

# Synthesis and Characterization of Novel Poly(aryl ether ketone ketone)s Containing the *o*-Dibenzobene Moiety

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**ABSTRACT:** The synthesis of a novel chloro monomer containing the 1,2-dibenzoylbenzene moiety was described. The chloro monomer was reacted with 4-(4-hydroxyphenyl)-1(2*H*)-phthalazinone compound in the presence of excess anhydrous potassium carbonate in an aprotic solvent (Sulfolane), and high molecular weight amorphous poly(aryl ether ketone ketone) was synthesized. The polymers with high glass transition temperature were soluble in solvents such as chloroform and nitrobenzene at room temperature and easily cast into flexible, colorless, and transparent films. The 5% weight loss of the polymers was >400 °C. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1487–1492, 2001

**Key words:** engineering plastics; poly(aryl ether ketone ketone); synthesis

## INTRODUCTION

High molecular weight poly(aromatic ketone)s (PAKs) were first synthesized by Friedel–Crafts condensation of isophthaloyl and terephthaloyl chlorides with diphenyl ether in methylene chloride solution in the presence of aluminum chlorides<sup>1</sup> and later by reaction in liquid hydrogen fluoride solvent.<sup>2</sup> PAKs exhibit high thermal stability and excellent electrical and mechanical properties. But, these materials are highly crystalline and show very poor solubility in all common solvents at ambient temperature. Rose<sup>3</sup> found that the nucleophilic substitution method

can be used to produce high-molecular weight poly(ether ether ketone) (PEEK). The commercial interest in this material is that it can be used 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 the reaction can be carried out at lower temperature in an aprotic polar solvent because these polymers are much more soluble.<sup>4</sup> An alternative to the bisphenoxide displacement reaction has been recently reported by Kricheldorf and Bire<sup>5</sup> in which the phenoxide is prepared by desilylation of trimethylsilyl phenyl ethers, with cesium fluoride as the catalyst. Amorphous high molecular weight meta-substituted polymers have been prepared by the condensation of 1,3-bis-(4-chlorobenzoyl) benzene with a number of bisphenoxides.<sup>6</sup> Hay and Singhe<sup>7</sup> have recently reported the syn-

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thesis of amorphous, high molecular weight, thermooxidatively stable poly (aryl ether ketone)s with high glass transition temperatures. These high molecular weight materials are prepared from fluoro monomers containing the 1,2-dibenzoylbenzene moiety that undergo facile fluoro-displacement polymerization with bisphenates in the presence of excess anhydrous potassium carbonate in *N,N*-dimethylacetamide (DMAc).

In this paper, a novel chloro monomer containing the 1,2-dibenzoylbenzene moiety was synthesized and the chloro-displacement polymerization with 4-(4-hydroxyphenyl)-1(2*H*)-phthalazinone (DHPZ), a bisphenate-like compound, in the presence of excess anhydrous potassium carbonate in sulfolane was carried out. The reactivity of the monomer, and the solubility and thermal stability of the polymers were also discussed.

## EXPERIMENTAL

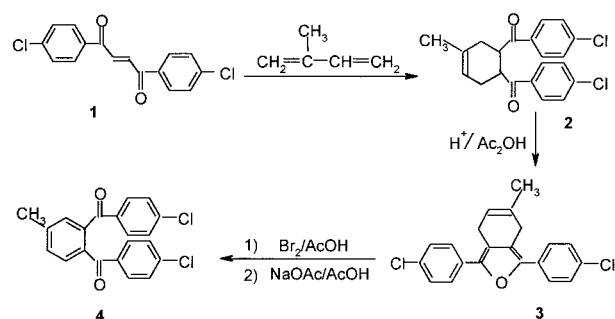
### Monomer Synthesis

#### 1,2-Bis (4-chlorobenzoyl) ethylene (1)

Aluminum chloride (0.60 mol, 79.83 g) was added to chlorobenzene (1.84 mol, 207 g, 187.1 mL). The resulting suspension was gently heated to 50 °C, and then fumaryl chloride (0.23 mol, 25 mL) was added in a dropwise manner into the system over a period of 5 to 8 min. The resulting carmine reaction mixture was refluxed for 15 min, and the mixture was poured onto conc. hydrochloric acid with crushed ice. The semi-solid was filtered off, washed with ethanol, digested in ethanol, and finally recrystallized from toluene to give pale yellow needles of **1**; mp 151–153 °C; <sup>1</sup>H-NMR (200 MHz), δ = 7.51(d, 4H, 2 ortho C<sub>6</sub>H<sub>2</sub>Cl), 8.00 (d, 4H, 2 ortho C<sub>6</sub>H<sub>2</sub>CO), 8.02 (s, 2H, CH=CH); MS: 306 (4.7), 305 (0.7), 304 (7.9), 269 (5.8), 165 (4.6), 141(31), 139 (100).

#### 4,5-Bis (4-chlorobenzoyl)-1-methyl-cyclohexene (2)

2-Methyl-1, 3-butadiene (26mmol, 1.77 g) was added to a cooled solution of 1,2-bis (4-chlorobenzoyl) ethylene (10 mmol, 6.08 g) in 50 mL of benzene. The intensely yellow reaction mixture was heated at reflux until a colorless reaction mixture was achieved (10–12 h). The resulting product was recrystallized from ethanol to give white crystalline **2**; mp 131–132 °C; <sup>1</sup>H-NMR (200 MHz), δ = 1.70 (s, 3H, CH<sub>3</sub>), 1.82–2.39 (m, 4H, CH<sub>2</sub>), 3.88–4.12 (m, 2H, CHCO), 5.4–5.55 (s, 1H,



**Scheme 1** The synthesis route of BCBB.

CH=C), 7.35 (d, 4H, 2 ortho C<sub>6</sub>H<sub>2</sub>Cl), 7.86 (d, 4H, 2 ortho C<sub>6</sub>H<sub>2</sub>CO); MS: 372 (18.5), 233 (80.1), 205 (37.1), 139 (100), 111 (80.7), 77 (21.7).

#### 1,2-Bis (4-chlorophenyl)-7-methyl-4,5-dihydroisobenzofuran (3)

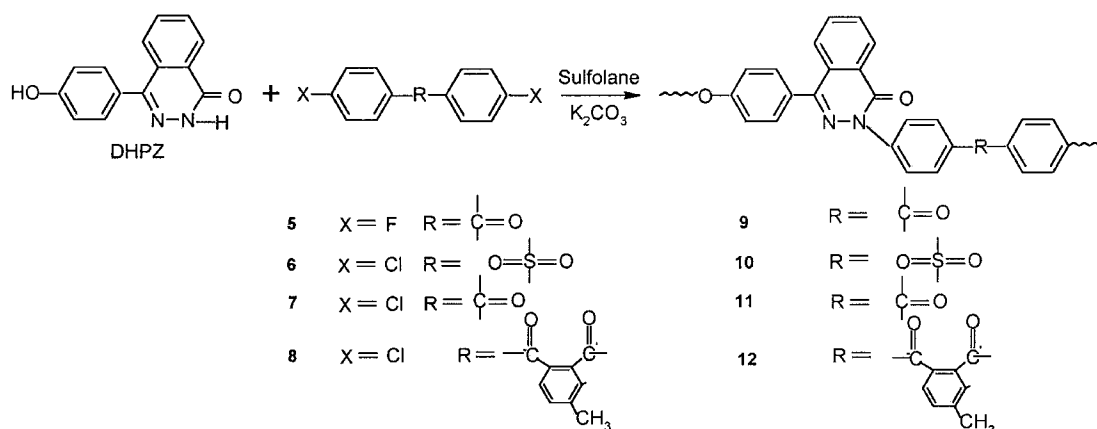
To 25 g reaction mixture of 4,5-bis (4-chlorobenzoyl)-1-methyl-cyclohexene in 200 mL of hot acetic anhydride, 0.5 g of 86% syrupy phosphoric acid was added. The reaction mixture was refluxed for 10 min and, on cooling, the insoluble furan crystallized immediately to give a quantitative yield of dihydroisobenzofuran **3**; mp 178–179 °C; <sup>1</sup>H-NMR (200 MHz), δ = 1.85 (s, 3H, CH<sub>3</sub>), 3.45 (s, 4H, CH<sub>2</sub>-CH=C), 5.55 (s, 1H, CH=C), 7.20 (d, 4H, 2 ortho C<sub>6</sub>H<sub>2</sub>Cl), 7.65 (d, 4H, 2 ortho C<sub>6</sub>H<sub>2</sub>CO).

#### 1,2-Bis (4-chlorobenzoyl)-4-methylbenzene (4)

The solution of bromine (62.65 mmol, 10 mL) in 60 mL of glacial acetic acid was added to a boiling solution of 1,2-bis (4-chlorophenyl)-7-methyl-4,5-dihydroisobenzofuran (25.0 mmol, 8.90 g) in glacial acetic acid (500 mL). The reaction mixture was refluxed for 15 min until the bromine was completely absorbed, and reflux continued for another 15 min after sodium acetate (250.6 mmol, 20.56 g) was added. Water (140 mL) was added to the refluxing mixture, and then it was allowed to cool for several hours. The white solid, 1,2-bis (4-chlorobenzoyl)-4-toluene, was filtered and recrystallized from ethanol; mp 147–148 °C; <sup>1</sup>H-NMR (200 MHz), δ = 2.40 (s, 3H, CH<sub>3</sub>), 7.30 (d, 4H, 2 ortho C<sub>6</sub>H<sub>2</sub>Cl), 7.45 (s, 4H, C<sub>6</sub>H<sub>3</sub>(CO)<sub>2</sub>(CH<sub>3</sub>)), 7.60 (d, 4H, 2 ortho C<sub>6</sub>H<sub>2</sub>CO).

### Polymer Synthesis

Polymerization reactions were conducted in three-necked flasks, which were generally equipped with



Scheme 2 The synthesis of PPEKK.

a nitrogen inlet, thermometer, Dean–Stark trap, and condenser. A typical synthesis of Phthalazine poly(ether ketone ketone) (PPEKK) is described as follows. The flask was charged with monomer BCBB (10 mmol, 3.69 g), DHPZ (10 mmol, 2.38 g), and sulfolane (20 mL). After toluene (40 mL) was mixed in the system, anhydrous potassium carbonate (14 mmol, 1.93 g) was added. The reaction mixture was then heated until the toluene began to reflux. A reflux temperature range was maintained between 135 and 140 °C until the presence of water was no long observed in the Dean–Stark trap. On dehydration and slow removal of toluene from the reaction mixture, the temperature was gradually increased to 200 °C. The reaction mixture was cooled and diluted with sulfolane (10 mL) when the viscosity increased dramatically, and several drops of weak acid (e.g., acetic acid) were added to neutralize phenoxide end groups. The reaction mixture was then coagulated in ~30 mL of water and filtered, redissolved in chloroform, and filtered again. The chloroform solution was concentrated and then coagulated in ethanol. The white fibrous polymer was filtered and dried in a vacuum oven at 80 °C for 48 h to give PPEKK in almost quantitative yield.

#### Characterization of Monomer and Polymers

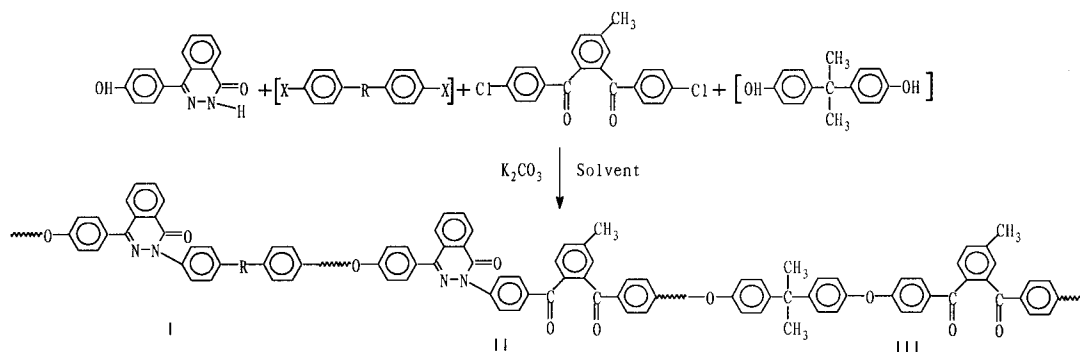
The proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra (200 MHz) was recorded on a Varian Gemini 200 instrument using tetramethylsilane as the internal standard, in deuteriochloroform as the solvent. The chemical shift ( $\delta$ ) is quoted in ppm. Mass spectra were recorded on a ZAB 2F HS spectrometer, ion source 240°C and 70-eV electron impact, direct inlet:  $m/e$  (assign-

ment). The infrared (IR) spectra of the monomer and polymer were recorded with Perkin-Elmer 1600 spectrophotometer. The inherent viscosity of the polymer was measured by viscometer at 25 °C. The glass transition temperature ( $T_g$ ) was determined by DuPont 2000 differential scanning calorimetry (DSC) at a heating rate of 10°C/min in an atmosphere of nitrogen. The thermooxidative stability was measured by thermogravimetric analysis (TGA) in an atmosphere of nitrogen at a heating rate of 10 °C/min. Sulfolane was refluxed over sodium hydroxide and activated carbon for 2 h and was distilled in vacuum. Chlorobenzene was refluxed and distilled over calcium chloride. 2-Methyl-1,3-butadiene and aluminum chloride were chemically pure reagents. Commercial bis(4-chlorophenyl)sulfone (DCS), 4,4'-difluorobenzophenone (DFB), and 4,4'-dichlorobenzophenone (DCB) were used as received without further purification. A bisphenol-like compound, 4(4-hydroxyphenyl)-1(2H)-phthalazinone (DHPZ), was synthesized according to the method of Jian et al.<sup>8</sup>

Table I Inherent Viscosity of Poly(ether ketone)<sup>a</sup>

Parameter	Dihalide			
	DCB	DCS	DFB	BCBB
Polymer number	9	10	11	12
$\eta_{inh}$ (dL/g)	0.18	0.36	0.66	0.35

<sup>a</sup> Reaction time, 4 h.



Phthalazinone poly(ether ketone ether ketone ketone) (PPEKEKK)

structural formula I + II, R:C=O, X:F.

Phthalazinone poly(ether sulfone ketone ketone) (PPESKK)

structural formula I + II, R:O=S=O, X:C1.

Phthalazinone poly(ether A ketone ketone) (PPEAKK)

structural formula II + III.

Phthalazinone poly(ether ketone ketone) (PPEKK)

structural formula II.

**Scheme 3** The synthesis of PPEKKs.

## RESULTS AND DISCUSSION

The new monomer 1,2-bis (4-chlorobenzoyl)-4-methylbenzene (BCBB) was synthesized as shown in Scheme 1. Chlorobenzene and fumaryl chloride were reacted in a Friedel–Crafts reaction to give 1,2-bis (4-chlorobenzoyl)-ethylene **1**. A Diels–Alder reaction of **1** with 2-methyl-1,3-buta-

diene in benzene gave the substituted cyclohexene **2** in excellent yield. Compound **2** was converted to the fully aromatized **4** in quantitative yield via the corresponding dihydroisobenzofuran intermediate **3**. The overall yield for the monomers was >90%. The high pure monomer was crystallized readily from acetone and ethanol. The carbonyls are trans,<sup>9</sup> and the pendant phe-

**Table II** Thermal Properties of Poly(aryl ether ketone ketone)

Polymer		Properties		
		$\eta_{inh}$ (dL/g)	$T_g$ (°C)	5% Weight Loss (°C)
PPEKK		0.37	213.8	425
	EK/EKK = 2/1	0.45	250.7	
PPEKEKK	EK/EKK = 1/1	0.38	228.8	426
	EK/EKK = 1/2	0.28	222.2	
	S/KK = 2/1	0.20	211.5	
	S/KK = 1/1	0.22	209.8	
PPESKK	S/KK = 1/1	0.22	209.8	400
	S/KK = 1/2	0.19	205.8	
	DHPZ/BPA = 2/1	0.60	213.4	
PPEAKK	DHPZ/BPA = 1/1	0.48	188.2	410
	DHPZ/BPA = 1/2	0.46	178.0	
	DHPZ/BPA = 1/2	0.46	178.0	

**Table III** The Solubility of Poly(aryl ether ketone ketone)<sup>a</sup>

Polymer	DMAc	CHCl <sub>3</sub>	DMF	DMSO	NMP	NB	TCE	THF	o-DCB	Py
PPEKK	+	+	+	-	+	±	+	±	-	+
PPEKEKK	EK/EKK = 2/1	+	+	-	+	+	+	±	-	±
	EK/EKK = 1/1	+	+	+	-	+	+	±	-	+
PPESKK	EK/EKK = 1/2	+	±	-	+	+	+	±	-	+
	KK/S = 2/1	+	+	+	-	+	+	±	-	+
	KK/S = 1/1	+	+	+	±	+	+	±	-	+
PPEAKK	KK/S = 1/2	+	+	+	±	+	+	+	±	+
	DHPZ/BPA = 2/1	±	+	+	-	+	±	+	±	±
PPEAKK	DHPZ/BPA = 1/1	+	+	+	-	+	+	+	±	+
	DHPZ/BPA = 1/2	+	+	+	-	+	+	+	+	+

<sup>a</sup> Key: +, fully soluble; ±, partially soluble; -, insoluble

nyls are clearly not coplanar with the central ring. Polymers containing these bulky substituents in the backbone would be expected therefore to be soluble and remain in solution during polymerization.

In the nucleophilic displacement polymerization reaction, an investigation of the reactivity of the chloro-substituted compounds DCS 6, DCB 7, BCBB 8, and DFB 5 with DHPZ was carried out in the presence of potassium carbonate in a sulfolane/toluene (1:2) solvent mixture. Four polymers (polymers 9–12) were synthesized (Scheme 2). For these four reactions, the solids composition was maintained at 30 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 after completion of bisphenoxide formation and dehydration, the polymerization systems were heated to 200 °C to effect the displacement reaction. After 4 h, the reactions were finished. The inherent viscosity of the four polymers is shown in Table I.

The dihalide monomers **5**, **6**, **7**, and **8** were reacted with DHPZ to yield poly(aryl ether ketone) **9**, **10**, **11**, and **12**, respectively (Table I). The inherent viscosity of polymer **9**, measured in chloroform at room temperature, was the highest and that of polymer **11** was the lowest. The inherent viscosities of polymers **10** and **12** were almost the same. This similarity indicates that the reactivity of BCBB with DHPZ is between that of DFB and DCB, but similar to that of DCS. That is, BCBB shows high reactivity with the bisphenol-like compound to form a poly(aryl ether ketone).

Four polymers were prepared by reactions of BCBB with various bisphenols (Scheme 3). In all

cases, high-molecular weight polymers were achieved within 5 h. All monomers were polymerized with bisphenoxides in sulfolane at 200 °C.

The glass transition temperature ( $T_g$ ) and the thermal stability of the polymer were also measured (Table II). At the same content of BCBB, the  $T_g$  of PPEKEKK is higher than that of PPEKK and PPEAKK. PPESKK should have a high  $T_g$  because it contains a sulfone group, but the low inherent viscosity led to a lower  $T_g$  of the polymer. The  $T_g$  of PPEAKK is the lowest because of the introduction of an aliphatic chain in the backbone.  $T_g$  also changed with the variation of the composition of polymers. The  $T_g$  of PPEKEKK increases with increasing DFK units, as expected because of the increasing rigidity of the backbone. The  $T_g$  of PPEAKK decreases with increasing amount of BPA units because of the increasing flexibility of the backbone. The  $T_g$  of PPESKK increases with increasing DCS units. Therefore, polymers with different  $T_g$  could be obtained easily by varying the structure and the composition. The TGA shows all of the polymers exhibit good thermal stability with 5% weight loss at >400 °C.

The solubility of the polymers in polar solvents is listed in Table III. The solubility of the polymers varied with the structure and the composition. The solubility of PPESKK increased with increasing content of sulfone group and that of PPEAKK decreased with decreasing content of BPA. The solubility of PPEKEKK does not change with the content of DFB. PPESKK shows the highest solubility because of the strong polarity of the sulfone group in the backbone.

All of the polymers are amorphous. The X-ray spectrum of PPEKK shows a diffuse scattering peak with no crystallization peak. Commercial PAEKs

are crystalline or semicrystalline, whereas PPEKKs are amorphous because of the irregularity of the backbone structure.

## CONCLUSION

A new 1,2-bis(4-chlorobenzoyl)-4-toluene monomer was synthesized, which undergoes reactions with bisphenates to produce amorphous poly(ether ketone)s with high glass transition temperatures. The polymerization reactions were conducted in sulfolane in the presence of  $K_2CO_3$  to give high molecular weight polymers that are soluble in some polar solvent. The decomposition temperature of the materials is  $>400\text{ }^\circ\text{C}$ , which indicates their high thermal stability.

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