

# Synthesis and Characterization of Poly(aryl ether ketone) Oligomers Terminated with Metallophthalocyanine to be Used for Oxidative Decomposition of TCP

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**ABSTRACT:** A series of metallophthalocyanine-terminated poly(aryl ether ketone) oligomers were synthesized from dicyanobenzene-terminated poly(aryl ether ketone) oligomers with different metal chloride and phthalonitrile. All polymers exhibited high glass transition temperature and good thermal stability. These polymers showed optical absorption in the visible region and had different colors in chloroform solution. Cobalt phthalocyanine-terminated poly(aryl ether ketone) oligomers exhibited good catalytic activity in oxida-

tive decomposition of 2,4,6-trichlorophenol (TCP) under  $H_2O_2$  and  $KHSO_5$ . The catalytic activity of  $KHSO_5$  is much better than  $H_2O_2$ , and more than 70% of initial TCP was decomposed within 7 h. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 434–438, 2009

**Key words:** poly(ether ketones); metal-polymer complexes; oligomers; synthesis

## INTRODUCTION

Phthalocyanines are known as excellent functional materials. Since the synthesis of phthalocyanines in the early 1930s, rich and varied chemistry and technology have developed around these interesting materials.<sup>1</sup> There are literally thousands of publication and patents related to phthalocyanine and its analogs.<sup>2–8</sup> Recently, for improving the solubility of phthalocyanine, more attention was paid to phthalocyanine-containing polymers. These phthalocyanine polymers, having various applications, for example, polyphthalocyanine for electroconductors and photoconductors materials,<sup>9–16</sup> phthalocyanine polymers for magnetic materials,<sup>17</sup> thermally stable polymers containing metallophthalocyanines,<sup>18</sup> phthalocyanine polymers for catalyzers,<sup>19,20</sup> and so on, have already been prepared. Metallophthalocyanine (M-Pc) has also attracted considerable interest because of its structural similarity to the active center of naturally occurring hemoenzymes. People studied a series of functional M-Pcs and their polymers as models for catalase, peroxidase, oxidase, and oxygenase.<sup>21–23</sup> In this work, we synthesized a series of poly(aryl ether ketone) oligomers terminated with metallophthalocyanine. Catalytic activity of

cobalt phthalocyanine in oxidative decomposition of 2,4,6-trichlorophenol (TCP) was also studied.

## EXPERIMENTAL

### Materials

Phthalonitrile and 4-nitrophthalonitrile (Aldrich Chemicals, Milwaukee, WI), 4,4'-isopropylidenediphenol (BPA) (Sinopharm Chemical Reagent Company, Shenyang, China), quinoline, toluene, chloroform, methanol, acetone, *N,N*-dimethylacetamide (DMAc), ethanol, and concentrated hydrochloric acid (36%) were obtained from commercial sources and used as received. 4,4'-Difluorobenzophenone was prepared in our laboratory according to the standard procedure.

### Instrumentation

FTIR spectra were recorded via the KBr pellet method using a Nicolet Impact 410 FTIR spectrophotometer. The elemental analysis was carried out with a Thermoquest CHNS-Ovelemental analyzer. The gel permeation chromatography (GPC) analysis was carried out using Waters 410 instrument with tetrahydrofuran as an eluent and polystyrene as the standard. The glass transition temperatures ( $T_g$ s) were determined by using a modulated DSC (Model Mettler DSC821<sup>e</sup>) instrument at a heating rate of 20°C/min under a nitrogen flow of 100 mL/min. The reported  $T_g$  values were recorded during the second scan. The thermogravimetric analysis was

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performed on a PerkinElmer Pyris 1 TGA analyzer under nitrogen atmosphere (100 mL/min) at a heating rate of 10°C/min. The UV-vis absorption spectrum was recorded on a UV2501-PC spectrophotometer.

#### Assay for TCP decomposition

A typical sample consisted of 50 mg TCP, 100 mg catalyst, and oxidant. H<sub>2</sub>O<sub>2</sub> or KHSO<sub>5</sub> was added as the oxidant. Reaction medium was adjusted to pH = 7 with a mixture of acetonitrile and phosphate buffer (1 : 3 v/v). The resulting mixture was stirred at 25°C. The oxidant was finally added to the reaction mixture. A portion reaction mixture (0.1 mL) was taken periodically and mixed with methanol 0.1 mL of methanol solution containing *n*-decyl alcohol as an internal standard. A 2- $\mu$ L portion of mixed solution was analyzed by gas chromatograph.

#### Synthesis of hydroxyl-terminated poly(aryl ether ketone) oligomers (1)

To 100-mL three-necked round-bottomed flask equipped with a magnetic stirring, a Dean-Stark trap and condenser and a nitrogen inlet, 4,4'-difluorobenzophenone (4.36 g, 0.020 mol), 4,4'-isopropylidenediphenol (BPA) (5.71 g, 0.025 mol, excess of 25%), DMAc (35 mL), K<sub>2</sub>CO<sub>3</sub> (3.73 g, 0.027 mol, excess of 35%), and toluene (20 mL) were added. Under an atmosphere of nitrogen, the solution was heated to 130–140°C and maintained at that temperature for 2 h to remove all water by means of a Dean-Stark trap through toluene. The polycondensation reaction was continued for 6 h at 150–160°C. Then, the viscous solution was slowly poured into water and stirred vigorously. The threadlike polymer was pulverized into a powder after cooling. Then, the powder was washed with hot methanol and water several times and dried at 110°C under vacuum for 24 h.

#### Synthesis of dicyanobenzene-terminated poly(aryl ether ketone) oligomers (2)

To a 250-mL three-necked flask equipped with a condenser and a nitrogen gas inlet, polymer 1 (2.0 g), K<sub>2</sub>CO<sub>3</sub> (0.6 g), 4-nitrophthalonitrile (0.6 g), and DMF (30 mL) were added. Under an atmosphere of nitrogen, the mixture was stirred for 24 h at room temperature. The reaction was worked up by filtering the undissolved salt and then slowly adding the filtrate to rapidly stirring water. The products were washed with hot methanol and water several times for removing the unreacted 4-nitrophthalonitrile and K<sub>2</sub>CO<sub>3</sub> and then were dried at 110°C under vacuum for 24 h.

#### Synthesis of metallophthalocyanine-terminated poly(aryl ether ketone) oligomers (3)

A typical reaction was carried out as follows: to a 100-mL three-necked flask equipped with a condenser and a nitrogen gas inlet, polymer 2 (1.0 g), phthalonitrile (0.3 g), CoCl<sub>2</sub>·H<sub>2</sub>O (0.1 g) (In this work, copper, zinc, cobalt, and nickel chloride were used), and 50 mL of quinoline were added. Under an atmosphere of nitrogen, the mixture was heated to 180–200°C for 6 h. After this period, the reaction mixture became dark blue. Then, the mixture was poured into a mixture of 100 mL of methanol and 10 mL of hydrochloric acid (11.8 mol/L) under vigorous stirring. The precipitated particles were washed with ethanol and water. Then, the precipitate was collected by filtration and extracted by chloroform with a Soxhelt extractor. The chloroform solution was concentrated and precipitated in methanol. A polymer was produced and dried at 110°C for 24 h.

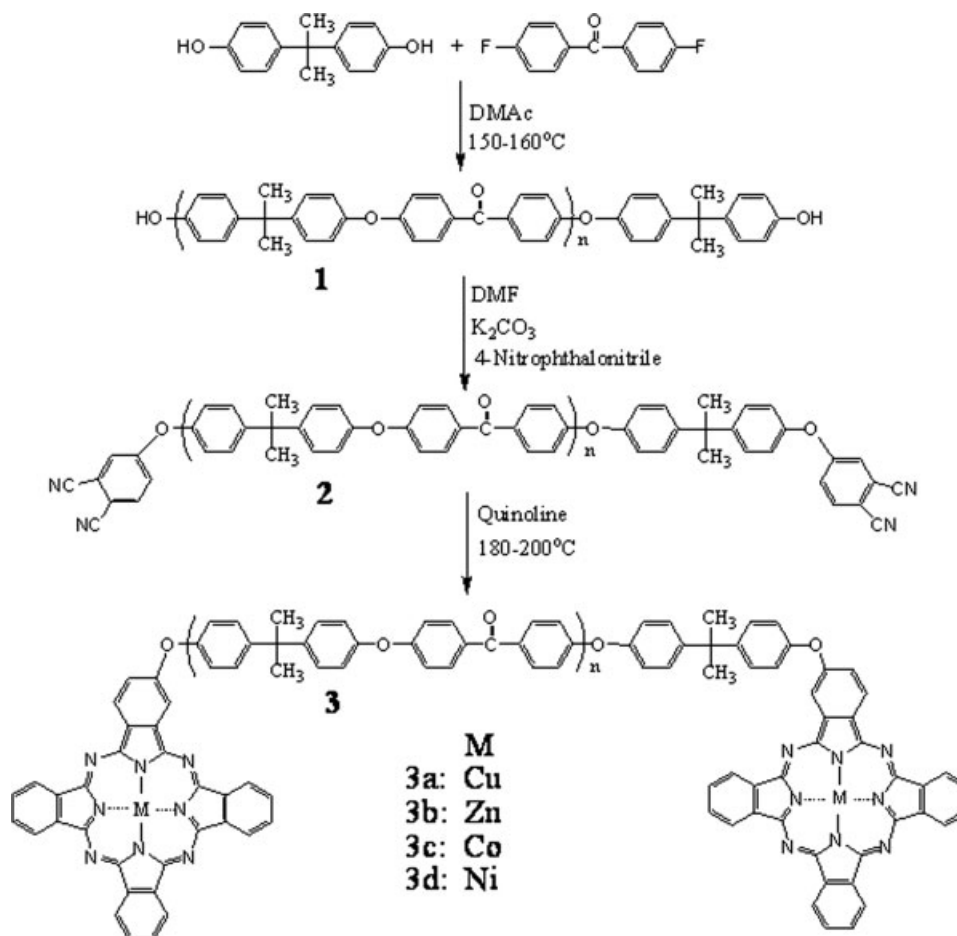
## RESULTS AND DISCUSSION

Hydroxyl-terminated poly(aryl ether ketone) oligomers (1) were prepared by condensation polymerization of 4,4'-isopropylidenediphenol and 4,4'-difluorobenzophenone in DMAc, with a 25% excess of 4,4'-isopropylidenediphenol (Scheme 1). The number-average molecular weight ( $M_n$ ) was 5000, and the polydispersity was 1.73 according to GPC. The glass transition temperature ( $T_g$ ) was 126°C.

Dicyanobenzene-terminated poly(aryl ether ketone) oligomers (2) was prepared by the reaction of polymer 1 and 4-nitrophthalonitrile, which was catalyzed by K<sub>2</sub>CO<sub>3</sub> in DMF (Scheme 1). The number-average molecular weight ( $M_n$ ) was 5180, and the polydispersity was 1.77 according to GPC. The glass transition temperature ( $T_g$ ) was 125°C.

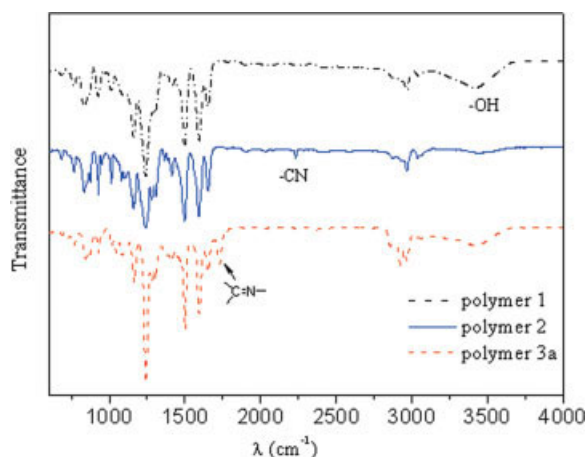
The chain structure of polymers 1 and 2 were confirmed by FTIR spectroscopes. The FTIR spectra of the polymers showed the characteristic absorption bands around 1654 cm<sup>-1</sup> due to aryl carbonyl groups and around 1220 cm<sup>-1</sup> based on aryl ether linkages (Fig. 1). In this IR spectrum, polymer 1 showed a characteristic band of hydroxy group absorption band around 3310 cm<sup>-1</sup>. After reaction, this characteristic absorption had disappeared, but the characteristic bands of cyano groups around 2223 cm<sup>-1</sup> had appeared.

As depicted in Scheme 1, a metal-complex ring can be formed either intermolecularly or intramolecularly. The formation of intermolecular metal-complex rings can cause crosslinking and insolubilization, which can be avoided by using excessive 1,2-dicyanobenzene followed by extracting with chloroform as described in the Experimental section. From the IR spectrum for copolymer 3a, it is clear that the



Scheme 1 Synthesis of polymers 1, 2, and 3.

peak at  $2227\text{ cm}^{-1}$  due to cyano groups has missed, and the characteristic bands of  $\text{C}=\text{N}$  groups around  $1720\text{ cm}^{-1}$  have appeared, indicating the complete reaction at this site. The contents of C, H, and N were obtained via elemental analysis (Table I).



**Figure 1** FTIR spectra of polymers 1, 2, and 3a. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

The properties of copolymers **3a–3d** are presented in Table II. From this table, it can be seen that the number-average molecular weights of the copolymers vary from 6770 to 7800, and the polydispersity values of the copolymers range from 1.47 to 1.58, respectively. From the same table, we can see that the  $T_g$  values vary from 152 to 161°C. These values are higher than those of the corresponding copolymers **3a–3d**. The 5 wt % weight loss temperatures vary from 393 to 434°C, which are similar to the corresponding values of polymer 1 and higher than polymer 2. These observations indicate that the metals existing in the polymers are responsible for better thermal stability. They were found to be soluble in common solvents (Table III).

The absorption spectra of copolymers **3a–3d** in dilute  $\text{CHCl}_3$  solution (5 mg/mL) are shown in Fig-

**TABLE I**  
Elemental Analysis Result of Polymers 3a–3d

Polymer	H (mol %)	C (mol %)	N (mol %)
<b>3a</b>	4.593	69.80	4.668
<b>3b</b>	4.007	68.73	3.165
<b>3c</b>	4.722	73.70	3.617
<b>3d</b>	4.975	76.56	4.889

**TABLE II**  
Properties of Polymers 1, 2, and 3a–3d

Polymer	$T_g$ (°C)	TGA-5% (°C)	$M_n$	Poly dispersity	$\lambda_{vu}$ (nm)	Color in the chloroform
1	126	419	5000	1.73	–	–
2	125	450	5180	1.77	–	–
3a	156	420	6920	1.47	680.5	Brown
3b	161	393	6850	1.58	710.5	Green
3c	152	421	6770	1.52	669.5	Yellow green
3d	152	434	7800	1.58	666.5	Green

ure 2. From the figure, it is clearly evident that the absorption of copolymers 3a and 3d are strong in the visible range, but moderate for the other polymers. These polymers containing metallophthalocyanine were found colored as expected. The colors of polymers 3a–3d in a chloroform solution are listed in Table III.

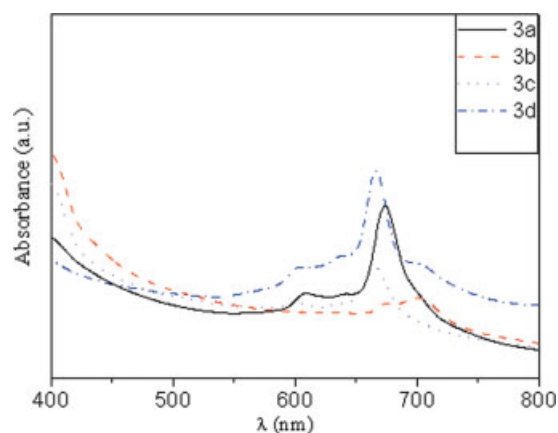
Recently, environmental problems arising from widespread of halogenated organic compounds in marine waters and soils are focused on social concern. There have been marked researches on decomposition and dehalogenation of these hazardous compounds by electrochemical, biochemical, and chemical method. Oxidative decomposition of TCP by metalloporphyrins and phthalocyanines electrostatically has been reported, in which high catalytic turnover and high stability were observed. Because much higher catalytic activity is expected when phthalocyanine complex is covalently bound to polymer chain, we have synthesized an active catalyst for TCP decomposition using cobalt phthalocyanine complex covalently bound to a polymer (3c).

The time course of  $\text{KHSO}_5$  and  $\text{H}_2\text{O}_2$  oxidation of TCP in the presence of polymer 3c was shown in Figure 3. From this figure, with the catalyst 3c and any oxidant, the conversion rate increases with the reaction time. To the oxidants mentioned earlier, the rate is much faster at the beginning of the reaction, and it is gradually slowed down at the end of the reaction. Besides, it is shown that the effect of

**TABLE III**  
Solubility of All Polymers

	Acetonitrile	THF	$\text{CHCl}_3$	DMF	NMP
1	–	+	+	+	+
2	–	+	+	+	+
3a	–	+	+	+	+
3b	–	+	+	+	+
3c	–	+	+	+	+
3d	–	+	+	+	+

+, soluble at room temperature; –, insoluble.  $\text{CHCl}_3$ , chloroform; THF, tetrahydrofuran; DMF, *N,N*-dimethylformamide; NMP, *N*-methyl-2-pyrrolidone.

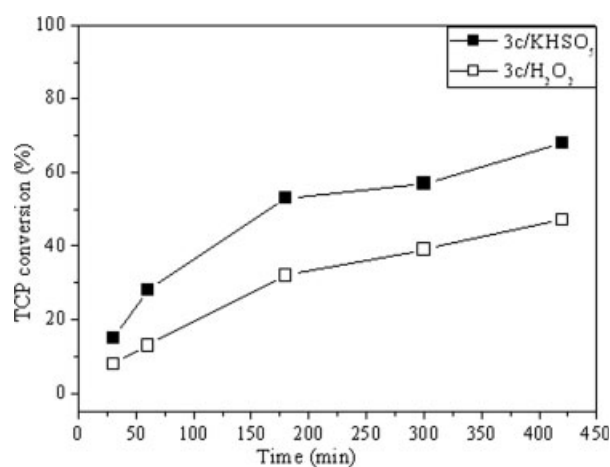


**Figure 2** UV-vis spectra of polymers 3a–3d in chloroform. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

$\text{KHSO}_5$  is much better than that of  $\text{H}_2\text{O}_2$  in the figure.

## CONCLUSIONS

A series of metallophthalocyanine-terminated poly(aryl ether ketone) oligomers were synthesized from dicyanobenzene-terminated poly(aryl ether ketone) oligomers with different metal chloride and phthalonitrile. All polymers exhibited high glass transition temperature and good thermal stability. These polymers showed optical absorption in the visible region and have different color in chloroform solution. Cobalt phthalocyanine-terminated poly(aryl ether ketone) oligomers exhibited good catalytic activity in oxidative decomposition of TCP under  $\text{H}_2\text{O}_2$  and  $\text{KHSO}_5$ . Furthermore, the latter compound is better than the former. The polymer can act as a catalyst of decompose TCP under four conditions.



**Figure 3** Time course of  $\text{KHSO}_5$  and  $\text{H}_2\text{O}_2$  oxidation of TCP in the presence of polymer 3c.

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