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Synthesis, Characterization and Thermal Degradation of Oligo-2-[(4-hydroxyphenyl) Imino Methyl]-1-naphtol and Oligomer-Metal Complexes

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The oxidative polycondensation of 2-[(4-hydroxyphenyl) imino methyl]-1-naphtol (4-HPIMN) has been accomplished by using NaOCl, H_2O_2 and air O_2 oxidants in aqueous alkaline medium. Optimum reaction conditions of the oxidative polycondensation and the main parameters of the process were established. At optimum reaction conditions, yield of the products were found to be 77.0%, 91.6% and 99.0% for H_2O_2, air O_2 and NaOCl oxidants, respectively. The structures of the obtained monomer and oligomer were confirmed by FT-IR, UV-Vis, ^1H- and ^{13}C-NMR and elemental analysis. The characterization was made by TG-DTA, SEC and solubility tests. The ^1H- and ^{13}C-NMR data shows that the polymerization proceeded by the C–C coupling of ortho positions according to –OH group of 4-HPIMN. The molecular weight distribution values of the product were determined by using size exclusion chromatography (SEC). The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of O-4-HPIMN were found to be 1777, 2225 and 1.252; 1790, 2250 and 1.257; 4540, 5139 g mol^{-1}, and 1.132 for NaOCl, H_2O_2 and air O_2 oxidants, respectively. According to TG analyses, the carbonaceous residue of 4-HPIMN and O-4-HPIMN was found to be 28.02% and 44.22% at 1000°C, respectively. Thermal analyses of O-4-HPIMN-Cd, O-4-HPIMN-Co, O-4-HPIMN-Cu, O-4-HPIMN-Fe, O-4-HPIMN-Mg, O-4-HPIMN-Mn, O-4-HPIMN-Ni, O-4-HPIMN-Pb and O-4-HPIMN-Zn oligomer-metal complex compounds were investigated in N_2 atmosphere between 15–1000°C.

Keywords oxidative polycondensation, oligo-2-[(4-hydroxyphenyl) imino methyl]-1-naphtol, oligomer metal complexes, thermal degradation

Introduction

The oligophenols and their Schiff base derivatives, which included –OH and –CH═N groups, have been used in various fields. They have useful properties such as paramagnetism, semi-conductivity, electrochemical cell and resistance to high energy (1–4). These

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compounds were attributed to new structures properties, adding to other functional groups. Polymer metal complex compounds can be prepared with the reaction of metal salts and polymers, which contain electro donor groups such as −OH and −CH═N (5). 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 cobalt (II) Schiff base complex compound was studied by Gupta et al. (6). 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. (7). The thermal and anti-microbial properties of oligophenols with a Schiff base substitute and their oligomer metal complex compounds were investigated by Kaya et al. (8). Anti-microbial activity of oligo-N-2-aminopyridinylsalicylaldimine and some oligomer-metal complexes was studied by Kaya et al. (9). The thermal stability of poly(acryloyl benzoic hydrazide) and its complexes with some transition metals was examined by Gad et al. (10). The thermal decomposition behavior of poly (acrylic acid) and its metal complexes were studied by Sebastian et al. (11). Kaya et al. studied thermal degradation of oligo-2-[(4-fluorophenyl) imino methylene] phenol and some of its oligomer-metal complexes (12). The conducting properties of poly(2-hydroxy-4-acryloxyacetophenone-phenylimine), poly(2-hydroxy-4-acryloyloxy-acetophenone-N-phenylimine-co-methacrylate) and their metal complexes were studied by Thamizharasi et al. (13). 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 (14). Therefore, the synthesis of oligomer-metal complexes and oligomer are very important in analytic, environmental, and food chemistry.

In this article, we have investigated the effects of different parameters such as temperature, times and initial concentration of NaOCl, H_2O_2 for the oligo-2-[(4-hydroxyphenyl) imino methyl]-1-naphtol in the medium alkaline. 4-HPIMN and O-4-HPIMN were characterized by using FT-IR, UV-Vis, ^{1}H-^{13}C-NMR, elemental analysis, TG-DTA and SEC techniques. Also, O-4-HPIMN-Pb, O-4-HPIMN-Co, O-4-HPIMN-Mg, O-4-HPIMN-Mn, O-4-HPIMN-Cd, O-4-HPIMN-Ni, O-4-HPIMN-Zn, O-4-HPIMN-Cu and O-4-HPIMN-Fe were characterized by using FT-IR, elemental analysis, and TG-DTA techniques.

Materials and Methods

Materials

2-hydroxy-1-naphtaldehyde, 4-aminophenol, methanol, ethanol, benzene, toluene, ethyl acetate, CH_2Cl_2, $CHCl_3$, CCl_4, acetone, hexane, THF, DMF, DMSO, H_2SO_4 (98%), KOH, hydrochloric acid (HCl, 37%) Co $(AcO)_2$ $4H_2O$, Ni $(AcO)_2$ $4H_2O$, Cu $(AcO)_2$ $4H_2O$, $FeSO_4$ $7H_2O$, $ZnCl_2$, $Pb(AcO)_2$ $3H_2O$, $MnSO_4$ H_2O, $MgSO_4$ $7H_2O$ and Cd $(AcO)_2$ $2H_2O$ were supplied from Merck Chem. Co. (Germany) and were used as received. Sodium hypochloride (NaOCl), (30% aqueous solution) was supplied from Paksoy Chemical Co. (Turkey).

Preparation of 2-[(4-Hydroxyphenyl) Imino Methyl]-1-naphtol (4-HPIMN)

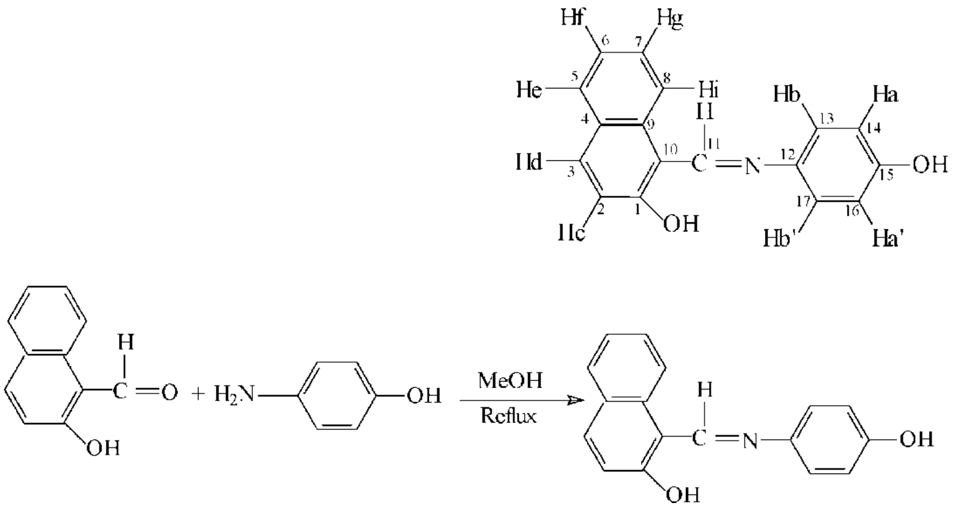
2-[(4-hydroxyphenyl) imino methyl]-1-naphtol was prepared by the condensation of 2-hydroxy-1-naphthaldehyde (0.56 g, 0.0052 mol) and 4-aminophenol (0.572 g, 0.0052 mol) in methanol 15 mL achieved by boiling the mixture under reflux for 3 h (Scheme 1). The precipitated 2-[(4-hydroxyphenyl) imino methyl]-1-naphtol was filtered and recrystallized from methanol and dried in vacuum desiccators (yield, 90%).

Anal. calcd. for 4-HPIMN: C, 77.57; H, 4.94; N, 5.32. Found: C, 77.25; H, 5.20; N, 5.00. FT-IR (KBr; cm^{-1}): v (CH=N) 1618 s; v (C–O) 1275 s; v (C=C) 1545, 1503, 1462 s; v (aromatic C-H) 3065 s; v (Ar-OH) 3375 s. UV-Vis (λ_{max}): 237, 324, 339 and 370 nm. ^{1}H-NMR (DMSO): δ ppm, 9.61 (s, 1H, –CH=N–); 16.11(s, 1H, naphtyl –OH); 9.76 (s, 1H, phenyl-OH); 6.92 (d, 2H, Ar-Haa′); 7.53 (d, 2H, Ar-Hbb′); 7.04 (d, 1H, Ar-Hc); 8.48 (d, 1H, Ar-Hd); 7.78 (d, 1H, Ar-He); 7.34 (t, 1H, Ar-Hf and 1H, Ar-Hg); 7.88 (d, 1H, Ar-Hi). ^{13}C-NMR (DMSO): ppm, 169.87 (C1-ipso), 120.67 (C2-H), 133.50 (C3-H), 129.39 (C4-H), 128.31 (C5-H), 122.46 (C6-H), 122.31 (C7-H), 127.08 (C8-H), 136.23 (C9-H), 108.96 (C10-ipso), 169.43 (C11-H), 154.26 (C12-ipso), 123.65 (C13-C17-H), 116.60 (C14-C16-H), 157.13 (C15-ipso).

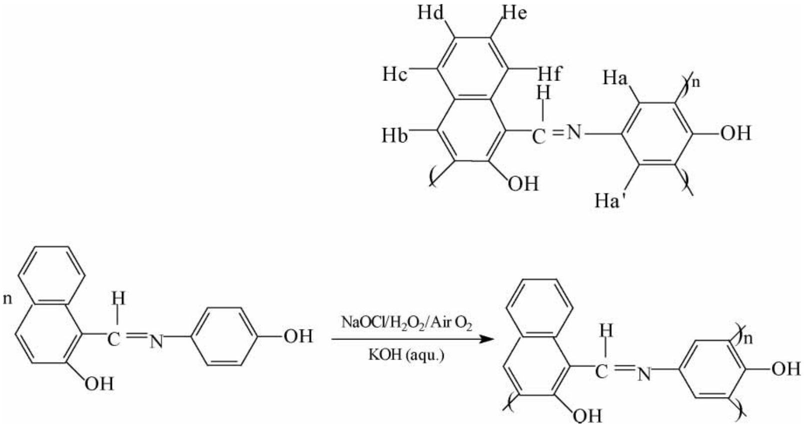
Synthesis of Oligo-2-[(4-hydroxyphenyl) Imino Methyl]-1-naphtol with H_2O_2, NaOCl and Air O_2 Oxidants

O-4-HPIMN was synthesized from the oxidative polycondensation reaction of 4-HPIMN with a water solution of H_2O_2 (30%), NaOCl (30%) and air O_2 as follows (Scheme 2) (9).

Anal. calcd. for O-4-HPIMN: C, 78.46; H, 3.85; N, 5.39. Found: C, 78.00; H, 4.15; N, 6.75. FT-IR (KBr; cm^{-1}): v (CH=N) 1630 s; v (C–O) 1273 s; v (C=C) 1594, 1513, 1449 s; v (aromatic C–H) 3080 s; v (Ar-OH) 3425 s. UV-Vis (λ_{max}): 252, 353 and 390 nm. ^{1}H-NMR (DMSO): δ ppm, 9.58 (s, 1H, –CH=N–); 15.82 (s, 1H, naphtyl -OH); 9.70 (s, 1H, phenyl-OH); 6.88 (s, 2H, Ar-Haa′), 7.89 (d, 1H, Ar-Hb) 7.26 (d, 1H, Ar-Hc) 7.80 (d, 1H, Ar-Hd) 7.95 (d, 1H, Ar-He) 8.50 (d, 1H, Ar-Hf). ^{13}C-NMR (DMSO): ppm, 167.22 (C1-ipso), 125.35 (C2-H), 133.00 (C3-H), 129.05 (C4-H), 127.72 (C5-H), 121.27 (C6-H), 120.47 (C7-H), 123.56 (C8-H), 135.74 (C9-H), 108.51 (C10-ipso), 166.74 (C11-H), 154.00 (C12-ipso), 121.54 (C13-C17-H), 118.85 (C14-C16-H), 156.75 (C15-ipso).



Scheme 1. Synthesis of 2-[(4-hydroxyphenyl) imino methyl]-1-naphtol.



Scheme 2. Synthesis of oligo-2-[(4-hydroxyphenyl) imino methyl]-1-naphtol.

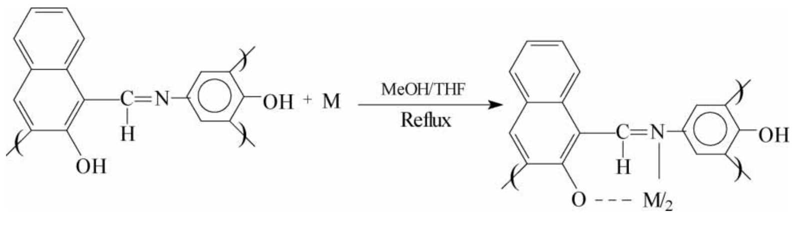
Synthesis of Oligo-2-[(4-hydroxyphenyl) Imino Methyl]-1-naphtol Metal Complexes

Solutions of Co $(AcO)_2$ $4H_2O$, Ni $(AcO)_2$ $4H_2O$, Cu $(AcO)_2$ $4H_2O$, $FeSO_4$ $7H_2O$, $ZnCl_2$, $Pb(AcO)_2$ $3H_2O$, $MnSO_4$ H_2O, $MgSO_4$ $7H_2O$ and Cd $(AcO)_2$ $2H_2O$ (1 mmol) in MeOH (10 mL) were added to a solution of O-4-HPIMN (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 MeOH/THF (1:1) and then dried in a vacuum oven.

Characterizations

O-4-HPIMN was dark brown in powder form, and was completely soluble in organic solvents such as DMF, THF, DMSO, methanol, and ethanol. O-4-HPIMN was insoluble in hexane, benzene, toluene, ethyl acetate, CH_2Cl_2, $CHCl_3$, CCl_4 and acetone. O-4-HPIMN-Cd, O-4-HPIMN-Co, O-4-HPIMN-Cu, O-4-HPIMN-Fe, O-4-HPIMN-Mg, O-4-HPIMN-Mn, O-4-HPIMN-Ni, O-4-HPIMN-Pb and O-4-HPIMN-Zn oligomer-metal complex compounds were insoluble in hexane, benzene, toluene, ethyl acetate, CH_2Cl_2, $CHCl_3$, CCl_4 and acetone. These oligomer metal complex compounds were partly soluble in DMSO and DMF.

The infrared and ultraviolet-visible spectra were measured by Perkin-Elmer FT-IR BX and UV-1208 Shimadzu, respectively. Elemental analysis was carried out with a LECO CHNS 932. The FT-IR spectra were recorded using a KBr disc



Scheme 3. Synthesis of metal complex compounds of oligo-2-[(4-hydroxyphenyl) imino methyl]-1-naphtol.

(4000–350 cm^{-1}). UV-Vis spectra of 4-HPIMN and O-4-HPIMN were determined by using DMSO. 4-HPIMN and O-4-HPIMN were characterized by using ^{1}H-NMR and ^{13}C-NMR spectra (Bruker Avance DPX-400 and 100.6 MHz, respectively) recorded at 25°C by using deuterated DMSO as solvent. TMS was used as internal standard. Thermal data were obtained by using a Perkin-Elmer Diamond Thermal Analysis system. The TG-DTA measurements were made between 15–1000°C (in N_2, rate 10°C/min). SEC analyses were performed at 30°C using DMF/MeOH (v/v, 4/1) as eluent at a flow rate of 0.4 ml/min. A refractive index detector was used as detector. The instrument (Shimadzu 10AVp series HPLC-SEC system) was calibrated with a mixture of polystyrene standards (Polymer Laboratories; the peak molecular weights, Mp, between 162 and 19880) using GPC software for the determination of the number-average molecular weight M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) of the polymer samples. For SEC investigations, a Macherey-Nagel GmbH & Co. was used (100Å and 7.7 nm diameter loading material) 3.3 mm i.d. × 300 mm columns. Metal analyses were determined by complexometric titration. The elemental analysis data of oligomer metal complexes are given in Table 1.

Results and Discussion

Synthesis of O-4-HPIMN

2-[(4-hydroxyphenyl) imino methyl]-1-naphtol was oxidized by air O_2, H_2O_2 and NaOCl oxidants in an aqueous alkaline medium. The conversion of 4-HPIMN was 77.0% at optimum reaction conditions, such as $[\text{4-HPIMN}]_0 = [\text{KOH}]_0 = [H_2O_2]_0 = 0.1$ mol/L, at 90°C for 3 h. The conversion of 4-HPIMN was 59.0% at the reaction conditions such as $[\text{4-HPIMN}]_0 = [\text{KOH}]_0 = [H_2O_2]_0 = 0.1$ mol/L at 50°C for 3 h. According to these values, with the increasing of reaction temperatures, the conversion to oligomer of

Table 1
Elemental analyses data and yields of 4-HPIMN, O-4-HPIMN and oligomer-metal complexes

	Calculated (%, found)				
Compounds	C	H	N	Metal	Yield, %
4-HPIMN	77.57 (77.25)	4.94 (5.20)	5.32 (5.00)	—	90
O-4-HPIMN	78.46 (78.00)	3.85 (4.15)	5.39 (6.75)	—	99
O-4-HPIMN-Cu	63.05 (62.80)	3.09 (2.90)	4.33 (4.40)	19.64 (18.68)	91
O-4-HPIMN-Ni	64.01 (63.75)	3.14 (3.01)	4.39 (4.27)	18.42 (18.24)	88
O-4-HPIMN-Co	63.96 (63.25)	3.14 (3.00)	4.39 (4.21)	18.48 (17.63)	73
O-4-HPIMN-Pb	43.66 (43.26)	2.14 (2.03)	3.00 (2.85)	44.35 (43.02)	96
O-4-HPIMN-Cd	54.78 (54.42)	2.69 (2.30)	3.76 (3.66)	30.19 (29.28)	75
O-4-HPIMN-Fe	64.59 (64.28)	3.17 (3.25)	4.43 (4.31)	17.68 (16.56)	87
O-4-HPIMN-Mn	64.78 (64.44)	3.18 (3.00)	4.45 (4.35)	17.45 (17.28)	90
O-4-HPIMN-Zn	62.69 (62.40)	3.07 (3.20)	4.30 (4.15)	20.10 (18.69)	53
O-4-HPIMN-Mg	71.75 (71.49)	3.52 (3.70)	4.92 (4.20)	8.55 (7.27)	82

4-HPIMN increased. Under the same conditions, increasing reaction times decreased the yield of oligomer. When the reaction times changed from 1 h to 25 h, the yield of O-4-HPIMN changed from 87% to 59% at the same conditions (such as $[\text{4-HPIMN}]_0 = [\text{KOH}]_0 = [\text{NaOCl}]_0 = 0.1\,\text{mol/L}$, at 80°C) for NaOCl oxidant. The same conditions, when the molar amount of NaOCl increased in two coatings, the total yield of O-4-HPIMN changed from 92.0% to 64.0%. The conversion of 4-HPIMN was 99.0% at optimum conditions such as $[\text{4-HPIMN}]_0 = [\text{NaOCl}]_0 = 0.1\,\text{mol/L}$ and $[\text{KOH}]_0 = 0.2\,\text{mol/L}$, at 60°C for 3 h. The conversion of 4-HPIMN was 90.0% at one other reaction condition such as $[\text{4-HPIMN}]_0 = [\text{NaOCl}]_0 = 0.1\,\text{mol/L}$ and $= [\text{KOH}]_0 = 0.2\,\text{mol/L}$ at 60°C for 25 h. The oxidative polycondensation reaction of 4-HPIMN, when air oxygen passed into 8.5 L/h rate at the reaction medium at 50°C, the product yield was 91.6%. When the molar amount of KOH increased in two coatings, the total yield of O-4-HPIMN changed from 91.6% to 79.1%. When the molar amount of KOH changed from 0.132 mol/L to 0.330 mol/L, the conversion of 4-HPIMN changed from 91.6% to 66.9% under the same conditions, such as the 8.5 L/h flow rate of air O_2 and at 50°C for 10 h. The conversion of 4-HPIMN to oligomer was decreased with an increase of oligomerization time under the same conditions. The reason for this may be conversion from oligomer to monomer at the high reaction times.

Structure of O-4-HPIMN

SEC analyses of O-4-HPIMN were performed at 30°C using DMF/Methanol (v/v, 4/1) as eluent at a flow rate of 0.4 ml/min. To the oxidant H_2O_2, M_n, M_w and PDI values of O-4-HPIMN was found to be 1790, 2250 g mol^{-1} and 1.257, respectively. Two peaks were observed in the chromatogram of O-4-HPIMN. 97% of the mass of O-4-HPIMN was low molecular weight ($M_n = 1277$, $M_w = 1367\,\text{g mol}^{-1}$, PDI = 1.070), but 3% of its weight was high molecular weight ($M_n = 7804$, $M_w = 10581\,\text{g mol}^{-1}$, PDI = 1.356). To oxidant air, O_2, M_n, M_w and PDI values of O-4-HPIMN were found to be 4540, 5139 g mol^{-1}, and 1.132, respectively. Two peaks were observed in the chromatogram of O-4-HPIMN. 75% of the mass of O-4-HPIMN was low molecular weight ($M_n = 1687$, $M_w = 2239\,\text{g mol}^{-1}$, PDI = 1.328) but 25% of its weight was high molecular weight ($M_n = 31261$, $M_w = 34397\,\text{g mol}^{-1}$, PDI = 1.100). In the oxidant NaOCl, M_n, M_w and PDI values of O-4-HPIMN were found to be 1777, 2225 g mol^{-1} and 1.252, respectively. Two peaks were observed in the chromatogram of O-4-HPIMN. 97% of the mass of O-4-HPIMN was low molecular weight ($M_n = 1222$, $M_w = 1307\,\text{g mol}^{-1}$, PDI = 1.070), but 3% of its weight was high molecular weight ($M_n = 7896$, $M_w = 10605\,\text{g mol}^{-1}$, PDI = 1.343). When reaction temperatures and reaction times increased, molecular weight distribution (MWD) of O-4-HPIMN increased, but the conversion of O-4-HPIMN decreased. The increasing of polymerization time, temperatures and oxidant concentrations increased the molecular weight and MWD of O-4-HPIMN.

The UV-Vis spectroscopic studies were carried out with DMSO solutions of the 4-HPIMN and O-4-HPIMN. In the 4-HPIMN spectra, K bands of phenol and $C_6H_5\text{-N}{=}$ were observed, 237 nm and 324 nm, respectively. A benzene band of 4-HPIMN and strength R band of $-\text{CH}{=}\text{N}-$ groups were observed, 339 and 370 nm, respectively. UV-Vis spectra of O-4-HPIMN, K and R bands were observed, 252 nm and 353 nm, respectively. The band of $-\text{CH}{=}\text{N}-$ group observed 390 nm. The UV-Vis spectra shows specific bands for λ_{max} assigned to aromatic and azometinic $\pi-\pi^*$ transitions at about 280 and 350 nm, respectively, (15). The shifting of the $-\text{CH}{=}\text{N}-$ group band from 370 nm to 390 nm has been demonstrated for the formation of the oligomeric conjuge π system.

The FT-IR spectral data of 4-HPIMN, O-4-HPIMN and oligomer metal complexes are given Table 2. The FT-IR spectra of 4-HPIMN and O-4-HPIMN, bands of OH and –CH=N groups were observed 3375 and 1618; 3425 and 1630 cm^{-1}, respectively. For monomer and oligomer, the shifting of –CH=N– and –OH groups bands from 3375 and 1618 to 3425 and 1630 cm^{-1}, respectively, have been demonstrated for the formation of oligomeric structure. In order to identify the structures of monomer and oligomer, the ^{1}H-NMR spectra were recorded in DMSO-d$_6$. ^{1}H-NMR and ^{13}C-NMR spectra of the monomer are given in Figures 1 and 2, respectively. In the ^{1}H-NMR spectra of 4-HPIMN and O-4-HPIMN, the signals of phenyl –OH, naphtyl —OH and –CH=N groups were observed 9.76, 16.11 and 9.61 ppm and 9.70, 15.82 and 9.58 ppm, respectively. The ^{1}H-^{13}C-NMR spectra results of the O-4-HPIMN confirm the formation of oligomer units. Other phenol derivatives were also polymerized, and the results are reported in the literature (16). Elemental analyses and FT-IR data of monomer, oligomer and oligomer-metal complex compounds are given in Table 1 and 2, respectively.

Crosslinking in the polymer structure is expected in those cases where the *ortho* positions in the corresponding monomer structure are unsubstituted. ^{13}C-NMR studies on O-4-HPIMN indicate that the linkage between any two adjacent phenyl rings is largely at *ortho* positions (Figures 3 and 4). The peak values for C2 and C14-C16 observed in 120.67 and 116.60 ppm in the monomer and 125.35, 118.85 ppm in the polymer, respectively. On the other hand, if the monomer connected at *meta* positions on the rings, the peaks of C3, C13 and C17 could shift downfield. However, the polymer spectrum in Figure 4 shows no such peak ruling out linkages at *meta* positions. There was no significant change in the peak position for C3, C13 and C17. 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* positions (Scheme 2).

Thermal Studies

The thermal degradation of monomer, oligomer and oligomer-metal complexes were studied by TG-DTA analyses at the N$_2$ medium and some data derived from TG curves are summarized in Table 3, where the thermal stability in terms of onset temperatures, 20 wt% losses and residues are given. The TG-DTA curves of monomer and oligomer are given in Figures 5 and 6. The initial degradation temperature and 55.78% wt loss of O-4-HPIMN was found to be 249 and 1000°C, respectively. This oligomer was formed and the carbines residue was high in the amount (44.22%) at 1000°C. Although the initial degradation temperature of the monomer was higher than the oligomer as a result of long conjugated band systems, the oligomer demonstrated higher resistance against high temperature than the monomer. The initial degradation temperature and 71.98% wt loss of 4-HPIMN was found to be 289 and 1000°C, respectively. The TGA curve of O-4-HPIMN (Figure 6) with a wt loss in the 50–100°C required adsorption water removal. According to TG analysis, although the initial degradation temperature of O-4-HPIMN was lower than the monomer, it was more stable than the monomer due to temperature and thermo-oxidative decomposition. According to DTA curves of the monomer and polymer, endothermic processes were observed in 232 and 206°C, respectively.

Table 2
FT-IR spectral data of 4-HPIMN, O-4-HPIMN and oligomer-metal complexes

	Wave number (cm^{-1})					
Compounds	–OH	–CH═N	–C═C	–C–O	Metal-O	Metal-N
4-HPIMN	3375	1618	1545, 1503,1462	1275	—	—
O-4-HPIMN	3425	1630	1594, 1513, 1449	1273	—	—
O-4-HPIMN-Cu	3421	1600	1540, 1432, 1432	1276	498	676
O-4-HPIMN-Ni	3350	1608	1570, 1540, 1441	1180	526	618
O-4-HPIMN-Co	3315	1617	1539, 1507, 1448	1272	538	667
O-4-HPIMN-Mn	3419	1623	1542, 1512, 1447	1112	505	606
O-4-HPIMN-Fe	3460	1623	1508, 1458	1151	512	616
O-4-HPIMN-Pb	3402	1610	1580, 1539, 1399	1267	533	668
O-4-HPIMN-Mg	3385	1616	1511, 1447	1274	530	663
O-4-HPIMN-Zn	3428	1624	1550, 1512	1271	505	663
O-4-HPIMN-Cd	3406	1635	1542, 1405	1268	537	668

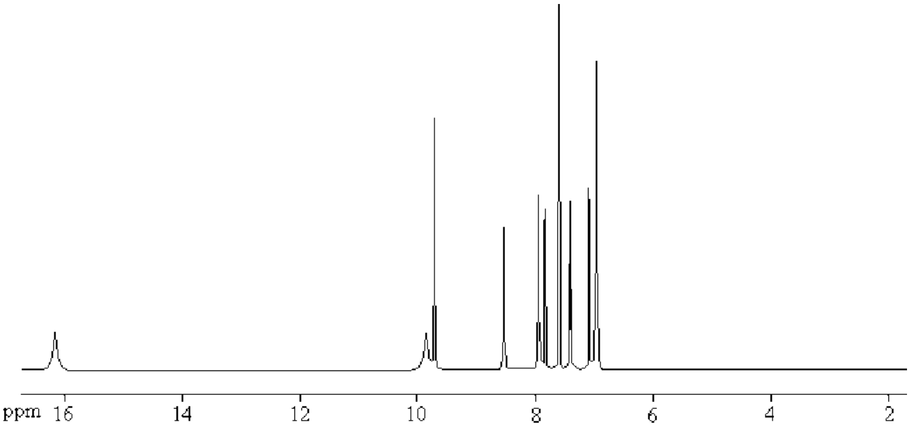


Figure 1. ^{1}H-NMR spectrum of 2-[(4-hydroxyphenyl) imino methyl]-1-naphtol.

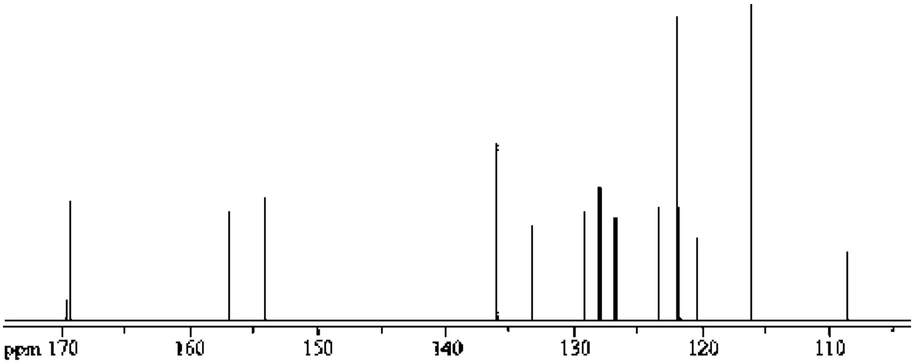


Figure 2. ^{13}C-NMR spectrum of 2-[(4-hydroxyphenyl) imino methyl]-1-naphtol.

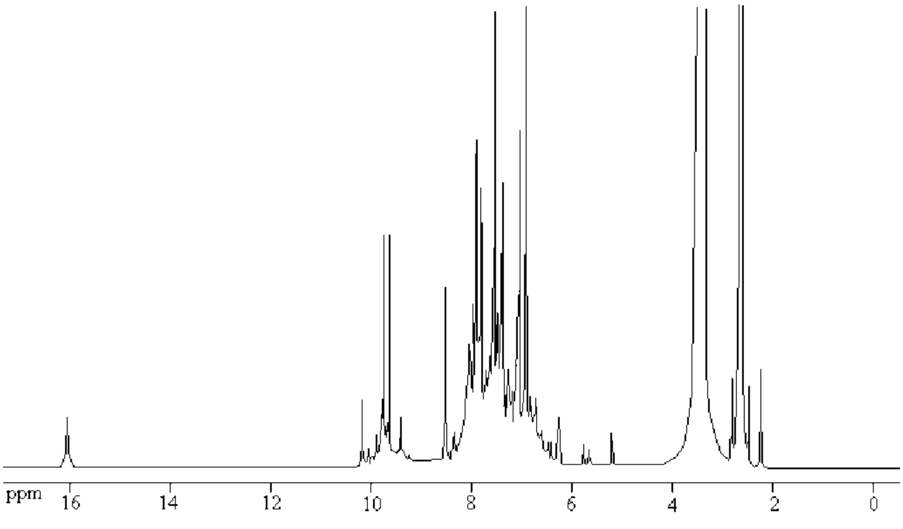


Figure 3. ^{1}H-NMR spectrum of oligo-2-[(4-hydroxyphenyl) imino methyl]-1-naphtol.

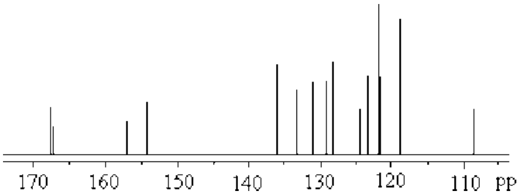


Figure 4. ^{13}C-NMR spectrum of oligo-2-[(4-hydroxyphenyl) imino methyl]-1-naphtol.

TG-DTA curves of O-4-HPIMN-Cd, O-4-HPIMN-Co, O-4-HPIMN-Cu, O-4-HPIMN-Fe, O-4-HPIMN-Hg, O-4-HPIMN-Mg, O-4-HPIMN-Mn, O-4-HPIMN-Ni, O-4-HPIMN-Pb and O-4-HPIMN-Zn oligomer-metal complex compounds are given Figures 7–15, respectively. A modification of the thermal stability by polycondensation or depending on the metal cation electro negativity is expected (15). Both oligomer and oligomer-metal complex compounds show onset temperature values in the 173–494°C range. The water presence is also seen in TG curves of oligomer-metal complex compounds (Figures 7–15) which appeared until 1%–15% wt losses in the 50–150°C range and required both crystallization (50–150°C) and coordination water (150–200°C) removal (15). This can also explain the differences, which appeared between the found and calculated elemental analysis values. O-4-HPIMN-Mg demonstrated lower thermal stability against thermo oxidative degradation than other oligomer-metal complex compounds.

Conclusions

2-[(4-hydroxyphenyl) imino methyl]-1-naphtol was converted to oligomer by oxidizing in air O_2, H_2O_2 and NaOCl at aqueous alkaline medium. Conversion to the 4-HPIMN

Table 3
Thermo oxidative degradation values of 4-HPIMN, O-4-HPIMN and oligomer-metal complex compounds

Compounds	$^{a}T_{on}$	$^{b}W_{max.}T$	20% Weight losses	% Carbine residue at 1000°C
4-HPIMN	287	—	308	28.02
O-4-HPIMN	250	—	275	44.22
O-4-HPIMN-Cu	206	221, 340 549	248	49.15
O-4-HPIMN-Ni	247	310	285	14.51
O-4-HPIMN-Co	253	296, 505, 804	258	13.48
O-4-HPIMN-Mn	494	635	662	71.83
O-4-HPIMN-Fe	236	249, 504	133	29.59
O-4-HPIMN-Pb	173	290, 387, 546	387	60.95
O-4-HPIMN-Mg	190	278, 342, 353	218	5.03
O-4-HPIMN-Zn	196	297, 542, 787	342	31.26
O-4-HPIMN-Cd	191	360, 518, 772, 922	418	39.52

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

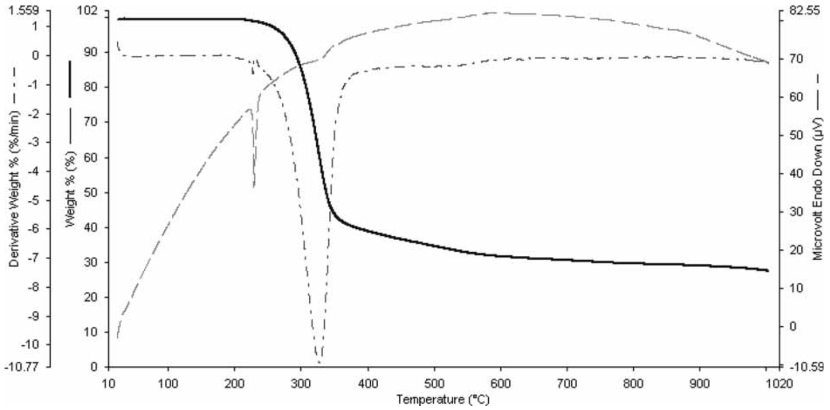


Figure 5. TG-DTG-DTA curves of 2-[(4-hydroxyphenyl) imino methyl]-1-naphtol.

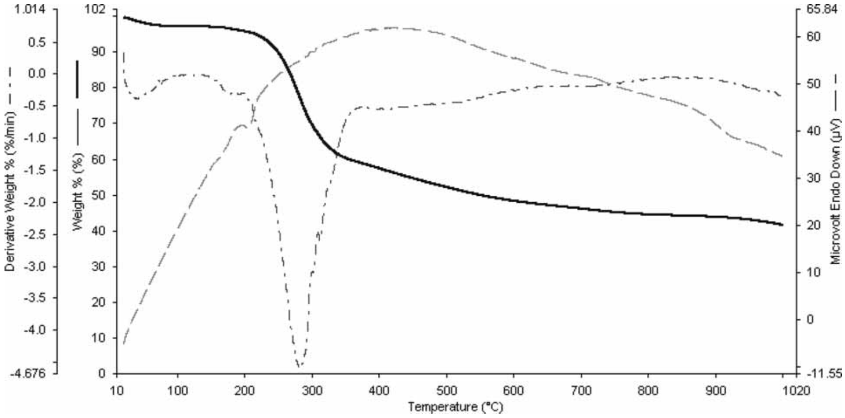


Figure 6. TG-DTG-DTA curves of oligo-2-[(4-hydroxyphenyl) imino methyl]-1-naphtol.

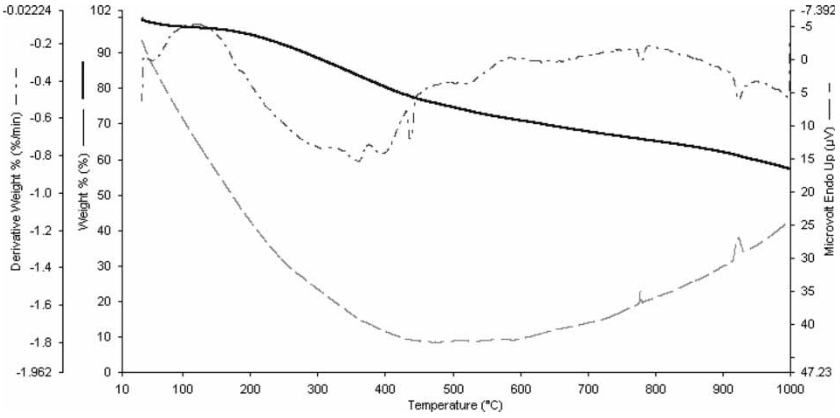


Figure 7. TG-DTG-DTA curves of O-2-HPIMN-Cd-complex.

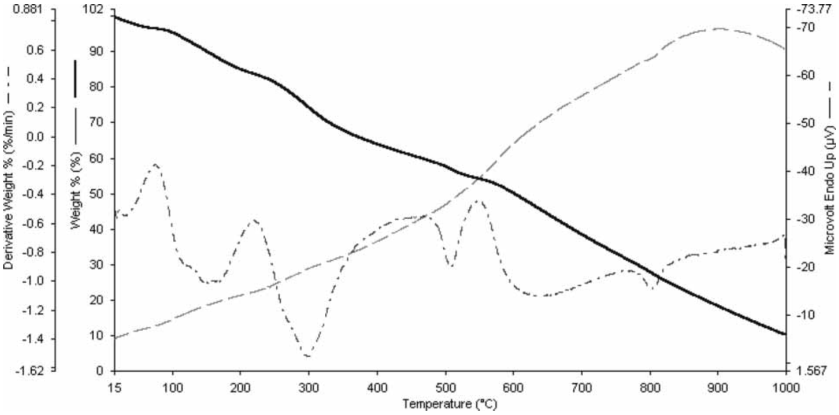


Figure 8. TG-DTG-DTA curves of O-2-HPIMN-Co-complex.

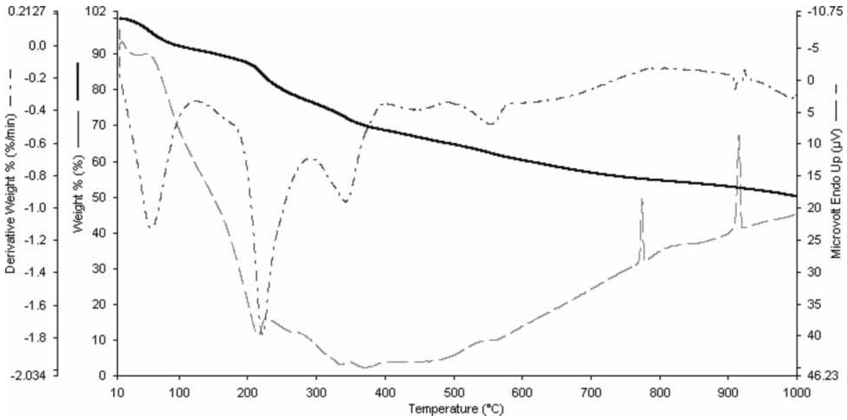


Figure 9. TG-DTG-DTA curves of O-2-HPIMN-Cu-complex.

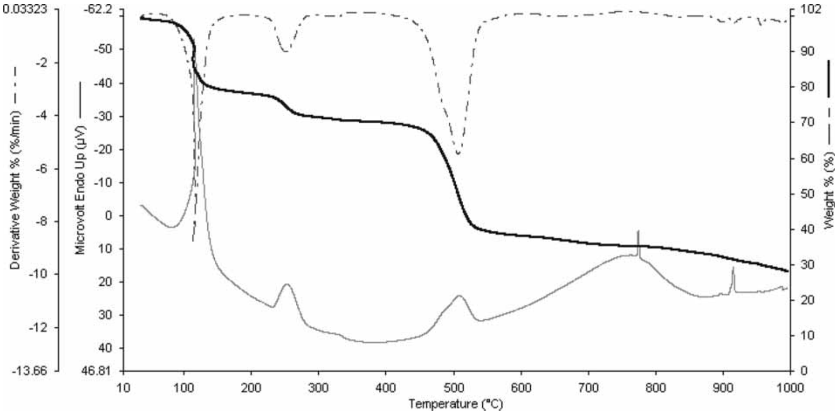


Figure 10. TG-DTG-DTA curves of O-2-HPIMN-Fe-complex.

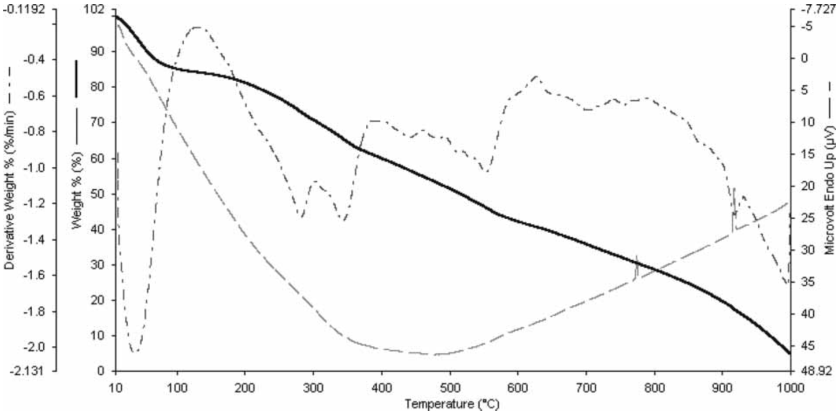


Figure 11. TG-DTG-DTA curves of O-2-HPIMN-Mg-complex.

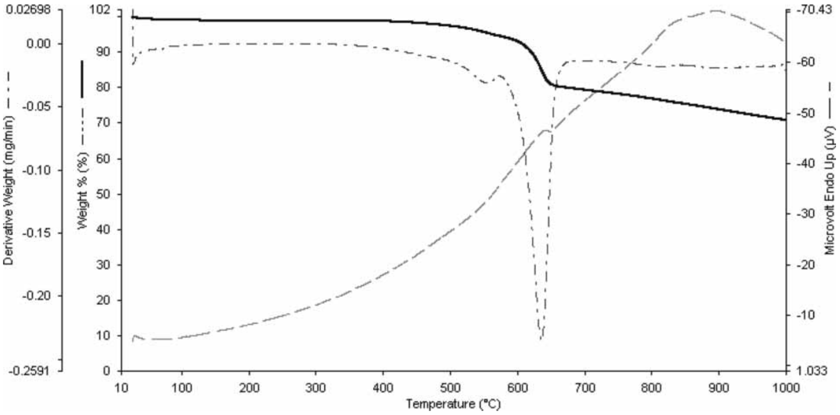


Figure 12. TG-DTG-DTA curves of O-2-HPIMN-Mn-complex.

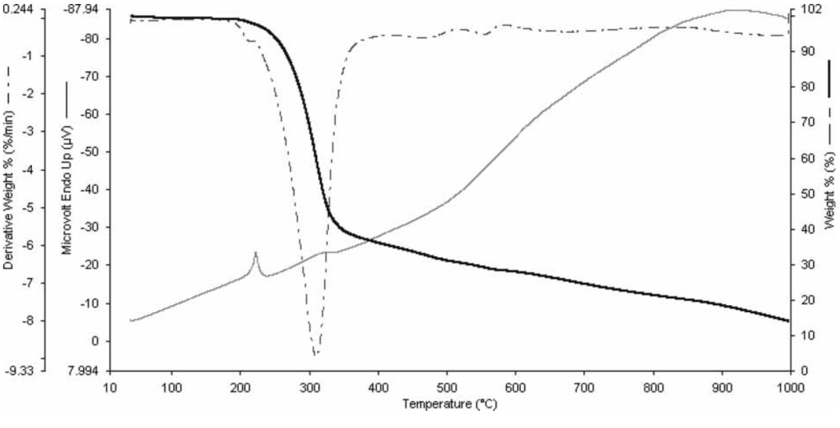


Figure 13. TG-DTG-DTA curves of O-2-HPIMN-Ni-complex.

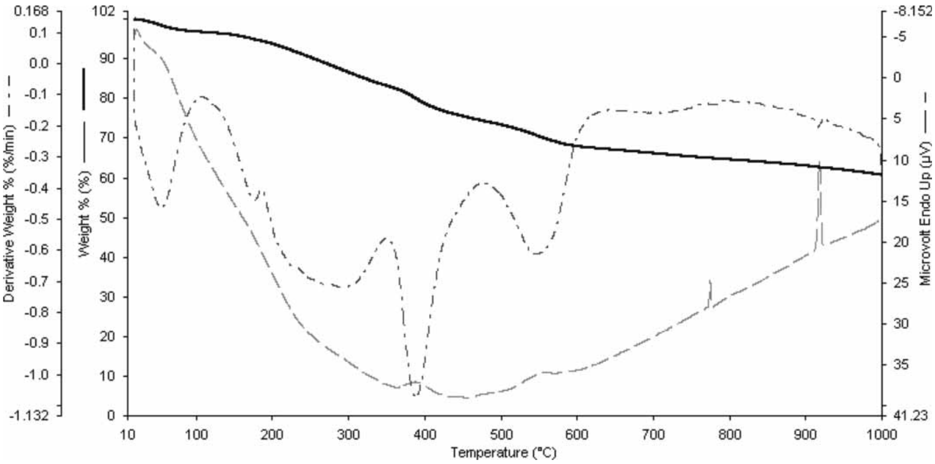


Figure 14. TG-DTG-DTA curves of O-2-HPIMN-Pb-complex.

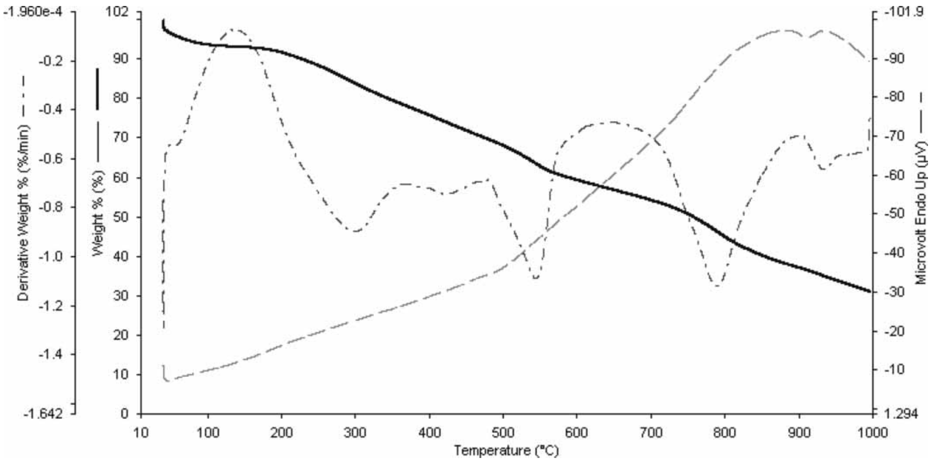


Figure 15. TG-DTG-DTA curves of O-2-HPIMN-Zn-complex.

oligomer was found to be 99% for the NaOCl oxidant. The M_n, M_w and PDI values of 4-HPIMN were found to be 1790, 2250 g mol^{-1} and 1.257, respectively, using the H_2O_2 oxidant; 4540, 5139 g mol^{-1}, and 1.132, respectively, using the air O_2 oxidant, and 1777, 2225 g mol^{-1} and 1.252, respectively, using the NaOCl oxidant. In the oxidative polycondensation reaction of 4-HPIMN, H_2O_2 demonstrated less activity than the NaOCl and air O_2 oxidants. The spectral analyses such as UV-Vis, FT-IR, ^{1}H and ^{13}C-NMR have demonstrated the ability to unite from *ortho* carbons of phenol ring each other of formation oligomers from oxidative polycondensation of 4-HPIMN. The results of TG-DTA analyses were shown to have enough resistance against thermo-oxidative degradation of oligo-2-[(4-hydroxyphenyl) imino methyl]-1-naphtol. The carbines residue of this oligomer was formed at high amount (44.22%) at 1000°C. According to TG analyses, weight losses of oligomer-metal complex compounds changed at 1000°C as follows: O-4-HPIMN-Mn > O-4-HPIMN-Pb > O-4-HPIMN-Cu > O-4-HPIMN-Cd > O-4-HPIMN-Zn > O-4-HPIMN-Fe > O-4-HPIMN-Ni > O-4-HPIMN-Co > O-4-HPIMN-Mg. As result, O-4-HPIMN-Mn and O-4-HPIMN-Pb demonstrated higher thermal stability against thermo oxidative degradation than monomer, oligomer and other oligomer-metal complex compounds.

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