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# Synthesis and Thermal Properties of a Novel Schiff Base Oligomer with a Double Azomethine Group and its Co(II) and Mn(II) Complexes

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Schiff base oligomer of N,N'-bis (2,4-dihydroxybenzylidene) 1,2-phenylenediamine (DHBPDA), with a double azomethine group, was synthesized from the oxidative polycondensation (OP) reaction with NaOCl as an oxidant in an aqueous alkaline medium at 90°C. About 75% DHBPDA was converted to O-DHBPDA. The structures of the products were studied by UV-Vis, FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and elemental analysis. According to Gel Permeation Chromatography (GPC) analysis of O-DHBPDA, the number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and PDI values were found to be 4328 g mol<sup>-1</sup>, 6228 g mol<sup>-1</sup> and 1.43, respectively. TG/DTA analyses were shown to be stable of O-DHBPDA against thermo-oxidative decomposition. During the polycondensation reaction, a part of the azomethine (-CH=N-) groups oxidized to aldehyde (CHO) group (10–12%). Oligomer-metal complexes of oligo-N,N'-bis (2,4-dihydroxybenzylidene) 1,2-phenylenediamine (O-DHBPDA) with Co(II) and Mn(II) were synthesized and characterized by FT-IR, UV-Vis, TG-DTA and Atomic Absorption Spectroscopy (AAS). The residue of DHBPDA, O-DHBPDA, O-DHBPDA-Co and O-DHBPDA-Mn were found to be 0%, 3.65%, 11.67%, and 9.20%, respectively at 1000°C.

**Keywords:** oxidative polycondensation; Schiff base oligomer; oligomer-metal complexes; thermal properties; oligo-N,N'-bis (2,4-dihydroxybenzylidene) 1,2-phenylenediamine

## 1 Introduction

In the last years, there has been increasing interest in the synthesis of new polymers with unusual thermal, optical and mechanical properties. Among these, polyazomethines were investigated with respect to their properties including thermal stability (1, 2), non-linear optical response (3), semi conductivity (4–6), syn–antiisomerization (7) and film or fiber forming ability (8). In some polyazomethines, liquid crystals in nematic phase were also evidenced even at room temperature (9). Due to this broad range of properties, such polymers are generally used to get optical devices, semi-conducting materials (10) and more recently, as catalytic support (11). The branch of polymer–metal complexes has been developed as an interdisciplinary area involving chemistry, electrochemistry, metallurgy, environmental protection, and material science (12, 13).

Also, polymer-metal complex compounds have useful properties such as thermal stability, ion selectivity, conductivity, and antimicrobial properties. Catalytic activity of styrene-allylchloride copolymer supported cobalt (II) Schiff base complex compound was studied by Gupta et al. (14). Conductivity properties of Cu (II) and Ni (II) complex compounds of poly(2-hydroxy-4-methacryloyloxybenzophenone) were studied by Kaliyappan et al. (15). Antimicrobial properties of oligophenols with a Schiff base substitute and their oligomer-metal complex compounds were investigated by Kaya et al. (16, 17). Thermal properties of polymer-metal complex compounds were investigated and reported in the literature (18–21). For nearly 50 years, researchers have worked to integrate M (salen)-type complexes into polymers and oligomers in the hope of generating materials with favorable characteristics (22).

In this paper, the Schiff base monomer (DHBPDA) was prepared by a common condensation method of an aldehyde and diamine. The new oligo Schiff base (O-DHBPDA) was synthesized from the oxidative polycondensation of DHBPDA with NaOCl in an aqueous alkaline medium. The characterization of synthesized monomer and oligomer was carried out using FT-IR, UV-Vis, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR, elemental analysis and Gel Permeation Chromatography

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(GPC) techniques. The new oligomer-metal complexes were synthesized using O-DHBPDA and Co(II) and Mn(II) metal acetates and characterized by spectroscopic methods. Thermal properties of monomer, oligomer and oligomer-metal complexes were studied by TG-DTA techniques.

## 2 Experimental

### 2.1 Materials

2,4-dihydroxybenzaldehyde,  $\text{Mn}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$  were supplied from Fluka Chemical Co. and were used as received. 1,2-Phenylenediamine, ethanol, benzene, *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), NaOCl (15%, aqueous solution), hydrochloric acid (HCl, 37%) and KOH were supplied from Merck and used without further purification.

### 2.2 Characterizations

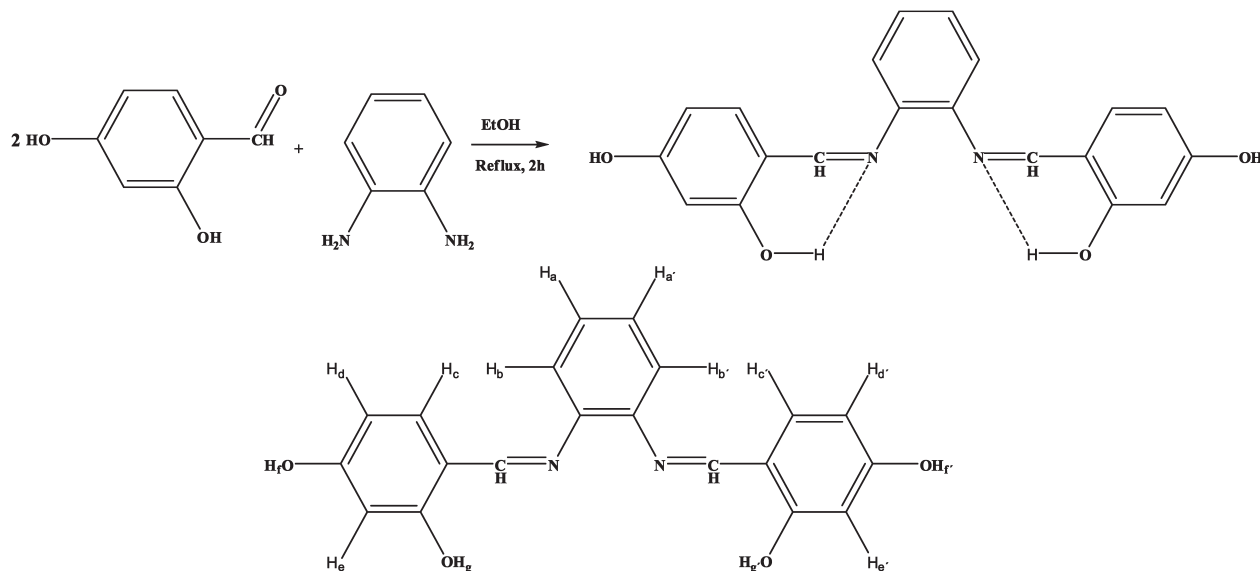
The infrared and UV-Vis. spectra were measured using a Perkin-Elmer RX-1FT-IR and Perkin-Elmer Lambda 25 UV-Vis spectrometers, respectively. The FT-IR spectra were recorded using KBr discs ( $4000\text{--}400\text{ cm}^{-1}$ ). Elemental analysis was carried out with LECO-CHNS-932 (at Tübitak-Atal Lab.). The monomer and oligomer were characterized by using  $^1\text{H-NMR}$  spectra (Bruker Biospin 300 MHz spectrometer, USA) recorded at  $25^\circ\text{C}$  using deuterated DMSO as a solvent. Tetramethylsilane was used as an internal standard. In addition, a  $^{13}\text{C-NMR}$  spectrometer was used for oligomer characterization at  $25^\circ\text{C}$  by using  $\text{CDCl}_3$  as a solvent. The number-averaged molecular weight ( $M_n$ ), mass-averaged molecular weight ( $M_w$ ), and polydispersity index values (PDI) of O-DHBPDA were determined by Gel

Permeation Chromatography (GPC) on a Shimadzu LC apparatus. For GPC investigations, the Machery-Nagel GmbH & Co. 7.7 mm i.d.  $\times$  300 mm columns were employed with  $0.5\text{ ml min}^{-1}$  of DMF as mobile phase and polystyrene standards. A refractive index detector (RID) operated at  $30^\circ\text{C}$  was used to analyze the oligomer. Differential thermal analyses (DTA) and thermogravimetry (TG) of the samples were performed with Setaram Labsys Thermal Analyzers in air medium, starting from  $50^\circ\text{C}$  up to  $1000^\circ\text{C}$  with the heating rate of  $10^\circ\text{C min}^{-1}$ . Metal analyses were carried out by AAS Perkin-Elmer 3100 in a solution prepared by decomposition of the complexes with  $\text{HNO}_3$  followed by dilution with deionized water.

### 2.3 Synthesis of *N,N'*-bis (2,4-dihydroxybenzylidene) 1,2-phenylenediamine (DHBPDA)

DHBPDA was prepared by the condensation of 2,4-dihydroxybenzaldehyde (17.22 g, 0.12 mol) and 1,2-phenylenediamine (6.49 g, 0.06 mol) in ethanol (100 ml) achieved by boiling the mixture and stirred under reflux for 2 h (Scheme 1). The solvent was evaporated under reduced pressure and unreacted phenylenediamine was separated from the mixture by extraction with benzene. The precipitated monomer was dried in vacuum desiccators. (Color, yellow; m.p.  $220\text{--}222^\circ\text{C}$ ; yield: 90%).

Anal. calcd. for DHBPDA: C, 68.96; H, 4.59; N, 8.06. Found for DHBPDA: C, 68.70; H, 4.72; N, 8.10. UV-Vis in DMSO ( $\lambda_{\text{max}}$ ): 230, 251, 320, and 333 nm. FT-IR (KBr;  $\text{cm}^{-1}$ ): 3178 (-OH str.); 3083 (Ar-H str.); 1630 (-CH=N-str.); 158 (Ar, -C=C-);  $1262\text{ cm}^{-1}$  (phenolic C-O bonding str.).  $^1\text{H-NMR}$  (DMSO): ppm, 13.40 (broad -OH<sub>gg'</sub>); 10.30 (broad -OH<sub>ff'</sub>); 8.75 (-CH=N-); 7.50–7.40 (d, Ar-H<sub>cc'</sub>); 7.38–7.28 (m, Ar-H<sub>bb'</sub>, Ar-H<sub>aa'</sub>); 6.43–6.37 (Ar-H<sub>dd'</sub>); 6.30 (Ar-H<sub>ee'</sub>).

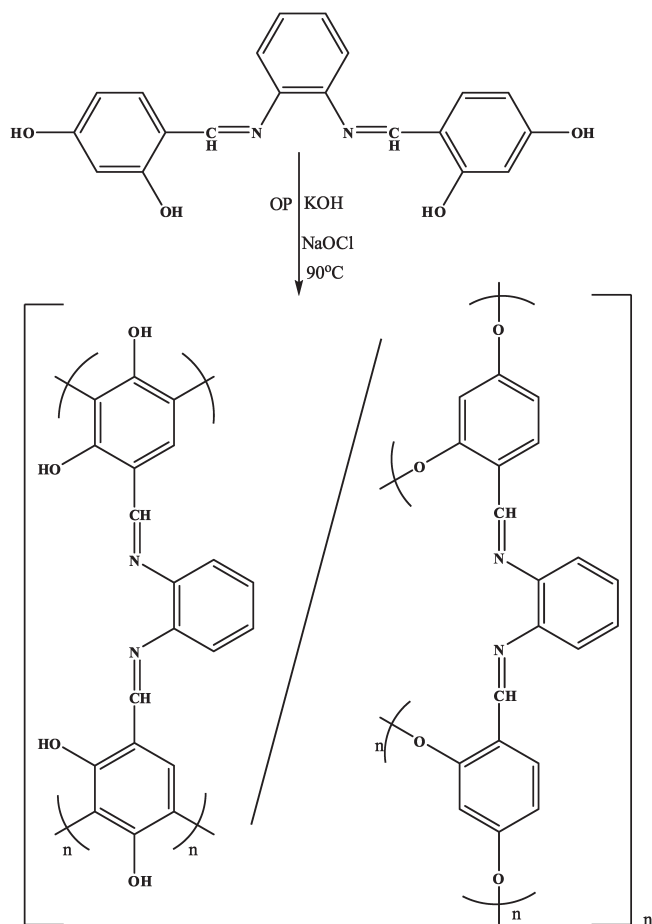


Sch. 1. Synthesis of *N,N'*-bis (2,4-dihydroxybenzylidene) 1,2-phenylenediamine.

#### 2.4 Synthesis of Oligo-*N,N'*-bis (2,4-dihydroxybenzylidene) 1,2-phenylenediamine (O-DHBPDA)

O-DHBPDA was synthesized through oxidative polycondensation of DHBPDA by using an aqueous solution of NaOCl (51 ml, 15%). The Schiff base monomer (14.9 g) was dissolved in an aqueous solution of KOH (10%, 0.17 mol) placed into a 250 ml three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and an addition to funnel containing NaOCl. After heating to 60°C for 15 min, NaOCl was added dropwise over about 45 min. The reaction mixture was stirred at 90°C for 13 h. It was cooled to room temperature and then 0.17 mol of HCl (37%) was added to the reaction mixture. The mixture was filtered and washed with hot water (3 × 50 ml) for separating from mineral salts. Unreacted monomer was separated from the product by washing with methanol and then the product dried in the oven at 110°C (Scheme 2). (color, dark brown; m.p. > 30°C; yield 75%).

Anal. calc. For O-DHBPDA: C, 69.70; H, 3.45; N, 8.15. Found for O-DHBPDA: C, 65.80; H, 3.68; N, 7.85. UV-Vis in DMSO ( $\lambda_{\max}$ ): 224, 250, 350, and 368 nm (400–600 nm). FT-IR (KBr;  $\text{cm}^{-1}$ ): 3380–3200 (-OH); 3062



Sch. 2. Synthesis of oligo-*N,N'*-bis (2,4-dihydroxybenzylidene) 1,2-phenylenediamine.

(Ar-H); 1619 (-CH=N- str.); 1582 (Ar, -C=C-); 1276  $\text{cm}^{-1}$  (phenolic C-O bonding str.).  $^1\text{H}$  NMR (DMSO):  $\delta$  ppm, 14.60–12.70 (broad-H); 9.90 (s, -CHO); 9.10–8.10 (m, -CH=N-); 8.00–6.90 (m, Ar-H<sub>aa'</sub>, Ar-H<sub>bb'</sub>, Ar-H<sub>cc'</sub>); 6.85–6.25 (m, Ar-H<sub>dd'</sub>, Ar-H<sub>ee'</sub>).  $^{13}\text{C}$ -NMR (CDCl<sub>3</sub>): ppm, 191.8 (CHO, aldehyde); 165.5–162.5 (-CH=N-); 162.0–160.0 (C-OH) 159.5.0–155.0 (C-O-C); 154.0–152.0 (Ar, C-N=C); 145.0–140.0 (C-C) and 135.0–103.0 ppm (Ar, C-H).

#### 2.5 Synthesis of Oligo-*N,N'*-bis (2,4-dihydroxybenzylidene) 1,2-phenylenediamine Metal Complexes

##### 2.5.1 Co(II) Complexes

A hot solution of Co(AcO)<sub>2</sub> · 4H<sub>2</sub>O (11.6 mmol, 2.89 g) in H<sub>2</sub>O (20 ml) was added dropwise to a hot solution of O-DHBPDA (5.8 mmol/unit, 2.00 g) in DMF (20 ml). The mixture was stirred and heated at 60–70°C for 5 h. The precipitated complex was filtered through a gooch crucible (por 3) and washed with cold ethanol and H<sub>2</sub>O, then dried in vacuum oven.

(Color, black; m.p. > 250°C; yield 60.7%).

Found for O-DHBPDA-Co(II); 9.9% Co(II) by AAS. UV-Vis in DMSO ( $\lambda_{\max}$ ): 245, 300, 340, and 400–700 nm. FT-IR (KBr;  $\text{cm}^{-1}$ ): 3376–3200 (-OH); 3060 (Ar-H); 1606 (-CH=N- str.); 1573 (Ar, -C=C-, str.); 1260  $\text{cm}^{-1}$  (phenolic C-O bonding str.).

##### 2.5.2 Mn(II) Complexes

A hot solution of Mn(AcO)<sub>2</sub> · 4H<sub>2</sub>O (11.6 mmol, 2.84 g) in H<sub>2</sub>O (20 ml) was added dropwise to a hot solution of O-DHBPDA (5.8 mmol/unit, 2.00 g) in DMF (20 ml). The mixture was stirred and heated at 60–70°C for 5 h. The precipitated complex was filtered from por 3 gooch crucible and washed with cold ethanol and H<sub>2</sub>O, then dried in vacuum oven.

(Color, black; m.p. > 250°C; yield 57.5%).

Found for O-DHBPDA-Mn(II); 6.3% Mn(II) by AAS. UV-Vis. in DMSO ( $\lambda_{\max}$ ): 244, 336, and 400–700 nm. FT-IR (KBr;  $\text{cm}^{-1}$ ): 3380–3205 (-OH); 3066 (Ar-H str.); 1603 (-CH=N- str.); 1565 (Ar, -C=C-, str.), 1267  $\text{cm}^{-1}$  (phenolic C-O bonding str.).

### 3 Results and Discussions

#### 3.1 Solubility

The solubility of monomer, oligomer and oligomer-metal complexes was studied at room temperature. All of the compounds were insoluble in water and diethylether. Monomer was dissolved in acetone but oligomer was not. O-DHBPDA was partially soluble in CHCl<sub>3</sub> and THF solvents. In addition, it was completely soluble in DMF and DMSO solvents. The oligomer-metal complexes were poorly soluble in DMF and completely soluble in DMSO.

**Table 1.** The number average weight ( $M_n$ ), mass average molecular weight ( $M_w$ ), polydispersity index (PDI) and % values of OP products of DHPDA

Compound	Total			Fraction I				Fraction II			
	$M_n$	$M_w$	PDI	$M_n$	$M_w$	PDI	%	$M_n$	$M_w$	PDI	%
O-DHPDA	4328	6228	1.43	3910	4298	1.10	88	19759	20319	1.03	12

The insolubility of oligomer-metal complexes can be explained by the bonding formation of metal-nitrogen and metal-oxygen. The insolubilities of complexes are important for easy separation from the reaction mixture while used as catalysts.

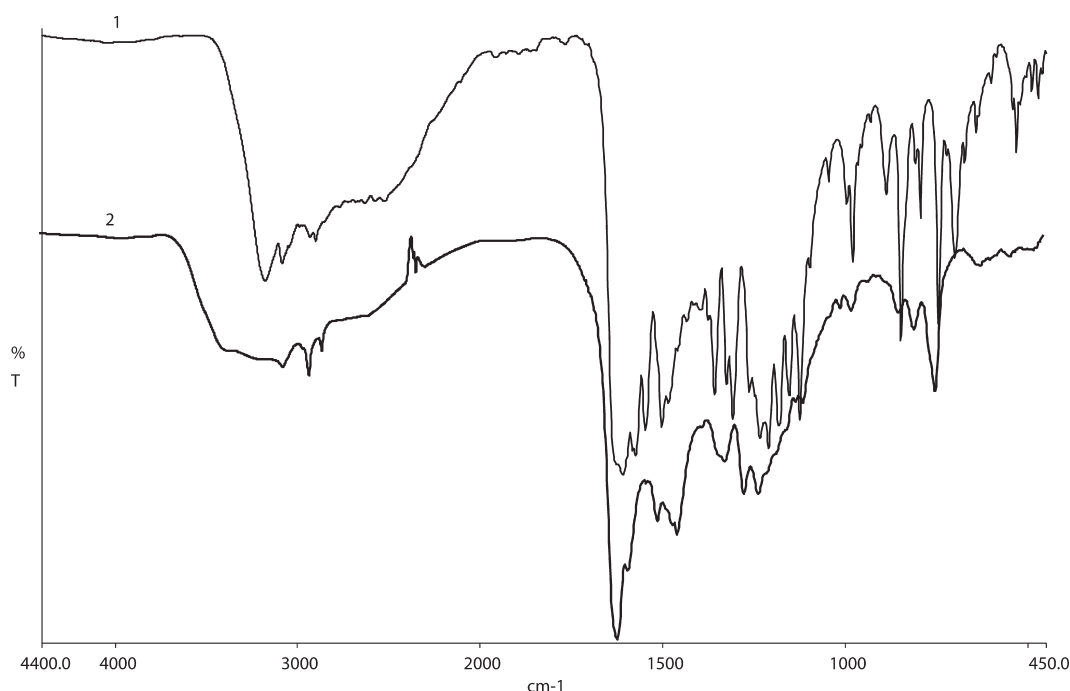
### 3.2 Structure of DHPDA, O-DHPDA and O-DHPDA-metal Complexes

According to GPC analysis of O-DHPDA, the number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and PDI values were found to be 4328 g mol<sup>-1</sup>, 6228 g mol<sup>-1</sup>, and 1.43, respectively. At the molecular weight distribution of O-DHPDA, two peaks were observed; low molecular weight (fraction I) and high molecular weight (fraction II) are given in Table 1.

The electronic spectra of monomer, oligomer and oligomer-metal complexes were recorded in DMSO solvent. The absorption bands of monomer and oligomer were observed at 230, 251, 320, 333 nm and 224, 253, 350, 368 nm, respectively. The bands at 230;224 nm were attributed to conjugation between the benzene ring and nonbonding

electrons of nitrogen in the azomethine group. The bands at 251;253 nm and 320, 333;350, 368 nm were assigned to the benzene  $\pi-\pi^*$  and the imines  $\pi-\pi^*$  transitions for monomer and oligomer, respectively. As being different from monomer, the oligomer's absorption region in 400–600 nm can be caused by its long polymer structure system (23). In the oligomer-metal complexes spectra, the low intensity absorption bands in 500–700 nm range are consisted of d–d transitions of the metal ions.

Figure 1 shows the infrared spectra of monomer and oligomer. Similar to the spectra of monomer, at the spectra of O-DHPDA, the absorption bands of -OH, Ar-C-H, azomethine -CH=N-, aromatic -C=C-, phenolic C-O groups were observed at 3380–3200, 3062, 1619, 1582, 1276 cm<sup>-1</sup>, respectively. On the other hand, the FT-IR spectrum of O-DHPDA was different in the reduction of the band strength and numbers from the FT-IR spectrum of DHPDA due to the increase in molecular weight after oxidative polycondensation. For the free ligands, the broad bands in the 2800–2700 cm<sup>-1</sup> range are assigned to the OH group vibration (ortho position) associated intramolecularly (O-H...N) with the nitrogen atom of the CH=N group

**Fig. 1.** The FT-IR spectra of DHPDA (1) and O-DHPDA (2).

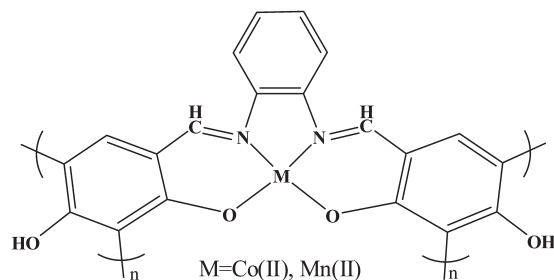
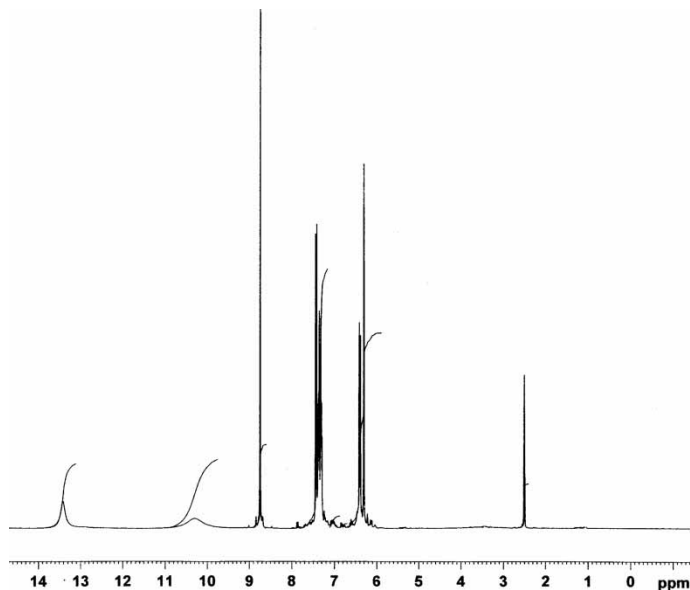
**Table 2.** The FT-IR spectral data of the O-DHBPDA and its metal complexes

Compound	Wavenumber (cm <sup>-1</sup> )					
	OH	Ar-CH	CH=N	-C-O	M-N	M-O
O-DHBPDA	3380–3200	3062	1619	1276	—	—
O-DHBPDA-Co	3376–3200	3060	1606	1260	550	505
O-DHBPDA-Mn	3380–3205	3066	1603	1267	549	495

(24). Both the FT-IR spectra of monomer and oligomer showed the absorption bands at 2700–2800 cm<sup>-1</sup> region, attributed to the intramolecular hydrogen bond (Scheme 2). The monomer absorption bands intensity at 750–850 cm<sup>-1</sup> decreased after oxidative polycondensation, and can be attributed to the phenylene (C-C linkage) units chain of the oligomer (23).

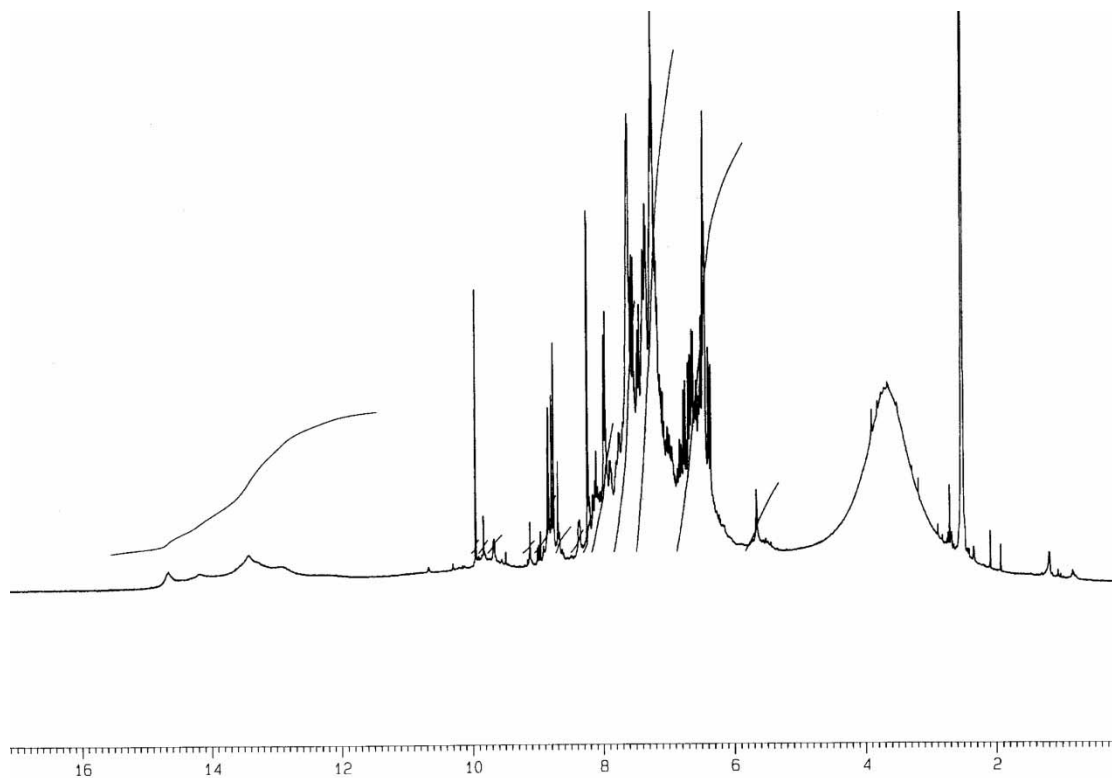
The FT-IR spectral data of O-DHBPDA and its Co(II) and Mn(II) complexes were given in Table 2. When the spectral data were compared, the azomethine (-CH=N-) and phenolic C-O bands shifted to a lower frequencies. As a result of coordination of the azomethine nitrogen and ortho position of hydroxyl oxygen atoms to metal ions, the -CH=N- and C-O bonds of the complexes shift towards lower values (25). In addition, at the FT-IR spectra of oligomer-metal complexes (not shown), the low intensity bands observed at the 549–550 cm<sup>-1</sup> and 495–509 cm<sup>-1</sup> region can be related with the M-N and M-O stretching. Furthermore, at the FT-IR spectra of oligomer-metal complexes were not observed vibrations bands at 2700–2800 cm<sup>-1</sup> range due to the disappearance of intramolecular hydrogen bonds after coordination of (-CH=N-) nitrogen atom to metal ions (Scheme 3).

Additional structural information can be deduced from the <sup>1</sup>H NMR (Fig. 2) spectra of DHBPDA and <sup>1</sup>H-NMR (Fig. 3) and <sup>13</sup>C-NMR (Fig. 4) spectra of O-DHBPDA, recorded in DMSO-d<sub>6</sub>. At the <sup>1</sup>H NMR spectra of O-DHBPDA, the chemical shifts of -OH, -CH=N and Ar-H were observed at 14.60–12.70 ppm (broad), 9.10–8.10 ppm (m) and 8.00–6.90 ppm (m, Ar-H<sub>aa'</sub>, Ar-H<sub>bb'</sub>, Ar-H<sub>cc'</sub>); 6.85–6.25 ppm (m, Ar-H<sub>dd'</sub>, Ar-H<sub>ee'</sub>), respectively. The <sup>1</sup>H-NMR spectrum

**Sch. 3.** Synthesis of oligo-N,N'-bis(2,4-dihydroxybenzylidene) 1,2-phenylenediamine metal complexes.**Fig. 2.** <sup>1</sup>H-NMR spectrum of DHBPDA.

of monomer show very sharp peaks. After oxidative polycondensation, however, the peaks become broad and also increased in number. These cases are attributed to polymerization. The decreases in integral ratio of aromatic protons; H<sub>dd'</sub>-H<sub>ee'</sub> to H<sub>cc'</sub> at the <sup>1</sup>H-NMR spectra of O-DHBPDA is attributed to the C-C (phenylene) coupling at *ortho* and *para* positions to hydroxyl groups (Scheme 2). In addition, the decreases in integral ratio of hydroxyl protons to azomethine protons (or phenylenediamine protons) at the <sup>1</sup>H NMR spectra of O-DHBPDA indicating that a little amount of C-O-C (oxyphenylene) coupling caused by the participating of hydroxyl groups in the polymerization reaction. At the <sup>1</sup>H NMR spectra of O-DHBPDA, a new sharp peak was observed at 9.90 ppm which assigned to the aldehyde (CHO) proton. On the other hand, in the <sup>1</sup>H NMR spectrum of O-DHBPDA, the integral ratio of azomethine protons to aldehyde protons, indicating that 10–12% of azomethine group oxidized to aldehyde after polycondensation.

According to <sup>13</sup>C-NMR spectra of O-DHBPDA (Fig. 4), the results were observed as follows: 191.8 ppm (CHO, aldehyde); 165.5–162.5 (-CH=N-); 162.0–160.0 (C-OH) 159.5.0–155.0 (C-O-C); 154.0–152.0 (Ar, C-N=C); 145.0–140.0 (C-C) and 135.0–103.0 ppm (Ar, C-H). The new signals at 140–145 ppm range and 155–160 ppm range at the <sup>13</sup>C-NMR spectra of O-DHBPDA were attributed to the C-C (phenylene) and the C-O-C (oxyphenylene) coupling, respectively, after polycondensation. Other phenol derivatives were also polymerized, and the results have been reported in the literatures (26). Crosslinking in polymer structure is expected in those cases in which the *ortho* and *para* positions in the corresponding monomer structure are unsubstituted. <sup>13</sup>C-NMR studies on O-DHBPDA indicate that the linkage between any two adjacent phenyl rings is largely at the *ortho* and *para* positions.



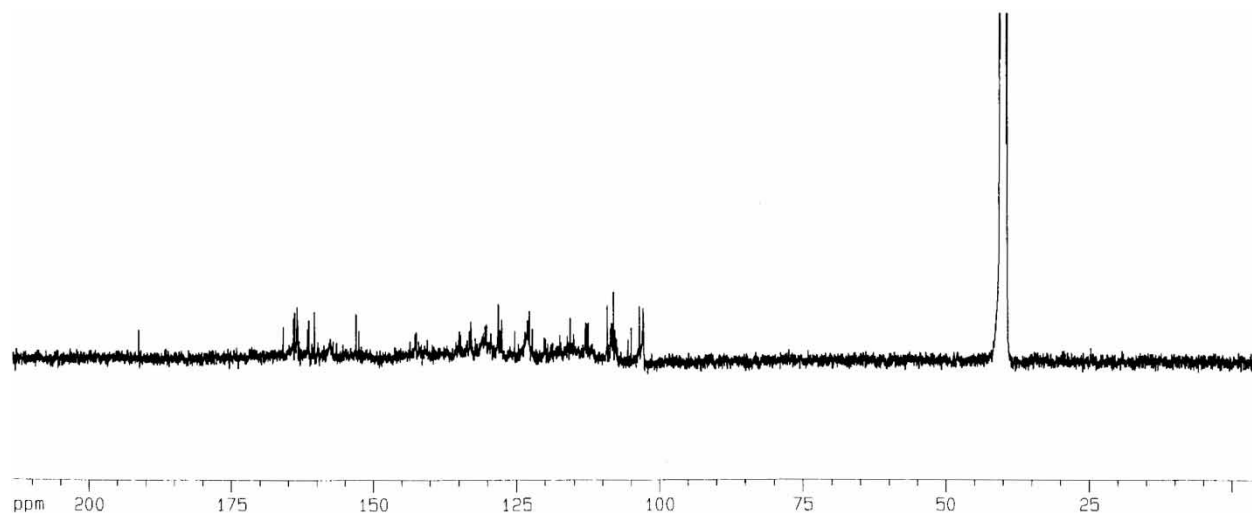
**Fig. 3.**  $^1\text{H-NMR}$  spectrum of O-DHBPDA.

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 (27).

Although a part of azomethine ( $-\text{CH}=\text{N}-$ ) group was oxidized to carboxylic ( $-\text{COOH}$ ) group after the oxidative polycondensation of Schiff bases (16, 17), in this study the

azomethine group was oxidized only to aldehyde group. This idea can be supported by  $^1\text{H-NMR}$  (9.9 ppm) and  $^{13}\text{C-NMR}$  (191.8 ppm) spectral data.

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  analyses results suggest the polymerization of the monomer by OP may be take place through C-O-C and C-C type coupling similar to the results



**Fig. 4.**  $^{13}\text{C-NMR}$  spectrum of O-DHBPDA.

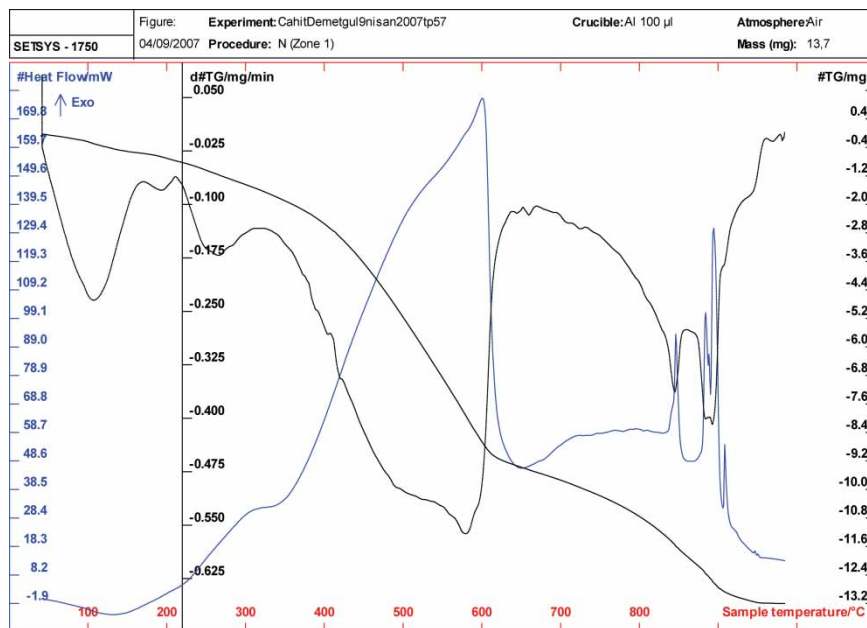


Fig. 5. TG, DTG, and DTA curves of O-DHBPDA.

reported in the literature (23, 27, 28) and the structures of the oligomer can be given as in Scheme 2.

According to the elemental analyses results of metal ions for O-DHBPDA-Co and O-DHBPDA-Mn complexes by AAS, were found to be less than the expected values. This case can be explained by the C-O-C coupling from the  $\text{OH}_{\text{gg}}$  and the oxidation of some azomethine groups to aldehyde, after polycondensation.

### 3.3 Thermal Analyses of DHBPDA, O-DHBPDA and O-DHBPDA-Metal Complexes

TG, DTG, and DTA curves of O-DHBPDA, O-DHBPDA-Co and O-DHBPDA-Mn were given in Figures 5–7. Also the thermal degradation results were given in Table 3. The thermal analyses of these compounds were measured at the air medium, starting from 50°C up to 1000°C with the

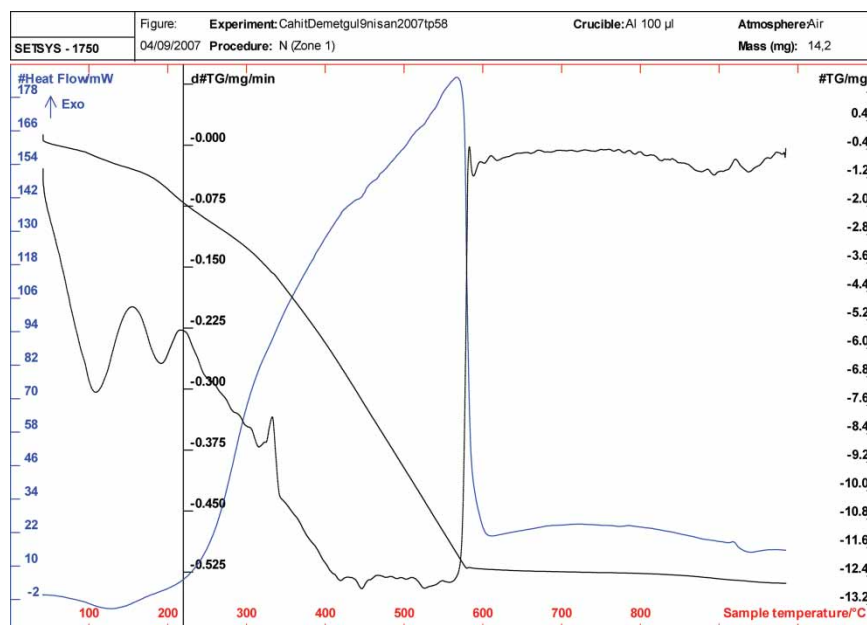


Fig. 6. TG, DTG, and DTA curves of O-DHBPDA-Co.



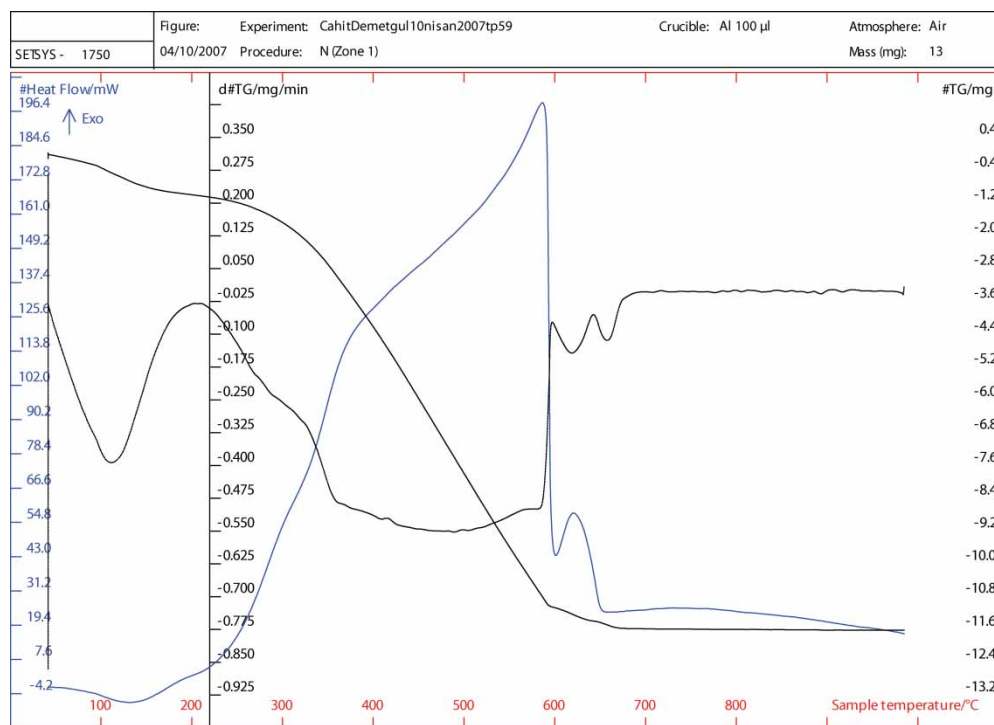


Fig. 7. TG, DTG, and DTA curves of O-DHBPDA-Mn.

heating rate of  $10^{\circ}\text{C min}^{-1}$ . According to DTG curve of the O-DHBPDA (Fig. 5),  $T_{\text{max}}$  and maximum weight losses were found to be 580 and between 320 and  $640^{\circ}\text{C}$ . As is seen in Table 3, the level of residue quantities of DHBPDA, O-DHBPDA, O-DHBPDA-Co and O-DHBPDA-Mn are 0% (not shown), 3.65%, 11.67%, and 9.20%, respectively at  $1000^{\circ}\text{C}$ . According to TG curves of DHBPDA (not shown), O-DHBPDA (Fig. 5), O-DHBPDA -Co (Fig. 6) and O-DHBPDA-Mn (Fig. 7), the thermal degradation was finished at 755, 950, 600, and  $660^{\circ}\text{C}$ , respectively. Because of long conjugated band systems, oligomer demonstrated partly higher resist against high temperature than monomer. The high thermal stability of O-DHBPDA demonstrated to be formed of C-C (phenylene) and C-O-C (oxyphenylene) coupling systems.

The presence of water can be seen in TGA curves of O-DHBPDA, O-DHBPDA-Co, and O-DHBPDA-Mn

**Table 3.** Thermooxidative degradation values of O-DHBPDA and O-DHBPDA-metal complexes

Compound	20%, °C (wt loss)	50%, °C (wt loss)	Residue% (at $1000^{\circ}\text{C}$ )	DTA ( $^{\circ}\text{C}$ )	
				Exo peaks	Endo peaks
O-DHBPDA	383	533	3.65	305,600, 840,900	—
O-DHBPDA-Co	216	426	11.67	558	—
O-DHBPDA-Mn	358	440	9.20	583,625	—

compounds (Fig. 5–7), showing 6, 15, and 10 wt.% losses in the  $50\text{--}150^{\circ}\text{C}$  and  $50\text{--}200^{\circ}\text{C}$  range, respectively, and corresponding to the loss of water of crystallization ( $50\text{--}150^{\circ}\text{C}$ ) and coordination water ( $150\text{--}200^{\circ}\text{C}$ ) (29, 30).

According to DTA curves of the compounds, there were one, two and more than two exothermic peaks for oligomer-Co, oligomer-Mn and oligomer, respectively. There were not observed endothermic peaks at DTA curves of oligomer and oligomer-metal complexes.

As a result, oligomer has shown a sufficient thermal resistance against the high temperature. For these reason, the syntheses of Schiff base substitute oligophenol and oligomer are very important to prepare new thermally stable materials.

#### 4 Conclusions

The new oligomer Schiff base [oligo-N,N'-bis (2,4-dihydroxybenzylidene) 1,2-phenylenediamine] was synthesized from the oxidative polycondensation of N,N'-bis (2,4-dihydroxybenzylidene) 1,2-phenylenediamine with NaOCl in an aqueous alkaline medium. The synthesized oligomer contains hydroxyl and double azomethine group, which can be difficult to achieve by conventional polycondensation method. The  $M_n$ ,  $M_w$ , and PDI values of O-DHBPDA were found to be  $4328\text{ g mol}^{-1}$ ,  $6228\text{ g mol}^{-1}$  and 1.43, respectively. The monomer and the oligomer were characterized by elemental analyses, UV-Vis, FT-IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopic studies, which revealed that the oligomer synthesized by OP is composed of oxyphenylene

(C-O-C) and phenylene (C-C) units. Oligomer-metal complexes were synthesized from O-DHBPDA and Co(II), Mn(II) metal acetates and characterized by spectroscopic techniques. The oligomer-metal complexes were poorly soluble in DMF and completely soluble in DMSO. The insolubilities of complexes are important for using as catalysts by easy separation from the reaction mixture. During the polycondensation reaction, a part of the azomethine (-CH=N-) groups oxidized to aldehyde (CHO) group (10–12%). The residue of DHBPDA, O-DHBPDA, O-DHBPDA-Co, and O-DHBPDA-Mn were 0%, 3.65%, 11.67%, and 9.20%, respectively at 1000°C.

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