A versatile synthesis of isomeric hyperbranched polyetherketones

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Summary

Hyperbranched polyetherketones with opposing fluoro and hydroxy terminal groups have been synthesised from the corresponding AB_2 monomers. The choice of A and B in these monomer units has been shown to be important and affects properties such as molecular weight, solubility, and glass transition temperature.

Introduction

While examples of highly branched polymers are prevalent in nature (1) the utilization of this concept in synthetic polymer chemistry has been neglected until recently. The synthesis of new macromolecular architectures where the ratio of branches to monomer units approaches unity can be conveniently divided into two separate fields. A major effort has been directed to the preparation of "perfect" dendritic macromolecules by step-wise divergent (2) or convergent (3) synthetic approaches. While highly defined structures are obtained which are excellent for investigating the new and improved properties of these highly branched systems the materials are obtained in only limited quantities after much effort. To alleviate this problem a number of groups have investigated the one-step polymerization of AB_2 monomers (4). This leads to hyperbranched macromolecules which due to their polydispersity and less perfect branching can be considered a separate field of study. The physical properties of these hyperbranched materials are not well understood but have been shown to be unusual and to resemble those found for dendritic macromolecules (5). An ideal polymerization of an AB_2 type monomer gives a hyperbranched macromolecule with a single A functionality and (DP + 1) B functional groups. Therefore unlike normal linear polymers the choice of reactive functionalities A and B on the initial monomer unit is very important. To determine what effect this has on the structure and physical properties of hyperbranched macromolecule we have investigated the synthesis of two AB_2 monomers and their polymerization to give "isomeric" hyperbranched polye-

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therketones. Comparison of the structure and physical properties of these materials gives some insight into the effect of choosing A and B in the initial AB_2 monomer.

Experimental

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 disks. ^{1}H NMR spectra were recorded on solutions with a Bruker AM 200 (200-MHz). ^{13}C NMR spectra were recorded at 50 MHz on a Bruker AM 200 (200-MHz) spectrometer, with the solvent carbon signal as 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 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 micron Waters columns (300 x 7.7 mm) connected in series in order of increasing pore size (100 A, 1000 A, 10^5 A, and 10^6 A) were used with THF as solvent.

3,5-Difluoro-4'-methoxybenzophenone (1). To a mixture of anisole (2.29 g, 21.0 mmol) and aluminum chloride (3.07 g, 23.0 mmol) in dry 1,2-dichloroethane (10 ml) was added dropwise 3,5-difluorobenzoyl chloride (3.00 g, 17.0 mmol) in 1,2-dichloroethane (5 ml). The reaction mixture was stirred at room temperature under nitrogen for 3 hours. Water (10 ml) was then added and stirring continued overnight. The reaction mixture was then poured into water (250 ml) and extracted with CH_2Cl_2 (3 x 100 ml), 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 1 as a colorless oil: yield 88%; IR 1650, 1600, 1350, and 1160 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.85 (s, 3H, OCH_3), 6.95 and 7.77 (ABq, 4H, J = 10 Hz, PhH), 6.97 (complex t, 1 H, J = 6 Hz, PhH), and 7.22 (complex d, 2 H, J = 6 Hz, PhH); ^{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), and 192.01 (t); mass spectra (EI), m/z 248.

3,5-Difluoro-4'-hydroxybenzophenone (2). The methoxybenzophenone (1) was dissolved in glacial acetic acid (25 ml), 48% HBr (15 ml) was added, and the mixture was heated at reflux for 4 hours. The reaction mixture was cooled, evaporated to dryness, water (100 ml) added and the mixture extracted with ether (3 x 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 then to 1:3 ether/CH_2Cl_2. The phenol 2 was obtained as an off white solid: yield 91%; mp 134-135 C, IR 3400-3000, 1640, 1595, 1450, and 1370 cm^{-1}; ^{1}H NMR (D$_6$-acetone) δ 6.94 and 7.71 (ABq, 4H, J = 8 Hz, PhH), 7.13 (complex t, 1 H, J = 6 Hz, PhH), and 7.25 (complex d, 2 H, J

= 6 Hz, PhH); ^{13}C NMR (D$_6$-acetone) δ 107.02 (t), 112.63 (q), 115.80, 128.23, 132.12, 141.21 (t), 160.46 and 165.42 (ABq), 162.69, and 192.21 (t); mass spectra (EI), m/z 234, Anal. Calcd. for C$_{13}$H$_8$F$_2$O$_2$: C, 66.7; H, 3.44. Found: C, 66.5; H, 3.40.

3,5-Dimethoxy-4'-fluorobenzhydrol (3). A solution of 3,5-dimethoxybenzaldehyde (10.0 g, 60.0 mmol) in dry THF (20 ml) was added dropwise to a 2.0 M ether solution of 4-fluorophenylmagnesium bromide (35 ml). The reaction was then heated at reflux under nitrogen for two hours. After cooling to room temperature the reaction was hydrolyzed with water (10 ml), filtered and the filtrate evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:1 hexane/CH$_2$Cl$_2$ increasing to CH$_2$Cl$_2$ to give the benzhydrol **3** as a colorless oil: yield 87%; IR 3600-3200, 1600, 1505, 1475, and 1160 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.75 (d, 1H, 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), and 6.99 and 7.31 (complex ABq, 4H, J = 9 Hz, PhH); ^{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, and 164.51; mass spectra (EI), m/z 262.

3,5-Dimethoxy-4'-fluorobenzophenone (4). To a mixture of pyridinium chlorochromate (12.9 g, 60.0 mmol) and sodium acetate (1.50 g) in CH$_2$Cl$_2$ (60 ml) was added the benzhydrol **4** (13.5 g, 51.5 mmol) in CH$_2$Cl$_2$ (25 ml). The reaction mixture was stirred under nitrogen at room temperature for 30 minutes during which time a thick black oil had separated out. The solution was decanted from this oil and the oil washed with CH$_2$Cl$_2$ and the combined organics evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:2 hexane/CH$_2$Cl$_2$ increasing to CH$_2$Cl$_2$ to give the benzophenone **4** as a colorless oil: yield 84%; IR 1650, 1595, 1370, and 1175 cm^{-1}; ^{1}H 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), and 7.11 and 7.82 (complex ABq, 4H, J = 9 Hz, PhH); ^{13}C NMR (CDCl$_3$) δ 55.46, 104.56, 107.63, 115.32 (d), 132.56 (d), 133.60, 139.23, 160.51, 162.78, 167.83, and 194.76; mass spectra (EI), m/z 260.

3,5-Dihydroxy-4'-fluorobenzophenone (5). The dimethylether **4** (11.0 g, 42.3 mmol) was dissolved in glacial acetic acid (150 ml), 48% HBr (90 ml) added, and the mixture heated at reflux under nitrogen for 20 hours. The black solution was then cooled, poured into water (500 ml) and extracted with ether (5 x 100 ml). The combined ether extracts were dried and evaporated to dryness. The crude product was purified by flash chromatography eluting with CH$_2$Cl$_2$ gradually increasing to ether to give the dihydroxy derivative **5** as an off-white solid: yield 91%; mp 142-143 C, IR 3500-3100, 1640, 1595, and 1170 cm^{-1}; ^{1}H NMR (D$_6$-acetone) δ 6.62 (t, 1 H, J = 3 Hz, ArH), 6.73 (d, 2 H, J = 3 Hz, ArH), and 7.27 and 7.85 (complex ABq, 4H, J = 9 Hz, PhH); ^{13}C NMR (D$_6$-acetone) δ 107.14, 108.62,

115.72 (d), 132.94 (d), 134.68, 139.94, 159.02, 163.11, 168.10, and 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.

Preparation of fluoro-terminated polyetherketone (6). To a mixture of 3,5-difluoro-4'-hydroxybenzophenone 2 (3.00 g, 12.8 mmol) and potassium carbonate (2.80 g) was added dry N-methylpyrrolidone (20 ml) and dry toluene (15 ml). The reaction mixture was then heated at reflux under nitrogen for 3 hours 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 was then continued for three hours. The reaction mixture was then poured into water (800 ml) and the precipitate collected and twice reprecipitated into methanol (500 ml). This gave the polyetherketone 6 as an off-white solid: yield 91%; IR 1660, 1595, 1350, and 1260 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.90-7.25 (complex m, 5 H), and 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, and 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 hydroxy-terminated polyetherketone (7). This was prepared from 3,5-dihydroxy-4'-fluorobenzophenone (5) using a similar procedure as above. The crude product was purified by initial precipitation into water (pH 1) followed by two reprecipitated into water (500 ml). This gave the polyetherketone 7 as an off-white solid: yield 84%; IR 3500-3100, 1640, 1600, 1360, and 1210 cm^{-1}; ^{1}H NMR (D$_6$-DMSO) δ 6.48 (br s), 6.56 (br s), 6.76, 6.84, and 6.96 (br s), 7.18 and 7.82 (d), and 10.22 (br s); ^{13}C NMR (D$_6$-DMSO) 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, and 193.47; Anal. Calcd. for $C_{13}H_8O_3$: C, 73.6; H, 3.80. Found: C, 73.3; H, 4.04.

Results and Discussion

Polyetherketones are an important class of engineering plastics which have attracted a considerable amount of interest recently and have been commercialized by a number of companies. The most versatile synthesis of polyetherketones involves the reaction of a phenol with an activated aryl fluoride in the presence of a suitable base (6). Therefore to obtain isomeric hyperbranched polyetherketones requires the synthesis and polymerization of two, essentially opposite, AB$_2$ monomers. For a fluoro-terminated product A = OH and B = F, conversely for a hydroxy-terminated derivative A = F and B = OH. Based on a benzophenone building block our two monomer units would therefore be 3,5-difluoro-4'-hydroxybenzophenone 2 and 3,5-dihydroxy-4'-fluorobenzophenone 5. The synthesis of 2 starts from the commercially available 3,5-difluorobenzoyl chloride which under standard Friedel Crafts acylation conditions gives the benzophenone 1 on reaction with anisole. Cleavage of the methyl ether of 1 by reaction with HBr in glacial acetic acid gives the desired difluoro-hydroxy monomer 2 in 80% overall yield after purification (Scheme 1).
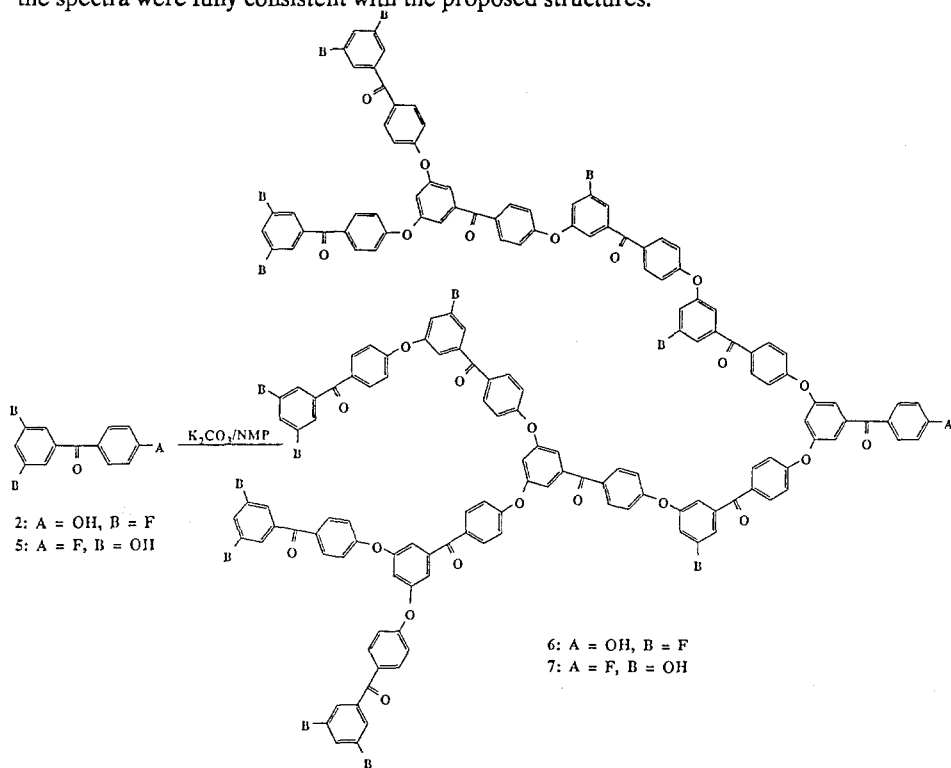
SCHEME 1

1   **2**
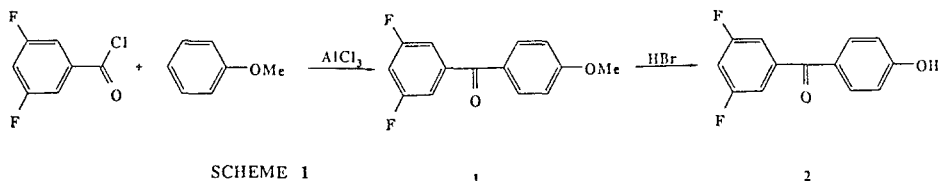
Due to the meta substitution of the hydroxy groups, Friedel Crafts chemistry was unsuitable for the synthesis of the corresponding monomer unit **5**, therefore a different synthetic approach was required. Reaction of the Grignard reagent prepared from 1-bromo-4-fluorobenzene with 3,5-dimethoxybenzaldehyde gave the coupled alcohol derivative **3** which was oxidized with pyridinium chlorochromate to give the desired benzophenone building block **4** in 84% yield after purification. The methyl ethers of **4** were cleaved under the same conditions as above to give the "opposite" fluoro-dihydroxy monomer unit **5** in 91% yield (Scheme 2).

3   **4**

HBr

SCHEME 2   **5**
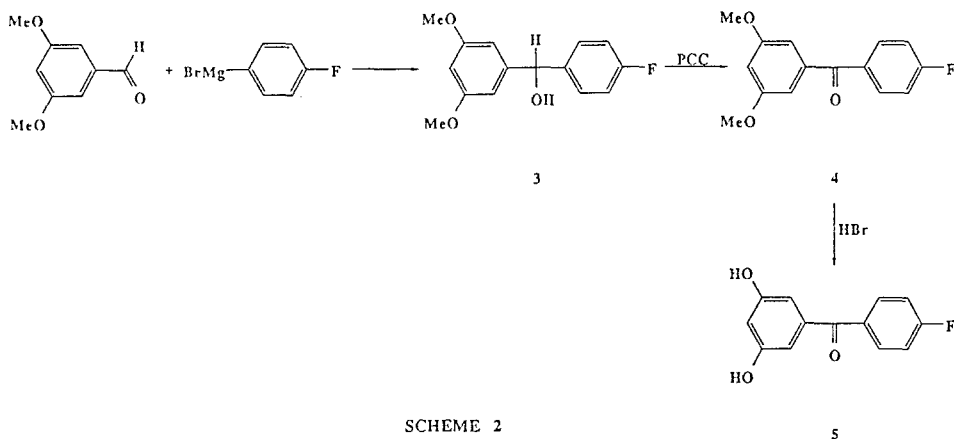
The polymerization of **2** and **5** were initially performed in dry dimethylsulphoxide in the presence of potassium carbonate, however the products obtained from both polymerizations were of low molecular weight. McGrath (7) has reported that a superior system for obtaining high molecular weight polyetherketones is potassium carbonate in a toluene/N-methylpyrrolidone mixture. Therefore reaction of 3,5-difluoro-4'-hydroxybenzophenone **2** with an excess of potassium carbonate in a 3:4 mixture of toluene and N-methylpyrrolidone was found to give the fluoro-terminated hyperbranched polyetherketone **6** in 91% yield. Similarly reaction of 3,5-dihydroxy-4'-fluorobenzophenone **5** under the same conditions as above gave the corresponding hydroxy-terminated hyperbranched polyetherketone **7** in 84% yield (Scheme 3).

The molecular weights of macromolecules **6** and **7** were determined by gel permea-
tion chromatography using tetrahydrofuran as the carrier solvent. The fluoro-terminated
macromolecule **6** gave a molecular weight of 20 000 with a polydispersity of 1.8 whereas
the hydroxy-terminated polyetherketone was found to have a molecular weight of 95 000
with a polydispersity of 2.2. The reason for the difference in molecular weights is not
known at this time but may be due to the relative reactivity of the fluoro and/or hydroxy
groups in either the meta and para positions. These molecular weights are with respect to
polystyrene standards and it has been shown that these values usually underestimate the
true molecular weight (8). Preliminary work suggests that the actual molecular weights
are considerably higher. In addition to gel permeation chromatography the two isomeric
polyetherketones were fully characterized by ^{1}H, ^{13}C NMR and infra-red spectroscopy,
the spectra were fully consistent with the proposed structures.

SCHEME 3

On comparison with the linear polyetherketone **8** prepared by the polymerization of
4'-fluoro-3-hydroxybenzophenone the hyperbranched polyetherketones **6** and **7** were
exceptionally soluble. Both polymers have high solubilities in typical solvents such as THF

and acetone. However a major difference between the two polymers were in their solubilities in very polar and non-polar solvents. The hydroxy-terminated polyetherketone 7 was very soluble in dimethylformamide and, surprisingly, aqueous K_2CO_3 or KOH solutions whereas the fluoro-terminated polyetherketone 6 was only sparingly soluble in DMF and totally insoluble in aqueous solutions. Conversely the fluoro-terminated polyetherketone 6 was soluble in solvents such as dichloromethane and 1,2-dichloroethane whereas the hydroxy-terminated derivative was insoluble. The enhanced but different solubilities found for 6 and 7 is in agreement with similar results obtained for "perfect" dendritic macromolecules where the solubility of the macromolecule was found to be dependent on the surface functional group.

A difference was also observed in the thermal behavior of these two macromolecules. The glass transition temperature of the fluoro-terminated polyetherketone 6 was observed at 162 C while the hydroxy-terminated polyetherketone 7 had a much lower T_g of 127 C. Since the interior building blocks of both polymers are the same this difference must be due to the terminal groups only. Both macromolecules had thermal stabilities similar to the linear polyetherketone 8 with >95% of their mass remaining after heating up to 500 C at 20 C/min under nitrogen.

The synthesis of isomeric hyperbranched polyetherketones from their respective AB_2 monomers has been demonstrated. The choice of A and B determines the final terminal groups of these macromolecules which has in turn been shown to dramatically affect the molecular weight, solubility and thermal properties of these hyperbranched systems. Future work will determine the degree of branching, examine the reactivity of the terminal groups and further elaborate the effect of these groups on physical properties.

Acknowledgements

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