

**SYNTHESIS, CHARACTERIZATION, THERMAL DEGRADATION AND
ELECTRICAL CONDUCTIVITY OF POLY-4-[(PYRIDIN-2-YL-IMINO)METHYL]
BENZENE-1,3-DIOL AND POLYMER-METAL COMPLEXES**

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ABSTRACT. Poly-4-[(pyridin-2-yl-imino)methyl]benzene-1,3-diol (P-4-PIMBD) was synthesized via the oxidative polycondensation reaction by using sodium hypo chloride (NaOCl) oxidant in an aqueous alkaline medium at 70 °C. The yield of the polymer was found to be 68 %. The structures of the compounds were confirmed by FT-IR, UV-Vis, ¹H-NMR and ¹³C-NMR and elemental analysis. The synthesized compounds were characterized by TGA-DTA and solubility tests. ¹H and ¹³C NMR data shows that the polymerization proceeded by the C-C coupling of *ortho* and *para* positions according to -OH groups of 4-[(pyridin-2-yl-imino)methyl]benzene-1,3-diol (4-PIMBD). According to size exclusion chromatography (SEC) measurements, the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of P-4-PIMBD were found as 9400, 12800 g mol⁻¹ and 1.362, respectively. The polymer-metal complex compounds were synthesized with acetates salts of Cd, Co, Cu, Zn and Ni. Thermal analyses of these metal-complex compounds investigated in N₂ atmosphere between 15-1000 °C. Also, FT-IR spectra and electrical conductivities of polymer-metal complexes were measured by four-point technique.

KEY WORDS: Poly-4-[(pyridin-2-yl-imino)methyl]benzene-1,3-diol, Thermal analysis, Oxidative polycondensation, Electrical conductivity

INTRODUCTION

Polyimines or Schiff base polymers, which are also named polyazines, were first reported by Adams *et al.* in 1923 [1]. Research interest in polyazomethines continues owing to their different characteristics such as chelating properties [2, 3], thermal stability [4, 5], liquid crystal properties as well as intrinsic conductivity [6-10]. Polyazomethines are generally synthesized by polycondensation reactions, a method that has some disadvantages, among them being the necessity to ensure special reaction conditions such as high temperature and the use in some cases of special catalysts [11]. Recently, a new method of synthesizing polyazomethines was reported, that is, oxidative polycondensation of monomers containing azomethine links [12]. Because of the use of oxidants such as NaOCl, H₂O₂ and air O₂, there are some significant advantages of this method. For example, these oxidants are cheap and easily available. Phenols and Schiff base substituted phenols were polymerized easily by using these oxidants [13]. Polymer metal complex compounds have useful properties such as catalytic activity, thermal stability, ion selectivity, conductivity and anti-microbial properties. Catalytic activity of a styrene-allylchloride copolymer supported Co(II) Schiff base complex compound was studied by Gupta *et al.* [14]. The thermal and conductivity properties of Zn(II), Ni(II), Th(II), Cd(II), Mg(II) complex compounds of poly (8-acryloxyquinoline) were studied by Kaliyappan *et al.* [15]. The thermal and anti-microbial properties of oligophenols with a Schiff base substitute and their polymer-metal complex compounds were investigated by Kaya *et al.* [16]. The thermal stability of poly(acryloyl benzoic hydrazide) and its complexes with some transition metals was examined by Gad *et al.* [17]. The thermal decomposition behavior of poly(acrylic acid) and its metal complexes were studied by Sebastian *et al.* [18]. Kaya *et al.* studied thermal degradation

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of oligo-2-[(4-fluorophenyl) imino methylene] phenol and some of its oligomer-metal complexes [19]. The conducting properties of poly(2-hydroxy-4-acryloxyacetophenone-phenylimine), poly(2-hydroxy-4-acryloyloxyacetophenone-N-phenylimine-co-methacrylate) and their polymer-metal complexes were studied by Thamizharasi *et al.* [20]. More functional oligophenols may be used to clean poisonous heavy metals in industrial wastewater. In addition, Schiff base compounds had been used for the determination of transition metals in some natural food samples [21]. Therefore, the syntheses of polymer-metal complexes and azomethine polymers are very important in analytic, environmental and food chemistry.

In this study, the structures of 4-PIMBD and P-4-PIMBD were characterized by using FT-IR, UV-Vis, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, elemental analysis, TGA and DTA. The molecular weight distribution of P-4-PIMBD was determined by SEC technique. For characterization of the polymer-metal complexes were made FT-IR, DTA and TG analyses. The electrical conductivities of P-4-PIMBD and polymer-metal complexes measured with four-point technique. The aim of this study was to synthesize polyazomethine and polymer-metal complex compounds and to investigate their thermal and conductivity properties.

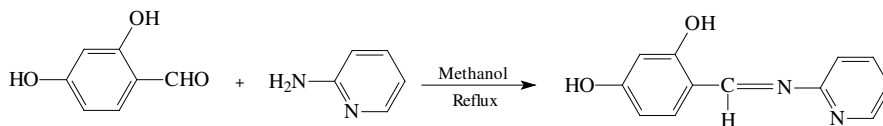
EXPERIMENTAL

Materials

All chemicals 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).

Synthesis of 4-PIMBD

4-PIMBD was prepared by the condensation of 1,4-dihydroxybenzaldehyde (1.38 g, 0.01 mol) with 2-aminopyridine (0.94 g, 0.01 mol) in methanol (25 mL) achieved by boiling the mixture under reflux for 3 h at 70 °C (Scheme 1). The precipitated 4-PIMBD was filtered, recrystallized from methanol and dried in a vacuum desiccator (yield 80 %). $^1\text{H-NMR}$ (DMSO) δ : 13.50 (s, 1H, -OH); 9.35 (s, 1H, -CH=N-); 5.94 (s, 1H, Ar-Ha); 6.47 (d, 1H, Ar-Hb); 8.49 (d, 1H, Ar-Hc); 6.64 (d, 1H, Ar-Hd); 7.90 (t, 1H, Ar-He); 7.37 (t, 1H, Ar-Hf); 9.28 (d, 1H, Ar-Hg). $^{13}\text{C-NMR}$ (DMSO) δ : 165.69 (C1-OH-*ipso*), 102.67 (C2-H), 159.97 (C3-OH-*ipso*), 108.64 (C4-H), 133.32 (C5-H), 115.68 (C6-*ipso*), 191.48 (C7-H), 163.74 (C8-*ipso*), 122.49 (C9-H), 137.68 (C10-H), 112.29 (C11-H), 147.69 (C12-H).

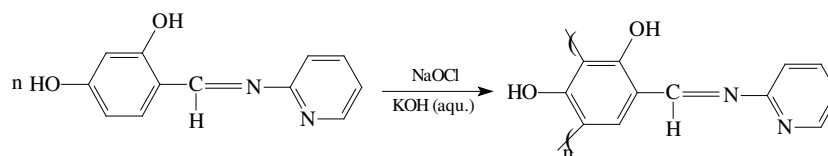


Scheme 1. Synthesis of 4-[(pyridin-2-yl-imino)methyl]benzene-1,3-diol.

Synthesis of P-4-PIMBD with NaOCl in an aqueous alkaline medium

P-4-PIMBD was synthesized through oxidative polycondensation of 4-PIMBD with an aqueous solution of NaOCl (oxidant) (30 %) [12]. The 4-PIMBD (0.138 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

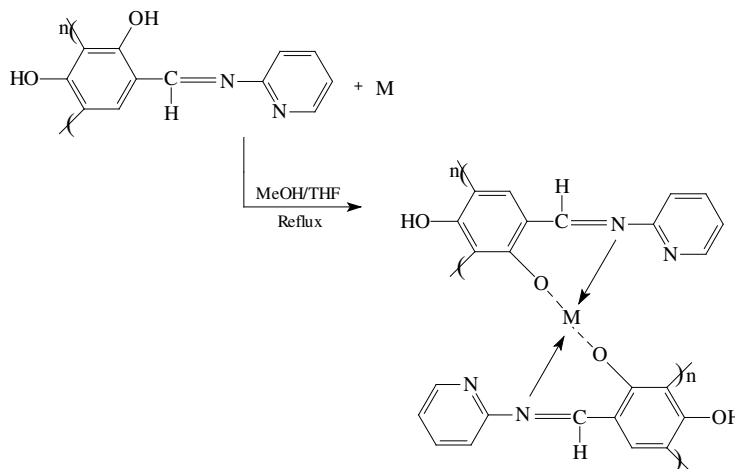
funnel containing NaOCl. After heating to 40 °C, NaOCl was added dropwise over about 20 min. The reaction mixtures were stirred at the various temperatures and durations (Scheme 2). The reaction mixtures were cooled to room temperature, and then 0.001 mol HCl (37 %) was added. For the separation of mineral salts and unreacted monomers, the mixture was filtered and washed with hot water (3 x 25 mL) and then dried in an oven at 110 °C. ¹H-NMR (DMSO) δ: 11.50 (s, 1H, -OH); 9.83 (s, 1H, -OH); 9.94 (s, 1H, -CH=N-); 8.15 (s, 1H, Ar-Hc); 6.44 (d, 1H, Ar-Hd); 7.01 (t, 1H, Ar-He); 6.87 (t, 1H, Ar-Hf); 7.93 (d, 1H, Ar-Hg). ¹³C-NMR (DMSO) δ: 168.05 (C1-OH-ipso), 112.57 (C2-ipso), 163.88 (C3-OH-ipso), 136.27 (C4-ipso), 136.52 (C5-H), 115.25 (C6-ipso), 195.25 (C7-H), 166.24 (C8-ipso), 124.47 (C9-H), 144.55 (C10-H), 113.89 (C11-H), 154.32 (C12-H).



Scheme 2. Synthesis of poly-4-[(pyridin-2-yl-imino)methyl]benzene-1,3-diol.

Syntheses of poly-4-[(pyridin-2-yl-imino)methyl]benzene-1,3-diol-metal complexes

Solutions of $M(\text{OAc})_2 \cdot x\text{H}_2\text{O}$ (M : Co, Ni, Cu, Zn and Cd; x : 4 and 2) (1 mmol) in MeOH (10 mL) were added to a solution of P-4-PIMBD (2 mmol/unit) in THF (20 mL). The mixture was stirred and heated at 70 °C for 5 h (Scheme 3). The precipitated complex was filtered, washed with cold methanol/THF (1:1) and dried in a vacuum oven at 110 °C.



Scheme 3. Syntheses of polymer-metal complex compounds.

Structure of P-4-PIMBD

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) were determined by size exclusion chromatography (SEC) techniques of the Shimadzu Co. For SEC investigations we used an SGX (100 Å and 7 nm diameter loading

material) 3.3 mm i.d. x 300 mm column; eluent: DMF/methanol (v/v, 4/1, 0.4 ml/min), polystyrene standards. A refractive index detector was used to analyze the polymer at 25 °C. SEC analyses of P-4-PIMBD were performed at 30 °C using DMF/methanol (v/v, 4/1) as eluent at a flow rate of 0.4 mL/min.

Elemental analysis was carried out with Carlo Erba 1106 (Carlo Erba Co.). The ultraviolet-visible spectra of the compounds were measured by Perkin Elmer Lambda 25. The infrared spectra were measured by a Perkin Elmer FT-IR Spectrum One. The FT-IR spectra were recorded using universal ATR sampling accessory (4000-550 cm^{-1}). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra (Bruker Avance DPX-400 and 100.6 MHz, respectively) were recorded at 25 °C by using deuterated DMSO as a solvent. TMS was used as internal standard. Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between 20-1000 °C (in N_2 , rate 10 °C/min).

Electrical properties

Conductivity was measured on a Keithley 2400 Electrometer. 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 dessicator [7].

RESULTS AND DISCUSSION

Structure of P-4-PIMBD

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) were determined by size exclusion chromatography (SEC). In the oxidant NaOCl, M_n , M_w and PDI values of P-4-PIMBD were found to be 9400, 12800 g mol^{-1} and 1.362, respectively. Two peaks were observed in the chromatogram of P-4-PIMBD. 75 % of the mass of P-4-PIMBD was low molecular weight ($M_n = 2650$, $M_w = 3000$ g mol^{-1} , PDI = 1.132), but 25 % of its weight was high molecular weight ($M_n = 67300$, $M_w = 93100$ g mol^{-1} , PDI = 1.383). When reaction temperatures and reaction times increased, molecular weight distribution (MWD) of P-4-PIMBD increased, but the conversion of P-4-PIMBD decreased. The increasing of polymerization time, temperatures and oxidant concentrations increased at the molecular weight and MWD of P-4-PIMBD.

4-PIMBD was bright yellow color in crystal form and was completely soluble in organic solvents such as methanol, ethanol, acetone, THF, CH_2Cl_2 , DMF, and DMSO but it was partly soluble in ethyl acetate, chloroform, 1-butanol, 2-propanol and acetonitrile. It was insoluble in toluene, benzene, CCl_4 , heptane and hexane. P-4-PIMBD was dark brown in powder form and was completely soluble in organic solvents such as THF, DMF and DMSO. It was partly soluble in acetone and methanol but it was insoluble in chloroform, acetonitrile, ethanol, 1-butanol, 2-propanol, ethyl acetate, toluene, benzene, CCl_4 , heptane and hexane. Polymer-metal complex compounds were insoluble in any of selected organic solvents.

The UV-vis spectroscopic studies were carried out with methanol and DMSO solutions of the 4-PIMBD and P-4-PIMBD, respectively. In the UV-vis spectra of 4-PIMBD spectra, K bands of phenol and $\text{C}_6\text{H}_5\text{-N=}$ were observed in 205 nm and 296 nm, respectively. A benzene band of 4-PIMBD and R band of -CH=N- groups were observed, 232 and 351 nm, respectively. UV-vis spectra of P-4-PIMBD, K and R bands were observed, 235 nm and 346 nm, respectively. The band of -CH=N- group observed 372 nm. The UV-vis spectra shows specific bands for λ_{max} assigned to aromatic and azometinic $\pi\text{-}\pi^*$ transitions at about 280 and 350 nm,

respectively [22]. The shifting of the -CH=N- group band from 351 nm to 372 nm has been demonstrated for the formation of the polymeric conjugated π -system.

In the FT-IR spectra of 4-PIMBD and P-4-PIMBD, bands of -OH and -CH=N groups were observed 3252 and 1615; 3153 and 1608 cm^{-1} , respectively. Elemental analyses and FT-IR data of monomer, polymer and polymer-metal complex compounds are given in Table 1 and 2, respectively. In the $^1\text{H-NMR}$ spectra of 4-PIMBD and P-4-PIMBD, the signals of phenyl -OH and -CH=N groups were observed 13.50 and 9.35 ppm and 11.50, 9.83 and 9.94 ppm, respectively. The $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra results of the P-4-PIMBD confirm the formation of polymer units. Other phenol derivatives were also polymerized, and the results are reported in the literature [23]. Crosslinking in the polymer structure is expected in those cases where the *ortho* and *para* positions in the corresponding monomer structure are unsubstituted. $^{13}\text{C-NMR}$ studies on P-4-PIMBD indicate that the linkage between any two adjacent phenyl rings is largely at *ortho* and *para* positions. The peak values of C2 and C4 atoms observed in 102.67 and 108.64 ppm in the monomer and 112.57, 136.27 ppm in the polymer, respectively. According to *meta* carbon atom of monomer, there was much a little change such as 3.2 ppm in the peak value of C5- *meta* carbon. Although the hydroxyl groups are involved in the formation of free radicals leading to polymer formation, they do not appear to be involved in bond formation. Thus, the phenyl rings in the polymer appear to be linked primarily at *ortho* and *para* positions [23, 24] (Scheme 2).

Table 1. Elemental analyses data and yields of monomer, polymer and polymer-metal complex compounds.

Compounds	Calculated (found) (%)				Yield, %
	C	H	N	Metal	
4-PIMBD	67.29 (67.10)	4.67 (4.50)	13.08 (12.90)	-	80
P-4-PIMBD	67.93 (67.69)	3.77 (3.54)	13.21 (12.95)	-	68
P-4-PIMBD-Cu	52.45 (52.05)	2.55 (3.00)	10.20 (10.00)	23.15 (21.50)	85
P-4-PIMBD-Zn	52.10 (51.85)	2.53 (2.30)	10.13 (9.75)	23.66 (22.88)	70
P-4-PIMBD-Cd	44.53 (44.15)	2.16 (2.00)	8.66 (8.25)	34.76 (34.45)	72
P-4-PIMBD-Ni	53.40 (53.10)	2.60 (2.18)	10.38 (10.00)	21.76 (21.10)	65
P-4-PIMBD-Co	53.35 (53.02)	2.59 (2.44)	10.37 (10.05)	21.83 (21.04)	74

Table 2. FT-IR spectral data of monomer, polymer and polymer-metal complex compounds.

Compounds	Wavenumber (cm^{-1})						
	-OH	Ar-C-H	-CH=N	-C=C	-C-O	Metal-O	Metal-N
4-PIMBD	3252	3050	1615	1589,1517, 1498	1244	---	---
P-4-PIMBD	3153	3083	1608	1594, 1474,1437	1218	---	---
P-4-PIMBD-Cd	3201	3098	1605	1580, 1537,1482	1232	553	672
P-4-PIMBD-Co	3225	3025	1588	1541,1467,1436	1220	560	652
P-4-PIMBD-Cu	3203	3043	1585	1538, 1467,1429	1219	570	625
P-4-PIMBD-Ni	3216	3015	1591	1540, 1467,1436	1217	550	645
P-4-PIMBD-Zn	3192	3093	1602	1587, 1543,1435	1225	580	663

Thermal analyses of 4-PIMBD and P-4-PIMBD

TG-DTG-DTA curves and data of monomer, polymer and polymer-metal complex compounds are given in Figures 1, 2, 3 and Table 3. The onset temperature, 50 % and 56.98 % weight loss of 4-PIMBD was found to be 109, 700 and 1000 $^{\circ}\text{C}$, respectively. The onset degradation temperature and 44.27 % weight loss of P-4-PIMBD was found to be 206 and 1000 $^{\circ}\text{C}$,

respectively. In TGA curve of P-4-PIMBD observing of weight loss such as 13.6 % in the 50 - 150 °C assigned to removal of absorbed water. Because of long conjugated band systems, polymer demonstrated higher resistance against high temperature than monomer. According to TG analysis, both onset temperature of P-4-PIMBD was higher than monomer and it was more stable than monomer through to temperature and thermal decomposition. It formed carbines residue at high amount such as 55.73 % at 1000 °C. P-4-PIMBD-Cu compound demonstrated higher thermal stability according to other polymer-metal complex compounds. The onset temperature of P-4-PIMBD-Ni compound was found to be 338 °C. The onset temperature and 37.65 % weight loss of P-4-PIMBD-Cu compound was found to be 227 and 1000 °C, respectively. According to TGA curves, to be high of thermal stability of polymer-metal complex compounds may be indicate the formation of metal-oxygen valance 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 (Figures 1 and 2), showing between 5.0 and 19.5 wt.% losses in the 50-200 °C range and corresponding to the loss of water of crystallization (50-150 °C) and coordination water (150-200 °C). This can also explain the differences appeared between the found and calculated elemental analysis values. P-4-PIMBD-Zn demonstrated lower thermal stability against thermal degradation than other polymer-metal complex compounds. According to TG analyses weight loses of polymer-metal complex compounds changed at 1000 °C as follows: P-4-PIMBD-Cu > P-4-PIMBD-Ni > P-4-PIMBD-Co > P-4-PIMBD-Cd > P-4-PIMBD-Zn.

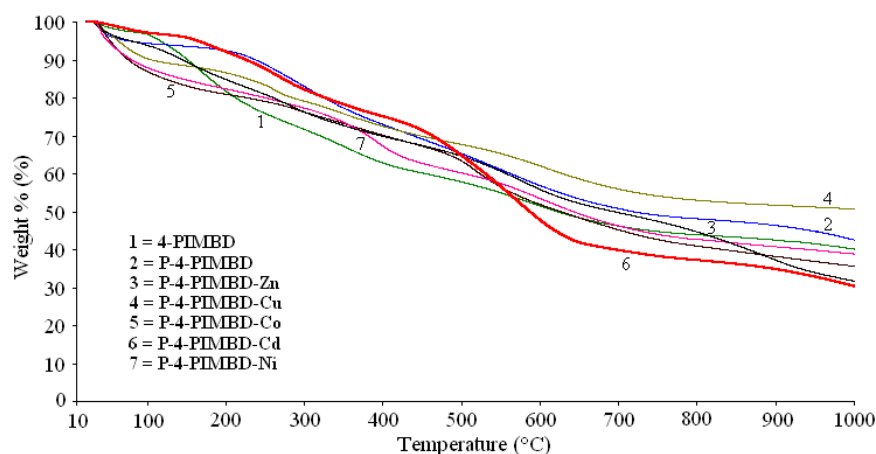


Figure 1. TGA curves of monomer, polymer and polymer-metal complex compounds.

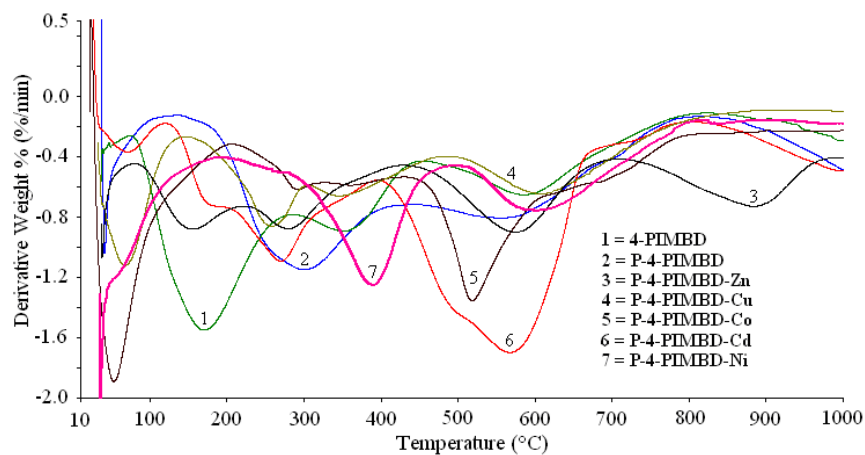


Figure 2. DTG curves of monomer, polymer and polymer-metal complex compounds.

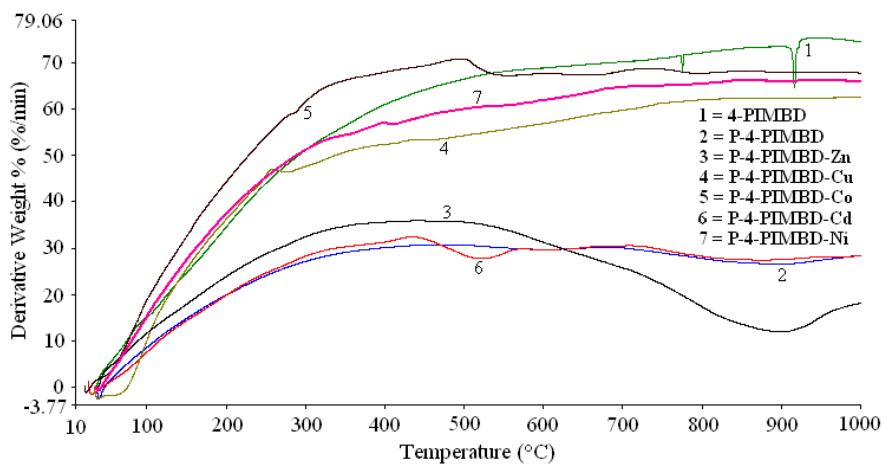


Figure 3. DTA curves of monomer, polymer and polymer-metal complex compounds.

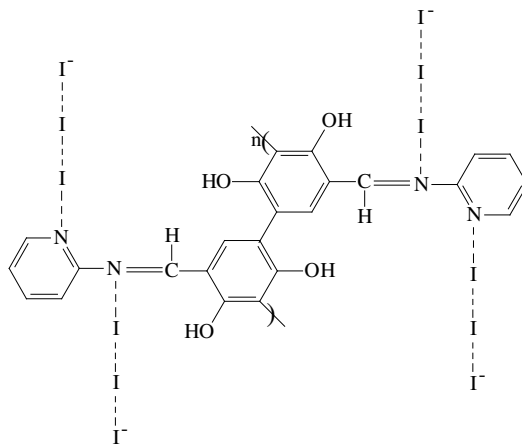
Table 3. Thermal decomposition values of monomer, polymer and polymer-metal complex compounds.

Compounds	TGA			DTA			
	^a T _{on}	^b W _{max} .T	20 % weight loss	50 % weight loss	% Carbene Residue at 1000°C	Exo	Endo
4-PIMBD	109	169, 351, 582	236	700	43.02	-	-
P-4-PIMBD	206	299	243	-	55.73	-	-
P-4-PIMBD-Cu	227	258, 342, 604	486	-	62.35	260	-
P-4-PIMBD-Co	255	517	509	-	54.85	-	-
P-4-PIMBD-Cd	185	268, 564	359	610	33.72	436, 716	-
P-4-PIMBD-Ni	338	290, 593	437	-	56.23	-	-
P-4-PIMBD-Zn	120	152, 277, 575, 887	317	797	37.11	437	-

^aThe onset temperature. ^bMaximum weight temperature.

Electrical properties of polymer and polymer-metal complex compounds

Polymer and polymer-metal complex compounds have conductivities of 10^{-11} - 10^{-10} S/cm. When doped with iodine, their conductivities could be increased by about eight orders of magnitude (up to 10^{-5} S/cm). Figure 4 shows the doping results for P-4-PIMBD and P-4-PIMBD-Co, P-4-PIMBD-Ni, P-4-PIMBD-Zn, P-4-PIMBD-Cd and P-4-PIMBD-Cu complex compounds with iodine for the various times at 25 °C. Although the structure of P-4-PIMBD and P-4-PIMBD-Co, P-4-PIMBD-Ni, P-4-PIMBD-Zn, P-4-PIMBD-Cd and P-4-PIMBD-Cu differ, little significant difference in conductivity was observed. This effect may possibly be due to all of them actually belonging to the same class of polymer and polymer-metal complexes. In the doping of polymer with iodine, it was found that the conductivity of P-4-PIMBD first increases greatly with doping time, but then tends to level off. The maximal (or saturated) conductivity values of P-4-PIMBD and P-4-PIMBD-Co, P-4-PIMBD-Ni, P-4-PIMBD-Zn, P-4-PIMBD-Cd and P-4-PIMBD-Cu were found to be 2.53×10^{-9} , 2.59×10^{-6} , 1.90×10^{-5} , 3.83×10^{-7} , 1.33×10^{-6} and 9.14×10^{-8} S/cm (shown in Figure 4). According to these values, the highest conductivity was observed in P-4-PIMBD-Ni compound. The increasing conductivity could indicate that a charge-transfer complex between P-4-PIMBD and dopant iodine is continuously formed. Consequently, Figure 4 not only shows the conductivity/doping time relationship but also indicate how quickly the doping reaction takes place. The 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. In order to exclude the influence of doping conditions, the conductivity of doped P-4-PIMBD and P-4-PIMBD-Co, P-4-PIMBD-Ni, P-4-PIMBD-Zn, P-4-PIMBD-Cd and P-4-PIMBD-Cu have been related with doping extent (shown in Figure 4). The highest conductivity was observed in P-4-PIMBD-Zn compound. Diaz *et al.* had suggested the conductivity mechanisms of Schiff base polymers for doping with iodine [7]. Nitrogen is a very electronegative element and it is capable of coordinating an iodine molecule. Coordination of iodine during P-4-PIMBD doping is as follows (Scheme 4): on the nitrogen atom coordination of iodine with Schiff base polymers and pyridine solutions had been suggested at the literatures [25 - 27].



Scheme 4. Coordination of iodine during P-4-PIMBD doping.

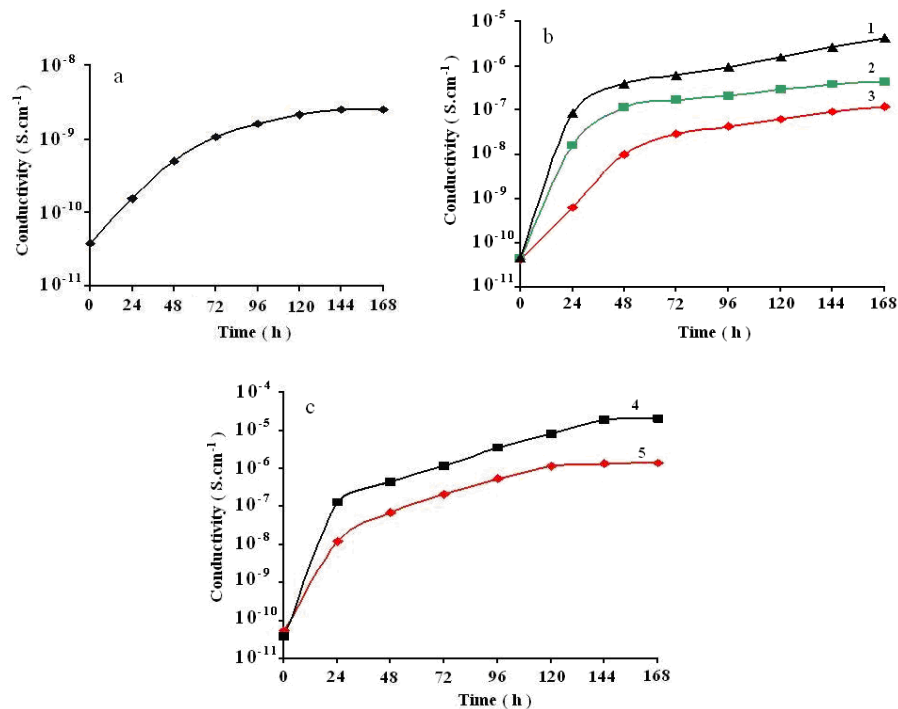


Figure 4. Electrical conductivity of I₂-doped (a) polymer, (b) [P-4-PIMBD-Co (1), P-4-PIMBD-Zn (2) and P-4-PIMBD-Cu (3)] and (c) [P-4-PIMBD-Ni (4) and P-4-PIMBD-Cd (5)] vs. doping time at 25 °C.

CONCLUSIONS

The polymer of 4-[(pyridin-2-yl-imino)methyl]benzene-1,3-diol was synthesized with NaOCl oxidant in an aqueous alkaline medium. The maximum yield of P-4-PIMBD was 68 %. The M_n , M_w and PDI values of 4-PIMBD were found to be 9400, 12800 g mol⁻¹ and 1.362, respectively. The spectral analyses such as ¹H-NMR and ¹³C-NMR have demonstrated the ability to unite from *ortho* and *para* carbons of phenol ring each other in the formation of polymer from oxidative polycondensation of 4-PIMBD. The results of TG-DTA measurements showed to have enough resistance against thermal decomposition of P-4-PIMBD. The carbene residue of polymer formed is at high amount such as 55.73 % at 1000 °C. According to TG analyses, weight losses of polymer-metal complex compounds changed at 1000 °C as follows: P-4-PIMBD-Cu > P-4-PIMBD-Ni > P-4-PIMBD-Co > P-4-PIMBD-Cd > P-4-PIMBD-Zn. As a result, P-4-PIMBD-Cu demonstrated higher thermal stability against thermal degradation than monomer and other polymer-metal complex compounds.

REFERENCES

1. Grigoras, M.; Antonoaia, N.C. *Eur. Polym. J.* **2005**, 41, 1079.
2. Marcu, M.; Cazacu, M.; Vlad, A.; Racles, C. *Applied Organometallic Chem.* **2003**, 17, 693.
3. Cazacu, M.; Marcu, M.; Vlad, A.; Toth, A.; Racles, C. *J Polym. Sci. Part A: Polym. Chem.* **2003**, 41, 3169.
4. Racles, C.; Cozan, V.; Cazacu, M.; Földes, E.; Sajo, I. *High Performance Polym.* **2002**, 14, 397.
5. Marin, L.; Cozan, V.; Bruma, M.; Grigoras, V.C. *Eur. Polym. J.* **2006**, 42, 1173.
6. Shukla, U.; Rao, K.V.; Rakshit, A.K. *J Appl. Polym. Sci.* **2003**, 88, 153.
7. Diaz, F.R.; Moreno, J.; Tagle, L.H.; East, G.A.; Radic, D. *Synt. Metals.* **1999**, 100, 187.
8. Sun, S.J.; Chang, T.C.; Li, C.H. *Eur. Polym. J.* **1993**, 29, 951.
9. Aly, K.; Khalaf, A.A.; Alkskas, I.A. *Polym. J.* **2003**, 39, 1035.
10. El-Shekeil, A.; Al-Aghbari, S. *Polym. Int.* **2004**, 53, 777.
11. Grigoras, M.; Catanescu, O.C.; Colotin, G. *Macromol. Chem. Phys.* **2001**, 202, 2262.
12. Kaya, İ.; Gül, M. *Eur. Polym. J.* **2004**, 40, 2025.
13. Kaya, İ.; Şenol, D. *J. Appl. Polym. Sci.* **2003**, 90, 442.
14. Gupta, K.C.; Abdulkadir, H.K.; Chand, S.J. *J. Macromol. Sci. Part A: Pure and Appl. Chem.* **2003**, A40, 475.
15. Kaliyappan, T.; Raman, A.; Kannan, P.J.; Kannan, P. *J. Macromol. Sci. Part A: Pure and Appl. Chem.* **1999**, A36, 517.
16. Kaya, İ.; Cihangiroğlu, N. *J. Polym. Res.* **2004**, 11, 37.
17. Gad, A.M.; El-Dissouky, A.; Mansour, E.M.; El-Magrophy, A. *Polym. Deg. and Stab.* **2000**, 68, 153.
18. Sebastian, N.; George, B.; Mathew, B. *Polym. Deg. and Stab.* **1998**, 60, 371.
19. Kaya, İ.; Bilici, A. *J. Macromol. Sci. Part A: Pure and Appl. Chem.* **2006**, 43, 719.
20. Thamizharasi, A.; Venkata, R.R.A.; Balasubramanian, A. *Eur. Polym. J.* **1998**, 34, 503.
21. Fakhari, A.R.; Khorrami, A.R.; Naeimi, H. *Talanta.* **2005**, 66, 813.
22. Cazacu, M.; Marcu, M.; Vlad, A.; Rusu, G.I.; Avadanei, M. *J. Organometallic Chem.* **2004**, 689, 3005.
23. Ayyagari, M.S.; Marx, K.A.; Tripathy, S.K.; Akkara, J.A.; Kaplan, D.L. *Macromolecules* **1995**, 28, 5192.
24. Kaya, İ.; Bilici, A. *Synt. Metals.* **2006**, 156, 736.
25. Sakai, H.; Matsuyama, T.; Maeda, Y.; Yamoaka, H. *J. Chem. Phys.* **1981**, 75, 5155.
26. Reid, C.; Mulliken, R.S. *J. Am. Chem. Soc.* **1954**, 76, 3869.
27. Tassaing, T.; Besnard, M. *J. Phys. Chem. A*, **1997**, 101, 2803.