

# Preparation and Properties of New Soluble Aromatic Polyimides from 2,2'-Bis(3,4-dicarboxyphenoxy)biphenyl Dianhydride and Aromatic Diamines

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Received 30 June 1997; accepted 1 December 1997

**ABSTRACT:** A new aromatic tetracarboxylic dianhydride having a crank and twisted noncoplanar structure, 2,2'-bis(3,4-dicarboxyphenoxy)biphenyl dianhydride, was synthesized by the reaction of 4-nitrophthalonitrile with biphenyl-2,2'-diol, followed by hydrolysis and cyclodehydration. The biphenyl-2,2'-diyl-containing aromatic polyimides having inherent viscosities up to 0.66 dL/g were obtained by the conventional two-step procedure starting from the dianhydride monomer and various aromatic diamines. Most of the polyimides were readily soluble in amide-type solvents such as *N,N*-dimethylacetamide and *N*-methyl-2-pyrrolidone. The aromatic polyimides had glass transition temperatures in the range of 205–242°C, and began to lose weight around 415°C, with 10% weight loss being recorded at about 500°C in air. © 1998 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 36: 2021–2027, 1998

**Keywords:** 2,2'-bis(3,4-dicarboxyphenoxy)biphenyl dianhydride; aromatic polyimides; solubility; thermal behavior

## INTRODUCTION

Aromatic polyimides were developed in the early 1960s, and since then have been of great technological importance due to their outstanding thermal and electrical properties.<sup>1,2</sup> Aromatic polyimides are normally insoluble in organic solvents, and have extremely high glass transition or melting temperatures, which preclude melt processing. Hence, one of the drawbacks in using aromatic polyimides is their poor processability, and a great deal of efforts have been made to improve the processing characteristics of these intractable polyimides.<sup>3,4</sup> One of the successful approaches to improve solubility and processability of polyimides with minimal detrimental effect on their high thermal stability is the introduction of bulky phe-

nyl pendant groups along the polymer backbone. Some organo-soluble aromatic polyimides have been demonstrated by using aromatic diamines having phenyl substituents,<sup>5–11</sup> as well as phenylated aromatic tetracarboxylic dianhydrides.<sup>12–14</sup>

The other effective approach to organo-soluble high-temperature polymers we developed recently is the incorporation of crank and twisted noncoplanar structure into the polymer backbone. For example, highly kinked and cranked bulky aromatic diamines, 2,2'-bis(4-aminophenoxy)biphenyl and 2,2'-bis(4-aminophenoxy)-1,1'-binaphthyl, were effectively used to prepare soluble aromatic polyamides and polyimides, with various aromatic dicarboxylic acids and tetracarboxylic dianhydrides, respectively.<sup>15,16</sup> Such aromatic dicarboxylic acids, 2,2'-bis(4-carboxyphenoxy)biphenyl and 2,2'-bis(4-carboxyphenoxy)-1,1'-binaphthyl, were also prepared for the production of soluble aromatic polyamides.<sup>17</sup>

To make a comparison of the properties of the above-mentioned aromatic polyimides derived

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*Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 36, 2021–2027 (1998)  
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from 2,2'-bis(4-aminophenoxy)biphenyl and aromatic tetracarboxylic dianhydrides<sup>16</sup> with those of the isomeric counterpart, a new aromatic tetracarboxylic dianhydride having a crank and twisted noncoplanar structure, 2,2'-bis(3,4-dicarboxyphenoxy)biphenyl dianhydride, was synthesized in the present study. The dianhydride monomer was used to prepare new soluble biphenyl-2,2'-diyl-containing aromatic polyimides by the conventional two-step method with various aromatic diamines. The properties of these polymers such as solubility and thermal behavior were then discussed.

## EXPERIMENTAL

### Materials

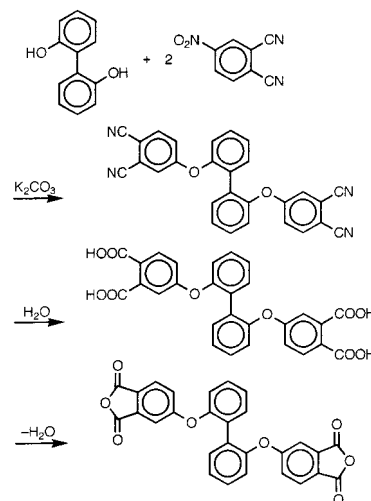
Reagent-grade aromatic diamines such as *m*-phenylenediamine (**2a**), *p*-phenylenediamine (**2b**), and bis(4-aminophenyl)methane (**2c**) were purified by distillation under reduced pressure. Bis(4-aminophenyl) ether (**2d**) was purified by sublimation, while bis(4-aminophenyl) sulfone (**2e**) was done by recrystallization from ethanol.

*N,N*-Dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO) were purified by distillation under reduced pressure over calcium hydride. Potassium carbonate was dried at 150°C under vacuum.

### Monomer Synthesis

#### 2,2'-Bis(3,4-dicyanophenoxy)biphenyl (BPCN)

In a three-necked flask equipped with a nitrogen inlet, a Dean–Stark trap, and a condenser, were placed 9.31 g (50 mmol) of biphenyl-2,2'-diol and 15.0 g (108 mmol) of dried potassium carbonate with 100 mL of DMSO and 100 mL of benzene. The mixture was heated with stirring at 120°C for 6 h under a thin stream of nitrogen to remove the by-product of water by azeotropic distillation with benzene. After the benzene had been removed, the mixture was cooled and to this was added 17.66 g (102 mmol) of 4-nitrophthalonitrile. The reaction was carried out with stirring at 40°C for 40 h under nitrogen, and the reaction mixture was poured into 1 L of cold water. The precipitate was collected by filtration and dried. The product was purified by recrystallization from ethanol to afford 15.90 g (78%) of pale-yellow needles, m.p. 155–156°C. The infrared (IR) spectrum (KBr) exhibited absorption bands at 2234 (C≡N) and 1250



Scheme 1.

$\text{cm}^{-1}$  (C—O—C). The  $^{13}\text{C}$ -nuclear magnetic resonance (NMR) spectrum ( $\text{CHCl}_3\text{-d}_1$ ) showed peaks  $\delta$  at 160.92, 150.62, 135.18, 131.99, 130.36, 129.39, 126.30, 121.04, 120.83, 117.14, 115.14, 114.76, and 108.58 ppm.

ANAL. Calcd for  $\text{C}_{28}\text{H}_{14}\text{N}_4\text{O}_2$ : C, 76.70%; H, 3.22%; N, 12.78%. Found: C, 76.14%; H, 3.05%; N, 12.75%.

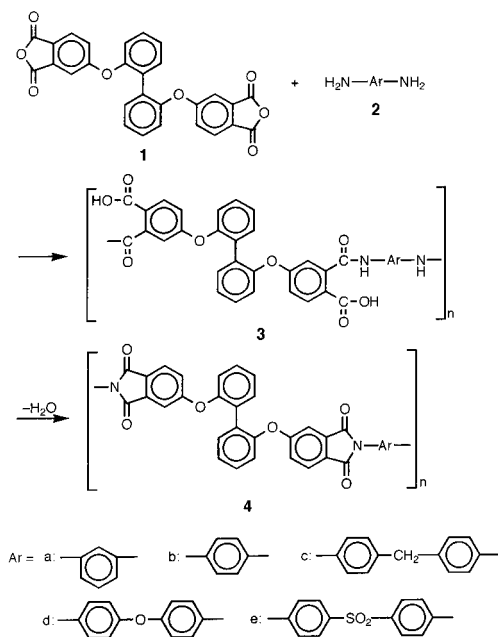
#### 2,2'-Bis(3,4-dicarboxyphenoxy)biphenyl (BPCA)

A mixture of 22.4 g (400 mmol) of potassium hydroxide and 8.13 g (20 mmol) of BPCN in 200 mL of methanol and 200 mL of water was stirred at a refluxing temperature until no further ammonia was generated. The time spent to reach this stage was about 4 days. The solution thus formed was cooled, and the pH value was adjusted with dilute hydrochloric acid to near 3. The white precipitate formed was filtered and dried under vacuum. The yield was 10.28 g (100%). The compound had an endothermic peak due to thermal cyclodehydration at about 190°C (by DSC). The IR spectrum (KBr) showed absorptions at 3200 (O—H), 1710 (C=O), and 1265  $\text{cm}^{-1}$  (C—O—C).

The product was used for the subsequent cyclodehydration without further purification.

#### 2,2'-Bis(3,4-dicarboxyphenoxy)biphenyl Dianhydride (1)

A mixture of 2.63 g (5.5 mmol) of BPCA and 1.5 mL of acetic anhydride in 30 mL of acetic acid was refluxed with stirring for 5 h. The solution formed was cooled, and a solid separated out. The solid



Scheme 2.

was removed by filtration and dried under vacuum. The yield was 1.98 g (81%), mp 188–190°C. The IR spectrum (KBr) exhibited absorption bands at 1852 and 1770 (C=O), and 1265  $\text{cm}^{-1}$  (C—O—C). The  $^{13}\text{C}$ -NMR spectrum (DMSO- $d_6$ ) showed peaks  $\delta$  at 163.73, 151.35, 133.89, 133.42, 130.39, 129.44, 127.85, 125.95, 124.36, 120.87, 120.55, and 111.98 ppm.

ANAL. Calcd for  $\text{C}_{28}\text{H}_{14}\text{O}_8$ : C, 70.30%; H, 2.95%. Found: C, 70.38%; H, 2.81%.

### Polymer Synthesis

#### Polyimide 4b from 1 and 2b

To a solution of 0.216 g (2.0 mmol) of aromatic diamine **2b** in 8 mL of DMAc, 0.963 g (2.0 mmol) of tetracarboxylic dianhydride **1** was added at once at 0–5°C under nitrogen. The mixture was stirred at that temperature for 1 h, giving a solution, and then at 20–25°C for 5 h. A half volume of the reaction solution was poured into 300 mL of methanol. The precipitated polymer was collected by filtration and dried under vacuum at room temperature. The inherent viscosity of polyamic acid **3b** was 0.57 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30°C.

The polyamic acid film was obtained by casting the reaction solution onto a glass plate and drying under vacuum at room temperature overnight. The polyamic acid in the form of film was converted to polyimide **4b** by successive heating under vacuum at 100, 200, and 300°C for 1 h each. The inherent viscosity of **4b** was 0.66 dL/g, measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C. The IR spectrum of **4b** (film) exhibited characteristic imide absorption bands at 1779 and 1717 (C=O), 1367 (C—N), and 725  $\text{cm}^{-1}$  (imide ring).

The other polyimides were prepared by an analogous procedure.

Table I. Synthesis of Aromatic Polyimides

Diamine	Polyamic acid		Polyimide				
	Code	$\eta_{\text{inh}}^a$ (dL/g)	Code	$\eta_{\text{inh}}^b$ (dL/g)	Elemental Analysis <sup>c</sup> (%)		
					C	H	N
<b>2a</b>	<b>3a</b>	0.33	<b>4a</b>	0.21	73.90 (74.18)	3.12 (3.30)	4.87 (5.09)
<b>2b</b>	<b>3b</b>	0.57	<b>4b</b>	0.66	73.95 (74.18)	3.14 (3.30)	4.98 (5.09)
<b>2c</b>	<b>3c</b>	0.41	<b>4c</b>	0.54	76.09 (76.87)	3.63 (3.78)	4.37 (4.37)
<b>2d</b>	<b>3d</b>	0.57	<b>4d</b>	0.47	74.23 (74.76)	3.33 (3.45)	4.41 (4.36)
<b>2e</b>	<b>3e</b>	0.10	<b>4e</b>	0.14	68.64 (69.56)	2.97 (3.21)	4.13 (4.06)

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMAc at 30°C.

<sup>b</sup> Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C.

<sup>c</sup> The data given in parentheses are the calculated values.

**Table II.** Solubility of Aromatic Polyimides<sup>a</sup>

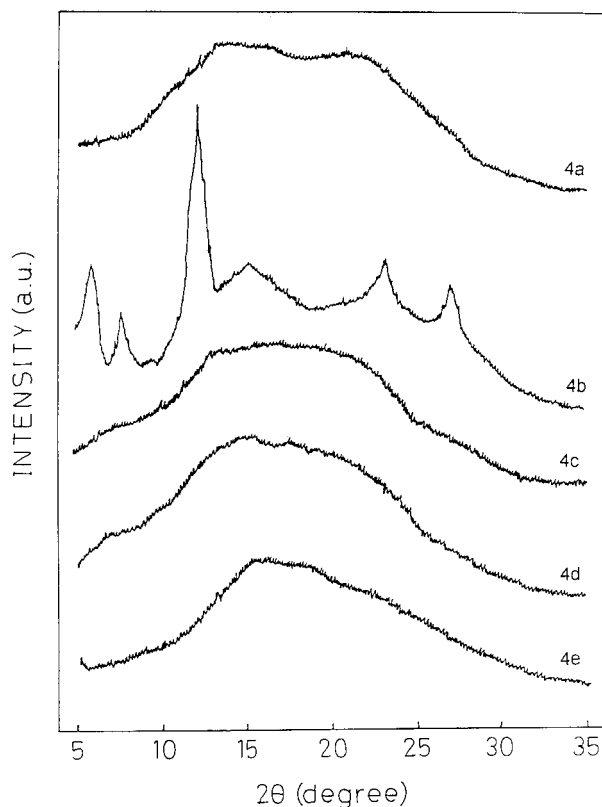
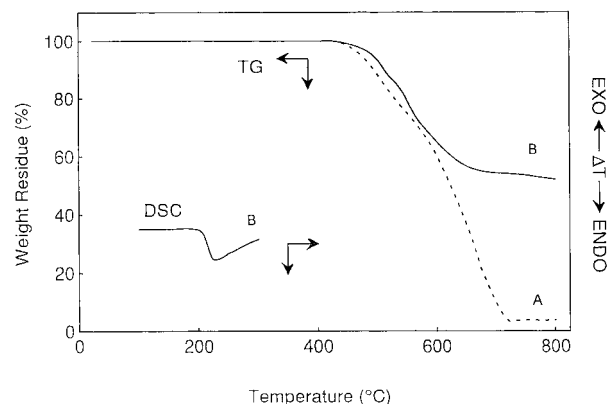
Solvent	Polymer				
	4a	4b	4c	4d	4e
NMP <sup>b</sup>	++	—	++	++	++
DMAc	±	—	++	±	++
Pyridine	++	—	—	±	±
<i>m</i> -Cresol	±	—	—	—	—
DMSO	—	—	—	—	—

<sup>a</sup> Solubility: (++) soluble at room temperature, (±) partly soluble, and (—) insoluble.

<sup>b</sup> *N*-methyl-2-pyrrolidone.

### Measurements

IR and <sup>13</sup>C-NMR spectra were recorded on a JASCO FT/IR-5000 spectrophotometer and a JEOL FX-90Q spectrometer, respectively. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed with DSC-41M and TGA-40M Shimadzu thermal analyzers, respectively. Wide-angle X-ray diffraction patterns

**Figure 1.** X-ray diffraction diagrams of aromatic polyimides.**Figure 2.** DSC and TG curves of polyimide 4a: (A) in air, and (B) in nitrogen. DSC and TG heating rate = 10°C/min.

were obtained at room temperature on a Rigaku-dennki RU-200 apparatus with nickel-filtered CuK $\alpha$  radiation (50 kV, 180 mA).

## RESULTS AND DISCUSSION

### Monomer Synthesis

Takekoshi et al. already reported the synthesis of aromatic ether-containing tetranitriles by the nitro substitution reaction of 4-nitrophthalonitrile with several bisphenols, and of the corresponding tetracarboxylic dianhydrides as well.<sup>18</sup> This route was applied in the present study to the synthesis of a new aromatic tetracarboxylic dianhydride, 2,2'-bis(3,4-dicarboxyphenoxy)biphenyl dianhydride (**1**), as shown in Scheme 1.

The aromatic tetranitrile containing ether linkage BPCN was synthesized readily starting from 4-nitrophthalonitrile and biphenyl-2,2'-diol in a high yield of 78%, according to a slight modification of the procedure of Takekoshi et al.<sup>18</sup> using potassium carbonate as a base in DMSO–benzene mixture. The tetranitrile compound was then hydrolyzed with aqueous potassium hydroxide, giving the corresponding tetracarboxylic acid BPCA, which in turn was converted to the aromatic ether-containing tetracarboxylic dianhydride **1** in a high yield of 81% by the chemical cyclodehydration with acetic anhydride.

The chemical structures of all of the newly synthesized compounds were confirmed by means of elemental analysis, as well as by IR and <sup>13</sup>C-NMR spectroscopic techniques. Concerning the synthesis of the tetracarboxylic acid BPCA, the

**Table III.** Thermal Behavior of Aromatic Polyimides

Polymer	$T_g^a$ (°C)	$T_d^b$ (°C)		$T_{10}^b$ (°C)	
		In Air	In Nitrogen	In Air	In Nitrogen
<b>4a</b>	205	415	420	495	520
<b>4b</b>	— <sup>c</sup>	425	425	520	520
<b>4c</b>	213	415	415	500	505
<b>4d</b>	206	425	435	545	530
<b>4e</b>	242	435	435	535	555

<sup>a</sup> Determined by DSC at a heating rate of 10°C/min in nitrogen.

<sup>b</sup>  $T_d$  (decomposition-starting temperature) and  $T_{10}$  (10% weight loss temperature) determined by TG at a heating rate of 10°C/min.

<sup>c</sup> No  $T_g$ , but a polymer melting temperature of 390°C was observed.

disappearance of a characteristic nitrile stretching band at 2234  $\text{cm}^{-1}$  with the appearance of a strong carboxylic stretching at 1710  $\text{cm}^{-1}$  on the IR spectrum clearly revealed the completion of hydrolysis of the tetranitrile compound BPCN. The cyclodehydration of BPCA to the corresponding tetracarboxylic dianhydride **1** was also supported from the observation on the IR spectrum that the strong absorption band due to carboxylic function shifted from 1710  $\text{cm}^{-1}$  (free acid) to 1770  $\text{cm}^{-1}$  (anhydride). The elemental analysis values of all the compounds were in good agreement with the calculated values for the proposed structures. But the  $^{13}\text{C}$ -NMR spectra of BPCN and compound **1** exhibited 13 and 12 peaks, respectively, owing to overlapping of some peaks.

### Polymer Synthesis

The conventional two-step procedure starting from aromatic diamines and tetracarboxylic dianhydrides is a convenient method for the preparation of polyimides.<sup>1,2</sup> New biphenyl-2,2'-diyl-containing polyimides **4a–4e** were synthesized in two steps from the aromatic tetracarboxylic dianhydride **1** with aromatic diamines **2a–2e** through the ring-opening polyaddition and subsequent thermal cyclodehydration (Scheme 2).

Table I summarizes the results of the synthesis of new polyimides. The ring-opening polyaddition in DMAc at room temperature readily afforded the precursor polyamic acids **3a–3e** having inherent viscosities of 0.10–0.57 dL/g, suggesting the formation of the polymers with moderate molecular weights. Polymer **3e** had lower viscosity than the others, which could be attributed to the low nucleophilic nature of aromatic diamine **2e** having electron-withdrawing group. Colorless trans-

parent films of the polyamic acids were obtained by casting the resulting polymer solutions.

The thermal conversion of the precursor polyamic acids **3a–3e** to polyimides **4a–4e** was carried out by successive heating of the precursors in the form of films at 100, 200, and 300°C under vacuum for 1 h each. The polyimides were readily obtained with inherent viscosities of 0.14–0.66 dL/g. Most polyimide films were light yellow and transparent, while polyimide **4b** gave a yellow translucent film due to its crystallinity.

The formation of polyimides was confirmed by elemental analysis and IR spectroscopy. The elemental analysis values of these polyimides agreed well with the calculated values for the proposed structures (Table I). In the IR spectra, the polyimides exhibited characteristic imide absorption bands at about 1780, 1720, 1370, and 725  $\text{cm}^{-1}$ .

### Polymer Characterization

The solubility of the aromatic polyimides was studied qualitatively, and the solubility behavior is shown in Table II. Polyimides **4c** and **4e** having methylene and sulfone connecting groups, respectively, dissolved readily in *N*-methyl-2-pyrrolidone (NMP) and DMAc. Polyimide **4a** with *m*-phenylene unit was also soluble in NMP and pyridine, while polymer **4b** with symmetric *p*-phenylene structure was quite insoluble in any organic solvents. Nevertheless, the solubility of polyimides was found to be improved by the introduction of bulky, cranked, and twisted noncoplanar biphenyl-2,2'-diyl unit into the polymer backbone.

Figure 1 shows the X-ray diffraction diagrams of the aromatic polyimides. These diagrams revealed that polyimide **4b** with symmetric *p*-phe-



**Table IV.** Comparison of Properties of Isomeric Polyimides

$\left[ \begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{N} \quad \text{Ar}' \quad \text{N}-\text{Ar}- \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array} \right]_n$		Solubility <sup>a</sup>			$T_g$ (°C)	$T_{10}^b$ (°C)
Ar	Ar'	H <sub>2</sub> SO <sub>4</sub>	NMP	DMAc		
		—	—	—	—	545
		++	++	++	200	530
		++	++	++	235	510
		++	—	—	—	520
		++	++	±	213	500
		++	++	++	242	535

<sup>a</sup> Solubility: (++) soluble at room temperature, (±) partly soluble, and (—) insoluble.<sup>b</sup>  $T_{10}$ : 10% weight loss temperature in air.

nylene structure had a fair degree of crystallinity, whereas all the other polyimides were amorphous. Thus, the amorphous nature of these polymers was reflected in their good solubility, and this also could be attributed to the incorporation of bulky and kinked biphenyl-2,2'-diyl unit along the polymer backbone.

The thermal behavior of the aromatic polyimides was evaluated by means of DSC and TG. Figure 2 depicts typical DSC and TG curves of polymer **4a**, and the thermal behavior data are summarized in Table III. The glass transition temperatures of amorphous polyimides **4a** and **4c–4e** were in the range of 205–242°C, depending

on the structure of the diamine component. Crystalline polyimide **4b** had a melting temperature of 390°C, but no glass transition temperature was detected even after the sample was quenched from 400°C. All the polyimides were stable up to 415°C in both air and nitrogen atmospheres, and the temperatures at 10% weight loss were above 495°C on the TG curves.

The properties of the new aromatic polyimides were compared with those of the isomeric counterpart polyimides derived from 2,2'-bis(4-aminophenoxy)biphenyl and various aromatic tetracarboxylic dianhydrides reported previously.<sup>16</sup> Table IV summarizes the comparison of

the properties of the two sets of isomeric polyimides. There was no obvious difference in solubility between the present polyimides and the isomeric counterparts. In addition, the glass transition temperatures and the thermal stability with respect to decomposition temperatures of the present polyimides were almost comparable to those of the isomeric pairs of polyimides.

## CONCLUSIONS

A new polyimide-forming tetracarboxylic dianhydride having a crank and twisted noncoplanar structure, 2,2'-bis(3,4-dicarboxyphenoxy)biphenyl dianhydride, was successfully synthesized in three steps starting from 4-nitrophthalonitrile and biphenyl-2,2'-diol. The dianhydride monomer was subjected to the polycondensation with various aromatic diamines, giving polyimides. The introduction of bulky, cranked, and twisted noncoplanar biphenyl-2,2'-diyl unit into the polymer backbone improved solubility of the polyimides in organic solvents. The aromatic polyimides had glass transition temperatures of 205–242°C and 10% weight loss temperatures above 495°C in air, indicating high thermal stability.

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