Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Polymer 44 (2003) 7299–7309

polymer

www.elsevier.com/locate/polymer

The synthesis and characterization of oligo-N-4-aminopyridine, oligo-2-[(pyridine-4-yl-imino) methyl] phenol and its some oligomer–metal complexes

İsmet Kaya*, Sermet Koyuncu

Department of Chemistry, Faculty of Sciences and Arts, Çanakkale Onsekiz Mart University, Çanakkale 17100, Turkey

Received 8 May 2003; received in revised form 19 August 2003; accepted 10 September 2003

Abstract

The product and the oxidative polycondensation reaction conditions of oligo-4-aminopyridine were studied by using NaOCl as oxidant. Oligo-4-aminopyridine (4-OAP) was synthesized from the oxidative polycondensation of 4-aminopyridine (4-AP) in an aqueous solution medium acidic and neutral between 25 and 60 °C by using NaOCl as oxidant. About 85% of 4-AP was converted to 4-OAP. The number average molecular weight, (M_n) mass average molecular weight (M_w) and polydispersity index (PDI) values of 4-OAP synthesized were found to be 270, 850 g mol^{-1} and 3.15, respectively, using NaOCl. The respective values of the Schiff base were 1721, 2256 g mol^{-1} and 1.31, respectively, using air oxygen and 2173, 2372 g mol^{-1} and 1.09, respectively, using NaOCl and 2749, 6432 g mol^{-1} and 2.33, respectively, using H_2O_2. At the optimum reaction conditions, the yield of oligo-2-[(pyridine-4-yl-imino) methyl] phenol (OPMP) were found to be 86% (H_2O_2) and 89% (NaOCl) and 95% (air oxygen). The 4-OAP and OPMP were characterized by ^{1}H NMR, FT-IR, UV–Vis and elemental analysis. TG analysis showed to be stable of 4-OAP against thermo-oxidative decomposition. The weight loss of 4-OAP and its Schiff base oligomer was found to be 50, 86.39 and 71.78% at 525, 625 and 1000 °C, respectively. Also, new oligomeric Schiff base was synthesized from condensation of 4-AP with salicylaldehyde and their structures and properties were determined. During polycondensation reaction, a part of the azomethine (–CH=N–) groups oxidized to carboxylic (–COOH) group. Thus, soluble fraction in water of oligo-2-[(pyridine-4-yl-imino) methyl] phenol involved in carboxylic (–COOH) (11%) group. Besides, the structure and properties of oligomer–metal complexes of oligo-2-[(pyridine-4-yl-imino) methyl] phenol (OPMP) with Cu(II), Ni(II) and Co(II) were studied.

Keywords: Oligo-2-[(pyridine-4-yl-imino) methyl] phenol; Oligo-N-4-aminopyridine; Oxidative polycondensation

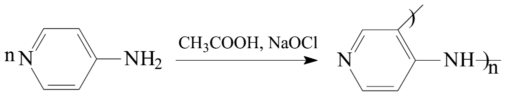
1. Introduction

The Schiff base substitute oligophenols and their derivatives, including conjuge bonding and active hydroxyl group, have been used in various fields. They have useful properties such as paramagnetism, semi-conductive, electrochemical cell and resisting to high energy. Because of these properties, they were used to prepare composites with resistance at high temperature, thermostabilisator, graphite materials, and epoxy oligomer and block copolymers, adhesives, photo resists, anti-microbial agent and antistatic materials [1–8]. The halogen and sulphur derivatives of oligophenols were used to prepare the composite materials enduring to flame of the specific detergents such as lead storing battery cathodes [9]. Addition of other functional groups to these compounds profited new useful properties. More functional oligophenols may be used for cleaning of poisonous heavy metals in the industrial wastewaters. Therefore, the syntheses of oligomer–metal complexes are very important at analytic and environmental chemistry. The prodigious growth of the published literature on Schiff base complexes dictates certain limitations as far as spectral and magnetic investigations are concerned. It seemed advantageous to attempt to design and prepare a polymer-bound chelating ligand, which would be able to form complexes with a variety of transition metals. Therefore, they have a large range of applications. Also, coordination compounds of salicylaldehyde Schiff base have proven to be an excellent model system to study the enzymatic reactions of pyridoxal phosphate, because both these systems

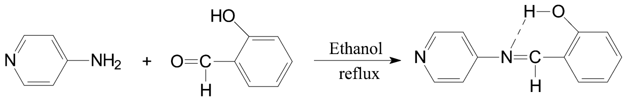
---

* Corresponding author. Tel.: +90-286-21800181858; fax: +90-286-2180033.
E-mail address: kayaismet@hotmail.com (I. Kaya).

0032-3861/$ - see front matter Crown Copyright © 2003 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.09.011



Scheme 1.



Scheme 2.

effectively catalyze transamination and racemization reaction [10].

The purpose of this paper is to report on the preliminary synthesis and characterization of 4-OAP and OPMP by oxidative polycondensation method. For this purpose, we determined the oxidative polycondensation reaction conditions of 4-OAP and OPMP. In the first part, both we have investigated to the oligo-4-aminopyridine the effects of different parameters such as temperature, initial concentration of 4-AP, NaOCl and acetic acid and we have studied the OPMP, the effects of different parameters such as temperature, initial concentration of PMP, NaOCl, H_2O_2 and alkaline. In the second part, synthesized 4-OAP and OPMP were characterized by using FT-IR, UV–Vis, ^1H NMR, elemental analysis, DTA-TG and size exclusion chromatography (SEC) techniques. In the third part, the new oligomer–metal complexes were synthesized from OPMP with Cu(II), Ni(II) and Co(II) and characterized by spectral techniques.

2. Materials and methods

2.1. Materials

4-Aminopyridine (4-AP), salicylaldehyde (SA), 1,4-dioxane, ethanol, benzene, acetone, ethyl acetate, *n*-heptane, pyridine, $CHCl_3$, CCl_4, tetrahydrofurane (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO), H_2SO_4, toluene, hydrochloric acid (HCl), KOH, H_2O_2 (35%, aqueous solution), Cu $(CH_3COO)_2{\cdot}H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$ and Ni $(CH_3COO)_2{\cdot}4H_2O$ were supplied from Merck Chemical Co. (Germany) as chromatographic grade and they were used as received. Sodiumhypochloride (NaOCl), (30%, aqueous solution) was supplied from Paksoy Co. (Turkey).

2.2. The oxidative polycondensation of 4-AP with NaOCl [11]

The 4-aminopyridine (0.6 g, 64 mmol) was dissolved in an aqueous solution of acetic acid (10%, 0.5 ml). At 25 °C, NaOCl (2.95 ml, 30%) was added drop wise over about 40 min. The reaction mixture was stirred at 25 °C for 1 h (Scheme 1, Table 1). The mixture was neutralized with 2.26 g KOH (10%, 40 mmol). Then, oligo-4-aminopyridine was separated by extraction with ethyl acetate and precipitated. Unreacted monomer was separated from the reaction products by washing cold $CHCl_3$. The crude product was washed with water (50 ml × 3), filtered and dried in the oven at 105 °C.

Anal. calcd for O-4AP: C, 65.21; H, 4.34; N, 30.40. Found for 4-OAP: C, 63.62; H, 4.81; and N, 31.51. For 4-OAP, FT-IR (KBr; cm^{-1}): 3490 (N–H); 1323 (C–N); 1421–1560 (C=C); 3097 (aromatic C–H); 1293 (aromatic-N). For O-4AP, UV–Vis (λ_{max}): 223, 240, 275 and 291 nm. ^1H NMR (DMSO): δ ppm, 6.65 (s, 1H, N*H*); 8.97 (d, 1H, Ar-*Ha*); 7.87 (d, 1H, Ar-*Hb*); 8.91 (s, 1H, Ar-*Hc*).

2.3. Preparation of 2-[(pyridine-4-yl-imino) methyl] phenol (PMP)

2-[(Pyridine-4-yl-imino) methyl] phenol was prepared by the condensation of salicylaldehyde (0.025 mol) and 4-aminopyridine (0.025 mol) in ethanol (15 ml) achieved by

Table 1
The oxidative polycondensation of 4-aminopyridine with NaOCl in an aqueous CH_3COOH and neutral medium

Sample number	$[4\text{-AP}]_0$ (mol l^{-1})	$[CH_3COOH]_0$, (mol l^{-1})	$[NaOCl]_0$ (mol l^{-1})	Temperature, (°C)	Time, (h)	Conversion of 4-AP, (%)
1	0.93	–	1.90	25	1	56
2	0.93	–	2.80	25	1	68
3	0.93	–	1.90	40	1	58
4	0.93	–	1.90	25	2	22
5	0.93	0.11	1.90	25	1	44
6	0.93	0.26	1.90	25	1	51
7	0.93	0.31	1.90	25	1	65
8	0.93	0.72	1.90	25	1	84
9	0.93	0.31	2.80	25	1	58
10	0.93	0.31	1.90	32	1	67
11	0,93	0.31	1.90	40	1	82
12	0.93	0.31	1.90	60	1	52
13	0.93	0.31	1.90	25	2	49
14	1.24	0.31	2.50	40	1	62
15	1.75	0.31	3.53	40	1	56

Table 2
The oxidative polycondensation of 2-[(pyridine-4-yl-imino) methyl] phenol with air oxygen in an aqueous KOH

Sample number	$[PMP]_0$, (mol l^{-1})	[KOH], (mol l^{-1})	$V_{\text{air, oxygen}}$ (l h^{-1})	Temperature, (°C)	Time, (h)	Conversion of PMP, (%)	Reaction products, (%)	
							Fraction I	Fraction II
1	0.75	0.75	8.5	70	10	84	58	26
2	0.75	0.75	8.5	75	10	87	64	23
3	0.75	0.75	8.5	80	10	94	72	22
4	0.75	0.75	8.5	85	10	80	61	19
5	0.75	0.75	8.5	90	10	72	54	18
6	0.75	1.50	8.5	80	10	86	71	15
7	0.75	0.75	8.5	80	25	95	83	12

Table 3
The oxidative polycondensation of 2-[(pyridine-4-yl-imino) methyl] phenol with NaOCl in an aqueous KOH

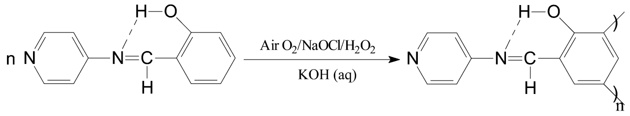
Sample number	$[PMP]_0$, (mol l^{-1})	$[KOH]_0$, (mol l^{-1})	[NaOCl], (mol l^{-1})	Temperature, (°C)	Time, (h)	Conversion of PMP, (%)	Reaction products	
							Fraction I	Fraction II
1	0.75	0.75	0.75	50	5	26	–	26
2	0.75	0.75	0.75	60	5	34	–	34
3	0.75	0.75	0.75	70	5	52	20	32
4	0.75	0.75	0.75	80	5	69	40	29
5	0.75	0.75	0.75	90	5	81	58	23
6	0.75	0.75	0.75	95	5	70	51	19
7	0.75	0.75	1.50	90	5	76	50	26
8	0.75	1.50	0.75	90	5	71	50	21
9	0.75	0.75	0.75	90	10	86	64	22
10	0.75	0.75	0.75	90	15	88	69	19
11	0.75	0.75	0.75	90	25	89	76	13

boiling the mixture under reflux for 3 h (Scheme 2). The precipitated 2-[(pyridine-4-yl-imino) methyl] phenol was filtered and recrystallized from ethanol and dried in a vacuum desiccators.

Anal. calcd for PMP: C, 72.72; H, 5.05; N, 14.14. Found for PMP: C, 73.25; H, 5.52; N, 13.50. For PMP, FT-IR (KBr, cm^{-1}): ν (O–H) 3304 s, ν (C–H aryl) 3077 m, ν (C–H aliphatic) 2925, 2698 s, ν (C=N) 1648 s, ν (aromatic, C=C) 1558–1450 m. UV–Vis (λ_{max}): 234, 273 and 330 nm.

2.4. *The synthesis of oligo-2-[(pyridine-4-yl-imino) methyl] phenol with air oxygen*

PMP (3.000 g, 1.515×10^{-2} mol) was dissolved in an aqueous solution of KOH (10%) (0.848 g, 1.515×10^{-2} mol). The reaction mixture was stirred at the various temperatures (Table 2). The air oxygen was passed into rate 8.5 l h^{-1} during the course of the reaction. The compound was obtained according to the published procedure (Scheme 3) [12]. It was cooled to room temperature and then 1.515×10^{-2} 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 by washing ethanol from the product and the product dried in the oven at 110 °C. The product separated two fractions. The first (OPMP-I) was insoluble in water but the second fraction (OPMP-II) was soluble in water.



Scheme 3.

Anal. calcd for OPMP: C, 73.45; H, 4.08; N, 14.29. Found for OPMP: C, 74.05; H, 4.25; N, 13.90. FT-IR (KBr, cm^{-1}): ν (O–H) 3346 s, ν (C–H aryl) 3085 m, ν (C–H aliphatic) 2920 s, ν (C=N) 1647 s, ν (aromatic, C=N) 1375 s, ν (C–O) 1299 s, ν (aromatic, C=C) 1599–1420 m. UV–Vis (λ_{max}): 237, 274 and 362 nm. ^{1}H NMR (DMSO): δ ppm, 9.00 (s, 1H, OH); 8.05 (s, 1H, CH=N); 6.96 (s, 1H, Ar-Ha); 7.12 (s, 1H, Ar-Hb); 6.57 (d, 2H, pyridinyl-Hcc′); 8.36 (d, 2H, pyridinyl-Hdd′).

2.5. *The synthesis of oligo-2-[(pyridine-4-yl-imino) methyl] phenol with NaOCl*

The PMP (3.000 g, 1.515×10^{-2} mol) was dissolved in an aqueous solution of KOH (10%, 0.848 g, 1.515×10^{-2} mol). After heating at 60 °C for 30 min, NaOCl (30% aqueous solution) was added drop wise over

Table 4
The oxidative polycondensation of 2-[(pyridine-4-yl-imino) methyl] phenol with H_2O_2 at neutral medium

Sample number	$[PMP]_0$, (mol l^{-1})	$[H_2O_2]_0$ (mol l^{-1})	Temperature, (°C)	Time, (h)	Conversion of PMP, (%)
1	0.5	0.5	50	5	62
2	0.5	0.5	60	5	83
3	0.5	0.5	65	5	86
4	0.5	0.5	70	5	74
5	0.5	0.5	75	5	70
6	0.5	0.5	80	5	65
7	0.5	0.5	85	5	57
8	0.5	0.5	90	5	45
9	0.5	0.5	95	5	33
10	0.5	1.0	65	5	78
11	0.5	0.5	65	10	81
12	0.5	0.5	65	25	82

about 20 min. The reaction mixture was stirred at the various temperatures (Table 3). The mixture was neutralized with 0.5 ml HCl (37%) at room temperature. The compound was obtained according to the published procedure (Scheme 3) [12]. The mixture was filtered and washed with hot water (3 × 50 ml) for separating from mineral salts. Unreacted monomer was separated by washing ethanol from the product and the product dried in the oven at 110 °C. The product separated two fractions. The first (OPMP-I) was insoluble in water but the second fraction (OPMP-II) was soluble in water.

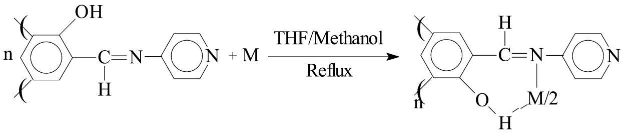
2.6. The synthesis of oligo-2-[(pyridine-4-yl-imino) methyl] phenol with H_2O_2

The PMP (3.000 g, 1.515×10^{-2} mol) was dissolved in distilled water. After heating at 50 °C for 30 min, H_2O_2 (35% aqueous solution) was added drop wise over about 20 min. The reaction mixture was stirred at the various temperatures (Table 4). The compound was obtained according to the published procedure (Scheme 3). The mixture was filtered and washed with hot water (3 × 50 ml) for separating from mineral salts and unreacted monomer and dried in the oven at 110 °C.

2.7. Syntheses of oligo-2-[(pyridine-4-yl-imino) methyl] phenol metal complexes [13]

2.7.1. Cobalt(II) complex

A solution of Co $(AcO)_2 \cdot 4H_2O$ (1×10^{-3} mol, 0.250 g) in methanol (10 ml) was added to a solution of oligo-2-[(pyridine-4-yl-imino)methyl] phenol (OPMP) (2×10^{-3} mol/unit, 0.400 g) in DMF (20 ml) (Scheme 4). The mixture was stirred and heated at 70 °C for 5 h. The precipitated complex was filtered and washed with cold DMF/methanol (1:1), then dried in vacuum oven (yield 69%, mp > 250 °C).



Scheme 4.

Anal. calcd for OPMP-Co: M, 23.14. Found for OPMP-Co: M, 21.15. For OPMP-Co, FT-IR (KBr, cm^{-1}): ν (O–H) 3355 s, ν (C–H aryl) 3018–3028 m, ν (C–H aliphatic) 2940 s, ν (C=N) 1638 s, ν (aromatic, C=C) 1585–1497 s, ν (M–O) 529 and ν (M–N) 595. UV–Vis (λ_{max}): 255, 270, 327, 362 and 641 nm. μ_{Eff}: diamagnetic.

2.7.2. Nickel(II) complex

A solution of Ni $(AcO)_2 \cdot 4H_2O$ (1×10^{-3} mol, 0.250 g) in methanol (10 ml) was added to a solution of oligo-2-[(pyridine-4-yl-imino) methyl] phenol (OPMP) (2×10^{-3} mol/unit, 0.400 g) in DMF (20 ml) (Scheme 4). The mixture was stirred and heated at 70 °C for 5 h. The precipitated complex was filtered and washed with cold DMF/methanol (1:1), then dried in vacuum oven (yield 78%, mp > 250 °C).

Anal. calcd for OPMP-Ni: M, 22.84. Found for OPMP-Ni: M, 20.00. For OPMP-Ni, FT-IR (KBr, cm^{-1}): ν (O–H) 3352 s, ν (C–H aryl) 3018–3033 m, ν (C–H aliphatic) 2945 s, ν (C=N) 1640 s, ν (aromatic, C=C) 1580–1496 s, ν (M–O) 526 and (M–N) 589. UV–Vis (λ_{max}): 252, 268, 327, 358 and 641 nm. μ_{Eff}: diamagnetic.

2.7.3. Copper(II) complex

A solution of Cu $(AcO)_2 \cdot H_2O$ (1×10^{-3} mol, 0.200 g) in methanol (10 ml) was added to a solution of oligo-2-[(pyridine-4-yl-imino) methyl] phenol (OPMP) (2×10^{-3} mol/unit, 0.400 g) in DMF (20 ml) (Scheme 4). The mixture was stirred and heated at 70 °C for 5 h. The precipitated complex was filtered and washed with cold DMF/methanol (1:1), then dried in vacuum oven (yield 86%, mp > 250 °C).

Anal. calcd for OPMP-Cu: OPMP-Cu: M, 24.47. Found for OPMP-Cu: M, 21.50. For OPMP-Cu, FT-IR (KBr, cm^{-1}): ν (O–H) 3354 s, ν (C–H aryl) 3014–3026 m, ν (C–H aliphatic) 2950 s, ν (C=N) 1640 s, ν (aromatic, C=C) 1583–1496 s, ν (M–O) 524 and (M–N) 592. UV–Vis (λ_{max}): 254, 275, 327, 361 and 641 nm. μ_{Eff}: diamagnetic.

2.8. Characterization techniques

The infrared and UV–Vis spectra were measured by Perkin–Elmer FT-IR BX and Shimadzu UV-1208, respectively. Elemental analysis was carried out with a Carlo Erba 1106. The FT-IR spectra were recorded using KBr disc (4000–350 cm^{-1}). UV–Vis spectra of 4-OAP and OPMP were determined by using DMSO. OPMP was characterized by using a ^{1}H NMR spectra (Bruker AC FT-NMR 400 MHz spectrometer) was recorded at 25 °C by using deuterated DMSO as solvent and TMS as internal standard. Thermal data were obtained by using STA 409C NETZSCH-Geratebau GmbH Thermal Analysis. TG-DTA measurements were made between 20 and 1000 °C (in air, rate 10 °C min^{-1}). The number average molecular weight (M_n), mass average molecular weight (M_w) and polydispersity index (PDI) were determined by size SEC of Shimadzu Co. For SEC investigations were used a SGX (100 Å and 7 nm diameter loading material) 7.7 mm i.d. × 300 mm columns; eluent: DMF (0.4 ml min^{-1}), polystyrene standards. A refractive index detector (RID) (at 25 °C) was used to analyze the product. Magnetic measurements were carried out by the Gouy method using Hg [Co(SCN)$_4$] as calibrant. Molar conductance of the oligomer–metal complexes was determined in DMSO (ca. 10^{-3} M) at room temperature using a Jenway Model 4070 conductivity meter.

3. Results and discussion

3.1. The investigation of synthesis conditions of OPMP

The conditions for oxidative polycondensation reaction of 4-AP with NaOCl solution in aqueous acidic and neutral medium are given in Table 1. The oxidative polycondensation reaction of 4-AP immediately formed in an aqueous solution and solution turned into brown by adding of NaOCl oxidant. When $[\text{4-AP}]_0 = 0.93$ mol l^{-1}, the conversion of 4-AP oligomer by $[\text{NaOCl}]_0 = 1.90$ mol l^{-1} at 25 °C for 1 h was 56.0%. However, while $[\text{4-AP}]_0 = 0.93$ mol l^{-1}, $[CH_3COOH]_0 = 0.72$ mol l^{-1} the conversion of 4-AP oligomer by $[\text{NaOCl}]_0 = 1.90$ mol l^{-1} at 25 °C for 1 h was 84.0% (see Table 1). Oligomer of 4-AP has not been formed at alkaline medium.

As seen in Table 1, in these reactions, the yield of oligomer was dependent on initial concentrations of CH_3COOH and NaOCl. The maximum yield (84.0%) of 4-OAP formed at the concentrations of 4-AP (0.93 mol l^{-1}), NaOCl (1.90 mol l^{-1}) and CH_3COOH (0.72 mol l^{-1}), at 25 °C for 1 h. The conversion of 4-AP increased from 56.0 to 68.0%, when increased concentration of NaOCl from 1.90 to 2.80 mol l^{-1} under the neutral condition (Table 1). Also, the yield of oligomer was affected by increasing the concentration of acetic acid. 4-APs know relatively higher active than phenols in oxidative polycondensation. As seen in Table 1, oligomer product 4-AP's formed in the presence of NaOCl.

Because of electron-donor effect of phenylazomethine, 2-[(pyridine-4-yl-imino) methyl] phenol has not oxidized at neutral and acidic medium by H_2O_2, air oxygen and NaOCl. But, PMP is oxidized by H_2O_2, air oxygen and NaOCl in an aqueous alkaline medium. In this reaction, medium was brown, because of phenylazomethine-phenoxy radicals. However, the oxidative polycondensation reaction of PMP immediately was formed in an aqueous alkaline solution and the solution turned into brown by adding oxidants such as NaOCl and H_2O_2 and air oxygen. When $[\text{PMP}]_0 = [\text{KOH}]_0 = 0.75$ mol l^{-1}, the conversion of PMP to oligomer by air oxygen at 80 °C for 10 h was 94.0% (see Table 2). While the conversion of PMP to oligomer was 94.0% at 80 °C for 10 h, the conversion of it was 72.0% at 90 °C for 10 h. The reason for this may be depolymerization to monomer of oligomer at high temperatures. For air oxygen oxidant, the maximum yield (95.0%) of OPMP formed at the concentrations of PMP (0.75 mol l^{-1}) at 80 °C for 25 h (Table 2). At this process, air oxygen was more reactive than NaOCl and H_2O_2. Also, reaction products were separated to two fractions. PMP is known relatively active than oligo-2-hydroxy-1-naphthaldehyde (OHNA) in oxidative polycondensation [14].

The conditions of oxidative polycondensation reaction of PMP with 30% NaOCl solution in aqueous alkaline medium are given in Table 3. The conversion of PMP was 81.0% at optimum conditions such as $[\text{PMP}]_0 = [\text{KOH}]_0 = [\text{NaOCl}]_0 = 0.75$ mol l^{-1}, at 90 °C for 5 h. The conversion of PMP was 89.0% at the reaction conditions such as $[\text{PMP}]_0 = [\text{KOH}]_0 = [\text{NaOCl}]_0 = 0.75$ mol l^{-1} at 90 °C for 25 h. The various conditions of PMP are given for NaOCl oxidant in Table 3. OPMP was soluble in water, because of the azomethine (–CH=N) group turned into carboxylic (–COOH) group (for oxidants NaOCl and air oxygen).

The conditions of oxidative polycondensation reaction of PMP with 30% H_2O_2 solution in aqueous medium are given in Table 4. The conversion of PMP was 86.0% at optimum conditions such as $[\text{PMP}]_0 = [H_2O_2]_0 = 0.50$ mol l^{-1}, at 65 °C for 5 h. The conversion of PMP was 65.0% at the reaction conditions such as $[\text{PMP}]_0 = [H_2O_2]_0 = 0.75$ mol l^{-1} at 80 °C for 5 h. While the conversion of PMP to oligomer was 86.0% at 65 °C for 5 h, the conversion of it was 45.0% at 90 °C for 5 h. The reason for this may be depolymerization to monomer of oligomer at high temperatures. The various conditions of PMP are given for H_2O_2 oxidant in Table 4. The second fraction had not been formed at H_2O_2 medium (Table 4). The oxidative polycondensation method is simple and easy for the synthesis of oligophenols with Schiff base substitute. Also, the synthesis of different molecular weight distribution oligomers is possible to be dependent on oxidant concentration, temperature and reaction times. While the second fractions occurred at the oxidative polycondensation reactions of PMP by using NaOCl and air O_2, the one fraction formed at the H_2O_2

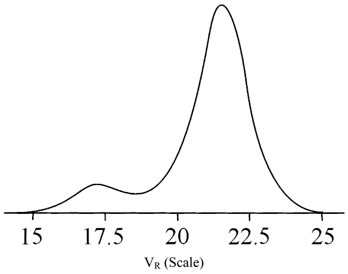


Fig. 1. The molecular weight distribution curves of the condensation product of 4-OAP.

oxidant. However, one fraction formed at oxidative polycondensation reactions of 4-AP. According to these results, NaOCl and air O_2 are better oxidants than H_2O_2, for oxidative polycondensation of oligophenols.

3.2. Solubility

The oxidative polycondensation product of 4-AP with NaOCl in aqueous acidic medium was light brown solid powder. 4-OAP was soluble in H_2SO_4, tetrahydrofuran, dimethylformamide, DMSO and 1, 4-dioxane. However, 4-OAP was poorly soluble in aqueous NaOH, toluene and chlorinated solvents, such as $CHCl_3$ and CCl_4. OPMP was completely soluble in DMF, DMSO, H_2SO_4 and aqueous alkaline solution but it was partly soluble in acetone, methanol, ethyl acetate and pyridine. However, it is insoluble in THF, ethanol and 1, 4-dioxane. The new oligomer–metal complexes were partly soluble in DMSO but they broken into an aqueous alkaline solution and conc. H_2SO_4. Insoluble parts of these oligomer–metal complexes, it is clear that formation of metal–oxygen valans and metal–nitrogen coordination bonds between oligomer–metal ions.

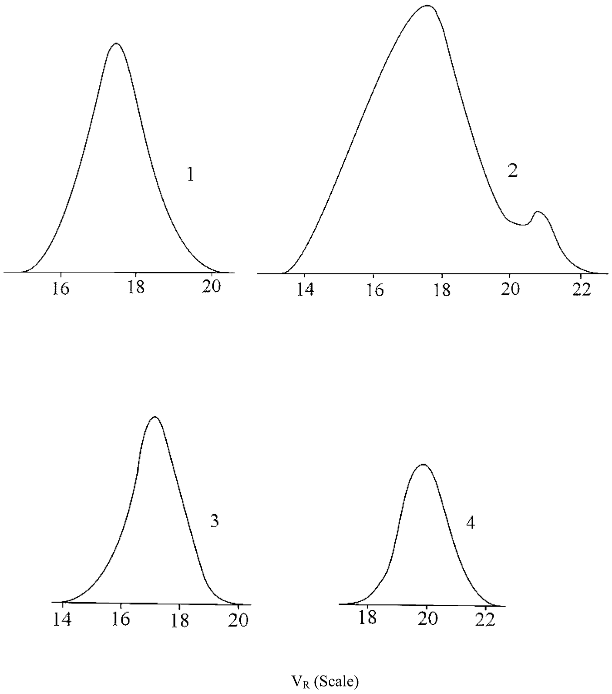
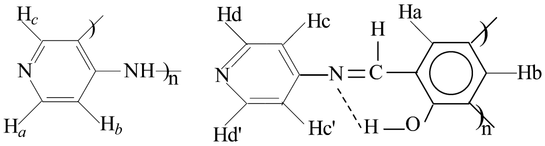


Fig. 2. The molecular weight distribution curves of the condensation product of (1), OPMP-I, (NaOCl, as oxidant) (2) OPMP-I, (H_2O_2, as oxidant) (3) OPMP-I (air oxygen, as oxidant) and (4) OPMP-II, (air oxygen, as oxidant).



Scheme 5(a) and (b).

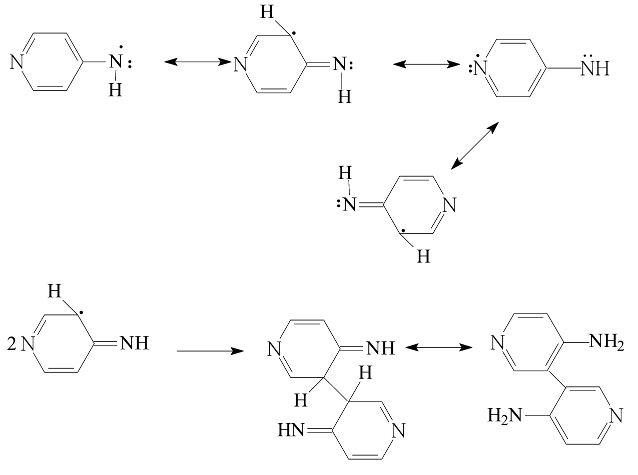
3.3. Structure of 4-OAP and OPMP

According to molecular weight distribution (Fig. 1), the number average molecular weight (M_n), mass average molecular weight (M_w) and PDI values of 4-OAP (as oxidant, NaOCl) were found to be 270, 850 g mol^{-1} and 3.15, respectively. At the molecular weight distribution of 4-OAP, two peaks were observed (Fig. 1). 96.0% of OAP's mass was low molecular weight (M_n : 425 g mol^{-1}, M_w : 520 g mol^{-1} and PDI: 1.22) but 4.0% of its weight was high molecular weight (M_n : 2750 g mol^{-1}, M_w : 4560 g mol^{-1} and PDI: 1.66). According to molecular weight distribution (Fig. 2), the number average molecular weight (M_n), mass average molecular weight (M_w) and PDI values of OPMP (as oxidant, NaOCl) were found to be 2173, 2372 g mol^{-1} and 1.09, respectively. At the molecular weight distribution of OPMP, H_2O_2), two peaks were observed (Fig. 2). 5.0% of OPMP's mass was low molecular weight (M_n : 390 g mol^{-1}, M_w : 430 g mol^{-1} and PDI: 1.11) but 95.0% of its weight was high molecular weight (M_n : 1615 g mol^{-1}, M_w : 2325 g mol^{-1} and PDI: 1.44). The M_n, M_w and PDI values of OPMP (as oxidant, air O_2) were found to be 1721, 2256 g mol^{-1} and 1.31, respectively. The M_n, M_w and PDI values of OPMP-II (as oxidant, air O_2) were found to be 436, 450 g mol^{-1} and 1.05, respectively.

At the FT-IR spectra of the oligomers, the characteristic peaks of the functional groups were observed: Phenyl-OH group at 3345 cm^{-1}, aromatic –CH groups at 3082 cm^{-1}, –CH bonding of azomethine group at 2920 cm^{-1}, –CH=N group at 1647 cm^{-1} and aromatic ring and –C=C double bond at 1599–1600, 1482–1493, 1450–1454 and 1380–1398 cm^{-1}, respectively. The characteristic peaks clearly show the binding of functional groups of the synthesized products [11].

The electronic spectra of 4-OAP, PMP and OPMP were recorded in DMSO solvent. The UV–Vis spectra of PMP and OPMP were observed the same bands in 234, 273, 330 and 237, 274, 362 nm, respectively. K bands belong to phenol, benzene and C_6H_5 –CH=N– groups were observed in 234, 273 and 237, 274 nm, respectively. R bands of CH=N group were observed in 330 and 362 nm.

In order to identify the structures of 4-OAP and OPMP (Scheme 5(a) and (b)), the ^1H NMR spectra were recorded



Scheme 6.

in DMSO-d_6. The FT-IR spectral data of the 4-OAP and OPMP confirm the results of the ^{1}H NMR spectra. The OH signals in the Schiff base oligomers appeared at much lower field because of intermolecular H-bonding (Scheme 5(b)). This case is also supported by the FT-IR bands at 2745–2766 cm^{-1}. During polycondensation reaction, a part of the azomethine (–CH=N) group oxidized to carboxylic (–COOH) group. Thus, reaction product, that is, azomethine (–CH=N) of oligo-2-[(pyridine-4-yl-imino) methyl] phenol, involves to carboxylic (–COOH) (11%) groups. The stretching vibration of carbonyl group was observed in 1720 cm^{-1} at the FT-IR spectra. According to ^{1}H NMR, proton of carboxyl group was observed in 16.0 ppm. The ^{1}H NMR and FT-IR results showed the formation of oligomeric macromolecules from PMP unit by the polymerization on C_3 and C_5 position (Scheme 5(b)).

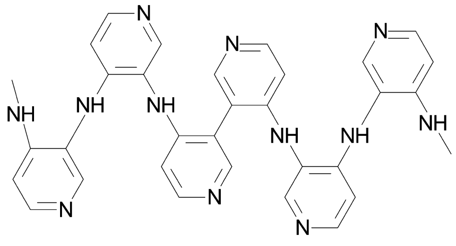
The mezomeric structures of monomer radical units and monomer (4-AP) and dimmer Inter conversion combinations of radical units are proposed as follows (Scheme 6):

According to the spectral and SEC analyses, 4-OAP's formula is given as follows (Scheme 7):

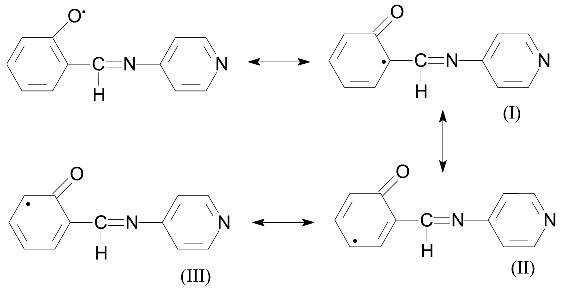
The mezomeric structures of monomer radical units are proposed as follows (Scheme 8):

Inter-conversion combinations of radical units of PMP and its dimmer are proposed as follows (Scheme 9):

According to the spectral and SEC analyses, OPMP's formula is given as follows (Scheme 10):



Scheme 7. The structure of 4-OAP.



Scheme 8.

Dutta et al. [15] had been synthesized to Schiff base oligomer with 4-nitroaniline and 4-hydroxybenzaldehyde, according to polycondensation reaction and they had been investigated some properties of Schiff base oligomer. Aly et al. [16] had been synthesized new conducting polyazomethine polymers containing main chain cycloalkanone and pyridine moieties according to polycondensation and they had been investigated some properties such as thermal and semi-conductivity. Yousef [17] had been reported to results concerning the electro-oxidative polymerization of 3-[1-(2-aminophenylimino)-ethyl]-6-methylpyran-2, 4-dione in acidic aqueous solution containing 1.0 M H_2SO_4.

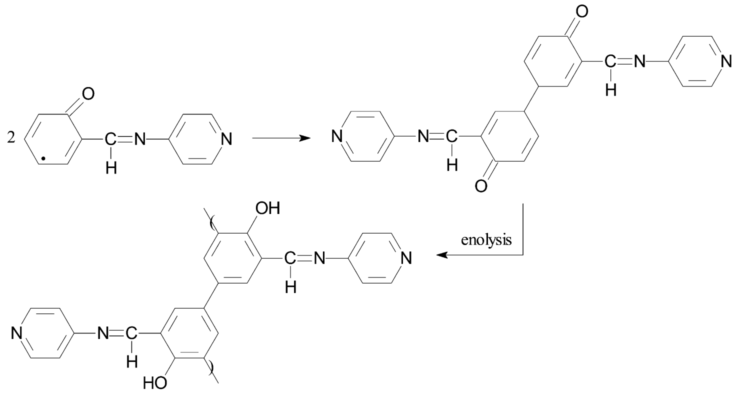
Polymers with azomethine structure containing 1, 5-naphthyl or 1,4-phenyl moieties had been synthesized through polycondensation of some dialdehydes with diamines. Both monomers and polymers had been characterized by IR and ^{1}H NMR techniques. Thermogravimetric analyses had been made for all the synthesized polymers in order to study their thermal behaviors [18].

Novel synthesis of a new poly (Schiff base sulfide) polymer by nucleophilic displacement polymerization of N, N′-bis(*p*-chloro-benzylidine)-2,6-diaminopyridine with sodium sulfide had been carried out. The monomer and the polymer had been characterized by using spectroscopic techniques [19]. Poly-Schiff base containing bisthiazole rings had been prepared from terephthalaldehyde and 2,2′-diamino-4,4′-bisthiazole [20]. According to other electrochemical techniques, the oxidative polycondensation reaction conditions are more simple and easy.

3.4. The structures of oligomer–metal complexes

The Co^{+2} complex of OPMP showed absorptions at 15,600, 27,624, 30,581, 37,037 and 39,216 cm^{-1}. The absorption at 33,333 cm^{-1} is assigned to cobalt–cobalt interaction [21]. The presence of one coordinated water molecule has already been confirmed by FT-IR spectral data. Thus the local symmetry around each cobalt is octahedral considering the metal–metal interaction.

The Ni^{+2} complex of OPMP showed absorptions at 15,600, 27,933, 30,581, 37,313 and 39,683 cm^{-1}. The presence of one coordinated water molecule has already been confirmed by FT-IR spectral data. Thus the local symmetry around each nickel is octahedral considering the metal–metal interaction. The Cu^{+2} complex of OPMP showed absorptions at 15,600, 27,701, 30,581, 36,363 and



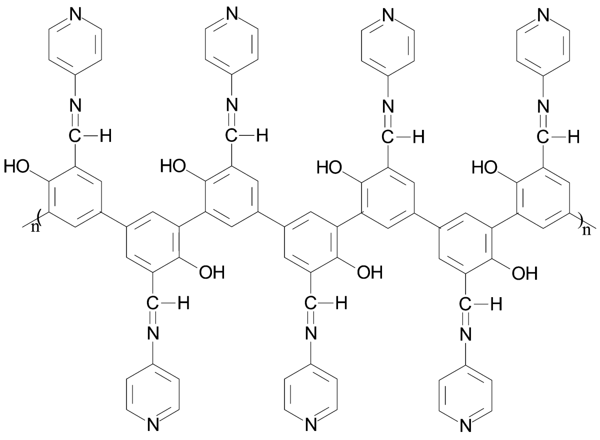
Scheme 9.

Table 5
The thermo-oxidative degradation values of 4-OAP, OPMP and Schiff base oligomer–metal complexes

Oligomer and oligomer–metal complex	TGA (°C)					DTA (°C)		
	Tstart	50% W. loss	1000 °C Weight loss	T_{max}, (°C)	W_{max}, (mg/min)	Initial temperature	Exo. peak	Endo peak
4-OAP	215	525	86.39	300	1.23	103	293, 584	407
PMP	140	220	96.38	232	1.32	260	–	158
OPMP	220	625	71.78	325	1.15	138	270, 575	535
OPMP-I-Co^{+2}	212	535	81.87	320	0.95	260	700	–
OPMP-I-Cu^{+2}	163	450	63.25	415	1.10	270	695	–
OPMP-I-Ni^{+2}	190	395	73.27	365	1.25	280	690	–

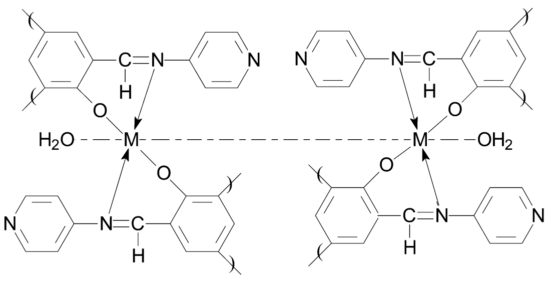
39,370 cm^{-1}. The presence of one coordinated water molecule has already been confirmed by FT-IR spectral data. Thus the local symmetry around each copper is octahedral considering the metal–metal interaction.

The pyridine ring breathing mode of vibration in the oligomer is located at 975 cm^{-1}, which is raised by 10–15 cm^{-1} in the oligomer–metal complexes, indicating the coordination of pyridine ring nitrogen [12]. In the spectra of these complexes stretch band (3346–3355 cm^{-1}) of OH group was partly lower than oligomers. The stretch band of –CH=N group shifted to 1638–1640 cm^{-1}, as a result of coordination of the azomethine nitrogen atom with metal ions. The –CH=N vibration shifts to lower frequency in the complexes by 10–12 cm^{-1}, suggesting involvement of nitrogen in the coordination [22]. The structure of Schiff base oligomer–metal complexes was demonstrated as follows (Scheme 11):



Scheme 10. The structure of OPMP.

Three polymer-Fe^{+2} complexes had been synthesized from Fe^{+2} and poly(Schiff base)s. The poly(Schiff base)s had been prepared from 2,2′-diamino-4,4′-bithiazole with phthalaldehyde, 5,5′-methylene-bis(salicylaldehyde) and terephthalaldehyde, respectively, and had been characterized by spectroscopic techniques. The magnetic behavior of these polymer-Fe^{+2} complexes had been examined as a function of magnetic field strength and temperature (5–300 K), respectively [23].



Scheme 11. The structure of Schiff base oligomer–metal complexes.

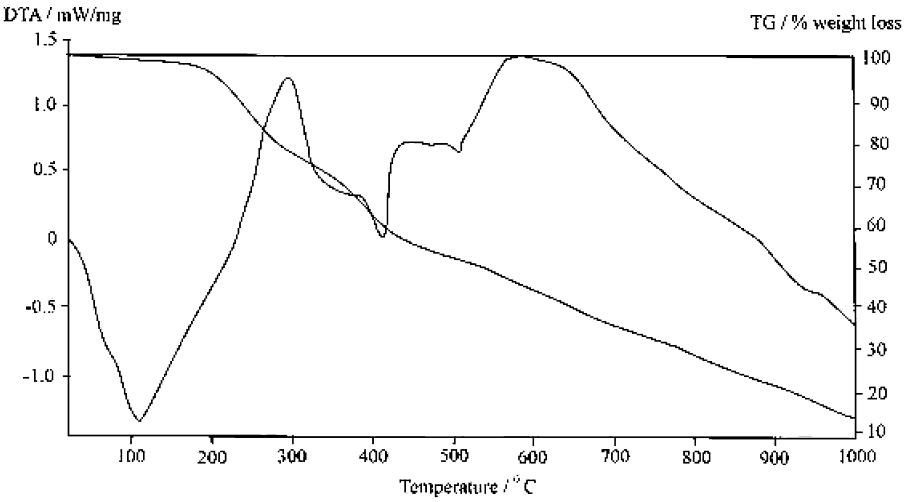


Fig. 3. TG-DTA curves of the 4-OAP.

3.5. Thermal analyses of oligomer and its oligomer–metal complexes

The thermal analyses (DTA-TG) of the prepared 4-OAP and OPMP were measured under air atmosphere in the temperature ranges 20–1000 °C, in order to investigate the thermal stability. Figs. 3 and 4 show the DTA-TG curves for the 4-OAP and OPMP. Also, the thermal analyses of metal complexes of OPMP were studied by DTA-TG analyses at the air medium. The results of these analyses are given in Table 5. Fifty percent of mass of 4-OAP, OPMP was lost at 525 and 625 °C, respectively. The weight loss of 4-OAP was found to be 86.39% at 1000 °C. Thermal degradation lasted to a high speed between 293 and 407 °C (26%). OPMP demonstrated more resistance than 4-OAP against to temperature at the same condition. 71.78% of OPMP's mass was lost at 1000 °C. Thermal degradation of OPMP was lasted to a weak speed (0.75 mg $\min^{-1}$). OPMP-Cu oligomer complex was demonstrated to more resistance than its Schiff base oligomer–metal complexes. The degradation temperatures and residues of OPMP-Cu, OPMP-Co and OPMP-Ni oligomer complexes were found to be 163, 212 and 190; 36.75, 18.13 and 26.73%, respectively. According to these parameters, Cu^{+2} and Ni^{+2} complexes were demonstrated to more resistance than Co^{+2} against to temperature.

DTA results of oligomer and its metal complexes are given in Table 5. It is seen that Table 5, stretch exothermic process of 4-OAP and OPMP started at 293, 270 °C and T_{max} was at 584 and 575 °C, respectively. Endothermic

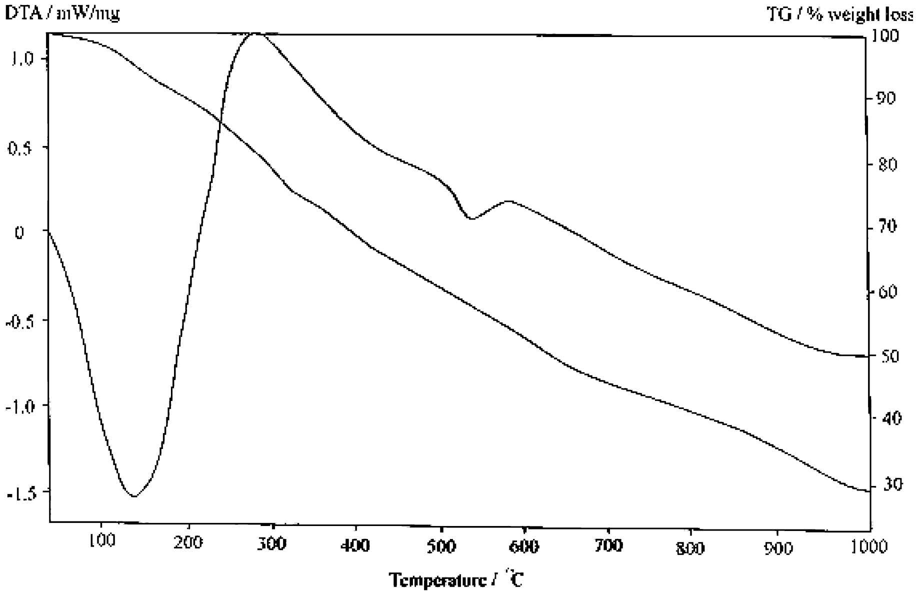


Fig. 4. TG-DTA curves of the OPMP.

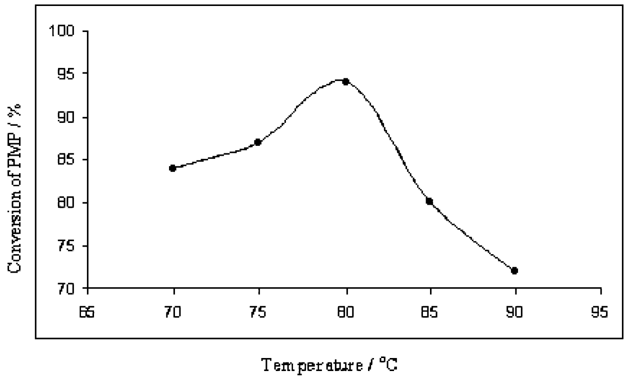


Fig. 5. According to temperature, % conversion of PMP with air O_2 oxidant at the oxidative polycondensation reaction.

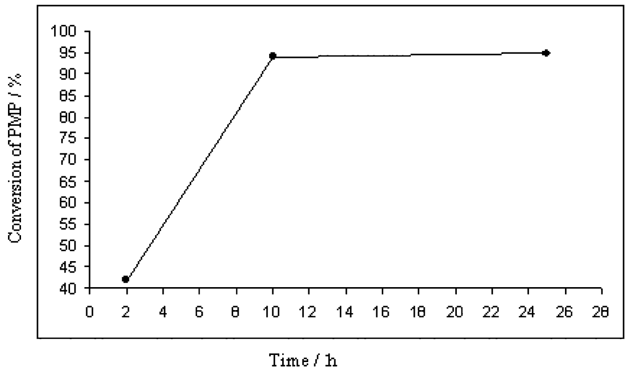


Fig. 6. According to times, % conversion of PMP with air O_2 oxidant at the oxidative polycondensation reaction.

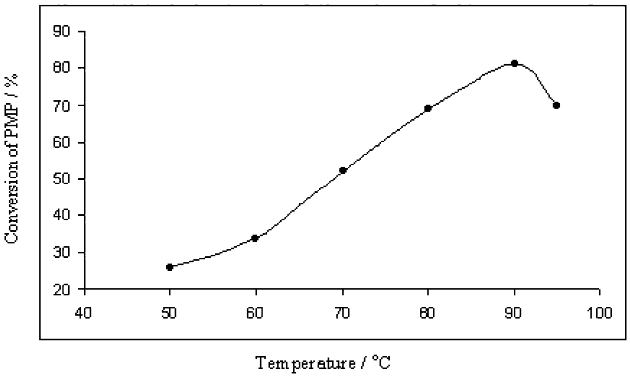


Fig. 7. According to temperature, % conversion of PMP with NaOCl oxidant at the oxidative polycondensation reaction.

process of 4-OAP started at 534 °C. T_{max} values of oligomer–metal complexes were between 650 and 740 °C. According to circumstances activity, metals catalyzed to thermo-oxidative degradation of OPMP as follows: $Cu^{+2} > Ni^{+2} > Co^{+2}$.

3.6. Kinetics study of PMP and 4-AP

The polymerization of PMP under the mentioned condition is influenced, as expected, by the effected temperatures and times at the air O_2, NaOCl and H_2O_2 oxidants (see Figs. 5–10). The polymerization of 4-AP under the mentioned condition is influenced, as expected, by the effected temperatures and times at NaOCl oxidants (see Fig. 11). It is seen that Figs. 5–11, % the effects of the reaction times and temperatures on the yield for the PMP and 4-AP were investigated. The % conversion of PMP and 4-AP affected from temperatures and times according to selected oxidants.

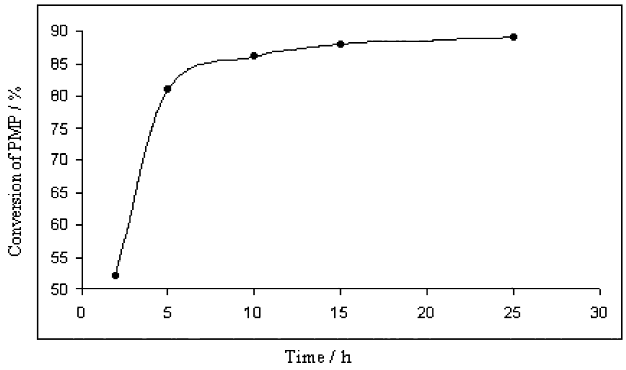


Fig. 8. According to times, % conversion of PMP with NaOCl oxidant at the oxidative polycondensation reaction.

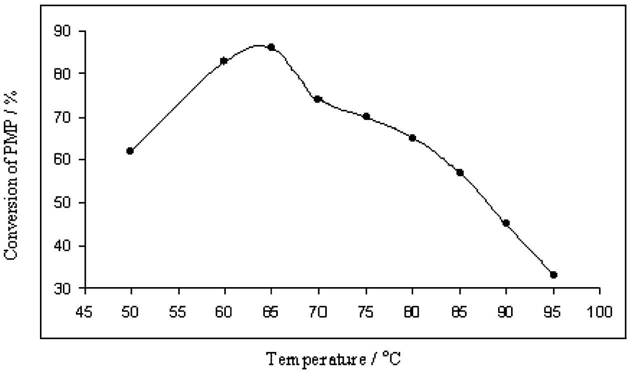


Fig. 9. According to temperature, % conversion of PMP with H_2O_2 oxidant at the oxidative polycondensation reaction.

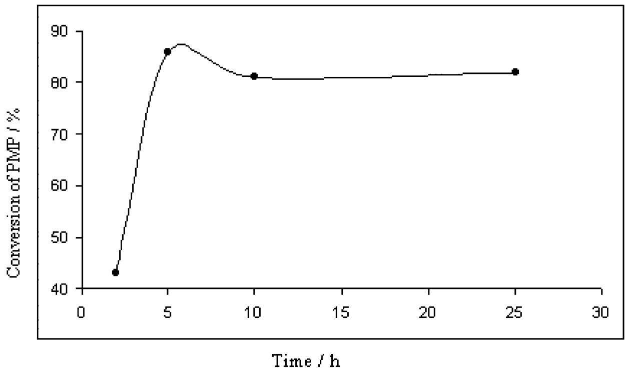


Fig. 10. According to times, % conversion of PMP with H_2O_2 oxidant at the oxidative polycondensation reaction.

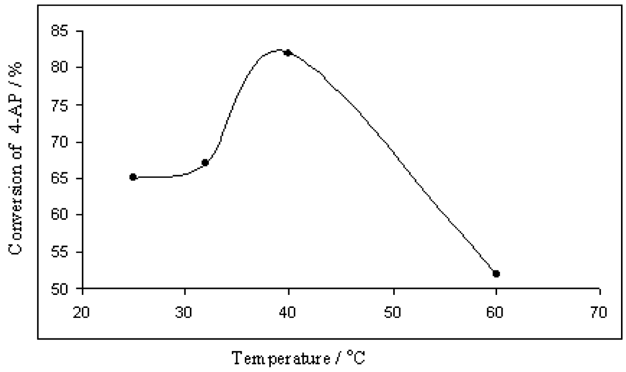


Fig. 11. According to temperature, % conversion of 4-AP with NaOCl oxidant at the oxidative polycondensation reaction.

4. Conclusion

We determined the optimum conditions of the oxidative polycondensation reaction of 4-AP with NaOCl. M_n, M_w and PDI values of 4-OAP were found to be 250, 800 g mol^{-1} and 3.20 respectively, using NaOCl. According to DTA-TG, 4-OAP was resistant against thermo-oxidative degradation, and carbonaceous residue values of 4-OAP were found to be 13.61% at 1000 °C. According to chemical and spectral analyses, synthesized oligo-2-[(pyridine-4-yl-imino) methyl] phenol macromolecules were appointed to formation from units bonding with *o*- and *p*-carbons of azomethinphenol. A part of azomethine (–CH=N) groups of oligomer were partly converted to carboxylic (–COOH) groups by the effects of oxidants such as NaOCl and air oxygen. The azomethine (–CH=N) group of OPMP-II involved to carboxylic (–COOH) (11%) group. The number average molecular weight (M_n) and mass average molecular weight (M_w) and PDI values of OPMP were found to be 2749 and 6432 g mol^{-1} and 2.33, respectively, using H_2O_2. According to these values, 90% of 2-[(pyridine-4-yl-imino) methyl] phenol turned into oligo-2-[(pyridine-4-yl-imino) methyl] phenol. Network structure oligomer–metal complexes were synthesized from oligo-2-[(pyridine-4-yl-imino) methyl] phenol with Co^{+2}, Cu^{+2} and Ni^{+2}, and their structure and the properties were determined. According to TG and DTA curves, oligomers and oligomer–metal complexes demonstrated high stability against thermo-oxidative degradation.

Acknowledgements

The authors thank Çanakkale Onsekiz Mart University Grants Commission for a research grant (Project Nu: 2001-b/19).

References

[1] Seriven EF. Chem Soc Rev 1983;12:129.
[2] Vaidya EI. J Am Chem Soc Polym Prepr 1986;27:101.
[3] Bayer E. Angew Chem 1957;69:107. Bayer E. Chem Ber 1957;90: 2325.
[4] Balto BA. J Macromol Sci Chem 1980;A14:107.
[5] Cosellato U, Vigato PA, Vidali M. J Coord Chem Rev 1977;23:31.
[6] Walter CI, Anderson HL, Sanders JK. J Chem Soc Commun 1964;4: 58.
[7] Sahni KS, Reedijk J. Coord Chem Rev 1984;59:1.
[8] Kaya İ, Vilayetoğlu AR, Topak H. J Appl Polym Sci 2002;85(9):2004.
[9] Patel MN, Patıl SH. J Macromol Sci Chem 1981;A16(8):1429.
[10] Maslen HS, Waters TN. Coord Chem Rev 1975;17:137.
[11] Kaya İ, Gülel R, Şenol D. Synthesis, characterization and optimum reaction conditions of oligo-3-aminopyridine and its Schiff base oligomer. Polymer Analysis and Characterization, 289B; 2003. Accepted for publication.
[12] Kaya İ, Vilayetoğlu AR, Mart H. Polymer 2001;42(11):4859.
[13] Kaya İ, Demir HÖ, Vilayetoğlu AR. Synth Met 2002;126(2,3):183.
[14] Kaya İ, Şenol D. J Appl Polym Sci 2003;90(2):442.
[15] Dutta PK, Jain P, Sen P, Triredi R, Sen PK, Dutta J. Eur Polym J 2003; 39(5):1007.
[16] Aly KI, Khalaf AA. J Appl Polym Sci 2000;77(6):1218.
[17] Yousef US. Eur Polym J 2000;36:1629.
[18] Catanescu O, Grigoras M, Colotin G, Dobreanu A, Hurduc N, Simionescu CI. Eur Polym J 2001;37(11):2213.
[19] Misra M, Das D, Padhi KB, Panigrahi AK, Mohanty AK. J Macromol Sci—Pure Appl Chem 1998;A35(5):867.
[20] Sun WL, Gao XS, Lu FC. J Appl Polym Sci 1997;64(12):2309.
[21] Lever ABP. Inorganic electronic spectroscopy, Elsevier, London.
[22] Schmidtke HH. Z Anorg Allg Chem 1965;339:103.
[23] Weng JA, Sun WL, Jiang LM, Shen ZQ. Macromol Rapid Commun 2000;21(15):1099.