

# Synthesis, Characterization, Thermal Stability, Conductivity, and Band Gap of a New Aromatic Polyether Containing an Azomethine as a Side

İsmet Kaya, Mehmet Yıldırım

Department of Chemistry, Faculty of Sciences and Arts, Çanakkale Onsekiz Mart University, 17020 Çanakkale, Turkey

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**ABSTRACT:** In this study, the oxidative polycondensation reaction conditions of 4-[(4-methylphenyl)iminomethyl]phenol (4-MPIMP) were studied by using oxidants such as air O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and NaOCl in an aqueous alkaline medium between 50 and 90°C. The structures of the synthesized monomer and polymer were confirmed by FTIR, UV-vis, <sup>1</sup>H-<sup>13</sup>C-NMR, and elemental analysis. The characterization was made by TGA-DTA, size exclusion chromatography (SEC), and solubility tests. At the optimum reaction conditions, the yield of poly-4-[(4-methylphenyl)iminomethyl]phenol (P-4-MPIMP) was found to be 28% for air O<sub>2</sub> oxidant, 42% for H<sub>2</sub>O<sub>2</sub> oxidant, and 62% 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 values of P-4-MPIMP were found to be 4400 g mol<sup>-1</sup>, 5100 g mol<sup>-1</sup>, and 1.159, using H<sub>2</sub>O<sub>2</sub>, and 4650 g mol<sup>-1</sup>, 5200 g mol<sup>-1</sup>, and 1.118, using air O<sub>2</sub>, and 5100 g mol<sup>-1</sup>, 5900 g mol<sup>-1</sup>, and 1.157,

using NaOCl, respectively. According to TG analysis, the weight losses of 4-MPIMP and P-4-MPIMP were found to be 85.37% and 72.19% at 1000°C, respectively. P-4-MPIMP showed higher stability against thermal decomposition. Also, electrical conductivity of the P-4-MPIMP was measured, showing that the polymer is a typical semiconductor. The highest occupied molecular orbital and the lowest unoccupied molecular orbital energy levels and electrochemical energy gaps (*E<sub>g</sub>*) of 4-MPIMP and P-4-MPIMP were found to be -5.76, -5.19; -3.00, -3.24; 2.76 and 1.95 eV, respectively. According to UV-vis measurements, optical band gaps (*E<sub>g</sub>*) of 4-MPIMP and P-4-MPIMP were found to be 3.34 and 2.82 eV, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2282–2289, 2007

**Key words:** oxidative polycondensation; poly-4-[(4-methylphenyl)iminomethyl]phenol; air O<sub>2</sub>; NaOCl; H<sub>2</sub>O<sub>2</sub>; thermal analysis; conductivity and band gap

## INTRODUCTION

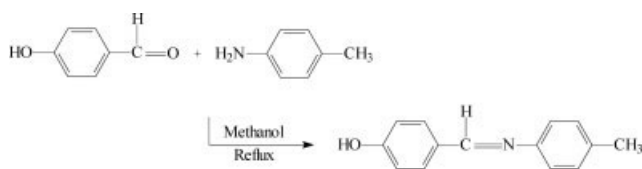
Polyimines, which are also known as polyazomethines, contain —HC=N— groups in their structures. By now, this class of polymers attracted much attention because of their useful properties and wide application fields. The first polyazomethines were prepared by Adams et al. from terephthalaldehyde, benzidine, and dianisidine.<sup>1</sup> In the period from 1950 to 1959, Marvel et al. prepared a number of polyazines and polyazomethines from aromatic dialdehydes with hydrazine and *o*-phenylenediamine and examined their chelate formation and thermal stability.<sup>2–4</sup> The compositions that were synthesized up to early 1967 were summarized and reviewed.<sup>5,6</sup> In another study, Morgan et al. described the synthesis of a variety of aromatic polyazomethines and copolyazomethines by solution and melt methods.<sup>7</sup>

Polyimines containing conjugated bonding and active hydroxyl group have been studied for more

than 60 years and they have been used in various fields due to useful properties such as paramagnetism, semiconductivity, electrochemical cell, and resistance to high energy. They are used to prepare composites with high positive temperature coefficient of resistance, thermostabilisators, graphite materials, epoxy oligomer and block copolymers, photo resists as well as materials, which are anti-static and enduring to flame.<sup>8–16</sup> By adding of other functional groups to these compounds, they can generate new useful properties. These types of polymers have been studied with their thermal, optical, electrical, and electrochemical properties by Kaya and Koyuncu.<sup>17</sup> In recent years, considerable effort has been directed toward the synthesis of conjugated polymers with low optical band gaps (*E<sub>g</sub>*), since they show intrinsic electrical conductivity.<sup>18–20</sup>

In this study, we investigated the optical and electrochemical band gaps, as well as electrical conductivity after the synthesis and characterization of P-4-MPIMP. In the first part, we determined the optimum reaction conditions by the changing of experimental parameters. To characterize the P-4-MPIMP, we used FTIR, UV-vis, <sup>1</sup>H and <sup>13</sup>C-NMR, elemental

Correspondence to: İ. Kaya (kayaismet@hotmail.com).



**Scheme 1** Synthesis of 4-[(4-methylphenyl)iminomethyl]phenol.

analysis, and size exclusion chromatography (SEC) techniques. Thermal stabilities of P-4-MPIMP were studied by TG-DTA techniques. Electrochemical properties of Schiff base and polymer were determined by cyclic voltammetry and the HOMO, LUMO, and electrochemical energy gaps ( $E_g'$ ) were calculated from oxidation and reduction onset values. The optical band gap ( $E_g$ ) of the Schiff base and polymer were calculated from their absorption edges. Electrical properties of doped and undoped polymer were determined by four-point probe technique at room temperature and atmospheric pressure using Keithley 2400 conductivity instrument (Keithley, Ohio, USA).

## MATERIALS AND METHODS

### Materials

4-Hydroxybenzaldehyde, *p*-toluidine, dioxane, methanol, ethanol, 1-butanol, 2-propanol, acetonitrile, benzene, toluene, ethyl acetate, heptane, hexane,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , tetrahydrofuran, THF, dimethylformamide, DMF, dimethylsulfoxide, DMSO,  $\text{H}_2\text{SO}_4$ , NaOH,  $\text{H}_2\text{O}_2$  (30% aqueous solution), KOH, and HCl were supplied by Merck Chemical (Germany) and they were used as received. Thirty percent aqueous solution of sodium hypo chloride NaOCl was supplied by Paksoy Chemical (Turkey).

### Preparation of 4-[(4-methylphenyl)iminomethyl]phenol (4-MPIMP)

4-MPIMP was prepared by the condensation of 4-hydroxybenzaldehyde (1.22 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 4-[(4-methylphenyl)iminomethyl]phenol was filtered, recrystallized from methanol, and dried in vacuum desiccators with yield of 85%.

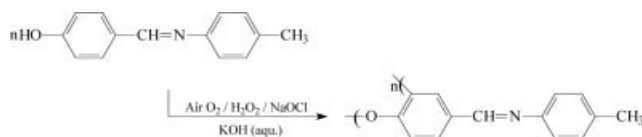
Calcd. for 4-MPIMP: C, 79.62; H, 6.16; N, 6.64. Found: C, 79.50; H, 6.00; N, 6.50. UV-vis ( $\lambda_{\text{max}}$ ): 201, 225, 291, and 320 nm. FTIR ( $\text{cm}^{-1}$ ):  $\nu$  (O—H) 3223 s,  $\nu$  (C—H aliphatic) 2916 m,  $\nu$  (C—H Phenyl) 3027 m,  $\nu$  (C=N) 1605 s,  $\nu$  (C=C phenyl) 1587, 1504, 1441 s,  $\nu$  (C—O) 1283 s.  $^1\text{H}$  NMR (DMSO):  $\delta$  ppm, 8.45 (s, 1H, —CH=N—); 10.06 (s, 1H, —OH); 6.89 (d, 2H, Ar-Haa'), 7.77 (d, 2H, Ar-Hbb'), 7.12 (d, 2H, Ar-

Hcc'), 7.19 (d, 2H, Ar-Hdd'), 2.31 (s, 3H, —CH<sub>3</sub>).  $^{13}\text{C}$  NMR (DMSO): ppm, 159.52 (C1-ipso), 116.01 (C2, 6-H), 131.05 (C3, 5-H), 128.24 (C4-ipso), 161.03 (C7-H), 149.83 (C8-ipso), 121.39 (C9, 13-H), 130.02 (C10, 12-H), 135.04 (C11-ipso), 21.18 (C14-H<sub>3</sub>).

### Synthesis of poly-4-[(4-methylphenyl)iminomethyl]phenol with NaOCl, $\text{H}_2\text{O}_2$ , and air $\text{O}_2$ in aqueous alkaline medium

P-4-MPIMP was synthesized through oxidative polycondensation of 4-[(4-methylphenyl)iminomethyl]phenol with aqueous solutions of NaOCl (30%),  $\text{H}_2\text{O}_2$  (30%), and air  $\text{O}_2$ , respectively. These oxidants were choiced because of being cheap and easy to provide.<sup>16</sup> The 4-MPIMP (0.211 g; 0.001 mol) was dissolved in an aqueous solution of KOH (10%, 0.001 mol) and placed into a 50-mL three-necked round-bottom flask (Scheme 2). It was fitted with a condenser, thermometer, stirrer, and an addition funnel containing NaOCl or  $\text{H}_2\text{O}_2$ . After heating to 40°C, NaOCl and  $\text{H}_2\text{O}_2$  were added drop by drop over about 20 min. The reaction mixtures were then heated to various temperatures while stirring for different durations and are given in Table I. Temperature range of 50–90°C was chosen at the polymerization reactions based on the previous studies in which this temperature range was used to obtain the optimal yields.<sup>21,22</sup> The air was passed into an aqueous solution of NaOH (20%) before being sent through the reaction tube to prevent water loss in the reaction mixture and to neutralize  $\text{CO}_2$  in the air (Scheme 2). The reaction mixtures were cooled to room temperature, and then 0.001 mol HCl (37%) was added. For the separation of mineral salts and unreacted monomers, the mixture was filtered and washed in 25 mL of hot water for three times and then dried in an oven at 110°C.

Calcd. for P-4-MPIMP: C, 80.38; H, 5.26; N, 6.70. Found: C, 80.05; H, 5.40; N, 6.54. UV-vis ( $\lambda_{\text{max}}$ ): 204, 260 and 338. FTIR ( $\text{cm}^{-1}$ ):  $\nu$  (O—H) 3305 s,  $\nu$  (C—H aliphatic) 2916 m,  $\nu$  (C—H Phenyl) 3035 m,  $\nu$  (C=N) 1580 s,  $\nu$  (C=C phenyl) 1512, 1479, 1445, s,  $\nu$  (C—O) 1280 s.  $^1\text{H}$  NMR (DMSO):  $\delta$  ppm, 8.45 (s, 1H, —CH=N—); 9.80 (s, 1H, —OH); 6.90 (d, H, Ar-Ha), 7.77 (d, H, Ar-Hb), 6.95 (d, H, Ar-Hc), 7.12 (d, H, Ar-Hdd'), 7.19 (d, 2H, Ar-Hee'), 2.31 (s, 3H, —CH<sub>3</sub>).  $^{13}\text{C}$  NMR (DMSO): ppm, 160.31 (C1-ipso), 127.50 (C2-ipso), 134.38 (C6-ipso), 115.63 (C2, 6-H, terminal), 130.31 (C3, 5-H), 149.22 (C4-ipso), 163.13



**Scheme 2** Synthesis of poly-4-[(4-methylphenyl)iminomethyl]phenol.

**TABLE I**  
**The Reaction Parameters of 4-[(4-Methylphenyl)iminomethyl]phenol<sup>a</sup> with NaOCl (Sample No.: 1–19), H<sub>2</sub>O<sub>2</sub> (Sample No.: 20–32), and Air O<sub>2</sub> (Sample No.: 33–37) in Aqueous KOH in the Oxidative Polycondensation Reaction**

Sample no.	Temperature (°C)	Times (h)	[KOH] <sub>0</sub> (mol L <sup>-1</sup> )	[NaOCl] <sub>0</sub> /[H <sub>2</sub> O <sub>2</sub> ] <sub>0</sub> (mol L <sup>-1</sup> )/Air O <sub>2</sub> (L/h)	% Yield of P-4-MPIMP
1	50	10	0.10	0.105	27
2	60	10	0.10	0.105	29
3	70	10	0.10	0.105	32
4	80	10	0.10	0.105	45
5	90	10	0.10	0.105	42
6	80	3	0.10	0.105	20
7	80	5	0.10	0.105	27
8	80	15	0.10	0.105	46
9	80	20	0.10	0.105	58
10	80	25	0.10	0.105	62
11	80	50	0.10	0.105	52
12	80	5	0.10	0.158	39
13	80	5	0.10	0.210	45
14	80	5	0.10	0.315	39
15	80	5	0.10	0.420	38
16	80	5	0.10	0.525	36
17	80	5	0.15	0.105	36
18	80	5	0.20	0.105	34
19	80	5	0.25	0.105	30
20	50	10	0.134	0.065	18
21	60	10	0.134	0.065	21
22	70	10	0.134	0.065	23
23	80	10	0.134	0.065	24
24	90	10	0.134	0.065	28
25	90	3	0.134	0.065	15
26	90	5	0.134	0.065	19
27	90	15	0.134	0.065	33
28	90	20	0.134	0.065	42
29	90	25	0.134	0.065	32
30	90	5	0.201	0.065	38
31	90	5	0.268	0.065	34
32	90	5	0.335	0.065	28
33	60	5	0.067	8.5	22
34	70	5	0.067	8.5	28
35	80	5	0.067	8.5	26
36	90	5	0.067	8.5	23
37	70	10	0.067	8.5	20

<sup>a</sup> Monomer concentration used in reactions was 0.067 mol L<sup>-1</sup>.

(C7-H), 158.91 (C8-*ipso*), 120.63 (C9, 13-H), 129.53 (C10, 12-H), 131.88 (C11-*ipso*), 20.78 (C14-H).

### Electrical properties

Conductivity was measured by a Keithley 2400 Electrometer. The pellets were pressed on hydraulic press at 1687.2 kg/cm<sup>2</sup>. Iodine doping was carried out by exposing the pellets to iodine vapor at atmospheric pressure and room temperature in a dessicator.<sup>20</sup>

### Electrochemical properties

Cyclic voltammetry (CV) measurements were carried out with a CHI 660B Electrochemical Analyzer (CH Instruments, Texas, USA) at a potential scan rate of 20 mV/s. All the experiments were performed in a dry

box filled with Ar 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 with respect to Ag wire or 0.38 V with respect to saturated calomel electrolyte (SCE). The voltammetric measurements were carried out for monomer and polymer in acetonitrile and DMSO, respectively.<sup>23</sup> The HOMO and LUMO energy levels and electrochemical energy gaps ( $E'_g$ ) were calculated from the oxidation and reduction onset values.

### Optical properties

The optical band gaps ( $E_g$ ) of monomer and polymer compounds were calculated from their absorption

**TABLE II**  
**The Number–Average Molecular Weight ( $M_n$ ), Mass–Average Molecular Weight ( $M_w$ ), polydispersity index (PDI), and % Values of Oxidative Polycondensation Products of P-4- MPIMP**

Compounds	Molecular weight distribution parameters														
	Total			Fraction I				Fraction II				Fraction III			
	$M_n$	$M_w$	PDI	$M_n$	$M_w$	PDI	%	$M_n$	$M_w$	PDI	%	$M_n$	$M_w$	PDI	%
P-4-MPIMP <sup>a</sup>	4650	5200	1.118	1750	2000	1.143	25	2200	2800	1.273	5	19,100	21,500	1.126	70
P-4-MPIMP <sup>b</sup>	5100	5900	1.157	1900	2350	1.237	30	1900	2400	1.263	10	24,000	27,700	1.154	60
P-4-MPIMP <sup>c</sup>	4400	5100	1.159	1600	1800	1.125	35	1850	2300	1.243	5	21,000	24,100	1.148	60

<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.

edges. Ultraviolet–visible (UV–vis) spectra were measured by Perkin Elmer Lambda 25 (Massachusetts, USA). The absorption spectra of monomer and polymer were recorded by using methanol and DMSO, respectively, at 25°C.

#### Solubility and characterization techniques

P-4-MPIMP is dark brown at powder forms and it is completely soluble in organic solvents such as acetone, THF, DMF, DMSO, aqueous alkaline, and concentrated H<sub>2</sub>SO<sub>4</sub>. P-4-MPIMP was found to be insoluble in methanol, ethanol, 1-butanol, 2-propanol, heptane, hexane, benzene, toluene, ethyl methyl ketone, 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 were measured by Perkin Elmer Spectrum One FTIR system. Elemental analysis was carried out with Carlo Erba 1106 (Carlo Erba, Italy). The FTIR spectra were recorded using universal ATR sampling accessory within the wavelengths of 4000–550 cm<sup>-1</sup>. 4-MPIMP and P-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. The tetramethylsilane was used as internal standard.<sup>22</sup> Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis. The TG-DTA measurements were made lease change 20–1000°C in N<sub>2</sub> at a rate of 10°C/min. The number–average molecular weight ( $M_n$ ), weight–average molecular weight ( $M_w$ ), and polydispersity index (PDI), values of polymer, were determined by size exclusion chromatography (SEC; Shimadzu, Japan). For SEC investigations a SGX (100 Å and 7 nm diameter loading material) 3.3 mm inside diameter × 300 mm columns was used with DMF (0.4 mL/min) as the eluent applied at polystyrene standards.<sup>21</sup> A refractive index detector was used to analyze the product at 25°C.

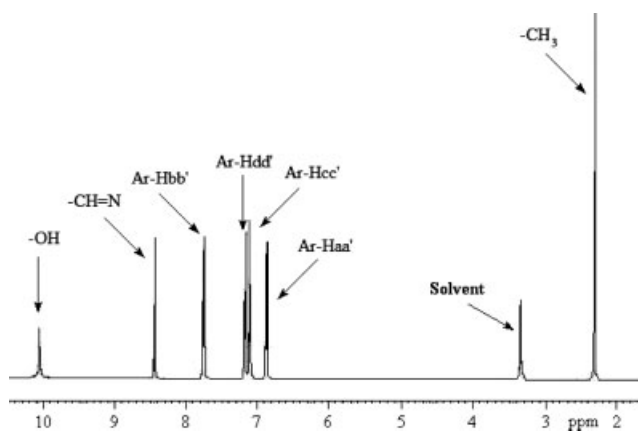
## RESULTS AND DISCUSSION

### The investigation of synthesis conditions of P-4-MPIMP

4-[(4-methylphenyl)iminomethyl]phenol was not oxidized at the neutral and organic mediums by air O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> (30% aqueous solution), and NaOCl (30% aqueous solution). When 4-MPIMP interacted with oxidants such as air O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and NaOCl in alkaline medium, brown phenoxy radicals precipitated immediately. The conditions of oxidative polycondensation reaction of 4-MPIMP with 30% NaOCl solution in aqueous alkaline medium are given in Table I. The yield of poly-4-[(4-methylphenyl)iminomethyl]phenol (P-4-MPIMP) was 42% at the NaOCl medium for 10 h at 90°C. As seen from Table I, the yield of products increased by increasing of temperatures possibly reaching a peak at ~ 80°C. A maximum yield of P-4-MPIMP at 62% was obtained with the reaction conditions of [KOH]<sub>0</sub> = 0.05, [4-MPIMP]<sub>0</sub> = 0.1, and [NaOCl]<sub>0</sub> = 0.105 mol/L at 80°C for 25 h. However, under the same conditions, when molar amount of alkaline and NaOCl oxidant were increased, the total yield of P-4-MPIMP decreased.

The oxidative polycondensation reaction conditions of 4-MPIMP with 30% H<sub>2</sub>O<sub>2</sub> solution in aqueous alkaline medium are given in Table I. The optimum yield of P-4-MPIMP was 42% at the conditions of [4-MPIMP]<sub>0</sub> = 0.067, [KOH]<sub>0</sub> = 0.134, and [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.065 mol/L, at 90°C for 20 h. With the same conditions, when molar amount of alkaline increased in two folds, total yield of P-4-MPIMP changed from 19 to 34%. The yield of P-4-MPIMP was 38% at the reaction conditions of [4-MPIMP]<sub>0</sub> = 0.067, [KOH]<sub>0</sub> = 0.201, and [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.065 mol/L at 90°C for 5 h. According to these values, the yield of P-4-MPIMP was increased by increasing reaction temperatures.

In the oxidative polycondensation reaction of 4-MPIMP, when air O<sub>2</sub> was introduced at a rate of 8.5 L/h to the reaction medium at 70°C, the yield of



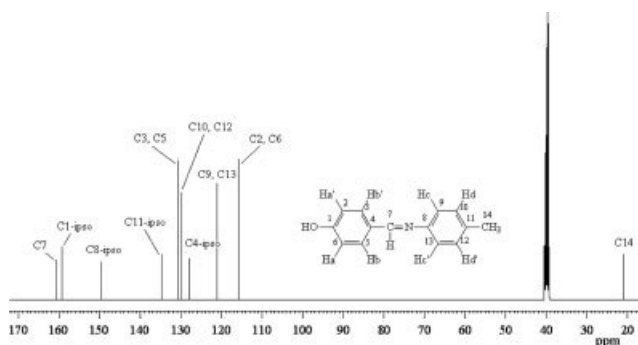
**Figure 1**  $^1\text{H}$  NMR spectrum of 4-[(4-methylphenyl)iminomethyl]phenol.

product was 28%. The yield of P-4-MPIMP was 23% at the reaction conditions of  $[4\text{-MPIMP}]_0 = [\text{KOH}]_0 = 0.067$  mol/L at  $90^\circ\text{C}$  for 5 h. The various conditions for P-4-MPIMP are given in Table I. As seen in Table I, the yields of the polymers in these reactions were dependent upon temperature, time as well as initial concentrations of alkaline and oxidants. At the same conditions, the yield of P-4-MPIMP was also found to be higher by using NaOCl as compared to air  $\text{O}_2$  and  $\text{H}_2\text{O}_2$  oxidants.

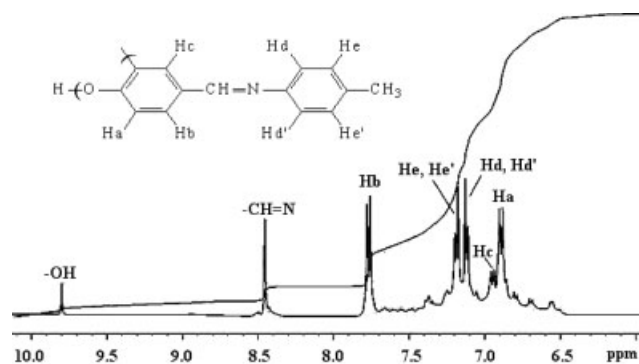
### Structure of P-4-MPIMP

According to SEC chromatograms, the values of number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) of P-4-MPIMP were calculated according to a Polystyrene standard calibration curve as given in Table II. According to the SEC analysis of the polymer, three fractions were observed in the chromatogram of products.

From our experiments, the UV-vis spectra of 4-MPIMP and P-4-MPIMP were found to be similar to each other. However, at the spectra of 4-MPIMP, K bands of phenol and  $\text{C}_6\text{H}_5\text{-N=}$  were observed in 225 and 291 nm, respectively. Benzene band of 4-



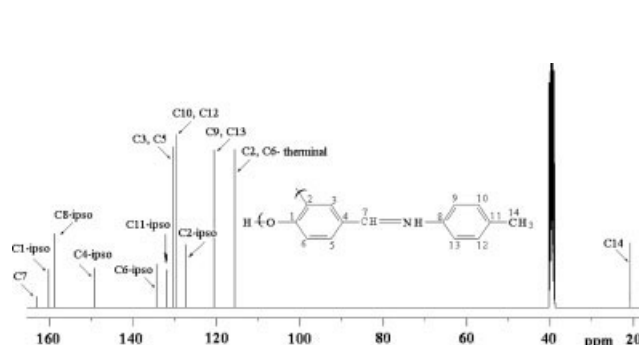
**Figure 2**  $^{13}\text{C}$  NMR spectrum of 4-[(4-methylphenyl)iminomethyl]phenol.



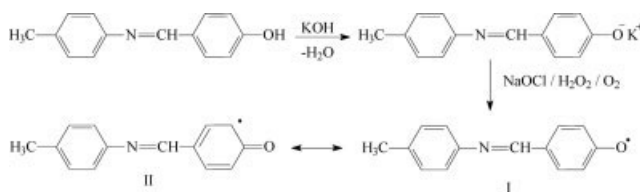
**Figure 3**  $^1\text{H}$  NMR spectrum of poly-4-[(4-methylphenyl)iminomethyl]phenol (enlargement of the plot from 6.5 to 10.0 ppm).

MPIMP and strength R band of  $-\text{CH}=\text{N}-$  groups were observed in 291 and 320 nm, respectively.  $\lambda_{\text{max}}$  values of P-4-MPIMP were observed in 204, 260, and 338. At the UV-vis spectra of P-4-MPIMP, K and R bands were observed in 260 and 338 nm, respectively. FTIR spectra of oxidative polycondensation product of 4-MPIMP shows differences only in the reduction of band strength and numbers when compared to the FTIR spectra of the original 4-MPIMP. At the FTIR spectra of 4-MPIMP and P-4-MPIMP, bands of  $-\text{OH}$ ,  $-\text{CH}=\text{N}$ , and  $-\text{CH}_3$  groups were observed in  $3223$ ,  $1605$ , and  $2916$   $\text{cm}^{-1}$ ;  $3305$ ,  $1580$ , and  $2916$   $\text{cm}^{-1}$ , respectively.

To identify the structures of monomer and polymer, the  $^1\text{H}$  NMR spectra were recorded in  $\text{DMSO}-d_6$ .  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the 4-MPIMP

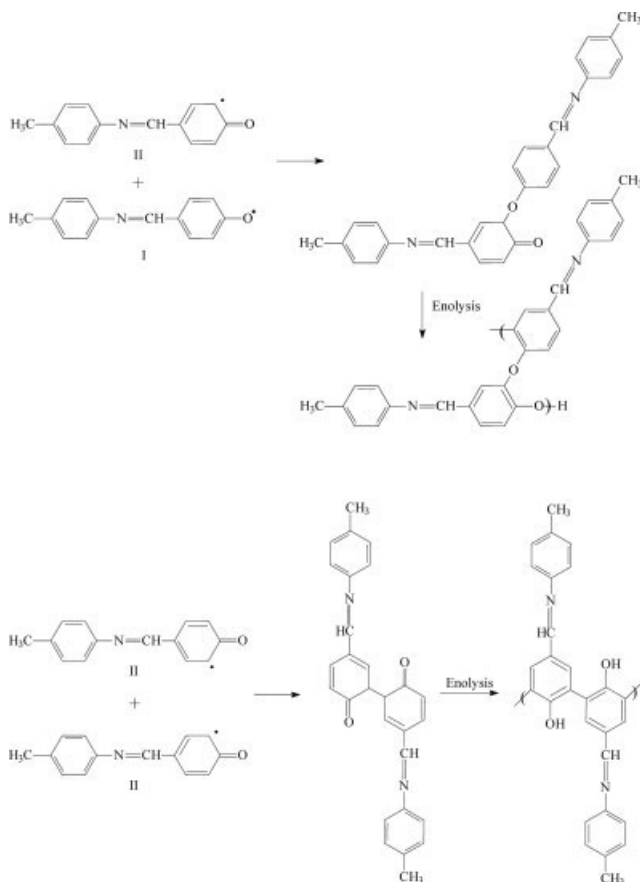


**Figure 4**  $^{13}\text{C}$  NMR spectrum of poly-4-[(4-methylphenyl)iminomethyl]phenol.

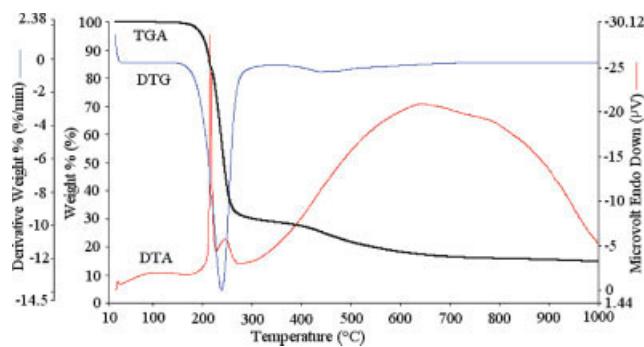


**Scheme 3** The reaction mechanism of phenoxy radical formation.

and P-4-MPIMP are given in Figures 1–4, respectively. In the  $^1\text{H}$  NMR spectra of 4-MPIMP and P-4-MPIMP, the signals of  $-\text{OH}$ ,  $-\text{CH}_3$ , and  $-\text{CH}=\text{N}$  groups were observed in 10.06, 2.31, and 8.45 ppm and 9.80, 2.31, and 8.45 ppm, respectively. Other phenol derivatives were also polymerized, and the results have been reported in the literatures.<sup>24</sup> Cross-linking in polymer structure is expected in those cases where the *ortho* positions and phenolic OH group in the corresponding monomer structure are unsubstituted.  $^{13}\text{C}$  NMR studies on P-4-MPIMP indicate that the linkage between any two adjacent phenyl rings is mainly at *ortho* positions and phenolic OH group. However, this type of linkage may strain the polymer backbone in such a manner that the phenyl rings are out of plane with respect to the adjacent rings. The peak values for C2 and C6 are



**Scheme 4** The reaction mechanism of polymer formation.

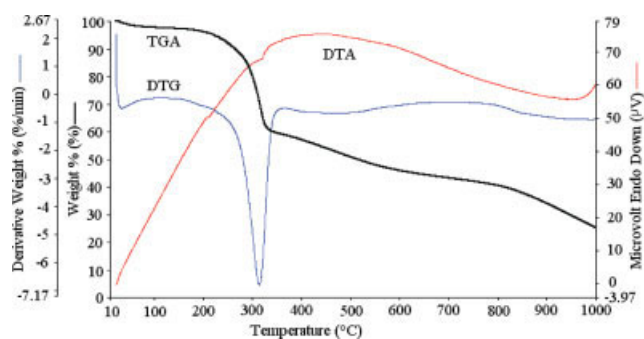


**Figure 5** TG-DTA curves of 4-[(4-methylphenyl)iminomethyl]phenol. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

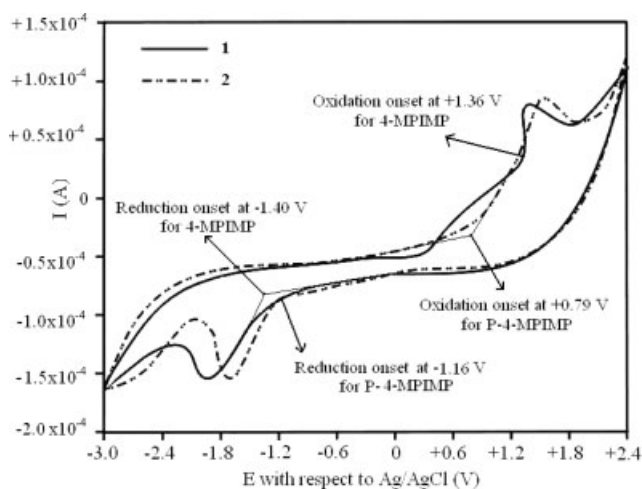
observed at 116.01 ppm in the monomer (Fig. 3) and at 127.50 (C2-*ipso*) and 134.38 ppm (C6-*ipso*) in the polymer (Fig. 4), respectively. These values are in agreement with the theoretically calculated peak position for *ortho* linkages on the ring.<sup>24</sup> It is seen that, in Figure 4, new peaks were observed in 127.50 and 134.38 ppm. Thus, the phenyl rings in the polymer appear to be linked primarily at the *ortho* positions and phenolic OH group. The reaction mechanism on the coupling selectivity has been studied by Kaya et al. and two possible reaction mechanisms (Schemes 3 and 4) for the C–C and C–O–C coupling have been proposed.<sup>25</sup> Furthermore, the decrease in the proton integration of  $-\text{OH}$  proton and observation of the peaks of C2 or C6 at 115.63 ppm has verified a C–O–C coupling system. According to  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR results of polymer, the formations of C–C and C–O–C coupling systems have been confirmed.

#### Thermal analyses of 4-MPIMP and P-4-MPIMP

The TGA-DTG-DTA curves of the monomer and the polymer are given in Figures 5 and 6, respectively. The initial degradation temperature, 50%, and the



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



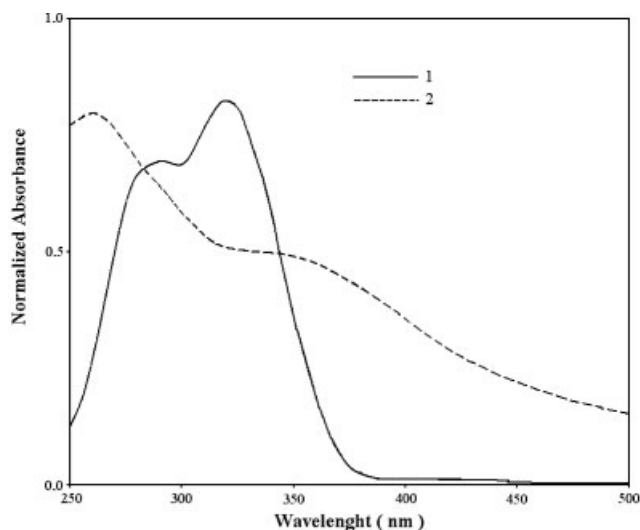
**Figure 7** Cyclic voltammograms of 4-MPIMP (1) and P-4-MPIMP (2).

maximum weight loss (85.37%) of 4-MPIMP was found to be 207, 242, and 1000°C, respectively. According to DTG curve,  $T_{\max}$  and maximum weight losses of the 4-MPIMP were found as 236 and between 145 and 335°C. According to DTA analysis, exothermic peaks were observed at the temperatures of 214, 246, and 660°C. The initial degradation temperature, 50%, and the maximum weight loss (72.19%) of P-4-MPIMP were found to be 272, 515, and 1000°C, respectively. The weight loss (3.5%) in the range of 50–140°C observing in TGA curve of P-4-MPIMP suggests the removal of adsorbed water. According to DTG curve,  $T_{\max}$  and maximum weight losses of the P-4-MPIMP were found as 313 and between 170 and 365°C. According to the TG analytical results, because of long conjugated  $\pi$ -band systems, the polymer demonstrated higher resistance against high temperature than the monomer.

### Electrochemical properties of 4-MPIMP and P-4-MPIMP

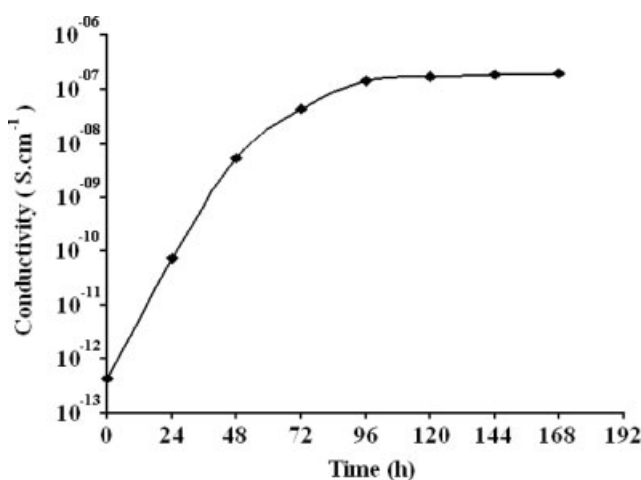
The voltammetric measurements of 4-MPIMP and P-4-MPIMP were carried out in acetonitrile and DMSO, respectively, as shown in Figure 7. The HOMO and LUMO energy levels and electrochemical energy gaps ( $E'_g$ ) were calculated from oxidation and reduction onset values as in the literature.<sup>26</sup> The HOMO and LUMO energy levels and electrochemical energy gaps ( $E'_g$ ) of 4-MPIMP and P-4-MPIMP were found to be -5.76, -5.19; -3.00, -3.24; 2.76 and 1.95 eV, respectively.

The absorption spectra of 4-MPIMP and P-4-MPIMP were recorded by using methanol and DMSO at 25°C (Fig. 8) and  $\lambda_{\max}$  and  $E_g$  values of 4-MPIMP and P-4-MPIMP were found to be 320 and 332 nm, and 3.34 and 2.82 eV, respectively.



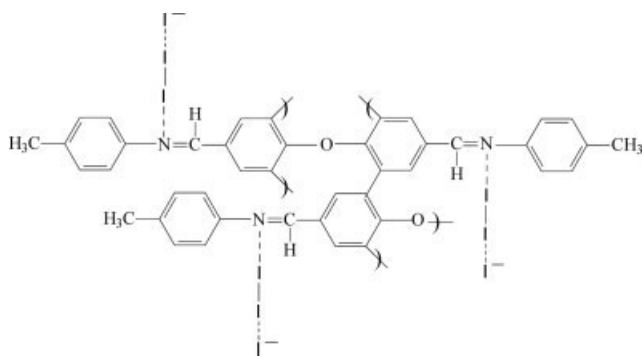
**Figure 8** Absorption spectra of 4-MPIMP (1) and P-4-MPIMP (2).

P-4-MPIMP has conductivities of  $10^{-13}$ – $10^{-12}$  S/cm. When doped with iodine at room temperature in a vacuum dessicator, its conductivities could be increased by about six orders of magnitude (up to  $10^{-7}$  S/cm). Figure 9 shows the results of P-4-MPIMP doped with iodine measured per 24 h at 25°C. These values agreed with the literature values.<sup>21,25</sup> In the doping of P-4-MPIMP with iodine, it was found that the conductivity of P-4-MPIMP first increased greatly with doping time, but then tended to level-off. The maximal or saturated conductivity was  $1.75 \times 10^{-7}$  S/cm (shown in Fig. 9). The increasing conductivity could indicate that a charge-transfer complex between P-4-MPIMP and dopant iodine is continuously being formed. Consequently, Figure 9 not only shows the conductivity/doping time relationship but also indicates how the doping



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





**Scheme 5** The nitrogen atom coordination of iodine with Schiff base polymers.

reaction takes place. The experiment results showed that a longer doping time was needed to obtain the maximal conductivity. As a result, the conductivity/doping time curve varied with doping conditions. To exclude the influence of doping conditions, the conductivity of doped P-4-MPIMP has been related with doping extent (shown in Fig. 9). Diaz et al. proposed a conductivity mechanism of Schiff base polymers for doping with iodine.<sup>20</sup> Nitrogen is a very electronegative element and it is capable of coordinating an iodine molecule. Coordination of iodine during P-4-MPIMP doping is as follows (Scheme 5): On the nitrogen atom coordination of iodine with Schiff base polymers and pyridine solutions.<sup>27–30</sup>

## CONCLUSION

The optimum reaction conditions and percentage yield values of P-4-MPIMP were determined by oxidants such as air O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and NaOCl in an aqueous alkaline medium. % yield values of P-4-MPIMP were found to be 28, 42, and 62% for air O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and NaOCl oxidants, respectively. According to these values, NaOCl demonstrated the highest activity at the oxidative polycondensation reaction of 4-MPIMP. The spectral analyses such as <sup>1</sup>H NMR and <sup>13</sup>C NMR have demonstrated to unity of *ortho*-carbons and phenolic —OH group of phenol ring to form polymer from oxidative polycondensation of 4-MPIMP. Thermal analysis results demonstrated that there were sufficient resistance against thermal degradation of synthesized polymer. This polymer lost half of its weight at 515°C. The properties of the monomer and the polymer with low potential band

gap characteristics were determined. The band gap value of the monomer was found to be higher than that of the polymer. This would be due to the presence of the azomethine group, an electron donor. This increased the HOMO more than the LUMO and therefore lowered the band gap. The observed band gaps were sufficiently low to make this polymer highly promising for photovoltaic applications.

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