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Poly(Aryl Ether Ketone)s Containing the 2-Naphthalenyl Moiety

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POLY(ARYL ETHER KETONE)S CONTAINING THE 2-NAPHTHALENYL MOIETY

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ABSTRACT

Amorphous, thermally stable poly(aryl ether ketone)s (PAKs) were prepared by the condensation polymerization of the novel dihalide 1,2-bis(4-fluorobenzoyl)-3,6-diphenyl-4,5-bis(2-naphthalenyl)-benzene and biphenols in dipolar aprotic solvents in the presence of potassium carbonate. The presence of pendant 2-naphthalenyl moieties was found to have no deleterious effects on the thermal stabilities or solubilities of the PAKs. The properties of these polymers are compared to those of PAKs prepared previously in this laboratory. Evidence of a single electron transfer reaction between hydroquinone and the novel dihalide involving the pendant 2-naphthalenyl moieties was found and was investigated through model reactions.

INTRODUCTION

Poly(aromatic ketone)s (PAK)s are a class of thermally stable engineering thermoplastics known for their excellent electrical and mechanical properties [1]. Commercially available polymers are highly crystalline, such as Victrex PEEK (ICI) and exhibit excellent solvent resistance. At present, PAKs are used as insulating materials, matrices for composite materials [1], and in electronics applications [2].

Bonner synthesized low molecular weight PAKs by the aluminum chloride mediated Friedel–Crafts acylation of diphenyl ether with terephthaloyl chloride in nitrobenzene [3]. The highly crystalline oligomers were insoluble and precipitated before high molecular weight polymer could form. Goodman et al. succeeded in synthesizing a high molecular weight PAK from isophathaloyl chloride and diphenyl ether using methylene chloride as the solvent [4]. Polyacylation reactions can also be performed in highly acidic media such as HF using BF_3 as the Lewis acid [5].

The synthesis of PAKs by nucleophilic displacement polymerization was initially unsuccessful due to the insolubility of the highly crystalline product [6]. Rose pioneered the use of diphenyl sulfone at high temperatures as a suitable reaction solvent and was able to synthesize high molecular weight semicrystalline PAKs by nucleophilic displacement polymerization [7].

A number of amorphous PAKs have been synthesized employing bisphenols such as 2,2-bis(4-hydroxyphenyl)propane (BPA) [8]. These polymers exhibit enhanced solubility, allowing the polymerizations to be performed at lower temperatures in dipolar aprotic solvents such as *N,N*-dimethyl acetamide (DMAc) and dimethylsulfoxide (DMSO). Recently we reported a series of amorphous, thermally stable PAKs incorporating the 1,2-dibenzoylbenzene moiety in the polymer backbone [9]. The coiled morphology of these polymers resulted in soluble PAKs with an entirely aromatic backbone. The work showed that as the bulkiness of the novel dihalide monomers was increased, so did the T_g of the respective polymers [9]. This paper describes our efforts to increase the T_g of our novel PAKs by further increasing the size of the dihalide monomer without negatively impacting the excellent properties already displayed by these polymers.

EXPERIMENTAL

General Methods

Melting points were recorded on a Fischer-Jones melting point apparatus. Flash chromatography was performed on silica gel 60 (70-230 mesh) from BDH. Inherent viscosity data were obtained using chloroform solutions with a concentration of 0.5 g/dL in a calibrated 1Å (176) Ubbelohde dilution viscometer at 25°C. Apparent molecular weights were determined by gel permeation chromatography using polystyrene standards with chloroform as the solvent using a Waters 510 HPLC with a UV detector (λ = 254 nm) and 4 μ-Styragel columns (10^5, 10^4, 500, and 100Å) in series. Glass transition temperatures (T_g) were measured using a Seiko 220 Differential scanning calorimeter (DSC) instrument at a heating rate of 20°C/min under a nitrogen atmosphere. The T_g was taken as the midpoint of the change in the slope of the baseline. All values reported are from the second run. Thermogravimetric analyses (TGA) were obtained using a Seiko 220 TG/DTA instrument. The 5% weight loss points were recorded using a heating rate of 10°C/min under atmospheres of nitrogen and air. All polymer samples were dried under a nitrogen atmosphere at the T_g (as determined by DSC) for 1 hour before performing TGA measurements. Young's moduli were recorded using a Seiko TMA/SS120. The polymer films used for these measurements were prepared as follows: 150 mg polymer was dissolved in 3 mL chloroform. The chloroform solutions were cast on glass plates using circular glass molds 1 inch in diameter. The chloroform was allowed to evaporate, and the films were dried at 85°C for 24 hours in a forced air oven. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Materials

Potassium cyanide, benzyltrimethyl ammonium hydroxide 40% solution in methanol (J. T. Baker), 1,3-diphenyl-2-propanone, 2-naphthaldehyde, ethylbenzene, 4-*tert*-butylphenol, tetramethylenesulphone (sulfolane) (Aldrich), hydrobromic acid (48% aqueous), ethanol (95%), methanol (ACP), toluene (spectro grade), anhydrous magnesium sulfate, and potassium carbonate (A&C Chemicals) were used as received. Phenol (Anachemia) was distilled under vacuum twice before use. Monomer quality Bisphenol A, 4,4′-dihydroxybiphenyl, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, and 9,9-bis(4-hydroxyphenyl)fluorene were donated by the General Electric Co. and were used as received. Hydroquinone, 4,4′-dihydroxydiphenylsulfone, and 4,4′-dihydroxybenzophenone (Aldrich) were sublimed under high vacuum before use. *N,N*-Dimethyl acetamide (DMAC), *N*-methyl pyrrolidinone (NMP), and *N*-cyclohexyl pyrrolidinone (CHP) (Aldrich) were distilled from calcium hydride and stored over 4Å molecular sieves.

Monomer Synthesis

1,2-Bis(2-naphthalenyl)ethan-1,2-dione, **2**

2-Naphthaldehyde **1** (50 g, 0.402 mol) was converted to 1,2-bis(2-naphthalenyl)-2-hydroxyethan-1-one as described in the literature [10]. Oxidation of the naphthoin to **2** was accomplished by the method of Floyd [11]. The crude 1,2-bis(2-naphthalenyl)-2-hydroxyethan-1-one was dissolved in DMSO (300 mL), and 48% HBr (aq) (25 mL) was added. The solution was heated to 55°C for 18 hours. When the solution was cooled to room temperature, the product **2** crystallized and was recovered by filtration. Recrystallization of **2** from a 50/50 mixture of benzene and methanol gave 30 g (60% yield) of yellow needle crystals: mp 157–158°C [lit. 158–159] [10].

2,5-Diphenyl-3,4-bis(2-naphthalenyl)cyclopentadien-1-one, **4**

A 500-mL three neck flask was charged with 1,3-diphenyl-2-propanone **3** (21.2 g, 0.101 mol), **2** (31.3 g, 0.101 mol), and triethylene glycol (50 mL). The solution was heated to 100°C in an oil bath and stirred until all the solids had dissolved. Benzyltrimethyl ammonium hydroxide 40% solution in methanol (5 mL) was added to the flask, and the reaction was stirred for 2 hours [12]. The product recrystallized from the solution as the flask was cooled. The solid was recovered by filtration and then recrystallized from ethanol to give 39.0 g of **4** (85% yield): mp 225–226°C [lit. 227–229°C] [13].

1,2-Bis(4-fluorobenzoyl)acetylene, **5**

This compound was prepared according to a previously published procedure [9]. 1,2-Bis(4-fluorobenzoyl)-3,6-diphenyl-4,5-bis(2-naphthalenyl)benzene, **6**.

A 1000-mL three neck flask was charged with 2,5-diphenyl-3,4-bis(2-naphthalenyl)cyclopentadien-1-one, **4** (30.0 g, 0.062 mol), 1,2-bis(4-fluorobenzoyl) acetylene, **5** (16.73 g, 0.062 mol), and ethylbenzene (300 mL). The solution was stirred under reflux for 8 hours and then cooled to room temperature. The solid precipitate was recovered by filtration and the ethylbenzene was evaporated under reduced pressure. The crude solid was recrystallized from ethylbenzene yielding 39.0 g of a fine white powder (89% yield): mp 218-219°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.64 (m, 3H), 7.49-7.51 (m, 2H), 7.40-7.41 (m, 1H), 7.18-7.35 (m, 9H), 6.94-7.00 (m, 3H), 6.76-6.86 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.44, 165.18 (d, $J_{C\text{-}F}$ = 250 Hz), 142.23, 142.18, 139.34, 139.92, 139.12, 137.78, 137.73, 135.97, 135.87, 134.49 (d, $J_{C\text{-}F}$ = 2.75 Hz), 132.06 (d, $J_{C\text{-}F}$ = 9.12 Hz), 132.09, 132.02, 131.36, 131.33, 130.94, 130.89, 130.67, 130.65, 130.51, 130.48, 128.89, 128.87, 128.77, 128.74, 127.62, 127.29, 126.73, 126.58, 126.47, 125.58, 125.53, 114.82 (d, $J_{C\text{-}F}$ = 21.9 Hz); MS (EI Direct inlet 350°C) *m/e* 726 (100, m^{*+}), 123 (45.2), 96 (13.5); Elemental analysis calculated for $C_{52}H_{32}F_2O_2$: C 89.89, H 4.68, F 5.47; found: C 89.71, H 4.73, F 5.02.

Model Reactions

1,2-Bis[4-(4-*tert*-butylphenoxy)benzoyl]-3,6-diphenyl-4,5-bis(2-naphthalenyl) benzene, 9

A 100-mL three neck flask was charged with **6** (1.000 g, 1.38 mmol), 4-*tert*-butylphenol (0.4547 g, 3.03 mmol), K_2CO_3 (0.4606 g, 3.33 mmol), toluene (3 mL), and DMAc (5 mL). The solution was heated to reflux, and water was removed by azeotropic distillation with toluene for 3 hours. The remaining toluene was then removed by distillation into the Dean-Stark trap. The temperature was increased to 155°C and the reaction was followed by TLC and HPLC for 3 hours, at which time all of the starting material, **6**, had been consumed. The solution was poured into 200 mL of aqueous methanol containing a few drops of glacial acetic acid, and the resulting precipitate was recovered by filtration. The crude product was recrystallized from xylenes/ethanol (50/50) yielding 1.308 g (96%) of the desired product **14**: mp 275-276.5°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.66 (m, 4H), 7.47-7.49 (m, 4H), 7.39-7.41 (m, 2H), 7.32-7.37 (m, 6H), 7.16-7.29 (m, 6H), 6.94-7.01 (m, 4H), 6.72-6.68 (M, 14H), 1.36 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.23, 161.42, 153.34, 147.05, 141.93, 139.48, 138.08, 136.27, 136.16, 132.76, 132.36, 131.85, 131.30, 131.02, 130.90, 130.75, 130.48, 129.00, 128.88, 127.61, 127.29, 126.62, 126.51, 126.40, 125.46, 119.16, 116.75, 34.34, 31.43; MS (EI Direct inlet 250°C) *m/e* 987 (15.10, M^{*+}), 761 (13.8), 307 (100.0), 253 (85.8), 210 (50.7); Elemental analysis calculated for $C_{72}H_{58}O_4$: C 87.60, H 5.92; found: C 87.52, H 5.87.

1,2-Bis(4-phenoxybenzoyl)-3,6-diphenyl-4,5-bis(2-naphthalenyl)benzene, 11

A 100-mL three neck flask was charged with **6** (1.0000 g, 1.38 mmol), phenol (0.2727 g, 2.90 mmol), K_2CO_3 (0.4606 g, 3.33 mmol), toluene (3 mL), and DMAc (5 mL). The solution was heated to reflux and dehydrated by distilling water off as an azeotrope with toluene. After 3 hours the remaining toluene was removed by distillation into the Dean-Stark trap. The reaction was heated to 155°C and followed by TLC and HPLC for 24 hours. At this time the reaction was quenched by pouring it into 200 mL of aqueous methanol containing a few drops of glacial acetic acid; the resulting precipitate was recovered by filtration. Two products and the starting material **6** were separated on a silica gel flash column with petroleum ether/ethyl acetate (10/1) as eluent. One-tenth of a gram of the starting material **6**, 10% of the original amount, was recovered directly from the flash column. This was followed by 0.118 g (10% yield) of a monosubstituted product **10** and 1.08 g (80% yield) of the expected disubstituted product **11**.

Compound **10**: mp 296-298°C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.51-7.93 (m, 9H), 7.34-7.46 (m, 5H), 7.08-7.27 (m, 9H), 6.78-6.96 (m, 14H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 196.17, 196.05, 164.80 (d, $J_{C\text{-}F}$ = 250 Hz), 142.35, 142.29, 142.19, 142.14, 138.79, 138.57, 138.50, 137.88, 137.84, 137.73, 137.69, 136.33, 136.28, 136.24, 136.18, 134.11, 132.45 (d, $J_{C\text{-}F}$ = 2.75 Hz), 132.12, 131.94, 131.05, 130.78 (d, $J_{C\text{-}F}$ = 9.1 Hz), 130.42, 130.33, 129.93, 129.04, 128.89, 127.73, 127.64, 127.40, 127.20, 126.89, 126.84, 126.25, 126.19, 125.97, 125.93, 124.61, 119.46, 117.34, 115.21 (d, $J_{C\text{-}F}$ = 22 Hz); MS (EI Direct inlet 230°C) *m/e* 801 (10.6, M^{*+}), 460 (10.9), 341 (9.9), 307 (100.0), 289 (57.7), 219 (20.9); Elemental analysis calculated for $C_{58}H_{37}FO_3$: C 86.98, H 4.66, F 2.37; found: C 86.91, H 4.70, F 2.55.

Compound **11**: mp 262-263°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 7.49-7.58 (m, 9H), 7.37-7.45 (m, 6H), 7.10-7.32 (m, 9H), 6.80-9.94 (m, 18H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 194.10, 159.22, 154.12, 140.87, 137.44, 137.37, 136.68, 135.19, 131.37, 130.99, 130.79, 129.90, 129.75, 129.30, 128.83, 127.96, 127.83, 126.63, 126.32, 126.08, 125.72, 125.14, 124.88, 123.56, 118.49, 116.30; MS (EI Direct inlet 200°C); *m/e* 875 (14.6, M^{*+}), 705 (4.07), 460 (12.4), 341 (8.5), 307 (100.0), 289 (60.3), 219 (25.9); Elemental analysis calculated for $C_{64}H_{42}O_4$: C 87.85, H 4.84, found: C 88.13, H 4.79.

Model Reaction in the Presence of Tetraphenylhydrazine [14]

A 100-mL three neck flask was charged with **6** (1.0000 g, 1.38 mmol), phenol (0.2727 g, 2.90 mmol), tetraphenylhydrazine (0.0135 g, 0.004 mmol), K_2CO_3 (0.4606 g, 3.33 mmol), toluene (3 mL), and DMAc (5 mL). The solution was heated to reflux and dehydrated by distilling water off as an azeotrope with toluene. After 3 hours the remaining toluene was removed by distillation into the Dean-Stark trap. The reaction was heated to 155°C and followed by TLC and HPLC for 24 hours. At this time the reaction mixture contained a mixture of 12% **6**, 11% **10**, and 75% **11**, as determined by HPLC. The reaction was quenched into aqueous methanol containing a few drops of glacial acetic acid. Isolation of the three materials was accomplished by flash chromatography, as described above.

1,2-Bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene, 12

This compound was synthesized according to a literature procedure [9].

1,2-Bis(4-phenoxybenzoyl)-3,4,5,6-tetraphenylbenzene, 13

A 100-mL three neck flask was charged with **12** (1.000 g, 1.59 mmol), phenol (0.3153 g, 3.35 mmol), K_2CO_3 (0.4606 g, 3.33 mmol), toluene (3 mL), and DMAc (5 mL). The solution was heated to reflux, and water was removed as an azeotrope with toluene for 3 hours. The remaining toluene was removed by distillation into the Dean-Stark trap. The reaction temperature was increased to 155°C and the reaction followed by TLC and HPLC until all of the starting material **12** was consumed (3 hours). The reaction was quenched by pouring into 200 mL of aqueous methanol which contained several drops of glacial acetic acid, and the resulting precipitate was recovered by filtration. The crude product **13** was recrystallized from xylenes/ethanol (50/50) yielding 1.30 g (92%) of the desired product: mp 399-400°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.59 (m, 4H), 7.31-7.34 (m, 4H), 7.11-7.14 (m, 2H), 6.72-6.92 (m, 28H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.34, 161.02, 155.92, 142.04, 139.28, 138.72, 138.68, 138.16, 133.00, 131.88, 131.19, 130.96, 129.80, 127.09, 126.87, 126.49, 125.85, 124.08, 119.59, 117.05; MS (EI Direct inlet (250°C)) *m/e* 775 (1.6, M^{*+}), 605 (1.9), 447 (1.7), 391 (27.7), 195 (31.7), 167 (44.7), 149 (100); Elemental analysis calculated for $C_{56}H_{38}O_4$: C 86.80, H 4.94; found: C 86.88, H 5.01.

Polymer Synthesis

A general method for the polymerization of **6** with all biphenols follows. A 50-mL reaction flask was charged with **6** (1.000 g, 1.38 mmol), BPA **7a** (0.3151 g, 1.38 mmol), K_2CO_3 (0.976 g, 7.1 mmol), DMAc (6 mL), and toluene (3 mL). The reaction mixture was heated to a gentle reflux (135°C), and this temperature was maintained for 3 hours to ensure complete dehydration. The reaction temperature was increased to 155°C by distilling the toluene into the Dean-Stark trap. The reaction was discontinued when the solution viscosity increased dramatically. The solution was diluted with DMAc (5 mL) and coagulated into aqueous methanol (150 mL) containing several drops of glacial acetic acid. The recovered polymer was dissolved in chloroform and filtered hot through a thin pad of Celite. The chloroform solution was concentrated and the polymer was coagulated in methanol (150 mL). The solid polymer was recovered by filtration and dried under vacuum (100°C) for 24 hours.

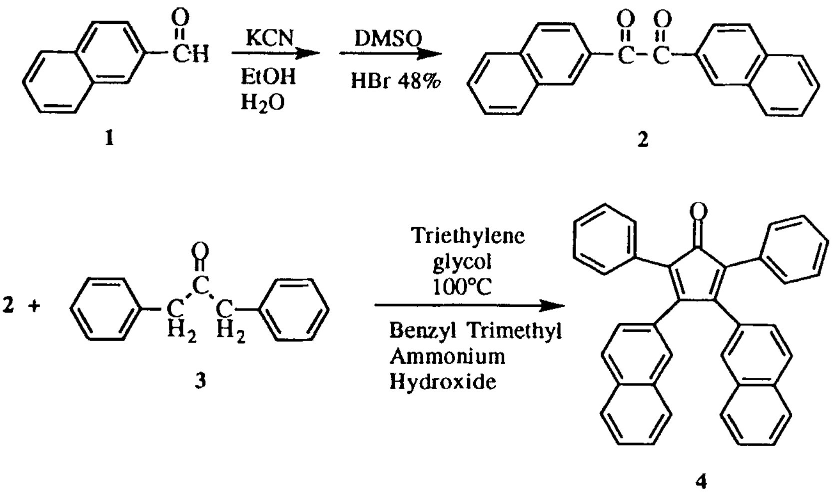
Polymerizations in solvents other than DMAc were performed in an identical manner, with the DMAc replaced by either NMP, CHP, or sulfolane.

DISCUSSION

Synthesis of 1,2-bis(4-fluorobenzoyl)-3,6-diphenyl-4,5-bis(2-naphthalenyl)-benzene **6** was accomplished as outlined in Schemes 1 and 2. 2-Naphthalenecarboxaldehyde **1** was reacted in a benzoin condensation followed by oxidation with HBr (48% aqueous) in DMSO. 1,2-Bis(2-naphthalenyl)ethan-1,2-dione **2** was condensed with 1,3-diphenyl-propan-2-one **3** in triethylene glycol in the presence of base to yield the tetra-substituted cyclopentadien-1-one **4**. The synthesis of dibenzoylacetylene **5** was accomplished following a literature procedure [9]. A Diels-Alder reaction between **4** and dibenzoyl-acetylene **5** in ethylbenzene yielded the desired monomer **6**. The reactions are facile and the overall yield is limited to 46% by the low yield obtained in the synthesis of 1,2-bis-2-naphthalenyl-ethan-1,2-dione **2**.

Polymerization Reaction

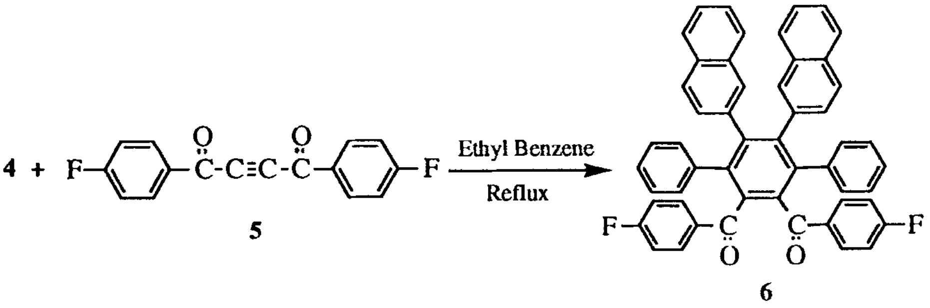
Monomer **6** was polymerized with commercial biphenols **7a–g** (Scheme 3) in DMAc in the presence of a small excess of potassium carbonate to yield polymers **8a–f** in greater than 90% yield. A typical reaction time including dehydration was 6



SCHEME 1.

hours; however, polymerization reactions with biphenols **7e** and **7f** required as much as 10 hours to achieve high molecular weight. This is a result of the lower reactivity of the phenate anions due to the strong electron-withdrawing nature of the bridging carbonyl and sulfonyl groups [1]. Polymers **8a–f** are amorphous and soluble in dipolar aprotic solvents as well as in common organic solvents such as chloroform and chlorobenzene. Transparent, colorless films were easily cast from chloroform solutions, which were tough and flexible. Attempts to synthesize polymer **8g** were unsuccessful, resulting in only low molecular weight oligomers. The reaction solutions were characterized by a black color which is considerably different from the tan color exhibited for all other polymer solutions. This was found not to be a solvent effect since polymerization reactions, which were attempted in DMAc, NMP, CHP, and sulfolane, all produced similar results.

Recently, it was reported that a single electron transfer reaction can occur under the conditions of condensation polymerization when the biphenol employed was hydroquinone [14]. The electron transfer reaction caused the reduction of a



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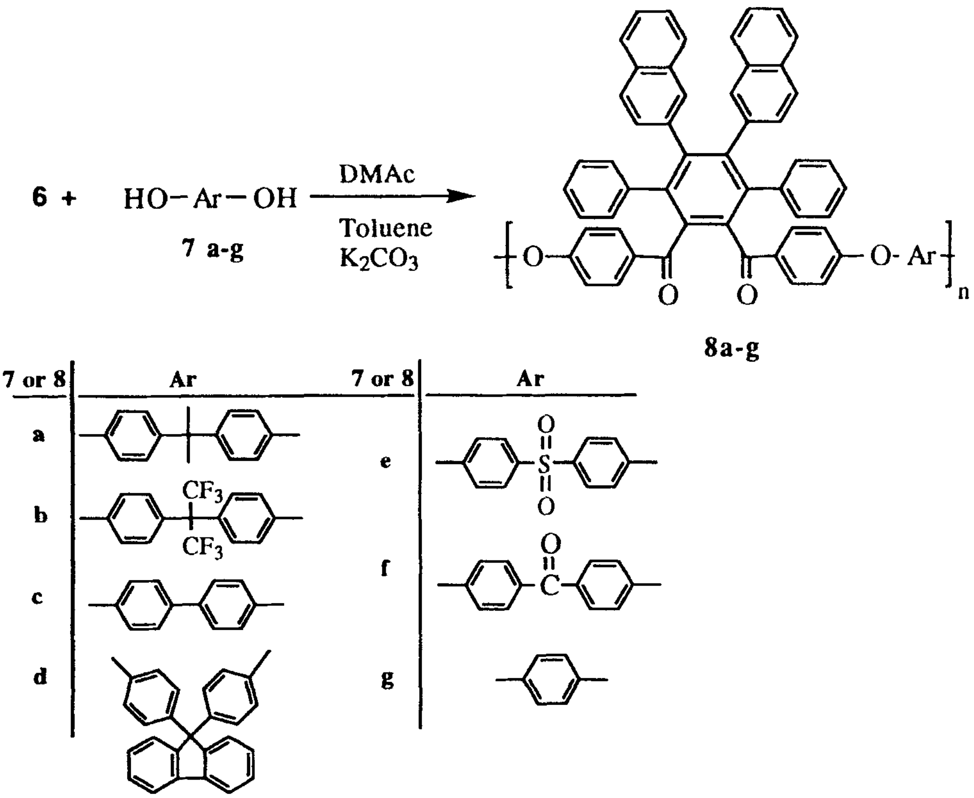
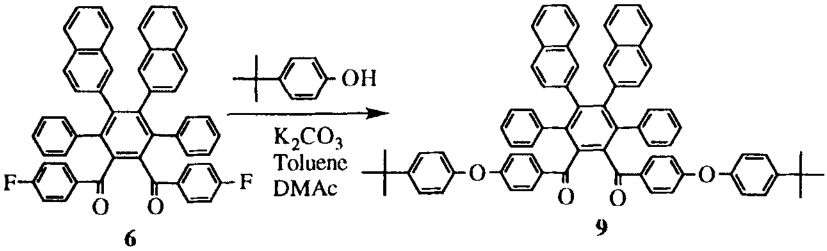


SCHEME 3.

carbon—halide bond when the activated halide was chlorine, destroying the reaction stoichiometry and preventing high polymer from forming [14]. Similar effects were not observed for monomers when the activated halide was fluorine. Model reactions involving a dichlorine monomer and phenol or 4-methylphenol showed that the electron transfer reaction occurred only in the presence of phenol [14].

Model reactions were performed with **6** and phenol or 4-*tert*-butylphenol. Compound **6** reacts quantitatively with 4-*tert*-butylphenol to give **9** (Scheme 4). However, in the presence of phenol, the solution rapidly becomes black, and after

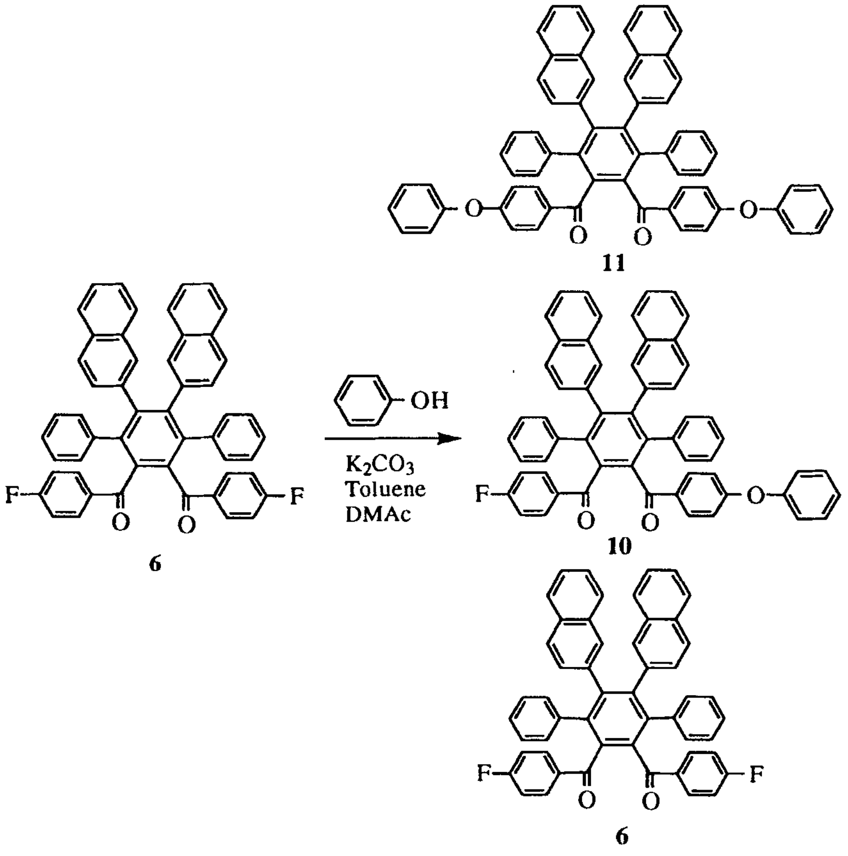


SCHEME 4.

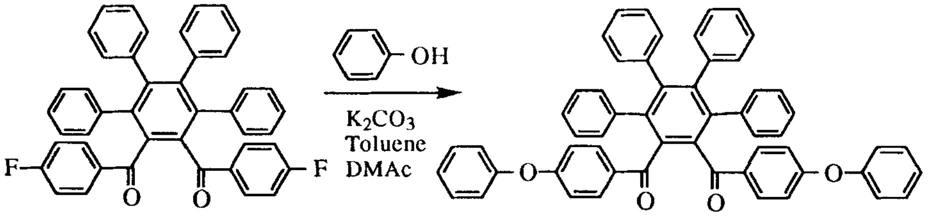
24 hours traces of **6** and two products **10**, a monosubstituted compound, and **11**, the expected disubstituted compound, were evident (Scheme 5). No traces of phenol were detected; however, HPLC indicated the presence of at least two highly polar substances in trace amounts (approximately 1% of total peak area). Flash chromatography of the reaction mixture resulted in the isolation of **6**, **10**, and **11**.

1,2-Bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene **12** reacted with hydroquinone **7g** to produce high molecular weight polymer without any complications [9]. A model reaction of **11** with phenol gave only one product, **13** (Scheme 6). This result indicates that the mechanism of electron transfer involves the 2-naphthalenyl moieties of **6**, and results in the consumption of a small amount of hydroquinone **7g**, destroying the stoichiometric balance of the polymerization reaction.

It was reported that the effect of the electron transfer reaction under condensation polymerization conditions can be prevented by the presence of a catalytic amount of tetraphenylhydrazine [14]. A model reaction of **6** with phenol in the presence of tetraphenylhydrazine resulted in a black solution and the recovery of a mixture of **6**, **10**, and **11**. The presence of tetraphenylhydrazine did not prevent the suspected electron transfer process from occurring in this case.



SCHEME 5.



12 13

SCHEME 6.

Polymer Properties

Table 1 contains data on the physical properties of polymers **8a–f**. All polymers show an inherent viscosity greater than 0.3 dL/g, indicating that high molecular weight polymers have been obtained. The values of the polymer T_gs range from 264 to 307°C as measured by DSC at a heating rate of 20°C/min. Polymer **8d**, synthesized from **6** and the fluorenone biphenol **7d**, yields the highest T_g polymer.

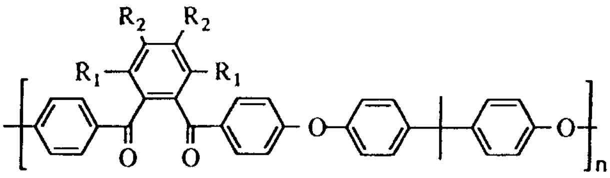
One objective of this work was to synthesize thermally stable, amorphous PAKs with glass transition temperatures greater than those of polymers **14a–c** (Fig. 1), synthesized previously in this laboratory [9]. Polymer **14a** has a T_g of 182°C (Table 2). The addition of a pair of pendant phenyl rings to the *o*-dibenzoylbenzene moiety of this polymer gives polymer **14b** and an increase in the polymer T_g of approximately 40°C. A similar increase in polymer T_g occurs going from **14b** to **14c** where two further pendant phenyl rings have been added. We were interested to see if the incorporation of larger pendant moieties, such as the 2-naphthalenyl group, into this polymer architecture would result in a further increase in the polymer T_g.

Table 3 compares the T_gs of polymers **8a–d** and **14c–f** (see Fig. 2 for structures of polymers **14c–f**). No increase in polymer T_g is evident when comparing polymers

TABLE 1. Properties of Polymers

Polymer	Inherent viscosity,[a] dL/g	T_g, °C[b]	TGA (°C),[c] 5% wt loss		Isothermal aging,[d] % wt loss
			N_2	Air	
8a	0.62	264	516	517	–
8b	0.37	275	535	529	0.9
8c	0.52	290	538	529	1.0
8d	0.51	310	546	535	1.0
8e	0.35	290	530	515	2.6
8f	0.63	271	532	519	1.1

[a] 0.5 g/dL in $CHCl_3$ at 25°C.
[b] Heating rate 20°C/min.
[c] Heating rate 10°C/min.
[d] 8 hours at 300°C under nitrogen atmosphere



14a $R_1=R_2=H$
14b R_1=phenyl $R_2=H$
14c $R_1=R_2$=phenyl

FIG. 1. Structure of polymers **14a-c**.

8a-d and **14c-f**. The additional size conferred by the pendant 2-naphthalenyl groups in **8a-d** does not result in an increase in the T_g of these PAKs.

All polymers showed excellent stability by thermogravimetric analysis in air and nitrogen atmospheres. The 5% weight loss points are greater than 500°C in all cases (Table 1). Isothermal aging of the polymers under nitrogen atmosphere for 8 hours at 300°C showed weight losses between 0.9 and 2.6% for polymers **8a-f**.

Young's moduli for polymers **8a-f** are given in Table 4. The moduli fall in the range of 1.2 to 2.5 GPa at room temperature and 1.0 to 1.3 GPa at 200°C. Young's moduli compare favourably with those of other engineering thermoplastics, both at room temperature and at 200°C. The T_gs of the polymers as measured from the tan δ are lower than the values measured by DSC, 257-298°C as compared to 264-307°C. This is due to the mild mechanical deformations inherent in the TMA/SS testing method [15]. The values consistently differ with the values measured by DSC by an average of 9°C. This behavior was observed for other PAKs reported by this laboratory [16].

Table 5 contains the gel permeation chromatography (GPC) data for polymers **8a-f**. The $\overline{M}_n$ and $\overline{M}_w$ values indicate high molecular weight polymers were formed but do not reflect true values due to the different morphologies of the PAKs and the polystyrene standards employed for the calibration curve. The polydispersity values are within the range expected for condensation polymers of this type.

Polymer Solubility

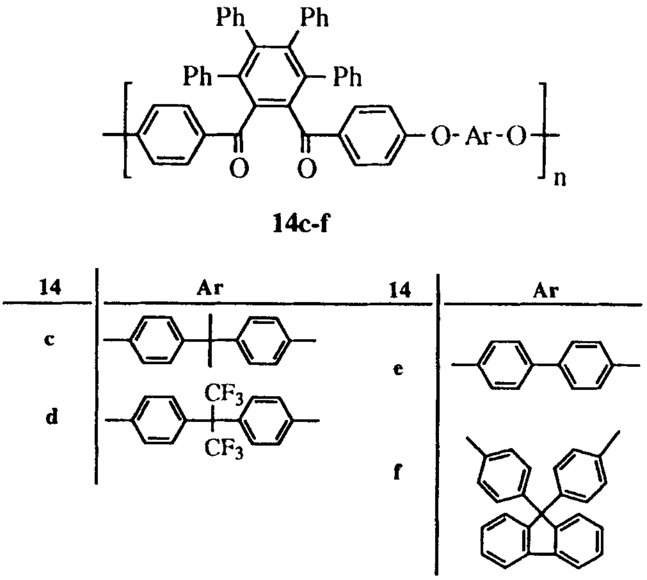
Polymers **8a-f** are soluble in chlorinated solvents such as chlorobenzene, *s*-tetrachloroethane, and chloroform, and common organic solvents such as 1,4-dioxane and toluene. This behavior is identical to the solubility of the PAKs previously reported by this laboratory [9].

TABLE 2. T_gs of Polymers **14a-c**

Polymer	T_g, °C [9]
14a	182
14b	221
14c	265

TABLE 3. Comparison of Polymer Glass Transition Temperatures

Polymer	T_g, °C	Polymer	T_g, °C [9]
8a	264	**14c**	265
8b	275	**14d**	278
8c	290	**14e**	292
8d	310	**14f**	313



14c-f

FIG. 2. Structure of polymers **14c-f**.

TABLE 4. Mechanical Properties for Polymers **8a-f**

Polymer	Young's modulus, GPa 20°C	Young's modulus, GPa 200°C	Tan δ, °C
8a	1.18	1.00	257
8b	2.53	1.25	260
8c	1.88	1.30	280
8d	1.53	1.26	298
8e	2.19	1.08	291
8f	2.11	1.22	261

TABLE 5. GPC Data for Polymers **8a–f**

Polymer	$\overline{M}_n$	$\overline{M}_w$	PD
8a	73,571	170,071	2.3
8b	47,738	108,477	2.3
8c	55,105	154,103	2.8
8d	73,896	169,127	2.3
8e	37,690	101,870	2.7
8f	68,894	164,845	2.4

CONCLUSIONS

A series of novel, amorphous poly(aryl ether ketone)s has been synthesized by the nucleophilic displacement polymerization of **6** with commercially available biphenols **7a–g** in DMAc. Only hydroquinone **7g** failed to give a high molecular weight polymer. This is believed to be due to a single electron transfer reaction between the 2-naphthalenyl groups of **6** and hydroquinone **7g**. Model reactions indicate that the presence of the 2-naphthalenyl moieties in **6** are necessary for the suspected electron transfer reaction to occur.

The polymers are amorphous and soluble in dipolar aprotic solvents and chlorinated solvents such as chloroform and chlorobenzene. The polymers exhibit glass transition temperatures between 264 and 307°C as measured by differential scanning calorimetry. When compared to the T_gs of PAKs synthesized previously in this laboratory, no increase in polymer T_g was conferred by the larger 2-naphthalenyl pendant groups of **6**.

The 5% weight loss temperatures in air and nitrogen atmospheres, as recorded by thermogravimetric analysis, were all in excess of 500°C. The polymers were cast into transparent, colorless films that were tough and flexible, and had Young's moduli between 1.2 and 2.5 GPa at room temperature and 1.0 and 1.3 GPa at 200°C.

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