

# Synthesis and Characterization of Imine Polymers Containing Aliphatic and Aromatic Groups and Some of Schiff Base-Metal Complexes

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**ABSTRACT:** In this study, the oxidative polycondensation reaction conditions of 2,2'-(2,5-dichloro-1,4-phenylene)bisnitrilomethylidene)diphenol (DCPMDP) were studied between 40 and 90°C using different times and concentrations in the alkaline medium to determine effect on the yield of these parameters. Polymerization of 2,2'-piperazine-1,4-diylbis[propane-3,1-diyl nitrilomethylidene)diphenol (PDMDP) was performed at two steps with graft polycondensation method. Additionally, seven different metal complexes were also synthesized from PDMDP with some metal salts. The structures of the compounds were confirmed by UV-vis, FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy analyses. The characterization

was made by TG-DTA, size exclusion chromatography (SEC), elemental analysis, and solubility tests. HOMO-LUMO energy levels and electrochemical band ( $E_g'$ ) gaps were determined from cyclic voltammetry (CV) measurements. Also, optical band ( $E_g$ ) gaps were calculated from UV-vis measurements. Electrical conductivity of doped and undoped monomer and oligomer were measured by four-point probe technique using an electrometer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3325–3336, 2011

**Key words:** oxidative polycondensation; polyimines; electrical conductivity; thermal analysis

## INTRODUCTION

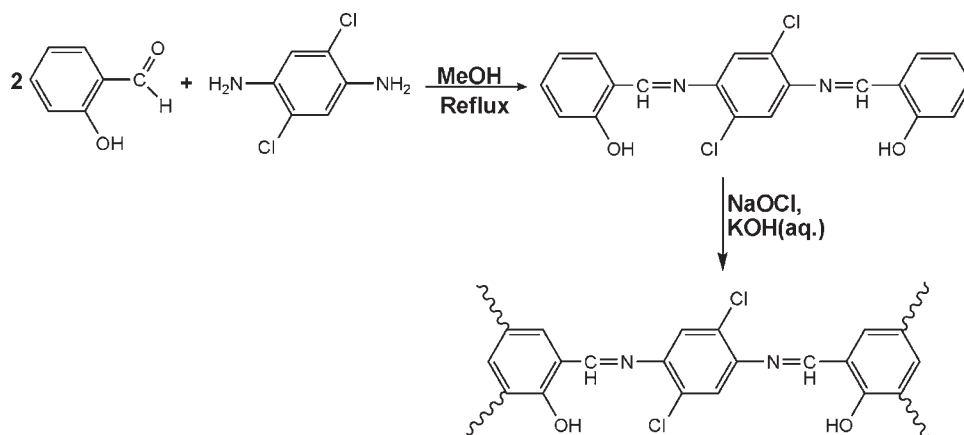
The poly(imines) are an example of conjugated polymers, also known as poly(azomethines) or as Schiff Base polymers.<sup>1</sup> Polyazomethines (PAMs), with a wide range of applications, have had continual increasing interest due to having a lot of properties such as high thermal stability and excellent mechanical strength as well as their semiconductivity, paramagnetism, electrochemical cell, resistance to high energy, and optoelectronic properties.<sup>2–4</sup> Oligophenols and their derivatives have been used in various fields because of their electron structure properties. Because of these properties, they were used to prepare composites with resistance to high temperature, thermostabilizations and graphite materials, epoxy oligomer and block copolymers, adhesives, photo resists, and antistatic materials.<sup>5–11</sup> Oligophenols and their —CH=N— containing derivatives have been synthesized by oxidative polycondensation method and presented in the literature with their several useful properties.<sup>7,12–15</sup> The oxidative polycondensation method is simply the reaction

of compounds including —OH groups and active functional groups (—NH<sub>2</sub>, —CHO, —COOH) in their structure with the oxidants as NaOCl, H<sub>2</sub>O<sub>2</sub>, and air in the aqueous alkaline and acidic medium.<sup>16</sup> Also, the conductivity and electrochemical properties of some poly Schiff bases and their metal complexes have been investigated by Kaya et al.<sup>17,18</sup>

In this article, we report the synthesis and characterization of polyimines which contain aromatic and aliphatic groups. In the first part, we synthesized aliphatic and aromatic Schiff base monomers by condensation reaction. And then, the synthesized aromatic monomer (DCPMDP) was converted into its polymer derivative through oxidative polycondensation (OP) reaction using NaOCl as oxidant. We have investigated the effects of different parameters such as temperature, concentration, and the reaction time for this oligomer in alkaline medium. In the second part, we synthesized poly(PDMDP) via graft polycondensation of the synthesized aliphatic monomer (PDMDP) with oligosalicylaldehyde (OSA) as in the literature.<sup>19</sup> And its Schiff base-metal complexes were synthesized with Cu<sup>+2</sup>, Co<sup>+2</sup>, Ni<sup>+2</sup>, Cd<sup>+2</sup>, Zn<sup>+2</sup>, Pb<sup>+2</sup>, and U<sup>+2</sup> metal salts.

Both the structures and properties of oligomer, polymer, and monomers were characterized by spectral techniques, conductivity, and cyclic voltammetry (CV). Thermal properties of all synthesized

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Scheme 1 Synthesis of DCPMPD and ODCPMPD.

compounds were determined by TG-DTA analysis. Molecular weights of the oligomer were measured by SEC analysis.

## EXPERIMENTAL

### Materials

Salicylaldehyde, 1,4-bis(3-aminopropyl)piperazine, 2,5-dichloro-1,4-*p*-phenylenediamine were supplied by Alfa Aesar. Methanol, ethanol, acetone, acetonitrile, ethyl acetate,  $\text{CHCl}_3$ , tetrahydrofuran (THF), hexane, 1-butanol, dimethylformamide (DMF), dimethylsulfoxide (DMSO),  $\text{H}_2\text{SO}_4$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  (30% aqueous solution), KOH, and HCl were supplied by Merck Chemical (Germany) and they were used as received.  $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ni}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Zn}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Pb}(\text{AcO})_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{Cd}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$  were supplied from Fluka. Sodium hypochlorite (NaOCl), (30%, aqueous solution) was supplied from Paksoy (Turkey).

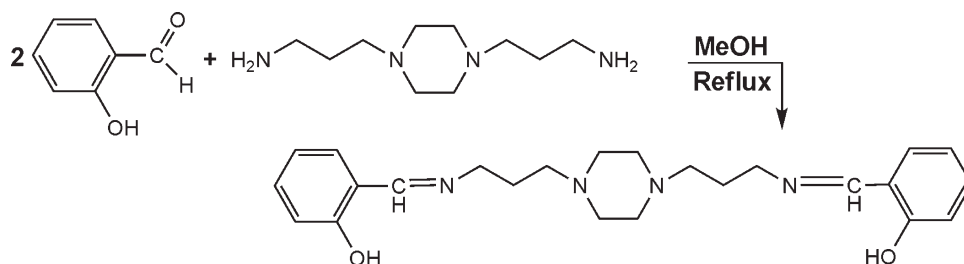
### Syntheses of DCPMPD and ODCPMPD

The 2,2'-[(2,5-dichloro-1,4-phenylene)bisnitrilomethylidene]diphenol (DCPMPD) was prepared by the condensation of salicylaldehyde (1.04 mL, 0.01 mol) with 2,5-dichloro-1,4-*p*-phenylenediamine (0.88 g, 0.005 mol) in methanol (50 mL) achieved by boiling the mixture

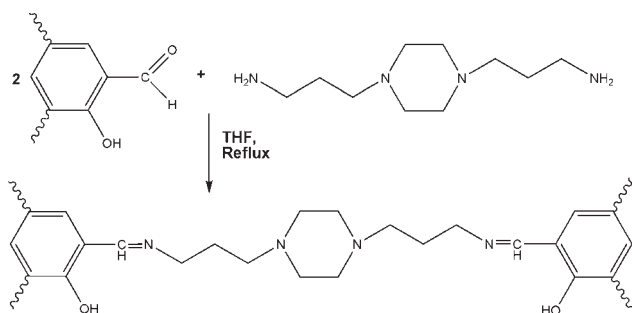
under reflux for 2 h at 70°C (Scheme 1). The precipitated 2,2'-[(2,5-dichloro-1,4-phenylene)bisnitrilomethylidene]diphenol was filtered, and recrystallized from methanol and dried in vacuum desiccator.

Calcd. For DCPMPD: C, 62.33; H, 3.63; N, 7.27. Found: C, 62.10; H, 3.50; N, 7.00. FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  3341,  $\nu(\text{C}-\text{H}$  Phenyl) 3058,  $\nu(\text{C}=\text{N})$  1609,  $\nu(\text{C}=\text{C}$  phenyl) 1563, 1485, 1470,  $\nu(\text{C}-\text{O})$  1281,  $\nu(\text{C}-\text{Cl})$  758.  $^1\text{H}$  NMR (DMSO):  $\delta$  ppm, 9.03 (s, 1H,  $-\text{CH}=\text{N}-$ ), 13.40 (s, 1H,  $-\text{OH}$ ), 6.88(m, 2H, Ar-Ha, Hb), 7.39 (t, 1H, Ar-Hc), 7.58 (d, 1H, Ar-Hd), 7.74 (s, 1H, Ar-He).  $^{13}\text{C}$  NMR (DMSO):  $\delta$  ppm, 160.59 (C1), 160.40 (C2), 145.59 (C3), 133.32 (C4-*ipso*), 132.89 (C5), 129.53 (C6), 119.89 (C7), 119.55 (C8-*ipso*), 117.04 (C9), 114.91 (C10).

Oligo-2,2'-[(2,5-dichloro-1,4-phenylene)bisnitrilomethylidene]diphenol (ODCPMPD) was synthesized through oxidative polycondensation of DCPMPD with aqueous solutions of NaOCl (30%) as the oxidant, as in the literature<sup>16</sup> (Scheme 1). Reactions were made in 250-mL three-necked round-bottom flasks which were fitted with condenser, thermometer, and magnetic stirrer. The reaction was performed between 40 and 90°C at different times and concentrations in the alkaline medium for to determine effects to be the yield of these parameters. After the reaction the mixture was neutralized with HCl (37%) (0.001 mol) at room temperature and unreacted monomer was separated from the reaction products



Scheme 2 Synthesis of PDMPD.



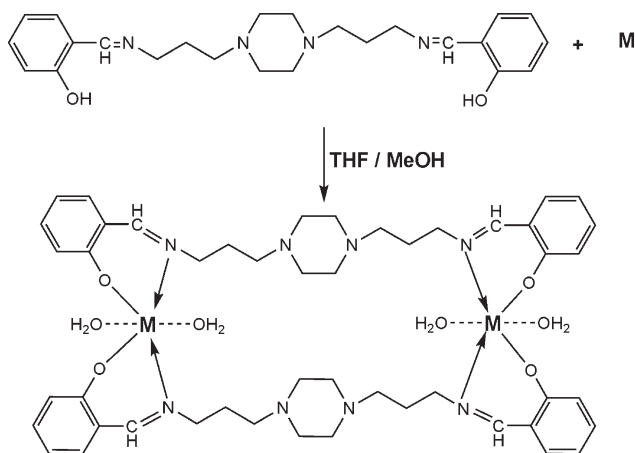
**Scheme 3** Synthesis of poly(PDMDP).

by washing with methanol. The mixture was filtered and washed with hot water ( $3 \times 25$  mL) to remove mineral salts.

Calcd. For ODCPMDP: C, 63.32; H, 2.11; N, 7.38. Found: C, 62.75; H, 2.25; N, 6.90. FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{O—H})$  3356,  $\nu(\text{C—H Phenyl})$  3048,  $\nu(\text{C=N})$  1605,  $\nu(\text{C=C phenyl})$  1567, 1514, 1491,  $\nu(\text{C—O})$  1279,  $\nu(\text{C—Cl})$  756.  $^1\text{H}$  NMR (DMSO):  $\delta$  ppm, 9.13 (s, 1H,  $-\text{CH=N}-$ ), 12.95 (s, 1H,  $-\text{OH}$ ), 6.48 (d, 1H, Ar-Ha), 7.61 (m, 2H, Ar-Hb, Hc), 7.02 (s, 1H, Ar-Hd), 8.01 (s, 1H, Ar-He).  $^{13}\text{C}$ -NMR (DMSO):  $\delta$  ppm, 161.01 (C1), 160.30 (C2), 148.62 (C3), 138.38 (C4), 134.97 (C5), 133.55 (C6), 132.90 (C7), 128.97 (C8-*ipso*), 121.15 (C9), 117.30 (C10), 119.90, and 119.64 (new peaks of C—C coupling system).

### Synthesis of PDMDP and Poly(PDMDP)

The 2,2'-piperazine-1,4-diylbis[propane-3,1-diyl nitrilomethylidene]diphenol (PDMDP) was synthesized by the condensation of salicylaldehyde (0.012 mol, 1.28 mL) with 1,4-bis(3-aminopropyl)piperazine (0.006 mol, 1.253 mL) in the 50 mL methanol achieved by boiling the mixture under reflux for 2 h (Scheme 2). The precipitated 2,2'-piperazine-1,4-diylbis[propane-3,1-diyl nitrilomethylidene]diphenol was filtered and recrystallized from the methanol and dried in a vacuum desiccator.



**Scheme 4** Synthesis of PDMDP-metal complexes.

**TABLE I**  
The Solubility Tests of all Compounds

Solvents	Compounds			
	DCPMDP	ODCPMDP	PDMDP	Poly(PDMDP)
Methanol	⊥	⊥	+	—
Ethanol	⊥	⊥	⊥	—
Acetone	+	⊥	+	—
Ethyl acetate	+	⊥	+	—
$\text{CHCl}_3$	+	⊥	+	—
Acetonitrile	+	—	+	—
n-hexane	⊥	—	—	—
Cyclohexane	⊥	—	—	—
DMSO	+	+	⊥	—
DMF	+	+	+	—
THF	+	+	+	—
1-butanol	⊥	⊥	⊥	—
$\text{H}_2\text{SO}_4$	+	⊥	—	⊥

+ : soluble at room temperature; ⊥ : partly soluble at room temperature; — : insoluble.

Calcd. For PDMDP: C, 70.58; H, 7.84; N, 13.72. Found: C, 70.25; H, 7.40; N, 13.35. FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{O—H})$  3350,  $\nu(\text{C—H Aromatic})$  3048,  $\nu(\text{C—H Aliphatic})$  2941, 2928, 2810,  $\nu(\text{C=N})$  1632,  $\nu(\text{C=C phenyl})$  1608, 1578, 1497,  $\nu(\text{C—O})$  1283.  $^1\text{H}$  NMR (DMSO):  $\delta$  ppm, 8.55 (s, 1H,  $-\text{CH=N}-$ ), 13.65 (s, 1H,  $-\text{OH}$ ), 6.88 (m, 2H, Ar-Ha, Hb), 7.32 (t, 1H, Ar-Hc), 7.42 (d, 1H, Ar-Hd), 3.60 (t, 2H, Ar-He), 1.78 (m, 2H, Ar-Hf), 2.33 (m, 6H, Ar-Hg, Hh, Hi).  $^{13}\text{C}$  NMR (DMSO):  $\delta$  ppm, 162.33 (C1), 161.41 (C2), 132.66 (C3), 132.02 (C4), 119.03 (C5), 118.80 (C6), 116.99 (C7), 56.75 (C8-*ipso*), 55.80 (C9), 53.29 (C10), 27.99 (C11).

Poly(PDMDP) was synthesized through graft polycondensation with two steps. In the first step, oligosalicylaldehyde (OSA) was synthesized as in the literature.<sup>19</sup> The synthesized oligomer (0.01 mol  $\text{U}^{-1}$ , 1.2 g) was dissolved in THF (15 mL). The 1,4-bis(3-aminopropyl)piperazine (0.005 mol, 1 g) was added to the mixture which was refluxed for 3 h (Scheme 3). Unreacted OSA was separated from the reaction products by filtering and then dried in a vacuum oven at  $60^\circ\text{C}$ .

Calcd. For Poly(PDMDP): C, 71.64; H, 6.46; N, 13.93. Found: C, 71.48; H, 6.42; N, 13.79. FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{O—H})$  3357,  $\nu(\text{C—H Aromatic})$  3060,  $\nu(\text{C—H Aliphatic})$  2942, 2828,  $\nu(\text{C=N})$  1624,  $\nu(\text{C=C phenyl})$  1580, 1497,  $\nu(\text{C—O})$  1278.

Poly(PDMDP) was insoluble in many organic solvents (except for  $\text{H}_2\text{SO}_4$ ). So, NMR measurement of this polymer was not made.

### Synthesis of PDMDP-metal complexes

#### General procedure

The solutions (2 mmol) of  $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cu}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Zn}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Pb}(\text{AcO})_2 \cdot 3\text{H}_2\text{O}$ ,

**TABLE II**  
**Oxidative Polycondensation Reaction Parameters of 2,2'-(2,5-dichloro-1,4-phenylene)bisnitrilomethylidene]diphenol with NaOCl in Aqueous KOH**

Run	Temp. (°C)	Time (h)	[DCPMDP] <sub>0</sub> (mol L <sup>-1</sup> )	[KOH] <sub>0</sub> (mol L <sup>-1</sup> )	[NaOCl] <sub>0</sub> (mol L <sup>-1</sup> )	%, yield of ODCPMDP
1	40	3	0.033	0.56	0.56	94
2	50	3	0.033	0.56	0.56	71
3	60	3	0.033	0.56	0.56	77
4	70	3	0.033	0.56	0.56	86
5	80	3	0.033	0.56	0.56	71
6	90	3	0.033	0.56	0.56	89
7	40	1	0.016	0.56	0.56	66
8	40	3	0.016	0.56	0.56	59
9	40	5	0.016	0.56	0.56	48
10	40	10	0.016	0.56	0.56	74
11	40	15	0.016	0.56	0.56	77
12	40	20	0.016	0.56	0.56	89

Ni(AcO)<sub>2</sub> · 4H<sub>2</sub>O, Cd(AcO)<sub>2</sub> · 2H<sub>2</sub>O, UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O in methanol (10 mL) were added to a PDMDP solution (2 mmol U<sup>-1</sup>) in THF (20 mL).<sup>20</sup> The mixtures were heated at 70°C and reactions were maintained for 3 h under reflux (Scheme 4). The precipitated complex was filtered, washed with cold MeOH/THF (1 : 1), and then dried in a vacuum oven.

#### Characterization techniques

The infrared spectra were measured by Perkin-Elmer FTIR Spectrum one. The FTIR spectra were recorded using universal ATR sampling accessory (4000–550 cm<sup>-1</sup>). Ultraviolet–visible (UV–vis) spectra were measured by Perkin-Elmer Lambda 25. UV–vis spectra of DCPMDP and ODCPMDP were measured by methanol as solvent. UV–vis spectra of aliphatic monomer and its metal complexes were measured by DMSO as solvent. PDMDP, DCPMDP, and ODCPMDP were characterized by using <sup>1</sup>H and <sup>13</sup>C NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) and recorded by using deuterated DMSO-d<sub>6</sub> as a solvent at 25°C. Tetramethylsilane was used as internal standard. Thermal data were obtained by use of a

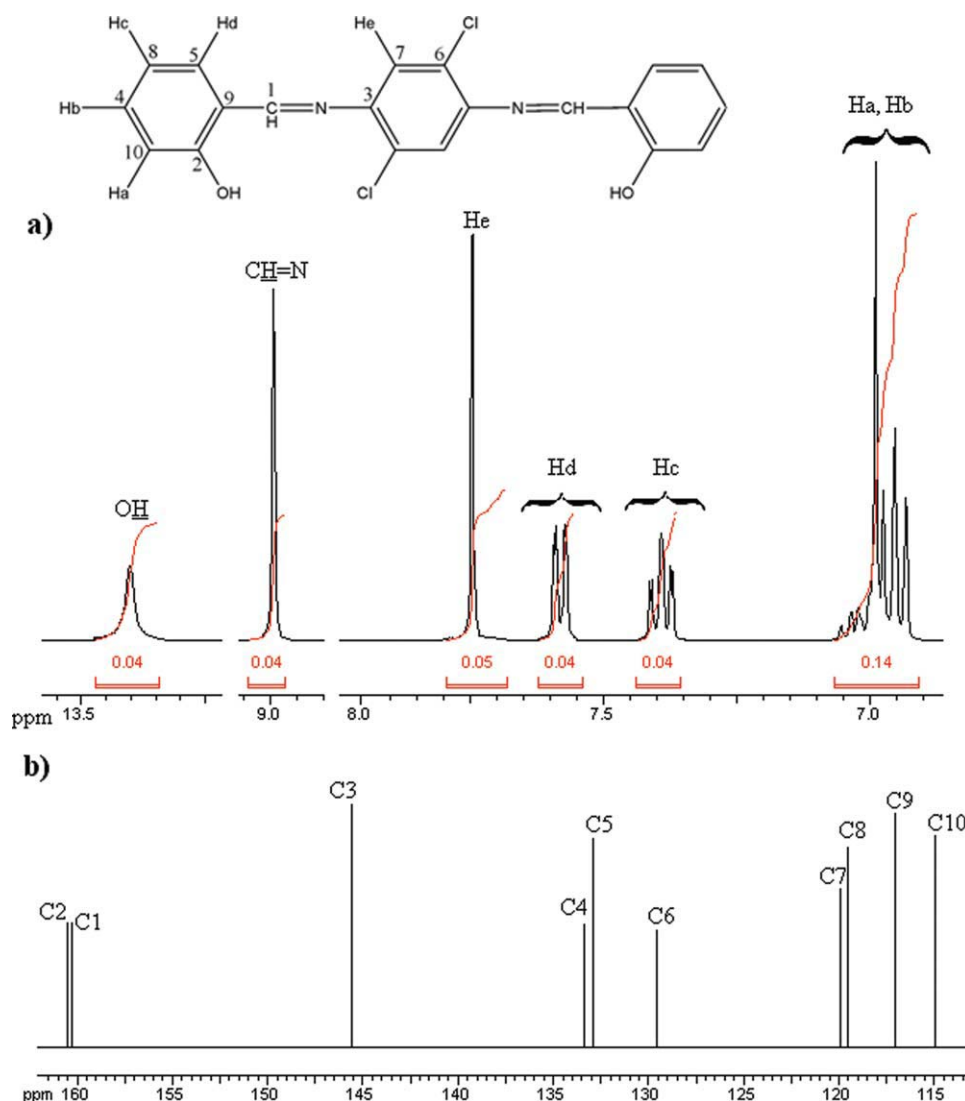
PerkinElmer Diamond Thermal Analysis system. TG-DTA measurements were made between 20 and 1000°C (in N<sub>2</sub>, 10°C min<sup>-1</sup>). DSC analyses of ODCPMDP and poly(PDMDP) were carried out by using Perkin-Elmer Pyris Sapphire DSC. DSC measurements were made between 30 and 420°C (in N<sub>2</sub>, rate 20°C min<sup>-1</sup>). The number average molecular weight (*M<sub>n</sub>*) and weight average molecular weight (*M<sub>w</sub>*) and polydispersity index (PDI) were determined by SEC (Shimadzu, Japan) with a SGX (100 Å and 7 nm diameter loading material) 7.7 mm i.d. × 300 mm columns, DMF eluent (0.4 mL min<sup>-1</sup>), polystyrene standards and a refractive index detector.

#### Electrical properties

Electrical conductivities were measured on a Keithley 2400 Electrometer using four-point probe technique. The pellets were pressed on a hydraulic press developing up to 1687.2 kg cm<sup>-2</sup>. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in a desiccator.<sup>21</sup> The optical band gaps (*E<sub>g</sub>*) of monomer and oligomer were calculated from their absorption edges.

**TABLE III**  
**The FT-IR Spectral Data of PDMDP and PDMDP-Metal Complexes**

Compounds	Functional groups (cm <sup>-1</sup> )				
	C–H (aliphatic)	C=C (aromatic)	–C=N	M–N	M–O
PDMDP	2941, 2928, 2810	1608, 1578, 1497	1632	–	–
PDMDP-Cd	2941, 2810	1575, 1544, 1498	1632	673	623
PDMDP-Co	2930, 2807	1596, 1537, 1447	1616	608	589
PDMDP-Cu	2935, 2809	1598, 1534, 1468	1619	602	575
PDMDP-Ni	2935, 2805	1541, 1469, 1446	1612	674	614
PDMDP-Pb	2931, 2816	1508	1629	653	614
PDMDP-U	2938, 2867	1537, 1467	1618	657	583
PDMDP-Zn	2981, 2862	1591, 1538, 1446	1629	691	612



**Figure 1** (a) <sup>1</sup>H NMR and (b) <sup>13</sup>C NMR spectra of DCPMDP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Electrochemical properties

Cyclic voltammetry (CV) measurements were carried out with a CH 660 C Electrochemical Analyzer (CH Instruments, TX) at a potential scan rate of 20 mV s<sup>-1</sup>. All the experiments were performed in a dry box filled with Ar at room temperature. The electrochemical potential of Ag was calibrated with respect to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple. The half-wave potential ( $E^{1/2}$ ) of (Fc/Fc<sup>+</sup>) measured in 0.1M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) DMSO solution is 0.39 V with respect to Ag wire or 0.38 V with respect to saturated calomel electrolyte (SCE).<sup>17</sup> The voltammetric measurements were carried out for DCPMDP, ODCPMDP, PDMDP, and PDMDP-metal complexes by DMSO. The HOMO and LUMO energy levels and electrochemical band gaps ( $E_g'$ ) of compounds were calculated from the oxidation and reduction peak maximum values.

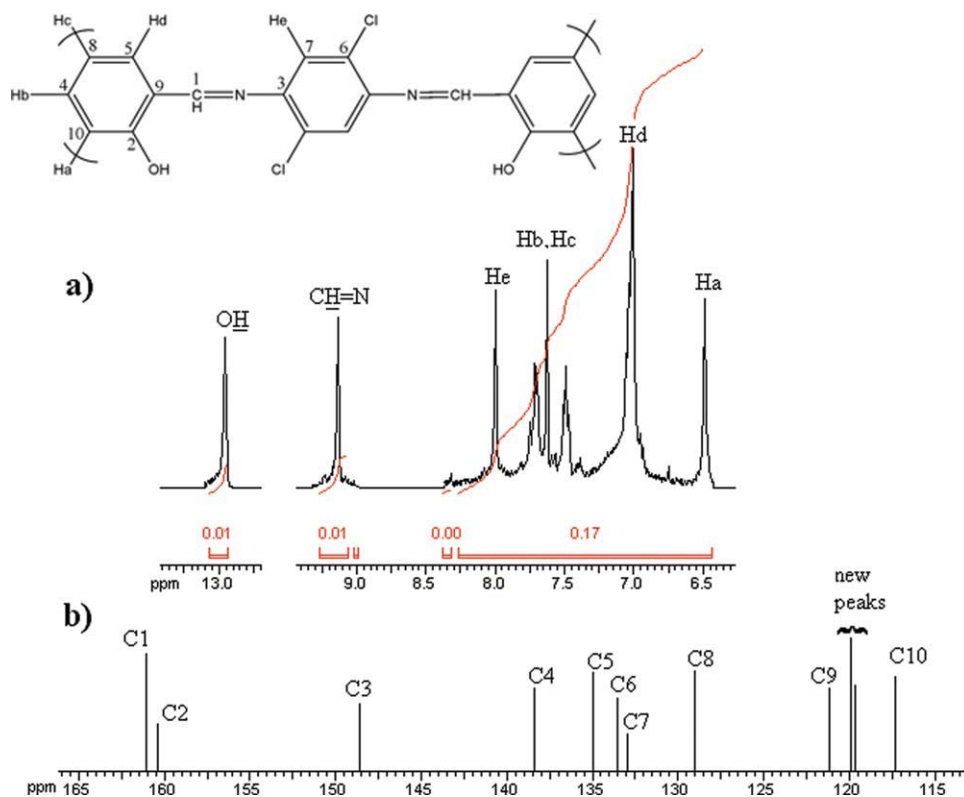
### Spectrochemical properties

Fluorescence measurements were obtained by use of a Shimadzu Spectrofluorophotometer RF-5301 PC. The synthesized DCPMDP and ODCPMDP were measured at fluorescence intensity values. We investigated for interactions in different solvents of synthesized compounds. For all fluorescence measurements the excitation and emission slit widths were at 5 nm. The intensity values, excitation, and emission spectra were measured for DCPMDP and ODCPMDP.

### Solubility properties

DCPMDP was yellow, the color of its oligomer ODCPMDP was dark brown. The synthesized PDMDP and poly(PDMDP) have brown colors. All compounds are at powder forms. The solubility tests of all compounds were done by using 1 mg sample





**Figure 2** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectrum of ODCPMDP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

and 1 mL solvent at  $25^\circ\text{C}$  and results are given in Table I. As shown in Table I the monomers are soluble in many solvents compared with their polymers. Although DCPMDP is completely soluble in acetonitrile its polymer is insoluble. Therefore, acetonitrile was used to separate unreacted monomers from the synthesized polymers after the polymerizations. Poly(PDMDP) is not soluble in any of the solvents but it is partly soluble in conc.  $\text{H}_2\text{SO}_4$ .

## RESULTS AND DISCUSSION

### The investigation of synthesis conditions of ODCPMDP

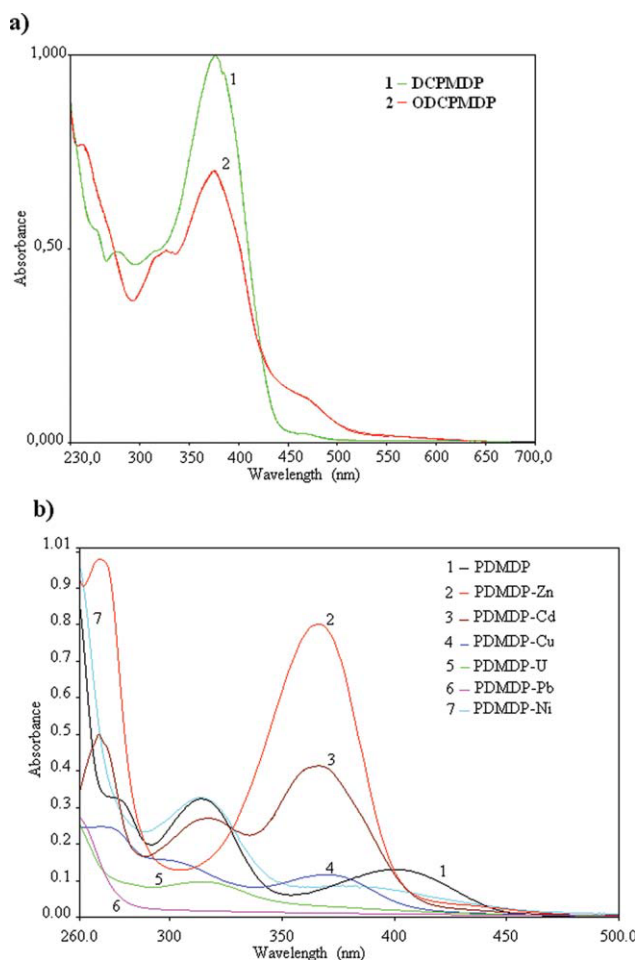
The oxidative polycondensation reaction conditions of ODCPMDP with 30% NaOCl solution in aqueous alkaline medium are given in Table II. The yield of ODCPMDP was 94% at the reaction conditions of  $[\text{DCPMDP}]_0 = 0.033$ ,  $[\text{KOH}]_0 = 0.56$  and  $[\text{NaOCl}]_0 = 0.56 \text{ mol L}^{-1}$  at  $40^\circ\text{C}$  for 3h. As seen from Table II, the highest yield of ODCPMDP is obtained at lower temperature. The yield of ODCPMDP was 89% at the reaction conditions of  $[\text{DCPMDP}]_0 = 0.016$ ,  $[\text{KOH}]_0 = 0.56$  and  $[\text{NaOCl}]_0 = 0.56 \text{ mol L}^{-1}$  at  $40^\circ\text{C}$  for 20 h. When reaction times changed from 1 to 20 h, the yield of ODCPMDP increased from 66 to 89%. According to these values, increasing the reac-

tion times increased the yield of ODCPMDP, at the low temperature.

### Spectral analyses of the synthesized compounds

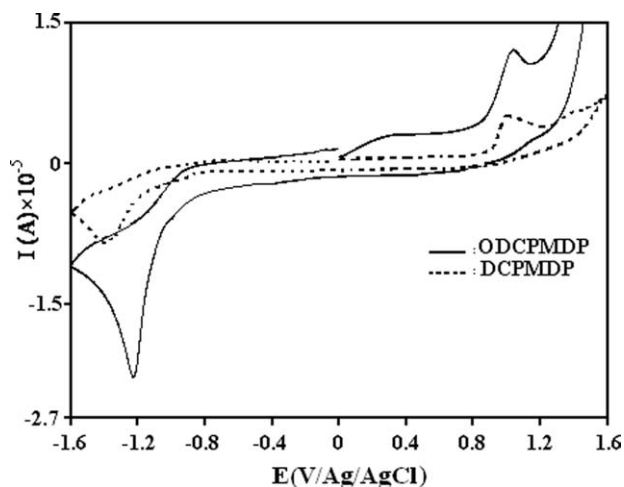
At the FT-IR spectra of DCPMDP and ODCPMDP, bands of  $-\text{OH}$  and  $-\text{CH}=\text{N}$  groups were observed in  $3341$  and  $1609 \text{ cm}^{-1}$ ;  $3356$  and  $1605 \text{ cm}^{-1}$ , respectively. At the FT-IR spectra of the PDMDP, the characteristic peaks of the functional groups were observed: Phenyl- $\text{OH}$  group at  $3350 \text{ cm}^{-1}$ ,  $-\text{CH}=\text{N}$  group at  $1632 \text{ cm}^{-1}$ , respectively. In the FT-IR spectra of the poly(PDMDP) its characteristic imine  $-\text{CH}=\text{N}$  vibrations were observed at  $1624 \text{ cm}^{-1}$ . The FT-IR spectra of poly(PDMDP) show a wide peak was at  $3350 \text{ cm}^{-1}$ . This band being the  $-\text{OH}$  group of the aromatic ring. As seen that the peak values changed after the polycondensation reaction due to their polyconjugated structures. The FT-IR spectral data of PDMDP and PDMDP-metal complexes are given in Table III. At the FTIR spectra of the Schiff base-metal complexes new peaks indicating metal-N and metal-O coordination were observed between  $575$  and  $691 \text{ cm}^{-1}$ . The structures of the synthesized Schiff base-metal complexes are confirmed by disappearing of the  $-\text{OH}$  peaks of PDMDP.

To identify the structures of DCPMDP, ODCPMDP, and PDMDP, the NMR spectra were recorded



**Figure 3** UV-vis spectra of DCPMDP, ODCPMDP and PDMDP-metal complexes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

in DMSO- $d_6$ .  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of DCPMDP and ODCPMDP are given in Figures 1 and 2, respectively. In the  $^1\text{H}$  NMR spectra of DCPMDP and ODCPMDP, the signals of  $-\text{OH}$  and  $-\text{CH}=\text{N}$  groups were observed in 13.40 and 9.03 ppm and 12.95 and 9.13 ppm, respectively. At the  $^1\text{H}$  NMR spectra of the polymers, the integration areas of  $-\text{OH}$  protons were used to determine the rate of the  $\text{C}-\text{O}-\text{C}$  coupling to  $\text{C}-\text{C}$  coupling. The neighboring



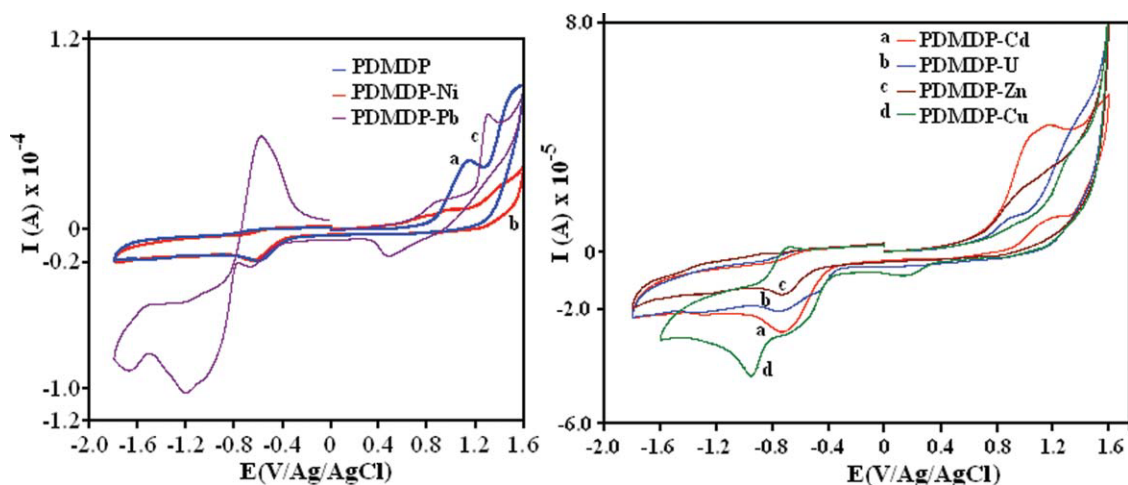
**Figure 4** Cyclic voltammograms of DCPMDP and ODCPMDP.

group of Hd proton causes the signal at 7.58 ppm to split into two in DCPMDP even though Hd proton signal of ODCPMDP is singlet. According to  $^1\text{H}$  NMR data, the polymerization of the DCPMDP largely maintained with  $\text{C}-\text{C}$  coupling from *para* position of hydroxyl group. In the  $^{13}\text{C}$  NMR spectra of DCPMDP and ODCPMDP, the peak values for C1, C2, C8, and C10 observed at 160.59, 160.40, 119.55, and 114.91 ppm in the monomer and 161.01, 160.30, 128.97, and 117.30 ppm in the oligomer, respectively. According to these results C2 peak values are close near for monomer and oligomer. It is shown that, the phenyl rings in the oligomer appear to be linked at *para* and *ortho* positions. So as structure of oligomer is confirmed by  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR data. As it is seen in Figure 1, because of  $\text{C}-\text{C}$  coupling system new peaks were observed at 119.90–119.64 ppm. These peaks are not present in the case of monomer. We can say that the observed results confirm the structures of the synthesized compounds.

The absorption spectra of DCPMDP, ODCPMDP, PDMDP, PDMDP-Cd, PDMDP-Co, PDMDP-Cu, PDMDP-U, and PDMDP-Zn were recorded by using methanol and dimethylsulfoxide at 25°C. Benzene

**TABLE IV**  
Optical and Electrochemical Values of the Compounds

Products	$\lambda_{\text{max}}$ (nm)	$E_g$ (eV)	$\lambda_{\text{onset}}$ (nm)	LUMO (eV)	HOMO (eV)	$(E_g')$ (eV)
DCPMDP	227, 277, 376, 468	2.76	450	-2.98	-5.41	2.43
ODCPMDP	227, 242, 326, 376, 473	2.32	534	-3.37	-5.52	2.15
PDMDP	253, 277, 314, 400	2.76	450	-3.78	-5.54	1.75
PDMDP-Cd	256, 316, 367	3	414	-3.66	-5.57	1.90
PDMDP-Ni	258, 313, 384	2.76	449	-3.74	-5.37	1.62
PDMDP-Cu	255, 305, 369	2.92	424	-3.79	-5.68	1.88
PDMDP-U	257, 262, 314	3.33	372	-3.63	-5.31	1.67
PDMDP-Zn	256, 268, 366	3.05	408	-3.67	-5.38	1.70
PDMDP-Pb	255, 259, 316	4.32	287	-3.73	-5.42	1.69



**Figure 5** Cyclic voltammograms of PDMDP and PDMDP-metal complexes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

bands of all synthesized compounds observed between 242 and 277 nm and strength R bands of imine groups were observed between 314 and 389 nm, respectively. The UV-vis spectra of DCPMDP and ODCPMDP are shown in Figure 3. According to these spectra, the absorption edges of the synthesized ODCPMDP shifted to higher wavelength values because of the polyconjugation in the structure. The synthesized oligomer has lower optical band gap compared to its monomer, as expected.  $\lambda_{\max}$  and the optical band gaps values were calculated as in the literature<sup>22</sup> and shown in Table IV.

The HOMO and LUMO energy levels and electrochemical band gaps ( $E'_g$ ) of compounds were calculated as in the literature.<sup>23</sup> The calculations were made by using the following equations.

$$E_{\text{HOMO}} = -(4.39 + E_{\text{ox}}) \quad (1)$$

$$E_{\text{LUMO}} = -(4.39 + E_{\text{red}}) \quad (2)$$

$$E'_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (3)$$

The voltammetric measurements of DCPMDP and ODCPMDP were carried out in DMSO, as shown in Figure 4. The voltammetric measurements of PDMDP and PDMDP-metal complexes were recorded in DMSO, as shown in Figure 5. According to the cyclic voltammetry (CV) measurements, the calculated HOMO-LUMO energy levels and the electrochemical band gaps ( $E'_g$ ) of DCPMDP, ODCPMDP, PDMDP and PDMDP-metal complexes were also shown schematically in Table IV.

For spectral characterization of DCPMDP and ODCPMDP, emission and excitation spectra were recorded in different solvents. Fluorescence measurements were performed in THF, methanol, DMF, DMSO, acetone, acetonitrile, and dichloromethane. Emission and excitation intensity values, Stoke's shift values, and fluorescence spectra of compounds were given in Tables V and VI, and

**TABLE V**  
Fluorescence Spectra Related Data of DCPMDP

Compound/solvents	$\lambda_{\text{Ex}}^a$	$\lambda_{\text{Em}}^b$	$\lambda_{\text{max}}(\text{Ex})^c$	$\lambda_{\text{max}}(\text{Em})^d$	$I_{\text{Ex}}^e$	$I_{\text{Em}}^f$	$\Delta\lambda_{\text{ST}}^g$
DCPMDP/DMF	441	556	440	550	75	77	110
DMSO	442	553	440	551	120	116	111
MeOH	488	563	457	563	275	111	106
THF	440	556	440	550	52	55	110
Acetone	434	554	434	550	41	43	116
Acetonitrile	433	566	425	558	27	30	133
Dichloromethane	433	558	433	555	31	32	122

<sup>a</sup> Excitation wavelength for emission.

<sup>b</sup> Emission wavelength for excitation.

<sup>c</sup> Maximum emission wavelength.

<sup>d</sup> Maximum excitation wavelength.

<sup>e</sup> Maximum excitation intensity.

<sup>f</sup> Maximum emission intensity.

<sup>g</sup> Stoke's shift.



TABLE VI  
Fluorescence Spectra Related Data of ODCPMDP

Compound/solvents	$\lambda_{\text{Ex}}^{\text{a}}$	$\lambda_{\text{Em}}^{\text{b}}$	$\lambda_{\text{max}}(\text{Ex})^{\text{c}}$	$\lambda_{\text{max}}(\text{Em})^{\text{d}}$	$I_{\text{Ex}}^{\text{e}}$	$I_{\text{Em}}^{\text{f}}$	$\Delta\lambda_{\text{ST}}^{\text{g}}$
ODCPMDP/DMF	487	569	484	504	75	242	20
DMSO	441	559	441	551	65	70	110
MeOH	456	566	454	563	506	507	109
THF	293	335	291	321	55	75	30
Acetone	434	553	433	551	35	37	118
Dichloromethane	435	560	433	553	29	30	120

<sup>a</sup> Excitation wavelength for emission.

<sup>b</sup> Emission wavelength for excitation.

<sup>c</sup> Maximum emission wavelength.

<sup>d</sup> Maximum excitation wavelength.

<sup>e</sup> Maximum excitation intensity.

<sup>f</sup> Maximum emission intensity.

<sup>g</sup> Stoke's shift.

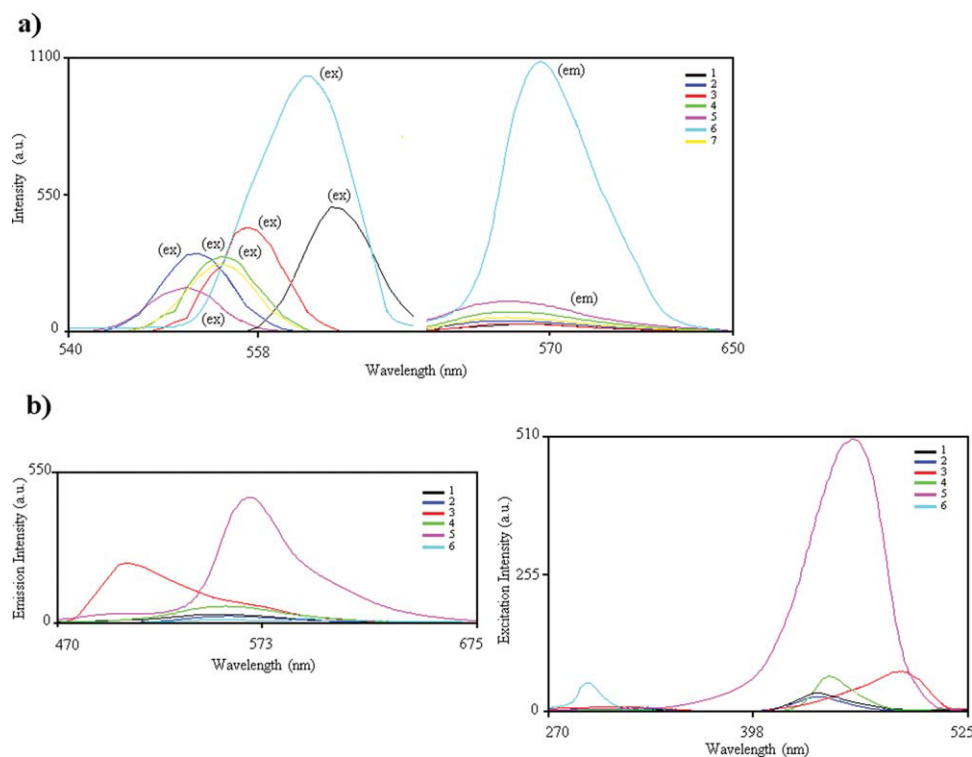
Figure 6, respectively. Stoke's shift ( $\Delta\lambda_{\text{ST}}$ ) values (the difference between excitation and emission maximum) calculated from the fluorescence spectra. The highest fluorescence intensity values were obtained for monomer and oligomer, when used methanol as solvent.

And finally, according to SEC chromatograms, the number average molecular weight ( $M_n$ ) and the weight average molecular weight ( $M_w$ ) values of ODCPMDP were calculated according to a polystyrene standard calibration curve. The  $M_n$ ,  $M_w$ , and

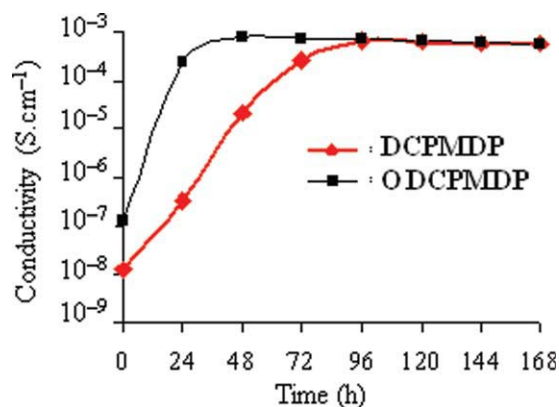
PDI values of ODCPMDP were found as  $M_n$ : 3350 g mol<sup>-1</sup>,  $M_w$ : 3400 g mol<sup>-1</sup>, PDI: 1.015 (determined by RI detector),  $M_n$ : 5600 g mol<sup>-1</sup>,  $M_w$ : 8500 g mol<sup>-1</sup>, PDI: 1.518 (determined by UV detector), respectively.

### Electrical conductivities

Electrical conductivities of the synthesized monomer and the oligomer and the changes of these values related to doping time with iodine were



**Figure 6** Fluorescence spectra of DCPMDP in different solvents (a) (1 = Acetonitrile, 2 = Acetone, 3 = Dichloromethane, 4 = DMF, 5 = DMSO, 6 = Methanol, 7 = THF). Fluorescence spectra of ODCPMDP in different solvents (b) (1 = Acetone, 2 = Dichloromethane, 3 = DMF, 4 = DMSO, 5 = Methanol, 6 = THF). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



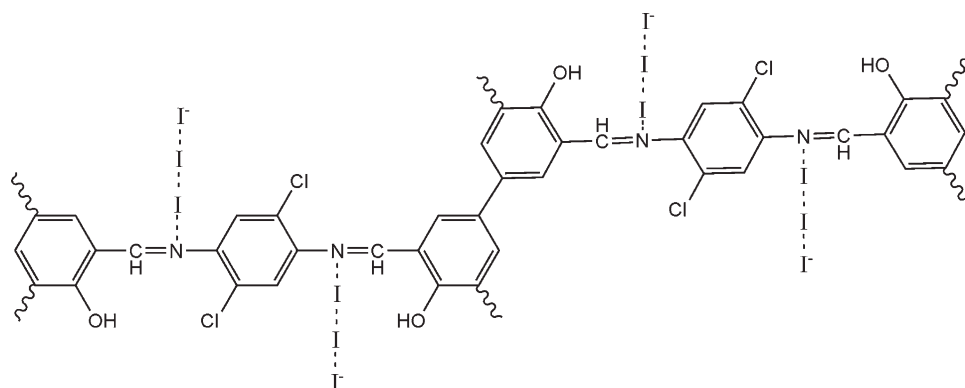
**Figure 7** Electrical conductivity of I<sub>2</sub>-doped DCPMPD and ODCPMPD versus doping time at 25°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

determined and the changes of the electrical conductivities are also given schematically in Figure 7. As seen in the Figure 7, DCPMPD has conductivity of  $10^{-8}$  S cm<sup>-1</sup>. When doped with iodine, the conductivities of DCPMPD increased up between to  $10^{-4}$  and  $10^{-3}$  S cm<sup>-1</sup>. The initial conductivity of the ODCPMPD is higher than DCPMPD. When doped with iodine, its conductivity could be increased by about four orders of magnitude (up to  $10^{-3}$  S cm<sup>-1</sup>). In the doping of the monomer and the oligomer with iodine, it was found that the conductivities firstly increase greatly with doping time, but then tend to level-off. Conductivity measurements of imine polymers have been previously studied and a considerable increase was reported when they doped with iodine.<sup>24</sup> Also coordination of iodine during ODCPMPD doping is as indicated in Scheme 5.

### Thermal studies

The thermal degradations of DCPMPD, ODCPMPD, PDMPD, poly(PDMPD), PDMPD-Cd, PDMPD-Co,

PDMPD-Cu, PDMPD-Ni, PDMPD-Pb, PDMPD-U, and PDMPD-Zn were studied by TG-DTG-DTA analyses at N<sub>2</sub> medium. According to TG, DTG, and DTA curves, thermal degradation data of all compounds calculated and are given in Table VII. The TG and DTG curves of PDMPD and PDMPD-metal complexes are given in Figures 8 and 9, respectively. The initial degradation temperatures (°C) are 196 and 176°C for ODCPMPD and DCPMPD, 263 and 258°C for PDMPD and poly-(PDMPD), respectively. Generally polymers have high internal resonance energy because of their long conjugated bond system. For this reason, polymers show higher resistance against high temperature according to the monomers. The high thermal stability of oligomer and polymer demonstrated to be formed of C—C coupling system. According to DTG and TG curves, thermal degradation of poly(PDMPD) was completed in one step and its char was found to be 42.64% at 1000°C. According to thermal analysis results, the initial degradation temperature of Ni complex was higher than other Schiff base-metal complexes. The TG curve of the PDMPD-metal complexes was carried out within a temperature range from 20°C up to 1000°C. The estimated mass losses were computed based on the TG results and the calculated values were computed using the results of microanalyses. The PDMPD-metal complexes give four stages of decomposition pattern. The temperature range 25–195°C which represents the loss of two molecules of water of crystallization and one molecule of acetate. The char amounts of PDMPD-metal complexes were changed between 4.07% with 47.50%. Although Ni complex was demonstrated higher degradation temperature, Pb complex was formed a char at higher amount, such as 47.50%. According to DSC thermogram, glass transition temperatures ( $T_g$ ) and changes of specific heat during glass transition ( $\Delta C_p$ ) of ODCPMPD and Poly(PDMPD) were found as 160 and 233°C; 0.058 and 0.032 J g<sup>-1</sup> °C<sup>-1</sup>, respectively.



**Scheme 5** Coordination of iodine during ODCPMPD doping.

TABLE VII  
TG and DTA Analysis Values of Compounds Synthesized

Compounds	TG (°C)					DTA (°C)	
	$T_{on}^a$	$T_{max}^b$	%20 Weight losses	%50 Weight losses	% Weight losses at 1000°C	Exo	Endo
DCPMDP	176	220,340	232	330	92.90	–	153,278,352
ODCPMDP	196	247,404	260	612	79.73	–	–
PDMDP	258	279,405	280	348	85.20	297	79
Poly(PDMDP)	263	343	385	921	57.36	–	–
PDMDP-Cd	241	300,527	292	404	79.16	275,308	478
PDMDP-Co	212	301,590,770	279	422	88.48	304,328	338,482
PDMDP-Cu	218	274,397	269	362	76.56	–	–
PDMDP-Ni	255	316	301	385	75.77	–	–
PDMDP-Pb	238	300,894	306	976	52.5	277,339,383	257,317,361
PDMDP-U	174	215,397,949	336	774	95.93	239,377	256
PDMDP-Zn	215	272,896	254	330	87.09	–	291

<sup>a</sup> The onset temperature.

<sup>b</sup> Maximum weight loss temperature.

## CONCLUSIONS

In this study, the oxidative polycondensation reaction conditions of 2,2'-(2,5-dichloro-1,4-phenylene) bisnitrilomethylidene]diphenol were examined between 40 and 90°C temperature in an aqueous alkaline medium by NaOCl and the optimum reaction conditions and percentage yield values of ODCPMDP were determined. Synthesis and characterization of DCPMDP, ODCPMDP, PDMDP, poly(PDMDP), and PDMDP-metal complexes were performed by using different spectral techniques. Electrochemical and optical properties of the synthesized compounds were also investigated. The electrochemical ( $E_g'$ ) and the optical ( $E_g$ ) band gap values of DCPMDP and ODCPMDP were found to be 2.43–2.15 eV and 2.76–2.36 eV, respectively. The  $E_g'$  and  $E_g$  values of the DCPMDP were found to be higher than that of the ODCPMDP.

The absorption edges of the synthesized ODCPMDP shifted to higher wavelength values because of the polyconjugation in the structure. According to electrical measurements, the initial conductivity of the ODCPMDP is higher than DCPMDP. Electrical conductivity measurements show that the synthesized oligomer is semiconductor. The synthesized DCPMDP and ODCPMDP were measured at fluorescence intensity values. The highest fluorescence intensity values are obtained in methanol, for monomer and oligomer. According to thermal data, because of long conjugated bond system, ODCPMDP and poly(PDMDP) demonstrated higher resistance against high temperature than their monomers. The initial degradation temperature of Ni complex was higher than other complex compounds. Pb complex was formed a char at high amount such as 47.5% at 1000°C.

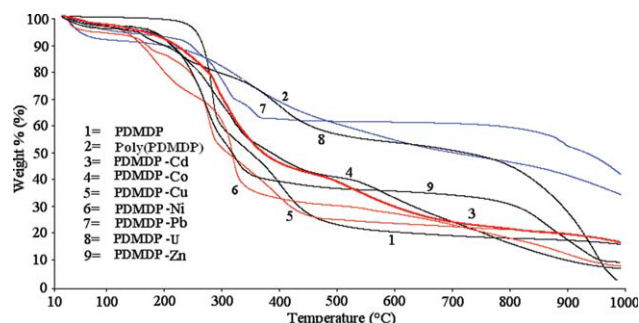


Figure 8 TG curves of PDMDP, poly(PDMDP), and PDMDP-metal complexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

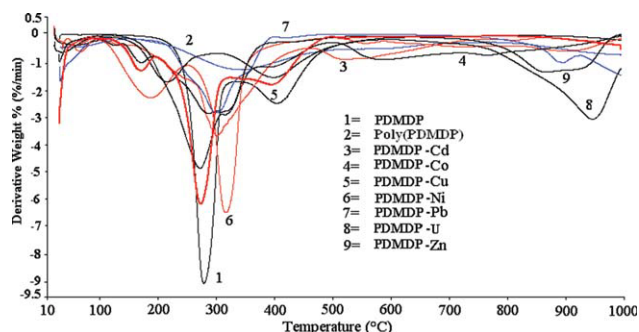


Figure 9 DTG curves of PDMDP, poly(PDMDP), and PDMDP-metal complexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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