR spectra in DMSO-d_6 of model compounds (a) **7**, (b) **6**, and (c) **5** as compared with (d) the hyperbranched poly(aryl ether oxadiazole) **P1**.

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.[20] 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 ^{1}H NMR, ^{13}C NMR, and HRMS. Figure 3 depicts the ^{1}H NMR spectra of compounds **5**, **6**, and **7** that resemble the terminal unit, the linear unit, and the dendritic unit, respectively. The peak assignments were based on the peak positions of compounds **4** and **5** as well as the auxiliary of 2D (H, H) and (C, H)-correlated NMR spectroscopy. Figure 3 also shows the ^{1}H NMR spectrum of the hyperbranched poly(aryl ether oxadiazole) **P1**. 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 ^{1}H 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 AB_2-type hyperbranched polymer possessing high molecular weight.[19,20] The DB is given by[20]

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

where D, L, and T represent the fractions of dendritic, linear, and terminal units, respectively. On the basis of this formula, the 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 AB_2 polycondensation.[21] The preference of linear product in the polycondensation reaction may result from steric hindrance because of the two hydroxyl groups of the AB_2 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 ^{1}H NMR spectra of model compounds **4** (terminal), **8** (linear), and **7** (dendritic) as well as polymer **P2**. A comparison of the ^{1}H 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 with relative integrations of 23.2, 54.1, and 22.7, 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 AB_2-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**.

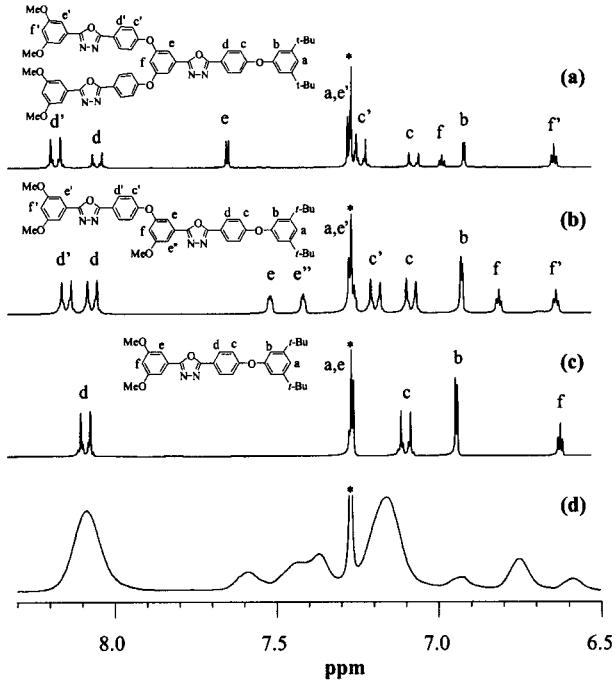


Figure 4. ^{1}H NMR spectra in $CDCl_3$ of model compounds (a) **7**, (b) **8**, and (c) **4** as compared with (d) the hyperbranched poly(aryl ether oxadiazole) **P2**. * Indicates a signal arising from $CHCl_3$.

Chemical Modification of Hyperbranched Poly(aryl ether oxadiazole) P1

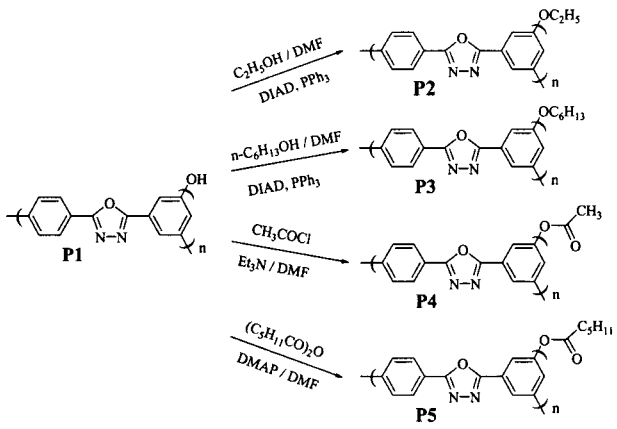
Hyperbranched polymers are characterized by their large number of chain-end groups. As shown in Scheme 5, different functional groups could be introduced into **P1** via reactions of the terminal phenolic groups. Using the Mitsunobu reaction,[22] the phenolic groups of **P1** were converted into ether 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**, respectively. These derivatives contain alkyl chain ends exhibiting ^{1}H 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.[23] 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.[24] Figure 5 indicates DSC thermograms for hyperbranched poly(aryl ether oxadiazole)s **P1**–**P5**. The T_g of **P1** that contains polar hydroxyl terminal groups is 286 °C, whereas the T_g values of **P2** and **P4** that contain less polar terminal groups, namely, ether and ester groups, are 183 and 220 °C, respectively. A further decrease in T_g to 121 and 146 °C is observed for **P3** and **P5**, respectively, because of the increasing length of the alkoxyl chain of the terminal ether or ester groups.

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_3OH 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_2Cl_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-



Scheme 5

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

Polymer	T_g (°C)	Solubility					
		Toluene	CH_2Cl_2	$CHCl_3$	THF	DMF	DMSO
P1	286	−	−	−	−	+	+
P2	183	−	+	+	±	±	−
P3	121	+	+	+	+	±	−
P4	220	−	+	+	±	+	−
P5	146	−	+	+	+	+	−

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

(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 ^1H 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.

The authors thank the National Science Council (ROC) (NSC 89-2113-M009-019) for their financial support.

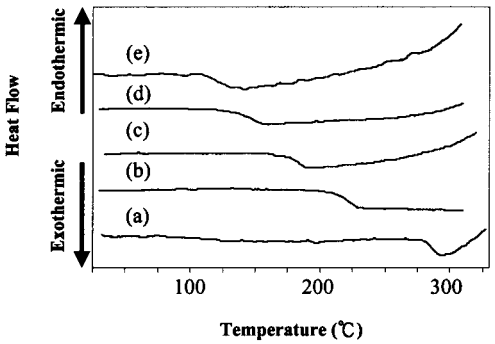


Figure 5. DSC thermograms of hyperbranched poly(aryl ether oxadiazole)s (a) **P1**, (b) **P4**, (c) **P2**, (d) **P5**, and (e) **P3**.

REFERENCES AND NOTES

1. (a) Malmström, E.; Hult, A. J Macromol Sci Rev Macromol Chem Phys 1997, C37, 555; (b) Kim, Y. H. J Polym Sci Part A: Polym Chem 1998, 36, 1685; (c) Voit, B. J. J. Polym Sci Part A: Polym Chem 2000, 38, 2505, and references cited in the reviews.
2. (a) Jayakannan, M.; Ramakrishnan, S. J Polym Sci Part A: Polym Chem 2000, 38, 261; (b) Drohmann, C.; Möller, M.; Gorbatsevich, O. B.; Muzafarov, A. M. J Polym Sci Part A: Polym Chem 2000, 38, 741; (c) Gong, C.; Fréchet, J. M. J. J Polym Sci Part A: Polym Chem 2000, 38, 2970; (d) Lin, Q.; Long, T. E. J Polym Sci Part A: Polym Chem 2000, 38, 3736; (e) Emrick, T.; Chang, H.-T.; Fréchet, J. M. J. J Polym Sci Part A: Polym Chem 2000, 38, 4850; (f) Wu, F.-I.; Shu, C.-F. J Polym Sci Part A: Polym Chem 2001, 39, 0000; (g) Yamanaka, K.; Jikei, M.; Kakimoto, M. Macromolecules 2000, 33, 1111; (h) Paulasaari, J. K.; Weber, W. P. Macromolecules 2000, 33, 2005; (I) Magnusson, H.; Malmström, E.; Hult, A. Macromolecules 2000, 33, 3099; (j) Markoski, L. J.; Thompson, D. S.; Moore, J. S. Macromolecules 2000, 33, 5315.
3. (a) Fréchet, J. M. J. Science 1994, 263, 1710; (b) Advances in Dendritic Molecules, Newkome, G. R., Ed.; JAI: Greenwich, CT, 1994; pp 1–67; Vol. 1; (c) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. Dendritic Molecules: Concepts, Syntheses, Perspectives; VCH: Weinheim, FRG, 1996; pp 1–36; (d) Zeng, F.; Zimmerman, S. C. Chem Rev 1997, 97, 1681; (e) Frey, H.; Lach, C.; Lorenz, K. Adv Mater 1998, 10, 279; (f) Crooks, R. M.; Zhao, M. Q.; Sun, L.; Chechik, V.; Yeung, L. K. Acc Chem Res 2001, 34, 181; (g) Hecht, S.; Fréchet, J. M. J. Angew Chem Int Ed Engl 2001, 40, 74.
4. (a) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. Polym J 1985, 17, 117; (b) Newkome, G. R.; Yao, Z.-Q.; Baker, G. R.; Gupta, V. K. J Org Chem 1985, 50, 2003.
5. (a) Hawker, C. J.; Fréchet, J. M. J. J Am Chem Soc 1990, 112, 7638; (b) Miller, T. M.; Neenan, T. X.

Chem Mater 1990, 2, 346; (c) Xu, Z. F.; Moore, J. S. Angew Chem Int Ed Engl 1993, 32, 1354.
6. (a) Rose, J. B. In High Performance Polymers: Their Origin and Development; Seymour, R. B.; Kirshenbaum, G. S., Eds.; Elsevier: New York, 1986; p 197; (b) Schulz, B.; Brehmer, L. In Polymeric Materials Encyclopedia; Salomone, J. C., Ed.; CRC: Boca Raton, FL, 1996; p 5595.
7. (a) Labadie, J. W.; Hedrick, J. L.; Ueda, M. In Step-Growth Polymers for High-Performance Materials; Hedrick, J. L.; Labadie, J. W., Eds.; ACS Symposium Series 624; American Chemical Society: Washington, DC, 1996; pp 210–225; Chapter 12; (b) Hergenrother, P. M.; Connell, J. W.; Labadie, J. W.; Hedrick, J. L. Poly(Arylene Ether)s Containing Heterocyclic Units. In Advances in Polymer Science: High Performance Polymers; Springer-Verlag: Heidelberg, 1994; Vol. 117, p 67.
8. (a) Attwood, Y. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R.; Rose, J. B.; Staniland, P. A. Polymer 1981, 22, 1096; (b) Singh, R.; Hay, A. S. Macromolecules 1992, 25, 1017; (c) Hay, A. S. Adv Polym Sci 1967, 4, 496.
9. (a) Hedrick, J. L.; Labadie, J. W. Macromolecules 1990, 23, 1561; (b) Hilborn, J. G.; Labadie, J. W.; Hedrick, J. L. Macromolecules 1990, 23, 2854; (c) Carter, K. R.; Miller, R. D.; Hedrick, J. L. Macromolecules 1993, 26, 2209; (d) Strukelj, M.; Hedrick, J. C. Macromolecules 1994, 27, 7511; (e) Bottino, F. A.; Di Pasquale, G.; Leonardi, N.; Pollicino, A. J Polym Sci Part A: Polym Chem 1995, 33, 843.
10. (a) Maier, G.; Hecht, R.; Nuyken, O.; Burger, K.; Helmreich, B. Macromolecules 1993, 26, 2583; (b) Maier, G.; Hecht, R. Macromolecules 1995, 28, 7558; (c) Maier, G.; Schneider, J. M. Macromolecules 1998, 31, 1798.
11. (a) Hedrick, J. L.; Twieg, R. Macromolecules 1992, 25, 2021; (b) Bottino, F. A.; Di Pasquale, G.; Pollicino, A. Macromol Rapid Commun 1999, 20, 405; (c) Bottino, F. A.; Di Pasquale, G.; Pollicino, A. Polym Bull 2000, 45, 345; (d) Bottino, F. A.; Di Pasquale, G.; Iannelli, P. Macromolecules 2001, 34, 33; (e) Hamciuc, C.; Hamciuc, E.; Bruma, M.; Klapper, M.; Pakula, T.; Demeter, A. Polymer 2001, 42, 5955.
12. (a) Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M. J Am Chem Soc 1993, 115, 356; (b) Chu, F.; Hawker, C. J Polym Bull 1993, 30, 265; (c) Hawker, C. J.; Chu, F. Macromolecules 1996, 29, 4370; (d) Martínez, C. A.; Hay, A. S. J Polym Sci Part A: Polym Chem 1997, 35, 2015; (e) Morikawa, A. Macromolecules 1998, 31, 5999.
13. (a) Srinivasan, S.; Twieg, R.; Hedrick, J. L.; Hawker, C. J. Macromolecules 1996, 29, 8543; (b) Hedrick, J. L.; Hawker, C. J.; Miller, R. D.; Twieg, R.; Srinivasan, S. A.; Trollsås, M. Macromolecules 1997, 30, 7607; (c) Gong, Z.-H.; Leu, C.-M.; Wu, F.-I.; Shu, C.-F. Macromolecules 2000, 33, 8527.
14. Klingsberg, E. J Am Chem Soc 1958, 80, 5786.
15. Huisgen, R.; Sauer, J.; Sturm, J. H.; Markgraf, J. H. Chem Ber 1960, 93, 2106.
16. (a) Bettenhausen, J.; Strohriegl, P. Adv Mater 1996, 8, 507; (b) Greczmiel, M.; Strohriegl, P.; Meier, M.; Brütting, W. Macromolecules 1997, 30, 6042.
17. (a) Carter, K. R. Macromolecules 1995, 28, 6462; (b) Carter, K. R. In Step-Growth Polymers for High-Performance Materials; Hedrick, J. L.; Labadie, J. W., Eds.; ACS Symposium Series 624; American Chemical Society: Washington, DC, 1996; Chapter 17; pp 276–291.
18. Hawker, C. J.; Fréchet, J. M. J. J Chem Soc Chem Commun 1990, 1010.
19. Flory, P. J. J Am Chem Soc 1952, 74, 2718.
20. Hawker, C. J.; Lee, R.; Fréchet, J. M. J. J Am Chem Soc 1991, 113, 4583.
21. Hölter, D.; Burgath, A.; Frey, H. Acta Polym 1997, 48, 30.
22. Mitsunobu, O. Synthesis 1981, 1.
23. Hawker, C. J.; Chu, F. Macromolecules 1996, 29, 4370.
24. Schmaljohann, D.; Häuβler, L.; Pötschke, P.; Voit, B. I.; Loontjens, T. J. A. Macromol Chem Phys 2000, 201, 49.