

Synthesis of Oligo-*ortho*-azomethinephenol and its Oligomer–Metal Complexes: Characterization and Application as Anti-microbial Agents

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ABSTRACT: The oxidative polycondensation reaction conditions and optimum parameters of *o*-phenylazomethinephenol (PAP) with oxygen (air) and NaOCl were determined in an aqueous alkaline solution at 60–98°C. The properties of oligo-*o*-phenylazomethinephenol (OPAP) were studied by chemical and spectra analyses. PAP was converted to dimers and trimers (25–60%) by oxidation in an aqueous alkaline medium. The number average molecular weight (M_n), mass average molecular weight (M_w), and polydispersity index (PDI) values were 1180 g mol⁻¹, 1930 g mol⁻¹, and 1.64, respectively. According to these values, 20–33% of PAP turned into OPAP. During the polycondensation reaction, a part of the azomethine (—CH=N—) groups oxidized to carboxylic (—COOH) group. Thus, a water-soluble fraction of OPAP was incorporated in the carboxylic (—COOH); (2–20%) group. Also, the structure and properties of oligomer–metal complexes of OPAP with Cu(II), Ni(II), Zn(II), and Co(II) were studied. Antimicrobial activities of the oligomer and its oligomer–metal complexes were tested against *B. cereus*, *L. monocytogenes*, *B. megaterium*, *B. subtilis*, *E. coli*, *Str. thermophilus*, *M. smegmatis*, *B. brevis*, *E. aeroginesa*, *P. vulgaris*, *M. luteus*, *S. aureus*, and *B. jeireseens*. Also, according to differential thermal analysis and thermogravimetric analysis, OPAP and its oligomer–metal complexes were stable throughout to temperature and thermo-oxidative decomposition. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2004–2013, 2002

Key words: oligo-*o*-phenylazomethinephenol; oxidative polycondensation; air oxygen; NaOCl; oligomer–metal complexes; antimicrobial activity

INTRODUCTION

The planar oligophenols and their derivatives, which include conjugate bonding and an active hydroxyl group, have been used in various fields.

They have electrochemical cells and several useful properties, such as paramagnetism, semiconductivity, and resistance to high energy. Because of these properties, these compounds are used to prepare composites with resistance to high temperature, thermostable materials,^{1,2} graphite materials,³ epoxy oligomers and block copolymers,^{4,5} adhesives,⁶ photoresistant materials,⁷ and anti-static materials.⁸ The halogen and sulfur deriva-

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tives of oligophenols were used to prepare composite materials that are resistant to the flame of specific agents, such as lead-storing battery cathodes.⁹ Addition of other functional groups to the structures of these compounds resulted in additional, new properties. These oligophenols, with added functions, may be used to clean poisonous heavy metals in industrial waste waters. Therefore, the synthesis of oligomer-metal complexes is very important for analytic and environmental chemistry situations.

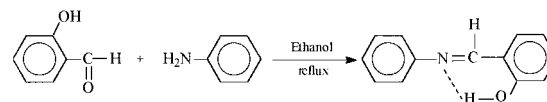
The prodigious growth literature published on Schiff base complexes indicates certain limitations with regard to spectral and magnetic investigations. It seemed advantageous to attempt to design and prepare a polymer-bound chelating ligand that would be able to form complexes with a variety of transition metals and therefore have a large range of applications. Also, coordination compounds of salicylaldehyde Schiff base have proven to be an excellent model system with which to study the enzymatic reactions of pyridoxal phosphate because both of these systems effectively catalyze transamination and racemization reactions.¹⁰

In the first part of this paper, we report our results on the effects of different parameters, such as temperature, flow rate of air (oxygen), and beginning concentrations of *o*-phenylazomethine phenol (PAP), NaOCl, and alkaline, on PAP. In the second part, the three fractions of oligo-*o*-phenylazomethine phenol (OPAP-I, OPAP-II, and OPAP-III) were characterized by Fourier transform infrared (FT-IR), ultraviolet-visible (UV-vis), proton nuclear magnetic resonance (¹H NMR), elemental analysis, thermogravimetric (TGA), differential thermal analysis (DTA), and high-pressure liquid chromatography (HPLC) techniques. In the third part, the new oligomer-metal complexes were synthesized, by reaction of OPAP-II with Cu(II), Ni(II), Zn(II), and Co(II), and then characterized by spectral techniques. Also, antimicrobial activities of oligomer and oligomer-metal complexes were investigated.

MATERIALS AND METHODS

Materials

Aniline, salicylaldehyde (SA), 1,4-dioxane, ethanol, benzene, acetone, ethyl acetate, *n*-heptane, tetrahydrofuran (THF), dimethylformamide



Scheme 1

(DMF), dimethyl sulfoxide (DMSO), H₂SO₄, toluene, Zn(CH₃COO)₂ · 2H₂O, Cu(CH₃COO)₂ · H₂O, Co(CH₃COO)₂ · 4H₂O, and Ni(CH₃COO)₂ · 4H₂O were supplied by Merck Chemical Company as chromatographic grade and were used as received. Hydrochloric acid (HCl) and sodium hypochloride (NaOCl; 30% solution in water) were supplied from Carlo Erba Company. KOH was supplied from Analar BDH Chemical Company.

Preparation of *o*-Phenylazomethinephenol (PAP)

PAP was prepared by the condensation of SA (0.025 mol) and aniline (0.025 mol) in ethanol (15 mL), which was achieved by boiling the mixture under reflux for 2 h (Scheme 1). The precipitated PAP was filtered, recrystallized from ethanol, and dried in vacuum desiccators (mp, 49°C; yield, 85%). For PAP, UV-vis (λ_{max}): 208, 220, 272, 324, 338 nm. Anal. Calcd for PAP: C, 79.19; H, 5.58; N, 7.11. Found for PAP: C, 79.25; H, 5.52; N, 7.02.

Synthesis of OPAP with Air (Oxygen)¹¹

PAP (3.94 g, 0.02 mol) was dissolved in an aqueous solution of KOH (10%; 1.12 g, 0.02 mol) and placed into a 100-mL, three-necked, round-bottomed flask. The flask was fitted with a condenser, thermometer, stirrer, and glass tubing over the condenser to deliver oxygen from air. The reaction mixture was heated (Table I). The air was delivered at a rate of 8.5 L/h during the course of the reaction. To avoid water loss in the reaction mixture and to unneutralize the CO₂ of air to KOH, air (oxygen) was passed into an aqueous solution of KOH (20%) before being sent through the reaction tubing (Scheme 2). The reaction mixture was cooled to room temperature and then 0.02 mol of HCl (37%) was added. The mixture was filtered and washed with hot water, to separate out mineral salts, and dried in an oven at 110°C. Unreacted monomer was separated from the reaction products by washing with cool *n*-heptane. The reaction product separated into three fractions. The first fraction (OPAP-I) was soluble in hot *n*-heptane and the second frac-

Table I Oxidative Polycondensation of *o*-Phenylazomethinphenol with Air (Oxygen) in Aqueous KOH

Sample	[PAP] ₀ , mol/L	[KOH] ₀ , mol/L	Air, L/h	T, °C	Time, h	Conversion of PAP, %	Reaction Products, %		
							OPAP-I	OPAP-II	OPAP-III
1	1.0	1.0	8.5	65	1	21	17	4	0
2	1.0	1.0	8.5	65	3	37	25	10	2
3	1.0	1.0	8.5	65	6	90	63	18	9
4	1.0	1.0	8.5	65	12	98	66	21	11
5	1.0	1.0	8.5	75	1	38	23	12	13
6	1.0	1.0	8.5	75	3	70	51	15	4
7	1.0	1.0	8.5	75	4	92	63	20	9
8	1.0	1.0	8.5	75	10	99	64	23	12
9	1.0	1.0	8.5	80	1	73	52	18	3
10	1.0	1.0	8.5	80	3	93	66	18	9
11	1.0	1.0	8.5	80	4	98	58	28	12
12	1.0	1.0	8.5	80	8	97	54	27	16
13	1.0	1.0	8.5	90	1	90	60	20	10
14	1.0	1.0	8.5	90	3	98	56	30	12
15	1.0	1.0	8.5	90	5	99	52	31	16
16	1.0	1.0	8.5	90	7	99	50	31	18
17	1.0	1.0	8.5	98	1	97	45	32	20
18	1.0	1.0	8.5	98	3	97	44	33	20
19	1.0	1.0	8.5	98	5	99	41	33	25
20	1.25	1.25	8.5	80	1	77	51	21	5
21	0.75	0.75	8.5	80	1	60	43	15	2
22	1.0	1.0	6.0	80	1	67	53	12	2
23	1.0	1.0	10.0	80	1	79	53	21	5

tion (OPAP-II) was insoluble in *n*-heptane. The third fraction (OPAP-III) was soluble in water.

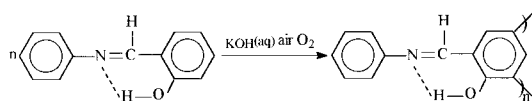
Anal. Calcd for OPAP-I: C, 80.00; H, 4.62; N, 7.18. Found for OPAP-I: C, 79.75; H, 4.72; N, 7.00. Anal. Calcd for OPAP-II: C, 80.00; H, 4.62; N, 7.18. Found for OPAP-II: C, 79.86; H, 4.70; N, 7.05. Anal. Calcd for OPAP-III: C, 80.00; H, 4.62; N, 7.18. Found for OPAP-III: C, 79.73; H, 4.85; N, 6.92.

For OPAP-I, UV-vis (λ_{\max}): 208, 222, 269, 328, 352 nm. For OPAP-II, UV-V (λ_{\max}): 208, 220, 270, 324, 338 nm. For OPAP-III, UV-vis (λ_{\max}): 208, 220, 269, 324, 3 nm.

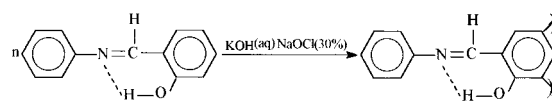
Synthesis of OPAP with NaOCl¹¹

OPAP was synthesized by oxidative polycondensation of PAP with an aqueous solution of NaOCl

(30%). The PAP (3.94 g, 0.02 mol) was dissolved in an aqueous solution of KOH (10%, 1.12 g, 0.02 mol) and placed into a 50-mL, three-necked, round-bottomed flask. The flask was fitted with a condenser, thermometer, stirrer, and an addition funnel containing NaOCl. After heating at 60°C for 30 min, NaOCl was added in a dropwise manner over ~ 20 min. The reaction mixture was heated at 90°C for 5 h. The mixture was neutralized with 3 mL of HCl (37%) at room temperature (Scheme 3). The mixture was filtered and washed with hot water, to separate out mineral salts, and dried in an oven at 110°C. Unreacted monomer was separated from the reaction products by washing with cool *n*-heptane. The reaction product separated to three fractions. The first fraction (OPAP-I) was soluble in hot *n*-heptane and the



Scheme 2



Scheme 3

second fraction (OPAP-II) was insoluble in *n*-heptane. The third fraction (OPAP-III) was soluble in water.

Syntheses of OPAP Metal Complexes

Cobalt (II) Complex

A solution of $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ (0.05 mol, 1.95 g) in methanol (10 mL) was added to a solution of OPAP-II (0.01 mol/unit, 1.92 g) in 1,4-dioxane (30 mL). The mixture was stirred and heated at 70°C for 3 h. The precipitated complex was filtered and washed with cold 1,4-dioxane/methanol (1 : 1), and then dried in vacuum oven (2.21 g, 69%; mp, > 250°C).

Anal. Calcd for OPAP-II-Co: M, 13.11. Found for OPAP-II-Co: M, 11.75. For OPAP-II-Co, UV-vis (λ_{max}): 208, 220, 272, 324, 340, and 642 nm. μ_{Eff} : 3.6.

Nickel (II) Complex

A solution of $\text{Ni}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ (0.005 mol, 1.14 g) in methanol (10 mL) was added to a solution of OPAP-II (0.01 mol/unit, 1.92 g) in 1,4-dioxane (30 mL). The mixture was stirred and heated at 70°C for 3 h. The precipitated complex was filtered and washed with cold 1,4-dioxane/methanol (1 : 1), and then dried in vacuum oven (2.20 g; 70%; mp, > 250°C).

Anal. Calcd for OPAP-II-Ni: M, 13.08. Found for OPAP-II-Ni: M, 11.02. For OPAP-II-Ni, UV-vis (λ_{max}): 208, 220, 272, 324, 341 and 640 nm. μ_{Eff} : diamagnetic.

Copper (II) complex

A solution of $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ (0.005 mol, 1.00 g) in methanol (20 mL) was added to a solution of OPAP-II (0.01 mol/unit, 1.92 g) in 1,4-dioxane (30 mL). The mixture was stirred and heated at 70°C for 3 h. The precipitated complex was filtered and washed with cold 1,4-dioxane/methanol (1 : 1), and then dried in a vacuum oven (2.32 g; 79%; mp, > 250°C).

Anal. Calcd for OPAP-II-Cu: M, 14.01. Found for OPAP-II-Cu: M, 12.23. For OPAP-II-Co, UV-vis (λ_{max}): 208, 220, 272, 324, 340, 640 nm. μ_{Eff} : 1.8.

Zinc (II) Complex

A solution of $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ (0.005 mol, 1.10 g) in methanol (10 mL) was added to a solution of

OPAP-II (0.01 mol/unit, 1.92 g) in 1,4-dioxane (30 mL). The mixture was stirred and heated at 70°C for 3 h. The precipitated complex was filtered and washed with cold 1,4-dioxane/methanol (1 : 1), and then dried in a vacuum oven (2.28 g; 75%; mp, > 250°C).

Anal. Calcd for OPAP-II-Zn: M, 14.36. Found for OPAP-II-Zn: M, 9.70. For OPAP-II-Co, UV-vis (λ_{max}): 208, 220, 272, 324, 339, 635 nm. μ_{Eff} : diamagnetic.

Preparation of Microbial Cultures

Bacillus megaterium DSM 32, *Bacillus subtilis* IMG 22, *Bacillus brevis* FMC 32, *E. coli* DM, Str. *thermophilus*, *M. smegmatis*, *M. luteus*, *E. Aeroginosa* CCM 2531, *P. vulgaris* DSM 50071, *S. aureus* COWAN 1, *L. monocytogenes* SCOTT A, *B. cereus*, and *B. jeoreseens* were used as the test organisms and yeast in an antimicrobial study. The bacteria and yeast strains were inoculated into nutrient broth (Difco) and malt extract broth (Difco) and incubated for 24 and 48 h, respectively. Using the Disc Diffusion method, the sterile Mueller Hinton Agar (Oxoid) for bacteria and Sabouraud Dextrose Agar for yeast were separately inoculated with the test microorganisms.^{12,13} The compounds were dissolved in CHCl_3 as 50- $\mu\text{g}/\text{disc}$ solutions and absorbed on sterile paper antibiotic discs, which were placed in wells (6 mm diameter) cut in the agar media. The plates were incubated at 32°C for bacteria (18–24 h) and at 25°C for yeast (72 h). The resulting inhibition zones on the plates were measured after 48 h. The control samples were only absorbed in CHCl_3 . The data reported in Table 7 are the average data of three experiments.

Characterization Techniques

The FT-IR and UV-vis spectra were measured with Shimadzu FT-IR 8300 and UV-160 instruments, respectively. Elemental analysis was carried out with a Carlo Erba 1106. The FT-IR spectra were recorded using KBr discs (4000–400 cm^{-1}). UV-vis spectra of OPAP-I, OPAP-II, and OPAP-III oligomers were determined with ethanol and THF. Oligomers were characterized by ^1H NMR spectra (Bruker AC FT-NMR 200 MHz spectrometer) that recorded at 25°C, using deuterated DMSO as solvent. Tetramethylsilane (TMS) was used as internal standard. Thermal data were obtained with a derivatograph MOM

Table II Oxidative Polycondensation of *o*-Phenylazomethinephenol with NaOCl in Aqueous KOH

Sample	[PAP] ₀ , mol/L	[KOH] ₀ , mol/L	[NaOCl] ₀ , mol/L	T, °C	Time, h	Conversion of PAP, %	Reaction Products, %		
							OPAP-I	OPAP-II	OPAP-III
1	1.0	1.0	1.0	60	3	90	69	15	6
2	1.0	1.0	1.0	70	3	96	71	17	8
3	1.0	1.0	1.0	80	3	99	65	21	13
4	1.0	1.0	1.0	90	3	99	63	22	14
5	1.0	1.0	1.0	95	1	100	60	24	16
6	1.0	1.0	1.0	70	5	75	58	12	5
7	1.0	1.0	1.0	70	7	99	65	23	11
8	1.0	1.0	1.0	70	3	100	60	24	16
9	1.25	1.25	1.25	70	3	98	70	18	10
10	0.75	0.75	0.75	70	3	81	62	13	6
11	1.0	1.0	1.5	70	3	100	65	15	16
12	1.0	1.0	2.0	70	3	100	54	18	17

Q-1500 from Kovo Company. The TGA measurements were made between 20 and 500°C (in air; rate, 5°C/min). The number average molecular weight (M_n), mass average molecular weight (M_w), and polydispersity index (PDI) were determined by HPLC with equipment from Kovo Company. The HPLC conditions were as follows: an SGX (100 Å and 7 mm diameter loading material) 3.3-mm i.d. × 150-mm columns; eluent, DMF (0.2 mL min⁻¹); polystyrene standards. A refractometric detector (at 25°C) was used to analyze the product. Magnetic measurements were made by the Gouy method using Hg[Co(SCN)₄] as calibrant. Molar conductances of the oligomer–metal complexes were determined in DMSO (~ 10⁻³ M) at room temperature using a Jenway Model 4070 conductivity meter. Metal analyses were carried out by titration with ethylenediaminetetraacetic acid (EDTA).

RESULTS AND DISCUSSION

Investigation of Synthesis Conditions of OPAP

Because of the electron-donor effect of phenylazomethine, PAP was not oxidized in neutral and acidic medium, with H₂O₂ and NaOCl, respectively, but, only in an aqueous alkaline medium with air (oxygen). In this reaction, the medium was brown because of the phenylazomethine–phenoxy radicals. The monomer completely turned into oligomer when air (oxygen; 8.5 L/h; 7 h) was passed into the reaction mixture at 65°C (Table I).

The monomer converted to oligomers (~ 100%) at 90–98°C within 2 h. The yields of OPAP-II and OPAP-III were increased under these conditions. As seen in Table I, total quantities of these fractions were 12, 19, 27, and 42% at 65, 75, 80, and 90°C, respectively, with exposure to 8.5 L/h air (oxygen) for 3 h. However, the yield of OPAP-III was affected by increasing temperature. For example, the yields of the second and the third fractions were 10 and 2%, respectively, at 60°C but 30 and 12%, respectively, at 90°C. Incubation time also affected yields. At 80°C, the yields of OPAP-I and OPAP-III were 18 and 3%, respectively, at after 1 h and 27 and 16%, respectively, after 8 h. OPAP-III was soluble in water because the azomethine (—CH=N) group turned into a carboxylic (—COOH) group. The oxidative polycondensation of PAP occurred in aqueous alkaline and neutral media at 85–98°C in the presence of NaOCl. NaOCl was more reactive than air (oxygen) for this reaction. Also, reaction products were separated to three fractions: the third fraction was also formed in the presence of NaOCl (Table II).

Solubility

The first fraction (OPAP-I) was soluble in common organic solvents such as CHCl₃, DMSO, conc. H₂SO₄, aqueous KOH, DMF, benzene, toluene acetone, THF, ethyl acetate, 1,4-dioxane, and pyridine. When OPAP-II was heated in DMF at 85°C for 10–12 h, 35–40% of its mass was soluble. When OPAP-III heated in water for 18–20 h,

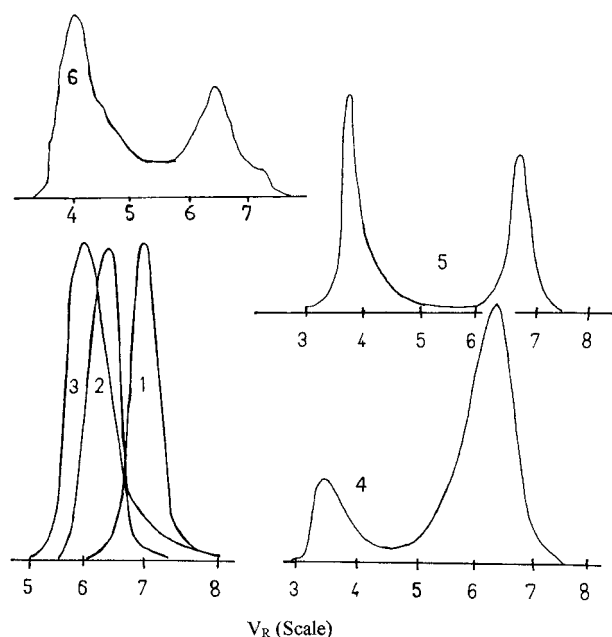


Figure 1 The molecular weight distribution curves of the condensation product of (1) PAP, (2) OPAP-I (NaOCl as oxidant), (3) OPAP-I (air [oxygen] as oxidant), (4) OPAP-II (air [oxygen] as oxidant), (5) OPAP-II* (air [oxygen] as oxidant), and (6) OPAP-III (air [oxygen] as oxidant).

50–60% of its mass was soluble. The reason for this difference is the formation of macromolecular structures by phenoxy radicals. OPAP-II was black brown. Also, it was completely soluble in 1,4-dioxane, DMF, DMSO, H_2SO_4 , and aqueous

alkaline solution, but it was partly soluble in acetone, THF, ethanol, ethyl acetate, and pyridine. OPAP-III was brown and because of carboxyl ($-COOH$) group, it was only soluble in H_2O and H_2SO_4 .

OPAP-II was reacted with Co^{+2} , Cu^{+2} , Zn^{+2} , and Ni^{+2} acetates to form oligomer-metal complexes that were either soluble or insoluble in water at room temperature. The new oligomer-metal complexes were partly soluble in DMF, but they were broken down in aqueous alkaline solution and conc. H_2SO_4 . The insolubility of these compounds indicates the formation of metal-oxygen valence and metal-nitrogen coordination bonds between oligomer-metal ions.

Structure of OPAP

According to molecular weight distribution (Figure 1), the M_n , M_w , and PDI values of OPAP-I were 550 g mol^{-1} , 700 g mol^{-1} , and 1.27, respectively. OPAP-I was di-trimers. The M_n , M_w , and PDI values of OPAP-II were 1180 g mol^{-1} , 1930 g mol^{-1} , and 1.64, respectively. At the molecular weight distribution of OPAP-II, two peaks were observed (Figure 1). Eighty percent of the mass of OPAP-II was low molecular weight (M_n , 550 g mol^{-1} ; M_w , 700 g mol^{-1} ; PDI, 1.27) but 20% of its weight was high molecular weight (M_n , 6570 g mol^{-1} ; M_w , 300 g mol^{-1} ; PDI, 1.11; see Table III).

The M_n , M_w , and PDI values of OPAP-III were 920 g mol^{-1} , 2200 g mol^{-1} , and 2.39, respectively. At the molecular weight distribution of OPAP-III, two peaks were observed (Figure 1). Thirty-five

Table III Number Average Molecular Weight (M_n), Mass Average Molecular Weight (M_w), and Polydispersity Index (PDI) Values of Oxidative Polycondensation Products of *o*-Phenylazomethinephenol

Product	Chromatographic Peak scale		Molecular Weight Distribution Parameters										
	I	II	Total			Fraction I				Fraction II			
			M_n	M_w	PDI	M_n	M_w	PDI	Yield, %	M_n	M_w	PDI	Yield, %
PAP	7.00	—	200	205	1.03	—	—	—	—	—	—	—	—
OPAP-I _(NaOCl)	6.67	—	420	460	1.10	—	—	—	—	—	—	—	—
OPAP-II _(NaOCl)	6.60	4.00	880	2070	2.35	730	890	1.22	80	6140	6900	1.11	20
OPAP-I _(O₂)	6.08	—	550	700	1.27	—	—	—	—	—	—	—	—
OPAP-II _(O₂)	6.54	3.66	1180	1930	1.64	550	700	1.27	80	6570	7300	1.11	20
OPAP-II _(O₂) ^a	6.67	3.36	1000	4150	4.15	510	580	1.14	50	6675	7740	1.16	50
OPAP-III _(O₂)	4.05	6.55	920	2200	2.39	730	850	1.16	35	6300	7100	1.11	65

^a When heated at 120°C for 12 h, insoluble fraction in 1,4-dioxane.

Table IV FT-IR Spectral Data for OPAP-II-Metal Complexes

Compound	Phenolic-OH	Ar-CH	Aliphatic-CH	CH=N	Aromatic, C=C	M-O	M-N
OPAP-II-Co	3435	3018–3028	2940	1612	1585–1496	420	505
OPAP-II-Cu	3380	3014–3026	2950	1610	1580–1496	475	486
OPAP-II-Ni	3420	3018–3033	2945	1605	1588–1493	495	460
OPAP-II-Zn	3430	3018–3028	2944	1612	1585–1490	425	510

percent of the mass of OPAP-III was low molecular weight (M_n , 730 g mol⁻¹; M_w , 850 g mol⁻¹; PDI, 1.16) but 65% of its weight was high molecular weight (M_n , 6300 g mol⁻¹; M_w , 7100 g mol⁻¹; PDI, 1.11; see Table III).

Characteristic peaks of functional groups were observed in the FT-IR spectra of the oligomers: phenyl-OH group at 3450–3420 cm⁻¹; aromatic-CH groups at 3060 cm⁻¹; —CH bonding of azomethine group at 2925 cm⁻¹; —CH=N group at 1618 cm⁻¹; and aromatic ring and —C=C double bonds at 1586–1600, 1483–1490, 1450–1454, and 1388–1398 cm⁻¹, respectively. The characteristic peaks clearly show the binding of functional groups of the synthesized products.¹⁴

The FT-IR spectrum of OPAP-III was somewhat different from those of OPAP-I and OPAP-II because carboxylic-OH and —C=O peaks were observed at 3292 and 1660 cm⁻¹, respectively, and a weak vibration band of —CH=N group was observed at 1581 cm⁻¹. Therefore, OPAP-III macromolecules include —CH=N and —COOH substituents. Also, bands for —OH and —C=O groups at 3292 cm⁻¹ (stretching vibration), 935–958 cm⁻¹ (bending vibration), and 1660 cm⁻¹ were not present in the FT-IR spectrum OPAP-III, indicating the formation of oligomer-metal complexes between —OH and —COOH groups and metal ions. In the spectra of these complexes, the stretch band (3400–3415 cm⁻¹) of the OH group was partly lower than in the spectra of oligomers. The stretch band of —CH=N group shifted to 1602 cm⁻¹ as a result of coordination of the azomethine nitrogen atom with metal ions. The FT-IR spectral data for the OPAP-II-metal complexes are given in Table IV.

The electronic spectra of PAP, OPAP-I, OPAP-II, and OPAP-III were recorded in THF solvent. The UV-vis spectra of PAP and OPAP-II showed similar bands at 208, 220, 272, 324, and 338 nm. K bands belonging to phenol, benzene, and C₆H₅—CH=N- groups were observed at 208, 272, and 220 nm, respectively. R bands for the CH=N

group were observed at 324–338 nm. In the oligomer-metal complexes, the low intensity bands in the 741–501-nm range are consistent with *d*→*d* transitions of the metal ions. To identify the structures of oligomers (Scheme 4), ¹H NMR spectra were recorded in DMSO-d₆. The ¹H NMR assignments are given in Table V. The FT-IR spectral data of the oligomers confirm the results of the ¹H NMR spectra. The OH signals in the Schiff base oligomers appeared at much lower field because of intermolecular H-bonding (Scheme 4). This case is also supported by the FT-IR bands at 2740–2760 cm⁻¹. During the polycondensation reaction, a part of the azomethine (—CH=N) group oxidized to carboxylic (—COOH), group. Thus, in the reaction product OPAP, the azomethine (—CH=N) group converts to the carboxylic (—COOH) group (0.5–20%). The ¹H NMR and FT-IR results showed the formation of oligomeric macromolecules from PAP unit by the polymerization on C₃ and C₅ position (Scheme 4).

Thermal Analyses of Oligomer and Its Oligomer-metal Complexes

The thermal degradation of OPAP-I, -II, and -III and their metal complexes was studied by TGA in air. The results of these analyses (Table VI) indicate that 5 and 50% of the mass of OPAP-I was lost at 170 and 263°C, respectively, and the total mass was lost between 300 and 350°C. A high rate of thermal degradation was noted at 281°C (1.28 mg/min). OPAP-II demonstrated more resistance than OPAP-I to temperature under the

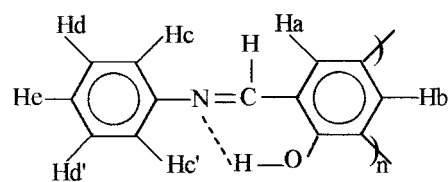
**Scheme 4**

Table V ^1H NMR Spectral Data for OPAPa

Compound	—OH	—CH=N—	a	b	cc'	dd'e	—COOH
OPAP-I	13.10 (s,1H)	8.90 (s,1H)	7.10 (s,1H)	7.60 (s,1H)	7.35 (d,2H)	6.92–7.26(m,3H)	—
OPAP-II	13.10 (s,1H)	8.90 (s,1H)	7.10 (s,1H)	7.62 (s,1H)	7.35 (d,2H)	6.90–7.35(m,3H)	—
OPAP-III	13.40 (s,1H)	8.93 (s,1H)	7.05 (s,1H)	7.64 (s,1H)	7.30 (d,2H)	7.10–7.45(m,3H)	12.65 (s,1H)

^a DMSO; δ , ppm; Me₄Si as internal standard.

same conditions: 50% of the mass of OPAP-II was lost at 541°C, and a low rate of thermal degradation was noted (0.90 mg/min). Metal complexes of OPAP-II were more resistant than their oligomers, with 5% mass loss of its metal complexes at 223–268°C.

According to these parameters, Cu⁺² and Ni⁺² complexes were more resistant than others to temperature; that is, 50% mass loss occurred at 580–600°C. The carbene residue of Cu⁺² and Ni⁺² complexes of OPAP-II was 58% at 500°C. The Cu⁺² complex of OPAP-II was more resistant than the Cu⁺² complex of OPAP-I, but it has a lower resistance than the Cu⁺² complex of OPAP-III. The carboxylic group in the structure of OPAP-III decreases the temperature resistance of OPAP-III and its metal complexes.

DTA results of oligomers and their metal complexes are given in Table VI. These data indicate that the stretch exothermic process of OPAP-II started at 468 °C and T_{max} was at 575°C. The exothermic process of oligomer-metal complexes started between 225 and 395°C, and T_{max} was 370–480°C. According to these results on activ-

ity, metals contributed to thermooxidative degradation of OPAP-II as follows: Zn⁺² > Co⁺² > Cu⁺² > Ni⁺².

Study of Antimicrobial Activities of Oligomer and Oligomer-metal Complexes

Fungicidal and bactericidal activities of the Schiff base substitute oligomer and its oligomer-metal complexes against photogenic fungi and bacteria are recorded in Table VII. It has been suggested that the oligomer with the N and O donor system might inhibit enzyme production because enzymes that require free hydroxyl groups for their activity appear to be especially susceptible to deactivation by the ions of the oligomer-metal complexes. The oligomer-metal complexes facilitate the diffusion of these ions through the lipid layer of spore membranes to the site of action, ultimately killing the spores by combining with —OH groups of certain cell enzymes. The variation in the effectiveness of different bi-radical agents against different organisms¹⁵ depends on the impermeability of the cell. The hydrocarbon

Table VI Thermooxidative Degradation Values of Oligomers and their Oligomer-Metal Complexes

Oligomer and Oligomer-metal Complexes	TGA				DTA			
	T_{start} , °C	5% Weight Loss Temp., °C	50% Weight Loss Temp., °C	% Weight Loss at 500°C	T_{max} , °C	W_{max} , mg/min	Initial Temp., °C	Exothermic Peak, °C
OPAP-I	106	170	263	100	281	1.28	—	—
OPAP-II	128	206	541	42.0	233	1.06	468	575
OPAP-III	126	218	700	39.0	295	1.30	475	586
OPAP-II-Zn ⁺²	112	235	680	42.5	335	1.21	225	370
OPAP-II-Co ⁺²	110	223	475	58.0	300	1.20	375	445
OPAP-II-Cu ⁺²	108	238	600	40.0	256	1.45	395	460
OPAP-II-Ni ⁺²	109	268	580	39.0	335	1.05	385	480
OPAP-III-Cu ⁺²	116	186	500	50.0	211	1.05	150	275, 390
OPAP-I-Cu ⁺²	105	236	300	81.0	278	1.12	217	275

Table VII Antimicrobial Effects of the OPAP-II and its Oligomer–Metal Complexes^a

Microorganism (inhibition zone ^b)	OPAP-II (O ₂)	OPAP-II (NaOCl)	OPAP-II–Zn	OPAP-II–Co	OPAP-II–Cu	OPAP-II–Ni
<i>B. cereus</i>	12	15	14	15	15	— ^c
<i>L. monocytogenes</i>	11	— ^c	7	14	14	— ^c
<i>B. megaterium</i>	— ^c	— ^c	— ^c	— ^c	— ^c	— ^c
<i>B. subtilis</i>	29	25	20	12	12	9
<i>E. coli</i>	— ^c	10	10	8	8	— ^c
<i>Str. thermophilus</i>	31	32	12	14	14	— ^c
<i>M. smegmatis</i>	13	14	15	16	16	— ^c
<i>B. brevis</i>	14	10	15	14	14	13
<i>E. aeroginesa</i>	11	9	15	17	17	13
<i>P. vulgaris</i>	13	12	17	19	19	— ^c
<i>M. luteus</i>	12	13	17	16	16	— ^c
<i>S. aureus</i>	19	14	15	11	11	— ^c
<i>B. jeoreseensis</i>	14	16	21	15	15	12

^a Compound conc 50 g disc.

^b Including disc diameter of 86 mm.

^c Compound has no any activity against the microorganism.

acts as a lipophilic group^{16,17} to drive the compound through the semipermeable membrane of the cell. Chelating reduces the polarity of the central ion mainly because of the partial sharing of its positive charge with the donor groups and possible π -electron delocalization within the entire chelate ring. This chelating increases the lipophilic nature of the central atom, which favors its permeation through the lipid layer of the membrane. In this study, OPAP-II demonstrated the highest biologic activity, affecting 11 types of microorganisms. Copper, cobalt, and zinc complexes of OPAP-II affected 12 types microorganisms, demonstrating high biologic activity. The OPAP-II–Ni complex affected four types of microorganisms. These results indicate that it is very important to synthesize Schiff base substitute phenols and oligomers to prepare new active agents.

CONCLUSION

According to chemical and spectral analyses, synthesized OPAP macromolecules were formed from units bonding with *o*- and *p*-carbons of azomethin-phenol. A part of the azomethine ($-\text{CH}=\text{N}$) groups of the oligomer were partly converted to carboxylic ($-\text{COOH}$) groups by the effects of oxidants such as NaOCl and air (oxygen). For example, the azomethine ($-\text{CH}=\text{N}$) group of OPAP-III converts to the carboxylic ($-\text{COOH}$)

group (2–20%). The number average molecular weight (M_n) and mass average molecular weight (M_w) values of OPAP-II were 1180 and 1930 g mol⁻¹, respectively. According to these values, 20–33% of PAP turned into OPAP. Network structure oligomer–metal complexes were synthesized from OPAP with Zn⁺², Co⁺², Cu⁺², and Ni⁺², and their the structure and the properties were determined. According to TG and DTA curves, oligomers and oligomer–metal complexes demonstrated high stability against thermooxidative degradation. OPAP-II and its oligomer–metal complexes affected 11 and 12 types microorganisms, respectively, as indicated by high biologic activity. For these reasons, Schiff base-substitute phenols and oligomers may be used to prepare new active agents.

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