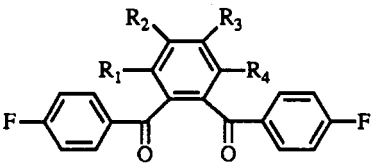
Synthesis of Novel Poly(ether ketone)s Containing the *o*-Dibenzoylbenzene Moiety

Introduction. Most of the reports on poly(aryl ether ketone)s that appear in the literature are aimed at the synthesis of crystalline polymers that can be used at elevated temperatures because of their high melting points. The polymers are very insoluble in common organic solvents, and therefore they are highly solvent-resistant materials.[1,2] High molecular weight poly(ether ether ketone) (PEEK) can be made 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 the precipitation of low molecular weight polymer from the solution.[2] Some amorphous poly(aryl ether ketone)s have been synthesized by using bisphenols such as 4,4′-(1-methylethylidene)bisphenol, and since these polymers are much more soluble, the reaction can be carried out at lower temperatures in an aprotic dipolar solvent.[3] Kricheldorf[4] has also synthesized a number of amorphous poly(aryl ether ketone)s by reaction of silylated bisphenols with fluoro ketones, and Hergenrother[5] has prepared a meta-substituted polymer that is also amorphous. All of these amorphous polymers are relatively soluble and have glass transition temperatures between 140 and 215 °C.

We describe herein the synthesis of the novel fluoro monomers **4**, **7**, and **10**, containing the 1,2-dibenzoylbenzene[6-8] moiety, which upon reaction with bisphenates in the presence of excess anhydrous potassium carbonate in *N*,*N*-dimethylacetamide (DMAc) gave high molecular weight amorphous poly(aryl ether ketone)s, which are very soluble in solvents such as chloroform and methylene chloride at room temperature and have glass transition temperatures ranging from 160 to 313 °C.

Results and Discussion. Two of the fluoroketone monomers were synthesized according to Scheme I. 1,2-Bis(*p*-fluorobenzoyl)ethylene (**1**), which was obtained from the reaction of fluorobenzene and aluminum chloride with fumaryl chloride,[7] undergoes a Diels–Alder reaction[8] with 1,3-butadiene in refluxing benzene to give cyclohexene **2** in quantitative yield. The reaction mixture changes from a bright yellow to a colorless solution, indicative of completion of the reaction. The isolated product was obtained in high purity, and no further purification was required. Reaction of cyclohexene **2** with a few drops of syrupy phosphoric acid in acetic anhydride gave dihydroisobenzofuran[9] **3** in quantitative yield. Treatment of compound **3** with 2 mol of bromine followed by sodium acetate in acetic acid gave bis(*o*-fluorobenzoyl)benzene (**4**) in excellent yield. In a similar manner, Diels–Alder reaction of compound **1** with *trans*,*trans*-1,4-diphenyl-1,3-butadiene in refluxing ethylbenzene gave diphenylcyclohexene **5** in quantitative yield. The sequence of steps



4 $R_1 = R_2 = R_3 = R_4 = H$
7 $R_2 = R_3 = H$, $R_1 = R_4 = C_6H_5$
10 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

for the aromatization of cyclohexene **2** was repeated for the synthesis of aromatic monomer **7** (98%) from diphenylcyclohexene **5**.

1,2-Bis(4-fluorobenzoyl)ethylene (**1**) was further employed in the synthesis of a tetraphenyl-substituted 1,2-dibenzoylbenzene monomer **10** (Scheme II). When the method of Lutz[10] was used, bromination of ethylene **1** gave vicinal bromide **8**, which upon treatment with triethylamine in acetone gave the bis(fluorobenzoyl)acetylene (**9**) in good yield. Diels–Alder reaction[11] of acetylene **9** with tetraphenylcyclopentadienone in benzophenone at reflux temperature gave 3,4,5,6-tetraphenyl-1,2-dibenzoylbenzene **10** in 95% yield.

The overall yield for the synthesis of each of the monomers described, without optimization, is above 90%.

Polymerization reactions involving the three fluoro diketone monomers **4**, **7**, and **10** were carried out with 4,4′-(1-methylethylidene)bisphenol (BPA) and excess potassium carbonate in DMAc. The high molecular weight polymers **11**–**13** were isolated as white fibrous materials in very good yield (95%) (Scheme III). Glass transition temperatures (T_g; by differential scanning calorimetry) of the three poly(ether ketone)s **11**–**13** (Table I) were determined, and values of 182, 221, and 268 °C, respectively, were obtained. The T_g's of the polyketones increase 40–45 °C with the addition of each pair of phenyl substituents on the benzene ring. The T_g of the poly(ether ketone) **11** is higher than its meta (T_g = 153 °C)[5] and para (T_g = 165 °C)[3] isomers, which have been synthesized previously. The higher T_g observed in the ortho polymer **11** as compared to its isomers could be a result of the restricted rotation present in the ortho isomer. This is illustrated by a molecular model of 1,2-dibenzoylbenzene (Figure 1a). Even more restriction to rotation is present in 1,2-dibenzoyl-3,6-diphenylbenzene (Figure 1b), which could account for the further increase in glass transition temperature observed for polymer **12** (T_g = 221 °C) compared to polymer **11** (T_g = 182 °C).

The three poly(ether ketone)s demonstrated excellent thermal stability by thermogravimetric analysis, with polymer decomposition temperatures ranging from 490 to 530 °C at 5% weight loss under an atmosphere of air and nitrogen (Table II). There seemed to be no significant difference in thermal stability under the two atmospheres.

Scheme I

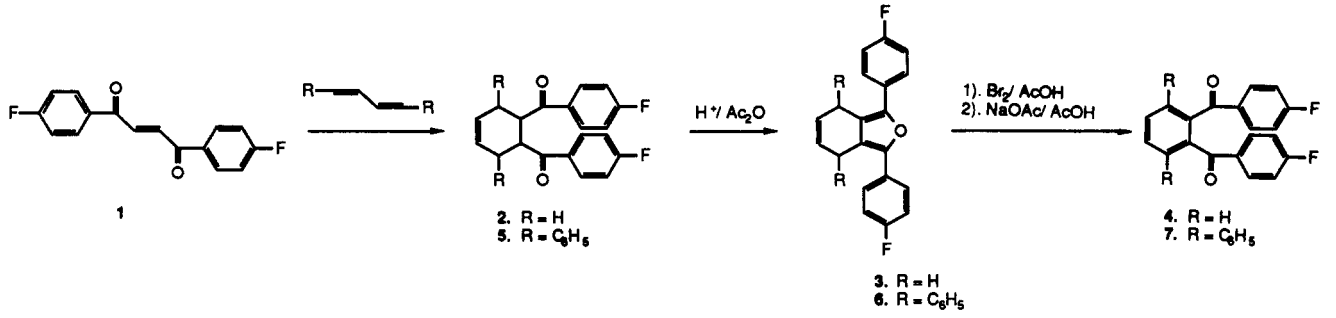


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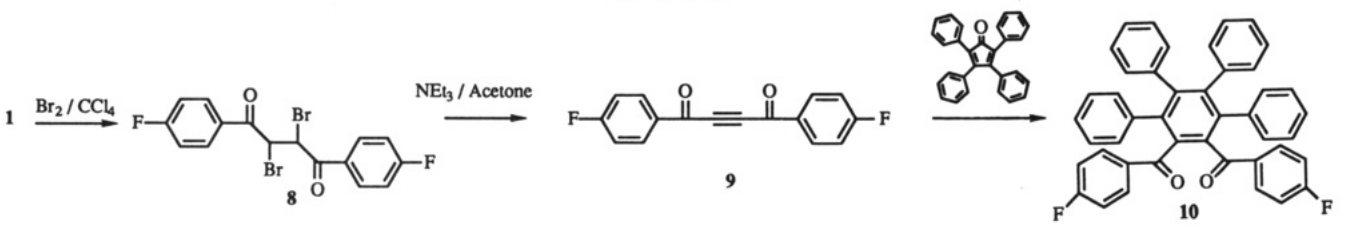
Table I
Properties of Poly(ether ketone)s 11–14

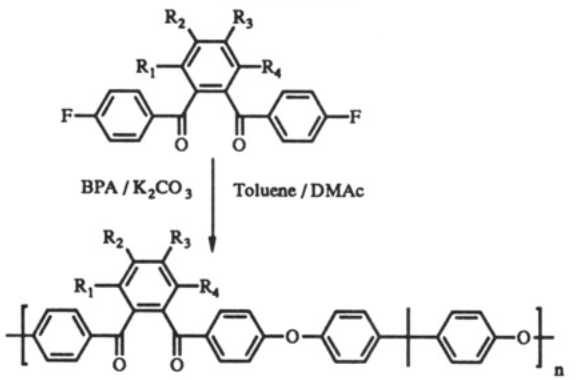
polymer	yield, wt %	η_{inh},[a] dL/g	T_g, °C	$\bar{M}_w$[b]	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$	TGA[c] for air/N_2, °C	film[d]
11[e]	95	0.48	182	32 400	17 100	1.9	483/483	flex
11[f]	85	0.36	160	24 530	8 760	2.8	476/477	flex
12	95	0.65	221	85 400	51 600	1.7	512/512	flex
13	96	0.47	268	44 000	27 300	1.6	520/523	flex
14	95	0.44	188	38 062	16 201	2.3	405/408	flex

[a] The inherent viscosities were measured at a concentration of 0.5 g/dL in chloroform at 25°C. [b] Determined by GPC (based on polystyrene standards). [c] Reported for 5% weight loss. [d] Films were cast from methylene chloride at 25 °C. [e] Polymer 11 obtained from direct polymerization of monomer 4. [f] Poly(ether ketone) 11 obtained from polymer 14.

Scheme II

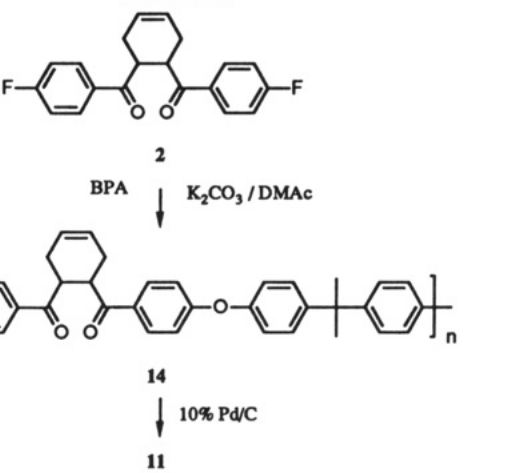


Scheme III



11 $R_1 = R_2 = R_3 = R_4 = H$
12 $R_2 = R_3 = H$, $R_1 = R_4 = C_6H_5$
13 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

Scheme IV



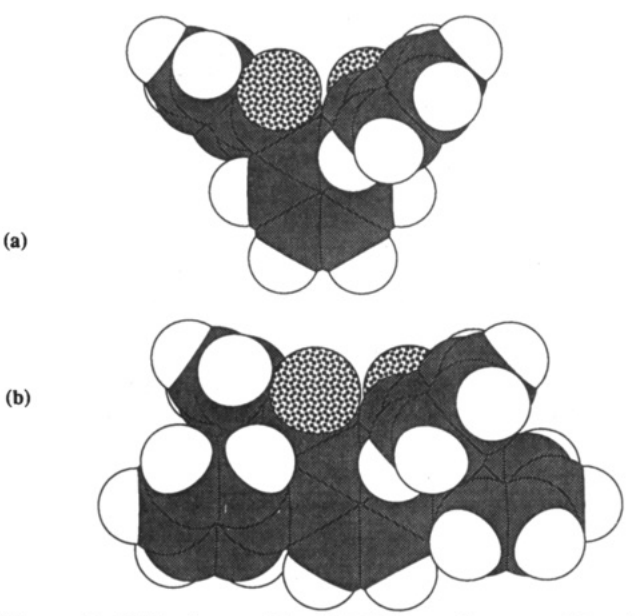
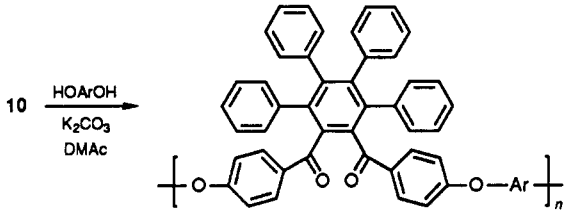


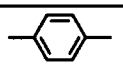
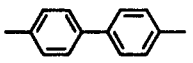
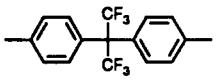
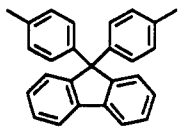
Figure 1. Molecular models of 1,2-dibenzoylbenzene (a) and 1,2-dibenzoyl-3,6-diphenylbenzene (b).

The polymer containing the most highly phenylated benzoylbenzene ring, poly(ether ketone) 13 synthesized from monomer 10 was the most thermally stable polymer. Tough, clear, and flexible films of polymers 11–13 were obtained by casting from methylene chloride solution at room temperature. Molecular weights of these polymers were determined by gel permeation chromatography using polystyrene standards, and their inherent viscosities are presented in Table I.

Alternatively, the synthesis of poly(ether ketone) 11 was effected by the polymerization of cyclohexene 2 with BPA and excess anhydrous potassium carbonate in DMAc and toluene solution, which gave a white fibrous polymer 14 (95%) when precipitated in methanol (Scheme IV). Dehydrogenation of polymer 14 with 10% Pd/C and a catalytic amount of elemental sulfur in diphenyl ether at the temperature of reflux for 30 h gave the fully aromatized poly(ether ketone) 11 (85%). Formal proof that this product had the structure assigned was based on the fact that, upon catalytic dehydrogenation of polymer 14, polymer 11 was obtained, which was by ^1H NMR studies identical with 11 obtained from monomer 4. The polymers 11 (from polymer 14) and 14 displayed glass transition temperatures of 160 and 188 °C, respectively. The discrepancy in glass transition temperature between the 1,2-dibenzoylbenzene polymer 11 (T_g = 160 °C) obtained from polymer 14 (T_g = 188 °C) and polymer 11 (T_g = 182 °C) synthesized by polymerization of monomer 4 could be due to some imperfections in the polymer chain arising in the dehydrogenation reaction of polymer 14. Some chain scission may also occur as indicated by a lowering of M_w, M_n, and inherent viscosity as evidenced in the dehydrogenation product 11 (from polymer 14) as seen in Table I.

Table II
Reaction of 3,4,5,6-Tetraphenylbis(4-fluorobenzoyl)benzene (10) with Various Bisphenates



-Ar-	η_{inh},[a] dL/g	T_g, °C	$\bar{M}_w$[b]	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$	TGA[c] for air/N_2, °C	film[d]
 15	0.49	273	25 600	16 000	1.6	542/543	flex
 16	0.73	292	43 400	25 300	1.7	536/536	flex
 17	0.44	278	37 860	12 300	3.1	546/548	flex
 18	0.55	313	87 900	48 500	1.8	523/528	flex

[a] The inherent viscosities were measured at a concentration of 0.5 g/dL in chloroform at 25 °C. [b] Determined by GPC (based on polystyrene standards). [c] Reported for 5% weight loss. [d] Films were cast in methylene chloride at 25 °C.

Other high molecular weight poly(aryl ether ketone)s with high glass transition temperatures were prepared by the reaction of 3,4,5,6-tetraphenylbis(4-fluorobenzoyl)benzene (**10**) with bisphenates in DMAc at 164 °C. Polymer properties are presented in Table II. As expected, polymers containing the 1,4-phenylene (polymer **15**) and 4,4′-biphenyl (polymer **16**) linkages have higher glass transition temperatures (273 and 292 °C) than polymer **13** (T_g = 268 °C), which contains the flexible isopropylidene moiety. Polymer **17** with the hexafluoroisopropylidene linkage also has a higher glass transition temperature (T_g = 278 °C; TGA for air/N_2 546/548) and is more stable than polymer **13** (TGA for air/N_2 520/523). Polymer **18** containing the 9,9-bis(4-hydroxyphenyl)fluorene moiety displayed the highest glass transition temperature (T_g = 313 °C) of any of the poly(aryl ether ketone)s synthesized to date. All the polymers form flexible films that are colorless and transparent.

In this study, we have synthesized some unique 1,2-bis(4-fluorobenzoyl)benzene monomers, which undergo reaction with bisphenates to give amorphous high-temperature polymers in excellent yields. Presently, work is in progress to synthesize other high-temperature polymers containing the *o*-dibenzoyl moiety from reactions with other bisphenates and along with further studies of the wide range of chemical and physical properties that can be achieved with these materials.

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