

# Synthesis, Characterization, Thermal Analysis, and Band Gap of Oligo-2-Methoxy-6-[(4-methylphenyl)imino]methylphenol

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**ABSTRACT:** The oxidative polycondensation reaction conditions of 2-methoxy-6-[(4-methylphenyl)imino]methylphenol (2M-4-MPIMP) by using oxidants such as air O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and NaOCl were studied in an aqueous alkaline medium between 30 and 90°C. The structures of synthesized monomer and oligomer were confirmed by FTIR, UV-vis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis. The characterization was made by TG-DTA, size exclusion chromatography (SEC), and solubility tests. At the optimum reaction conditions, the yield of oligo (O)-2M-4-MPIMP was 68% for air O<sub>2</sub> oxidant, 68% for H<sub>2</sub>O<sub>2</sub> oxidant, and 82% for NaOCl oxidant. According to the SEC analysis, the number-average molecular weight (*M<sub>n</sub>*), weight-average molecular weight (*M<sub>w</sub>*), and polydispersity index (PDI) values of O-2M-4-MPIMP were found to be 695, 1000 g mol<sup>-1</sup> and 1.439, using air O<sub>2</sub>, and 670, 795 g mol<sup>-1</sup> and 1.187, using NaOCl, and 645, 790 g mol<sup>-1</sup> and 1.225, using H<sub>2</sub>O<sub>2</sub>,

respectively. TG-DTA analyses were shown to be stable of O-2M-4-MPIMP against thermal decomposition. The weight losses of 2M-4-MPIMP and O-2M-4-MPIMP were found to be 98.46% and 89.54% at 1000°C, respectively. Also, electrical conductivity of the O-2M-4-MPIMP was measured, showing that the polymer is typical semiconductor. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of monomer and oligomer were determined from the onset potentials for *n*-doping and *p*-doping, respectively. Optical energy gaps (*E<sub>g</sub>*) of 2M-4-MPIMP and O-2M-4-MPIMP were calculated from UV-vis measurements. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3417–3426, 2007

**Key words:** oxidative polycondensation; oligo-2-methoxy-6-[(4-methylphenyl)imino]methylphenol; air O<sub>2</sub>, NaOCl; H<sub>2</sub>O<sub>2</sub>; thermal analysis; conductivity and band gap

## INTRODUCTION

Polymers with highly conjugated chains have attracted much attention in the last few years because they are materials of academic interest and also they are promising candidates for a wide variety of applications such as electronics,<sup>1</sup> optoelectronics,<sup>2</sup> and photonics.<sup>3</sup> Numerous articles have been published having polymers as a main subject conjugated systems of type polyacetylenes, polyphenylenes, polyphenylene vinylenes, polypyrrole, polythiophene, or polyaniline.<sup>1,4</sup> The oxidative polycondensation method is simply the reaction of compounds including —OH groups and active functional groups (—NH<sub>2</sub>, —CHO, and —COOH) in their structure with the oxidants such as NaOCl, H<sub>2</sub>O<sub>2</sub>, an air oxygen in the aqueous alkaline, and acidic medium.<sup>5</sup> Another class of this family, unfortunately

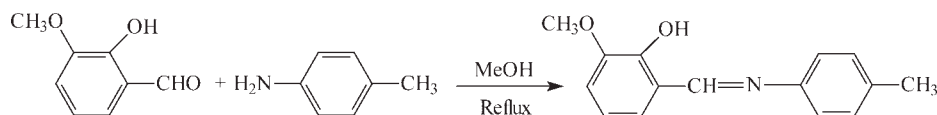
less examined, is that of polyimines (PIs), which are also known as polymeric Schiff bases, polymers that are synthesized by a polycondensation reaction between an amine or hydrazine with an aldehyde or diketone.<sup>6–9</sup> The PIs have attracted much attention not only as high performance fiber and film-forming polymers with remarkable thermal stability, high strength, and high modulus<sup>10–14</sup> but also as particularly promising electronic materials with semiconducting properties<sup>15–17</sup> nonlinear optical properties,<sup>18</sup> and ability to form chelates.<sup>19</sup>

In this article, we have investigated the effects of different parameters such as temperature, reaction time, and initial concentration of NaOCl and H<sub>2</sub>O<sub>2</sub> for the oligo-2-methoxy-6-[(4-methylphenyl)imino]methylphenol (2M-4-MPIMP). We have characterized 2M-4-MPIMP and O-2M-4-MPIMP by using FTIR, UV-vis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, elemental analysis, TG-DTA, and size exclusion chromatography (SEC) techniques. The electrical conductivity of the oligomer was measured after doping with I<sub>2</sub>. Also, electrochemical (*E'<sub>g</sub>*) and optical (*E<sub>g</sub>*) energy gaps of the monomer and oligomer were determined from cyclic voltammetry (CV) and UV-vis measurements.

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**Scheme 1** Synthesis of 2-methoxy-6-[(4-methylphenyl)imino]methylphenol.

## MATERIALS AND METHODS

### Materials

Methanol, *p*-toluidine, *o*-vanillin, dioxane, ethanol, 1-butanol, acetonitrile, benzene, toluene, ethyl acetate, heptane, hexane,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , tetrahydrofuran, THF, *N,N'*-dimethylformamide, DMF, dimethylsulfoxide, DMSO,  $\text{H}_2\text{SO}_4$  (98%), NaOH,  $\text{H}_2\text{O}_2$  (30% aqueous solution), KOH, and hydrochloric acid (HCl, 37%) were supplied from Merck Chemical (Germany) and they were used as received. Sodium hypochlorite (NaOCl), 30% aqueous solution, was supplied from Paksoy Chemical (Turkey). 2M-4-MPIMP was synthesized from condensation reaction of *o*-vanillin with *p*-toluidine and recrystallized in methanol.

### Preparation of 2M-4-MPIMP

2M-4-MPIMP was prepared by the condensation of *o*-vanillin (1.52 g, 0.01 mol) with *p*-toluidine (1.07 g, 0.01 mol) in methanol (50 mL) achieved by boiling the mixture under reflux for 2 h at 70°C (Scheme 1). The precipitated 2M-4-MPIMP was filtered, recrystallized from methanol, and dried in a vacuum desiccators (yield 96%).

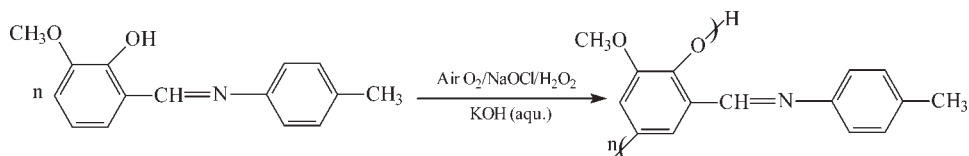
Calcd. for 2M-4-MPIMP: C, 74.69; H, 6.22; N, 5.81. Found: C, 74.55; H, 6.15; N, 5.70. UV-vis ( $\lambda_{\text{max}}$ ): 203, 225, 276, and 316 nm. FTIR ( $\text{cm}^{-1}$ ):  $\nu$  (O—H) 3261 s,  $\nu$  (C—H phenyl) 3029 m,  $\nu$  (C—H aliphatic) 2920 s,  $\nu$  (C=N) 1616 s,  $\nu$  (OCH<sub>3</sub>) 1456 s,  $\nu$  (C=C phenyl) 1595, 1575, 1509 s,  $\nu$  (C—O) 1255 s. <sup>1</sup>H NMR (DMSO):  $\delta$ , ppm, 13.35 (s, 1H, —OH), 8.93 (s, 1H, —CH=N—), 7.33 (d, 2H, Ar—Haa'), 7.28 (d, 2H, Ar—Hbb'), 7.13 (d, 1H, Ar—Hc), 6.91 (t, 1H, Ar—Hd), 7.23 (d, 1H, Ar—He), 3.84 (s, 3H, —OCH<sub>3</sub>), 2.35 (s, 3H, —CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO): ppm, 151.06 (C<sub>1</sub>-ipso-OH), 148.37 (C<sub>2</sub>-ipso-OCH<sub>3</sub>), 118.99 (C<sub>3</sub>—H), 115.95 (C<sub>4</sub>—H), 124.33 (C<sub>5</sub>—H), 119.69 (C<sub>6</sub>-ipso), 163.16 (C<sub>7</sub>—H), 145.67 (C<sub>8</sub>-ipso),

121.66 (C<sub>9</sub>—H), 130.43 (C<sub>10</sub>—H), 137.01 (C<sub>11</sub>-ipso), 56.36 (C<sub>12</sub>—OCH<sub>3</sub>), 21.08 (C<sub>13</sub>—CH<sub>3</sub>).

### Synthesis of oligo-2M-4-MPIMP with NaOCl, air O<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> in aqueous alkaline medium

O-2M-4-MPIMP was synthesized through oxidative polycondensation of 2M-4-MPIMP with solution of NaOCl (30%, in water), air O<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> (30%, in water) oxidants, respectively, (Scheme 2).<sup>20</sup> The 2M-4-MPIMP (2.41 g 0.01 mol) was dissolved in an aqueous solution of KOH (10%, 0.01 mol) and placed into a 50-mL three-necked round-bottomed flask. It was fitted with a condenser, thermometer, and stirrer and at addition to funnel containing NaOCl or H<sub>2</sub>O<sub>2</sub>. After heating to room temperature, NaOCl and H<sub>2</sub>O<sub>2</sub> were added drop by drop over about 30 min and mixture was heated between 30 and 90°C. The reaction mixtures were stirred at various temperatures and durations (Tables I and II). Air O<sub>2</sub> was passed into an aqueous solution of KOH (10%) before being sent through the reaction tube to prevent water loss in the reaction mixture and the neutralizing of CO<sub>2</sub> in the air to KOH (Scheme 2). The mixture was neutralized with HCl 0.01 mol (37%) at room temperature. Unreacted monomer was separated from the reaction products by washing with methanol. The mixture was filtered and washed with hot water (3 × 25 mL) for separating from mineral salts and then dried in the oven at 110°C.

Calcd. for O-2M-4-MPIMP: C, 75.00; H, 5.83; N, 5.83. Found: C, 74.40; H, 5.55; N, 5.72. UV-vis ( $\lambda_{\text{max}}$ ): 207, 228, 274, and 325. FTIR ( $\text{cm}^{-1}$ ):  $\nu$  (O—H) 3357 s,  $\nu$  (C—H phenyl) 3050 m,  $\nu$  (C—H aliphatic) 2920 s,  $\nu$  (C=N) 1622 s,  $\nu$  (OCH<sub>3</sub>) 1079 s,  $\nu$  (C=C phenyl) 1596, 1574, 1509 s,  $\nu$  (C—O) 1252 s. <sup>1</sup>H NMR (DMSO):  $\delta$ , ppm, 13.40 (s, 1H, —OH), 8.95 (s, 1H, —CH=N—), 7.33 (d, 2H, Ar—Haa'), 7.27 (d, 2H, Ar—Hbb'), 7.12 (d, 1H, Ar—Hc), 6.90 (t, 1H, end group, Ar—Hd), 7.23 (d, 1H, Ar—He), 3.85 (s, 3H,



**Scheme 2** Synthesis of oligo-2-methoxy-6-[(4-methylphenyl)imino]methylphenol.

**TABLE I**  
The Oxidative Polycondensation Reaction Parameters of 2-Methoxy-6-[(4-methylphenyl)imino]methylphenol<sup>a</sup> with NaOCl in Aqueous KOH

Sample no.	[KOH] <sub>0</sub> (mol L <sup>-1</sup> )	NaOCl (mol L <sup>-1</sup> )	Temp. (°C)	Times (h)	The yield of O-2-M-4-MPIMP (%)
1	0.01	0.01	40	3	63
2	0.01	0.01	50	3	71
3	0.01	0.01	60	3	77
4	0.01	0.01	50	3	80
5	0.01	0.01	80	3	82
6	0.01	0.01	90	3	74
7	0.01	0.01	80	1	67
8	0.01	0.01	80	5	77
9	0.01	0.01	80	10	73
10	0.01	0.01	80	15	70
11	0.01	0.01	80	25	57
12	0.01	0.02	40	3	44
13	0.01	0.02	50	3	49
14	0.01	0.02	60	3	53
15	0.01	0.02	70	3	58
16	0.01	0.02	80	3	60
17	0.01	0.02	90	3	57
18	0.01	0.02	80	1	31
19	0.01	0.02	80	3	25
20	0.01	0.02	80	5	48
21	0.01	0.02	80	10	34
22	0.01	0.02	80	15	28
23	0.01	0.02	80	25	26

<sup>a</sup> The initial concentration of 2-M-4-MPIMP was used as 0.01 mol L<sup>-1</sup>.

—OCH<sub>3</sub>), 2.33 (s, 3H, —CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO): ppm, 151.08 (C<sub>1</sub>-ipso-OH), 148.37 (C<sub>2</sub>-ipso-OCH<sub>3</sub>), 119.69 (C<sub>3</sub>-H), 118.98 (C<sub>4</sub>-ipso), 129.68 (new peak of C—C coupling system), 124.34 (C<sub>5</sub>-H), 115.93 (C<sub>6</sub>-ipso), 163.13 (C<sub>7</sub>-H), 145.65 (C<sub>8</sub>-ipso), 121.65 (C<sub>9</sub>-H), 130.42 (C<sub>10</sub>-H), 137.00 (C<sub>11</sub>-ipso), 56.35 (C<sub>12</sub>-OCH<sub>3</sub>), 21.08 (C<sub>13</sub>-CH<sub>3</sub>).

### Electrochemical properties

CV measurements were carried out with a CH Instruments 660B Electrochemical Analyzer at a potential scan rate of 20 mV/s. All the experiments were performed in a dry box under Ar atmosphere at room temperature. The electrochemical potential of Ag was calibrated with respect to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple. The half-wave potential ( $E^{1/2}$ ) of (Fc/Fc<sup>+</sup>) measured in 0.1M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) acetonitrile solution is 0.39 V vs. Ag wire or 0.38 V versus supporting calomel electrode (SCE). The voltammetric measurements were carried out for 2M-4-MPIMP and O-2M-4-MPIMP in acetonitrile and DMSO, respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the 2M-4-MPIMP and

O-2M-4-MPIMP were determined from the onset potentials of the *n*-doping ( $\phi'_n$ ) and *p*-doping ( $\phi'_p$ ), respectively, as shown in literature.<sup>21</sup>

### Optical properties

The optical band gaps ( $E_g$ ) of monomer and oligomer compounds were calculated from their absorption edges. Ultraviolet–visible (UV–vis) spectra were measured by PerkinElmer Lambda 25. The absorption spectra of monomer and oligomer were recorded by using methanol and DMSO, respectively, at 25°C.

### Electrical properties

Conductivity was measured on a Keithley 2400 Electrometer. The pellets were pressed on hydraulic press developing up to 1687.2 kg/cm<sup>2</sup>. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in a desiccator.<sup>22</sup>

**TABLE II**  
The Oxidative Polycondensation Reaction Parameters of 2-Methoxy-6-[(4-methylphenyl)imino]methylphenol<sup>a</sup> with H<sub>2</sub>O<sub>2</sub> (Sample Number: 1–15) and Air O<sub>2</sub> (Sample Number: 16–26) in Aqueous KOH

Sample no.	[KOH] <sub>0</sub> (mol L <sup>-1</sup> )	H <sub>2</sub> O <sub>2</sub> (mol L <sup>-1</sup> ) or Air O <sub>2</sub> (L h <sup>-1</sup> )	Temp. (°C)	Time (h)	The Yield of O-2-M-4-MPIMP (%)
1	0.01	0.01	40	3	43
2	0.01	0.01	50	3	49
3	0.01	0.01	60	3	62
4	0.01	0.01	70	3	68
5	0.01	0.01	80	3	60
6	0.01	0.01	90	3	57
7	0.01	0.01	70	1	27
8	0.01	0.01	70	5	48
9	0.01	0.01	70	10	41
10	0.01	0.01	70	15	36
11	0.01	0.01	70	25	33
12	0.01	0.02	40	3	27
13	0.01	0.02	50	3	28
14	0.01	0.02	50	1	21
15	0.01	0.02	50	5	24
16	0.01	8.5	30	3	52
17	0.01	8.5	40	3	64
18	0.01	8.5	50	3	68
19	0.01	8.5	60	3	43
20	0.01	8.5	70	3	42
21	0.01	8.5	80	3	30
22	0.01	8.5	90	3	29
23	0.01	8.5	50	1	37
24	0.01	8.5	50	5	44
25	0.01	8.5	50	10	33
26	0.01	8.5	50	15	18

<sup>a</sup> The initial concentration of 2-M-4-MPIMP was used as 0.01 mol L<sup>-1</sup>.

### Solubility and characterization techniques

O-2M-4-MPIMP was dark brown at powder form and it was completely soluble in organic solvents such as DMF, THF, DMSO, aqueous alkaline, and conc. H<sub>2</sub>SO<sub>4</sub>, but it was partly soluble in methanol, ethanol, and 1-butanol. O-2M-4-MPIMP was any insoluble in heptane, hexane, benzene, toluene, ethyl acetate, acetonitrile, CHCl<sub>3</sub>, CCl<sub>4</sub>, and dioxane. The solubility tests were done by using 1 mg sample and 1 mL solvent at 25°C. The infrared spectra was measured by PerkinElmer FTIR spectrum one. The FTIR spectra were recorded using ATR attachment (4000–550 cm<sup>-1</sup>). UV-vis spectra of 2M-4-MPIMP and O-2M-4-MPIMP were determined by using methanol and DMSO. Elemental analysis was carried out with a Carlo Erba 1106. 2M-4-MPIMP and O-2M-4-MPIMP were characterized by using <sup>1</sup>H and <sup>13</sup>C NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) and recorded by using deuterated DMSO-*d*<sub>6</sub> as a solvent at 25°C. Tetramethylsilane was used as an internal standard. Thermal data were obtained by using a PerkinElmer Diamond Thermal Analysis system. The TG-DTA measurements were made between 15 and 1000°C (in N<sub>2</sub>, rate 10°C/min). The number-average molecular weight (*M<sub>n</sub>*), weight-average molecular weight (*M<sub>w</sub>*), and polydispersity index (PDI) were determined by SEC techniques of Shimadzu. For SEC, investigations were used a SGX (100 Å and 7-nm diameter loading material) 3.3 mm i.d. × 300 mm columns; eluent: DMF (0.4 mL/min), polystyrene standards. A refractive index detector (at 25°C) was used to analyze the oligomer.

## RESULTS AND DISCUSSION

### The investigation of synthesis conditions of O-2M-4-MPIMP

2M-4-MPIMP is not oxidized at the normal condition in the neutral aqueous and organic medium by air O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> (30% aqueous solution), and NaOCl (30% aque-

ous solution). When 2M-4-MPIMP interacted by oxidizes such as air O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and NaOCl, it immediately precipitated phenoxy radicals with brown adding to alkaline solution. The conditions of oxidative polycondensation reaction of 2M-4-MPIMP with 30% NaOCl solution in aqueous alkaline medium are given in Table I. The yield of O-2M-4-MPIMP was 82% at the NaOCl medium for 3 h at 80°C. The yield of O-2M-4-MPIMP was 63% at the reaction conditions such as [KOH]<sub>0</sub> = [2M-4-MPIMP]<sub>0</sub> = [NaOCl]<sub>0</sub> = 0.01 mol/L at 40°C for 3 h. At the same conditions (at 80°C and 3 h), when molar amount of NaOCl oxidant increased in two coating, total yield of 2M-4-MPIMP changed from 82 to 60%. That is, increasing of oxidant amount decreased in the yield of O-2M-4-MPIMP.

The oxidative polycondensation reaction conditions of 2M-4-MPIMP with 30% H<sub>2</sub>O<sub>2</sub> solution in aqueous alkaline medium are given in Table II. The yield of O-2M-4-MPIMP was 68% at optimum conditions such as [2M-4-MPIMP]<sub>0</sub> = [KOH]<sub>0</sub> = [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.01 mol/L at 70°C for 3 h. At the same conditions, when molar amount of alkaline increased in two coating, total yield of 2M-4-MPIMP changed from 62% to 15%. The yield of O-2M-4-MPIMP was 27% at the reaction conditions such as [2M-4-MPIMP]<sub>0</sub> = [KOH]<sub>0</sub> = [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.01 mol/L at 70°C for 1 h. According to these values, yield of O-2M-4-MPIMP decreased increasing of reaction temperatures and time. The oxidative polycondensation reaction conditions of 2M-4-MPIMP with air O<sub>2</sub> oxidant in an aqueous alkaline medium are given in Table II. At the oxidative polycondensation reaction of 2M-4-MPIMP, when air O<sub>2</sub> passed into 8.5 L/h rate at the reaction medium at 30°C for 3 h, the yield of product was 52%. The yield of O-2M-4-MPIMP was 68% at optimum conditions such as [2M-4-MPIMP]<sub>0</sub> = [KOH]<sub>0</sub> = 0.01 mol/L and 8.5 L h<sup>-1</sup> rate at 50°C for 3 h. As is seen from Table I and II, in these reactions the yield of the oligomer was dependent upon temperature, times, and initial concentrations of alkaline and oxidants. At the same conditions, the yield of O-2M-4-MPIMP with NaOCl was higher than that of air O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>.

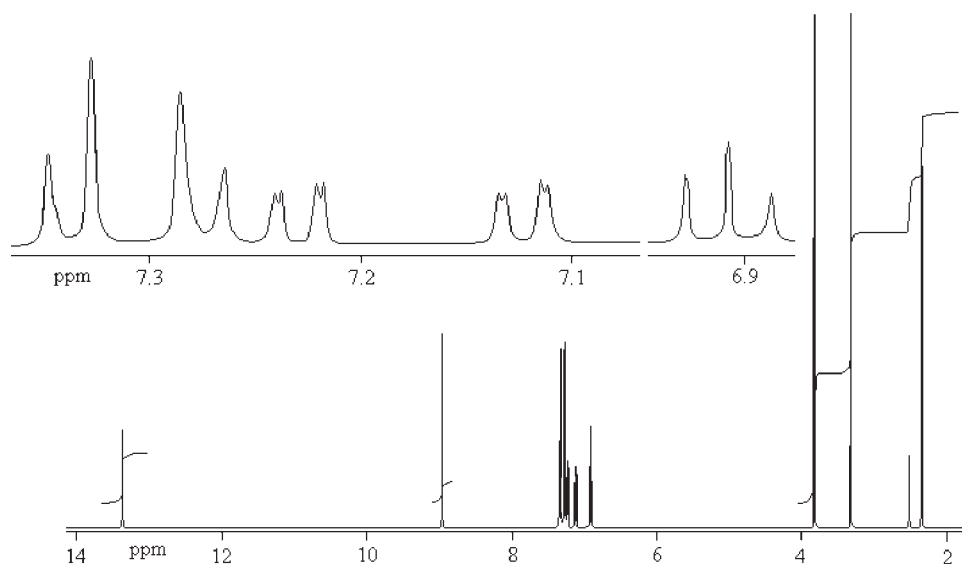
TABLE III  
The Number-Average Molecular Weight (*M<sub>n</sub>*), Weight-Average Molecular Weight (*M<sub>w</sub>*), Polydispersity Index (PDI) and % Values of O-2-M-4-MPIMP

Compounds	Molecular weight distribution parameters															
	Total			Fraction I				Fraction II				Fraction III				
	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>	PDI	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>	PDI	%	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>	PDI	%	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>	PDI	%	
O-2-M-4-MPIMP <sup>a</sup>	695	1000	1.439	560	1100	1.964	96	21300	23140	1.086	4	–	–	–	–	
O-2-M-4-MPIMP <sup>b</sup>	670	795	1.187	790	1000	1.266	96	14695	15380	1.047	4	–	–	–	–	
O-2-M-4-MPIMP <sup>c</sup>	645	790	1.225	630	965	1.532	76	2170	2810	1.295	19	20840	22050	1.058	5	

<sup>a</sup> Air O<sub>2</sub> oxidant.

<sup>b</sup> NaOCl oxidant.

<sup>c</sup> H<sub>2</sub>O<sub>2</sub> oxidant.



**Figure 1** <sup>1</sup>H NMR spectrum of 2-methoxy-6-[(4-methylphenyl)imino]methylphenol.

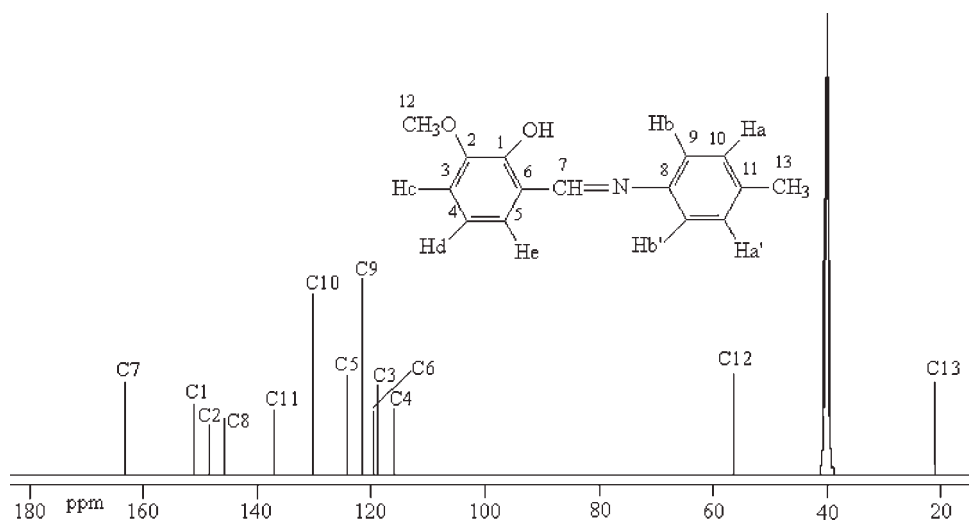
### Structure of O-2M-4-MPIMP

According to SEC chromatograms, the values of number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) of O-2M-4-MPIMP were calculated according to a polystyrene standard calibration curve and are given in Table III. It is seen that, two fractions observed in oligomer by air O<sub>2</sub> and NaOCl oxidants but three fractions determined for H<sub>2</sub>O<sub>2</sub> oxidant. An important section of products had little molecular weight distribution.

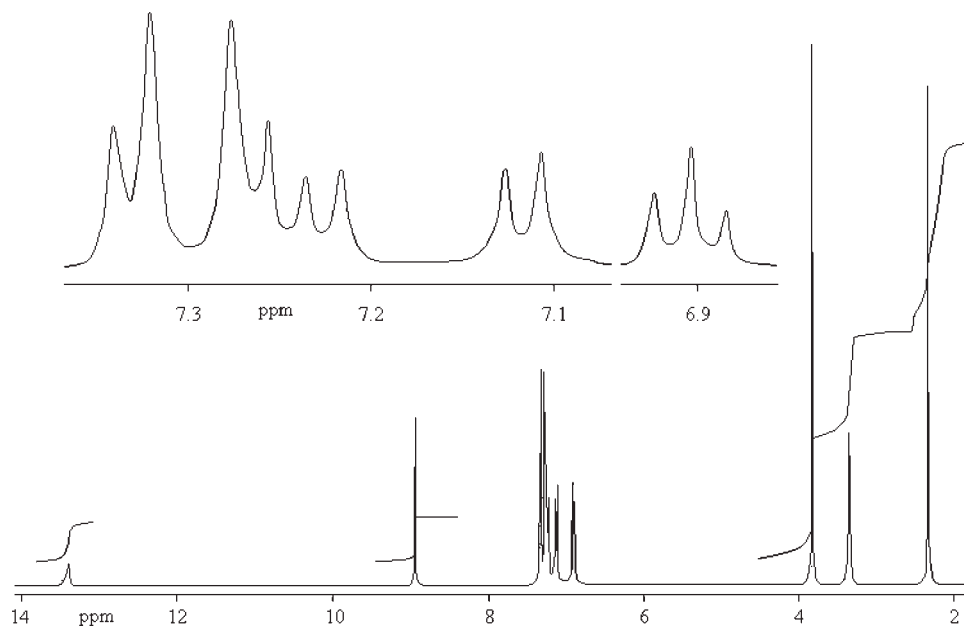
The UV-vis spectra of 2M-4-MPIMP and O-2M-4-MPIMP were similar to one together. However, at the spectra of 2M-4-MPIMP, K bands of phenol, and C<sub>6</sub>H<sub>5</sub>-N= were observed in 205 and 225 nm, respectively. Benzene band of 2M-4-MPIMP and strength R band of -CH=N- groups were observed in 276 and 316 nm, respectively.  $\lambda_{\max}$  values of O-2M-4-

MPIMP were observed in 207, 228, 274, and 325 nm. UV-vis spectra of O-2M-4-MPIMP, K, and R bands were observed in 274 and 325 nm, respectively. Because of conjugated band systems, azomethine group of oligomer shifted to higher field.

At the FTIR spectra of oxidative polycondensation, product of 2M-4-MPIMP are only different by reduction of band strength and peak numbers from the FTIR spectra of 2M-4-MPIMP. At the FTIR spectra of 2M-4-MPIMP and O-2M-4-MPIMP, bands of -OH, -CH=N, and aliphatic -CH<sub>3</sub> groups were observed in 3261, 1616, and 2920 cm<sup>-1</sup>; 3357, 1622, and 2925 cm<sup>-1</sup>, respectively. To identify the structures of monomer and oligomer, the <sup>1</sup>H NMR spectra were recorded in DMSO-*d*<sub>6</sub>. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the 2M-4-MPIMP and O-2M-4-MPIMP are given in Figures 1-4, respectively. At the <sup>1</sup>H NMR spectra of 2M-4-MPIMP and



**Figure 2** <sup>13</sup>C NMR spectrum of 2-methoxy-6-[(4-methylphenyl)imino]methylphenol.

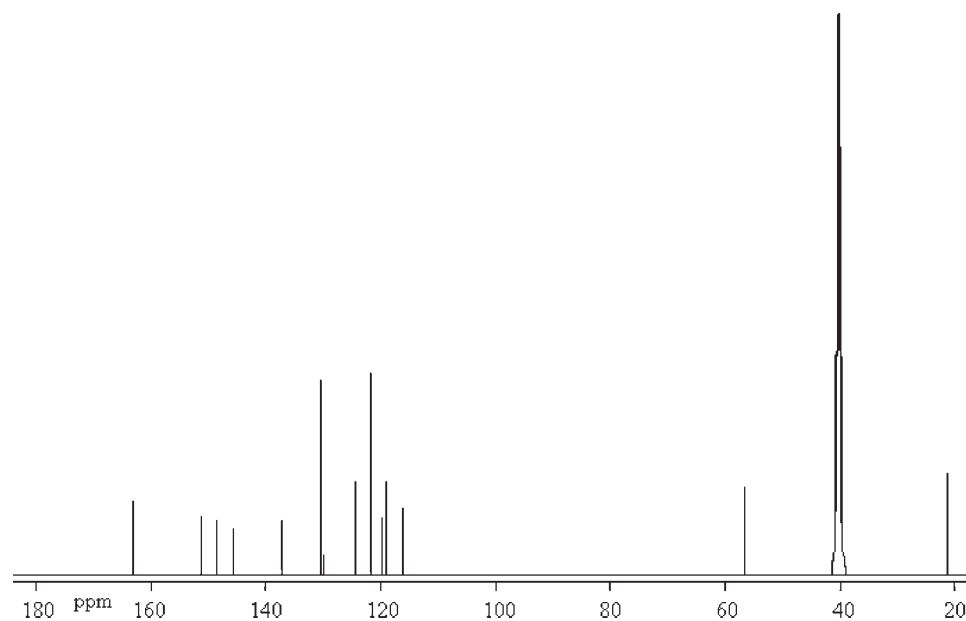


**Figure 3**  $^1\text{H}$  NMR spectrum of oligo-2-methoxy-6-[(4-methylphenyl)imino]methylphenol.

O-2M-4-MPIMP, the signals of  $-\text{OH}$ ,  $-\text{CH}=\text{N}$ , and  $-\text{OCH}_3$  groups were observed in 13.35, 8.93, and 3.84 ppm and 13.40, 8.95, and 3.85 ppm, respectively. It is seen from Figure 4 that because of C—C coupling system, a new peak is observed in 129.68 ppm. The  $^{13}\text{C}$  NMR spectrum of O-2M-4-MPIMP has been demonstrated C—C and C—O—C coupling systems.<sup>20</sup> Interconversion combinations of radical units and formation of dimer, trimer, tetramer, and pentamer units are proposed as follows (Scheme 3). The SEC results spectral data and the results of FTIR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectra of the O-2M-4-MPIMP have supported together.

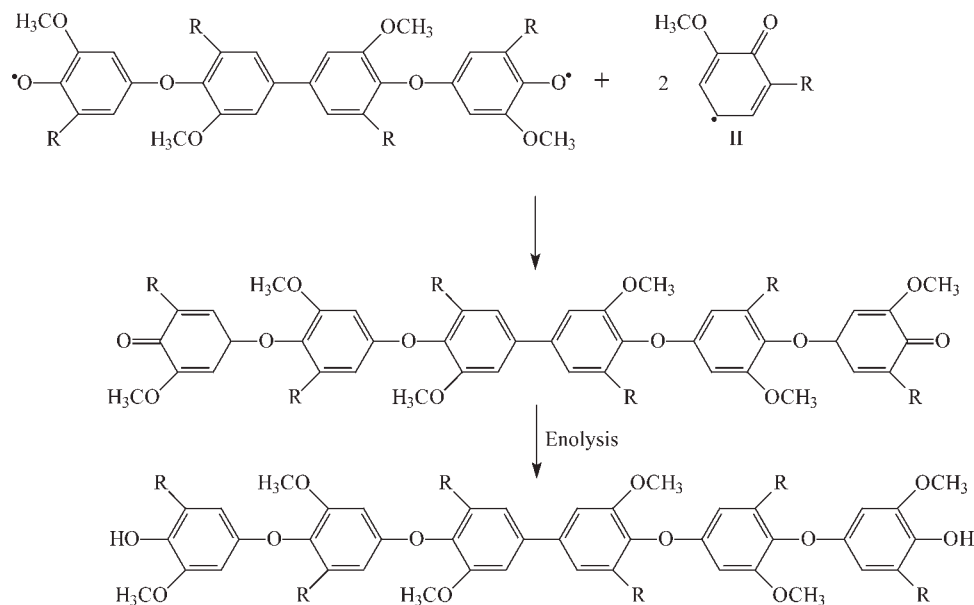
#### Thermal analyses of 2M-4-MPIMP and O-2M-4-MPIMP

TG/DTA curves of monomer and oligomer were given in Figures 5 and 6. The initial degradation temperature, 50 and 98.46% weight loss of 2M-4-MPIMP found to be 209, 233, and 1000°C, respectively. According to DTG curve, thermal degradation of 2M-4-MPIMP was formed at one step.  $T_{\text{max}}$  value of 2M-4-MPIMP was observed in 250°C. According to DTA analysis, exothermic peaks observed in 100, 260, and 672°C. The initial degradation temperature,



**Figure 4**  $^{13}\text{C}$  NMR spectrum of oligo-2-methoxy-6-[(4-methylphenyl)imino]methylphenol.





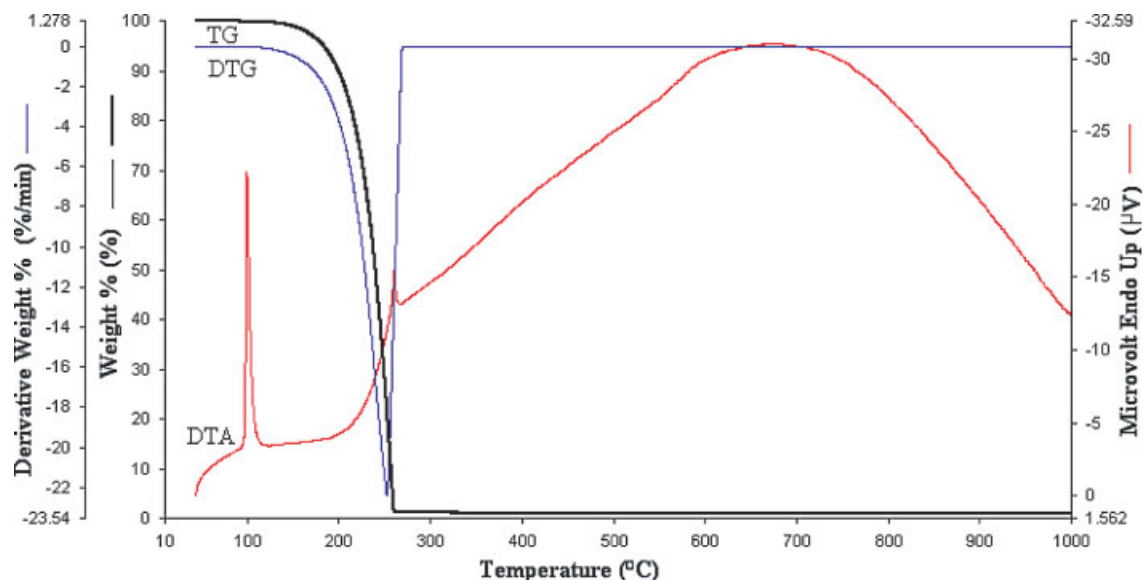
Scheme 3 (Continued from previous page)

50 and 89.54% weight loss of O-2M-4-MPIMP found to be 214, 257, and 1000°C, respectively. According to DTG curve,  $T_{max}$  value of O-2M-4-MPIMP was observed in 255°C. According to DTA analysis, exothermic peaks observed in 83, 256, and 760°C. Because of long conjugated band systems, oligomer demonstrated higher resist against high temperature than monomer. According to TG analysis, although initial degradation temperature of O-2M-4-MPIMP was lower than monomer, it was more stable than monomer through to temperature and thermal decomposition. Carbinic residue was formed at high

amount such as 10.46% at 1000°C. Because of long conjugated band systems, oligomer demonstrated partly higher resist against high temperature than monomer. The high thermal stability of O-2M-4-MPIMP demonstrated to be formed of C—C and C—O—C coupling systems.

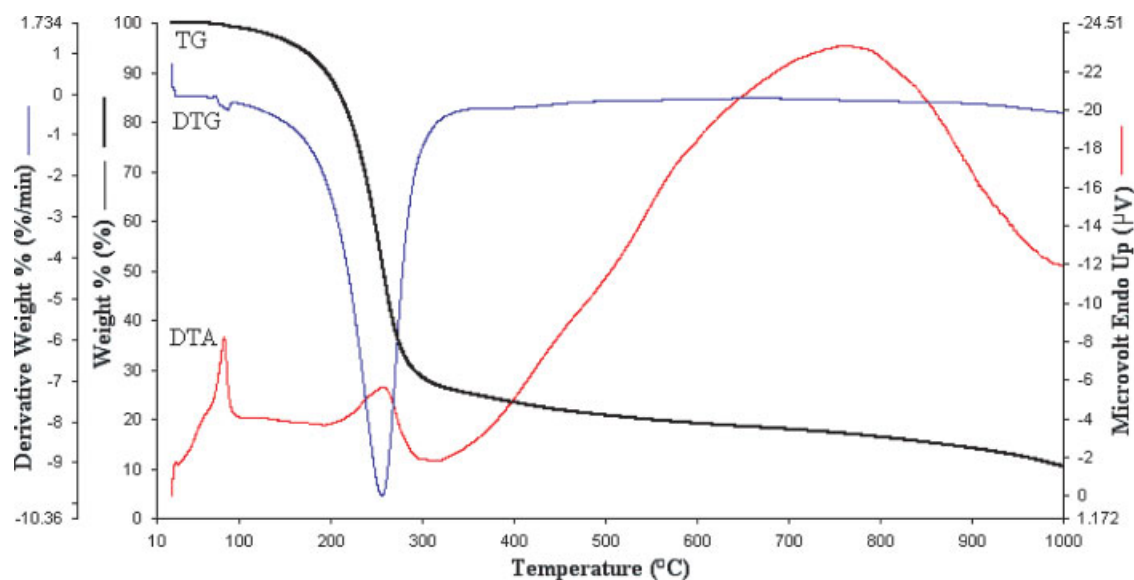
#### Electrochemical properties of 2M-4-MPIMP and O-2M-4-MPIMP

The voltammetric measurements of 2M-4-MPIMP and O-2M-4-MPIMP were carried out in acetonitrile



**Figure 5** TG–DTG–DTA curves of 2-methoxy-6-[(4-methylphenyl)imino]methylphenol. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]





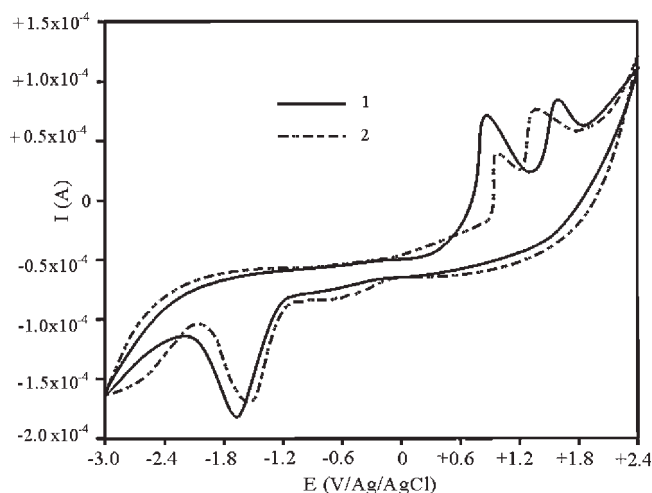
**Figure 6** TG-DTG-DTA curves of oligo-2-methoxy-6-[(4-methylphenyl)imino]methylphenol. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

and DMSO, respectively. The HOMO and LUMO energy levels of the 2M-4-MPIMP and O-2M-4-MPIMP were determined from the onset potentials of the  $n$ -doping ( $\phi_n'$ ) and  $p$ -doping ( $\phi_p'$ ), respectively (Fig. 7). The HOMO and LUMO energy levels and electrochemical energy gaps<sup>21</sup> ( $E_g'$ ), ( $E_g' = \Delta\phi = \phi_p' - \phi_n'$ ) of 2M-4-MPIMP and O-2M-4-MPIMP were found to be  $-6.03$ ,  $-6.12$ ;  $-2.67$ ,  $-2.75$ ;  $3.45$  and  $3.27$  eV, respectively.

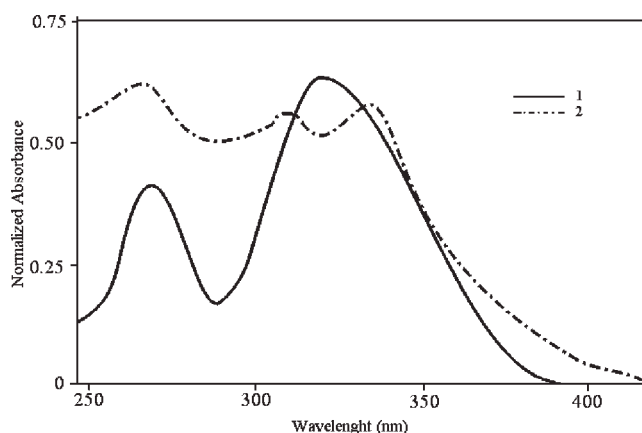
The absorption spectra of 2M-4-MPIMP and O-2M-4-MPIMP were recorded by using methanol and DMSO at  $25^\circ\text{C}$  (Fig. 8) and  $\lambda_{\text{max}}$  and  $E_g$  values of 2M-4-MPIMP and O-2M-4-MPIMP were found to be  $318$  and  $334$  nm and  $3.25$  and  $3.08$  eV, respectively.

O-2M-4-MPIMP has conductivities of  $10^{-8} - 10^{-7}$  S/cm. When doped with iodine, their conductivities

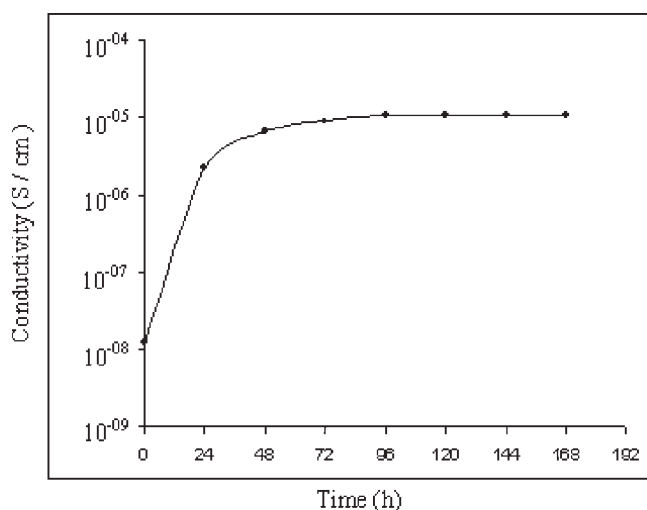
could be increased by about eight orders of magnitude (up to  $10^{-3}$  S/cm). Figure 9 shows the results of O-2M-4-MPIMP doped with iodine at various times at  $25^\circ\text{C}$ . Although the structure of O-2M-4-MPIMP differs, little significant difference in conductivity was observed. This effect may possibly be because of all actually belonging to the same class of oligomer. In the doping of O-2M-4-MPIMP with iodine, it was found that the conductivity of O-2M-4-MPIMP first increases greatly with doping time, but then tends to level-off. The maximal (or saturated) conductivity was  $1.07 \times 10^{-5}$  S/cm (shown in Fig. 9). The increasing conductivity could indicate that a charge-transfer complex between O-2M-4-MPIMP and dopant iodine is continuously formed. Consequently, Figure 9 not only shows the conductivity/doping



**Figure 7** Cyclic voltammograms of 2M-4-MPIMP (1) and O-2M-4-MPIMP (2).



**Figure 8** Absorption spectra of 2M-4-MPIMP (1) and O-2M-4-MPIMP (2).

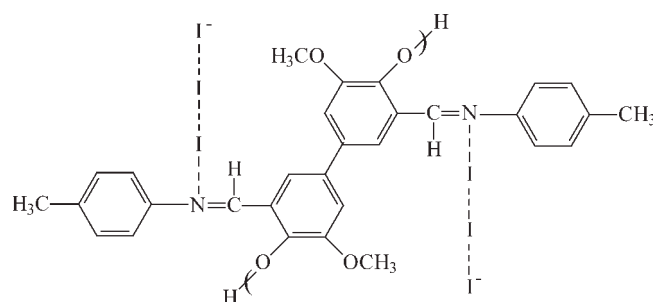


**Figure 9** Electrical conductivity of I<sub>2</sub>-doped O-2M-4-MPIMP versus doping time at 25°C.

time relationship but also indicates how quickly the doping reaction takes place. Our experiments showed that a longer doping time is needed to obtain the maximal conductivity. As a result, the conductivity/doping time curve varies with doping conditions. To exclude the influence of doping conditions, the conductivity of doped O-2M-4-MPIMP has been related with doping extent (shown in Fig. 9). Diaz et al. had been suggested the conductivity mechanisms of Schiff base polymers for doping with iodine.<sup>23</sup> Nitrogen is a very electronegative element and it is capable of coordinating an iodine molecule. On the nitrogen atom coordination of iodine with Schiff base, polymers and pyridine solutions had been suggested at the literatures as follows (Scheme 4).<sup>24–26</sup>

## CONCLUSIONS

O-2M-4-MPIMP with Schiff base substitute is synthesized by oxidants such as air O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and NaOCl in an aqueous alkaline medium. The yield of O-2M-4-MPIMP was found to be 68, 68, and 82% for air O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and NaOCl oxidants, respectively. At the oxidative polycondensation reaction of 2M-4-MPIMP, NaOCl demonstrated to higher activity than H<sub>2</sub>O<sub>2</sub> and air O<sub>2</sub>. The <sup>13</sup>C NMR data have demonstrated to unite from *para*-carbons of phenol ring each other of formation oligomer from oxidative polycondensation of 2M-4-MPIMP. Thermal analysis results have demonstrated to be enough resistance against thermal degradation of synthesized oligomer. The carbines residue of O-2M-4-MPIMP was found at high amount such as 10.46% at 1000°C. Properties of monomer and oligomer with potential low-band gap characteristics were determined. The band gap value of monomer was higher than oligomer. This is



**Scheme 4** Coordination of iodine during O-2M-4-MPIMP doping.

a result of the azomethine group that is an electron donor. This increases the HOMO more than the LUMO and therefore lowers the band gap. The observed band gaps are sufficiently low to make this oligomer highly promising for photovoltaic applications.

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