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Hyperbranched Poly(ether ketones): Manipulation of Structure and Physical Properties

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ABSTRACT: Hyperbranched poly(ether ketones), with a variety of chain end functional groups and controllable degrees of branching, are prepared by the polymerization of AB_2, AB_3, and AB_4 monomers. It is found that the choice of A and B, or the incorporation of dendritic and linear units into the AB_x monomer structure, dramatically affects the degree of branching. Depending on the structure of the monomer unit, degrees of branching ranging from 15 to 71% can be obtained. For determining the degree of branching for fluoro-terminated hyperbranched poly(ether ketones), a new technique based on ^{19}F NMR has been developed. Evaluation of the physical properties of the hyperbranched poly(ether ketones) with different degrees of branching has shown that thermal properties are independent of macromolecular architecture but depend heavily on the nature of the chain end functional groups, with glass transition temperatures ranging from 97 to 290 °C. The solubility of the hyperbranched poly(ether ketones) is also shown to depend heavily on the nature of the chain ends, and by varying the chain ends, poly(ether ketones) soluble in either hexane or aqueous solutions could be obtained. The water-soluble derivatives were shown to act as unimolecular micelles.

Introduction

Three-dimensional polymers, such as dendritic and hyperbranched macromolecules, have received considerable attention recently.[1] Though related, there are a number of similarities and differences between these two families of three-dimensional macromolecules. The similarities arise from AB_x monomers being used to prepare both materials. This results in highly branched structures that contain a large number of chain end functional groups. For AB_2 monomers, this value is equal to the degree of polymerization plus one. However, the synthetic approaches employed for both families of macromolecules are distinctly different and this leads to dramatic variation in structure. While the essentially "perfectly" branched and monodisperse dendrimers are prepared by either a step-wise divergent[2] or convergent[3] approach, hyperbranched macromolecules are prepared in a one-step polymerization process that gives irregular and polydisperse structures.[4] A result of this one-step approach is that hyperbranched macromolecules are much more readily available at lower costs than comparable dendritic macromolecules, and this is highly desirable for many applications.

In examining possible applications for dendritic and hyperbranched macromolecules, a number of authors have taken advantage of the many interesting physical properties of these materials. For example, very low melt[5] and intrinsic viscosity[6] values are observed for dendrimers, which suggests that these materials have little, if any, intermolecular entanglements even at high molecular weights. The large number of chain end functional groups present in both dendrimers and hyperbranched macromolecules have also been shown to dramatically affect physical properties such as the glass transition temperature,[7] solubility,[8] and chemical reactivity.[9] Engineering of these unique features can give "dendrimeric boxes" capable of molecular encapsulation,[10] or the shape and functionality of a dendrimer can be controlled to give defined vectors for gene therapy.[11] A number of hyperbranched macromolecules have also been examined for use in coating technologies[12] or as property modifiers for commodity linear polymers.[13]

In this paper we report the synthesis, characterization, and physical properties of a variety of hyperbranched poly(ether ketones) based on a 3,4′,5-trioxybenzophenone repeat unit. The effect of using "isomeric" AB_2 monomers, in which the A and B functional groups are reversed, is examined for the first time. A new concept for manipulating the structure of hyperbranched macromolecules based on the use of AB_x ($x > 2$) monomer units, incorporating dendritic or linear units, is also presented. The physical properties of these hyperbranched poly(ether ketones) are investigated, and the effect of changes in the chain end functional group and the degree of branching are evaluated.

Experimental Section

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer as thin films on NaCl. ^1H NMR spectra were recorded in solution with a Bruker AM 200 (200-MHz) spectrometer, with the TMS proton signal as an internal standard. ^{13}C NMR spectra were recorded at 50 MHz on a Bruker AM 200 (200-MHz) spectrometer with the solvent carbon signal as the internal standard. ^{19}F NMR spectra were recorded on solutions at 188 MHz on a Bruker AM 200 (200-MHz) spectrometer, with the fluorobenzene signal as the internal standard. Mass spectra were obtained on a Kratos MS890 with EI ionization. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica gel for flash chromatography was Merck Kieselgel 60 (230−400 mesh). Size-exclusion chromatography was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer. Four 5-μm Waters columns (300 × 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10^5, and 10^6 Å) were used with THF as the solvent. UV−vis absorption spectra were taken on a Perkin-Elmer UV/vis Lambda 2 spectrometer. Glass transition temperatures (T_g) were recorded on a Perkin-Elmer DSC 7.

3,5-Difluoro-4′-methoxybenzophenone, 7. To a mixture of anisole (2.29 g, 21.0 mmol) and aluminum chloride (3.37 g,

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23.0 mmol) in dry 1,2-dichloroethane (10 mL) was added dropwise 3,5-difluorobenzoyl chloride, **6** (3.00 g, 17 mmol), in 1,2-dichloroethane (5 mL). The reaction mixture was stirred at room temperature under nitrogen for 3 h. Water (10 mL) was added and stirring continued overnight. The reaction mixture was then poured into water (250 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography, eluting with CH_2Cl_2 to give the benzophenone, **7**, as a colorless oil: 88%, IR 1650, 1600, 1350, 1160 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.85 (s, 3H, OCH_3), 6.95 and 7.77 (ABq, 4H, $J = 10$ Hz, ArH), 6.97 (complex t, 1H, $J = 6$ Hz, ArH), 7.22 (complex d, 2H, $J = 6$ Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 55.13, 106.71 (t), 112.21 (q), 113.56, 128.61, 132.20, 141.11 (t), 159.80, 163.51, 164.82 (d), 192.01 (t); mass spectra (EI), m/z 248.

3,5-Difluoro-4′-hydroxybenzophenone, 2. The methoxybenzophenone, 7 (3.00 g, 12.1 mmol), was dissolved in glacial acetic acid (25 mL), 48% HBr (15 mL) was added, and the mixture was heated at reflux for 4 h. The reaction mixture was cooled and evaporated to dryness, water (300 mL) was added, and the mixture was extracted with ether (3 × 50 mL). The combined extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography, eluting with 2:1 CH_2Cl_2/hexane, gradually increasing to CH_2Cl_2 and then to 1:3 ether/CH_2Cl_2. The phenol, **2**, was obtained as an off-white solid: 91%; mp 134−135 °C; IR 3400−3000, 1640, 1595, 1450, 1370, cm^{-1}; ^1H NMR (acetone-d_6) δ 6.94 and 7.71 (ABq, 4H, $J = 8$ Hz, ArH), 7.13 (complex t, 1 H, $J = 6$ Hz, ArH), 7.25 (complex d, 2H, $J = 6$ Hz, ArH); ^{13}C NMR (acetone-d_6) δ 107.02 (t), 112.63 (q), 115.80, 128.23, 132.12, 141.21 (t), 160.46 and 165.42 (ABq), 162.69, 192.21 (t); mass spectra (EI), m/z 234. Anal. Calcd for $C_{13}H_8F_2O_2$: C, 66.7; H, 3.44. Found: C, 66.5; H, 3.40.

3,5-Dimethoxy-4′-fluorobenzhydrol, 10. A solution of 3,5-dimethoxybenzaldehyde, **9** (10.0 g, 60 mmol), in dry THF (20 mL) was added dropwise to a 2.0 M ether solution of 4-fluorophenylmagnesium bromide, **8**, (35 mL, 70.0 mmol). The reaction was then heated at reflux under nitrogen for 2 h. After cooling to room temperature, the reaction was hydrolyzed with water (10 mL) and filtered, and the filtrate was evaporated to dryness. The crude product was purified by flash chromatography, eluting with 1:1 hexane/CH_2Cl_2, increasing to CH_2Cl_2, to give the benzhydrol, **10**, as a colorless oil: 87%; IR 3600-3200, 1600, 1505, 1475, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.75 (d, 1 H, $J = 2$ Hz, OH), 3.73 (s, 6 H, OCH_3), 5.65 (d, 1 H, $J = 2$ Hz, CHOH), 6.34 (t, 1 H, $J = 3$ Hz, ArH), 6.48 (d, 2 H, $J = 3$ Hz, ArH), 6.99 and 7.31 (complex ABq, 4 H, $J = 9$ Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 55.22, 75.38, 99.29, 104.38, 115.15 (d), 128.17 (d), 139.25, 146.10, 159.63, 160.79, 164.51; mass spectra (EI), m/z 262.

3,5-Dimethoxy-4′-fluorobenzophenone, 11. To a mixture of pyridinium chlorochromate (12.9 g, 60 mmol) and sodium acetate (1.50 g) in CH_2Cl_2 (60 mL) was added the benzhydrol, **10** (13.5 g, 51.5 mmol), in CH_2Cl_2 (25 mL). The reaction mixture was stirred under nitrogen at room temperature for 30 min, during which time a thick black oil separated out. The solution was decanted from this oil and the oil washed with CH_2Cl_2. The combined organic layers were evaporated to dryness. The crude product was purified by flash chromatography, eluting with 1:2 hexane/CH_2Cl_2, increasing to CH_2Cl_2, to give the benzophenone, **11**, as a colorless oil: 84%; IR 1650, 1595, 1370, 1175 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.79 (s, 6 H, OCH_3), 6.38 (t, 1 H, $J = 3$ Hz, ArH), 6.85 (d, 2 H, $J = 3$ Hz, ArH), 7.11 and 7.82 (complex ABq, 4 H, $J = 9$ Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 55.46, 104.56, 107.63, 115.32 (d), 132.56 (d), 133.60, 139.23, 160.51, 162.75, 167.83, 194.76; mass spectra (EI), m/z 260.

3,5-Dihydroxy-4′-fluorobenzophenone, 4. The dimethyl ether, **11** (11.0 g, 42.3 mmol), was dissolved in glacial acetic acid (150 mL), 48% HBr (90 mL) was added, and the mixture was heated at reflux under nitrogen for 20 h. The black solution was then cooled, poured into water (500 mL), and extracted with ether (5 × 100 mL). The combined ether extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography, eluting with CH_2Cl_2, gradually increasing to ether, to give the dihydroxy derivative, **4**, as an off-white solid: 91%; mp 142−143 °C; IR 3500-3100, 1640, 1596, 1170 cm^{-1}; ^1H NMR (acetone-d_6) δ 6.62 (t, 1 H, $J = 3$ Hz, ArH), 6.73 (d, 2 H, $J = 3$ Hz, ArH), 7.27 and 7.85 (complex ABq, 4 H, $J = 9$ Hz, ArH); ^{13}C NMR (acetone-d_6) δ 107.14, 108.62, 115.72 (d), 132.94 (d), 134.68, 139.94, 159.02, 163.11, 168.10, 194.80; mass spectra (EI), m/z 232. Anal. Calcd for $C_{13}H_9FO_3$: C, 67.2; H, 3.91. Found: C, 67.1; H, 3.82.

3,5-Difluoro-4′-phenoxybenzophenone, 16. To a mixture of 3,5-difluoro-4′-hydroxybenzophenone, **2** (3.00 g, 12.8 mmol), *N*-methylpyrrolidone (30 mL), and potassium carbonate (3.0 g, 21.7 mmol) was added fluorobenzene (10 g, 104 mmol). The reaction mixture was then heated at reflux under nitrogen for 4 h. Water (500 mL) was added, and the crude product was extracted with ether (4 × 100 mL). The combined extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography, eluting with CH_2Cl_2 to give **16** as an off-white oil: 72%; ^1H NMR ($CDCl_3$) δ 7.04 (d, ArH), 7.07−7.42 (complex, ArH), 7.80 (d, ArH); ^{13}C NMR ($CDCl_3$) δ 1.74 (t), 112.7 (q), 117.2, 120.3, 124.9, 130.1, 130.5, 132.4, 141.2 (q), 155.3, 160.2 and 165.1 (ABq), 162.3, 193.0; ^{19}F NMR ($CDCl_3$) δ −108.2 (s).

3-Fluoro-4′-5-diphenoxybenzophenone, 17. To a mixture of 3,5-difluoro-4′-phenoxybenzophenone, **17**, (2.00 g, 6.45 mmol), *N*-methylpyrrolidone (20 mL), and potassium carbonate (2.0 g, 14.5 mmol) was added phenol (0.60 g, 6.45 mmol). The reaction mixture was heated at reflux under nitrogen for 4 h and cooled, and water (400 mL) was added. The mixture was extracted with ether (4 × 100 mL). The combined extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography, eluting with CH_2Cl_2 to give **17** as an off-white oil: 65%; ^1H NMR ($CDCl_3$) δ 6.85 (t, ArH), 6.90 (t, ArH), 7.02 (d, ArH), 7.04−7.27 (complex, ArH), 7.33−7.47 (complex, ArH), 7.80 (d, ArH); ^{13}C NMR ($CDCl_3$) δ 109.0 (d), 111.0 (d), 115.1, 117.2, 119.7, 120.3, 124.7, 130.1, 130.9, 132.5, 140.7 (d), 155.5 (d), 159.0 (d), 160.5, 162.1, 165.5, 193.4; ^{19}F NMR ($CDCl_3$) δ −109.6 (s).

3,5-Dimethoxy-4′-(phenoxy-d_5)benzophenone, 24. To a mixture of *N*-methylpyrrolidone (20 mL) and toluene (12 mL) was added the dimethyl ether, **11** (1.90 g, 7.31 mmol), phenol-d_6 (1.00 g, 10.6 mmol, 1.45 equiv), and potassium carbonate (1.50 g). The reaction mixture was then heated at reflux for 1.5 h, with water being collected in a Dean-Stark trap. The solution was cooled, water (500 mL) was added, and the mixture was extracted with ether (3 × 50 mL). The combined extracts were dried and evaporated to dryness. To crude product was purified by flash chromatography, eluting with 2:1 hexane/CH_2Cl_2, gradually increasing to CH_2Cl_2, to give the benzophenone, **24**, as a colorless oil: 93%; ^1H NMR ($CDCl_3$) δ 3.81 (s, MeH), 6.65 (t, ArH), 6.89 (d, ArH), 7.01 and 7.83 (ABq, ArH); ^{13}C NMR ($CDCl_3$) δ 55.5, 104.4, 107.6, 117.0, 120.0, 131.7, 132.4, 139.8, 160.5, 161.7, 195.1.

3,5-Dihydroxy-4′-(phenoxy-d_2)benzophenone, 21. The dimethyl ether, **24** (2.50 g, 7.37 mmol), was dissolved in a mixture of glacial acetic acid (100 mL) and HBr (50 mL, 48% aq), and the solution was heated at reflux for 16 h. After cooling, water (500 mL) was added and the mixture was extracted with ether (3 × 50 mL). The combined extracts were then dried and evaporated to dryness. The crude product was purified by flash chromatography, eluting with 1:4 hexane/CH_2Cl_2, gradually increasing to CH_2Cl_2, and then 2:1 ether/CH_2Cl_2 to give **21** as an off white solid: 92%; ^1H NMR ($CDCl_3$) δ 6.50 (t, ArH), 6.58 (d, ArH), 7.06 and 7.77 (ABq, ArH), 7.13 (d, ArH), 7.23 (t, ArH), 9.22 (s, OH); ^{13}C NMR ($CDCl_3$) δ 106.5, 107.7, 117.1, 120.0, 124.6, 130.2 (t), 131.9, 132.2, 139.3, 155.1, 158.5, 160.9, 194.1.

3-Hydroxy-4′-(phenoxy-d_2)-5-(phenoxy-d_5)benzophenone, 22, and 3,5-Bis(phenoxy-d_5)-4′-(phenoxy-d_2)benzophenone, 23. To a mixture of *N*-methylpyrrolidone (20 mL) and toluene (15 mL) was added the diphenol, **21** (0.54 g, 1.75 mmol), potassium carbonate (1.0 g), and copper powder (3.0 g). The mixture was heated at reflux for 1 h, with water collected in a Dean-Stark trap. Bromobenzene-d_5 (0.80 g, 5.1 mmol) was added, and stirring and heating were continued for 2 h. The distillate was then removed until the temperature of the reaction mixture approached 200 °C; heating was continued for 1 h. Water (300 mL) was added, the mixture was extracted with ether (3 × 50 mL), and the combined extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography, eluting with 2:1 hexane/CH_2Cl_2, gradually increasing to CH_2Cl_2, to give the triphenoxy derivative, **23** (0.21 g): 43%; ^{1}H NMR (DMSO-d_6) δ 6.99 and 6.78 (ABq, ArH), 7.08 (d, ArH), 7.11 (s, ArH), 7.22 (t, ArH); ^{13}C NMR (DMSO-d_6) δ 117.0, 117.8, 119.9, 124.5, 127.6, 130.0 (complex), 131.7, 131.9, 144.7, 145.7, 155.1, 156.8, 160.6, 192.1. Further elution with 2:1 ether/hexane then gave the hydroxy derivative, **22** (0.10 g): 22%; ^{1}H NMR (DMSO-d_6) δ 6.64 (complex, ArH), 6.84 (t, ArH), 7.05 and 7.76 (ABq, ArH), 7.12 (d, ArH), 7.23 (t, ArH), 10.10 (s, OH); ^{13}C NMR (DMSO-d_6) δ 108.8, 109.4, 111.3, 117.1, 120.0, 124.6, 130.0 (complex), 131.3, 132.3, 139.7, 155.0, 155.7, 158.2, 158.8, 161.1, 193.7.

3,5-Diphenoxy-4′-methoxybenzophenone, 25. To a mixture of 3,5-difluoro-4′-methoxybenzophenone, **6** (3.00 g, 12.1 mmol), *N*-methylpyrrolidone (30 mL), toluene (20 mL), and potassium carbonate (4.50 g, 32.6 mmol) was added phenol (4.50 g, 47.9 mmol). The reaction mixture was heated at reflux for 2 h, with water being collected in a Dean-Stark trap. After this time, the distillate was removed until the temperature of the reaction mixture had reached ca. 200 °C. Stirring and heating were then continued for 3 h. The reaction mixture was poured into water (600 mL) and extracted with ether (3 × 100 mL). The combined extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography, eluting with 4:1 hexane/CH_2Cl_2, gradually increasing to CH_2Cl_2, to give **25** as an off-white solid: 60%; ^{1}H NMR ($CDCl_3$) δ 3.82 (s, OMe), 6.86 (t, ArH), 6.90 (d, ArH), 7.02−7.13 (complex, ArH), 7.31 (d, ArH), 7.35 (d, ArH), 7.80 (d, ArH); ^{13}C NMR ($CDCl_3$) δ 55.6, 112.0, 113.5, 113.9, 119.2, 124.0, 129.4, 129.9, 132.4, 140.8, 156.1, 158.4, 163.4, 193.0.

3,5-Bis[4-[(3,5-difluorophenyl)carbonyl]phenoxy]-4′-methoxybenzophenone, 26. To a mixture of 3,5-diphenoxy-4′-methoxybenzophenone, **25** (3.90 g, 9.85 mmol), and aluminum chloride (5.0 g, 37 mmol) in 1,2-dichloroethane (30 mL) was added 3,5-difluorobenzoyl chloride, **6** (5.00 g, 28.3 mmol, 2.9 equiv), in 1,2-dichloroethane (10 mL) dropwise at room temperature. The reaction mixture was stirred at room temperature under nitrogen for 4 h. Water (10 mL) was then added and stirring continued for 12 h. The mixture was poured into water (300 mL) and extracted with ether (4 × 100 mL). The combined extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography, eluting with 4:1 hexane/CH_2Cl_2, gradually increasing to CH_2Cl_2 to give **26** as a colorless oil, 75%; ^{1}H NMR ($CDCl_3$) δ 3.81 (s, MeH), 6.96 and 7.77 (ABq, ArH), 7.23 (complex, ArH), 7.29 and 7.89 (ABq, ArH), 7.36−7.52 (complex, ArH), ^{13}C NMR ($CDCl_3$) δ 107.9 (t), 112.8 (d), 113.3 (d), 114.8, 114.9, 116.7, 118.7, 128.1, 132.1, 133.2, 141.6 (t), 142.6, 157.4, 161.4 and 165.5 (ABq), 161.4, 162.5, 192.5, 193.0; ^{19}F NMR ($CDCl_3$) δ −107.9.

3,5-Bis[4-[(3,5-difluorophenyl)carbonyl]phenoxy]-4′-hydroxybenzophenone, 24. The methyl derivative, **26** (5.00 g, 7.40 mmol), was dissolved in a mixture of glacial acetic acid (100 mL) and hydrobromic acid (50 mL, 48%). The reaction mixture was heated at reflux for 6 h and then poured into water (400 mL). The crude product was extracted with ether (4 × 100 mL). The combined extracts were dried, evaporated to dryness, and purified by flash chromatography, eluting with 2:1 hexane/CH_2Cl_2, gradually increasing to 8:1 CH_2Cl_2/ether. Recrystallization from a mixture of tetrahyrofuran and diethyl ether gives **24** as a white solid: 56%; ^{1}H NMR ($CDCl_3$) δ 6.91 (d, ArH), 7.23 (complex, ArH), 7.29 (d, ArH), 7.36 (t, ArH), 7.38 (t, ArH), 7.42 (t, ArH), 7.47 (t, ArH), 7.51 (t, ArH), 7.74 (d, ArH), 7.89 (d, ArH), 10.45 (s, OH); ^{13}C NMR ($CDCl_3$) δ 107.8 (t), 112.8 (q), 114.6, 115.7, 116.4, 118.4, 127.6, 131.6, 132.9, 141.2 (t), 142.2, 157.0, 161.0, 163.0, 160.2 and 165.1 (ABq), 192.1, 192.7; ^{19}F NMR ($CDCl_3$) δ −108.2.

3-Fluoro-5-phenoxy-4′-methoxybenzophenone, 28. To a mixture of 3,5-difluoro-4′-methoxybenzophenone, **7** (2.50 g, 10.1 mmol), *N*-methylpyrrolidinone (15 mL), and toluene (15 mL) was added phenol (1.10 g, 11.7 mmol) and cesium carbonate (3.90 g, 12.0 mmol). The reaction mixture was heated at reflux for 2 h, and water was collected in a Dean-Stark trap. Water (500 mL) was added, and the mixture was extracted with dichloromethane (3 × 100 mL). The combined extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography, eluting with CH_2Cl_2 to give **28** as a colorless oil: 50%; ^{1}H NMR ($CDCl_3$) δ 3.84 (s, MeH), 6.84 (t, ArH), 6.89 (t, ArH), 6.93 and 7.80 (ABq, ArH), 7.03−7.18 (complex, ArH), 7.32−7.41 (complex, ArH); ^{13}C NMR ($CDCl_3$) δ 55.5, 108.8 (d), 110.9 (d), 113.7, 114.9 (d), 119.7, 124.5, 129.2, 130.1, 132.5, 141.1 (d), 155.7, 158.9, 163.6, 160.5 and 165.4 (d), 193.3; ^{19}F NMR ($CDCl_3$) δ −109.7.

3-[4-[(3,5-Difluorophenyl)carbonyl]phenoxy]-5-fluoro-4′-methoxybenzophenone, 29. To a mixture of the methyl ether, **28** (1.60 g, 4.97 mmol), and aluminum chloride (1.0 g, 7.5 mmol) in 1,2-dichloroethane (10 mL) was added 3,5-difluorobenzoyl chloride, **6** (1.20 g, 7.10 mmol), in 1,2-dichloroethane (5 mL) dropwise at room temperature under nitrogen. The mixture was then stirred at room temperature under nitrogen for 3 h. Water (10 mL) was added dropwise, the reaction mixture was stirred overnight and then poured into water (500 mL). The crude product was extracted with ether (3 × 100 mL), and the combined extracts were dried and evaporated to dryness. Purification by flash chromatography, eluting from CH_2Cl_2, gradually increasing to 2:1 CH_2Cl_2/ether, gave **29** as a colorless oil: 65%; ^{1}H NMR ($CDCl_3$) δ 3.87 (s, MeH), 6.95 and 7.80 (ABq, ArH), 7.00−7.07 (complex, ArH), 7.15 and 7.86 (ABq, ArH), 7.28 (complex, ArH); ^{13}C NMR ($CDCl_3$) δ 55.8, 107.8 (t), 111.0 (d), 113.2 (q), 114.5, 116.8, 118.5, 129.4, 132.1, 133.0, 141.0 (t), 142.0 (d), 157.0 (d), 160.9, 160.8 and 165.8 (d), 160.5 and 165.5 (ABq), 192.3, 192.8; ^{19}F NMR ($CDCl_3$) δ −108.7, 107.9.

3-[4-[(3,5-Difluorophenyl)carbonyl]phenoxy]-5-fluoro-4′-hydroxybenzophenone, 30. The methyl ether derivative, **29** (1.50 g, 3.25 mmol), was dissolved in glacial acetic acid (20 mL) and hydrobromic acid (15 mL, 48%). The mixture was heated at reflux under N_2 for 5 h. Water (400 mL) was added, and the mixture was extracted with ether (4 × 100 mL). The combined extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography, eluting with CH_2Cl_2/hexane 4:1, gradually increasing to CH_2Cl_2/ether 1:2, to give **30** as a colorless liquid: 83%; ^{1}H NMR ($CDCl_3$) δ 6.99 and 7.78 (ABq, ArH), 7.15 and 7.86 (ABq, ArH), 7.04−7.09 (complex, ArH), 7.28 (complex, ArH), 8.84 (s, OH); ^{13}C NMR ($CDCl_3$) δ 108.1 (t), 111.1 (d), 113.2 (q), 116.1 116.9, 118.5, 128.3, 132.0, 133.6, 133.8, 141.0 (t), 141.9 (d), 156.7 (d), 161.0, 162.1, 160.5 and 165.5 (d), 160.2 and 165.2 (ABq), 193.7, 194.0; ^{19}F NMR ($CDCl_3$) δ −108.5, −107.7.

General Procedure for the Preparation of Fluoro-Terminated Hyperbranched Poly(ether ketone), 3. To a mixture of 3,5-difluoro-4′-hydroxybenzophenone, **2**; (3.00 g, 12.8 mmol), and potassium carbonate (2.80 g) were added dry *N*-methylpyrrolidone (20 mL) and dry toluene (15 mL). The reaction mixture was then heated at reflux under nitrogen for 3 h, with the water being collected in a Dean-Stark trap. After this time, the distillate was collected and removed until the temperature of the reaction mixture had reached ca. 200 °C. Stirring and heating were then continued for 3 h. The reaction mixture was poured into water (800 mL), and the precipitate was collected and reprecipitated twice from THF into methanol (500 mL). This gave the fluoro-terminated hyperbranched poly(ether ketone), **3**, as an off-white solid: 91%; IR 1660, 1595, 1350, 1260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.90−7.25 (complex m, 5 H), 7.65 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 106.7, 108.1, 110.5, 113.9, 114.7, 117.1, 129.9, 130.8, 140.1, 157.6, 159.4, 159.9, 192.6. Anal. Calcd for $C_{13}H_7FO_2$: C, 72.9; H, 3.30. Found: C, 72.8; H, 3.35.

Preparation of Phenolic-Terminated Hyperbranched Poly(ether ketone), 5. This was prepared from 3,5-dihydroxy-4′-fluorobenzophenone, **4**, using a procedure similar to that above. The crude product was purified by initial precipitation into water (pH = 1) followed by reprecipitation from THF into 1:2 hexane/ether twice. This gave the phenolic-terminated hyperbranched poly(ether ketone), **5**, as an off-white solid: 84%; IR 3500-3100, 1640, 1600, 1360, 1210 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.48 (br s), 6.56 (br s), 6.76, 6.84, and

6.96 (br s), 7.18 and 7.82 (d), 10.22 (br s); ^{13}C NMR (DMSO-d_6) δ 107.58, 110.42, 110.91, 112.76, 117.78, 131.65, 132.33, 139.91, 156.22, 158.37, 158.94, 160.40, 193.47. Anal. Calcd for $C_{13}H_8O_3$: C, 73.6; H, 3.80. Found: C, 73.3; H, 4.04.

Linear Poly(4-oxybenzophenone), 34. To a mixture of *N*-methylpyrrolidone (20 mL) and toluene (15 mL) was added 4-fluoro-4′-hydroxybenzophenone, **1** (3.00 g, 13.9 mmol), and potassium carbonate (2.80 g, 20.1 mmol). The mixture was stirred at reflux under N_2 for 2 h, with water being collected in a Dean-Stark trap. The distillate was then removed from the trap until the temperature reached a ca. 200 °C. Stirring was continued for another 2 h at this temperature. The mixture was poured into water (500 mL), filtered, and dried to give **34** as an off-white solid: 94%.

General Procedure for Functionalization of Fluoro-Terminated Hyperbranched Poly(ether ketone): *p*-(Methyl)phenoxy-Terminated Poly(ether ketone), 38. To a mixture of dry *N*-methylpyrrolidone (20 mL) and dry toluene (15 mL) were added 3,5-difluoro-4′-hydroxybenzophenone, **3** (3.00 g, 12.8 mmol), and potassium carbonate (2.8 g, 20 mmol). The reaction mixture was then heated at reflux under nitrogen for 3 h, with water being collected in a Dean-Stark trap. After this time, the distillate was collected and removed from the trap until the temperature of the reaction mixture reached ca. 200 °C. Stirring and heating was then continued for another 3 h when *p*-cresol (7.80 g, 72.2 mmol), K_2CO_3 (5 g), NMP (5 mL), and toluene (12 mL) were added. The mixture was stirred at reflux for 1.5 h. Collected distillate was removed from the trap, and the reactants were stirred and heated for 2 h and poured into water (500 mL). The precipitate was filtered out, washed with hot water four times, and reprecipitated from THF into a mixture of 2:1 ether/hexane to give **38** as an off-white solid: 85%; ^{1}H NMR ($CDCl_3$) δ 2.33, 6.98, 7.15, 7.73; ^{13}C NMR ($CDCl_3$) δ 32.8, 117.5, 119.8, 120.2, 130.5, 132.5, 135.0, 141.5, 157.6, 159.8, 160.3, 160.5, 160.9, 193.3.

***p*-(Ethoxycarbonyl)phenoxy-Terminated Hyperbranched Poly(ether ketone), 39.** The polymer, **39**, was prepared from 3,5-difluoro-4′-hydroxybenzophenone, **2**, and ethyl *p*-hydroxybenzoate using the same procedure as for **38**: 89%; ^{1}H NMR ($CDCl_3$) δ 1.35, 4.34, 7.04, 7.20, 7.80, 8.03; ^{13}C NMR ($CDCl_3$) δ 14.3, 61.8, 110.7, 113.0, 115.9, 118.7, 119.0, 131.9, 132.6, 141.0, 157.5, 159.7, 160.2, 160.9, 160.6, 166.0, 193.0.

Benzophenone-Terminated Hyperbranched Poly(ether ketone), 31a. The poly(ether ketone), **31a**, was prepared from 3,5-difluoro-4′-hydroxybenzophenone, **2**, and 4-hydroxybenzophenone using the same procedure as for **38**: 91%; ^{1}H NMR ($CDCl_3$) δ 6.90, 7.27, 7.57, 7.64; ^{13}C NMR ($CDCl_3$) δ 114.7, 116.0, 116.6, 118.0, 119.0, 119.5, 128.4, 129.9, 132.6, 138.9, 141.7, 157.8, 159.9, 160.5, 161.0, 162.2, 176.0, 193.8, 196.0.

Octyloxy-Terminated Hyperbranched Poly(ether ketone), 32. The polymer, **32**, was prepared from 3,5-difluoro-4′-hydroxybenzophenone, **2**, and potassium octoxide using the same procedure as for **38** except that the product was purified by precipitation into methanol: 71%; ^{1}H NMR ($CDCl_3$) δ 1.29 (complex), 4.00 (complex), 6.64, 6.78, 6.88, 7.03, 7.10, 7.49, 7.83; ^{13}C NMR ($CDCl_3$) δ 13.83, 22.42, 25.78, 29.11, 31.58, 67.64, 114.03, 115.22, 119.3, 128.1, 129.8, 132.6, 140.8, 158.2, 160.2, 161.9, 193.4.

***p*-(Carboxyl)phenoxy-Terminated Hyperbranched Poly(ether ketone), 33.** The polymer, **33**, was obtained by heating a mixture of the ester-terminated polymer, **39** (10.0 g, 26.5 mmol equiv), tetrahydrofuran (50 mL), methanol (20 mL), water (50 mL), and potassium hydroxide (5.0 g, 91 mmol) at reflux for 10 h. The tetrahydrofuran and methanol were removed by evaporation, and water (50 mL) was added, followed by heating at reflux for 4 h. The mixture was then cooled and acidified with hydrochloric acid. The precipitate was filtered out and washed with distilled water (3 × 100 mL) to give the carboxylic acid derivative, **33**, as an off-white solid: 85%; ^{1}H NMR (acetone-d_6 and D_2O) δ 6.24, 6.42, 6.90, 7.60, 7.88; ^{13}C NMR (acetone-d_6 and D_2O) δ 114.0, 117.8, 118.6, 119.3, 120.4, 130.6, 131.6, 131.9, 133.8, 140.8, 157.4, 160.8, 173.1, 193.6. Neutralization with aqueous sodium hydroxide followed by removal of the water and drying gave the carboxylate salt, **40**.

General Procedure for Functionalization of Phenolic-Terminated hyperbranched Poly(ether ketone): Benzoyl-Terminated Poly(ether ketone), 36. The phenolic-terminated poly(ether ketone), **5** (2.00 g, 9.40 mmol), was dissolved in dry tetrahydrofuran (30 mL), and benzoyl chloride (1.82 g, 12.9 mmol, 1.5 equiv) and (dimethylamino)pyridine (1.74 g, 14.3 mmol, 1.65 equiv) were added. The solution was stirred at room temperature under N_2 for 4 h and then heated at reflux for 2 h. The reaction mixture was poured into water (300 mL), and the precipitate was filtered out and dried. The crude product was purified by precipitating from THF into water and then hexane to give **41** as an off-white solid: 83%; ^{1}H NMR ($CDCl_3$) δ 7.13, 7.20, 7.45, 7.60, 7.90, 8.15; ^{13}C NMR ($CDCl_3$) δ 117.3, 118.1, 119.4, 128.7, 130.2, 132.0, 132.7, 134.0, 140.3, 151.7, 156.5, 160.7, 164.6, 193.1.

Acetate-Terminated Hyperbranched Poly(ether ketone), 35. The poly(ether ketone), **42**, was produced from the phenolic-terminated poly(ether ketone), **5**, and acetyl chloride using the same procedure as for **41**: 85% ^{1}H NMR ($CDCl_3$) δ 2.30, 6.63, 6.76, 6.86, 7.01, 7.06, 7.10, 7.79, 7.84: ^{13}C NMR ($CDCl_3$) δ 21.5, 108.3, 111.3, 111.8, 113.7, 117.3, 131.6, 132.2, 140.0, 156.2, 158.5, 159.0, 161.2, 194.1.

Benzophenone-Terminated Hyperbranched Poly(ether ketone), 31b. The poly(ether ketone), **31b**, was prepared from 3,5-dihydroxy-4′-fluorobenzophenone, **4**, and 4-fluorobenzophenone using the same procedure as for **38**: 88%; ^{1}H NMR ($CDCl_3$) δ 7.09, 7.13, 7.46, 7.49, 7.74, 7.84; ^{13}C NMR ($CDCl_3$) δ 114.8, 116.8, 118.0, 118.5, 121.8, 128.3, 131.4, 132.4, 133.1, 137.5, 141.0, 157.0, 160.7, 193.4, 195.3.

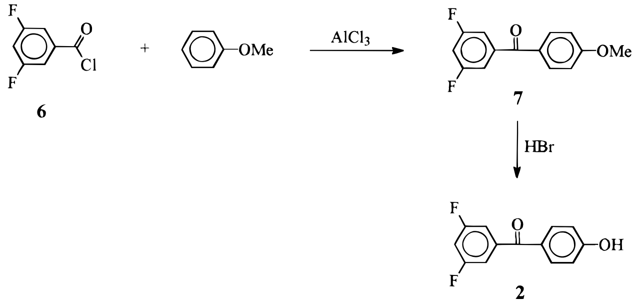
Results and Discussion

The synthetic procedure used for the one-step synthesis of hyperbranched poly(ether ketone)s is derived from a reaction developed by McGrath[14] for the preparation of linear poly(arylene ether nitriles). In this procedure, the polymeric linkages are formed by reaction of a phenolic group with an activated aryl fluoride in the presence of a suitable base such as potassium carbonate. A solvent mixture of *N*-methylpyrrolidinone and toluene is initially employed to remove the water formed during the reaction, thus promoting polymer formation.

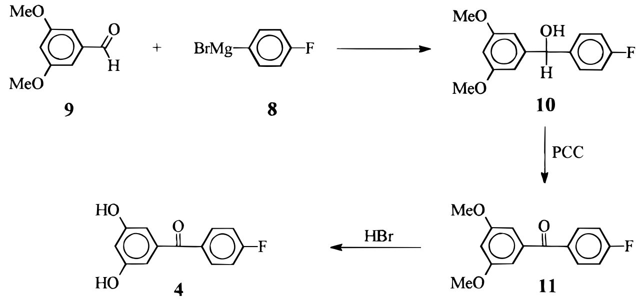
In designing monomer units compatible with the above synthetic strategy, we encountered a characteristic of hyperbranched and dendritic macromolecules. Unlike the synthesis of linear polymers from AB monomers, where the choice of A and B is not important since the groups are interchangeable, polymerization of AB_2 monomers gives different hyperbranched macromolecules depending on the nature of A and B. Therefore, while 4-fluoro-4′-hydroxybenzophenone, **1**, is the AB monomer for linear poly(ether ketone), the synthesis of the corresponding hyperbranched poly(ether ketone) can be accomplished from two distinctly different AB_2 monomers. Polymerization of 3,5-difluoro-4′-hydroxybenzophenone, **2**, gives the fluoro-terminated hyperbranched poly(ether ketone), **3**, while 3,5-dihydroxy-4′-fluorobenzophenone, **4**, gives the phenolic-terminated hyperbranched poly(ether ketone), **5**. To determine the effect of "switching" the A and B functionalities on the physical properties and structure of the hyperbranched poly(ether ketones), the synthesis and polymerization of both AB_2 monomers was examined.

The synthesis of 3,5-difluoro-4′-hydroxybenzophenone, **2**, starts from the commercially available 3,5-difluorobenzoyl chloride, **6**, and is outlined in Scheme 1. The desired difluoro monomer, **2**, was obtained in 80% overall yield after purification. The synthesis of the "inverted" AB_2 monomer 3,5-dihydroxy-4′-fluorobenzophenone, **4**, was accomplished by reaction of the

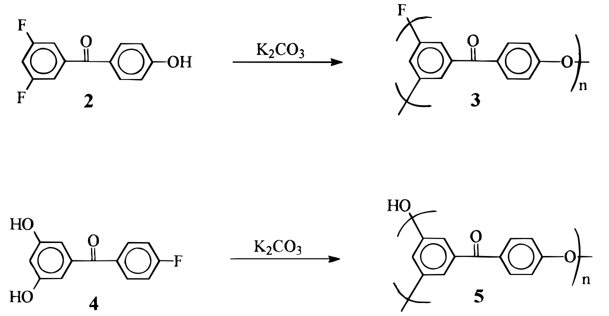
Scheme 1



Scheme 2



Scheme 3



Grignard reagent, **8**, with 3,5-dimethoxybenzaldehyde, **9**, followed by oxidation and deprotection (Scheme 2).

As mentioned previously, the polymerization conditions of choice were similar to those reported by McGrath.[14] In the case of **2**, this gave the fluoro-terminated hyperbranched poly(ether ketone), **3**, in 91% yield which was shown to have a polystyrene equivalent molecular weight, M_n, of 20 000 (PD = 1.8). In contrast, polymerization of **4** gave the corresponding phenolic-terminated hyperbranched poly(ether ketone), **5**, in 84% yield (M_n = 43 000; PD = 2.2). It should be noted that due to the highly branched nature of dendritic and hyperbranched macromolecules, the molecular weights determined by polystyrene standards have been shown to underestimate true molecular weights.[15] As shown graphically in Scheme 3 the internal repeat units of **3** and **5** are the same but the macromolecules differ in the nature of their end groups and potentially in their degree of branching.

The concept of degree of branching, or DB, in hyperbranched macromolecules, was introduced to better define the structure of these unusual polymers.[15,16] Unlike dendritic macromolecules, which are essentially perfectly branched and have a degree of branching approaching 100%, hyperbranched macromolecules have a much more irregular structure. This is due to the one-step synthetic strategy used in their synthesis. Theoretically, such an approach can lead to degrees of branching anywhere from 0% to 100%. For a complete

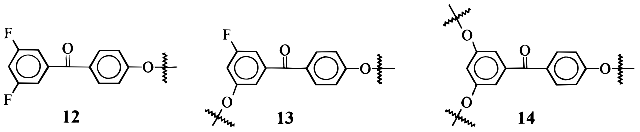
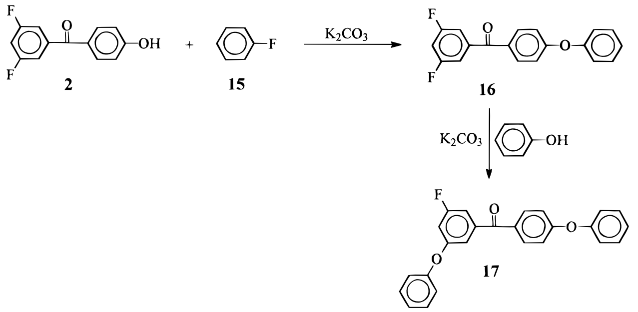


Figure 1. Structure of repeat units in fluoro-terminated hyperbranched poly(ether ketone) **3**.

Scheme 4



understanding of these materials, it is therefore very important that the degree of branching for hyperbranched macromolecules be determined. Determination of the degree of branching for the hyperbranched macromolecules, **3** and **5**, will allow some insight into the effect of monomer structure on DB.

For **3** consideration of the overall structure reveals three different types of subunits (Figure 1). These include “terminal”, **12**, with two fluoro groups; “linear”, **13**, which has one fluoro group; and “dendritic”, **14**, which has no fluoro groups. A fundamental difference between the three subunits is therefore the number of fluoro groups. The chemical environment of the fluorine atoms of **12** and **13** will be substantially different, allowing the relative percentage of **12** and **13** to be evaluated by ^{19}F NMR spectroscopy. To determine the feasibility of this approach, model compounds for both the terminal and linear subunits were synthesized. Examination of the ^{19}F NMR spectra for these models, in comparison with the ^{19}F NMR spectrum of the fluoro-terminated hyperbranched poly(ether ketone), should allow the resonance for the linear and terminal subunits to be identified and quantified.

The model compounds **16** and **17** were prepared as outlined in Scheme 4. Examination of the ^{19}F NMR spectra of **16** and **17** showed a distinct difference (Figure 2). The two fluorine atoms of **16** are equivalent and appear as a sharp singlet at −108.1 ppm while the single fluorine atom of **17** appears at −109.5 ppm. When compared with the ^{19}F NMR spectrum of **3**, the resonance at lowest field (−107.7 ppm) can be assigned to the terminal subunits while the resonance at highest field (−108.4 ppm) is due to linear subunits. Integration allows the relative percentage of linear and terminal subunits in **3** to be determined.

We now consider the definition for degree of branching:

$$\mathrm{DB} = \frac{(\text{no. of dendritic units}) + (\text{no. of terminal units})}{\text{total number of units}} \qquad (1)$$

Since the number of dendritic units is theoretically equal to the number of terminal units plus one, at high molecular weights the above equation simplifies to

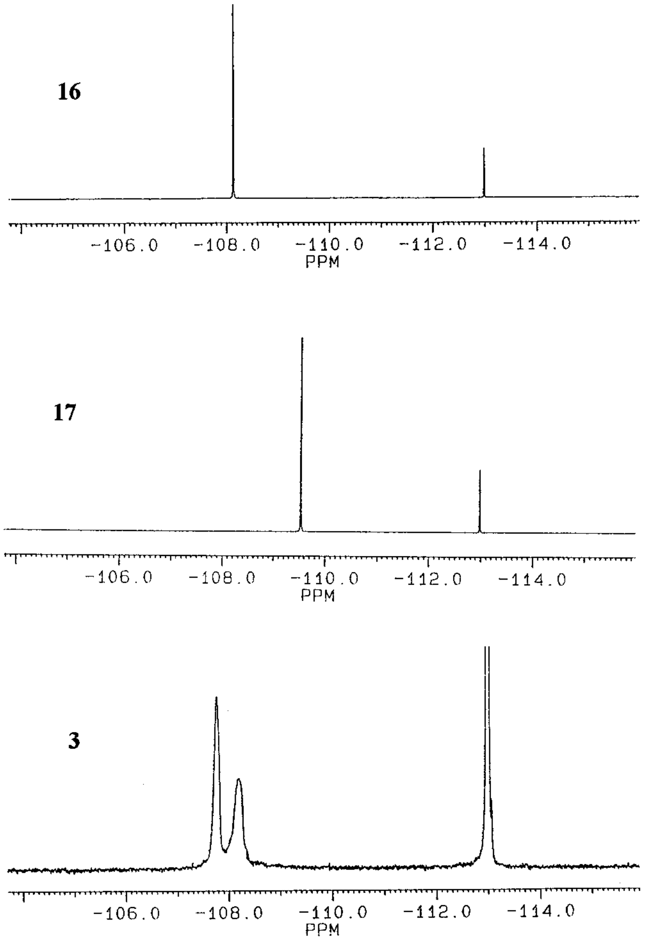


Figure 2. 188-MHz ^{19}F NMR spectra of terminal model compound **16** and linear model compound **17**, compared with the fluoro-terminated hyperbranched poly(ether ketone), **3**.

$$\mathrm{DB} = \frac{2 \times (\text{no. of terminal units})}{2 \times (\text{no. of terminal units}) + (\text{no. of linear units})} \qquad (2)$$

Using the values obtained for the relative percentage of terminal and linear subunits, the degree of branching for the fluoro-terminated hyperbranched poly(ether ketone), **3**, was found to be 0.49 or 49%.

A similar analysis of the phenolic-terminated poly(ether ketone), **5**, also reveals three different subunits, **18**−**20** (Figure 3). There are no unique fluoro groups to aid determination of the degree of branching, and differences in the ^{1}H and ^{13}C NMR spectra of the subunits and model compounds were examined. To simulate the polymer backbone, the model compounds were substituted with phenoxy groups and, for simplification of the ^{1}H NMR, deuterated phenoxy groups were introduced. The synthesis of the model compounds **21**−**23** is detailed in Scheme 5. Interestingly, cleavage of the methyl ethers resulted in exchange of the ortho and para deuterium atoms of the phenoxy ring. Presumably, this occurs by protonation of the aromatic ring under the strongly acidic reaction conditions with protonation being directed to the ortho and para positions by the oxygen substituent. Fortuitously, the resonances for these protons did not overlap with any resonances for the benzophenone nucleus and therefore did not hinder evaluation of the degree of branching.

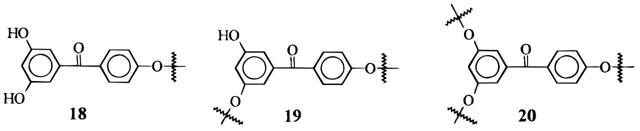


Figure 3. Structure of repeat units in hydroxy-terminated hyperbranched poly(ether ketone) **5**.

Scheme 5

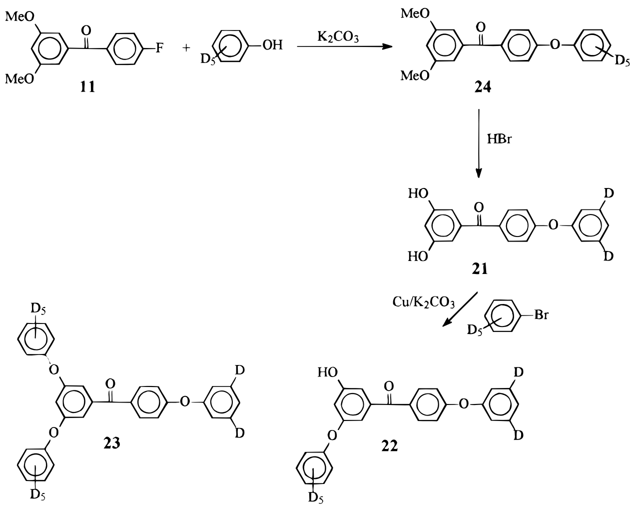


Figure 4 shows the ^{1}H NMR spectra for the model compounds, **21**−**23**. Distinct resonances for the terminal model compound, **21**, are observed at 6.49 and 6.58 ppm (H_d and H_e) while the corresponding protons for the linear model compound, **22** (H_a/H_b and H_c), appear at 6.65 and 6.84 ppm, respectively. When the ^{1}H NMR spectra of these model compounds are compared with the phenolic-terminated poly(ether ketone), **5**, excellent agreement is observed. The large resonances at 6.70 and 6.88 ppm are due to protons H_a, H_b, and H_c of the linear subunit, while the minor peaks at 6.45 and 6.55 ppm are due to protons H_d and H_e of the terminal subunit. Integration of these well-resolved resonances allows the relative percentage of the terminal and linear subunit to be determined. From these values, and eq **2**, the degree of branching for the phenolic-terminated hyperbranched poly(ether ketone), **5**, was calculated to be 0.15 or 15%. Similarly, the ^{13}C NMR spectra of the model componds, **21**−**23**, showed unique resonances depending on the substituents of the trisubstituted phenyl ring. For example, the linear model, **22**, has three resonances at 109.5−111.0 ppm while the terminal model, **21**, has two characteristic resonances at 108.2 and 108.8 ppm. These resonances are well removed from other resonances in the ^{13}C NMR spectra and show good agreement with the observed resonances in the region 108−109 and 110−112 ppm for the phenolic-terminated hyperbranched poly(ether ketone), **5** (Figure 5). Integration allows the relative percentage of terminal and linear subunits to be calculated and from these results a degree of branching of 0.14, or 14%, was determined for the phenolic-terminated hyperbranched poly(ether ketone), **5**. This result is in excellent agreement with the ^{1}H NMR results and confirms the very low degree of branching for **5**. In fact, this is the lowest reported degree of branching for a hyperbranched macromolecule and is in direct contrast to the fluoro-terminated hyperbranched poly(ether ketone), **3**, for which a degree of branching of 0.49 was obtained. The effect of such a difference in degree of branching on the structure of the hyperbranched poly(ether ketones) can be better appreciated if the number of branch points per repeat unit is considered. For **3**, there is a

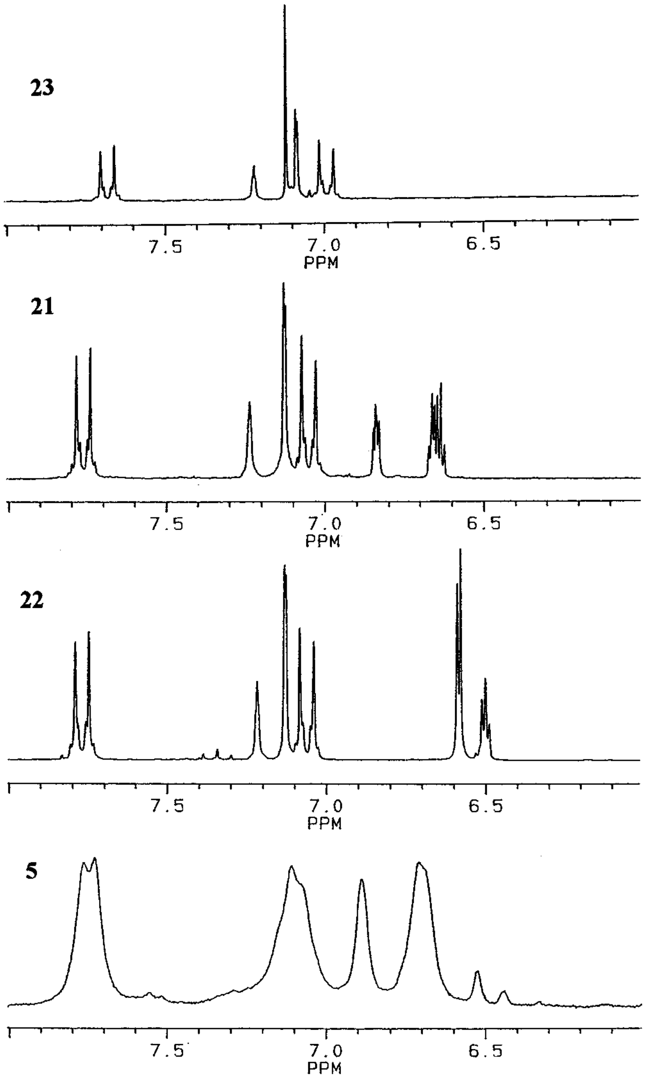


Figure 4. 200-MHz ^{1}H NMR spectra of dendritic model compound **23**, linear model compound **21**, and terminal model compound **22**, compared with the hydroxy-terminated hyperbranched poly(ether ketone), **5**.

branch point at every second repeat unit, while for **5**, there is a branch point at approximately every seven repeat units. This would lead to a highly branched and globular structure for **3** while **5** would more resemble a lightly branched linear polymer.

In an effort to further manipulate the degree of branching and to examine the effect of using more complex AB$_x$ monomers on the structure of hyperbranched macromolecules the synthesis of AB$_4$ and AB$_3$ monomers, based on 3,5-difluoro-4′-hydroxybenzophenone, **2**, was examined. In designing the AB$_4$ monomer, **24**, a dendritic unit was deliberately included in the structure in an attempt to enhance branching and therefore obtain a fluoro-terminated hyperbranched poly(ether ketone) with a higher degree of branching than was obtained from the corresponding AB$_2$ monomer, **2**. Starting from **7** the synthesis of **24** is outlined in Scheme 6. The structure of the monomer, **24**, was confirmed by NMR spectroscopy; specifically, the ^{13}C NMR spectrum shows two different carbonyl groups while the ^{19}F spectrum shows only a single resonance which correlates with all four fluoro groups being in the same chemical environment.

In contrast, the AB$_3$ monomer, **27**, was designed to include a linear unit and its presence would be expected to lead to a lower degree of branching when compared to the corresponding AB$_2$ monomer. A synthetic strategy, similar to that for **24**, was employed for the synthesis of the AB$_3$ monomer, **27**, as shown in Scheme 7. The structure of **27** was confirmed by a variety of spectroscopic techniques and, as for the AB$_4$ monomer, ^{13}C and ^{19}F NMR spectroscopy proved to be very instructive. Of particular note is the ^{19}F NMR spectrum which shows two singlets, in the ratio of 2:1, at −107.9 and −108.8 ppm for the difluoro-substituted phenyl ring and the monofluoro-substituted phenyl ring of **27**, respectively. When compared to the fluoro-terminated hyperbranched poly(ether ketone), **3**, the correlation with the dendritic and linear subunits is even closer than for the models discussed previously and confirms the peak assignments for **3** (Figure 6).

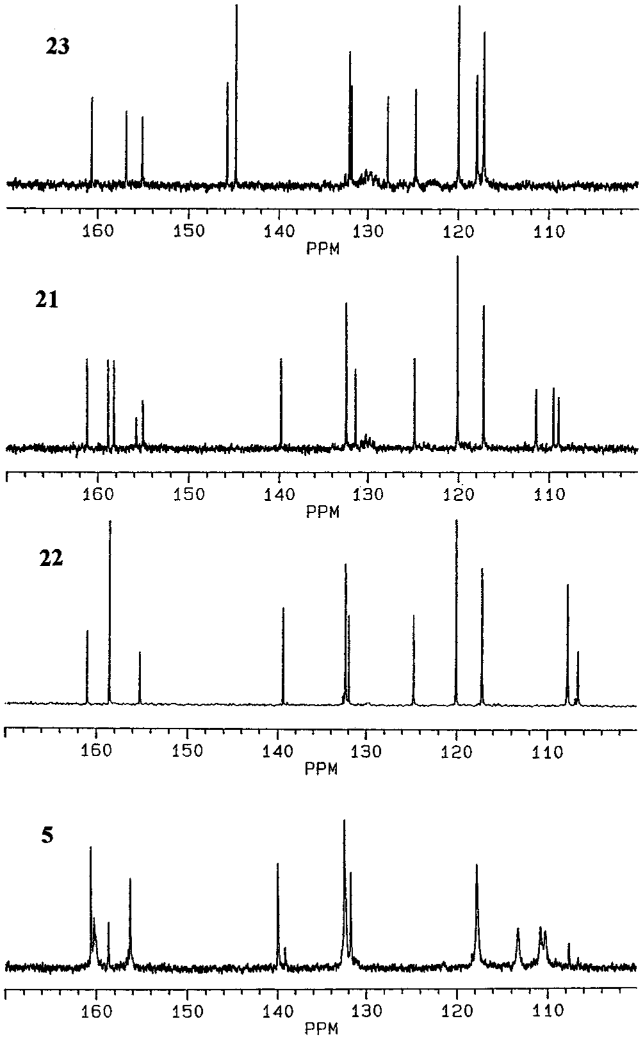
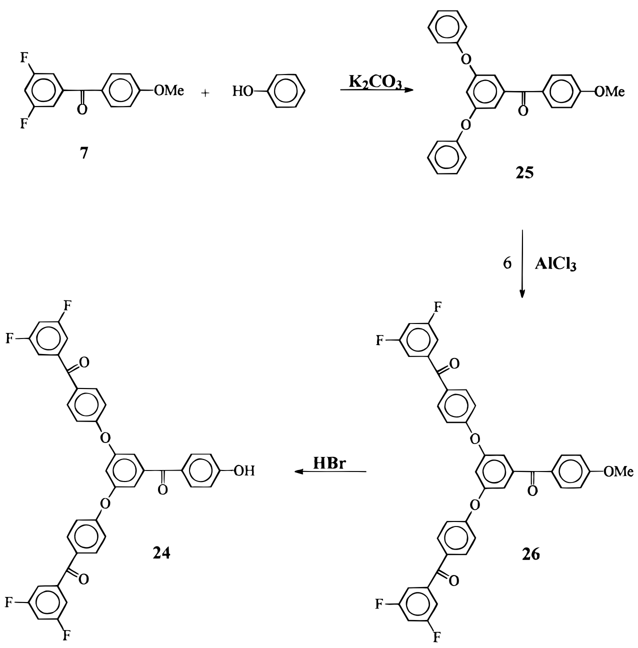


Figure 5. Comparison of the 75-MHz ^{13}C NMR spectra for the linear, terminal, and dendritic model compounds **21**−**23**, respectively, with the hydroxy-terminated hyperbranched poly(ether ketone), **5**.

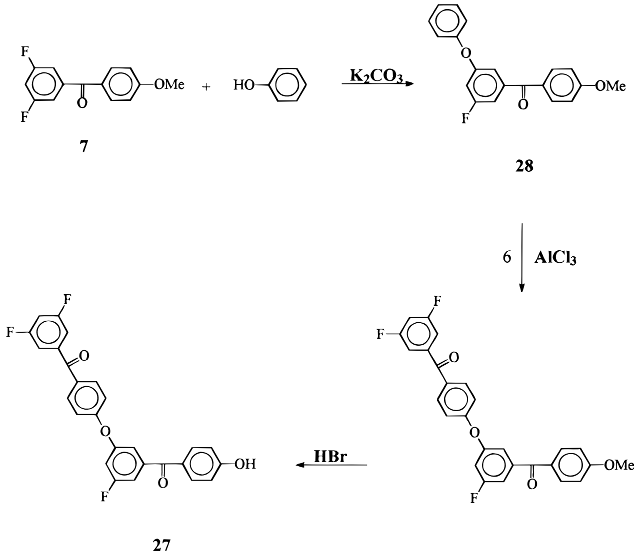
Polymerization of **24** and **27** was conducted under the same conditions as for the AB$_2$ monomer, **2**, to give the fluoro-terminated hyperbranched poly(ether ketones), **29** and **30**, in 84 and 88% yield, respectively. Interestingly, **29** was found to have a molecular weight, M_n, of 55 000 (PD = 2.1) while the hyperbranched poly(ether ketone), **30**, derived from the AB$_3$ monomer gave a M_n of 45 000 (PD = 1.9).

Analysis of the degree of branching for the fluoro-terminated hyperbranched poly(ether ketones), **29** and

Scheme 6



Scheme 7



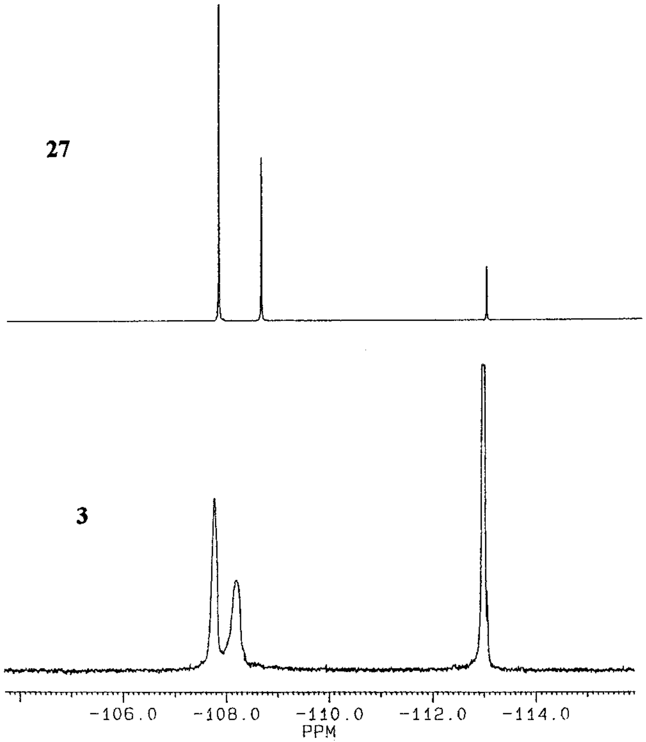


Figure 6. 188-MHz ^{19}F NMR spectra of AB$_3$ monomer **27**, compared with the fluoro-terminated hyperbranched poly(ether ketone), **3**.

30, by ^{19}F NMR spectroscopy revealed degrees of branching significantly different from that obtained for the AB$_2$ monomer. For the fluoro-terminated hyperbranched poly(ether ketone), **29**, obtained from the AB$_4$ monomer a degree of branching of 0.71, or 71%, is found while the fluoro-terminated hyperbranched poly(ether ketone), **30**, obtained from the AB$_3$ monomer gives a degree of branching of 0.38, or 38%. Comparison with the degree of branching of 0.49 found for the AB$_2$ monomer reveals that the introduction of a dendritic unit into the monomer structure does lead to an increase in the degree of branching while the introduction of a linear unit into the monomer structure leads to a decrease in the degree of branching. This result is consistent with transetherification, leading to the same DB for all monomers, being only a minor process during the preparation of the fluoro-terminated poly(ether ketones). A similar observation has been made by Kakimoto[23] during the synthesis of dendritic poly(ether ketones) and has been ascribed to the relatively mild polymerization conditions coupled with the moderate activating effect of the carbonyl group. Therefore the degree of branching for hyperbranched macromolecules can be manipulated and controlled by the synthesis and polymerization of AB$_x$ monomers containing preformed linear or dendritic subunits. Of particular note is the fact that the fluoro-terminated hyperbranched poly(ether ketones), **3**, **29**, and **30**, effectively constitute macromolecular isomers which contain the same repeat units and the same fluoro chain ends but differ in their degree of branching.

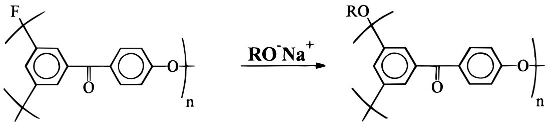
Functional Group Modification of Hyperbranched Poly(ether ketones)

Hyperbranched macromolecules are characterized by a large number of chain end groups, the number of which is equal to the degree of polymerization plus one. Previous studies[4,8] have shown that the chain end groups of hyperbranched macromolecules play an important role in determining the final physical properties of these novel materials. To investigate the effect of chain ends in hyperbranched poly(ether ketones), functionalization reactions for both the fluoro-terminated and phenolic-terminated macromolecules were investigated.

The modification of the fluoro-terminated hyperbranched poly(ether ketone), **3**, was accomplished by nucleophilic displacement of the activated fluoro groups at the chain ends. A variety of substituted phenolic and alcoholic groups could be introduced at the chain ends by reaction of the isolated and purified polymer with a nucleophile and potassium carbonate or by addition of the nucleophile to the reaction mixture at the conclusion of the polymerization (Scheme 8). Both strategies resulted in essentially the same extent of functionalization and the same molecular weights for the final polymer.

For the phenolic-terminated hyperbranched poly(ether ketone), **5**, two different strategies were employed for functionalization of the chain ends (Scheme 9). The

Scheme 8



3

Scheme 9

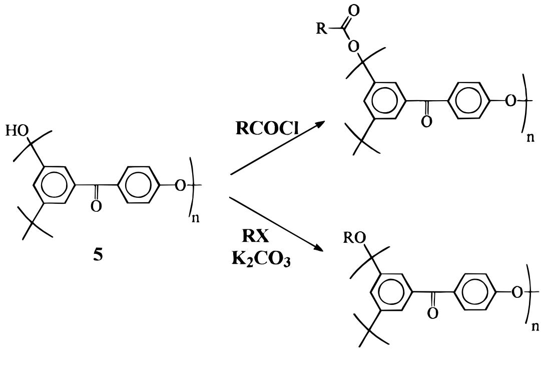
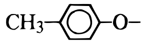
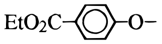
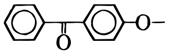
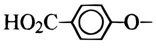
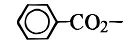
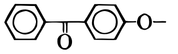


Table 1. Glass Transition Temperatures of Hyperbranched Poly(ether ketone) Derivatives

Compd	R	T_g(°C)
3	F-	162
5	HO-	127
38		139
39		154
31a		117
32	$CH_3(CH_2)_7$-O–	97
33		290
36		147
35	CH_3-CO_2–	118
31b		119

phenolic groups could be readily acylated with a variety of acid chlorides to give the corresponding ester derivatives or arylated by reaction with activated aryl fluorides. Interestingly, this last procedure allowed the same chain ends to be introduced (**31b**), for example benzophenone, as could be introduced by reaction of the fluoro-terminated hyperbranched poly(ether ketone) with the corresponding phenolic derivatives (**31a**). It should be noted that in all the above modification reactions the use of excess reagents resulted in essentially complete (>95%) functionalization which was confirmed by a variety of spectroscopic techniques.

Physical Properties of Chain End Modified Macromolecules

A number of researchers have shown the dramatic effect that changes in the end groups have on the glass transition temperature and solubility of hyperbranched and dendritic macromolecules.[4,8] Similar results were observed for the hyperbranched poly(ether ketones) prepared above. As shown in Table 1, the glass transition temperature of hyperbranched poly(ether ketones), based on a 3,4′,5-trioxybenzophenone as a repeat unit, undergoes dramatic changes on varying the chain end functional groups. For example, the glass transition temperature increases from 97 to 290 °C, an increase in nearly 200 °C, on going from an octyloxy end group, **32**, to a *p*-(carboxy)phenoxy end group, **33**. Another interesting feature is the close agreement between the glass transition temperatures of the benzophenone-terminated hyperbranched poly(ether ketones), **31a** and **31b** (117 and 119 °C), which were prepared by different synthetic strategies from the fluoro-terminated and phenolic-terminated hyperbranched poly(ether ketones), respectively. While these materials have exactly the same building blocks and chain ends, they do have significantly different degrees of branching, 49% compared to 15%, which illustrates that thermal properties, such as T_g, are not influenced by the degree of branching. Further support for the independence of thermal properties and macromolecular architecture came from a study of the fluoro-terminated hyperbranched poly(ether ketones), **3**, **30**, and **29**, prepared from AB_2, AB_3, and AB_4 monomers. For these three samples, which have degrees of branching of 49, 39, and 71%, a glass transition temperature of 162 °C was observed in each case. The phenolic and fluoro-terminated poly(ether ketones) were stable to 480 °C in N_2 with 10% weight loss occurring at over 500 °C. When compared to their linear analogs, which have a high degree of crystallinity, all the hyperbranched poly(ether ketones) were completely amorphous, which illustrates another important property difference between linear polymers and hyperbranched or dendritic macromolecules. This lack of crystallinity is due to the highly branched nature of these materials, which disrupts crystal formation and has been observed by a number of other workers.[4,22]

Solubility Behavior

On comparison with the linear poly(ether ketone), **34**, which has very limited solubility, the hyperbranched poly(ether ketones), **3** and **5**, were exceptionally soluble in a wide range of solvents. Both polymers have high solubilities in typical solvents such as tetrahydrofuran and *N*-methylpyrrolidinone. However, the different chain ends did result in a major difference between the two polymers when their solubilities in very polar and nonpolar solvents was examined. The phenolic-terminated poly(ether ketone), **5**, was very soluble in dimethylformamide, dimethyl sulfoxide, and surprisingly, aqueous K_2CO_3 or KOH solutions, whereas the fluoro-terminated poly(ether ketone), **3**, was only sparingly soluble in DMF and totally insoluble in DMSO and aqueous solutions. Conversely, in relatively nonpolar solvents such as chloroform and 1,2-dichloroethane the fluoro-terminated poly(ether ketone), **3**, was extremely soluble whereas **5** was totally insoluble. Even more dramatic solubility changes were observed on modification of the chain ends. For example, modification of the phenolic-terminated poly(ether ketone), **5**, with acetyl chloride results in the acetyl derivative, **35**, which is insoluble in aqueous base and soluble in chloroform and 1,2-dichloroethane, while the octyl-terminated material, **32**, was soluble in hexane and the carboxy derivative, **33**, was readily soluble in water. The enhanced and variable solubilities of hyperbranched poly(ether ketones), when compared to their linear analogs, are in agreement with similar results obtained for dendritic and hyperbranched macromolecules where the solubility was found to be dependent on both the surface functional groups and the highly branched structure of these materials.

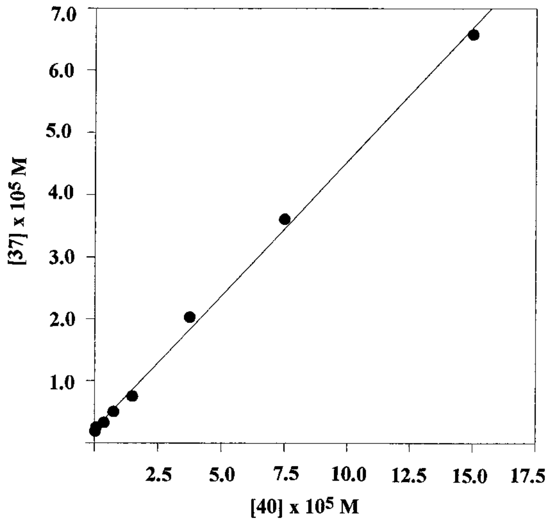


Figure 7. Plot of the saturation concentration of 1,4-diaminoanthraquinone, **37**, versus the concentration of the carboxylate-terminated hyperbranched poly(ether ketone), **40**, in water.

Previously, Kim and Webster[17] have shown that hyperbranched polyphenylene derivatives, terminated by carboxylate groups, are capable of solubilizing small hydrophobic organic molecules. Newkome[18,19] and Hawker[20] have examined this effect in more detail in the synthesis of dendritic micelles or unimolecular micelles. These authors have taken advantage of the highly branched, three-dimensional structure of hyperbranched/dendiritic macromolecules combined with the numerous chain ends to prepare globular materials that resemble traditional micelles. An interesting feature of these unimolecular micelles is that they are strict structures which do not suffer from a critical micelle concentration (CMC) and so can solubilize hydrophobic molecules at extremely low concentrations. To determine whether hyperbranched macromolecules, based on a poly(ether ketone) core, could also function as unimolecular micelles, the carboxylate-terminated hyperbranched poly(ether ketone), **40**, was prepared from the corresponding fluoro-terminated derivative (DB = 49%). The hydrophobic compound used for this study was 1,4-diaminoanthraquinone, **37**, which gives an absorption at 585 nm, and the methodology used for examining the solubilizing ability of **40** was the same as detailed previously.[20] Using the above procedure a saturated concentration in water for 1,4-diaminoanthraquinone, **37**, of 1.9×10^{-6} M was observed, which correlates well with the literature value of 1.7×10^{-6} M.[21] In a aqueous solution of the hyperbranched poly(ether ketone) ([40] = 1.4×10^{-4} M), the saturation concentration of **37** was determined to be 7.9×10^{-5} M, approximately a 40-fold increase when compared to pure water. Increasing the concentration of **40**, was shown to result in a linear increase in the saturation concentration of 1,4-diaminoanthraquinone, **37**, and no critical micelle concentration was observed for this system even at concentrations in the micromolar range (Figure 7).

Conclusion

The synthesis of a variety of hyperbranched poly(ether ketones) based on 3,4′,5-trioxybenzophenone as the repeat unit has been demonstrated. It is found that the choice of the A and B groups in the starting AB_2 monomer is important and dramatically affects the physical properties and structure of the hyperbranched poly(ether ketone) obtained. In the case of 3,5-difluoro-4′-hydroxybenzophenone, **2**, a fluoro-terminated hyperbranched poly(ether ketone), **3**, is obtained which has a glass transition temperature of 162 °C and analysis by ^{19}F NMR spectroscopy revealed a degree of branching of 49%. In contrast, polymerization of 3,5-dihydroxy-4′-fluorobenzophenone, **4**, gave the corresponding phenolic-terminated hyperbranched poly(ether ketone), **5**, which was found to have a T_g of 127 °C, and analysis of ^1H and ^{13}C NMR spectroscopy revealed a degree of branching of only 15%. The degree of branching could be further manipulated by the synthesis and polymerization of AB_4 and AB_3 monomers units based on the same building blocks but containing a preformed dendritic unit and linear unit, respectively. By inclusion of a dendritic unit the degree of branching for the fluoro-terminated poly(ether ketone) could be increased to 71% while inclusion of a linear unit resulted in a decrease in the degree of branching to 39%. It was found that the glass transition temperature of the hyperbranched poly(ether ketones) was independent of the degree of branching but was dramatically affected by changes in the chain end functional groups. The chain end functional groups were also found to have a dendritic influence on the solubility of the hyperbranched poly(ether ketones) with the carboxylate-terminated material being soluble in water and acting like unimolecular micelles.

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