Synthesis and Physical Properties of Soluble, Amorphous Poly(ether ketone)s Containing the *o*-Dibenzoylbenzene Moiety

Rina Singh[†] and Allan S. Hay*

Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6

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ABSTRACT: The synthesis of novel fluoro monomers **4**, **7a**, and **10** containing the 1,2-dibenzoylbenzene moiety is described. The three monomers were isolated in very high yields. These fluoro monomers undergo reactions with bisphenols in the presence of excess anhydrous potassium carbonate in an aprotic solvent (*N,N*-dimethylacetamide) to give high molecular weight amorphous poly(aryl ether ketone)s which are very soluble in solvents such as chloroform and toluene at room temperature, have glass transition temperatures ranging from 160 to 313 °C, and are easily cast into flexible, colorless and transparent films. The 5% weight losses by thermogravimetric analysis for these materials were all above 500 °C.

Introduction

High molecular weight poly(aromatic ketone)s (PAK) were first synthesized by Friedel–Crafts condensation of isophthaloyl and terephthaloyl chlorides with diphenyl ether in methylene chloride solution in the presence of aluminum chloride[1] and later by reaction in liquid hydrogen fluoride solvent.[2] They comprise a class of polymers exhibiting high thermal stability and excellent electrical and mechanical properties. These materials are highly crystalline and very insoluble in all common solvents at ambient temperatures. The alternate synthesis of PAK by nucleophilic substitution was for a long time unsuccessful because the polymers precipitate from solution during polymerization. Rose found that the nucleophilic substitution method could be used to produce high molecular weith poly(ether ether ketone) (PEEK)[3] by the condensation of 4,4′-difluorobenzophenone with hydroquinone in the presence of potassium carbonate only if the reaction is carried out in diphenyl sulfone solvent above 300 °C to avoid precipitation of low molecular weight polymer from solution. The current commercial interest in this material is as an insulating material and as a high-temperature matrix resin for composites. Several amorphous PAKs have been synthesized by using bisphenols such as 4,4′-(1-methylethylidene)bisphenol (BPA), and since these polymers are much more soluble, the reaction can be carried out at lower temperatures in an aprotic dipolar solvent.[4] An alternative to the bisphenoxide displacement reaction was recently reported by Kricheldorf,[5] in which the phenoxide was generated by desilylation of trimethyl silyl phenyl ethers with cesium fluoride as the catalyst. The catalyst is continually regenerated by the subsequent reaction of the phenoxide with the activated aromatic fluoride. Amorphous high molecular weight meta-substituted polymer has been prepared by the condensation of 1,3-bis(4-chlorobenzoyl)benzene with a number of bisphenoxides.[6]

Our interest in the PAK family of engineering thermoplastics has been directed toward the synthesis of amorphous, high molecular weight, thermooxidatively stable materials with high glass transition temperatures. We recently reported[7] the synthesis of poly(aryl ether ketone)s with the above properties. These high molecular weight materials were prepared from fluoro monomers containing the 1,2-dibenzoylbenzene moiety which underwent facile fluoro-displacement polymerization with bisphenates in the presence of excess anhydrous potassium carbonate in *N,N*-dimethylacetamide (DMAc). The polymerization reactions yielded polymers that were colorless and fibrous and that were found to be readily soluble in ordinary organic solvents such as chloroform and toluene at room temperature. Solution casting the materials at room temperature from chloroform gave transparent and colorless, flexible films. In this paper we will discuss and describe our further work on these poly(aryl ether ketone)s including the mechanical properties of the polymers.

Results and Discussion

The monomers 1,2-bis(4-fluorobenzoyl)benzene **4** and 1,2-bis(4-fluorobenzoyl)-3,6-diphenylbenzene (**7a**) were synthesized according to the method described by Adams.[8,9] Fluorobenzene and fumaryl chloride were reacted in a Friedel–Crafts reaction to give 1,2-bis(4-fluorobenzoyl)ethylene (**1a**)[9] (Scheme I). A Diels–Alder reaction of monomer **1a** with 1,3-butadiene in benzene or *trans,trans*-1,4-diphenyl-1,3-butadiene in ethylbenzene gave in excellent yield the substituted cyclohexenes **2** and **5a**, respectively. Monomers **2** and **5a** were converted to the fully aromatized compounds **4** and **7a** in quantitative yield via the corresponding dihydroisobenzofuran[10] intermediates **3** and **6a**, respectively. In a sequence of reactions similar to that above the 1,2-bis(4-chlorobenzoyl)ethylene (**1b**) was converted to substituted cyclohexene **5b** which was then aromatized to the chloro monomer **7b** via the dihydroisobenzofuran intermediate **6b**. The overall yields for the monomers are above 90%. Compound **7b** crystallizes readily from ethanol. Single crystals were grown from it, and an X-ray crystallographic analysis was performed. The crystal structure of **7b** is illustrated in Figure 1a, and a space-filling model[11] of it is shown in Figure 1b. The carbonyls are trans as depicted in the X-ray structure, and the pendant phenyls are clearly not coplanar with the central ring; hence, polymers containing these bulkly substituents in the polymer backbone would not be expected to crystallize and would be expected therefore to be soluble and remain in solution during polymerization.

1,2-Bis(4-fluorobenzoyl)ethylene (**1a**) was further employed in the synthesis of the tetraphenyl-substituted 1,2-dibenzoylbenzene monomer **10** (Scheme II). Using the method of Lutz,[12] bromination of ethylene **1a** gave vicinal bromide **8**, which upon treatment with triethylamine in acetone gave bis(4-fluorobenzoyl)acetylene (**9**) in excellent yield. Diels–Alder reaction[13] of acetylene **9** with tetraphenylcyclopentadienone in benzophenone at reflux tem-

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[†] Central Research, Dow Chemical Co., Midland, MI 48674.

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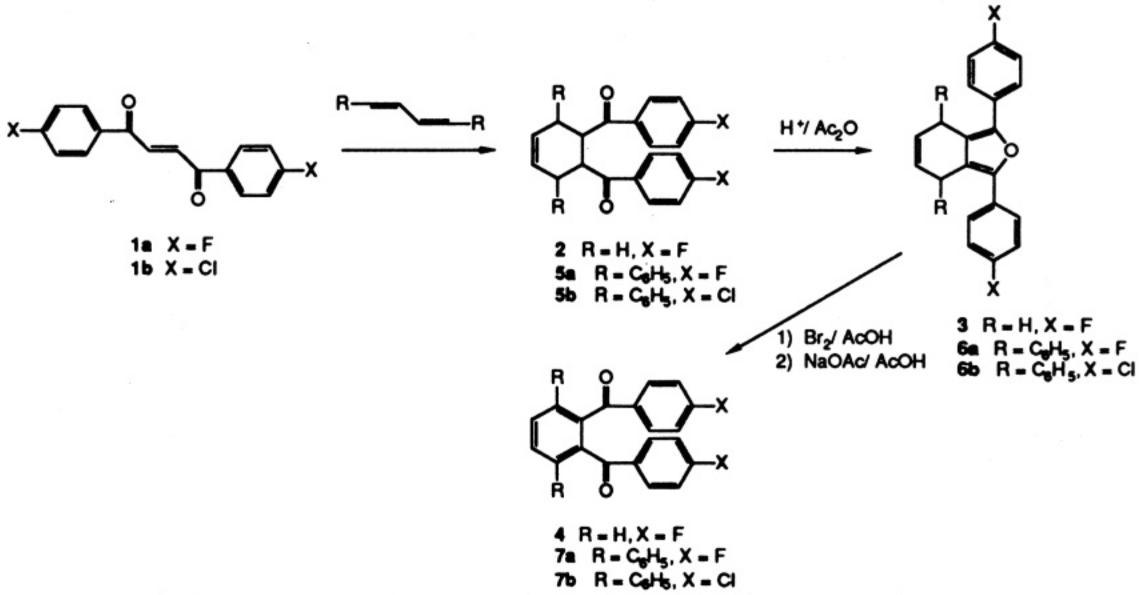
Scheme I



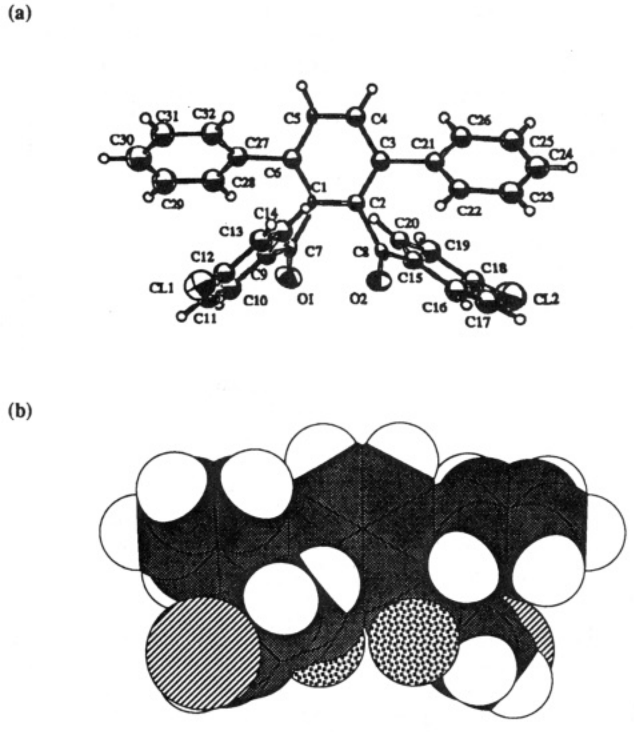


Figure 1. (a) X-ray structure and *crystallographic* numbering scheme for 1,2-bis(4-chlorobenzoyl)-3,6-diphenylbenzene (**7b**). (b) Space-filling model of **7b** generated by molecular modeling using the crystal coordinates.

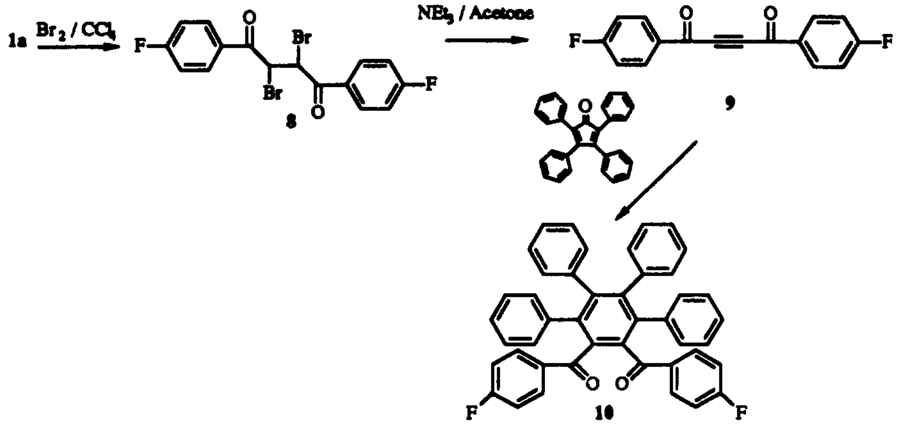
perature gave 1,2-dibenzoyl-3,4,5,6-tetraphenylbenzene (**10**) in 95% yield. The overall yield for the synthesis of monomer **10**, without optimization, is above 90%.

In the nucleophilic displacement polymerization reaction, an investigation of the rates of reactivity of the fluoro-substituted monomer **7a** versus the chloro-substituted monomer **7b** with BPA **11a** was carried out in the presence of potassium carbonate in a DMAc/toluene (2/1) solvent mixture (Scheme III). For both reactions, the solid composition was maintained at 25 wt %, and any water present or generated during the bisphenoxide formation was removed as an azeotrope with toluene. The reactions were maintained at the reflux temperature of 135 °C for 30 min, and, upon completion of bisphenoxide formation and dehydration, the polymerization reactions were heated to 164 °C to effect the displacement reaction. After a period of 2 h a dramatic increase in the viscosity indicated the formation of high molecular weight poly(ether ketone) **13a** from monomer **7a**. To acquire high molecular weight polymer from the chloro monomer **7b**, the reaction was conducted for a much longer period of time (18 h). The glass transition temperature of polymer **13a** obtained from either monomer (**7a** or **7b**) was 220 °C, and the inherent viscosities measured in chloroform at room temperature were 0.65 dL/g (from monomer **7a**) and 0.68 dL/g (from monomer **7b**). The ^{1}H NMR spectra of the polymers were identical from both reactions and are shown in Figure 2a. The 2D ^{1}H–^{1}H COSY spectrum (6.6–7.7 ppm) of poly(ether ketone) **13a** shown in Figure 2b confirms the chemical shift assignment for the aromatic region shown in the 1D ^{1}H NMR spectrum (Figure 2a).

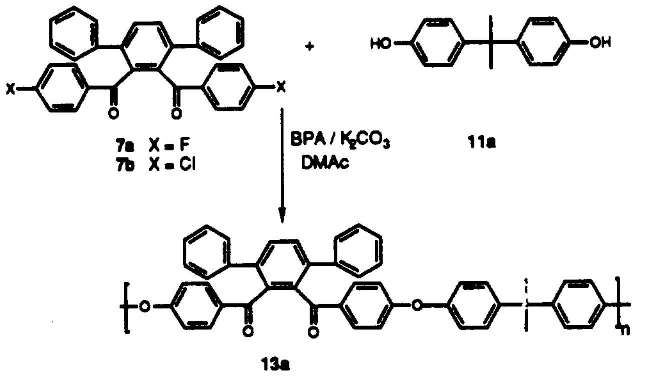
Due to the enhanced reactivity of the fluoro monomer **7a** compared to the chloro monomer **7b**, polymerization reactions of fluoro monomers **4**, **7a**, and **10** with various bisphenols were conducted in the presence of excess potassium carbonate and DMAc (Scheme IV). In all cases, high molecular weight polymer was achieved within 2 h. In all of the above polymerization reactions, the polymer solutions were cooled, diluted, coagulated in excess methanol, and filtered (coagulation in methanol was performed twice). The polymers were all dried under reduced pressure at 120 °C for 48 h. The bisphenols employed in the synthesis are shown in Scheme IV (**11a–e**). Monomers **4** and **7a** reacted with bisphenols (**11a–c**) to give high molecular weight polymers **12a–c** and **13a–c**, respectively. In addition, fluoro monomer **10** reacted with bisphenols **11a–e** to give high molecular weight poly(ether ketone)s **14a–e**. All three fluoro monomers polymerized with bisphenoxides in DMAc at the temperature of reflux. There was no difference in the rates of reactivity of the three fluoro monomers toward the various bisphenols.

The glass transition temperatures (T_g's) reported (Table I) were determined by differential scanning calorimetry (DSC) at a heating rate of 20 °C/min under an atmosphere of nitrogen. In all cases, the midpoint of the change in the slope of the base line was taken as the T_g. The glass transition temperature of the poly(ether ketone) **12a** (182 °C) is higher than its meta (T_g = 153 °C)[6] and para (T_g = 165 °C)[4] isomers, which have been synthesized previously. The higher T_g observed in the ortho polymer **12a**

Scheme II



Scheme III



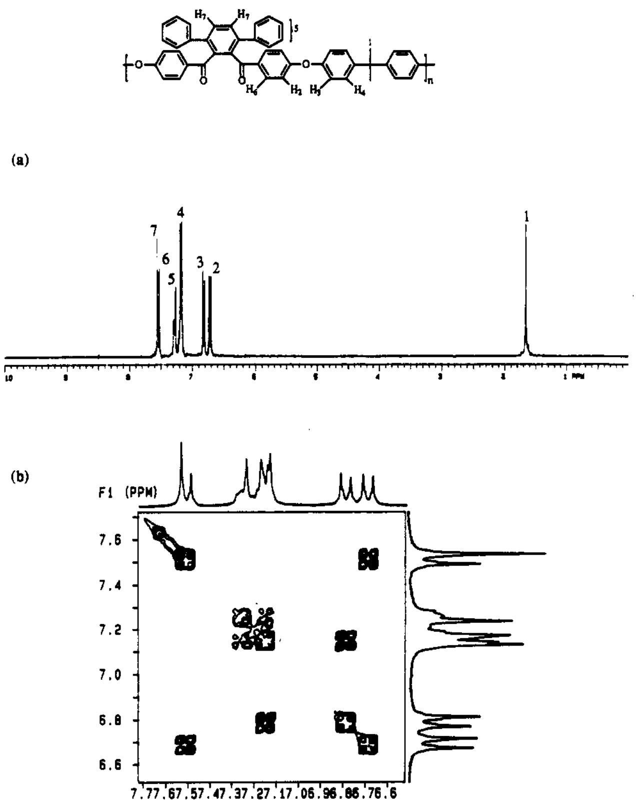


Figure 2. (a) 1D ^{1}H NMR (200 MHz, CDCl$_3$) spectrom of poly(ether ketone) **13a** from either **7a** or **7b**. (b) 2D ^{1}H–^{1}H COSY spectrum (6.6–7.7 ppm) of poly(ether ketone) **13a** acquired at 300 MHz (CDCl$_3$). Diagonal aromatic proton resonances in the 2D ^{1}H NMR spectrum are labeled in the 1D ^{1}H NMR spectrum.

as compared to its isomers has been attributed to the restricted rotation of the adjacent benzoyl groups,[7] thus resulting in a polymer with a more rigid backbone. Similar increases in glass transition temperatures due to steric hindrance in the ortho isomers of polyimides have been reported previously.[14] The glass transition temperatures of the poly(ether ketone)s increase (40–45 °C) with the addition of each pair of phenyl substituents on the central benzene ring. The T_g's ranged from 182–313 °C depending on the bisphenol and activated difluoride monomer used in the polymer synthesis (Table I). The tetraphenyl-substituted polymer series **14** showed the highest T_g's (265–313 °C), with **14e** (313 °C) containing the fluorene bisphenol moiety being somewhat higher than the polymers derived from the other bisphenols. Figure 3 shows the DSC curves of poly(ether ketone)s **14b–e**.

Apparent molecular weights determined by GPC using polystyrenes as standards have been reported for the poly(ether ketone)s shown in Table I.[7] However, to ascertain exact molecular weights for the poly(ether ketone)s, end-capped PAKs **15–23** (Scheme V) were prepared with a degree of polymerization of $n \simeq 25$, 50, and 70 monomer units/chain. The three monomers **4**, **7a**, and **10a** were polymerized with excess anhydrous potassium carbonate in DMAc and toluene solution with 4,4′-(1-methylethylidene)bisphenol (BPA) **11a** in the presence of 3,5-di-*tert*-butylphenol as an end-capping agent to give poly(aryl ether ketone)s **15–23** with 3,5-di-*tert*-butylphenyl terminal groups. The exact number-average molecular weights determined by ^{1}H NMR studies[15] for the capped materials and apparent molecular weights determined by gel permeation chromatography using polystyrenes as standards are shown in Table II. Attempts to correlate the apparent molecular weights determined by GPC with the exact molecular weights determined by ^{1}H NMR failed. The end-capped PAKS **18–23** derived from monomers **7a** and **10** gave polymers which could be solution cast from chloroform at room temperature to give flexible, clear and colorless films. End-capped PAK **15** synthesized from monomer **4** with a degree of polymerization of ~25 monomer units gave a brittle film, whereas PAKs **16** and **17** gave flexible films upon solution casting from chloroform at room temperature. All of the capped PAKs showed an intense singlet for the protons in the isopropylidene moiety at δ 1.66 and a weaker singlet for the di-*tert*-butyl group at δ 1.29, and from the ratios of the peak areas the number-average molecular weights for the polymers were calculated. The increases in the chain length of the capped materials (**15–17**, **18–20**, and **21–23**) are reflected in the increases in the inherent viscosities (Table II). The glass transition temperatures of the capped materials were observed to be identical to those of the uncapped materials shown in Table I.

Scheme IV

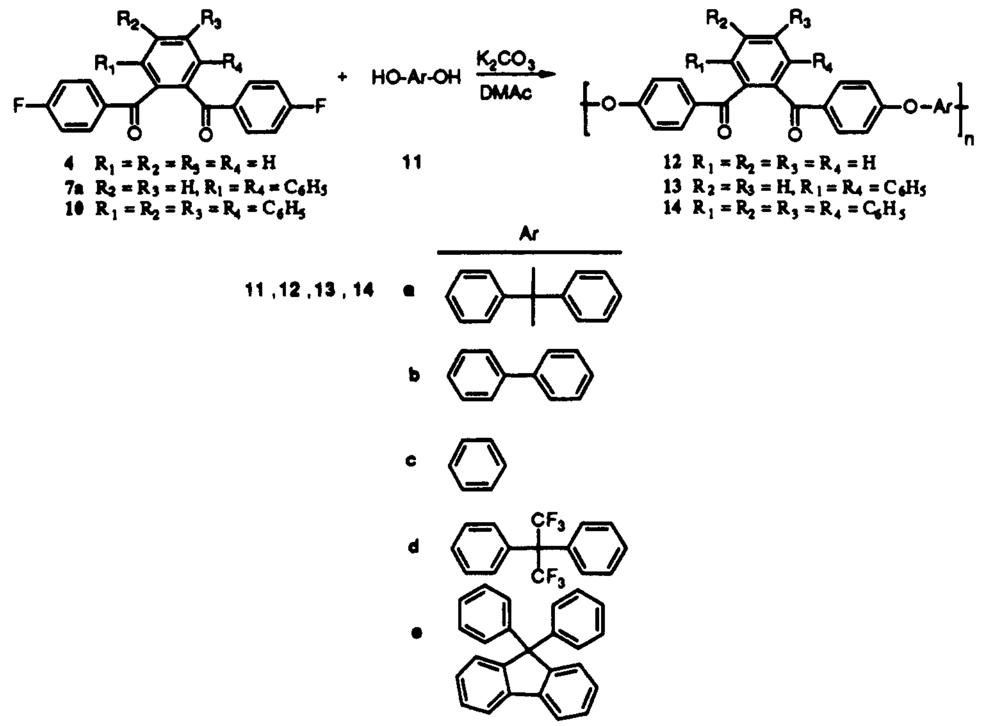


Table I
Properties of Poly(ether ketone)s 12–14

polymer	η_{inh}[a]	T_g, °C
12a	0.48	182
12b	0.42	190
12c	0.43	185
13a	0.65	221
13b	0.56	240
13c	0.35	240
14a	0.47	265
14b	0.73	292
14c	0.49	273
14d	0.44	278
14e	0.55	313

[a] The inherent viscosities were measured at a concentration of 0.5 g/dL in chloroform at 25 °C.

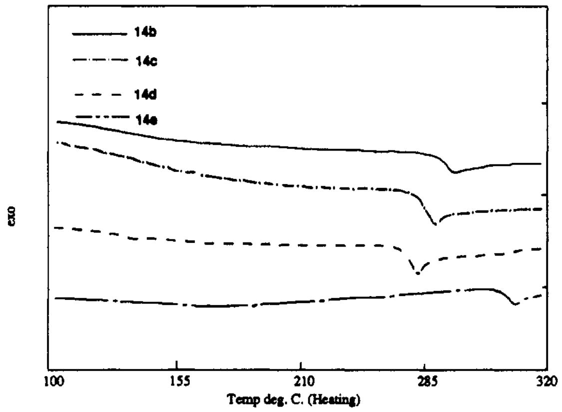


Figure 3. DSC of polymers **14b–e** under an atmosphere of N_2.

The glass transition temperatures determined by DSC (Table I) were in good agreement with those determined from dynamic mechanical thermal analysis as shown, for example, for poly(aryl ether ketone) **14a** in Figure 4. None of the polymers synthesized show any crystalline behavior even after extensive annealing above the T_g. Table III presents modulus data for the films from poly(aryl ether ketone)s from each of the difluoride monomers with the various bisphenols. The moduli of the materials range from 1.78 to 3.92 GPa at 25 °C and are lower at higher temperatures (100 or 200 °C), 0.81–2.97 GPa. The materials are all tough and show ductile mechanical behavior with no failure at 40% elongation. Poly(aryl ethers) from 1,3- and 1,4-bis(4-chlorobenzoyl)benzene have been shown[6] to have moduli of 2.62 and 2.13 GPa, respectively. The ortho isomer, polymer **12a**, has a modulus (2.10 GPa) similar to that of the para isomer.[6]

The poly(ether ketone)s demonstrated excellent thermooxidative stability by thermogravimetric analysis, with 5% weight losses above 500 °C under atmospheres of air and nitrogen[7] (Figure 5). The poly(aryl ether ketone)s containing *o*-dibenzoylbenzene moieties **14b–e** synthesized from monomer **10** are the most thermally stable by TGA. Isothermal aging (TGA) was done under an atmosphere of nitrogen over an 8-h period to assess the long-term thermal stability of the polymers (Table IV). From the aging experiments, the materials show weight losses in the range of 0.22–0.56%. Polymer **14e**, by isothermal aging, has the highest weight loss (0.56%) which is in agreement with variable-temperature TGA studies, indicating that it is the least thermally stable polymer in the series.

All of the polymers synthesized are amorphous; the glass transition temperatures increase with increasing numbers of pendant phenyl groups and the solubility of the polymers also increase. It might be expected that the free volume in the polymers would increase as the bulky phenyl groups are added. In order to confirm this, we determined the permeation of oxygen in the poly(aryl ether ketone)s **17**, **20**, and **23**. Oxygen permeation (Table V) at 20 °C increases with increasing phenyls in the polymer chain which is indicative of the larger free volume associated with poly(aryl ether ketone) **23** containing four phenyls, which has an O_2 permeation value of 2.82. Polymer **20**, which has two pendant phenyls, has an O_2 permeation of 1.27, and polymer **17** having no pendant phenyls has an even lower O_2 permeation, 1.03. From these O_2 permeation results it can be concluded that polymer **17** has a smaller free volume, which results from better interchain packing. Interestingly, polymer **17** having no pendant phenyls has

Scheme V

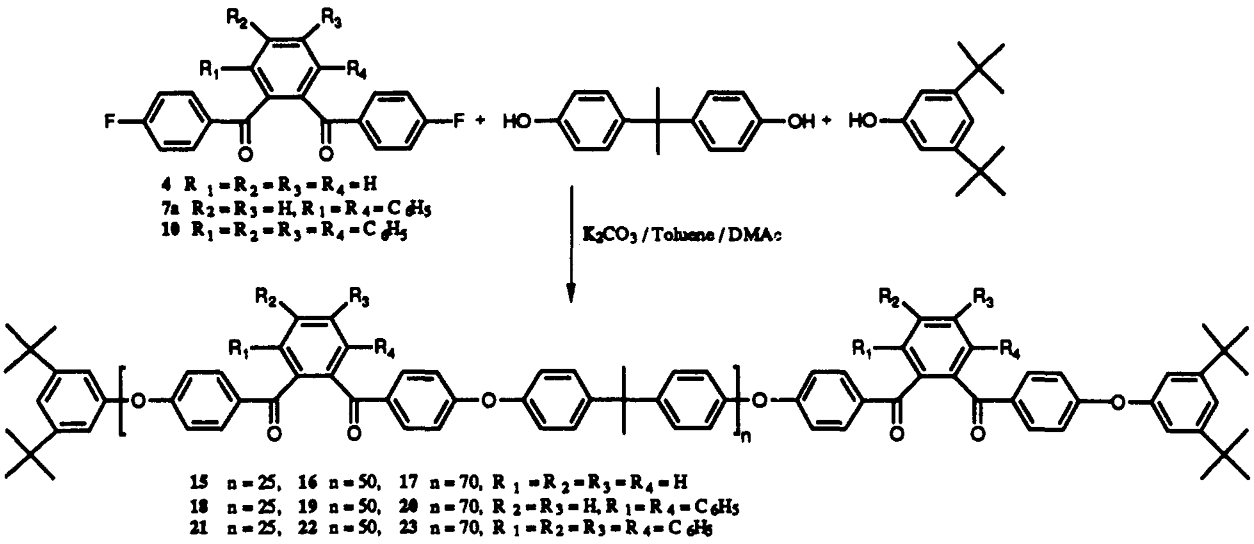


Table II
Exact Molecular Weights of Poly(aryl ether ketone)s Determined via ^{1}H NMR Studies

polymer	$n^{a,b}$	$\bar{M}_n$, ×10^4	$\bar{M}_w$,^{c} ×10^4	$\bar{M}_n$,^{c} ×10^4	η_{inh},^{d} dL/g
15	36	1.91	0.96	0.43	0.19
16	64	3.33	0.96	0.43	0.21
17	79	4.10	1.98	0.94	0.44
18	36	2.47	3.35	1.32	0.30
19	48	3.26	4.27	1.60	0.38
20	69	4.65	5.36	1.86	0.49
21	36	3.03	3.13	1.20	0.25
22	55	4.57	3.28	1.36	0.30
23	81	6.70	4.01	1.62	0.49

[a] The number of monomer units (*n*) was experimentally designed for 25 units for polymers **15**, **18**, and **21**, 50 units for polymers **16**, **19**, and **22**, and 70 units for polymers **17**, **20**, and **23**. [b] The exact number of monomer units (*n*) was determined by ^{1}H NMR measurements. [c] Determined by GPC measurements using polystyrenes as standards. [d] Inherent viscosities were measured at a concentration of 0.5 g/dL in chloroform at 25 °C.

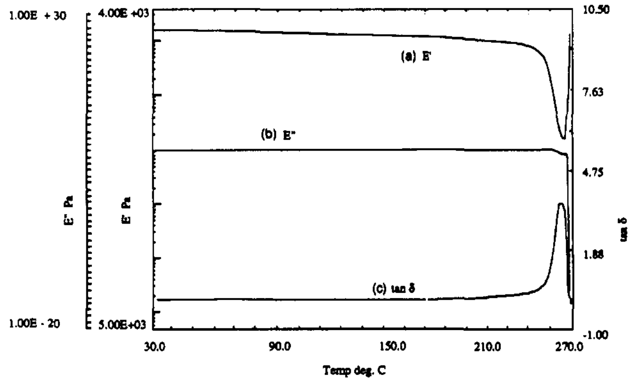


Figure 4. Thermomechanical analysis for poly(aryl ether ketone) **14a**: (a) modulus (E') vs temperature; (b) storage modulus (E'') vs temperature; (c) tan δ vs temperature.

a O_2 permeation (1.03) similar to that of polycarbonate[16] (1.05, 20 °C) and poly(aryl ether ketone) **23** containing four pendant phenyls is approximately 5 times lower in O_2 permeation than poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO) (11.1).[16] An increase in the temperature, from 20 to 78.5 °C, provides energy[17] to "loosen" the polymer structure (polymer **23**) or to increase segmental mobility which increases the penetrant diffusion rate from 2.82 (20 °C) to 6.9 (78.5 °C). Extrapolation of these results to 200 °C indicates the O_2 permeation of polymer **23** should further increase to 22.5 at that temperature.

Table III
Moduli of Polymers at 25 and 200 °C[a]

polymer	modulus for temp 25 °C/200 °C, GPa	polymer	modulus for temp 25 °C/200 °C, GPa
12a	2.10/1.93	**14a**	1.78/0.81
12b	2.29/1.96	**14b**	2.56/2.01
12c	2.27/1.92	**14c**	2.57/2.12
13a	3.92/2.97	**14d**	2.32/1.99
13b	3.21/2.83	**14e**	2.03/1.83
13c	3.33/3.00		

[a] The moduli for polymers **12a–c** are reported at 25 and 100 °C.

Table IV
Thermal Properties of Poly(aryl ether ketone)s 14b–e

poly(aryl ether ketone)	isothermal aging at 400 °C,[a] wt loss %/h	TGA for N_2,[b] °C
14b	0.29	536
14c	0.22	543
14d	0.19	548
14e	0.56	528

[a] Isothermal aging were performed under an atmosphere of N_2 on materials that were not end-capped. [b] Reported for 5% weight loss.

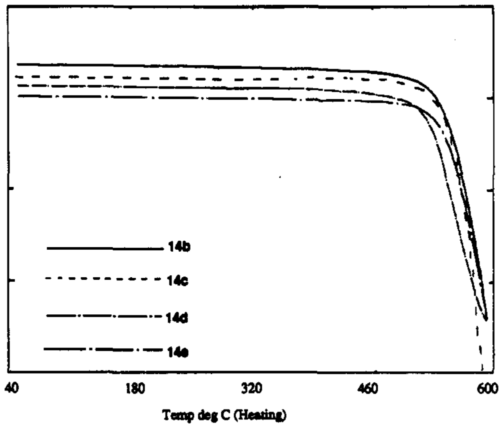
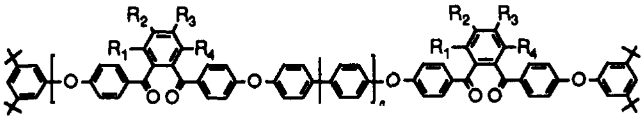


Figure 5. TGA thermograms (weight loss vs temperature) for poly(aryl ether ketone) **14b–e** under an atmosphere of N_2.

Conclusion

Some unique 1,2-bis(4-fluorobenzoyl)benzene monomers have been synthesized which undergo reaction with bisphenates to give amorphous high-temperature poly(ether ketone)s in excellent yields. The polymerization

Table V
Oxygen Permeation at 20 °C



poly(aryl ether ketone)	$P^{a} \times 10^{13}$
17 ($R_1 = R_2 = R_3 = R_4 = H$)	1.03
20 ($R_2 = R_3 = H$; $R_1 = R_4 = C_6H_5$)	1.27
23 ($R_1 = R_2 = R_3 = R_4 = C_6H_5$)	2.82
	6.9 at 78.5 °C
	22.5 at 200 °C[b]

[a] *P* in cm^3·cm/cm^2·s·Pa. [b] Calculated.

reactions were conducted in DMAc in the presence of K_2CO_3 to give high molecular weight polymers. A variety of bisphenols were used along with ketones with zero, two, and four pendant phenyl groups on the central ring. Increases in glass transition temperatures of 40–45 °C occurred in the polymers with increasing pendant phenyls in the 1,2-bis(4-fluorobenzoyl)benzene monomers. The materials had decomposition temperatures above 500 °C by thermogravimetric analysis, indicative of their high thermal stability. All of the polymers form flexible, colorless and transparent films.

Experimental Section

General Methods. The ^{1}H NMR 1D spectra (200 MHz) were recorded on a Varian XL-200 instrument using tetramethylsilane as the internal standard, in deuteriochloroform as the solvent. The chemical shift (δ) and coupling constant (J) data are quoted in ppm and hertz, respectively. The 2D experiments (COSY and COLOC) were done on a Varian XL-200 or XL-300 instrument. Mass spectra were recorded on a ZAB 2F HS spectrometer, ion source 240 °C and 70-eV electron impact, direct inlet: *m/e* (assignment). LRMS with specific ion monitoring to ascertain purity was performed. Thin-layer chromatography was performed on silica gel (Kieselgel 60F 254) aluminum-backed plates. Generally, all compounds isolated were solids. All solvents were reagent grade unless otherwise stated. Triethylamine was refluxed and distilled over calcium hydride. *N*,*N*-Dimethylacetamide was refluxed and distilled over barium oxide. Chlorobenzene, fluorobenzene, 1,4-diphenyl-1,3-butadiene, tetraphenylcyclopentadienone, and 3,5-di-*tert*-butylphenol were purchased from Aldrich and used without further purification. 1,3-Butadiene was purchased from Fluka. Bisphenols 4,4′-(1-methylethylidene)bisphenol (BPA), 4,4′-dihydroxybiphenyl, and 9,9′-bis(4-hydroxyphenyl)fluorene were kindly supplied by General Electric Co. and 4,4′-(hexafluoroisopropylidene)diphenol and hydroquinone were purchased from Aldrich Chemical Co. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. UV spectra were performed on a SP 800 Unicam ultraviolet spectrophotometer with a deuterium lamp.

1,2-Bis(4-fluorobenzoyl)ethylene (1a). To a solution of fluorobenzene (0.52 mol, 50 g, 48.83 mL) in carbon disulfide (500 mL) was added aluminum chloride (0.651 mmol, 86.8 g). The resulting suspension was gently refluxed under an atmosphere of nitrogen. Fumaryl chloride (0.26 mol, 28.2 mL) was added over a period of 15–20 min. The resulting dark orange reaction mixture was refluxed for 18 h, and the residue was poured onto crushed ice (1 kg) and concentrated hydrochloric acid (15.0 mL). The semisolid was filtered off, washed with ethanol, digested in ethanol, and recrystallized from toluene to give pale yellow needles of compound **1a** in 96% yield: mp 115 °C; ^{1}H NMR (200 MHz) δ 7.18 (t, J = 8.4 Hz, 4 H, 2 ortho C_6H_2F), 7.97 (s, 2 H, $CH{=}CH$), 8.08 (dd, J. 8.7 Hz, 4 H, 2 ortho C_6H_2CO); MS (CI with NH_3) *m/e* (calcd for $C_{16}H_{11}O_2F_2$, 273.0727; found, 273.0727) 290 (100), 273 (84), 272 (18), 244 (3), 166 (4), 123 (10).

1,2-Bis(4-chlorobenzoyl)ethylene (1b). The synthesis of 1,2-bis(4-chlorobenzoyl)ethylene (**1b**) was done in a manner similar to that described for the synthesis of 1,2-bis(4-fluorobenzoyl)ethylene (**1a**). The yield was 96% after recrystallization from toluene: mp 151–153 °C; ^{1}H NMR (200 MHz) δ 7.51 (d, J = 8.3 Hz, 4 H, 2 ortho C_6H_2Cl), 8.00 (d, J = 8.3 Hz, 4 H, 2 ortho C_6H_2CO), 8.02 (s, 2 H, $CH{=}CH$); MS (EI) *m/e* (calcd for $C_6H_{10}O_2Cl_2$, 304.0057; found, 304.0057) 306 (4.7), 305 (0.7), 304 (7.9), 269 (5.8), 165 (4.6), 141 (31), 139 (100).

4,5-Bis(4-fluorobenzoyl)cyclohexene (2). To a cooled solution of 1,3-butadiene (22.1 mmol, 1.19 g) in 50 mL of benzene was added 1,2-bis(4-fluorobenzoyl)ethylene (**1a**; 11.0 mmol, 3 g). The intensely yellow reaction mixture was heated at reflux in a glass pressure bomb until a colorless reaction mixture resulted (10–12 h). The reaction mixture was concentrated under reduced pressure, and the resulting residue was recrystallized from ethanol to give a white crystalline compound **2** in 100% yield: mp 118–120 °C; ^{1}H NMR (200 MHz) δ 2.12–2.32 (m, 2 H, $C\mathit{H}_2CHCO$), 2.52–2.63 (m, 2H, $C\mathit{H}_2CHCO$), 4.01–4.21 (m, 2 H, CHCO), 5.85 (s, 2 H, $CH{=}CH$), 7.16 (dd, J = 8.8 Hz, 4 H, 2 ortho C_6H_2F), 8.04 (dd, J = 8.8 Hz, 4 H, 2 ortho C_6H_2CO); MS (CI with NH_3) *m/e* (calcd for $C_{20}H_{17}O_2F_2$, 327.1196) 344 (11.3), 328 (21.6), 327 (100), 326 (4.2), 309 (1.9), 123 (0.84).

1,3-Bis(4-fluorophenyl)-4,7-dihydroisobenzofuran (3). To a reaction mixture of 25 g of 4,5-bis(4-fluorobenzoyl)cyclohexene (**2**) in 200 mL of hot acetic anhydride was added 0.5 g of 86% sirupy phosphoric acid. The reaction mixture was refluxed for 10 min, and, upon cooling, the insoluble furan crystallized immediately to give a quantitative yield of dihydroisobenzofuran **3**: mp 175–176 °C; ^{1}H NMR (200 MHz) δ 3.44 (s, 4 H, CH_2-$CH{=}CH$), 5.94 (s, 2 H, $CH{=}CH$), 7.07 (dd, J = 8.5 Hz, 4 H, 2 ortho C_6H_2F), 7.69 (dd, J = 8.5 Hz, 4 H, 2 ortho C_6H_2CO); MS (EI) *m/e* (calcd for $C_{20}H_{14}OF_2$, 308.1012; found, 308.1012) 308 (100), 277 (7.1), 211 (8.9), 185 (12.9), 183 (32), 123 (57).

1,2-Bis(4-fluorobenzoyl)benzene (4). To a boiling solution of 1,3-bis(4-fluorophenyl)-4,7-dihydroisobenzofuran (**3**; 35.4 mmol, 10.9 g) in glacial acetic acid (500 mL) was added a solution of bromine (70.8 mmol, 11.3 mL) in 60 mL of glacial acetic acid. The reaction mixture was refluxed for 15 min until the bromine was completely absorbed; then sodium acetate (283.2 mmol, 23.23 g) was added, and reflux was continued for another 15 min. To the refluxing mixture was added water (150 mL), and then it was allowed to cool for several hours. The white solid was filtered and recrystallized from ethanol to give, quantitatively, 1,2-bis(4-fluorobenzoyl)benzene (**4**): mp 90–91 °C; ^{1}H NMR (200 MHz) δ 7.06 (dd, J = 8.8 Hz, 4 H, 2 ortho C_6H_2F), 7.61 (s, 4 H, $C_6H_4(CO)_2$), 7.74 (dd, J = 8.8 Hz, 4 H, 2 ortho C_6H_2CO); MS (EI) *m/e* (calcd for $C_{20}H_{12}O_2F_2$, 322.0805; found, 322.0805) 322 (46.1), 227 (62.6), 170 (28.3), 123 (100).

1,2-Bis(4-fluorobenzoyl)-3,6-diphenylcyclohex-4-ene (5a). To a solution of 1,2-bis(4-fluorobenzoyl)ethylene (**1a**; 73.5 mmol, 20 g) in ethylbenzene (500 mL) was added *trans*,*trans*-1,4-diphenyl-1,3-butadiene (73.5 mmol, 15.16 g). The reaction mixture was refluxed for 18 h, cooled, and concentrated to give a white granular solid. Upon recrystallization from ethanol, cyclohexene **5a** was isolated as fine needlelike white crystals in quantitative yield: mp 170–172 °C; ^{1}H NMR (200 MHz) δ 3.80 (m, 1 H, $C\mathit{H}C_6H_5$), 4.12 (m, 2 H, $C\mathit{H}C_6H_5$ and $C\mathit{H}CO$), 4.73 (q, J = 6.0 Hz, 1 H CHCO), 6.04 (m, 2 H, $CH{=}CH$), 6.75 (dd, J = 8.8 Hz, 2 H, ortho C_6H_2F), 6.95 (dd, J = 8.6 Hz, 2 H, ortho C_6H_2F), 7.22 (m, 5 H, C_6H_5), 7.25 (m, 5 H, C_6H_5), 7.45 (dd, 2 H, ortho C_6H_2CO), 7.90 (dd, 2 H, ortho C_6H_2CO); MS (EI) *m/e* (calcd for $C_{32}H_{24}O_2F_2$; 478.1744; found, 478.1743) 478 (3.6), 461 (10.2), 355 (24.9), 338 (8.8), 251 (10.3), 206 (13.8), 123 (100).

1,2-Bis(4-chlorobenzoyl)-3,6-diphenylcyclohex-4-ene (5b). The synthesis of 1,2-bis(4-chlorobenzoyl)-3,6-diphenylcyclohex-4-ene (**5b**) was done in a manner similar to that described for the synthesis of 1,2-bis(4-fluorobenzoyl)-3,6-diphenylcyclohex-4-ene (**5a**). The yield was quantitative after recrystallization from ethanol: mp 126–127 °C; ^{1}H NMR (200 MHz) δ 3.81 (m, 1 H, CHC_6H_5), 4.10 (m, 2 H, CHCO and CHC_6H_5), 4.69 (q, J = 6.0 Hz, 1 H, CHCO), 6.05 (m, 2 H, $CH{=}CH$), 6.94 (m, 2 H, C_6H_5), 7.08 (d, J = 8.8 Hz, 2 H, ortho C_6H_2Cl), 7.23–7.25 (m, 8 H, C_6H_5 and C_6H_3), 7.32 (d, J = 8.8 Hz, 2 H, ortho C_6H_2Cl), 7.45 (d, J = 8.8 Hz, 2 H, ortho C_6H_2CO), 7.81 (d, J = 8.8 Hz, 2 H, ortho C_6H_2CO); MS (EI) *m/e* (calcd for $C_{32}H_{24}O_2Cl_2$, 510.0902; found, 510.0902) 514 (12.2), 512 (10.6), 510 (50.8), 494 (33.2), 475 (22.3).

1,3-Bis(4-fluorophenyl)-4,7-dihydro-4,7-diphenylisobenzofuran (6a). To a reaction mixture of 1,2-bis(4-fluorobenzoyl)-

3,6-diphenylcyclohex-4-ene (**5a**; 25 g) in 800 mL of hot acetic anhydride was added 0.5 g of 86% sirupy phosphoric acid. The reaction mixture was refluxed for 20 min, and, upon cooling, the insoluble furan crystallized immediately to give a quantitative yield of dihydroisobenzofuran **6a**: mp 250–251 °C; ^{1}H NMR (200 MHz) δ 4.87 (d, J = 2.2 Hz, 2 H, 2 CHC_6H_5), 5.95 (d, J = 2.2 Hz, 2 H, CH=CH), 6.95 (t, J = 8.6 Hz, 4 H, 2 ortho C_6H_2F), 7.24 (m, 10 H, 2 C_6H_5), 7.50 (dd, J = 8.6 Hz, 4 H, 2 meta C_6H_2F); MS (EI) *m/e* (calcd for $C_{32}H_{22}F_2O$, 460.1638; found, 460.1637) 460 (100), 458 (26), 355 (13), 191 (11), 123 (98).

1,3-Bis(4-chlorophenyl)-4,7-dihydro-4,7-diphenylisobenzofuran (6b). To a reaction mixture of 15 g of 1,2-bis(4-chlorobenzoyl)-3,6-diphenylcyclohex-4-ene (**5b**) in 600 mL of hot acetic anhydride was added 0.4 g of 86% sirupy phosphoric acid. The reaction mixture was refluxed for 20 min, and, upon cooling, the insoluble furan crystallized immediately to give a quantitative yield of dihydroisobenzofuran **6b**: mp 238–239 °C; ^{1}H NMR (200 MHz) δ 4.86 (d, J = 2.4 Hz, 2 H, 2CH(C_6H_5)), 5.94 (d, J = 2.4 Hz, 2 H, 2CH=CH), 7.15–7.43 (m, 14 H, 2 C_6H_5 and 2 C_6H_2Cl), 7.48 (d, J = 8.8 Hz, 4 H, 2 C_6H_2Cl); MS (EI) *m/e* (calcd for $C_{32}H_{22}OCl_2$, 492.1041; found, 492.1041) 496 (5.1), 495 (10.5), 494 (33.7), 492 (96.7), 490 (100), 353 (10.4), 352 (10.5), 351 (23.2), 315 (24.1), 313 (16.1).

1,2-Bis(4-fluorobenzoyl)-3,6-diphenylbenzene (7a). To a boiling solution of 1,3-bis(4-fluorophenyl)-4,7-dihydro-4,7-diphenylisobenzofuran (**6a**; 7.3 mmol, 3.4 g) in glacial acetic acid (75 mL) was added a solution of bromine (14.6 mmol, 0.75 mL) in 5 mL of glacial acetic acid. The reaction mixture was refluxed for 15 min until the bromine was completely absorbed; then sodium acetate (58 mmol, 4.8 g) was added, and reflux was continued for another 15 min. To the refluxing mixture was added water (150 mL), and then it was allowed to cool slowly for several hours. The white solid was filtered and recrystallized from ethanol to give quantitatively compound **7a**: mp 156–157 °C; ^{1}H NMR (200 MHz) δ 6.84 (dd, J = 8.8 Hz, 4 H, 2 ortho C_6H_2F), 7.14–7.29 (m, 10 H, 2 C_6H_5), 7.57 (dd, J = 8.8 Hz, 4 H, 2 ortho C_6H_2CO), 7.62 (s, 2 H, $C_6H_2(CO)_2(C_6H_5)_2$); MS (EI) *m/e* (calcd for $C_{22}H_{20}O_2F_2$, 474.1431; found, 474.1432) 474 (27), 458 (3.3), 457 (3.6), 380 (5.7), 379 (20.1), 351 (11.3), 349 (4.9), 335 (4.4), 322 (6.2), 123 (100).

1,2-Bis(4-chlorobenzoyl)-3,6-diphenylbenzene (7b). To a boiling solution of 1,3-bis(4-chlorophenyl)-4,7-dihydro-4,7-diphenylisobenzofuran (**6b**; 8.5 mmol, 4.2 g) in glacial acetic acid (75 mL) was added a solution of bromine (17.0 mmol, 0.87 mL) in 5 mL of glacial acetic acid. The reaction mixture was refluxed for 15 min until the bromine was completely absorbed; then sodium acetate (68 mmol, 5.5 g) was added, and reflux was continued for another 15 min. To the refluxing mixture was added water (150 mL), and then it was allowed to cool slowly for several hours. The white solid was filtered and recrystallized from ethanol to give, quantitatively, compound **7b**: mp 180–181 °C; ^{1}H NMR (200 MHz) δ 7.14 (d, J = 8.3 Hz, 4 H, 2 ortho C_6H_2Cl), 7.19–7.25 (m, 10 H, 2 C_6H_5), 7.48 (d, J = 8.3 Hz, 4 H, 2 ortho C_6H_2CO), 7.62 (s, 2 H, $C_6H_2(C0)_2(C_6H_5)_2$); MS (EI) *m/e* (calcd for $C_{32}H_{20}O_2Cl_2$, 506.0840; found, 506.0841) 510 (3.9), 508 (18.3), 506 (24.8), 399 (0.5), 397 (11.1), 395 (29), 371 (0.26), 369 (4.4), 367 (15.2), 358 (0.26), 353 (1.6), 351 (4.9), 306 (0.12), 304 (10.5), 302 (11.8), 179 (2.7), 141 (32), 139 (100).

1,2-Bis(4-fluorobenzoyl)-1,2-dibromoethylene (8). 1,2-Bis-(4-fluorobenzoyl)ethylene (**1a**; 25.7 mmol, 7 g) was dissolved in carbon tetrachloride (200 mL) to which was added a solution of bromine (25.7 mmol, 1.32 mL) in carbon tetrachloride (5 mL). The reaction mixture was stirred under an atmosphere of nitrogen for 30 min and concentrated under reduced pressure to give a white solid. Recrystallization of the solid from a mixture of petroleum ether and ethyl acetate (2/1) gave quantitatively 1,2-bis(4-fluorobenzoyl)-1,2-dibromoethylene (**8**): mp 84–85 °C; ^{1}H NMR (200 MHz) δ 5.70 (s, 2 H, 2 CHBr), 7.19 (dd, J = 8.8 Hz, 4 H, 2 ortho C_6H_2F), 8.06 (dd, J = 8.8 Hz, 4 H, 2 ortho C_6H_2CO); MS (EI) *m/e* (calcd for $C_{16}H_{10}O_2Br_2F_2 \cdot HBr$, 349.9754; found, 349.9753) 352 (1.2), 350 (1.5), 273 (11.8), 272 (46.1), 244 (32), 149 (21), 124 (43.1), 123 (100).

1,2-Bis(4-fluorobenzoyl)acetylene (9). To a solution of 1,2-bis(4-fluorobenzoyl)-1,2-dibromoethylene (**8**; 16.3 mmol, 7.0 g) in reagent-grade acetone (200 mL) under an atmosphere of nitrogen was added triethylamine (32.6 mmol, 4.5 mL). After stirring the reaction mixture for 10 min at reflux temperature, the quaternary salt was filtered and the filtrate concentrated under reduced pressure. The reaction can be conducted at room temperature, and the time required to reach completion is 2 h. The product was recrystallized from ethanol to give 1,2-bis(4-fluorobenzoyl)acetylene (**9**): mp 98–99 °C; ^{1}H NMR (200 MHz) δ 7.22 (dd, J = 8.9 Hz, 4 H, 2 ortho C_6H_2F), 8.22 (dd, J = 8.9 Hz, 4 H, 2 ortho C_6H_2CO); MS (EI) *m/e* (calcd for $C_{16}H_8O_2F_2$, 270.0492; found, 270.0492) 270 (26.6), 243 (2.1), 242 (10.3), 214 (57.4), 147 (38.5), 123 (100).

1,2-Bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (10). 1,2-Bis(4-fluorobenzoyl)acetylene (**9**; 18.6 mmol, 5.0 g) and tetraphenylcyclopentadienone (18.6 mmol, 7.15 g) in benzophenone (70 g) were refluxed for 2 h under an atmosphere of nitrogen. The reaction mixture was cooled to 30 °C and poured into a large volume (300 mL) of methanol. The tan precipitate was washed with methanol (2 × 25 mL) and refluxed in toluene/charcoal to give a white crystalline compound **10** in 89% yield: mp 318–320 °C; ^{1}H NMR (200 MHz) δ 6.77–6.91 (m, 24 H, 4 C_6H_5 and 2 ortho C_6H_2F), 7.60 (dd, J = 8.5 Hz, 4 H, 2 ortho C_6H_2CO); MS (EI) *m/e* (calcd for $C_{44}H_{28}O_2F_2$, 626.2057; found, 626.2059) 626 (48.9), 531 (15.2), 503 (21.4), 488 (10.7), 487 (24.1), 475 (4.3), 435 (11), 425 (4.6), 407 (6.1), 378 (2.6), 363 (2.3), 123 (100). The reaction could also be conducted in 1,2,4-trichlorobenzene and ethylbenzene. Ethylbenzene required longer reaction times (4 h) compared to 1,2,4-trichlorobenzene (2 h) and benzophenone.

X-ray Crystallographic Analysis of Compound 7b. A colorless fragment crystal of $C_{32}H_{20}O_2Cl_2$ having dimensions of 0.080 × 0.130 × 0.240 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite-monochromated Cu Kα radiation and at 1.75 kW. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 12 carefully centered reflections in the range $53.19 < 2\theta < 60.13°$, corresponded to a monoclinic cell with dimensions a = 7.946 (3) Å, b = 24.474 (5) Å, c = 13.964 (3) Å, v = 2610 (1) Å^3, and β = 106.06 (2)°. For z = 4 and FW = 507.41, the calculated density is 1.291 g/cm^3. The data were collected at a temperature of 20 °C using the ω–2θ scan technique to a maximum 2θ value of 110.1°. The structure was solved by direct methods using the MITHRIL software. The non-hydrogen atoms were refined either anisotropically or isotropically. The final cycle of full matrix least-squares refinement was based on 1203 observed reflections and 115 variable parameters and converged with R = 0.083 and R_w = 0.058.

Polymer Synthesis. Polymerization reactions were conducted in three-neck flasks which were generally equipped with a nitrogen inlet, thermometer, Dean-Stark trap and condenser. A typical synthesis of poly(aryl ether ketone) **14a** is described, based on 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (**10**). The flask was charged with (4.79 mmol, 3 g) of monomer **10**, bisphenol (BPA) **11a** (4.79 mmol, 1.09 g), and *N,N*-dimethylacetamide (16 mL). Toluene (8 mL) was added, followed by potassium carbonate (9.58 mmol, 1.32 g). The reaction mixture was then heated until the toluene began to reflux. An optimum reflux temperature range was achieved between 135 and 140 °C. The reaction mixture was maintained at this range until the presence of water was no longer observed in the Dean-Stark trap, which took approximately 1 h. Upon dehydration and slow removal of toluene from the reaction mixture, the temperature gradually increased to 165 °C. The reaction was refluxed at this temperature for 1 h. Completion or near completion of polymerization was qualitatively estimated by the point where the viscosity increased dramatically. The reaction mixture was cooled and diluted with DMAc (8 mL), and several drops of weak acid (e.g., acetic acid) were added to neutralize phenoxide end groups. The polymer solution was then coagulated in about 30 mL of methanol and filtered, redissolved in chloroform, and filtered hot through a thin layer of Celite. The chloroform solution was concentrated and then coagulated in methanol (30 mL). The white fibrous polymer was filtered and dried in a vacuum oven (120 °C) for 48 h to give poly(aryl ether ketone) **14a** in almost quantitative yield.

Poly(aryl ether ketone)s Capped with 3,5-Di-*tert*-butylphenol. A typical end-capping reaction involved a three-neck flask equipped with a nitrogen inlet, thermometer, Dean-

Stark trap, and condenser. The synthesis of poly(aryl ether ketone) **23** with a degree of polymerization of $n \sim 70$ monomer units/chain is described. To the flask was added 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (**10**; 15.97 mmol, 10 g), bisphenol (BPA) **11a** (15.75 mmol, 3.59 g), and potassium carbonate (31.94 mmol, 4.4 g). The dry mixture was mixed thoroughly and to this was added DMAc (54 mL) and toluene (27 mL). Further mixing of the solution was done at room temperature for a period of 2 h. The reaction mixture was then heated until the toluene began to reflux at 140 °C. The reaction mixture was heated at this temperature for 1 h and then gradually increased to 165 °C. The reaction mixture was refluxed at this temperature for 1 h. Completion of polymerization was estimated by the point where the viscosity increased dramatically. The polymerization reaction was worked up in a manner similar to that in the case of poly(aryl ether ketone) **14a** to give polymer **23**. From ^{1}H NMR studies, the exact number of monomer units/chain was found to be 81.

Poly(aryl ether ketone) 15: ^{1}H NMR (200 MHz) δ 1.29 (s, 36 H, 4 $C(CH_3)_3$), 1.66 (s, 6 H, 2 CH_3), 6.92 (d, $J = 6.6$ Hz, 4 H, 2 C_6H_4O), 6.96 (d, $J = 6.6$ Hz, 4 H, 2 $C(CH_3)_2C_6H_4O$), 7.23 (d, $J = 8.9$ Hz, 2 $C_6H_4O(CH_3)_2$), 7.56 (s, 4 H, C_6H_4 and 2 CO), 7.71 (d, $J = 8.9$ Hz, 2 COC_6H_4O); UV (CCl_3H) λ_{max} 300 nm (ϵ 1.18×10^6), 245 nm (ϵ 1.58×10^6).

Poly(aryl ether ketone) 18: ^{1}H NMR (200 MHz) δ 1.29 (s, 36 H, 4 $C(CH_3)_3$, 1.66 (s, 6 H, 2 CH_3), 6.69 (d, $J = 8.8$ Hz, 4 H, 2 OC_6H_4OCO), 6.83 (d, $J = 8.8$ Hz, 4 H, 2 $OC_6H_4C(CH_3)_2$), 7.19 (d, $J = 8.8$ Hz, 2 $(CH_3)_2C_6H_4$), 7.15–7.29 (m, 10 H, 2 C_6H_5), 7.52 (d, $J = 8.8$ Hz, 4 H, 2 COC_6H_4), 7.56 (s, 2 H, $C_6H_2C_6H_2(C_6H_5)_2$); UV (CCl_3H) λ_{max} 288 nm (ϵ 1.48×10^6), 250 nm (ϵ 1.22×10^6).

Poly(aryl ether ketone) 21: ^{1}H NMR (200 MHz) δ 1.29 (s, 36 H, 4 $C(CH_3)_3$), 1.66 (s, 6 H, 2 CH_3), 6.74 (dd, $J = 8.8$ Hz, 4 H, 2 C_6H_4O), 6.83 (dd, $J = 8.8$ Hz, 4 H, 2 C_6H_4O), 6.80–6.87 (m, 20 H, 4 C_6H_5), 7.17 (dd, $J = 8.8$ Hz, 4 H, 2 $C_6H_5C(CH_3)_2$), 7.57 (dd, $J = 8.8$ Hz, 4 H, 2 COC_6H_4); UV (CCl_3H) λ_{max} 287 nm (ϵ 1.92×10^6), 250 nm (ϵ 1.76×10^6).

Polymer Characterization. Inherent viscosity measurements were determined by using a Ubbelohde dilution viscometer. Apparent molecular weights were determined by gel permeation chromatography using polystyrene standards with chloroform as the solvent on a Waters 510 HPLC with a UV detector and with four μ-Styragel columns (500, 10^4, 10^5, and 100 Å) in series. Glass transition temperatures were measured on a Mettler FP80 at a heating rate of 20 °C/min for the variable-temperature scans. Isothermal aging and variable-temperature scans (TGA) were performed on a Seiko TG/DTA 220. Dynamic mechanical behavior was measured on a Seiko 120 thermomechanical analyzer thermal stress–strain analyzer (TMA/SS) with a heating rate of 10 °C/min. Films for the mechanical analyzer were cast from chloroform at room temperature and were dried in an oven at 90 °C for 24 h. Oxygen permeation measurements were made on a Mocon's Ox-tran 100 twin, and the films employed for these measurements were developed and treated in a manner similar to that above.

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