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Synthesis, characterization, conductivity, band gap and thermal analysis of poly-2-[(4-mercaptophenyl) imino methyl] phenol and some of its polymer–metal complexes

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Abstract

The oxidative polycondensation reaction conditions of 2-[(4-mercaptophenyl) imino methyl] phenol (4-MPIMP) was studied in an aqueous alkaline medium between 30 and 90 °C by using oxidants such as air O_2, NaOCl and H_2O_2. Polymer–metal complex compounds were synthesized from the reactions of poly-2-[(4-mercaptophenyl) imino methyl] phenol (P-4-MPIMP) with Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} and Zr^{4+} ions. The structures of these monomer and polymer were identified from UV–vis, FT-IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. While thermal analysis of P-4-MPIMP and polymer–metal complexes were made by TGA–DTA, the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of this polymer were determined by size exclusion chromatography (SEC). According to TG–DTA analyses, P-4-MPIMP–Cu was found to be higher stable than other synthesized polymer and polymer–metal complexes. While conductivity measurements of polymer and polymer–metal complexes were done by electrometer using four point probe techniques, electrochemical and optical band gap values of 4-MPIMP, P-4-MPIMP and polymer–metal complexes were determined by using cyclic voltammetry and UV–vis measurements. Conductivity and band gap values show that this polymer and polymer–metal complexes are a typical semiconductor.
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Keywords: 2-[(4-Mercaptophenyl) imino methyl] phenol; Polymer and polymer–metal complexes; Band gap; Conductivity; Thermal analysis

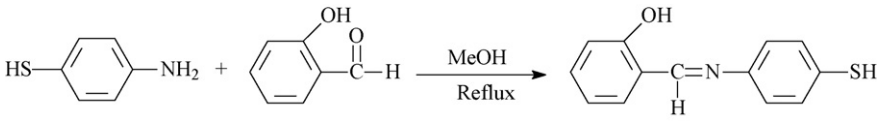
1. Introduction

In the recently, imine oligomers or polymers including hydroxyl group (–OH) have useful properties such as paramagnetism, semiconductivity, electrochemical cells and resistance to high energy. Because of these properties, they were used to prepare composites with resistance to high temperature, thermostabilisators and graphite materials, epoxy oligomer and block copolymers adhesives, fotoresists and antistatic materials [1–7]. These oligomers profit to new properties to their structures adding to other functional groups. For example, the halogen and sulphur derivatives of oligophenols were used to prepare of the composite materials enduring to flame of the specific detergents such as lead storing battery cathodes [3]. Imine oligomers and polymers including hydroxyl (–OH) group were synthesized via oxidative polycondensation reactions by using NaOCl, H_2O_2 and air O_2 as oxidant in an aqueous medium at various temperatures [9–11]. Due to including azomethine (–C=N) and hydroxyl (–OH) groups, when hydroxyl (–OH) group is placed in *ortho* position in phenyl ring, imine polymers and oligomers have the capability of coordination with different metal ions and they can be used for cleaning of poisonous heavy metals in the industrial waste waters. Therefore, the synthesis of these type polymers or oligomers and their metal complexes is very important for analytical and environmental chemistry.

Schiff base oligomers including conjugated bounding have attracted a great deal of attention due to their unusual electrical, electrochemical and optical properties [12]. –CH=N group is isoelectronic with the –CH=CH group in these oligomers and the incorporation of nitrogen atoms into the conjugated system is another approach to form classes of materials with equally interesting electronic and optical properties [13]. Optical

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Scheme 1. Synthesis of 2-[(4-mercaptophenyl) imino methyl] phenol.

and electrical properties of these oligomer and oligomer–metal complexes have become an increasingly interesting area of semiconducting and optical materials because these materials possess great potential for device applications such as Schottky diode, solid state devices and optical sensor [8]. Finally, electrical and electrochemical properties and thermal stability of these oligomer or polymers and their metal complexes will establish the industrial applicability of these materials.

In this article, we synthesized imine polymer including hydroxyl (–OH) and thiol (–SH) groups and its nine polymer–metal complexes and investigated to oxidative polycondensation reaction parameters, thermal, electrochemical, optical and electrical properties. The synthesized monomer and polymer were characterized by using FT-IR, UV–vis, ^{1}H NMR, ^{13}C NMR, TG–DTA and SEC techniques. Polymer–metal complexes were characterized by using FT-IR, UV–vis, TG–DTA and elemental analysis. Electrochemical properties of polymer and polymer–metal complex compounds were determined by cyclic voltammetry. While the HOMO and LUMO energy levels and electrochemical energy gaps (E'_g) were calculated from oxidation and reduction onset values, optical band gap (E_g) of this polymer and polymer–metal complex compounds were calculated from their absorption edges. Electrical properties of compounds were determined by four-point probe technique at room temperature and atmospheric pressure. On the other hand an important increase of the conductivity was attained when iodine was employed as a doping agent.

2. Experimental

2.1. Materials

2-Aminothiophenol and salicylaldehyde were supplied from Fluka Chemical Co. Tetrahydrofuran, THF, *N*,*N*′-dimethylformamide, DMF and dimethylsulfoxide, DMSO, benzene, acetone, ethyl acetate, hexane, heptane, KOH, HCl (37%), H_2O_2 (30% aqueous solution), CCl_4, $CHCl_3$, Cu $(CH_3COO)_2{\cdot}H_2O$, Pb $(CH_3COO)_2{\cdot}3H_2O$, Co $(CH_3COO)_2{\cdot}4H_2O$, Zn $(CH_3COO)_2{\cdot}2H_2O$, Cd $(CH_3COO)_2{\cdot}2H_2O$, Ni $(CH_3COO)_2{\cdot}4H_2O$, $CrCl_3{\cdot}6H_2O$, $MnCl_2$ and $ZrCl_4$ were supplied from Merck Chemical Co. (Germany) and they were used as received. Sodium hypo chloride (NaOCl) (30% aqueous solution) was supplied from Paksoy Chemical Co. (Turkey).

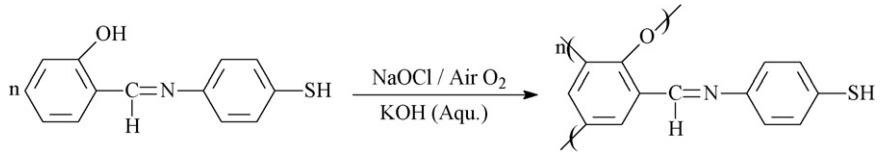
2.2. Preparation of 2-[(4-mercaptophenyl) imino methyl] phenol

2-[(4-Mercaptophenyl) imino methyl] phenol (4-MPIMP) was prepared by the condensation of salicylaldehyde (1.22 g, 0.01 mol) with 4-aminothiophenol (1.25 g, 0.01 mol) in methanol (25 ml). Mixture was refluxed by boiling for 3 h at 70 °C (Scheme 1). 2-[(4-Mercaptophenyl) imino methyl] phenol (4-MPIMP) precipitated as yellow crystals in the reaction mixture, then filtered and again recrystallized from methanol and dried in vacuum desiccator (yield 90%).

UV–vis (λ_{max}): 204, 239, 269 and 328 nm. ^{1}H NMR (DMSO): δ (ppm), 13.20 (s, 1H, –O<u>H</u>), 8.59 (s, 1H, –C<u>H</u>=N–), 7.19 (d, 2H, Ar–Haa′), 7.33 (d, 2H, Ar–Hbb′), 7.04 (d, 1H, Ar–Hc), 7.38 (t, 1H, Ar–Hd), 6.96 (t, 1H, Ar–He), 7.40 (d, 1H, Ar–Hf), 3.55 (s, 1H, –S<u>H</u>). ^{13}C NMR (DMSO): δ (ppm), 161.12 (C1-ipso), 117.29 (C2), 133.26 (C3), 119.19 (C4), 132.34 (C5), 129.47 (C6-ipso), 162.13 (C7), 146.16 (C8-ipso), 121.96 (C9, 13), 130.46 (C10, 12), 133.68 (C11-ipso).

2.3. Synthesis of poly-2-[(4-mercaptophenyl) imino methyl] phenol (4-MPIMP) with NaOCl and air O_2 in aqueous alkaline medium

P-4-MPIMP was synthesized via oxidative polycondensation of 4-MPIMP with aqueous solution of NaOCl (30%) and air oxidants, respectively (Scheme 2) [9]. The 4-MPIMP (2.29 g 0.01 mol) was dissolved in an aqueous solution of KOH (30%, 0.03 mol) and placed into a 50 ml three-necked round-bottom flask. It was fitted with a condenser, thermometer, and stirrer and at addition to funnel containing NaOCl. NaOCl was 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 1. The air passed into an aqueous solution of KOH (20%) before being sent through the reaction tube to the neutralizing of CO_2 in the air with KOH. The reaction mixtures were cooled to room temperature, and then 0.03 mol HCl (37%) was added. For the separation of mineral salts, the mixture was filtered and washed in 25 ml of hot water for three times. Then, unreacted monomer was separated from the reaction products by washing with ethanol and dried in a vacuum oven at 60 °C.



Scheme 2. Synthesis of poly-2-[(4-mercaptophenyl) imino methyl] phenol.

Table 1
The oxidative polycondensation reaction parameters of 2-[(4-mercaptophenyl) imino methyl] phenol (4-MPIMP)[a] with NaOCl (sample number: 1–15) and air O_2 (sample number: 16–25) in aqueous KOH

Sample number	$[KOH]_o$ (mol L^{-1})	$[NaOCl]_o$ (mol L^{-1}) or air O_2 (L/h)	Temp. (°C)	Time (h)	Yield of P-4-MPIMP (%)
1	0.15	0.075	30	3	71
2	0.15	0.075	30	5	74
3	0.15	0.150	30	5	65
4	0.15	0.225	30	5	60
5	0.15	0.075	30	10	84
6	0.15	0.075	30	15	80
7	0.15	0.075	30	20	75
8	0.15	0.075	40	5	66
9	0.15	0.075	50	5	58
10	0.15	0.075	60	5	50
11	0.20	0.075	60	5	43
12	0.25	0.075	60	5	39
13	0.15	0.075	70	5	43
14	0.15	0.075	80	5	39
15	0.15	0.075	90	5	37
16	0.15	8.5	30	10	68
17	0.15	8.5	40	10	72
18	0.15	8.5	50	10	81
19	0.15	8.5	60	10	70
20	0.15	8.5	70	10	34
21	0.15	8.5	80	10	17
22	0.15	8.5	90	10	11
23	0.15	8.5	50	5	32
24	0.15	8.5	50	15	68
25	0.15	8.5	50	20	57

[a] The initial concentration of 4-MPIMP was used as 0.05 mol L^{-1}.

UV–vis (λ_{max}): 206, 242, 274 and 345 nm. ^{1}H NMR (DMSO): δ (ppm), 14.10 (s, 1H –O<u>H</u>), 8.75 (s, 1H, –C<u>H</u>=N–), 7.30 (d, 2H, Ar–Ha), 7.53 (d, 2H, Ar–Hb), 6.96 (s, 1H, Ar–Hc), 7.81 (d, 1H, Ar–Hd), 7.45 (t, 1H, Ar–Hd), 6.90 (t, 1H, Ar–He), 7.94 (s, 1H, Ar–Hf), 7.63 (d, 1H, Ar–Hf), 2.50 (s, 1H, –S<u>H</u>). ^{13}C NMR (DMSO): δ (ppm), 160.96 (C1-ipso), 117.00 (C2), 132.89 (C3), 119.33 (C4), 131.80 (C5), 129.34 (C6-ipso), 163.75 (C7), 146.64 (C8-ipso), 122.45 (C9, 13), 128.16 (C10, 12), 136.05 (C11-ipso) and new peaks 134.20 and 126.46 ppm.

2.4. Synthesis of P-4-MPIMP–metal complex compounds

A solutions of Cu $(CH_3COO)_2{\cdot}H_2O$, Pb $(CH_3COO)_2{\cdot}3H_2O$, Co $(CH_3COO)_2{\cdot}4H_2O$, Zn $(CH_3COO)_2{\cdot}2H_2O$, Cd $(CH_3COO)_2{\cdot}2H_2O$, Ni $(CH_3COO)_2{\cdot}4H_2O$, $CrCl_3{\cdot}6H_2O$, $MnCl_2$ and $ZrCl_4$ (0.250 mol) in methanol (20 ml) was added to a solution of poly-2-[(4-mercaptophenyl) imino methyl] phenol (P-4-MPIMP) (0.5 mol, according to a polymer unit) in THF (30 ml) (Scheme 3). The mixture was stirred and heated at 70 °C for 5 h. The precipitated complex was filtered and washed with cold methanol, then dried in the oven.

2.5. Electrical properties

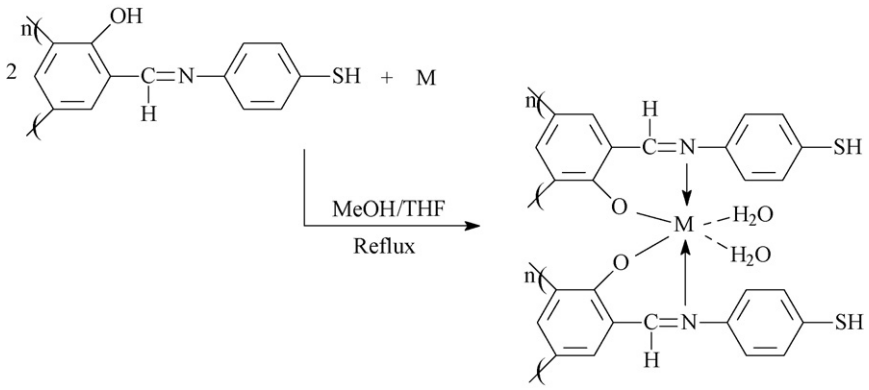
Electrical properties of doped and undoped polymer and polymer–metal complex compounds were determined by four-point probe technique at room temperature and atmospheric pressure using Keithley 2400 conductivity instrument (Keithley, Ohio, USA). The pellets were pressed on hydraulic press developing up to 1687.2 kg/cm^2. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in a desiccator [6].

2.6. Optical properties

The optical band gaps (E_g) of monomer, polymer and its polymer–metal complex compounds were calculated from their absorption edges. Ultraviolet–visible (UV–vis) spectra were measured by Perkin-Elmer Lambda 25 (Massachusetts, USA). The absorption spectra of monomer, polymer and polymer–metal complexes were recorded by using methanol and DMSO, respectively, at 25 °C [14].

2.7. 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 dry box under Ar atmosphere at room temperature. The electrochemical potential of Ag was calibrated with respect to the ferrocene/ferrocenium (Fc/Fc^+) couple. The half-wave potential ($E^{1/2}$) of (Fc/Fc^+) measured in 0.1 mol/L tetrabutylammonium hexafluorophosphate ($TBAPF_6$) acetonitrile solution is 0.39 V versus Ag wire or 0.38 V versus saturated calomel electrolyte (SCE). The voltammetric measurements were carried out for monomer, polymer and polymer–metal complexes in acetonitrile and DMSO, respectively. The HOMO and LUMO energy levels of the 4-MPIMP and P-4-MPIMP were



Scheme 3. Synthesis of poly-2-[(4-mercaptophenyl) imino methyl] phenol–metal complex compounds.

determined from the onset potentials of the n-doping (ϕ'_n) and p-doping (ϕ'_p), respectively [15,16].

2.8. Solubility and characterization techniques

4-MPIMP was yellow in powder form and was completely soluble in polar organic solvents such as methanol, ethanol, acetone, THF, acetonitrile, 1-butanol, chloroform, DMF, and DMSO. 4-MPIMP was insoluble in nonpolar organic solvents such as heptane and hexane. P-4-MPIMP was light brown in powder form and was completely soluble in organic solvents such as chloroform, DMF and DMSO. P-4-MPIMP was partly soluble in acetone, THF and dioxane. P-4-MPIMP was insoluble in ethanol, methanol, acetonitrile, 1-butanol, heptane and hexane. Polymer–metal complex compounds were insoluble in benzene, toluene, hexane, chloroform, ethyl acetate, CH_2Cl_2, CCl_4 and acetone, methanol, ethanol. These polymer–metal complex compounds were partly soluble in DMSO and DMF.

The infrared spectra were measured by Perkin-Elmer Spectrum One FT-IR system. The FT-IR spectra were recorded using ATR attachment (4000–550 cm^{-1}). Elemental analysis was carried out with Carlo Erba 1106 (Carlo Erba Co., Italy). UV–vis spectra of 4-MPIMP and P-4-MPIMP were recorded in methanol and DMSO, respectively. 4-MPIMP and P-4-MPIMP were also characterized by using ^1H and ^{13}C NMR (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) the NMR spectra values and recorded by using deuterated DMSO-d_6 as a solvent at 25 °C. The tetramethylsilane was used as internal standard. Thermal data were obtained by using Perkin-Elmer Diamond Thermal Analysis. The TG–DTA measurements were made lease change 20–1000 °C in N_2 at a rate of 10 °C/min. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined by size exclusion chromatography, SEC (Shimadzu Co., Japan). For SEC investigations a SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. × 300 mm columns was used with DMF/methanol (v/v, 4/1, 0.4 ml/min) as the eluent applied at polystyrene standards. A refractive index detector (at 25 °C) was used to analyze the product.

3. Results and discussion

3.1. Synthesis of P-4-MPIMP

The optimum reaction conditions of 2-[(4-mercaptophenyl) imino methyl] phenol were investigated in an aqueous alkaline medium by using air O_2 and NaOCl as oxidant. When 4-MPIMP interacted with these oxidants in an aqueous alkaline medium, brown phenoxy radicals immediately precipitated in the solution medium. But, when using H_2O_2 oxidant, brown phenoxy radicals was not formed under the same conditions. The oxidative polycondensation reaction conditions of 4-MPIMP with 30% NaOCl solution in an aqueous alkaline medium are given in Table 1. The yield of P-4-MPIMP was 84% at conditions such as $[4\text{-MPIMP}]_0 = 0.05$, $[KOH]_0 = 0.15$ and $[NaOCl]_0 = 0.075$ mol/L, at 30 °C for 10 h. It is seen in Table 1, that the yield of polymer decreased by increasing the reaction temperature. But the yield of polymer increased by increasing reaction times at the same reaction temperatures. Under the same conditions, when initial molar amount of NaOCl increased, the yield of P-4-MPIMP changed from 74% to 65%. The yield of P-4-MPIMP was 37% at conditions such as $[4\text{-MPIMP}]_0 = 0.05$, $[KOH]_0 = 0.15$ and $[NaOCl]_0 = 0.075$ mol/L, at 90 °C for 5 h. The oxidative polycondensation reaction conditions of 4-MPIMP with air O_2 in aqueous alkaline medium are given in Table 1. The yield of P-4-MPIMP was 81% at the reaction conditions such as $[4\text{-MPIMP}]_0 = 0.05$ mol/L $[KOH]_0 = 0.15$ mol/L and air O_2 (flow rate = 8.5 L/h), at 50 °C for 10 h. When reaction temperatures increased from 50 to 90 °C, the yield changed from 81% to 11%, respectively, at the same conditions. According to these values, it can be concluded that by increasing temperatures and reaction times, the yields decreased. As is seen from Table 1, the yields of these reactions were dependent upon temperature, times and initial concentrations of NaOCl and KOH. For the yield of P-4-MPIMP air O_2 and NaOCl were better oxidants according to H_2O_2, at the same conditions. The changes of the yield of P-4-MPIMP depending on temperature, time, initials concentrations of KOH and NaOCl oxidant, are given in Figs. 1 and 2.

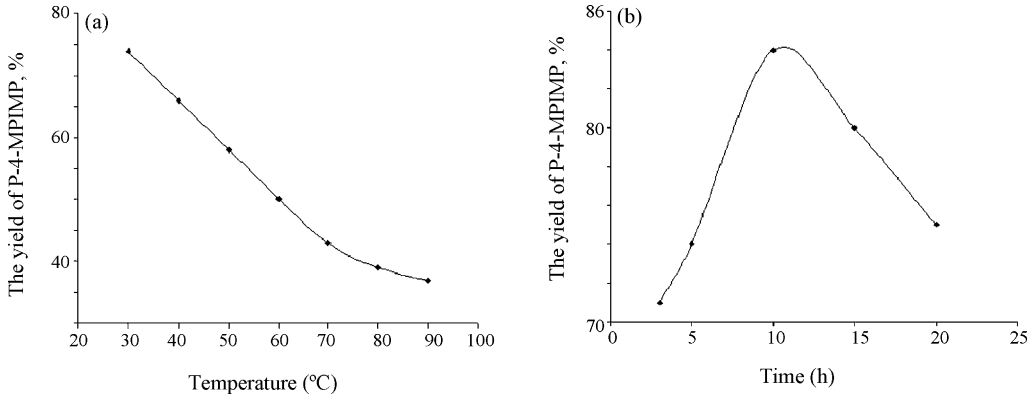


Fig. 1. The effects of temperature (a) and times (b) on % yield of P-4-MPIMP with NaOCl oxidant at the oxidative polycondensation reaction.

3.2. Structure of P-4-MPIMP

SEC analyses of P-4-MPIMP were performed at 30 °C using DMF/methanol (v/v, 4/1) as eluent at a flow rate of 0.4 ml/min. In the case of oxidant air O_2, M_n, M_w and PDI values of P-4-MPIMP were found to be 5750, 6200 g mol^{-1} and 1.078, respectively. Three peaks were observed in the chromatogram of P-4-MPIMP. Seventy-three percent of the mass of P-4-MPIMP was low molecular weight (Frc. I: M_n = 825, M_w = 1050 g mol^{-1}, PDI = 1.273) but 27% of its weight was high molecular weight (Frc. II (15%): M_n = 52,300, M_w = 58,250 g mol^{-1}, PDI = 1.114; Frc. III (12%): M_n = 74,000, M_w = 76700 g mol^{-1}, PDI = 1.037). When NaOCl was used as an oxidant, M_n, M_w and PDI values of P-4-MPIMP were found to be 5250, 5700 g mol^{-1} and 1.086, respectively. Three peaks were observed in the chromatogram of P-4-MPIMP. Seventy percent of the mass of P-4-MPIMP was low molecular weight (Frc. I: M_n = 1050, M_w = 1300 g mol^{-1}, PDI = 1.238) but 30% of its weight was high molecular weight (Frc. II (15%: M_n = 32,500, M_w = 33,600 g mol^{-1}, PDI = 1.034; Frc. III (15%): M_n = 67300, M_w = 74450 g mol^{-1}, PDI = 1.100).

In the FT-IR spectra of oxidative polycondensation product of 2-[(4-mercaptophenyl) imino methyl] phenol are only different by reduction of band strength and number of bands from the FT-IR spectra of 4-MPIMP. In the FT-IR spectra of 4-MPIMP and P-4-MPIMP, bands of –OH and –CH=N groups were observed in 3360 and 1610 cm^{-1}; 3382 and 1615 cm^{-1}, respectively. According to UV–vis measurements, –CH=N bands of 4-MPIMP and P-4-MPIMP were observed in 328 and 345 nm, respectively. Because of conjugated band systems, azomethine group of polymer shifted to higher field. In order to identify the structures of monomer and polymer, the ^{1}H NMR and ^{13}C NMR spectra were recorded in DMSO-d_6. ^{1}H NMR and ^{13}C NMR spectra of the monomer and polymer are given in Figs. 3–5, respectively. In the ^{1}H NMR spectra of 4-MPIMP and P-4-MPIMP, the signals of –OH and –CH=N groups were observed in 13.20 and 8.59 ppm and 14.10 and 8.75 ppm, respectively. Elemental analyses and FT-IR data of monomer, polymer and polymer–metal complex compounds are given in Tables 2 and 3, respectively. The theoretical calculations of polymer–metal complex compounds were made according to two units of polymer. The bands of –OH and –CH=N groups of polymer–metal complex compounds were observed between 3359–3317 cm^{-1} and 1613–1600 cm^{-1}, respectively.

Other phenol derivatives were also polymerized, and the results reported in the literatures [17]. Cross-linking in polymer structure is expected in those cases where the *ortho* and *para* positions in the corresponding monomer structure are unsubstituted. ^{1}H NMR and ^{13}C NMR studies on P-4-MPIMP indicate that the linkage between any two adjacent phenyl rings is largely

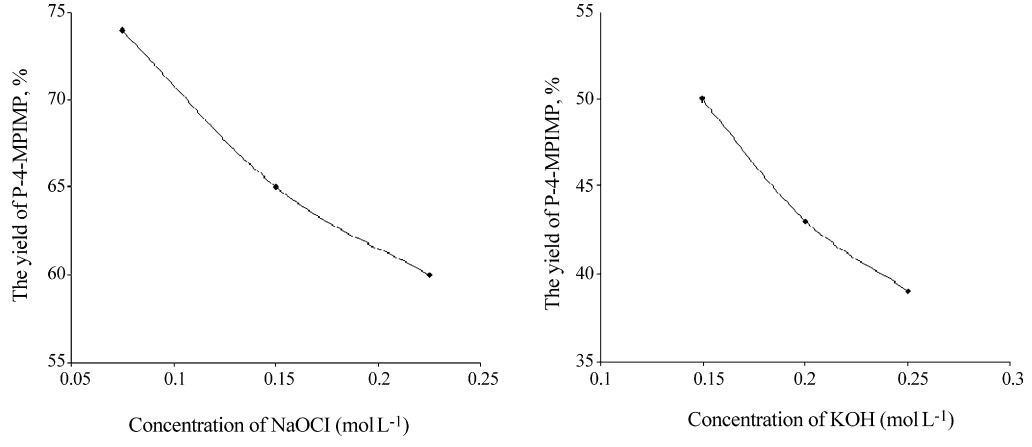


Fig. 2. The effects of concentration of NaOCl and KOH on % yield of P-4-MPIMP at the oxidative polycondensation reaction.

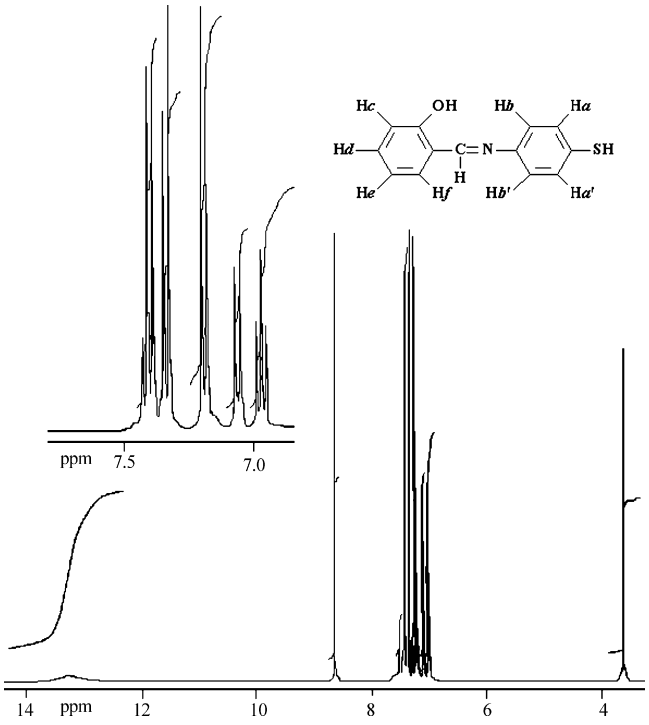


Fig. 3. ^{1}H NMR spectrum of 2-[(4-mercaptophenyl) imino methyl] phenol.

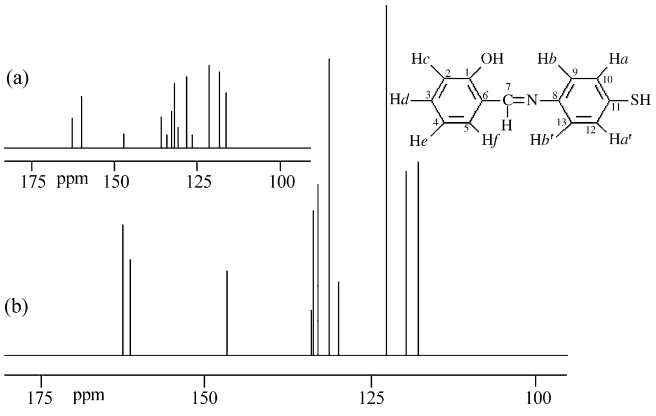


Fig. 4. ^{13}C NMR spectrum of P-4-MPIMP (a) and 4-MPIMP (b).

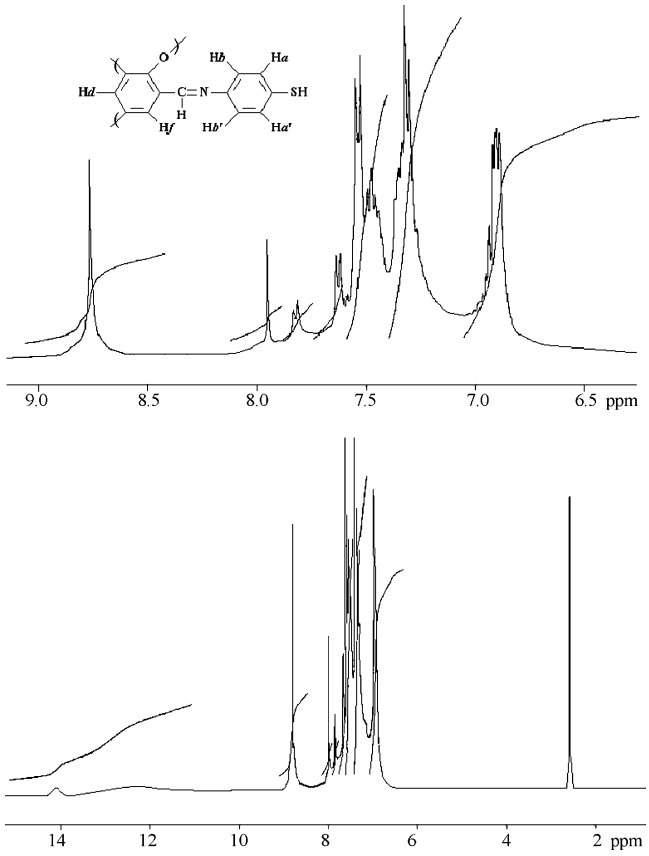
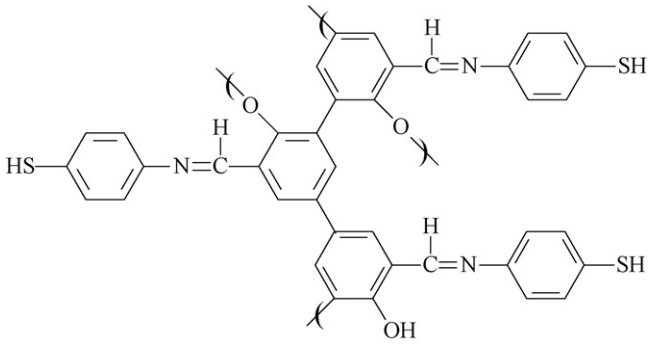


Fig. 5. ^{1}H NMR spectrum of poly-2-[(4-mercaptophenyl) imino methyl] phenol.

at *ortho* and *para* positions (Fig. 4). 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 C4 observed in 117.29 and 129.47 ppm in the monomer and new peaks 126.46 and 134.20 ppm in the polymer, respectively. The hydroxyl groups are involved in the formation of free radicals leading to polymer formation and C–O–C coupling system appeared according to proton integration of peak at the ^{1}H NMR spectrum of polymer. Thus the phenyl rings in the polymer appears to be linked primarily at *ortho* and *para* positions and oxyphenylene. The ^{1}H NMR and ^{13}C NMR results showed that the polymeriza-

Table 2
Elemental analyses data and yields of monomer, polymer and polymer–metal complex compounds

Compounds	Calculated (%, found)					Yield (%)
	C	H	N	S	Metal	
4-MPIMP	68.42 (68.37)	4.38 (4.25)	6.15 (6.00)	14.04 (13.90)	–	90
P-4-MPIMP	69.03 (63.00)	3.55 (3.35)	6.19 (6.05)	14.16 (14.00)	–	84
P-4-MPIMP–Cd	54.99 (54.70)	3.35 (3.15)	4.93 (4.76)	11.28 (11.00)	19.81 (19.40)	39
P-4-MPIMP–Mn	61.18 (60.82)	3.73 (3.59)	5.49 (5.32)	12.55 (12.45)	10.77 (10.50)	46
P-4-MPIMP–Cr	61.54 (61.32)	3.75 (3.63)	5.52 (5.36)	12.62 (12.38)	10.26 (10.00)	33
P-4-MPIMP–Co	60.71 (60.41)	3.70 (3.48)	5.45 (5.27)	12.45 (12.30)	11.47 (11.26)	60
P-4-MPIMP–Ni	60.74 (60.41)	3.70 (3.40)	5.45 (5.22)	12.46 (12.28)	11.42 (11.21)	64
P-4-MPIMP–Zn	59.96 (59.78)	3.65 (3.44)	5.38 (3.15)	12.30 (12.10)	12.56 (12.34)	33
P-4-MPIMP–Zr	57.12 (56.90)	3.47 (3.21)	5.13 (5.00)	11.72 (11.59)	16.70 (16.42)	39
P-4-MPIMP–Pb	47.12 (46.90)	2.87 (2.70)	4.23 (4.08)	9.66 (9.44)	31.19 (13.00)	43
P-4-MPIMP–Cu	60.17 (60.00)	3.67 (3.49)	5.40 (5.27)	12.34 (12.18)	12.25 (12.05)	62



Scheme 4. The structure of poly-2-[(4-mercaptophenyl) imino methyl] phenol.

tion of P-4-MPIMP was proposed by C–C and C–O–C coupling from *ortho* and *para* positions according to –OH group and oxyphenylene, respectively [17]. The reaction mechanism on the coupling selectivity has been studied by Kaya and co-workers and three possible reaction mechanisms for the C–C and C–O–C coupling selectivity. Interconversion combinations of radical units have been proposed as literature (Scheme 4) [18,19].

3.3. Electrochemical properties of 4-MPIMP and P-4-MPIMP and polymer–metal complex compounds

The voltammograms of 4-MPIMP, P-4-MPIMP and polymer–metal complexes were carried out in acetonitrile and DMSO, respectively. The electrochemical HOMO and LUMO energy gaps (E'_g) of all compounds were determined from oxidation and reduction onset values and are shown in Figs. 6–8 and Table 4. The onset potentials of the n-doping (ϕ'_n) and p-doping (ϕ'_p), can be used to determine LUMO and HOMO energy levels of monomer and polymer [17]. HOMO, LUMO energy levels and energy gaps (E'_g) of 4-MPIMP and P-4-MPIMP were found to be between −5.85 and −5.82, −2.63 and −2.87, 3.22 and 2.95 eV, respectively.

The absorption spectra of monomer, polymer and polymer–metal complex compounds were recorded by using methanol and DMSO, respectively, at 25 °C and are given in Table 4 and Fig. 9. The optical band gap (E_g) values of

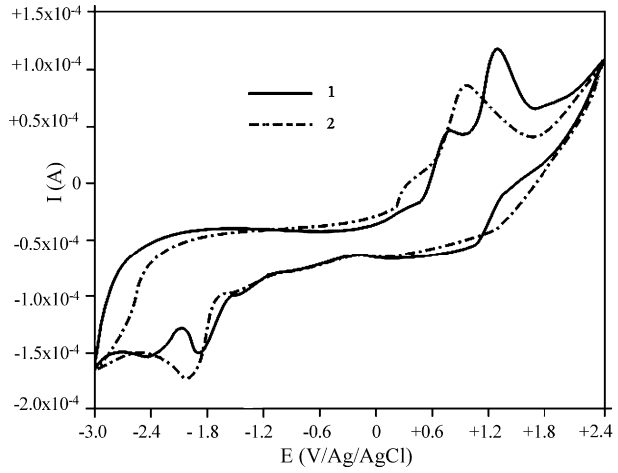


Fig. 6. Cyclic voltammograms of 4-MPIMP (1) and P-4-MPIMP (2).

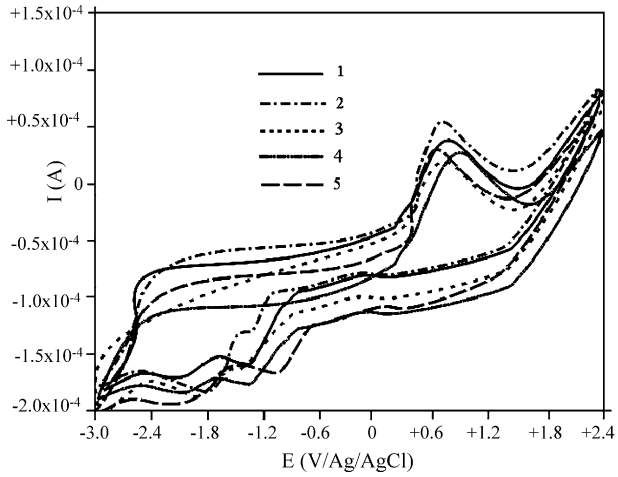


Fig. 7. Cyclic voltammograms of P-4-MPIMP–Co (1), P-4-MPIMP–Ni (2), P-4-MPIMP–Cd (3), P-4-MPIMP–Zn (4) and P-4-MPIMP–Cu (5).

4-MPIMP, P-4-MPIMP, P-4-MPIMP–Co, P-4-MPIMP–Ni, P-4-MPIMP–Cu, P-4-MPIMP–Cd, P-4-MPIMP–Pb, P-4-MPIMP–Zn, P-4-MPIMP–Cr, P-4-MPIMP–Mn and P-4-MPIMP–Zr were found to be 3.12, 3.01, 2.94, 2.99, 2.59, 2.99, 2.63, 2.52, 2.86, 2.96 and 3.15, respectively. According to these values, E_g

Table 3
FT-IR spectral data of monomer, polymer and polymer–metal complex compounds

Compounds	Wave number (cm^{-1})						
	–OH	–CH=N	–C=C	–CO	–SH	–M–O	–M–N
4-MPIMP	3360	1610	1588, 1485	1281	2554	–	–
P-4-MPIMP	3382	1615	1585, 1484	1283	2560	–	–
P-4-MPIMP–Cd	3336	1611	1583, 1486	1280	2562	560	650
P-4-MPIMP–Mn	3359	1610	1586, 1489	1279	2587	563	605
P-4-MPIMP–Cr	3317	1613	1589, 1489	1229	2578	588	615
P-4-MPIMP–Co	3351	1600	1578, 1483	1229	2577	555	650
P-4-MPIMP–Ni	3341	1607	1583, 1485	1237	2588	595	612
P-4-MPIMP–Zn	3340	1606	1579, 1487	1234	2609	590	620
P-4-MPIMP–Zr	3351	1608	1582, 1491	1234	2603	590	610
P-4-MPIMP–Pb	3326	1612	1587, 1489	1224	2569	595	625
P-4-MPIMP–Cu	3357	1606	1578, 1484	1226	2592	580	610

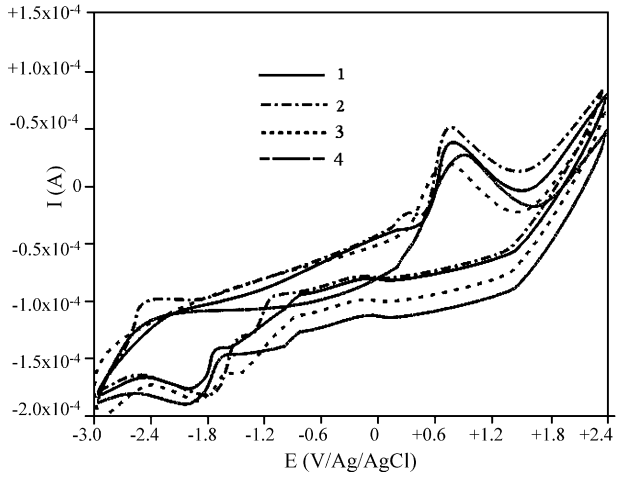


Fig. 8. Cyclic voltammograms of P-4-MPIMP–Pb (1), P-4-MPIMP–Cr (2), P-4-MPIMP–Mn (3) and P-4-MPIMP–Zr (4).

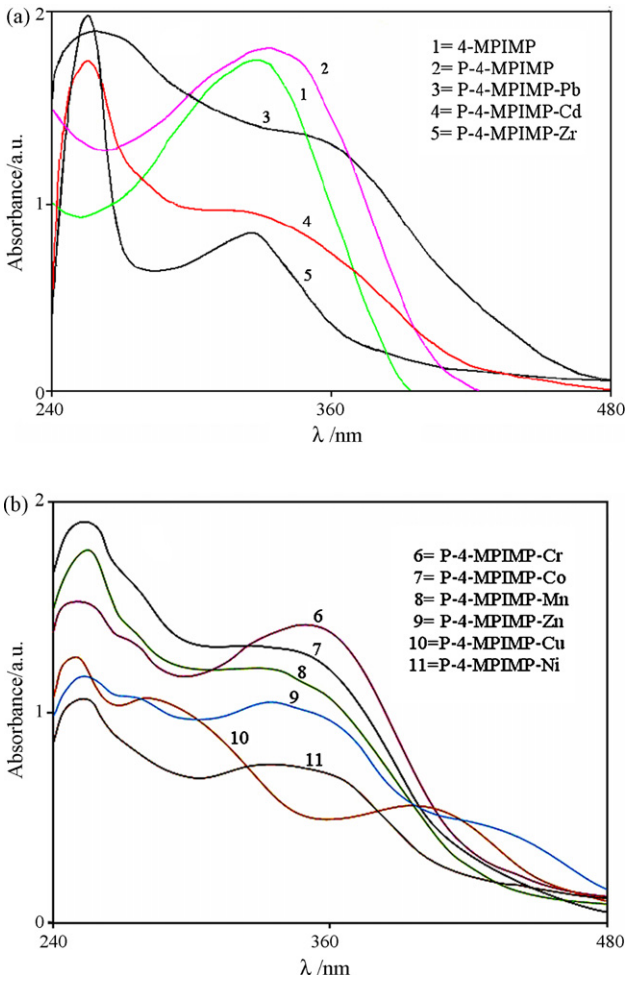


Fig. 9. Absorption spectra of 'a'—(1) 4-MPIMP, (2) P-4-MPIMP, (3) P-4-MPIMP–Pb, (4) P-4-MPIMP–Cd, (5) P-4-MPIMP–Zr and 'b'—(6) P-4-MPIMP–Cr, (7) P-4-MPIMP–Co, (8) P-4-MPIMP–Mn, (9) P-4-MPIMP–Zn, (10) P-4-MPIMP–Cu, (11) P-4-MPIMP–Ni.

value of P-4-MPIMP–Zn was lower than other polymer–metal complex compounds.

P-4-MPIMP and polymer–metal complex compounds have conductivities of 10^{-11} to 10^{-10} S/cm. When doped with iodine, conductivities of the compounds could be increased. Fig. 10 shows the doping results of P-4-MPIMP, P-4-MPIMP–Co, P-4-MPIMP–Ni, P-4-MPIMP–Cu, P-4-MPIMP–Cd, P-4-MPIMP–Pb, P-4-MPIMP–Zn, P-4-MPIMP–Cr, P-4-MPIMP–Mn and P-4-MPIMP–Zr complex compounds with iodine for the various times at 25 °C. Although the structures of P-4-MPIMP, P-4-MPIMP–Co, P-4-MPIMP–Ni, P-4-MPIMP–Cu, P-4-MPIMP–Cd, P-4-MPIMP–Pb, P-4-MPIMP–Zn, P-4-MPIMP–Cr, P-4-MPIMP–Mn and P-4-MPIMP–Zr differ, little significant differences in conductivity were observed. This effect may possibly be due to all of them actually belonging to the same class of polymer and polymer–metal complex compounds. In the doping P-4-MPIMP with iodine, it was found that the conductivity of P-4-MPIMP first increases greatly with doping time, but then tends to level-off. The maximal (or saturated) conductivity was 7.91×10^{-10} S/cm (shown in Fig. 10). The increasing conductivity could indicate that a charge-transfer complex between P-4-MPIMP and dopant iodine is continuously formed. Consequently, Fig. 10 not only shows the conductivity/doping time relationship but also indicates how quickly the doping reaction takes place. The experimental results 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.

Table 4
HOMO, LUMO energy levels, electrochemical (E'_g) and optical band gaps (E_g) and λ_{max} (nm) values of monomer, polymer and polymer–metal complex compounds

Products	HOMO (eV)	LUMO (eV)	(E'_g) (eV)	λ_{max} (nm)	E_g (eV)
4-MPIMP	−6.02	−2.68	3.34	328	3.12
P-4-MPIMP	−5.64	−2.62	3.02	345	3.01
P-4-MPIMP–Co	−5.52	−2.84	2.68	346	2.94
P-4-MPIMP–Ni	−5.51	−2.86	2.65	335	2.99
P-4-MPIMP–Cd	−5.52	−2.77	2.75	342	2.99
P-4-MPIMP–Zn	−5.49	−3.22	2.27	445	2.52
P-4-MPIMP–Cu	−5.48	−3.24	2.24	428	2.59
P-4-MPIMP–Pb	−5.47	−2.92	2.55	364	2.63
P-4-MPIMP–Cr	−5.49	−2.81	2.69	358	2.86
P-4-MPIMP–Mn	−5.46	−2.93	2.53	336	2.96
P-4-MPIMP–Zr	−5.52	−2.62	3.20	334	3.15

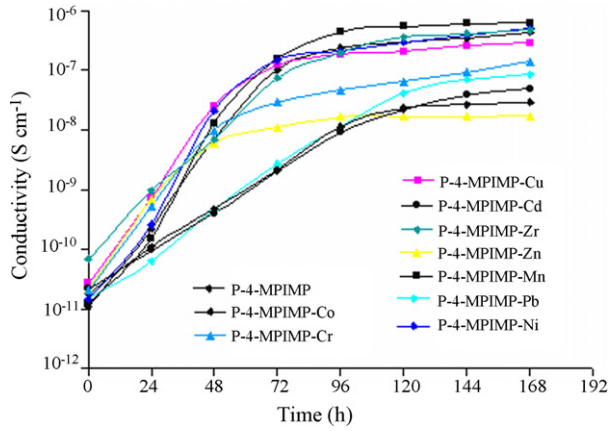
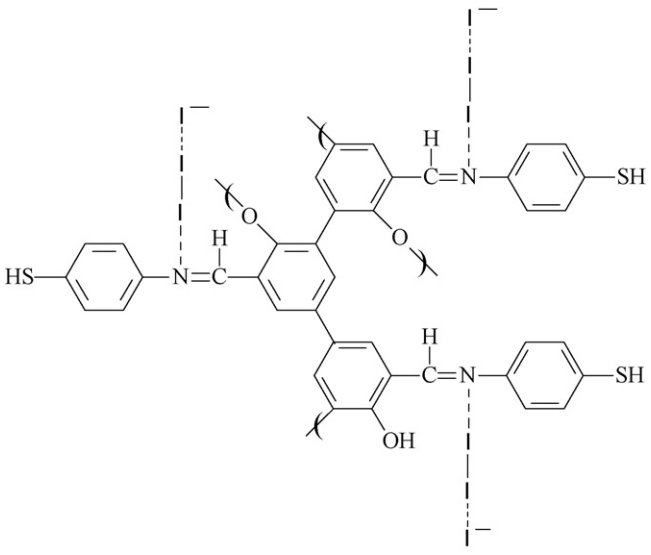


Fig. 10. Electrical conductivities changes of I_2-doped P-4-MPIMP and polymer–metal complexes vs. doping time at 25 °C.

In order to exclude the influence of doping conditions, the conductivity of doped polymer and polymer–metal complex compounds have been related with doping extent (shown in Fig. 10). The maximal (or saturated) conductivity values of P-4-MPIMP, P-4-MPIMP–Co, P-4-MPIMP–Ni, P-4-MPIMP–Cu, P-4-MPIMP–Cd, P-4-MPIMP–Pb, P-4-MPIMP–Zn, P-4-MPIMP–Cr, P-4-MPIMP–Mn and P-4-MPIMP–Zr were found to be 5.37×10^{-7}, 4.39×10^{-8}, 5.91×10^{-7}, 4.10×10^{-7}, 6.10×10^{-8}, 8.29×10^{-8}, 2.19×10^{-8}, 9.76×10^{-8}, 7.85×10^{-7} and 6.12×10^{-7} S/cm, respectively (shown in Fig. 10). According to these values, the highest conductivity was observed in P-4-MPIMP–Mn compound. Diaz et al. had been suggested the conductivity mechanisms of Schiff base polymers for doping with iodine [6]. Nitrogen atom is a very electronegative 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 had been suggested in the literatures as follows [20–22].



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

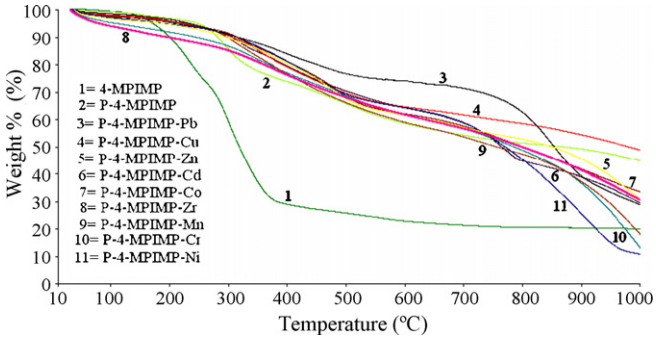


Fig. 11. TGA curves of monomer, polymer and polymer–metal complex compounds.

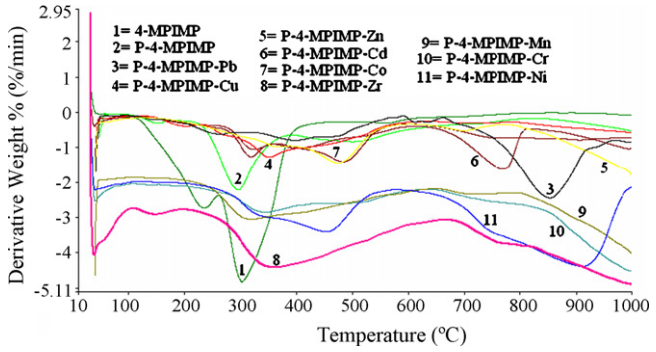


Fig. 12. DTG curves of monomer, polymer and polymer–metal complex compounds.

3.4. Thermal analyses

The thermal degradations of 4-MPIMP, P-4-MPIMP, P-4-MPIMP–Co, P-4-MPIMP–Ni, P-4-MPIMP–Cu, P-4-MPIMP–Cd, P-4-MPIMP–Pb, P-4-MPIMP–Zn, P-4-MPIMP–Cr, P-4-MPIMP–Mn and P-4-MPIMP–Zr were studied by TGA–DTG–DTA analyses at N_2 medium and thermal analyses results and the curves of these analyses are given in Table 5 and Figs. 11–13, respectively. The initial degradation temperature of P-4-MPIMP was higher than 4-MPIMP. Thermal stability of oligo-benzylidene-3′-hydroxyaniline that synthesized from the condensation reaction of benzaldehyde with 3-aminophenol was lower than poly-2-[(4-mercaptophenyl) imino methyl] phenol. The initial degradation temperature and carbines residues

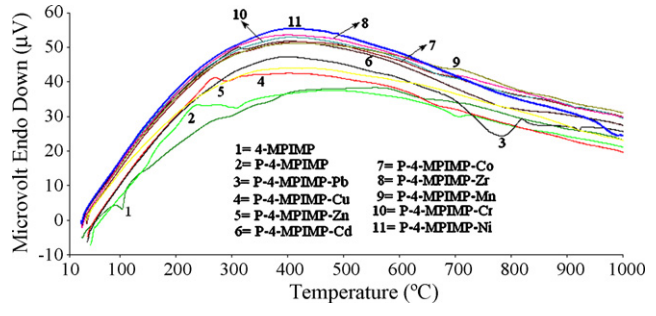


Fig. 13. DTA curves of monomer, polymer and polymer–metal complex compounds.

Table 5
Thermal decomposition values of monomer, polymer and polymer–metal complex compounds

Compounds	TGA					DTA	
	T_{on}[a]	$W_{max.}T$[b]	20% Weight loss	50% Weight loss	% Carbine Resi. at 1000 °C	exo	endo
4-MPIMP	172	232, 302	237	322	19.96	–	103
P-4-MPIMP	257	294, 500	348	920	46.71	–	308, 700
P-4-MPIMP–Co	271	323, 480	430	747	36.73	–	–
P-4-MPIMP–Ni	316	453, 907	426	738	14.73	–	
P-4-MPIMP–Cd	281	317, 404 767	437	787	34.00	–	–
P-4-MPIMP–Zn	309	472, 695	440	896	34.78	–	–
P-4-MPIMP–Cu	269	350	411	–	50.85	–	–
P-4-MPIMP–Pb	219	392, 849	470	863	30.29	–	775
P-4-MPIMP–Cr	284	336	423	803	21.99	–	–
P-4-MPIMP–Mn	258	316, 701	406	800	21.45	–	–
P-4-MPIMP–Zr	291	357	447	915	40.54	–	–

[a] The onset temperature.
[b] Maximum weight temperature.

of oligo-benzylidene-3′-hydroxyaniline had been found to be 120 °C and 40.54%, respectively, at 1000 °C [23]. Both the initial degradation temperature (257 °C) and carbines residues of poly-2-[(4-mercaptophenyl) imino methyl] phenol were higher than that. This polymer formed carbines residue at high amount such as 46.71% at 1000 °C. Because of long conjugated band systems, polymer demonstrated higher resistance against high temperature according to monomer. The high thermal stability of P-4-MPIMP demonstrated to be formed of C–C coupling system. P-4-MPIMP–Pb compound demonstrated higher thermal stability according to other polymer–metal complex compounds. The initial degradation temperature and 50.85% weight loss of P-4-MPIMP–Cu compound was found to be 269 and 1000 °C, respectively. According to TGA curves of compounds, to be high of thermal stability of polymer–metal complex compounds may be indicate the formation of metal–oxygen and metal–nitrogen coordination bond between polymer–metal ions. The presence of water can be seen in TGA and DTG curves of polymer–metal complex compounds (Figs. 11 and 12), showing between 1.5 and 9.5% wt. losses in the 100–175 °C range and corresponding to the loss of water of crystallization (50–150 °C) and coordination water (150–200 °C) (Scheme 3) [24].

4. Conclusion

Poly-2-[(4-mercaptophenyl) imino methyl] phenol was synthesized by using air and NaOCl in an aqueous alkaline medium. The yield of P-4-MPIMP was found to be 84 and 81%, respectively, for NaOCl and air O_2 oxidants. The M_n, M_w and PDI values of P-4-MPIMP were found to be 5750, 6200 g mol^{-1} and 1.078, respectively, using air O_2 and 5250, 5700 g mol^{-1} and 1.086, using NaOCl, respectively. At the oxidative polycondensation reaction of 4-MPIMP, both air O_2 and NaOCl demonstrated to high activities. The spectral analyses such as ^{1}H NMR and ^{13}C NMR have demonstrated to unite from *ortho* and *para* carbons and oxyphenylene of phenol ring each other of formation polymer from oxidative polycondensation of 4-MPIMP. The conductivity value of P-4-MPIMP–Zn compound was higher than P-4-MPIMP, P-4-MPIMP–Co, P-4-MPIMP–Ni, P-4-MPIMP–Cu, P-4-MPIMP–Cd, P-4-MPIMP–Pb, P-4-MPIMP–Cr, P-4-MPIMP–Mn and P-4-MPIMP–Zr compounds. The optical band gap values of monomer and polymer were higher than polymer–metal complex compounds. This is 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 polymer and polymer–metal complex compounds highly promising for photovoltaic applications. According to TGA–DTG–DTA analyses, both polymer and polymer–metal complex compounds demonstrated high stability against thermal degradation.

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