

## SYNTHESIS, CHARACTERIZATION AND THERMAL DEGRADATION OF OLIGO-2-[(4-IODOPHENYLIMINO)METHYL]PHENOL AND OLIGOMER-METAL COMPLEXES

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**ABSTRACT.** The conditions for oxidative condensation of 2-[(4-iodophenylimino)methyl]phenol (IPIMP) were studied with air and NaOCl as oxidants in an aqueous alkaline medium between 50 and 90 °C. Size exclusion chromatography (SEC) showed that the number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ) and polydispersity index (PDI) values, respectively, were 1250, 1300 g mol<sup>-1</sup> and 1.040 for oxidation with NaOCl and 2200, 2500 g mol<sup>-1</sup> and 1.136 for oxidation by air. With the optimum reaction conditions, the yield of OIPIMP was found to be 67 % with NaOCl, and 29 % with air, as oxidant. The OIPIMP was characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FT-IR, UV-Vis and elemental analysis. Metal complexes of the oligomer were shown to be more thermally stable than OIPIMP itself.

**KEY WORDS:** Oligo-2-[(4-iodophenylimino)methyl]phenol, Thermal analysis, Oxidative polycondensation, Oligomer-metal complexes

### INTRODUCTION

Oligophenols containing conjugated bonding and active hydroxyl groups have been studied for more than 60 years because of useful properties such as paramagnetism, semiconductivity, and electrochemical properties. Because of these properties, they are used to prepare composites having high thermal stability [1], graphite materials, adhesives, epoxy oligomer and block copolymers, photoresists [2], and materials which are antistatic [3] and flame resistant [4-6]. Schiff base polymers show anti-microbial activities against various bacteria, yeast and fungus [7, 8]. Oligophenols which have a high loading of a particular functional group may be used for removal of poisonous heavy metals in the industrial waste waters. Because of their use as sensors [9], the synthesis of oligomer-metal complexes is very important in analytical and environmental chemistry. It seemed advantageous to attempt to design and prepare a polymer-bound chelating ligand, which would be able to form complexes with a variety of transition metals and therefore have a large range of applications [10, 11].

In this paper, we describe the effects of various reaction parameters on the preparation of oligo-2-[(4-iodophenylimino)methyl]phenol in order to determine the optimum reaction conditions. The IPIMP and OIPIMP were characterized by FT-IR, UV-Vis, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectroscopy, elemental analysis and SEC. Oligomer-metal complexes were synthesized from the reactions of OIPIMP with Co(II), Ni(II) and Cu(II) acetates. The thermal stabilities of OIPIMP and its oligomer-metal complexes were studied by TG-DTA.

### EXPERIMENTAL

#### Materials

4-Iodoaniline (4-IA), salicylaldehyde (SA), methanol (MeOH), ethanol, benzene, acetone, toluene, heptane, hexane, tetrahydrofuran, THF, *N,N'*-dimethylformamide, DMF, dimethylsulfoxide, DMSO, H<sub>2</sub>SO<sub>4</sub>, NaOH, KOH, hydrochloric acid (HCl, 37 %),

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$\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ ,  $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$  and  $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$  were supplied by Merck Chemical Co. (Germany) and they were used as received. Sodium hypochlorite ( $\text{NaOCl}$ , (30 %, aqueous solution) was obtained from Paksoy Co. (Turkey). IPIMP was synthesized by the condensation reaction of 4-iodoaniline with salicylaldehyde.

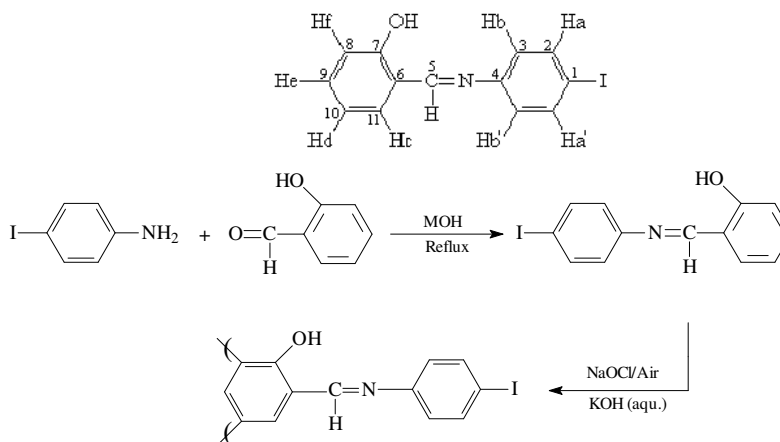
#### Syntheses of 2-[(4-iodophenylimino)methyl]phenol Schiff base

4-IA (0.025 mol) and SA (0.025 mol) were dissolved in MeOH (15 mL) and the mixture was stirred at 70 °C for 3 h (Scheme 1). The precipitated 2-[(4-iodophenylimino)methyl]phenol was filtered off, recrystallized from MeOH and dried in a vacuum desiccator (yield 97 %).

Calcd. for IPIMP: C, 48.30; H, 3.10; N, 4.33. Found: C, 48.00; H, 2.95; N, 4.00. FT-IR (KBr;  $\text{cm}^{-1}$ ):  $\nu(\text{CH}=\text{N})$  1616 s;  $\nu(\text{C}-\text{O})$  1282 s;  $\nu(\text{C}=\text{C})$  1566, 1475, 1410 s;  $\nu(\text{aromatic C}-\text{H})$  3050 s;  $\nu(\text{Ar}-\text{OH})$  3432 s;  $\nu(\text{C}-\text{I})$  743 s. UV-Vis ( $\lambda_{\text{max}}$ ): 209, 237, 273, 325 and 345 nm.  $^1\text{H-NMR}$  ( $\text{DMSO}-d_6$ ):  $\delta$  [For designation of H atoms see Scheme 1] 12.90 (s, 1H, OH), 8.96 (s, 1H, CH=N), 7.80 (d, 2H, Ar-Haa'), 7.24 (d, 2H, Ar-Hbb'), 7.66 (d, 1H, Ar-Hc), 6.96 (t, 1H, Ar-Hd), 7.43 (t, 1H, Ar-He), 6.98 (d, 1H, Ar-Hf).  $^{13}\text{C-NMR}$  ( $\text{DMSO}-d_6$ ):  $\delta$  119.7 (C1-*ipso*), 138.6 (C2), 124.2 (C3), 148.3 (C4-*ipso*), 164.3 (C5), 117.0 (C6-*ipso*), 160.7 (C7-*ipso*), 117.1 (C8), 137.5 (C9), 133.0 (C10), 134.0 (C11).

#### Synthesis of oligo-2-[(4-iodophenylimino)methyl]phenol with NaOCl or air

OIPIMP was synthesized via oxidative polycondensation of IPIMP with a solution of NaOCl (30 %, in water) and air as oxidants (Scheme 1) [11-13]. The IPIMP (0.200 g,  $6.2 \times 10^{-4}$  mol) was dissolved in an aqueous solution of KOH (0.140 g,  $2.48 \times 10^{-3}$  mol, 0.2 mL) heated to 40 °C and NaOCl was added drop by drop over about 20 min. The reaction mixtures were stirred at various temperatures and durations (Table 1). Alternatively, the air was passed into an aqueous solution of KOH (20 %) before passage through the reaction tube to prevent water loss in the reaction mixture and remove  $\text{CO}_2$  (Table 1). The mixture was neutralized with  $2.48 \times 10^{-3}$  mol HCl (0.2 mL, 37 %) at room temperature. Unreacted monomer was separated from the reaction products by washing with MeOH. The mixture was filtered and washed with hot water (3 x 25 mL) to remove mineral salts and then dried in an oven at 105 °C.



Scheme 1. Synthesis of 2-[(4-iodophenylimino)methyl]phenol and oligo-2-[(4-iodophenylimino)methyl]phenol.

Table 1. The oxidative polycondensation of 2-[(4-iodophenylimino)methyl]phenol<sup>a</sup> using NaOCl (sample number: 1–16) and air (sample number: 17–24) in an aqueous KOH.

Sample number	[KOH] (mol L <sup>-1</sup> )	[NaOCl] <sub>0</sub> (mol L <sup>-1</sup> )/Air (L h <sup>-1</sup> )	Temp. (°C)	Time (h)	The yield of OIPIMP (%)
1	0.168	0.042	60	5	60
2	0.168	0.042	70	5	63
3	0.168	0.042	80	5	53
4	0.168	0.042	90	5	43
5	0.168	0.042	70	1	52
6	0.168	0.042	70	3	67
7	0.168	0.042	70	7	49
8	0.168	0.042	70	10	31
9	0.168	0.084	70	1	64
10	0.168	0.084	70	3	52
11	0.168	0.084	70	7	49
12	0.168	0.084	70	10	37
13	0.168	0.084	60	5	49
14	0.168	0.084	70	5	48
15	0.168	0.084	80	5	52
16	0.168	0.084	90	5	59
17	0.248	8.5	60	5	18
18	0.248	8.5	70	5	21
19	0.248	8.5	80	5	24
20	0.248	8.5	90	5	29
21	0.248	8.5	90	1	21
22	0.248	8.5	90	3	25
23	0.248	8.5	90	7	20
24	0.248	8.5	90	10	16

a = The initial concentration of IPIMP was used as 0.042 mol L<sup>-1</sup>.

Calcd. for OIPIMP: C, 48.60; H, 2.49; N, 4.36. Found: C, 48.24; H, 2.55; N, 3.95. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$ (O-H) 3439 s;  $\nu$ (C-H aryl) 3055 m;  $\nu$ (C=N) 1617 s;  $\nu$ (aromatic, C-O) 1283 s;  $\nu$ (C-I) 748 s;  $\nu$ (aromatic, C=C) 1583, 1478, 1417 m. UV-Vis ( $\lambda_{\max}$ ): 245, 290, 332 and 355 nm. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>):  $\delta$  12.84 (s, 1H, OH), 8.95 (s, 1H, CH=N), 7.80 (d, 2H, Ar-H<sub>aa'</sub>), 7.20 (d, 2H, Ar-H<sub>bb'</sub>), 7.70 (d, 1H, Ar-H<sub>c</sub>), 6.95 (t, 1H, Ar-H<sub>d-terminal</sub>), 7.40 (t, 1H, Ar-H<sub>e</sub>), 6.99 (d, 1H, Ar-H<sub>f-terminal</sub>). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>):  $\delta$  119.8 (C1-*ipso*), 138.7 (C2), 124.2 (C3), 148.1 (C4-*ipso*), 173.5 (C5), 117.0 (C6-*ipso*), 166.4 (C7-*ipso*), 125.0 (C8), 137.7 (C9), 138.9 (C10), 134.3 (C11), 126.3 and 135.2 (new peaks).

#### Syntheses of oligo-2-[(4-iodophenylimino)methyl]phenol-metal complexes

**Cobalt(II) complex.** A solution of Co(AcO)<sub>2</sub>·4H<sub>2</sub>O (8.84 × 10<sup>-4</sup> mol, 0.220 g) in MeOH (15 mL) was added to a solution of OIPIMP (1.56 × 10<sup>-3</sup> mol/unit, 0.500 g) in THF (20 mL). The mixture was stirred and heated at 70 °C for 5 h (Scheme 2) and the precipitated complex filtered off, washed with cold MeOH/THF, and dried in vacuum oven (yield 76 %).

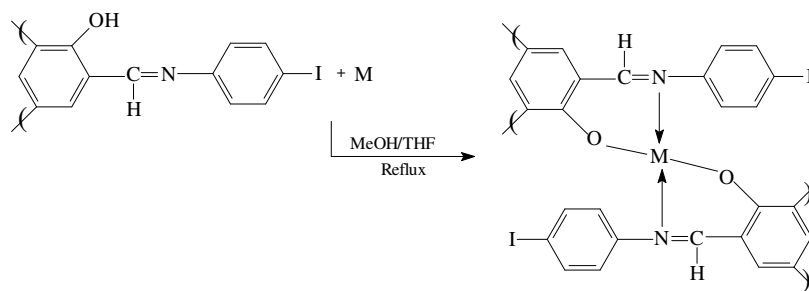
Calcd. for OIPIMP-Co: M, 15.51. Found: M, 14.95. UV-Vis ( $\lambda_{\max}$ ): 206, 237, 281, 343 and 383 nm. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$ (O-H) 3446 s,  $\nu$ (C-H aryl) 3057 m,  $\nu$ (C=N) 1604 s,  $\nu$ (aromatic, C-O) 1249 s,  $\nu$ (C-I) 822 s,  $\nu$ (aromatic, C=C) 1586, 1569, 1532, 1480, 1460 m,  $\nu$ (M-O) 519 s,  $\nu$ (M-N) 565 s.

*Nickel(II) complex.* This was prepared similarly from  $\text{Ni}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$  ( $8.48 \times 10^{-4}$  mol, 0.211 g) and OIPIMP ( $1.56 \times 10^{-3}$  mol/unit, 0.500 g) in THF (yield 88 %).

Calcd. for OIPIMP-Ni: M, 15.46. Found: M, 15.00. UV-Vis ( $\lambda_{\text{max}}$ ): 208, 237, 281, 341 and 388 nm. FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{O-H})$  3419 s,  $\nu(\text{C-H aryl})$  3054 m,  $\nu(\text{C=N})$  1614 s,  $\nu(\text{aromatic, C-O})$  1181 s,  $\nu(\text{C-I})$  824 s,  $\nu(\text{aromatic, C=C})$  1572, 1549, 1472, 1446 m,  $\nu(\text{M-O})$  525 s,  $\nu(\text{M-N})$  591 s.

*Copper(II) complex.* This was obtained from  $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$  ( $1.08 \times 10^{-3}$  mol, 0.215 g) and OIPIMP ( $1.56 \times 10^{-3}$  mol/unit, 0.500 g) in THF (yield 93 %).

Calcd. for OIPIMP-Cu: M, 16.53. Found: M, 16.15. UV-Vis ( $\lambda_{\text{max}}$ ): 206, 238, 280, 341 and 384 nm. FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{O-H})$  3445 s,  $\nu(\text{C-H aryl})$  3048 m,  $\nu(\text{C=N})$  1607 s,  $\nu(\text{aromatic, C-O})$  1183 s,  $\nu(\text{C-I})$  822 s,  $\nu(\text{aromatic, C=C})$  1530, 1510, 1482, 1462, 1441 m,  $\nu(\text{M-O})$  523 s,  $\nu(\text{M-N})$  587 s.



Scheme 2. Syntheses of oligo-2-[(4-iodophenylimino)methyl]phenol-metal complexes.

#### Characterization techniques

The Fourier transform infrared (FT-IR) and ultraviolet-visible (UV-Vis) spectra were obtained by use Perkin Elmer BX II and Perkin Elmer Lambda 25 instruments, and elemental analyses were with a Carlo Erba 1106 unit. The FT-IR spectra were recorded on KBr discs (4000-350  $\text{cm}^{-1}$ ). UV-Vis spectra were recorded from solutions in methanol and DMSO. IPIMP and OIPIMP in  $\text{DMSO-d}_6$  at 25 °C were characterized by  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively). Tetramethylsilane was used as internal standard. Thermal data were obtained by use of a Perkin Elmer Diamond Thermal Analysis system. TG-DTA measurements were made between 20-1000 °C (in  $\text{N}_2$ , 10 °C/min). The number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ) and polydispersity index (PDI) were determined by SEC (Shimadzu Co. Japan) with a Macherey-Nagel GmbH & Co. (Germany) (100 Å and 7 nm diameter loading material) 7.7 mm i.d. x 300 mm columns, DMF eluent (0.4  $\text{mL min}^{-1}$ ), polystyrene standards and a refractive index detector.

## RESULTS AND DISCUSSION

#### Conditions for synthesis of OIPIMP

Conditions for oxidative condensation of IPIMP with NaOCl in aqueous alkaline medium are given in Table 1. The condensation began immediately and the solution turned brown upon

addition of oxidant. When  $[\text{IPIMP}]_0 = [\text{NaOCl}]_0$  was 0.042 mol/L and  $[\text{KOH}]_0 = 0.168$  mol/L, the yield of OIPIMP was 67 % at 70 °C for 3 h. When  $[\text{IPIMP}]_0$  was 0.042 mol/L,  $[\text{KOH}]_0$  0.168 mol/L and  $[\text{NaOCl}]_0$  0.084 mol/L, the yield of OIPIMP was 64 % at 70 °C for 1 h. The yield of OIPIMP increased from 52 % to 64 %, when the concentration of the NaOCl was increased under the same conditions. The conditions for oxidative condensation with air in aqueous alkaline medium also are given in Table 1. The yield of OIPIMP was 29 % with reaction conditions  $[\text{IPIMP}]_0$  0.062,  $[\text{KOH}]_0$  0.248 mol/L and air 8.5 L/h at 90 °C for 5 h. The yield of OIPIMP was only 16 % with the same reaction conditions perhaps because of depolymerization of oligomer with high reaction times.

The electron-donor effect of azomethine group in 2-[(4-iodophenylimino)methyl]phenol appears to have facilitated the oxidation in alkaline medium by air and NaOCl. The brown color may suggest formation of phenoxy radicals. NaOCl is more reactive than air.

#### Solubility

The oxidative polycondensation products of IPIMP with NaOCl and air in aqueous alkaline medium were black solid powders. OIPIMP was soluble in  $\text{H}_2\text{SO}_4$ , THF, DMF, DMSO and acetone, poorly soluble in toluene, benzene and chlorinated solvents, such as  $\text{CHCl}_3$  and  $\text{CCl}_4$  and insoluble in aliphatic hydrocarbons such as heptane and hexane. OIPIMP formed oligomer-metal complexes with  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  acetates. These were insoluble in water at room temperature but soluble in DMSO.

#### Structure of OIPIMP

SEC measurements gave the values of number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) of OIPIMP by comparison with polystyrene as standard. When NaOCl was used as oxidant,  $M_n$ ,  $M_w$  and PDI values of OIPIMP was found to be 1250, 1300  $\text{g mol}^{-1}$  and 1.040, respectively. When the oxidant was air,  $M_n$ ,  $M_w$  and PDI values of OIPIMP were 2200, 2500  $\text{g mol}^{-1}$  and 1.136.

The electronic spectra of IPIMP and OIPIMP were recorded in methanol. The K band is assigned to the -OH and azomethine groups of IPIMP were observed in 237 and 325 nm, respectively. The B and R bands of IPIMP were observed in 273 and 345 nm. The R band of the -CH=N group of IPIMP was observed in 345 nm. The K bands belonging to -OH and azomethine groups of OIPIMP were observed in 245 and 332 nm, respectively. The R band of the -CH=N group of OIPIMP was observed in 355 nm. In the oligomer-metal complexes, the low intensity bands in the 450-550 nm range are consistent with d→d transitions of the metal ions.

In order to identify the structures of IPIMP and OIPIMP, the  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded in  $\text{DMSO-d}_6$ . The signals of -OH and -CH=N groups of IPIMP and OIPIMP were observed at 12.90 and 8.96 ppm and 12.84 and 8.95 ppm, respectively. The FT-IR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectral data of the OIPIMP indicate that the polymerization occurs via substitution at positions *ortho* and *para* to the OH group.

In independent work, a series of novel polyimide and poly (Schiff base) oligomers with azomethine [14] structures containing bithiazole rings was synthesized through polycondensation of some diamines with dianhydrides. All compounds had been characterized by FT-IR, elemental analysis and  $^1\text{H-NMR}$  techniques and thermogravimetric analyses [15].

#### Thermal analyses of compounds

DTA and TG analyses of IPIMP, OIPIMP, OIPIMP-Cu, OIPIMP-Ni and OIPIMP-Co compounds were made under an  $\text{N}_2$  atmosphere in the temperature range 20-1000 °C and the

results are given in Table 2. Figures 1 and 2 show the DTA and TG traces for the IPIMP and OIPIMP. Degradation of OIPIMP started at 237 °C and proceeded rapidly between 250 and 400 °C. The weight loss at 1000 °C was 99 %. Exothermic and endothermic peaks of monomer and oligomer were observed at 128, 278 °C and 118 °C, respectively. From DTG analysis the  $T_{\max}$  values of monomer and oligomer were observed at 271 and 274 °C, respectively. It is seen that Figure 1, monomer completely decomposed low a temperature such as 280 °C.

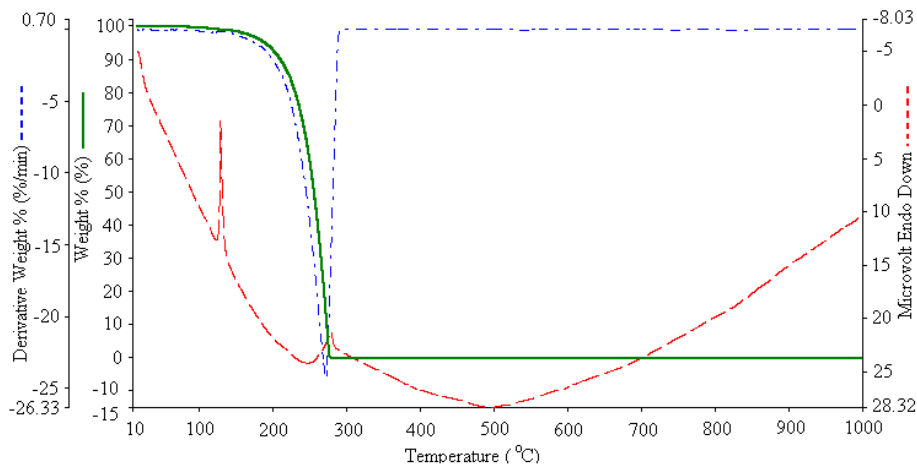


Figure 1. TG-DTG-DTA curves of IPIMP.

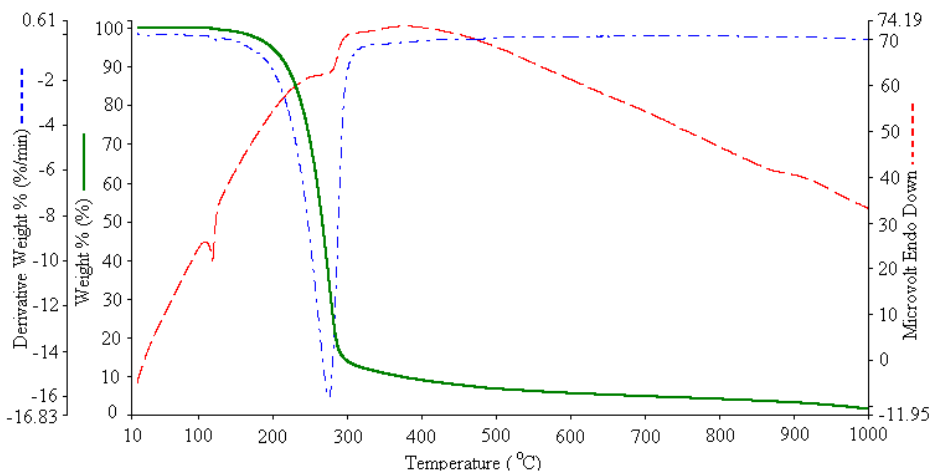


Figure 2. TG-DTG-DTA curves of OIPIMP.

Table 2. Thermal decomposition values of IPIMP, OIPIMP and oligomer-metal complex compounds.

Compounds	TGA (°C)					DTA (°C)	
	<sup>a</sup> T <sub>on</sub>	<sup>b</sup> T <sub>max</sub>	20 % weight loss	50 % weight loss	% Residual at 1000°C	Exo	Endo
IPIMP	230	271	231	255	-	128, 278	-
OIPIMP	232	274	242	267	1.23	-	118
OIPIMP-Cu	265	292, 745	338	693	33.83	327	243
OIPIMP-Ni	278	286, 367, 518	360	624	49.36	-	-
OIPIMP-Co	307	337, 617	510	740	35.25	342	283

<sup>a</sup>The onset temperature. <sup>b</sup>Maximum weight loss temperature (from the DTG curves).

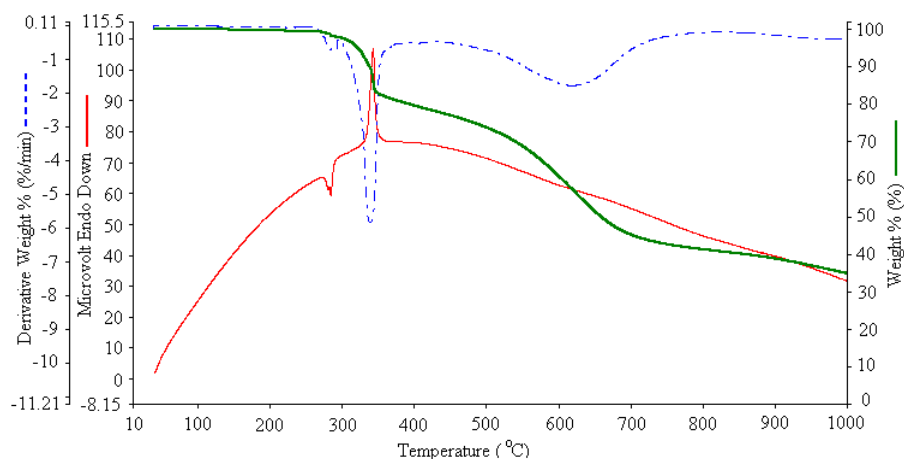


Figure 3. TG-DTG-DTA curves of OIPIMP-Co complex.

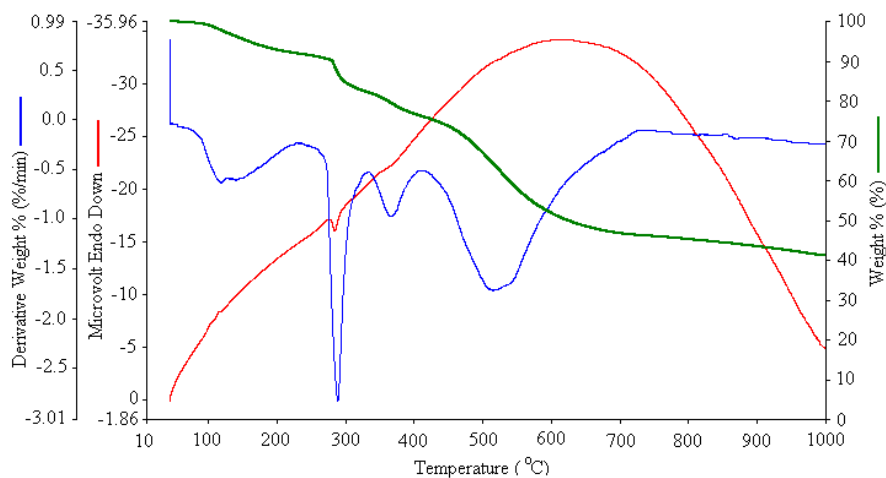


Figure 4. TG-DTG-DTA curves of OIPIMP-Ni complex.

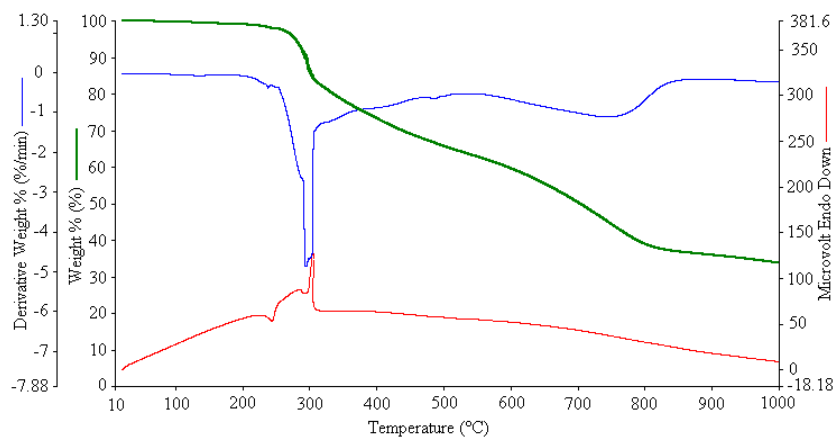


Figure 5. TG-DTG-DTA curves of OIPIMP-Cu complex.

### CONCLUSIONS

We have shown that the oxidative condensation of IPIMP proceeds by attack at the *ortho* and *para* positions and that NaOCl is a better oxidant than air. The structures of IPIMP and OIPIMP were characterized by spectral analyses. When NaOCl and air were used as oxidant, the yields of OIPIMP were 67 % and 29 %, respectively. NaOCl was more reactive than air. The complexes of OIPIMP with copper, nickel and cobalt were stable through to temperature and thermal decomposition. Total weight losses of the complexes of OIPIMP with copper, nickel and cobalt were 66.2 %, 50.6 % and 64.7 %, respectively, at 1000 °C. The highest residue was with OIPIMP-Ni but the initial degradation temperature of OIPIMP-Co was higher than that of other complexes. The complexes of OIPIMP with copper, nickel and cobalt are more stable thermally than the oligomer itself.

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