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## **Aryl ether-ketone segmented polypyromellitimides**

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(Received 26 July 1993)

### **SUMMARY:**

Aromatic ether-ketone segments have been incorporated into polyimide backbone to impart the well-known thermoplastic properties of polyether ketones. For this purpose three aromatic diamines containing ether and ketone connecting groups between aromatic rings have been prepared and polymerized with pyromellitic dianhydride to yield polyimides. The thermal behavior of the polyimide cast films has been investigated.

### **ZUSAMMENFASSUNG:**

Aromatische Ether-Keton-Sequenzen wurden in eine Polyimidkette eingebaut, um diesen die thermoplastischen Eigenschaften der Polyetherketone zu verleihen. Zu diesem Zweck wurden drei aromatische Diamine mit Ether- und Ketongruppen zwischen den aromatischen Ringen hergestellt und mit Pyromellitsäuredianhydrid kondensiert. Das thermische Verhalten von daraus hergestellten Polymerfilmen wurde untersucht.

### *Introduction*

Polyimides, especially polypyromellitimides, are known as one of the most thermo-resistant polymers, which have been used for electronics materials such as insulators and passivants. However, these excellent materials are not easily processed owing to their infusibility and insolubilities in common solvents.

There have been considerable efforts on the subject of the processibility including incorporation of oxyethylene<sup>1</sup>, aryl ether<sup>2</sup> and some aryl ether-ketone units<sup>3</sup>. Although aliphatic segments in the backbone impart chain mobility, these modifications always decrease the polymer degradation temperature (PDT)<sup>4</sup>.

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In the present study some new polypyromellitimides containing aromatic ether-ketone segments have been prepared and their thermal properties have been examined. Our goal is to combine the excellent thermal and mechanical properties of polyimides with the fairly good thermoplastic properties of aromatic ether ketones for improving the processibility of polyimides. In order to impart their properties into polyimides, three diamines with aromatic ether-ketone groups have been synthesized and reacted conveniently with pyromellitic dianhydride (PMDA).

### *Experimental*

All the chemicals were reagent grade; commercial products were used without any further purification.

NMR spectra were recorded with a Bruker 270 MHz spectrometer, in DMSO- $d_6$  using TMS as internal standard.

IR spectra were taken on a Pye-Unicam PU 9714 IR spectrometer with KBr discs.

Differential scanning calorimetry (DSC): Dupont S 99 Model 910 DSC (at 10 K/min heating rate).

Thermogravimetric measurements were made on a Perkin-Elmer TGS-2 Analyser under nitrogen flow with 10 K/min heating rate.

Viscosity measurements were carried out in DMF at  $30 \pm 0.02^\circ\text{C}$  (in 1 g/L concentrations), using a Cannon-Fenske viscometer.

Synthesis of p-nitrophenyl phenyl ether (NPPE) was carried out by the method given elsewhere<sup>5</sup>.

### *Synthesis of 4-(4-nitrophenoxy)phenyl-4-nitrophenyl ketone (1a)*

5.375 g (25.0 mmol) of NPPE and 4.175 g (25.0 mmol) of p-nitrobenzoic acid in 32.5 g (23 ml) of Eaton reagent (1 : 10  $\text{P}_2\text{O}_5$ /methane sulfonic acid) were placed in a tightly closed 100 ml flask. While stirring with a magnetic stirrer, the mixture was heated for 3 h in an oil bath at  $100^\circ\text{C}$ . At the end of this period, the content of the flask was poured into 500 ml of cold water. The precipitate was stirred until decolorization of the mixture (for about 30 min), then filtered and washed with water several times. The crude product was dispersed in 200 ml of 3%  $\text{Na}_2\text{CO}_3$  solution and mixed vigorously for 20 min to remove unreacted p-nitrobenzoic acid. The product was filtered, washed with excess of water and 20 ml of methanol to remove unreacted NPPE. Then it was dissolved in 150 ml of acetic acid and boiled with decolorizing charcoal for 10 min and filtered. On cooling, white crystals precipitated. Yield 3.8 g (41.7%), m. p.  $212^\circ\text{C}$  (soluble in acetic acid, toluene, dichloromethane, dioxane, N-methyl pyrrolidone, DMF, acetone, less soluble in  $\text{CCl}_4$ , xylene, insoluble in n-hexane and water).

*Aryl ether-ketone segmented polypyromellitimides*

$C_{19}H_{12}N_2O_6$ (364.31)	Calcd.	C 62.64	H 3.32	N 7.69
	Found	C 62.50	H 3.26	N 7.71

$^1H$ -NMR (DMSO- $d_6$ ):  $\delta$  = 7.3–8.24 (m, aromatic).

IR (KBr pellet) ( $cm^{-1}$ ): 1505 (asym.  $NO_2$  str.), 1340 (sym.  $NO_2$  str.), 1690 (C=O str.), 1240 (Ar-O-Ar str.).

*Synthesis of 4,4'-bis(p-nitrophenoxy)benzophenone (1b)*

Synthesis of p-nitrophenoxy-4-methylbenzene (NPPK) from p-cresol and p-nitro bromobenzene and its oxidation to 4-(4-nitrophenoxy)benzoic acid (NPBA) were carried out according to the procedure given in the literature<sup>6</sup>. The mixture of 5.18 g (20.0 mmol) of 4-(4-nitrophenoxy)benzoic acid (NPBA), 4.3 g (20.0 mmol) of 4-nitrophenyl phenyl ether (NPPE) and 26 g (20 ml) Eaton reagent were placed in a closed glass bottle and stirred at 100 °C for 3 h. Then the same procedure applied for **1a** was followed.

Yield 5.7 g (80.0%), m. p. 152 °C (soluble in acetic acid, DMF, N-methyl pyrrolidone, dioxane,  $CH_2Cl_2$ , acetone, less soluble in methanol, ethanol, insoluble in n-hexane, xylene and water).

$C_{25}H_{16}N_2O_7$ (456.41)	Calcd.	C 65.79	H 3.53	N 6.14
	Found	C 65.58	H 3.48	N 5.97

$^1H$ -NMR (DMSO- $d_6$ ):  $\delta$  = 7.15–8.20 (m, aromatic).

IR (KBr pellet) ( $cm^{-1}$ ): 1700 (C=O str.), 1510 ( $NO_2$  asym. str.), 1345 ( $NO_2$  sym. str.), 1250 (Ar—O—Ar str.).

(Note: This compound has been synthesized by F. Harenberg and co-workers in a different way<sup>7</sup> (m.p. 150–151 °C) by interaction of bis(4-bromophenyl) ketone and potassium salt of 4-nitrophenol).

*Synthesis of 1,4-bis(4-p-nitrophenoxybenzoyl)benzene (1c)*

3.32 g (20.0 mmol) of terephthalic acid, 8.6 g (40.0 mmol) of NPPE and 52 g (36 ml) of Eaton reagent were placed in a closed glass bottle and stirred at 120 °C for 6 h. The mixture was poured into 500 ml of cold water; after stirring for 20 min, the precipitate was filtered and washed with water. The crude product was dispersed in 200 ml of 3%  $Na_2CO_3$  solution and filtered. Then it was dispersed in 100 ml hot methanol and ether. The dried product was dissolved in 100 ml of DMF and boiled with decolorizing charcoal and filtered. On cooling white crystals separated was filtered, washed with methanol and ether, dried at 100 °C for 3 hours. Yield 5.0 g (44.6%), m. p. 261 °C (soluble in DMF, hot nitrobenzene, insoluble in water, benzene, xylene, acetone, chloroform, less soluble in diethylene glycol).

N. Bıçak, G. Koza

$C_{32}H_{20}N_2O_8$ (560.52)	Calcd.	C 68.57	H 3.60	N 5.00
	Found	C 69.10	H 3.57	N 4.86

$^1H$ -NMR (DMSO- $d_6$ ):  $\delta$  = 7.30–8.35 (m, aromatic).

IR (KBr pellet) ( $cm^{-1}$ ): 1690 (C=C str.), 1500 ( $NO_2$  asym. str.), 1340 ( $NO_2$  sym. str.), 1249 (Ar—O—Ar str.).

### *General procedure for the preparation of the corresponding diamines (2a, 2b and 2c)*

Preparation of the diamine **2a** was performed by reduction of the dinitro compound (**1a**) with sodium dithionite ( $Na_2S_2O_4$ ): 3.5 g (10.0 mmol) of **1a** was dispersed in 100 ml of ethanol in a 250 ml flask. A solution of 30 g of 85%  $Na_2S_2O_4$  in 40–50 ml water was added dropwise to the flask with stirring at 50–60 °C for 30 min. More dithionite was added until the color changed. 50 ml of water was added and stirring was continued for another 1 h. The mixture was boiled and ethanol was evaporated. The content of the flask was filtered and poured into 80 ml of concentrated hydrochloric acid. HCl salt of the diamine was filtered and dispersed in 50 ml water, and 10 ml of concentrated HCl solution was added and boiled for 5–10 min in order to destroy the possible bisulphite adducts.

The chilled mixture was neutralized with NaOH and left overnight. The white precipitate was filtered and recrystallized from methanol/pyridine (1 : 1 v/v) and dried at 70 °C for 3 h. Yield 2.93 g (86%), m. p. 188–191 °C (soluble in DMF, dioxane, N-methyl pyrrolidone and pyridine, less soluble in xylene, nitrobenzene and  $CH_2Cl_2$ , insoluble in methanol and water).

$C_{19}H_{16}N_2O_2$ (304.35)	Calcd.	C 74.98	H 5.30	N 9.20
	Found	C 74.80	H 5.26	N 9.18

$^1H$ -NMR (DMSO- $d_6$ ):  $\delta$  = 6.40–7.63 (m, 12 H, aromatic), 5.85 (s, 2H,  $NH_2$  of amino benzoyl unit,  $D_2O$  exch.), 5.1 (s, 2H,  $NH_2$  of amino phenoxy unit,  $D_2O$  exch.).

IR (KBr pellet) ( $cm^{-1}$ ): 3300–3400 (broad doublet,  $NH_2$  str.), 1650 (C=O str.), 1600 (N—H plane def.), 1255 (Ar—O—Ar str.).

The other two diamines were prepared by the same procedure; except for **2c**, N-methyl pyrrolidone was used instead of ethanol.

The yield for **2b** was 40.3%, m. p. 154 °C<sup>8</sup> (soluble in DMF, N-methyl pyrrolidone, pyridine, less soluble in dioxane, xylene and  $CH_2Cl_2$ ).

$C_{25}H_{20}N_2O_3$ (404.51)	Calcd.	C 75.74	H 5.08	N 7.07
	Found	C 76.50	H 5.01	N 7.10

$^1H$ -NMR (DMSO- $d_6$ ):  $\delta$  = 6.65–7.80 (m, 16 H aromatic), 5.32 (s, 4H,  $NH_2$ ,  $D_2O$  exch.).

### *Aryl ether-ketone segmented polypyromellitimides*

IR (KBr Pellet) ( $\text{cm}^{-1}$ ): 3300–3400 (broad doublet,  $\text{NH}_2$  str.), 1670 ( $\text{C}=\text{O}$  str.), 1600 ( $\text{N}-\text{H}$  plane def.), 1240 ( $\text{Ar}-\text{O}-\text{Ar}$  str.).

For 2c: Yield 78.2%, m. p. 229 °C (soluble in DMF, N-methyl pyrrolidone, pyridine, less soluble in dioxane, xylene, nitrobenzene).

$\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_4$ (500.55)	Calcd.	C 76.79	H 4.83	N 5.60
	Found	C 76.60	H 4.80	N 5.47

$^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ ):  $\delta$  = 6.6–7.9 (m, 20H, aromatic), 5.25 (s, 4H,  $\text{NH}_2$ ,  $\text{D}_2\text{O}$  exch.).

IR (KBr pellet) ( $\text{cm}^{-1}$ ): 3300–3400 (broad doublet,  $\text{NH}_2$  str.), 1680 ( $\text{C}=\text{O}$  str.), 1595 ( $\text{N}-\text{H}$  plane def.), 1240 ( $\text{Ar}-\text{O}-\text{Ar}$  str.).

(Note: This compound has been synthesized by a different route<sup>3</sup>, by interaction of 4-aminophenol and 4,4' difluorobenzophenone in the presence of excess of  $\text{K}_2\text{CO}_3$ . m. p. 226–230 °C).

### *General procedure for preparation of the pyromellitimides*

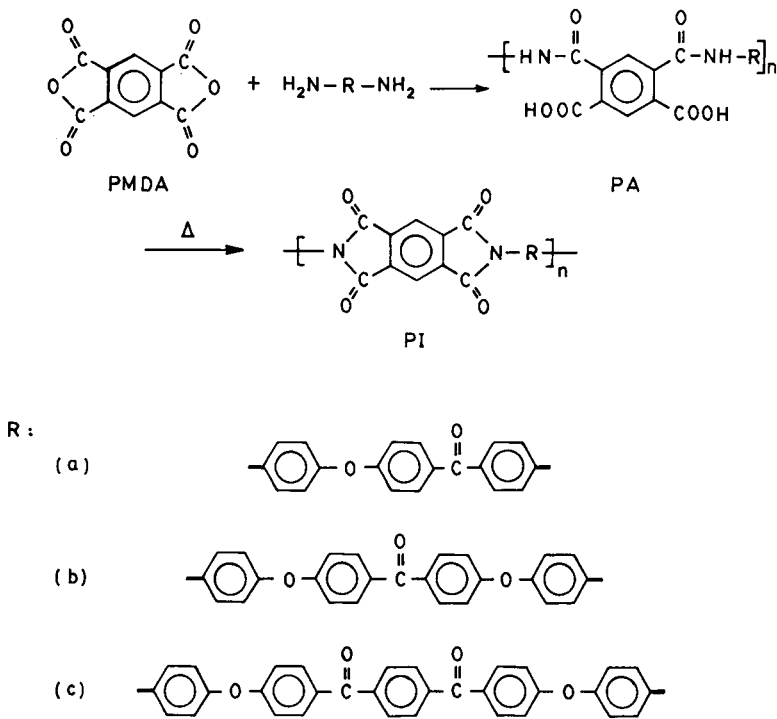
Polypyromellitimides were prepared by reacting PMDA with diamines in NMP, by the two step method<sup>9</sup> through polyamic acid. 0.436 g (2.0 mmol) of PMDA and 2 mmol of the corresponding diamine were dissolved in 10 ml of dry NMP in a closed bottle and stirred at room temperature for 14 h. A small amount of sample was taken for polyamic acid viscosity test. Polyamic acid films were cast from NMP on a plate glass and heated at 120 °C under nitrogen for 1 h. Cyclodehydration was completed by heating for 2 h at 300 °C in an oven. Thick films were scratched for tests.

In IR spectra,  $\text{C}=\text{O}$  str. vibrations of polyamic acids are in the 1650–1690  $\text{cm}^{-1}$  range. In the case of polyimides, these vibrations appear at 1710 and 1770  $\text{cm}^{-1}$  as double bands. Characteristic imide peaks are observed at 600 and 710  $\text{cm}^{-1}$  as peaks of medium intensity.

### *Results and discussion*

Three aromatic diamines having different ether and ketone connecting groups were prepared from their nitro analogues. The nitro compounds were obtained by condensation of p-nitrophenyl phenyl ether (NPPE) and aromatic carboxylic acids by means of Eaton reagent (1:10  $\text{P}_2\text{O}_5$ /methane sulfonic acid) at 100–120 °C (Scheme 1). Eaton reagent is a useful condensing agent for the preparation of aromatic ketones from aromatic ethers<sup>10</sup> and benzocrown ethers<sup>11</sup>. 1.3 g of the condensing agent were used for 1 mmol of carboxy unit.

Scheme 1. Preparation routes to nitro ether ketones and corresponding diamines.

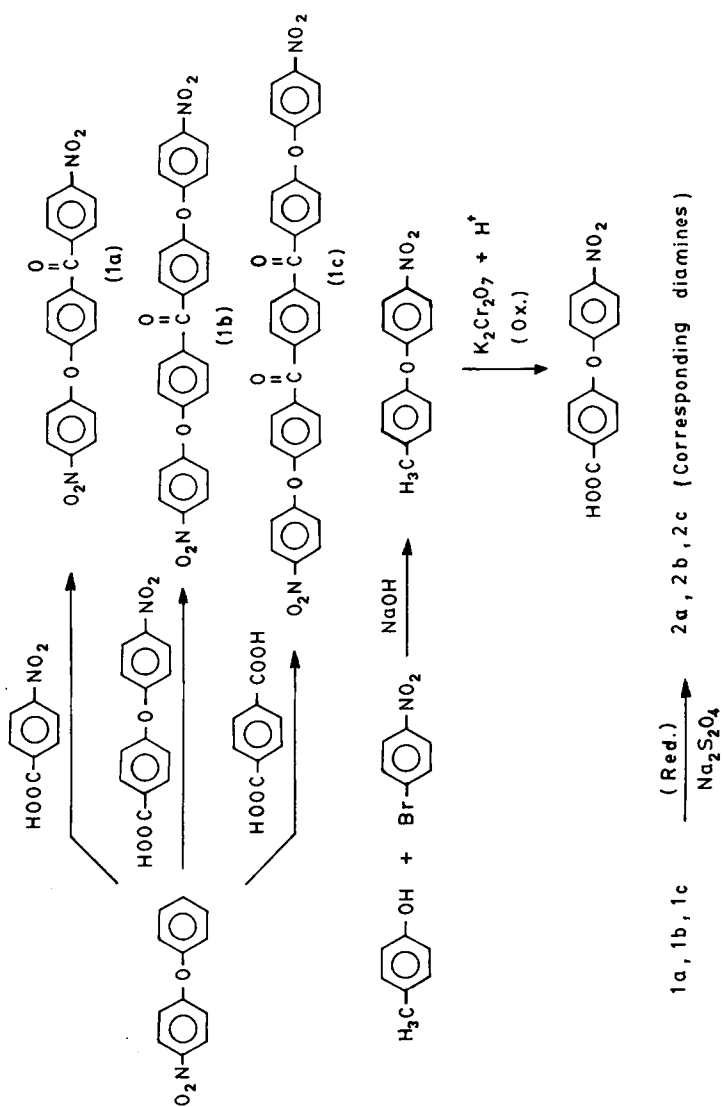


The use of this reagent instead of viscous polyphosphoric acid provides homogeneous reaction mixtures and gives almost parasubstituted products in high yields. Reduction of the nitro compounds by sodium dithionite gives corresponding diamines in which the ratio of ether to keto groups is 1/1, 2/1 and 2/2. As far as we know the dinitro compound **1a** and the corresponding diamine **1b** have not been described before in the literature.

The resulting diamines were reacted with PMDA to form polyamic acids, in NMP solution. Polyimides were obtained as cast films by cyclodehydration of the polyamic acid solutions at 300 °C (Scheme 2).

The polyimides obtained do not melt and are not soluble in common organic solvents. The polyimide PIa film is opaque and brittle, whereas PIb and PIc films are transparent. Degradation temperatures of the polyimides are about 580 °C as seen in Tab. 1. DSC measurements show that only PIb exhibits a glass transition temperature. PIc has also been prepared by Hergenrother's group<sup>3</sup> who demonstrated that it does not show any glassy state.

Scheme 2. Polypyromellitimides with ether ketone segments.



Tab. 1. Characteristics of the polyimides obtained.

Polyimide	$\eta$ inh <sup>a</sup> (mL/g)	PDT <sup>b</sup> (°C)	R <sup>c</sup> (%)	Tg (°C)	Film quality
PIa	28	579	56	—	opaque, brittle
PIb	21	575	55	223	transparent
PIc	24	580	56	—	transparent

<sup>a</sup> Inherent viscosities are based on the corresponding polyamic acids measured by a Cannon-Fenske viscometer in DMF at  $30 \pm 0.2^\circ\text{C}$ .

<sup>b</sup> Polymer degradation temperature.

<sup>c</sup> Percent chary residue at  $800^\circ\text{C}$  under nitrogen flow (10 K/min).

Consequently, incorporation of aromatic ether-ketone segments into polyimides does not change their well known thermal stability.

On the other hand, the amine component of the polyimide PIb contains two ether groups per one keto group, and this segment can be considered to be responsible for its glass transition.

This work was supported by İTÜ-UYG-AR merkezi. The authors would like to thank Professor G. Montaudo and Dr. C. Puglisi for their encouragements and TG measurements.

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