Synthesis and Properties of Poly(arylene ether)s Containing 1,8-Dibenzoylnaphthalene Units

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Received November 16, 1994; Revised Manuscript Received February 21, 1995®

ABSTRACT: High molecular weight, amorphous, soluble poly(arylene ether ketone)s are synthesized from 1,8-bis(4-fluorobenzoyl)naphthalene and a variety of aromatic bisphenols. The polymers are characterized by gel permeation chromatography and by ^{1}H and ^{13}C NMR. The glass transition temperatures range from 214 to 270 °C, measured by differential scanning calorimetry. The 5% weight loss from these polymers by thermogravimetric analysis occurs all above 476 °C in nitrogen and 478 °C in air. Young's moduli are between 0.70 and 4.40 GPa by thermomechanical analysis.

Introduction

Commercialization of poly(ether ether ketone) (PEEK) by ICI as the most prominent high-performance melt-processable engineering thermoplastic has promoted much research efforts in the area of poly(arylene ether ketone)s (PAEKs), aiming at improving overall properties of PEEK and searching for new materials with better properties.[1-3] A variety of PAEKs have been synthesized and evaluated for uses as coatings, adhesives, membranes, and structural composites. Structurally related PAEKs containing phenylenedicarbonyl units (A)[4] and biphenylenedicarbonyl units (B)[5] (Figure 1) have been synthesized by several groups, which allow systematical studies and comparisons of their glass transition temperatures (T_gs), thermal stabilities, and mechanical properties. Depending on the substitution patterns of A and B, the T_gs of isomeric polymers vary. For example, three isomeric PAEKs containing units A have T_gs varying in the order 1,2- > 1,4- > 1,3-substitutions. A similar effect is also seen in the series of PAEKs having isomeric groups B, for the T_gs varying in the order 4,4′- > 2,2′- > 3,3′-substitutions.[5] The relatively high T_gs for the less linear polymers with ortho-disubstituted phenylenes and 2,2′-disubstituted biphenylenes can be attributed to chain stiffness caused by the restricted rotation of two adjacent carbonyl groups. As to viscoelastic properties, it has been found that isomeric PAEKs containing units B have similar Young's moduli.[5e] Another noteworthy feature of 1,2-phenylenedicarbonyl and 2,2′-biphenylenedicarbonyl groups is their ability to undergo structural transformation to phthalazine or isoquinoline and phenanthrene rings upon chemical treatment with hydrazine or benzylnitrile and Lawesson's thionating agent, respectively.[6,7] Structural symmetry of the repeat unit has been correlated with the toughness of poly(arylene ether sulfone)s, with the most linear para-isomers being the toughest.[8] The effects of structural symmetry on gas transport properties of poly(arylene ether sulfone)s have also been studied. Polymers with unsymmetric structures have lower gas permeability and higher selectivity coefficients than their symmetric counterparts.[9] However, no similar studies have been done with isomeric PAEKs yet.

In spite of much work on the synthesis of new PAEKs, to date only the PAEKs containing the 1,5- and 2,6-naphthylenedicarbonyl units are known, such as polymers **8** and **9** (Figure 3).[4a] Introduction of methyl groups at the 2,6-positions of the 1,5-naphthalic unit improved the solubility and increased the T_g but decreased the thermooxidative stability of polymer **9**.[10] Among a dozen possible isomeric naphthylenedicarbonyls (C; Figure 1), the 1,8-naphthalic isomer is quite unique. Two carbonyl groups at the peri positions of naphthalene are almost as close to each other as those in other ortho-isomers (e.g., 1,2- and 2,3-isomers), which is expected to increase the T_gs of PAEKs in the same way as 1,2-phenylene- and 2,2′-biphenylenedicarbonyl groups do. As part of ongoing systematic studies of the effects of structural symmetry and the substitution pattern of the arylene core in PAEKs on the polymer properties, the synthesis and properties of a series of naphthalene-based poly(arylene ether ketone)s derived from 1,8-bis(4-fluorobenzoyl)naphthalene (**2**) and bisphenols are described herein.

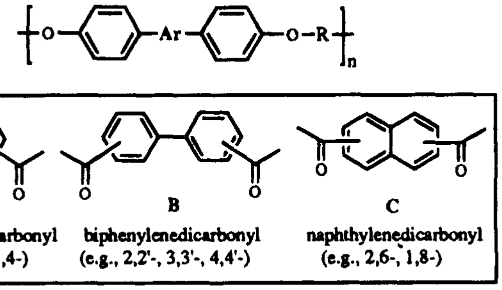


Figure 1. Poly(arylene ether)s containing different arylenedicarbonyl units.

Experimental Section

Materials. 1-Bromo-4-fluorobenzene, 1,2-acenaphthenequinone, 3,5-di-*tert*-butylphenol, 1,1,2,2-tetrachloroethane (TCE), tetramethylene sulfone ($TMSO_2$), toluene, fluorobenzene, aluminum chloride, and other common organic solvents were purchased from Aldrich Chemical Co. and used as received. Tetrahydrofuran (THF; Aldrich) was dried by refluxing over sodium wire prior to use. 4,4′-Isopropylidenediphenol (**3a**; Aldrich), 4,4′-(hexafluoroisopropylidene)diphenol (**3b**; Aldrich), and 9,9-bis(4-hydroxyphenyl)fluorene (**3d**; General Electric Co.) were recrystallized from toluene. 4,4′-Diphenol (**3e**; Aldrich) and 1,4-hydroquinone (**3c**; Aldrich) were purified by recrystallization from ethanol. *tert*-Butyl-1,4-hydroquinone (**3f**; Aldrich) was purified by sublimation.

Characterization. Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Infrared (IR) measurements were performed on a Bomem FTIR Michelson series instrument with a resolution of 4 cm^{-1}; the spectra were recorded after five scans. The ^{1}H and ^{13}C NMR spectra

® Abstract published in *Advance ACS Abstracts,* April 15, 1995.

were recorded in chloroform-*d* solutions on either a Varian Gemini 200 or a Bruker 400 instrument, and results are reported in ppm from tetramethylsilane on the δ scale. The coupling constants were assigned by assuming first-order spectra were obtained. Low-resolution mass spectra were obtained on a Du Pont 21−492B spectrometer. Molecular weights were determined relative to polystyrene standards using chloroform as an eluent at a flow rate of 1.0 mL/min on a Perkin-Elmer LC-250 GPC equipped with a PL gel column (5 μm) and a UV detector set at 254 nm wavelength. Inherent viscosity data were obtained with an Ubbelohde viscometer (size OB114) in a 0.5% (g/dL) chloroform solution at 25 °C. The glass transition temperatures (T_gs) of the polymers were obtained using a Seiko 220C DSC instrument at a heating rate of 10 °C/min in N$_2$ (50 mL/min). The T_g values were reported from the second scan, otherwise as indicated. The T_g was taken from the midpoint of the change in the slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 20 °C/min under either N$_2$ or air (200 mL/min). For all DSC and TG measurements, polymer pellets were lightly pressed, and a sample of 8−12 mg was used for each measurement.

Film Casting. Polymer films were cast from chloroform or TCE. A typical procedure is as follows: a polymer (150 mg) was dissolved in 2 mL of solvent. This solution was filtered and transferred into a glass ring (diameter = 6.5 cm, height = 2 cm, thickness = 0.2 cm) placed on a glass plate. The glass ring was covered with a glass plate, and the solvent was allowed to slowly evaporate at room temperature over 24 h. The resulting tough and flexible films were further dried in a vacuum oven. The oven temperature was gradually increased from 50 to 200 °C over a period of 2 days. The film thickness ranged from 0.060 to 0.090 mm.

Measurement of Mechanical Properties. A typical procedure to obtain Young's modulus measurements was performed as follows: a stamp was used to cut out a film strip (length = 5 mm, width = 2 mm, thickness = 0.07 mm) which was mounted between two chucks in a Seiko TMA/SS 120 instrument. For Young's modulus at 25 °C, the parameters were set as offset load = 10−20 g, load amplitude = 5−10 g, and cycling frequency = 0.05 Hz. After these data were collected for 30 min, the same film was used without changing the parameters to measure Young's modulus (E') variation with temperature by heating to a temperature 40 °C higher than the T_g of the polymer studied at a ramp rate of 3 °C/min in static air.

Monomer Synthesis. 1,8-Bis(4-fluorobenzoyl)naphthalene (2). In a flame-dried 1-L round-bottomed flask fitted with a mechanical stirrer, a reflux condenser, and a nitrogen provider was placed dry magnesium turnings (33.0 g, 1.40 mol). To the flask were added THF (100 mL) and 1-bromo-4-fluorobenzene (15.0 mL, 0.13 mol). The mixture was heated slowly up to reflux under nitrogen. The appearance of a brown coloration around the magnesium turnings indicated the beginning of the reaction forming the Grignard reagent. The stirring was turned on, and the rest of THF (400 mL) and 1-bromo-4-fluorobenzene (128 mL, 1.12 mol) were added dropwise. At the end of the addition, the mixture was stirred at room temperature for another hour. The mixture was diluted with 250 mL of THF. Acenaphthenequinone (95.0 g, 0.52 mol) was then added in small portions over 1 h. The exothermic reaction was controlled by means of an ice bath. After 1 h of reaction, TLC analysis (ethyl acetate/hexane, 40/60) showed the consumption of the starting material. Ice (300 g) was added in the reaction flask to hydrolyze the magnesium salt. The mixture of hydrolyzed product was then poured into a beaker containing aqueous acetic acid (10%, 1 L), resulting in the precipitation of white solids. The solids were filtered and recrystallized from toluene once. A small amount of the solids was further purified to characterize 1,2-dihydroxy-1,2-bis(4-fluorophenyl)acenaphthene (**1**): mp 191−193 °C (lit.[11] mp 220−221 °C, 153.5−154.5 °C); IR (KBr, cm^{-1}) 3570, 3510 (OH); ^{1}H NMR (400 MHz) δ 7.91 (d, 2 H, $J_{\mathrm{H-H}} = 8.30$ Hz), 7.66 (dd, 2 H, $J_{\mathrm{H-H}} = 8.28$ and 6.95 Hz), 7.36 (d, 2 H, $J_{\mathrm{H-H}} = 6.97$ Hz), 7.23 (m, 4 H), 7.03 (t, 4 H, $J_{\mathrm{H-H}} = J_{\mathrm{H-F}} = 8.65$ Hz), 2.06 (s, 2 H); ^{13}C NMR (100 MHz) δ 163.86, 161.40 ($J_{\mathrm{C-F}} = 247.2$ Hz), 145.32, 136.27, 131.26, 129.73, 129.65 ($J_{\mathrm{C-F}} = 8.9$ Hz), 129.01, 125.63, 121.71, 114.85, 114.64 ($J_{\mathrm{C-F}} = 21.1$ Hz), 89.42.

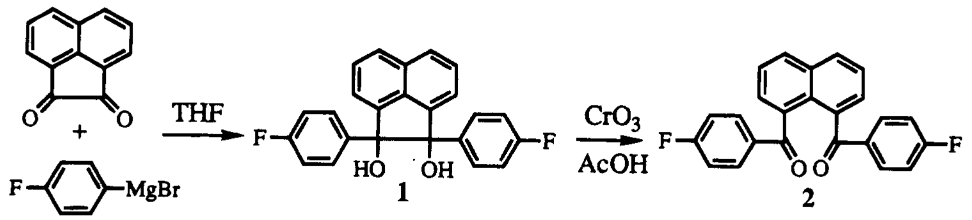
After filtration, the solids were mixed with CrO$_3$ (80.0 g, 0.53 mol) in 3 L of acetic acid in a beaker. The mixture was heated up until all solids dissolved and held at 90 °C overnight. TLC analysis (ethyl acetate/hexane, 40/60) showed the consumption of the diol. After cooling to room temperature, the solids were precipitated out upon addition to cold water. After filtration and rinsing with hot water, the product **2** was recrystallized three times from toluene/methanol (1:1, v/v) to yield white crystals: 122.0 g (65%); mp 166.0−168.0 °C (lit.[11] mp 166.5−167.5 °C); IR (KBr, cm^{-1}) 1665 (C=O); ^{1}H NMR (400 MHz) δ 8.07 (m, 2 H), 7.87 (dd, 4 H, $J_{\mathrm{H-H}} = 8.69$ Hz, $J_{\mathrm{H-F}} = 5.51$ Hz), 7.54 (m, 4 H), 7.07 (t, 4 H, $J_{\mathrm{H-H}} = J_{\mathrm{H-F}} = 8.64$ Hz); ^{13}C NMR (100 MHz) δ 196.30, 166.98, 164.45 ($J_{\mathrm{C-F}} = 254.8$ Hz), 136.68, 135.01, 134.03, 134.00 ($J_{\mathrm{C-F}} = 2.9$ Hz), 133.05, 132.96 ($J_{\mathrm{C-F}} = 9.4$ Hz), 132.08, 129.73, 124.98, 115.46, 115.24 ($J_{\mathrm{C-F}} = 21.9$ Hz); MS (relative intensity) m/e 249 ($\mathrm{M}^{\bullet +} - {}^{\bullet}\mathrm{COPhF}$, 100).

1,8-Bis(4-phenoxybenzoyl)naphthalene. In a dry 50-mL flask equipped with a stirbar, a Dean−Stark trap fitted with a condenser, and a nitrogen inlet were placed the difluoride **2** (5.000 g, 13.4 mmol) and phenol (2.525 g, 26.8 mmol). TMSO$_2$ (20 mL) and toluene (7 mL) were added to the flask. Potassium carbonate was then added to the suspension. The mixture was heated up to 140 °C and stirred for 2 h to distill off the azeotrope formed by water with toluene. The temperature was then increased to 180 °C, and the mixture was allowed to react overnight. The reaction was then stopped, and the solution was precipitated into a beaker containing methanol (200 mL). The white solids were filtered and then recrystallized twice from toluene/methanol (1:1, v/v) to afford 1,8-bis(4-phenoxybenzoyl)naphthalene as white crystalline solids: 5.58 g (80%); mp 181−182 °C; IR (KBr, cm^{-1}) 1649 (C=O), 1244 (C-O-C); ^{1}H NMR (200 MHz) δ 8.03 (dd, 2 H, $J_{\mathrm{H-H}} = 7.55$ Hz, $^{4}J_{\mathrm{H-H}} = 1.93$ Hz), 7.78 (dd, 4 H, $J_{\mathrm{H-H}} = 6.90$ Hz, $^{4}J_{\mathrm{H-H}} = 2.08$ Hz), 7.55 (m, 4 H), 7.38 (dd, 4 H, $J_{\mathrm{H-H}} = 8.46$ and 7.75 Hz), 7.17 (tt, 2 H, $J_{\mathrm{H-H}} = 7.35$ Hz, $^{4}J_{\mathrm{H-H}} = 1.22$ Hz), 7.07 (dd, 4 H, $J_{\mathrm{H-H}} = 8.60$ Hz, $^{4}J_{\mathrm{H-H}} = 1.20$ Hz), 6.90 (dd, 4 H, $J_{\mathrm{H-H}} = 6.97$ Hz, $^{4}J_{\mathrm{H-H}} = 2.11$ Hz); ^{13}C NMR (50 MHz) δ 196.15, 161.77, 155.18, 136.86, 134.76, 132.57, 131.92, 131.65, 129.88, 129.51, 128.67, 124.74, 124.48, 120.26, 116.57.

Polymer Synthesis. Polymerizations were typically carried out in a dry 50-mL, three-necked flask equipped with a stirbar, a Dean−Stark trap fitted with a condenser, and a nitrogen inlet. The following is a typical procedure. To the dried flask containing difluoride **2** (1.117 g, 3.00 mmol), bisphenol **3a** (0.685 g, 3.00 mmol), deoxygenated toluene (6 mL), and TMSO$_2$ (4 mL) was added finely ground potassium carbonate (1.036 g, 7.50 mmol). The mixture was stirred at 140−150 °C for 2 h under a strong flow of nitrogen to azeotrope off the water formed with toluene. The temperature was then increased to 180 °C. After 1 h of reaction and an apparent increase in the viscosity, TMSO$_2$ (4 mL) was added. The reaction was monitored by testing samples by GPC. After another hour, the reaction was complete, showing no increase in the molecular weight. The reaction mixture was cooled down to 150 °C, diluted with TCE (15 mL), and precipitated into methanol (200 mL) containing a few drops of concentrated HCl. The resulting fibrous polymer was dissolved in chloroform (70 mL), filtered through a thin bed of Celite to remove the inorganic salts, and reverse precipitated to remove low molecular weight fractions, yielding white fibrous polymer **4a**: 1.634 g.

4a: 96%; IR (film, cm^{-1}) 1661 (C=O), 1243 (C-O-C); ^{1}H NMR (200 MHz) δ 8.00 (d, 2 H, $J_{\mathrm{H-H}} = 7.96$ Hz), 7.75 (d, 4 H, $J_{\mathrm{H-H}} = 8.75$ Hz), 7.52 (m, 4 H), 7.22 (d, 4 H, $J_{\mathrm{H-H}} = 8.75$ Hz), 6.95 (d, 4 H, $J_{\mathrm{H-H}} = 8.61$ Hz), 6.87 (d, 4 H, $J_{\mathrm{H-H}} = 8.91$ Hz), 1.65 (s, 6 H); ^{13}C NMR (50 MHz) δ 196.29, 161.99, 153.20, 146.84, 137.05, 134.90, 132.75, 132.01, 131.82, 129.68, 128.84, 128.36, 124.93, 119.88, 116.72, 42.40, 31.07.

4b: 90%; IR (film, cm^{-1}) 1655 (C=O), 1247 (C-O-C); ^{1}H NMR (400 MHz) δ 8.03 (dd, 2 H, $J_{\mathrm{H-H}} = 8.00$ Hz, $^{4}J_{\mathrm{H-H}} = 1.48$ Hz), 7.84 (d, 4 H, $J_{\mathrm{H-H}} = 8.70$ Hz), 7.56 (dd, 2 H, $J_{\mathrm{H-H}} = 7.06$ Hz, $^{4}J_{\mathrm{H-H}} = 1.48$ Hz), 7.51 (t, 2 H, $J_{\mathrm{H-H}} = 7.82$ Hz), 7.40 (d, 4 H, $J_{\mathrm{H-H}} = 8.64$ Hz), 7.05 (d, 4 H, $J_{\mathrm{H-H}} = 9.09$ Hz), 6.99 (d, 4 H, $J_{\mathrm{H-H}} = 8.82$ Hz); ^{13}C NMR (100 MHz) δ 196.31, 160.55, 156.49, Scheme 1. Synthesis of Difluoride Monomer 2



136.92, 134.98, 133.13, 132.82, 131.97, 129.73, 128.87, 128.79, 124.95, 119.13, 117.90, 63.42.

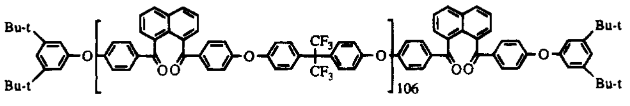
4c: 89%; IR (film, cm^{-1}) 1655 (C=O), 1236 (C-O-C); ^1H NMR (200 MHz) δ 8.00 (d, 2 H, J_{H-H} = 8.06 Hz), 7.80 (d, 4 H, J_{H-H} = 8.69 Hz), 7.52 (m, 8 H), 7.11 (d, 4 H, J_{H-H} = 8.61 Hz), 6.94 (d, 4 H, J_{H-H} = 8.89 Hz); ^{13}C NMR (50 MHz) δ 196.31, 161.69, 154.81, 136.89, 136.64, 134.87, 132.74, 132.22, 131.83, 129.68, 128.74, 128.47, 124.88, 120.61, 116.86.

4d: 92%; IR (film, cm^{-1}) 1654 (C=O), 1243 (C-O-C); ^1H NMR (200 MHz) δ 7.97 (d, 2 H, J_{H-H} = 7.82 Hz), 7.71 (d, 6 H, J_{H-H} = 8.64 Hz), 7.49–7.15 (m, 14 H), 6.87 (d, 4 H, J_{H-H} = 8.79 Hz), 6.82 (d, 4 H, J_{H-H} = 8.83 Hz); ^{13}C NMR (50 MHz) δ 196.33, 161.74, 154.36, 151.11, 142.10, 140.14, 137.12, 134.99, 132.85, 132.27, 131.92, 129.80, 128.93, 128.05, 127.89, 125.14, 126.21, 125.03, 120.48, 120.03, 117.06, 64.65.

4e: 85%; IR (film, cm^{-1}) 1654 (C=O), 1229 (C-O-C); ^1H NMR (400 MHz) δ 7.98 (d, 2 H, J_{H-H} = 7.94 Hz), 7.81 (d, 4 H, J_{H-H} = 8.70 Hz), 7.51 (m, 4 H), 7.08 (s, 4 H), 6.92 (d, 4 H, J_{H-H} = 8.69 Hz); ^{13}C NMR (100 MHz) δ 196.30, 161.89, 151.93, 136.99, 134.97, 132.79, 132.33, 131.82, 129.63, 128.70, 124.90, 121.86, 116.68.

4f: 90%; IR (film, cm^{-1}) 1655 (C=O), 1227 (C-O-C); ^1H NMR (200 MHz) δ 8.01 (dd, 2 H, J_{H-H} = 8.16 Hz, $^4J_{H-H}$ = 2.01 Hz), 7.84 (d, 4 H, J_{H-H} = 8.2 Hz), 7.52 (m, 4 H), 7.17 (s, 1 H), 6.95 (m, 6 H), 1.36 (s, 9 H); ^{13}C NMR (50 MHz) δ 196.67, 162.47, 162.19, 151.43, 151.32, 144.19, 137.29, 137.25, 135.26, 133.06, 132.54, 132.42, 132.37, 132.29, 132.09, 130.07, 129.97, 129.06, 125.14, 122.94, 120.31, 119.27, 119.23, 117.33, 116.60, 35.28, 30.39.

End-Capped Polymer 5. To a dry 50-mL, three-necked flask equipped with a stirbar, a Dean–Stark trap with a condenser, and a nitrogen provider containing difluoride **2** (1.729 g, 4.64 mmol), bisphenol **3b** (1.546 g, 4.60 mmol), 3,5-di-*tert*-butylphenol (0.019 g, 0.09 mmol), $TMSO_2$ (12 mL), and deoxygenated toluene (15 mL) was added finely ground potassium carbonate (1.383 g, 10.0 mmol). The mixture was heated up to 140–150 °C under a strong flow of nitrogen to remove the azeotrope. The temperature was then increased to 180 °C and held for 2 h until a viscous solution was formed, and GPC of samples taken from the reaction mixture showed no increase in the molecular weight. The reaction mixture was then allowed to cool down to 150 °C, diluted with TCE (15 mL), and precipitated into methanol (200 mL) containing a few drops of HCl. The resulting polymer was dissolved in chloroform (150 mL), filtered through a thin bed of Celite, and reverse precipitated, yielding white fibrous polymer **5**: 2.944 g (95%); IR (film, cm^{-1}) 1661 (C=O), 1244 (C-O-C); ^1H NMR (400 MHz) δ 8.02 (d, 2 H, J_{H-H} = 8.00 Hz), 7.84 (d, 4 H, J_{H-H} = 8.71 Hz), 7.53 (m, 4 H), 7.40 (d, 4 H, J_{H-H} = 8.60 Hz), 7.05 (d, 4 H, J_{H-H} = 8.95 Hz), 6.99 (d, 4 H, J_{H-H} = 8.74 Hz), 1.30 (s); ^{13}C NMR (100 MHz) δ 196.07, 160.31, 156.24, 136.67, 134.73, 132.88, 132.88, 132.57, 131.71, 129.49, 128.62, 128.54, 125.35, 124.70, 122.50, 118.89, 117.66, 63.66, 31.15. The calculation based on the ratio of two peaks at 1.30 and 8.02 ppm in the ^1H NMR spectrum gave a number of units (n) in the polymer of 106 or M_n = 70 800 (M_n = 52 700 by GPC). The inherent viscosity was 0.51 dL/g in chloroform at 25 °C.



End-capped Polymer 5

Purification of Polymer by Reverse Precipitation. In a large beaker a polymer (1.0 g) was dissolved in chloroform (50 mL) with stirring. To the chloroform solution was added dropwise through a dropping funnel methanol (about 50 mL), while the solution was stirred rapidly. To the point when the polymer precipitated out as a gummy residue at either the bottom of the beaker or around the stirring bar, the addition was stopped. After removal of the solvent, the polymer was redissolved in chloroform (10–20 mL) and precipitated into methanol. The resulting fibrous polymer was filtered and dried under reduced pressure at 60 °C.

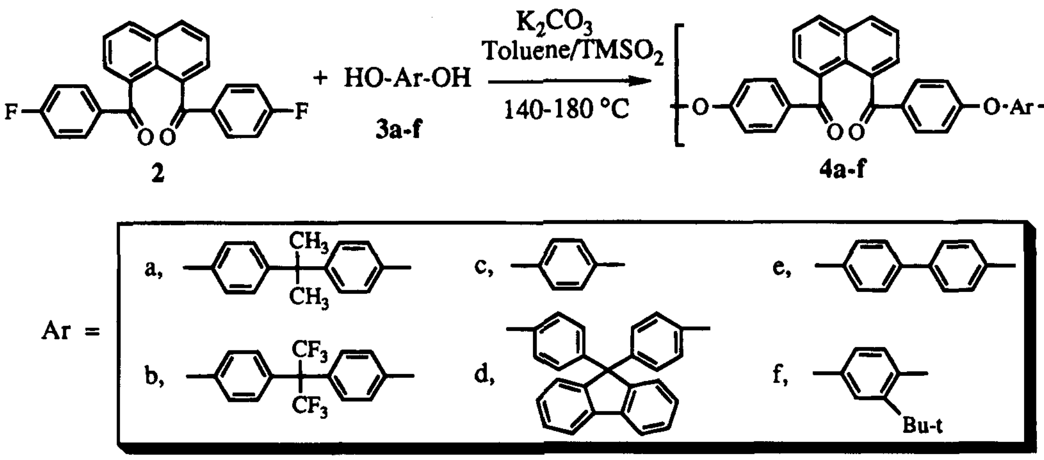
Results and Discussion

Between two common routes to poly(arylene ether ketone)s, the nucleophilic substitution of activated aromatic dihalides with bisphenols and the electrophilic substitution of arenes with 1,8-naphthalic acid or its derivatives, the former is the choice of the polymerization since the difluoride monomer containing a 1,8-naphthylenedicarbonyl unit can be readily prepared. In this approach, a variety of title polymers can be produced because of the availability of many bisphenols.

Monomer Synthesis. Direct acylation of fluorobenzene with 1,8-naphthalic anhydride failed to produce any products, which is presumably due to low reactivity of the acylium ion generated upon action with aluminum chloride.[12] This failure also implies the futile polymerization by the electrophilic substitution if using 1,8-naphthalic acid or anhydride. The Grignard reaction of 1,2-acenaphthenequinone with (4-fluorophenyl)magnesium bromide gave the pinacol **1** as a mixture of cis/trans isomers which, without further purification, was oxidized with chromic acid in acetic acid to afford the desired monomer **2** (Scheme 1). The high purity of difluoride **2** in an overall 65% yield was obtained after recrystallization three times from toluene/methanol (1:1, v/v). This simple process can be readily scaled up over 100 g without any difficulties. The monomer is very reactive toward nucleophilic displacement reaction. As a model reaction for polymerization, it reacted with 2 mol equiv of phenol at 180 °C in $TMSO_2$ in the presence of potassium carbonate. The expected product, 1,8-bis(4-phenoxybenzoyl)naphthalene, was isolated in high yield (>80% after twice recrystallization). The high yield and quantitative conversion observed in the displacement demonstrated that the conditions used in this model reaction ($TMSO_2$/toluene, 180 °C) are suitable for polymerization.

Polymer Synthesis. Polymerizations were carried out in $TMSO_2$ using a stoichiometric ratio of monomers in the presence of excess potassium carbonate (Scheme 2). The resulting water was removed together with toluene at 140 °C during the initial stage of polymerization. At the beginning of polymerization the solution concentration was kept high with about 45% solid contents. After complete dehydration (2 h) and raising the temperature to 180 °C, the reaction mixture became viscous and was diluted with $TMSO_2$ to ca. 22.5% solid contents. The progress of polymerization was then

Scheme 2. Synthesis of Naphthalene-Based Polymers 4a-f



monitored by running GPC of a small amount of samples. The prolonged heating at temperatures higher than 180 °C could cause polymer degradation, which is known for poly(arylene ether)s.[13] The resulting polymers were isolated by precipitation into methanol, washed, and purified by reverse precipitation to remove any small amounts of oligomers.

Polymer **5** with controlled molecular weight was also prepared from monomers **2** and **3b** in the presence of 3,5-di-*tert*-butylphenol as an end-capping agent. The number-average molecular weight (M_n) of this end-capped polymer was then determined by the ^1H NMR analysis and compared with the apparent M_n obtained by gel permeation chromatography (GPC) according to polystyrene standards.

Polymer Characterization and Properties. All polymers appear as the white to off-white fibrous solids and displayed excellent solubility in chlorinated hydrocarbons, *N,N'*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP). Free-standing, transparent, tough films could be cast from chloroform or TCE solution. The structures of all polymers were confirmed by IR and NMR spectroscopies. The carbonyl absorption for these polymers in IR was found in the region of 1654−1661 cm^{-1}. The most conclusive evidence comes from NMR data. The carbon-13 NMR spectrum of **4c** displays 13 distinguishable lines for each of the different carbon atoms and matches well with that of structurally related 1,8-bis(4-phenoxybenzoyl)naphthalene that has two extra lines as expected (Figure 2). A carbonyl peak was observed at 196 ppm for both. When necessary, the assignment is supported by 2D COSY experiments for other polymers. These spectral data clearly indicate the formation of expected PAEKs. GPC in chloroform relative to polystyrene standards showed that high molecular weight products were obtained (Table 1). The apparent weight-average molecular weights for **4a−f** ranged from 58 700 to 213 000. All GPC traces were monomodal with polydispersity factors varying between 1.94 and 2.20. The high molecular masses of polymers **4a−f** were also evidenced by their inherent viscosities ranging from 0.50 to 0.95 dL g^{-1} in chloroform (Table 1).

The end-capped polymer **5** had an inherent viscosity of 0.51 dL g^{-1} in chloroform. Its number-average molecular weight was determined to be 52R t700 by GPC, which is significantly less than the value (M_n = 70 800) calculated by the NMR analysis. Therefore, the exact molecular weights of these polymers should be higher than the apparent ones determined by GPC.

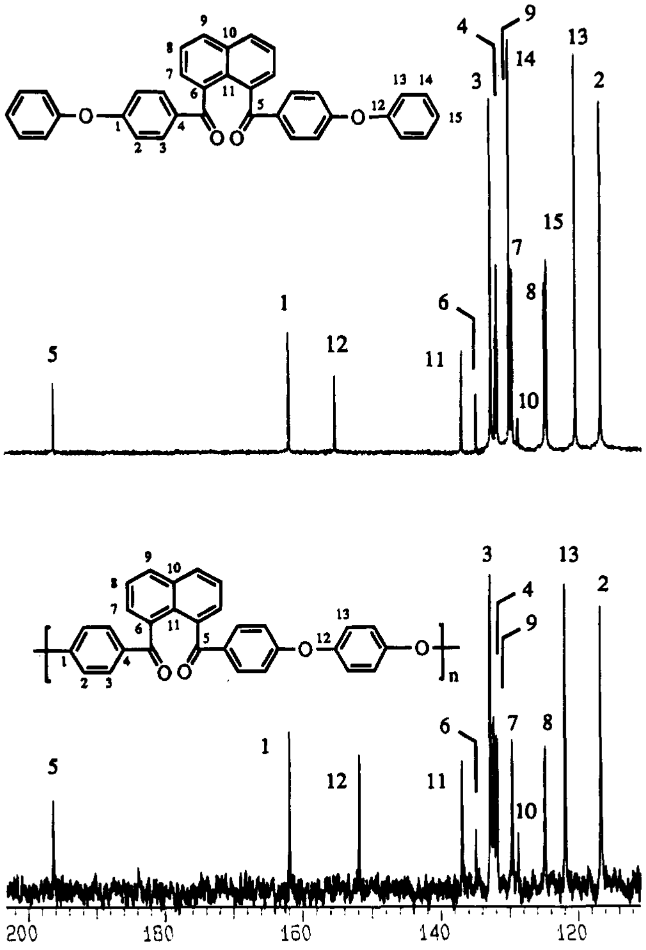


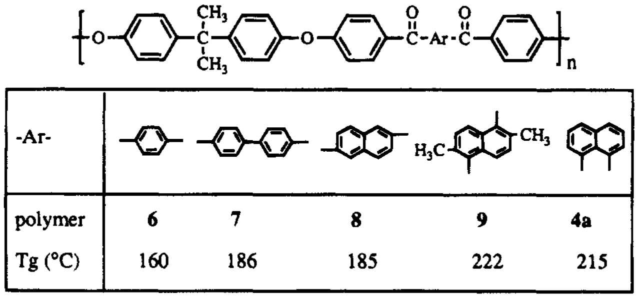
Figure 2. ^{13}C NMR (100 MHz) spectra of **4c** and 1,8-bis(4-phenoxybenzoyl)naphthalene.

None of these polymers showed any crystalline behavior as assessed by differential scanning calorimetry (DSC) and thermomechanical analysis in stress−strain mode (TMA/SS). The glass transition temperatures (T_gs) were observed between 214 and 270 °C by DSC depending on the units derived from bisphenol monomers (Table 1). Polymer **4d** containing a bulky cardo group has the highest T_g (270 °C), whereas others have T_gs all around 220 °C. The T_g values obtained from DSC agree well with tan δ (maximum) values obtained from TMA/SS. In general, introducing a rigid benzenoid into the polymer backbone is likely to increase the T_g. Polymer **8** derived from bisphenol **3a** and 2,6-bis(4-fluorobenzoyl)naphthalene has a T_g of 185 °C, higher

Table 1. Characterization of Polymers 4a-f

				T_g, °C		TG[d]		E'[e] (GPa)	
polymer 4	η_{inh}[a] (dL/g)	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	DSC[b]	TMA[c]	in N_2	in air	load A	load B
a	0.61	7.05	3.64	215	206	476	480	0.60	0.70
b	0.94	21.3	10.0	214	212	526	522	1.75	2.17
c	0.50	5.87	2.47	222	182	528	522	0.82	0.96
d	0.74	15.7	5.23	270	268	534	529	1.20	1.70
e	0.79	14.5	7.01	228	225	537	533	1.60	4.40
f	0.95	14.8	6.83	230	*f*	476	478	*f*	*f*

[a] Inherent viscosity taken in a 0.5% chloroform solution at 25 °C. [b] Second scan at a heating rate of 10 °C/min. [c] Tan δ value; heating rate of 10 °C/min. [d] Onset temperatures for 5% weight loss. [e] Young's modulus at 25 °C. Load A: offset = 10 g, amplitude = 5 g. Load B: offset = 20 g, amplitude = 10 g. [f] Not measured.



polymer	6	7	8	9	4a
Tg (°C)	160	186	185	222	215

Figure 3. Comparison of the T_gs of structurally related poly(arylene ether ketone)s.

than that of analogue **6** with a *p*-phenylene unit (160 °C)[4a] but very close to that of analogue **7** having a 4,4′-biphenylene unit (186 °C) (Figure 3).[5c] Considering the structures in the repeat unit, polymer **4a** is less symmetric than **8**. But its T_g is actually 30 °C higher than that (T_g = 185 °C) of **8**. This noticeable increase in T_g clearly demonstrates that two benzoyls at the 1,8-positions of naphthalene are in the fairly sterically congested environment, similar to those in the 1,2-phenylenedicarbonyl and 2,2′-biphenylenedicarbonyl structures (Figure 1). Such a steric hindrance causes the increased restriction of free rotation of the bond connecting the naphthylene and the carbonyl groups and reduces the overall chain mobility. Introducing a bulky, pendant *tert*-butyl group in the polymer also increases T_g, as demonstrated by a pair of polymers **4c** (T_g = 222 °C) and **4f** (T_g = 230 °C). However, the thermal stability decreases greatly due to the presence of the weaker C−H bond in the *tert*-butyl group. As assessed by thermogravimetry (TG), the 5% weight loss in both nitrogen and air occurred near 480 °C for **4f** and above 520 °C for **4c** containing no *tert*-butyl group. Polymer **4a** was also relatively less thermally stable, because of the presence of an aliphatic methyl group, than other wholly aromatic poly(ether ketone)s **4c**−**e** and its fluorinated analogue **4b**. Nevertheless, in spite of their high T_gs, these PAEKs should be stable enough for melt processing.

The solvent-cast thin films of polymers **4a**−**e** were clear, creasable, and tough. Young's moduli were measured by TMA in the tensile stress−strain mode (Table 1). Loads were chosen such that a linear stress−strain relationship was obtained. Two sets of Young's moduli were taken using different loads. With higher loads (offset = 20 g, amplitude = 10 g), relatively higher E' were observed in the range of 0.70−4.40 GPa at 25 °C. These values are typical for engineering thermoplastics such as polysulfones and poly(ether imide)s. At elevated temperatures, films of these polymers maintain good mechanical properties in the gigapascal range up to about 200 °C. The high E' value (4.4 GPa) was observed for polymer **4e**, due to biphenylene in the repeat unit. High tensile moduli have also been reported for other biphenyl-containing PAEKs.[5b,c,e,14] The relatively low Young's modulus for **4c** may be due to residual TCE solvent in the film or different film-casting conditions.

Conclusions

A series of 1,8-naphthalic-containing PAEKs **4** derived from 1,8-bis(4-fluorobenzoyl)naphthalene are all amorphous and readily soluble in chloroform, TCE, and NMP. Their T_gs should be relatively higher than those of analogues having 2,6-naphthalic units derived from 2,6-bis(4-fluorobenzoyl)naphthalene and the corresponding bisphenols. High thermostabilities should allow polymers **4** to be melt processed. Young's moduli of PAEKs **4** are found to be relatively lower than those of biphenyl-based PAEK analogues. The syntheses of other isomeric naphthalene-based PAEKs and the effects of structural symmetry of these isomeric PAEKs on gas transport properties will be reported in due course.

Acknowledgment. We gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada.

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MA946154E