Synthesis and Characterization of Isomeric Biphenyl Containing Poly(aryl ether-bisketone)s II.[†]   Polymers Derived from 3,3'-(4-Fluorobenzoyl)biphenyl and Bisphenols

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ABSTRACT: A series of amorphous and semicrystalline poly(aryl ether-bisketone)s have been synthesized from bisphenols and 3,3'-(4-fluorobenzoyl)biphenyl via nucleophilic aromatic substitution reactions. Model compound studies were carried out with a variety of substituted phenols, 3,3'-(4-fluorobenzoyl)biphenyl and 3,3'-(4-chlorobenzoyl)biphenyl. The bishalide monomers were prepared by the reaction of 3,3'-biphenyl dicarboxylic acid with thionyl chloride followed by Friedel–Crafts reaction with the appropriate aryl halide. Potassium carbonate mediated reaction of these monomers with a variety of bisphenols in dimethylacetamide or diphenylsulfone gave moderate to high molecular weight polymers in excellent yield. The high molecular weight polymers afforded tough films by compression molding. The glass transition temperatures, melting points and the thermal behaviors of the polymers were compared with the corresponding polymers derived from 4,4'-(4-fluorobenzoyl)biphenyl.
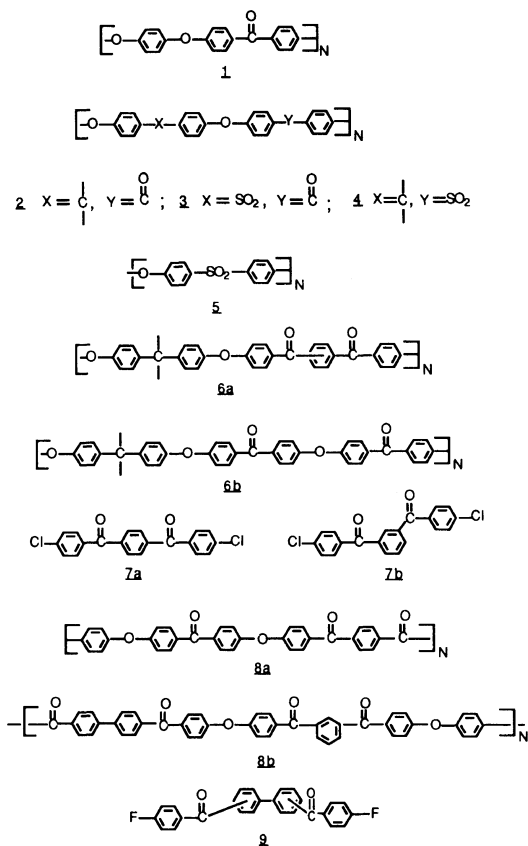   KEY WORDS   Nucleophilic Aromatic Substitution / Glass-Transition Temperatures / Annealing /

Poly(aryl ether-ketone)s belong to a class of materials known as engineering thermoplastics.[1,2] The introduction of crystallinity into a poly(aryl ether-ketone) backbone results in improving the solvent resistance and modulus. PEEK™, (1, poly(ether ether ketone)) an aromatic poly(ether-ketone) exhibits a relatively high degree of crystallinity and a melting point (T_m) of 335°C.[3a,4,5] On the other hand, PEEK suffers from poor creep behavior above its relatively low glass transition temperature (T_g) of 145°C.[6] Therefore, attempts have been made to either increase the glass transition temperature or to introduce crosslink sites into the PEEK backbone.[7–9] The amorphous poly(aryl ether-ketone)s, characterized by backbones containing sp³ or sp³d² hybridized atoms (e.g., 2 and 3, respectively), exhibit lower glass transition temperatures than the analogous amorphous poly(aryl ether-sulfone)s, 4 and 5.[10,11] In order to achieve higher T_gs and/or higher T_ms, two carbonyl groups, (in contrast to PEEK which contain one such group) have been incorporated into the polymer repeat unit (e.g., 6a and 6b).[2,12–15] Polymer 6a was synthesized by the reaction of bisphenol-A with either 7a or 7b via nucleophilic aromatic substitution reactions. Electrophilic aromatic substitution reactions have been used also for the synthesis of poly(aryl ether-ketone)s (e.g., 8a and 8b) containing two keto substituents.[16,17]
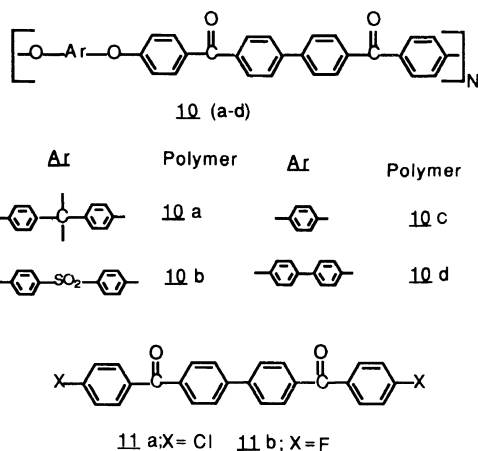
Aromatic polyethers containing a biphenyl group in the repeat unit exhibit excellent

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2 X = Ċ, Y = C̈ ; **3** X = SO₂, Y = C̈ ; **4** X = Ċ, Y = SO₂

5

6a

6b

Cl—C(O)—C(O)—Cl   **7a**   Cl—C(O)—C(O)—Cl **7b**

8a

8b

F—C(O)—C(O)—F   **9**

10 (a-d)

Ar	Polymer	Ar	Polymer
—C(CH₃)₂—	**10 a**	—	**10 c**
—SO₂—	**10 b**	—()—	**10 d**

11 a; X = Cl   **11 b; X = F**

thermo-oxidative stability and high toughness.[18] The synthesis and characterization of a series of poly(aryl ether-bissulfone)s containing a biphenyl moiety in the repeat unit have been reported. These polymers exhibit excellent thermal stabilities and some of the highest known T_gs for poly(aryl ether)s.[19] On the other hand, poly(aryl ether-ketone)s containing a biphenyl group are usually prepared from 4,4'-biphenol and readily available aromatic haloketone such as 4,4'-difluorobenzophenone, **7a** or **7b**. These polymers are semicrystalline in nature and exhibit high melting points. This results in processing difficulties, which has created a need for polymers with lower processing temperature while still maintaining thermal stability and toughness. In an attempt to achieve these objectives a series of four monomers, **9**, suitable for the preparation of poly(aryl ether-bisketone)s have been synthe-

sized. These monomers, which contain a biphenyl linkage and two keto groups were prepared from isomeric biphenyl dicarboxylic acids. Recently, the synthesis and characterization of poly(aryl ether-bisketone)s, **10**, derived from 4,4'-(4-fluorobenzoyl)biphenyl, **11b**, has been reported.[20] In this paper, we report the synthesis of bisketo functional monomers (derived from 3,3'-biphenyldicarboxylic acid), related model compound studies and polymers based upon isopropylidenebiphenol (bisphenol-A), hydroquinone, 4,4'-dihydroxy biphenyl (biphenol), 4,4'-dihydroxy diphenylsulfone (bisphenol-S) and 4,4'-dihydroxybenzophenone. The polymers have been characterized and the results from these studies have been compared with those of the corresponding polymers derived from **11b**.[20]

EXPERIMENTAL

Materials

Dimethylacetamide (DMAc) (Aldrich) was dried over calcium hydride and then distilled at reduced pressure. 4,4'-Isopropylidenebiphenol (bisphenol-A), kindly supplied by the Dow Chemical Co., was purified by recrystallization from toluene and dried at reduced pressure at 80°C for 24 h. Diphenyl sulfone (DPS), hydroquinone, biphenol and 4,4'-dihydroxydiphenyl sulfone (bisphenol-S) (Aldrich) were recrystallized from acetone. Copper powder, 3-iodo-

toluene and 4,4'-dihydroxybenzophenone (Aldrich) were used as received. Thionyl chloride was stirred over triphenyl phosphite and distilled prior to use. Anhydrous potassium carbonate (Fisher) was dried in an oven overnight at 100°C.

3,3'-Dimethylbiphenyl, **12.** A 2000 ml, one-necked, round bottomed flask fitted with a condenser was charged with 109 g (0.5 mol) of 3-iodotoluene and 127 g (2.0 mol) of copper powder. The reaction mixture was heated under reflux for a period of 24 h. The flask was cooled and 500 ml of anhydrous ether was added to the solid residue. The contents of the flask were filtered. Ether was removed from the filtrate by evaporation under reduced pressure. Finally, the desired compound was distilled as a colorless liquid at a distillation head temperature of 130°C (0.1 mmHg) (71.9% yield): mass spectrum (*m/z*) (relative intensity) 183 (34), 182 (100), 167 (65); ^{1}H NMR (CDCl$_3$) δ 7.18 (8H, m), 2.05 (6H, s); ^{13}C NMR (CDCl$_3$) δ 21.45, 124.25, 127.85, 127.89, 128.55, 138.09, 141.31.

3,3'-Biphenyldicarboxylic acid, **13.** A 1000 ml, glass container inside a Parr High Pressure Reactor was charged with 28.41 g (0.15 mol) of 3,3'-dimethylbiphenyl, 139.5 g (0.45 mol) of sodium dichromate, Na$_2$Cr$_2$O$_7$·2H$_2$O, and 500 ml of water. The reactor was assembled and the temperature of the reaction vessel was increased to 250°C. The oxidation reaction was carried out with vigorous stirring for a period of 24 h. At the completion of the reaction, the reaction vessel was cooled and the reaction mixture was filtered. The yellow colored filtrate was acidified with concentrated hydrochloric acid. The crude diacid, which precipitated upon acidification, was isolated by filtration. The residue was washed with copious quantities of water to remove excess hydrochloric acid. Any last traces of chromium salt was emoved from the crude diacid by extracting with water in a Soxhlet apparatus for 24 h. The crude product was dried at 80°C under reduced pressure (92% yield). The diacid was used for subsequent reactions without further purification. A small portion of the diacid was crystallized from tetrahydrofuran to afford a white crystalline solid: mp 334—336°C (lit.[21] 330—332°C); IR (KBr) 3097, 1690, 1286, 925 cm^{-1}; mass spectrum (*m/z*) (relative intensity) 242 (100), 225 (29), 152 (13); ^{1}H NMR (DMSO-d_6) δ 13.22 (s, 2H), 7.65 (m, 8H); ^{13}C NMR (DMSO-d_6) δ 127.24, 128.54, 129.34, 130.99, 131.68, 139.53, 167.01.

3,3'-Biphenyldicarbonyl chloride, **14.** A 1000-ml, three-necked, round bottomed flask fitted with a condenser, a nitrogen inlet and a mechanical stirrer was charged with 60.5 g (0.25 mol) of 3,3'-biphenyldicarboxylic acid, 600 ml of thionyl chloride (5.0 mol, excess) and 10 ml of dimethylformamide (DMF). A nitrogen blanket was maintained during the course of the reaction. The reaction mixture was heated under reflux for a period of 4 h. Upon the formation of the acid chloride, excess thionyl chloride was removed by distillation. The crude product was then crystallized (methylene chloride) to afford **14** as a white crystalline solid (89% yield): mp 147—149°C (lit.[21] 150°C); IR (KBr) 1749, 1592, 1193, 892, 749 cm^{-1}; mass spectrum (*m/z*) (relative intensity) 278 (15), 243 (100), 152 (39), 76 (10); ^{13}C NMR (CDCl$_3$) δ 129.89, 129.95, 131.16, 133.99, 134.29, 140.48, 168.33.

3,3'-Bis(4-chlorobenzoyl)biphenyl, **15.** A 1000-ml, three-necked, round bottomed flask fitted with a condenser, a nitrogen inlet and a mechanical stirrer was charged with 54.45 g (0.25 mol) of **14** and 500 ml of dry chlorobenzene. The reaction vessel was cooled in an ice bath and anhydrous aluminum chloride (52.8 g, 0.40 ml) was added in small increments to the reaction mixture. After the initial exotherm, the ice bath was removed and the mixture was refluxed for 10 h. The deep orange colored reaction mixture was then poured into strongly acidified cold water with vigorous stirring. The precipitated solid was collected by filtration at reduced pressure and washed with copious quantities of water followed by saturated aqueous sodium bicarbonate solu-

tion. The crude product was crystallized two times (methylene chloride) to afford **15** as white needles (30% yield): mp 139.7°C (DSC); IR (KBR) 1657, 1593, 1585, 1290, 856 cm^{-1}; mass spectrum (m/z) (relative intensity) 432 (73), 431 (30), 430 (99), 319 (83), 140 (32), 138 (100), 110 (38); ^{13}C NMR (CDCl$_3$) δ 128.61, 128.88, 129.17, 129.45, 131.37, 131.60, 135.77, 138.13, 139.28, 140.56, 195.30. *Anal.* Calcd. for C$_{26}$H$_{16}$O$_2$Cl$_2$: C, 72.56%; H, 3.72%; Cl, 16.28%. Found: C, 72.50%; H, 3.84%; Cl, 16.46%.

3,3'-Bis(4-fluorobenzoyl)biphenyl, **16**. Compound **16** was prepared by the procedure described for **15** by using 60.0 g (0.216 mol) of **14**, 55 g (0.58 mol) of fluorobenzene and 58.1 g (0.44 mol) of anhydrous aluminum chloride. The reaction mixture was refluxed for 18 h. The product was isolated in high yield and purified by recrystallization (methylene chloride) to afford white flakes (64% yield): mp 168.08°C (DSC) (lit.[23] 163.5—166.5°C); IR (KBr) 1658, 1601, 755 cm^{-1}; mass spectrum (m/z) (relative intensity) 398 (100), 303 (41), 123 (84), 95 (30); ^{1}H NMR (CDCl$_3$) δ 7.25 (m), 7.89 (m); ^{19}F NMR (CDCl$_3$) $\delta - 106.16$; ^{13}C NMR (CDCl$_3$) δ 115.55 (d, 21 Hz), 128.36, 128.94, 129.19, 131.02, 132.67 (d, 9 Hz), 133.65 (d, 3 Hz), 138.20, 140.37, 165.46 (d, 255 Hz), 194.92. *Anal.* Calcd. for C$_{26}$H$_{16}$O$_2$F$_2$: C, 78.38%; H, 4.02%; F, 9.65%. Found: C, 78.08%; H, 3.99%; F, 9.58%.

Model Compounds, **17(a—d)** *Synthesis.* A three-necked, 100-ml, round-bottomed flask fitted with a nitrogen inlet, a thermometer, and a Dean–Stark trap fitted with a condenser was charged with 0.005 mol of **15** or **16**, 0.01 mol of the desired phenol (4-*tert*-butylphenol or 4-phenylphenol) (Table I), 7.0 g (excess) of anhydrous potassium carbonate, 35 ml of DMAc and 20 ml of toluene. The reaction mixture was heated at solvent reflux at 145°C and water, the byproduct of the reaction, was removed by azeotropic distillation. The reaction mixture was heated to 160°C for 8 to 22 h and then cooled to room temperature. It was

filtered and the filtrate was distilled under reduced pressure to remove all solvents. If possible, the residue was dissolved in appropriate solvent and the solution was washed repeatedly with water, dried over anhydrous magnesium sulfate and the solvent was removed by rotary evaporation at reduced pressure. The crude product was purified by crystallization. For more acidic phenols such as phenol and 4-hydroxybenzophenone, in addition to the above mentioned solvents, diphenyl sulfone (15 g) was added to the reaction vessel. The reaction mixture was heated at solvent reflux at 160°C for a period of 18 h. Finally, the temperature was allowed to increase to 190°C by removing first toluene and then DMAc *via* the Dean-Stark trap. The reaction mixture was heated at that temperature for an additional 5 h and then cooled to room temperature. It was diluted with methylene chloride, filtered, and the filtrate was distilled under reduced pressure to remove all solvents except DPS. The solid residue was dissolved in appropriate solvent and percolated down a silica gel colomn to remove DPS and to isolate the desired ether. The crude product was purified by crystallization.

General Procedure for Polymer **18(a—e)** *Synthesis.* The polymers were prepared according to a previously published procedure.[20]

CHARACTERIZATION

Proton and carbon-13 NMR spectra were recorded using a General Electric QE-300 instrument. Fluorine-19 NMR was recorded using an IBM NR-80 instrument and fluorotrichloromethane as an internal standard. IR spectra were obtained with a Nicolet DxB FT-IR spectrophotometer. Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured either with a Du Pont DSC 2100 or a Perkin-Elmer DSC-7 at a heating rate of 10°C min^{-1}. Thermogravimetric analysis (TGA) of the polymer samples was conducted with a heat-

ing rate of 10°C min^{-1} in nitrogen. Dynamic mechanical behaviors of the polymers were assessed with a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) in the bending mode with a heating rate of 4°C min^{-1} (1 Hz). Wideangle X-ray scans of semicrystalline samples were run on a Phillips XRG-3000 instrument. Intrinsic viscosity measurements for the amorphous polymers were determined by using a Cannon-Ubbelohde dilution viscometer and solutions in either DMAc or aqueous concentrated sulfuric acid or chloroform (CHCl$_3$) (25°C).

RESULTS AND DISCUSSION

Monomer Synthesis

The carbonyl group is known to activate a fluorine atom in para orientation, towards nucleophilic aromatic substitution reactions. For example, 4,4'-difluorobenzophenone is used for the synthesis of PEEK and other poly(aryl ether-ketone)s.[2a,3] On the other hand, under similar reaction conditions, 4,4'-dichlorobenzophenone is thought to be an unsuitable monomer for poly(aryl ether) synthesis.[3a] This has been attributed to the low reactivity of the chlorine substituent due to its lower electronegativity as compared to a fluorine atom. It has been shown that the bischlorides 7a or 7b with two keto substituents, are suitable for polymer synthesis with bisphenol-A and other bisphenols.[2a,12] However, this list of bisphenols did not include more acidic compounds such as hydroquinone or 4,4'-dihydroxybenzophenone. In view of these earlier findings, both bischloro (15) and the bisfluoro (16) substituted compounds were synthesized for the present investigation in order to study the feasibility of using 15 as a suitable, yet less expensive monomer for polymer preparations. The bishalides, 15 and 16 were prepared starting from 3-iodotoluene (Scheme 1). In order to obtain monomer grade material, the crude chlorobisketone, 15 was crystallized four times from toluene. On the
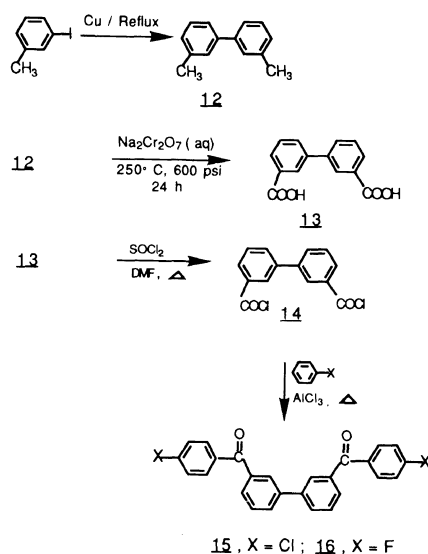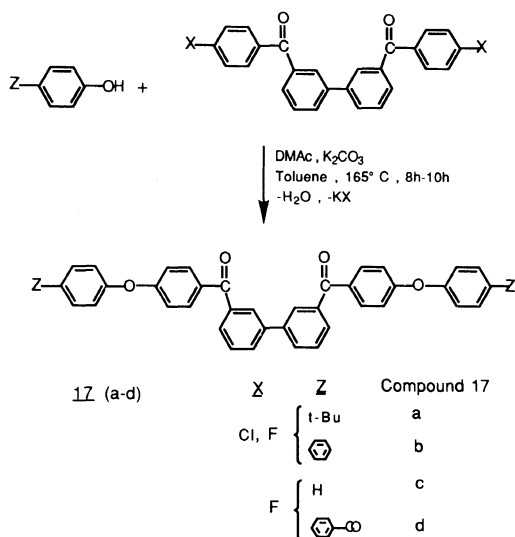

Scheme 1.

other hand, purification of 16 was relatively simple. It could be recrystallized from either toluene or methylene chloride to afford monomer grade material. The low yield of 15, and the highly cumbersome nature of its purification due to its poor solubility, allowed for the synthesis of the compound in small quantities for model compound studies only. The large scale preparation of 15 required for polymer synthesis was not undertaken.

Model Compound Studies

Model compound studies were carried-out by treating phenol or substituted phenols with 15 or 16 in DMAc in the presence of excess potassium carbonate (Scheme 2). The reaction of p-tert-butylphenol or 4-phenylphenol with either 15 or 16 required almost 48 h for completion and resulted in the formation of the desired product in essentially quantitative yield. This is in contrast to the significantly shorter times (8 to 10 h) needed for the completion of similar reactions of the same phenols with 11a and 11b.[20] These observations suggest the following. First, it is possible to use the bischloride, 15 or the bisfluoride, 16, to synthesize high molecular weight amorphous

Scheme 2.

polymers with bisphenol-A and 4,4'-dihydrox-ybiphenyl. Second, in order to achieve high molecular weight polymers significantly longer reaction times or higher reaction temperatures will be necessary. While the reaction of phenol with **16** was quantitative, the replacement of the chloro groups of **15** by phenoxide derived from phenol was not satisfactory. Only a 50% yield of the desired compound could be realized. This difference in reactivity of the phenoxide anion as compared with the anions derived from 4-*tert*-butylphenol and 4-phenyl-phenol towards chlorine displacement, may be attributed to the relative nucleophilicities of the anions under consideration.[24,25] The required set of data needed to support this contention is not available. However, it is possible to correlate the order of basicity of the phenoxide anions with their relative nucleophilicity.[26] A comparison of the relative acidity constants for phenol, 4-phenylphenol and 4-*tert*-butylphenol reveals the following order; 4-phenylphe-nol ~ 4-*tert*-butylphenol < phenol.[27] It there-fore follows that the order of the conjugate base strength and nucleophilicity is Ph–O^{2-} < 4-Ph–Ph–O^{2-} ~ 4-(CH$_3$)$_3$C–Ph–O^{2-}. Thus, the anion derived from phenol being a weak

nucleophile cannot replace the less reactive chlorine atoms of **15**, for the formation of the ether bonds *via* nucleophilic aromatic substitu-tion (S$_N$AR) reaction, whereas the more reac-tive nucleophiles can. It has been shown earlier that both S$_N$AR and substitution radical nu-cleophilic unimolecular (S$_{RN}$1) reactions com-plete leading to the formation of the desired bisether and side products when a weak nu-cleophile is allowed to react with a bischloro-diketone. Detailed discussions have been provided elsewhere.[28] This conclusion was further supported by carrying out the reaction of 4-hydroxybenzophenone (a stronger acid than phenol)[27] with **15** and **16**. The ether formation was quantitative with the more reactive bisfluoride, **16**, (Table I).

Besides elemental analysis, the structures of the model compounds were verified by MS analysis. Carbon-13 NMR analysis lent further support for the structure determination of **17(a—d)**. The observed ^{13}C absorbances (Table I) are in close agreement with the calculated values.[29]

Synthesis and DSC Analysis of Poly(aryl ether-bisketone)s **18(a—e)**

Polymerization of the bishalide, **16**, with bisphenol-A could be readily carried out in presence of excess potassium carbonate in a DMAc–toluene (2:1) solvent mixture (Scheme 3). A polymerization temperature of 165°C was sufficient to synthesize high molecular weight poly(aryl ether-bisketone)s in 24 h. This is in contrast to the shorter time (8 h) required for the synthesis of **10a** from bisphenol-A and **11b** under the same reaction conditions. This differ-ence, which was expected from the model com-pound studies, can possibly be attributed to the fact that the fluorine atoms are in a less favor-able electronic environment in **16** than in **11b**. Therefore it takes longer time to replace these atoms quantitatively to obtain a high molecular weight polymer. The high molecular weight nature of polymer **18a** was evident from the fact that it was possible to obtain tough, clear

Table I. Analytical data for model compounds **17** (**a**—**d**)

Compound 17	Phenol	Bishalide	% Yield*	mp	IR (KBr)	^{13}C NMR (CDCl$_3$)^d	Mass spectrum (m/z) (Relative intensity)	Elemental analysis	
								Calcd.	Found.
a	4-*tert*-Butylphenol	**15** or **16**	~89	149—151	2960, 1658, 1592, 1501, 1245	31.40, 34.40, 116.83, 119.69, 126.81, 128.28, 128.76, 129.02, 130.61, 131.32, 132.42, 138.73 140.33, 147.56, 152.08, 162.11, 195.07	658 (27), 644 (25), 643 (48), 314 (100), 253 (43), 237 (48)	C, 83.95 H, 6.43	C, 83.81 H, 6.35
b	4-Phenyl-phenol	**15** or **16**	~90	195—197	1645, 1592, 1488, 1272	117.28, 120.44, 126.95, 127.29, 128.38, 128.72, 128.83, 128.88, 129.12, 129.14, 130.80, 131.81, 132.55, 138.69, 140.23, 140.42, 154.91, 161.74, 195.21	699 (28), 698 (55), 349 (26), 274 (21), 273 (100), 152 (10)	C, 85.96 H, 4.87	C, 85.99 H, 4.80
c	Phenol	**16**	~85	62—64	1651, 1586 1488, 1239	117.19, 120.18, 124.58, 128.31, 128.78, 129.04, 130.01, 130.74, 131.71, 132.45, 138.74, 140.42, 155.46, 161.77, 195.12	546 (19), 198 (12), 197 (100), 141 (14)	C, 83.52 H, 4.76	C, 83.41 H, 4.60
d	4-Hydroxy-benzophenone	**16**	~87	168—170	1651, 1587, 1239	118.60, 118.75, 128.35, 128.42, 128.97, 129.24, 129.87, 131.02, 132.40, 132.57, 132.62, 132.95, 133.32, 137.64, 138.48, 140.51, 159.69, 160.13, 195.17, 195.42	379 (20), 378 (73), 301 (100), 198 (14)	C, 82.74 H, 4.57	C, 82.65 H, 4.45

* After one crystallization.

and finger-nail creasable films upon solution casting or compression moulding. A moderately high intrinsic viscosity value ($\eta = 0.67$ dl g^{-1}) in chloroform at room temperature further supported this observation. The polymer was amorphous and exhibited solubility behavior typical of poly(aryl ether)s with the same morphology (Table II). It was soluble in a variety of solvents including chlorinated hydrocarbons and tetrahydrofuran. On the other hand, the more linear counterpart **10a** (derived from bisphenol-A and **11b**) was insoluble in methylene chloride and tetrahydrofuran in spite of its amorphous nature.

Scheme 3.
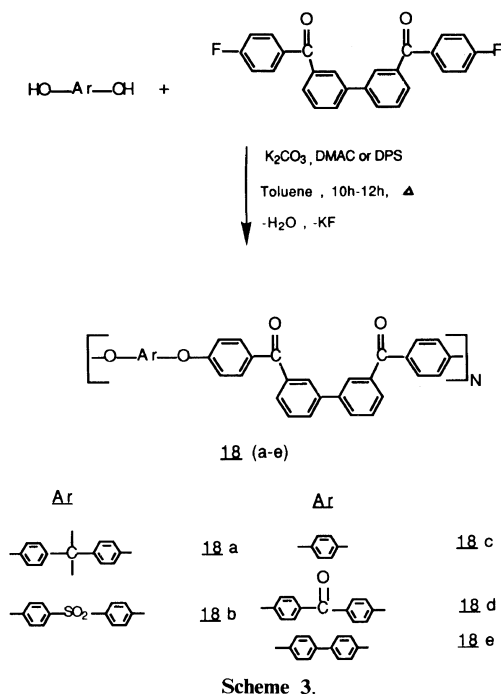
This indicates that the incorporation of the 3,3'-linkage lowers the solvent resistance of the polymer as compared to that of the 4,4'-linkage. The polymerization reaction of 4,4'-dihydroxybiphenyl and **16** in DMAc remained unsuccessful. Sufficient rise in the viscosity of the reaction mixture was not observed even after 48 h at 165°C. The lack of a sufficient reactivity of the bisphenoxide in the present instance can be attributed to its lower solubility in DMAc at the reaction temperature. The reaction was therefore conducted at a higher temperature (230°C) by adding diphenylsulfone to the reaction vessel. The reaction was allowed to continue for a period of 8 h. The resulting polymer **18e**, was insoluble in methylene chloride, chloroform and tetrahydrofuran. It exhibited partial solubility in hot DMAc and NMP. This is in contrast to the behavior of the corresponding linear poly(aryl ether-bisketone) **10d** (obtained from 4,4'-dihydroxybiphenyl and **11b**). Polymer **10d** was insoluble in all of the aforementioned solvents under reflux condition and exhibited

a high degree of crystallinity.[20] The poor solubility of the polymer **18e** in these conventional solvent allowed for the measurement of intrinsic viscosity in concentrated aqueous sulfuric acid solution only. Although an intrinsic viscosity value of $0.46 \, \mathrm{dl \, g^{-1}}$ was indicative of a moderately high molecular weight, only brittle film could be obtained upon compression molding. Further attempts at increasing the molecular weight by conducting the polymerization for longer time period (10 to 18 h), remained unsuccessful.

From our observations with these polymerization reactions, it was expected that the reactions of bisphenol-S, 4,4'-dihydroxybenzophenone and hydroquinone with **16** would require high reaction temperature and prolonged reaction times. Since the sulfone and the carbonyl moieties are strongly electron withdrawing, the resulting bisphenoxides from bisphenol-S and 4,4'-dihydroxybenzophenone can be regarded as weak nucleophiles in contrast to the bisphenoxides from bisphenol-A and 4,4'-dihydroxybiphenyl. Similar observations have been made for the reactions of the phenoxide from bisphenol-S and 4,4'-dihydroxybenzophenone with a variety of activated halides.[2a,d,18] Accordingly, the polymerization reactions were carried out only at elevated temperatures (230°C) for 8 to 10 h. In all cases, moderate to high molecular weight polymers could be prepared. The solubility behavior of the bisphenol-S functional polymer **18b** was same as that of the mono-ketone analogue, **3**. It was soluble in a wide variety of solvents including chlorinated hydrocarbons, tetrahydrofuran, DMAc and N-methylpyrrolidone (NMR) at room temperature. This is in contrast to the linear counterpart **10b**, which was soluble in boiling DMAc and NMP only. Similarly, polymer **18c**, obtained from hydroquinone and **16** was soluble in all solvents which are expected to dissolve amorphous poly(aryl ether)s (Table II). This solubility behavior is unlike the exceptional solvent resistance of **10c** (prepared from hydroquinone

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and 11b). Once again, these differences can be attributed to the highly kinked nature of the backbone due to the introduction of the

3,3′-linkage. In contrast, the poly(aryl ether-bisketone)s, 18d and 18e were soluble in hot DMAc and NMP only. This is due to the enhanced interchain forces, which results in improved solvent resistance in spite of the presence of the kinked 3,3′-links.

The molecular structures of the polymers were confirmed by both ^{13}C NMR and FT-IR. The ^{13}C NMR spectrum of the polymer 18a is shown in Figure 1. The observed peak positions were in agreement with calculated chemical shifts.[29] Furthermore, the absence of additional resonances due to end groups confirmed the high molecular weight nature of the polymers. The FT-IR spectra (film) of the polymers established the presence of the ether and keto linkages (absorbances at 1250 and 1655 cm^{-1}, respectively).
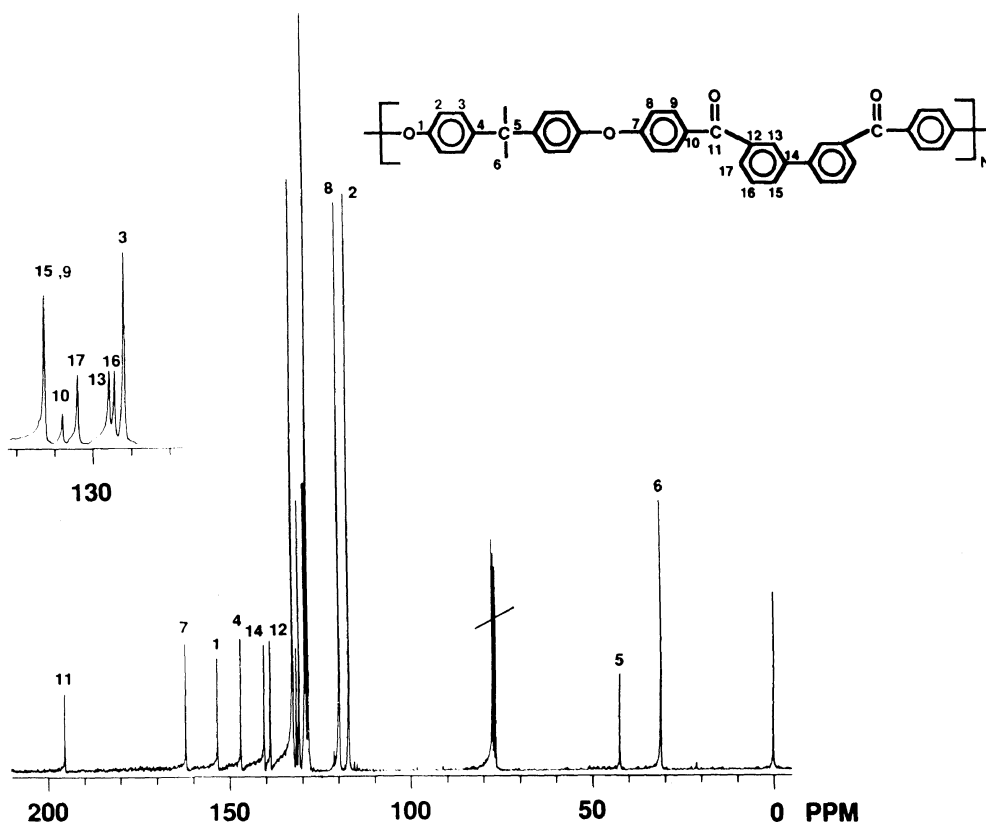
The glass transition temperatures of the

Table II. Solubility* behaviors of poly(aryl ether-bisketone)s 18 (a—e)^a

Polymers 18	Solvents				
	Methylene chloride	Chloroform	THF^b	DMAc^c	NMP^d
a	s	s	s	s	s
b	s	s	s	s*	s
c	s	s	s	s*	s
d	i	s	i	i	s*
e	i	i	i	i	s*

^{a} s, Soluble at RT: i, Insoluble at RT; s*, Soluble hot; *, 10% w/v.
^{b} Tetrahydrofuran.
^{c} Dimethylacetamide.
^{d} N-Methylpyrrolidone.

Figure 1. ^{13}C NMR spectrum of poly(aryl ether-bisketone) in CDCl$_3$ based on 18a.

Table III. Intrinsic viscosity data and glass transition temperatures of amorphous poly(aryl ether-bisketone)s

Polymer 18	Intrinsic viscosity values/(dl g^{-1}) (in chloroform at 25°C)	Glass transition temperatures/°C (DSC) (Heating rate 10°C min^{-1})
a	0.67	154
b	0.32	184
c	0.37	151
d	2.10[a]	182
e	0.46[b]	157

[a] Solvent, DMAc.
[b] Solvent, concentrated sulfuric acid.

poly(aryl ether-bisketone)s **18(a—e)**, were determined by DSC (Table III). Except for the more polar **18b** ($T_g = 184$°C) and **18d** ($T_g = 182$°C), the remaining polymers exhibited T_gs in the vicinity of 150°C. This was disappointing, because these values are not significantly higher than the reported value for poly(aryl ether-ketone), **2**, which contains only one keto group and is devoid of a biphenyl moiety.[2a] As expected, due to the presence of the 3,3′-linkage, the observed T_g values of 154°C for **18a** and 184°C for **18b** are approximately 30°C lower than those of the analogous linear amorphous poly(aryl ether-bisketone) **10a** and **10b**. This is consistent with earlier observations by Tanaka *et al.* with polyimide isomers.[30] The reason for the lower T_g of the meta isomers has been attributed to their higher configurational entropy due to a larger degree of conformational freedom of the main chains than the para linked polymers. The solubility behavior of the polymers discussed earlier was indicative of the semicrystalline nature for polymers **18d** and **18e**. Polymer **18d** exhibited a melting point endotherm at 238°C in the first heating. However, it did not recrystallize upon slow cooling and upon subsequent heating, a well-defined T_g could be observed only. The wide angle X-ray scan of the sample (Figure 3) revealed the low degree of crystallinity associated with this sample. On the other hand,
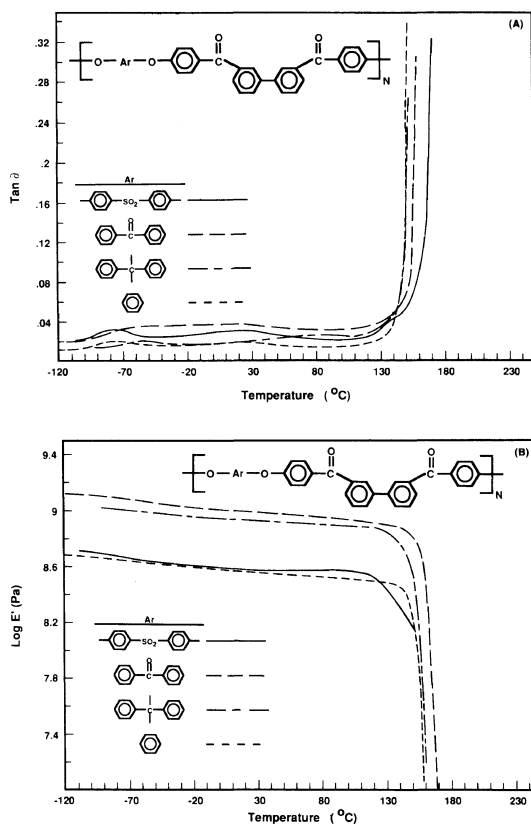
Figure 2. (A) tan δ *versus* temperature for various amorphous poly(aryl ether-bisketone)s. (B) Storage modulus (bending) *versus* temperature.

polymer **18e** with identical solubility properties did not show a melting point. In order to induce crystallinity, the polymer was annealed at 280°C for 24 h. Upon slow cooling (2.5°C min^{-1}) and reheating, an extremely weak melting point endotherm at 380°C could be observed. However, crystallinity could not be detected from the wide angle scan of the sample (Figure 3). This is in contrast to the high melting point ($T_m = 470$°C, first heating) observed for the corresponding polymer **10d** derived from the linear 4,4′-isomer.[20]

DMTA and Thermogravimetric Analysis of Poly(aryl ether-bisketone)s **18(a—e)**

The dynamic mechanical thermal analysis of the polymers (**18a—e**) corraborated the T_g data
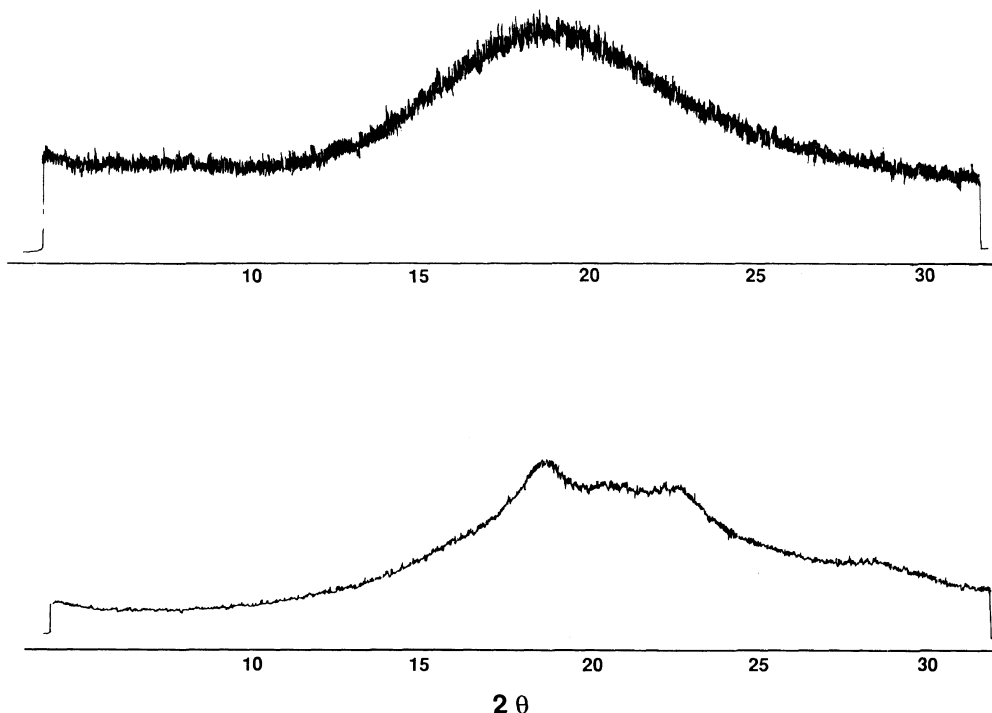
Figure 3. WDAX scans for **18d** (bottom) and **18e** (top).

obtained from DSC measurements. The dynamic mechanical behavior for the polymers is displayed in Figure 2. These data clearly show the moderately high T_g and good dimensional stability exhibited by these materials and also indicate a glassy morphology for this polymeric system (**18a—e**). In addition, a major low temperature secondary relaxation (β transition) in the vicinity of $-100°C$ can also be observed in all cases. Such transitions have been investigated by dynamic mechanical[31–33] and NMR techniques.[32] The observation of a β relaxation is believed to be associated with polymers which can exhibit ductile deformation.[31] In addition to these transitions, an additional weak peak can be observed for **18b**. It is likely that this is due to residual stress in the compression molded sample. This type of phenomenon has been observed earler with Udell™ polysulfone.[34]

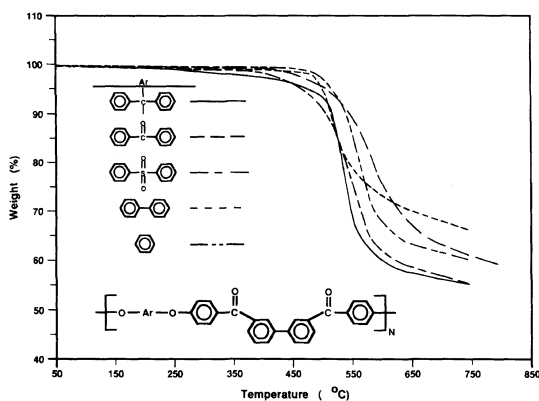The amorphous poly(aryl ether-bisketone)s were thermoformed by compression molding

Figure 4. TGA thermograms (weight loss *versus* temperature) for various poly(aryl ether-bisketone)s.

at approximately 70°C above the glass transition temperature. That this can be done is reflective of the excellent thermal stability of these materials. The thermal stability of the polymers, **18(a—e)** was further affirmed by thermogravimetric analysis in both the isothermal and dynamic modes. The variable

Table IV. Thermogravimetric analysis (nitrogen) of poly(aryl ether-bisketone)s

Polymer 18	Wt. loss on isothermal aging at 400°C/wt% h⁻¹	Polymer onset of decomposition temperature/°C	% Residue at 750°C
a	3.07	507	55.27
b	4.94	496	55.57
c	1.27	521	59.76
d	10.41	476	59.00
e	1.32	516	63.30

temperature thermograms of the polymers are shown in Figure 4. From an examination of the figure it is apparent that the poly(aryl ether-bisketone)s exhibit very good thermal stability with polymer decomposition temperature approaching 500°C, except for **18d**, which exhibits an onset of decomposition temperature at 476°C (Table IV). From an examination of the data in Table IV, it is clear that the polymers **18(a—e)** decompose with a significant amount (>50%) of char yield at 750°C. This would suggest a high level of flame retardant characteristics associated with these polymers.[35] Isothermal TGA (400°C, one hour, under nitrogen atmosphere) was also used to assess the thermal stability of the polymers (Table IV). The data consistent with the variable TGA scans, demonstrate that the poly(aryl ether-bisketone)s are materials of good thermal stability.

CONCLUSIONS

A series of high molecular weight poly(aryl ether-bisketone)s have been synthesized by the reaction of 3,3'-bis(4-fluorobenzoyl)biphenyl with suitable bisphenols. Polymer with amorphous and semicrystalline morphologies were obtained. The glass transition temperatures of the polymers were lower than those of the corresponding polymers prepared from the more linear 4,4'-bis(4-fluorobenzoyl)biphenyl, reflecting the increased stiffness of the 4,4'-linkage over that of the 3,3'-linkage. Some of the poly(aryl ether-bisketone)s exhibited improved solvent resistance over that observed for the monoketone analogues. In addition, all synthesized poly(aryl ether-bisketone)s possess excellent thermal stability, as evidenced from both dynamic and isothermal thermogravimetric analysis.

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