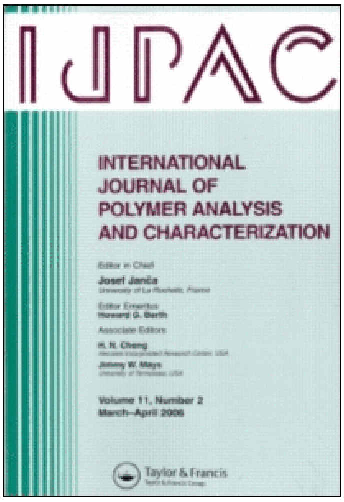

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The Oxidative Polycondensation of 4-[(Phenylimino) Methyl] Phenol Using NaOCl, Air Oxygen, and H_2O_2 at Alkaline and Neutral Medium: Synthesis and Characterization

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The Oxidative Polycondensation of 4-[(Phenylimino) Methyl] Phenol Using NaOCl, Air Oxygen, and H_2O_2 at Alkaline and Neutral Medium: Synthesis and Characterization

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Abstract: In this study, the oxidative polycondensation reaction conditions of 4-[(phenylimino) methyl] phenol (4-PIMP) with air oxygen, H_2O_2, and NaOCl oxidants in aqueous alkaline and neutral medium between 50° and 90°C were examined. 4-PIMP and its condensation product, oligo-4-[(phenylimino) methyl] phenol (O-4-PIMP), were characterized by ^1H-^{13}C-NMR, FT-IR, UV-vis techniques, and elemental analysis. At the optimum reaction conditions, the yield of oligo-4-[(phenylimino) methyl] phenol was found to be 73% for NaOCl, 65% for air O_2, and 70% for H_2O_2. According to size exclusion chromatography (SEC) analyses, the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) values of O-4-PIMP were 5268, 10320 g mol^{-1}, and 1.959, respectively, using air O_2; 8215, 17789 g mol^{-1}, and 2.165, respectively, using NaOCl; and 4800, 5260 g mol^{-1}, and 1.096, respectively, using H_2O_2. The carbon residues for 4-PIMP and O-4-PIMP were found to be 42.4% and 53.4%, respectively, at 1000°C by using TG-DTA analyses.

Keywords: Oligo-4-[(phenylimino) methyl phenol; Oxidative polycondensation; Thermal analysis

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INTRODUCTION

Recently, polyazomethine polymers have attracted more and more attention and have made great progress as new promising conducting or semi conducting materials because of their conjugated bonding and active hydroxyl groups.[1] They also have useful properties such as paramagnetism, electrochemical response, and resistance to high energy. Because of these properties, they are used to prepare composites that resist high temperature, thermal stabilizers, graphite materials, epoxy oligomers, block copolymers, adhesives, photoresists, and antistatic materials. The halogen and sulfur derivatives of oligophenols can serve as composite materials that endure heat in specific applications such as lead storage battery cathodes.[2–13] Many researchers have been trying to improve the properties of these polymers by adding some functional groups to their structures.

In this article, we examine the effects of different parameters such as temperature and initial concentration of NaOCl, H_2O_2, and alkaline for the formation of oligo-4-[(phenylimino) methyl] phenol. 4-PIMP and O-4-PIMP were characterized by using Fourior transform-infrared (FT-IR) spectroscopy, UV-vis spectroscopy, ^{1}H and ^{13}C-NMR (nuclear magnetic resonance), elemental analysis, and thermogravimetric-differential thermal analysis (TG-DTA). The molecular weight distribution of O-4-PIMP was determined by the size exclusion chromatography (SEC) technique.

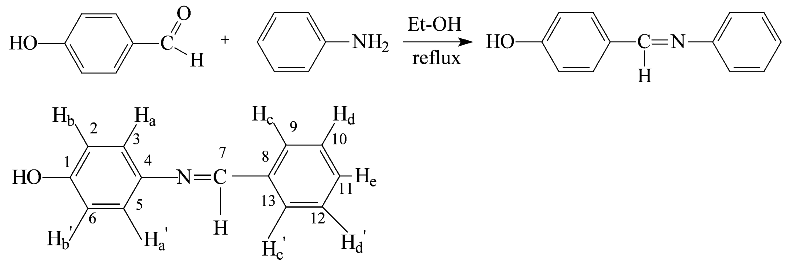
MATERIALS AND METHODS

Materials

4-Hydroxybenzaldehyde (4-HBA), aniline, 1,4-dioxane, methanol, ethanol, acetonitrile, benzene, toluene, acetone, ethyl acetate, heptane, CCl_4, $CHCl_3$, THF, DMF, DMSO, H_2SO_4, NaOH, KOH, and hydrochloric acid (37%, HCl) were supplied by Merck Chemical Co. (Germany) and used as received. Sodium hypochlorite (NaOCl) (30% aqueous solution) was supplied by Paksoy Chemical Co. (Turkey). 4-[(Phenylimino) methyl] phenol was synthesized by the condensation reaction of 4-hydroxybenzaldehyde with aniline and recrystallized in ethanol.

Preparation of 4-PIMP

4-[(Phenylimino) methyl] phenol (4-PIMP) was prepared by the condensation of 4-hydroxybenzaldehyde (6.720 g, 0.055 mol) with aniline (5 mL, 0.055 mol) in ethanol (50 mL) by boiling the mixture under reflux



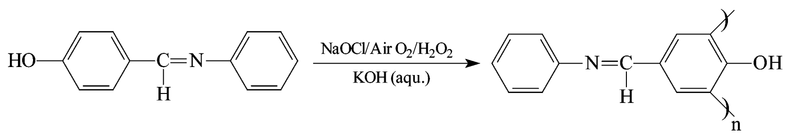
Scheme 1.

for 3 h at 70°C (Scheme 1). The precipitated 4-[(phenylimino) methyl] phenol was filtered, recrystallized from ethanol, and dried in a vacuum desiccator (yield 90%). The reaction for this condensation is shown in Scheme 1.

Analysis calculated for 4-PIMP: C, 79.19; H, 5.58; N, 7.11. Found: C, 78.80; H, 6.00; N, 6.95. UV-vis (λ_{max}): 206, 225, 273, and 314 nm. FT-IR (KBr, cm^{-1}): ν(O-H) 3447 s, ν(C-H phenyl) 2914 m, ν(C=N) 1602 s, ν(C=C phenyl) 1576, 1515, 1484, 1444 s, ν(C-O) 1286 s. ^{1}H-NMR (DMSO): δppm, 8.45 (s, 1H, -CH=N-); 10.15 (s, 1H, -OH); 7.78 (d, 2H, Ar-Haa′), 6.91 (d, 2H, Ar-Hbb′), 7.20 (dd, 2H, Ar-Hcc′) 7.39 (t, 3H, Ar-Hdd′e). ^{13}C-NMR (DMSO): ppm, 162.00 (C1-ipso), 118.45 (C2, 6-H), 133.80 (C3, 5-H), 129.00 (C4-ipso), 160.85 (C7-H), 153.25 (C8-ipso), 122.00 (C9, 13-H), 130.10 (C10, 12-H), 126.50 (C11-H).

Synthesis of O-4-PIMP with NaOCl, H_2O_2, and Air O_2 in Aqueous Alkaline Medium

Oligo-4-[(phenylimino) methyl] (O-4-PIMP) was synthesized through oxidative polycondensation of 4-[(phenylimino) methyl] phenol with aqueous solutions of NaOCl (30%), H_2O_2 (30%), and air.[11] The 4-PIMP (0.2 g 0.001 mol) was dissolved in an aqueous solution of KOH (10%, 0.001 mol) and placed in a 50 mL three-necked round-bottom flask (Scheme 2). It was fitted with a condenser, thermometer, stirrer, and an addition funnel containing NaOCl or H_2O_2. After heating to 40°C,



Scheme 2.

Table I. Oxidative polycondensation reaction parameters of 4-[(phenylimino) methyl] phenol with NaOCl in aqueous KOH

Sample number	$[\text{4-PIMP}]_0$ (mol L^{-1})	$[\text{KOH}]_0$ (mol L^{-1})	$[\text{NaOCl}]_0$ (mol L^{-1})	Temp. (°C)	Time (h)	Conversion of 4-PIMP, %
1	0.042	0.042	0.042	50	2	20
2	0.042	0.042	0.042	50	5	40
3	0.042	0.042	0.042	60	3	30
4	0.042	0.042	0.042	60	5	42
5	0.042	0.042	0.042	70	2	50
6	0.042	0.042	0.042	70	6	58
7	0.042	0.042	0.042	70	10	64
8	0.042	0.042	0.042	70	15	70
9	0.042	0.042	0.042	70	25	73
10	0.042	0.042	0.042	80	5	36
11	0.042	0.042	0.042	90	5	24
12	0.042	0.084	0.042	70	3	23
13	0.042	0.084	0.084	70	3	36
14	0.042	0.042	0.084	70	3	38
15	0.042	0.084	0.042	70	5	35
16	0.042	0.084	0.084	70	5	39
17	0.042	0.042	0.084	70	5	54
18	0.042	0.084	0.042	70	10	40
19	0.042	0.084	0.084	70	10	46
20	0.042	0.042	0.084	70	10	72

NaOCl and H_2O_2 were added drop by drop over about 20 min. The reaction mixtures were stirred at the various temperatures and durations (Tables I–III). Air was passed into an aqueous solution of KOH (20%) before being sent through the reaction tube to prevent water loss in the reaction mixture and to neutralize CO_2 in the air (Scheme 2). The reaction mixtures were cooled to room temperature, and then 0.087 mL HCl (37%) was added. For the separation of mineral salts and unreacted monomers, the mixture was filtered, washed with hot water (3 × 25 mL), and then dried in an oven at 110°C.

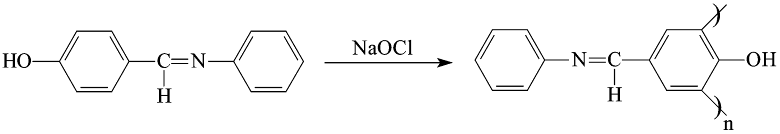
Analysis calculated for O-4-PIMP: C, 80.00; H, 4.62; N, 7.18. Found: C, 79.80; H, 5.38; N, 6.48. UV-vis ($\lambda_{\max}$): 238, 269, 287, and 366. FT-IR (KBr, cm^{-1}): ν(O-H) 3188 s, ν(C-H phenyl) 2962 m, ν(C=N) 1668 s, ν(C=C phenyl) 1597, 1453 s, ν(C-O) 1286 s. ^{1}H-NMR (DMSO): δ ppm, 9.34 (s, 1H, -CH=N-); 9.80 (s, 1H, -OH); 6.25–8.10 (m, 7H, Ar-H). ^{13}C-NMR (DMSO): ppm, 152.85 (C1-ipso), 144.00 (C2, 6-ipso), 134.94 (C3, 5-H), 135.00 (C4-ipso), 163.90 (C7-H), 153.95 (C8-ipso), 122.10 (C9, 13-H), 130.50 (C10, 12-H), 126.95 (C11-H).

Table II. Oxidative polycondensation reaction parameters of 4-[(phenylimino) methyl] phenol with air O_2 in aqueous KOH

Sample number	$[4\text{-PIMP}]_0$ (mol L^{-1})	$[\text{KOH}]_0$ (mol L^{-1})	Air O_2 (L h^{-1})	Temp. (°C)	Time (h)	Conversion of 4-PIMP, %
1	0.042	0.042	8.5	50	3	12
2	0.042	0.042	8.5	50	5	15
3	0.042	0.042	8.5	60	3	17
4	0.042	0.042	8.5	60	5	20
5	0.042	0.042	8.5	70	3	26
6	0.042	0.042	8.5	70	5	37
7	0.042	0.042	8.5	80	5	40
8	0.042	0.042	8.5	90	5	30
9	0.042	0.042	8.5	70	10	58
10	0.042	0.042	8.5	70	15	65
11	0.042	0.084	8.5	70	3	9
12	0.042	0.084	8.5	70	5	12
13	0.042	0.084	8.5	70	10	14
14	0.042	0.084	8.5	70	15	17

Table III. Oxidative polycondensation reaction parameters of 4-[(phenylimino) methyl] phenol with H_2O_2 in aqueous KOH

Sample number	$[4\text{-PIMP}]_0$ (mol L^{-1})	$[\text{KOH}]_0$ (mol L^{-1})	$[H_2O_2]_0$ (mol L^{-1})	Temp. (°C)	Time (h)	Conversion of 4-PIMP, %
1	0.042	0.042	0.042	50	2	33
2	0.042	0.042	0.042	50	5	38
3	0.042	0.042	0.042	60	3	43
4	0.042	0.042	0.042	60	5	58
5	0.042	0.042	0.042	70	5	66
6	0.042	0.042	0.042	70	10	69
7	0.042	0.042	0.042	70	15	70
8	0.042	0.042	0.042	80	5	41
9	0.042	0.042	0.042	90	5	34
10	0.042	0.084	0.042	70	3	26
11	0.042	0.084	0.084	70	3	30
12	0.042	0.042	0.084	70	3	37
13	0.042	0.084	0.042	70	5	32
14	0.042	0.084	0.084	70	5	40
15	0.042	0.042	0.084	70	5	51
16	0.042	0.084	0.042	70	10	35
17	0.042	0.084	0.084	70	10	44
18	0.042	0.042	0.084	70	10	57



Scheme 3.

Synthesis of O-4-PIMP with NaOCl in Neutral Medium

O-4-PIMP was synthesized through oxidative polycondensation of 4-PIMP (0.2 g 0.001 mol) with an aqueous solution of NaOCl (30%). It was placed in a 50 mL three-necked round-bottom flask equipped with a condenser, thermometer, stirrer, and also a funnel containing NaOCl (Scheme 3). After heating to 40°C, NaOCl was added drop by drop over about 20 min. The reaction mixture was stirred at various temperatures and times (Table IV). The mixture was filtered and washed with hot water (3 × 25 mL) to separate mineral salts and unreacted monomers and then dried in an oven at 110°C.

Instruments

The infrared and ultraviolet-visible spectra were measured via Perkin-Elmer FT-IR BX and Shimadzu UV-1208 spectrometers, respectively.

Table IV. Oxidative polycondensation reaction parameters of 4-[(phenylimino) methyl] phenol with NaOCl in aqueous neutral medium

Sample number	$[\text{4-PIMP}]_0$ (mol L^{-1})	$[\text{NaOCl}]_0$ (mol L^{-1})	Temp. (°C)	Time (h)	Conversion of 4-PIMP, %
1	0.042	0.042	50	2	5
2	0.042	0.042	50	5	7
3	0.042	0.042	60	3	7
4	0.042	0.042	60	5	9
5	0.042	0.042	70	2	8
6	0.042	0.042	70	6	10
7	0.042	0.042	80	3	12
8	0.042	0.042	80	5	15
9	0.042	0.042	80	10	20
10	0.042	0.042	80	15	18
11	0.042	0.042	90	5	6
12	0.042	0.084	80	3	15
13	0.042	0.084	80	5	18
14	0.042	0.084	80	10	24
15	0.042	0.084	80	15	21
16	0.042	0.126	80	10	19

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 O-4-PIMP and 4-PIMP were determined using tetrahydrofuran (THF). 4-PIMP and O-4-PIMP were also characterized by ^{1}H-NMR and ^{13}C-NMR spectra (Bruker Avance DPX at 400 and 100.6 MHz, respectively) recorded at 25°C by using deuterated dimothyl sulfoxide (DMSO-$_{d6}$) as a solvent. Tetramethylsilane (TMS) was used as internal standard. Thermal data were obtained by Perkin-Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between 20° and 1000°C (in N_2, rate 10°C/min). SEC analyses were performed at 30°C using dimethyl formamide (DMF) as eluent at a flow rate of 0.4 mL/min. min. A refractive index detector was used as a detector. The instrument (Shimadzu GPC-SEC system) was calibrated with a mixture of polystyrene standards using gel permeation chromatography (GPC) software for the determination of the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI).

RESULTS AND DISCUSSION

Investigation of Synthesis Conditions of O-4-PIMP

The effects of temperature, reaction duration, and initial concentrations of oxidants and alkaline on 4-[(phenylimino) methyl] phenol oligomerization behavior are shown in Tables I–III. 4-[(phenylimino) methyl] phenol was not oxidized in acidic medium by oxidants such as air oxygen, H_2O_2, and NaOCl, but it was oxidized in alkaline medium with NaOCl oxidant. It was also oxidized in the neutral medium with only NaOCl. When 4-PIMP was reacted with air oxygen in the alkaline medium, H_2O_2, or NaOCl, a brown precipitate was seen immediately.

The oxidative polycondensation reaction conditions of 4-PIMP with 30% NaOCl solution in aqueous alkaline medium are given in Table I. Oligomer yield of 4-PIMP solution was found to be 40.0% at the NaOCl medium for 5 h at 50°C. As can be seen in Table I, oligomer yield increases with increasing temperature. Under the same conditions, when the molar amount of NaOCl was doubled, total yield changed from 50.0% to 38.0% (see Table I). The conversion of 4-PIMP was found to be 73.0% under optimum conditions when $[\text{4-PIMP}]_0 = [\text{KOH}]_0 = [\text{NaOCl}]_0 = 0.042\,\text{mol/L}$, at 70°C for 25 h. The conversion of 4-PIMP was also 24.0% at the same concentrations of $[\text{4-PIMP}]_0$, $[\text{KOH}]_0$, and $[\text{NaOCl}]_0$, but at 90°C for 5 h. However, when the temperature was over 70°C, the conversion decreased slightly. Warm heating is possible benefit to chain propagation to obtain higher conversion, but higher temperatures usually resulted in deactivated species in azomethine polymerization. It was possible that chain transfer took place more easily at higher temperature.

The oxidative polycondensation reaction conditions of 4-PIMP with air O_2 in aqueous alkaline medium are given in Table II. For this reaction, when air oxygen was introduced at a rate of 8.5 L/h in the reaction medium at 80°C for 5 h, the yield of product was 40.0%. The conversion of 4-PIMP was 65.0% under optimum conditions when $[4\text{-PIMP}]_0 = [KOH]_0$ at 70°C for 15 h. As can be seen from Tables I and II, the yield of the oligomer was dependent on the temperature, initial concentration of monomer, and reaction duration. Under the same conditions, NaOCl showed higher activity than air O_2 and H_2O_2 for conversion of 4-PIMP to oligomer.

The oxidative polycondensation reaction conditions of 4-PIMP with H_2O_2 solution (30%) in alkaline medium are given in Table III. The conversion of 4-PIMP was 70.0% under optimum conditions when $[4\text{-PIMP}]_0 = [KOH]_0 = [H_2O_2]_0 = 0.042\,\text{mol/L}$, at 70°C for 15 h, and the conversion was 34.0% at the same concentrations of $[4\text{-PIMP}]_0$, $[KOH]_0$, and $[H_2O_2]_0$ but at 90°C for 5 h. It was seen that the polymerization of 4-PlMP was influenced by variables such as temperature, concentration of KOH, reaction duration, and the kind of oxidants. The conversion temperature can be optimized according to the oxidant.

The oxidative polycondensation reaction conditions of 4-PIMP with NaOCl solution (30%) in neutral mediums are given in Table IV. The highest conversion of 4-PIMP (24%) was obtained under the reaction conditions when $[4\text{-PIMP}]_0 = 0.042\,\text{mol/L}$ and $[NaOCl]_0 = 0.084\,\text{mol/L}$ at 80°C for 10 h. Under the same reaction conditions, NaOCl oxidant showed more activity in the alkaline medium than in the neutral medium for the conversion of 4-PIMP. 4-PIMP was not converted to oligomer by air O_2 and H_2O_2 oxidants. It was also seen that while *ortho*-azomethinephenol[8] was not converted to the oligomer, 4-[(phenylimino) methyl] phenol was converted to the oligomer. The highest conversion of benzylidene-3′-hydroxyaniline (B-3′-HA) has been obtained as 98% under the reaction conditions when $[\text{B-3}'\text{-HA}]_0 = [NaOCl]_0 = [KOH]_0 = 0.1015\,\text{mol/L}$ at 50°C for 5 h.[14]

Solubility

The color of O-4-PIMP was dark brown in the form of powder. While it was partly soluble in methanol and ethanol, it was completely soluble in organic solvents such as DMF, THF, DMSO, and acetone and in aqueous alkaline and concentrated H_2SO_4. It was completely insoluble in heptane, acetonitrile, benzene, toluene, ethyl acetate, $CHCl_3$, CCl_4, and 1,4-dioxane.

Structure of O-4-PIMP

SEC chromatograms of O-4-PIMP are given in Figure 1. Only one component was observed for air O_2 and two components were observed for NaOCl and H_2O_2 from this analysis. When air O_2 was used as oxidant, M_n, M_w, and PDI values of O-4-PIMP were found to be 5268, 10320 g mol^{-1}, and 1.959, respectively (Figure 1, curve a). With NaOCl, M_n, M_w, and PDI values of O-4-PIMP were found to be 8215, 17789 g mol^{-1}, and 2.165, respectively (Figure 1, curve b). Two components were observed in the chromatogram of O-4-PIMP; 59% of the weight of O-4-PIMP was of low molecular weight ($M_n = 1988$, $M_w = 3806$ g mol^{-1}, PDI = 1.915) and 41% of high molecular weight ($M_n = 37210$, $M_w = 81296$ g mol^{-1}, PDI = 2.185). With H_2O_2, M_n, M_w, and PDI values of O-4-PIMP were found to be 4800, 5260 g mol^{-1}, and 1.096, respectively

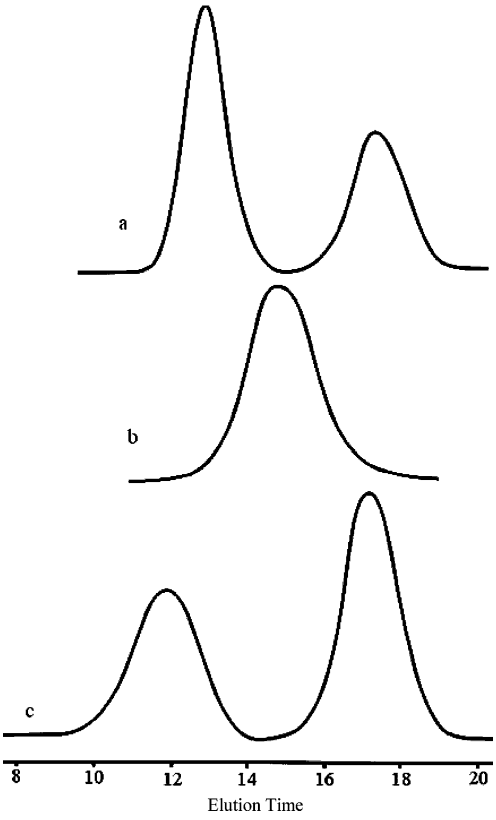


Figure 1. Chromatograms of the oxidative polycondensation products of 4-PIMP: a, H_2O_2, as oxidant; b, air O_2, as oxidant; c, NaOCl, as oxidant.

Table V. Number average-molecular weight (M_n), mass-average molecular weight (M_w), polydispersity index (PDI), and weight % of oxidative polycondensation products of 4-[(phenylimino) methyl] phenol

	Molecular weight distribution parameters														
	Total			Component I				Component II				Component III			
Compounds	M_n	M_w	PDI	M_n	M_w	PDI	%	M_n	M_w	PDI	%	M_n	M_w	PDI	%
O-4-PIMP[a]	6732	8237	1.224	67755	81346	1.200	20	14573	18552	1.273	40	2038	2550	1.251	40
O-4-PIMP[b]	4350	6562	1.509	17640	26893	1.524	45	1386	1859	1.341	55	—	—	—	—
O-4-PIMP[c]	4782	5624	1.176	66410	73561	1.108	10	16269	20076	1.234	42	1818	2256	1.241	48
O-4-PIMP[d]	7070	11340	1.604	22403	36365	1.623	60	1743	2149	1.233	40	—	—	—	—
O-4-PIMP[e]	7743	9195	1.188	62139	72917	1.173	25	15934	19306	1.211	45	1747	2225	1.273	30
O-4-PIMP[f]	7366	8967	1.217	74467	87919	1.180	20	15374	19972	1.299	42	1966	2440	1.241	38
O-4-PIMP[g]	6688	11317	1.692	20907	35873	1.716	60	2078	2776	1.336	40	—	—	—	—

[a] Table I, Sample no. 19.
[b] Table III, Sample no. 13.
[c] Table III, Sample no. 16.
[d] Table II, Sample no. 10.
[e] Table IV, Sample no 9.
[f] Table II, Sample no. 9.
[g] Table IV, Sample no. 14.

(Figure 1, curve c). Two components were observed in the chromatogram: 58% was of low molecular weight ($M_n = 1276$, $M_w = 1802$ g mol^{-1}, PDI = 1.412) and 42% of high molecular weight ($M_n = 15631$, $M_w = 16837$ g mol^{-1}, PDI = 1.077). The M_n, M_w, and PDI values of benzylidene-3′-hydroxyaniline (B-3′-HA) have been found as 2640, 5130 g mol^{-1}, and 1.142, respectively, for NaOCl oxidant.[14] These values of O-4-PIMP were lower for the same oxidant. The M_n, M_w, PDI, and weight % of some selected products are given in Table V. It can be seen from Table V that the values for different products varied, depending on the oxidants.

The UV-vis spectra were obtained with THF solutions of 4-PIMP and O-4-PIMP. For the spectrum of 4-PIMP, K bands of phenol and C_6H_5-N= were observed at 206 nm and 225 nm, respectively. Benzene band and -CH=N- band were observed at 273 and 314 nm, respectively. The λ_{max} values of O-4-PIMP were observed at 238, 269, 287, and 366 nm. For the UV-vis spectrum of O-4-PIMP, K and R bands were observed at 238 nm and 287 nm, respectively. The band of -CH=N- group was observed at 366 nm. The UV-vis spectrum showed specific bands for λ_{max} assigned to aromatic and azometinic π–π^* transitions at about 280 and 350 nm, respectively.[15]

A comparison of the FT-IR spectra of 4-PIMP and O-4-PIMP showed the main difference to be the width of the peaks. For the FT-IR spectra of 4-PIMP and O-4-PIMP, bands of -OH and –CH=N groups were observed at 3447 and 1602 cm^{-1} and at 3188 and 1668 cm^{-1}, respectively.

In order to identify the structures of the monomer and the oligomer, the ^{1}H and ^{13}C-NMR spectra were recorded in DMSO-d_6. For future reference, the spectra of the oligomer are given in Figures 2 and 3. According to the ^{1}H-NMR spectra of 4-PIMP and O-4-PIMP, the signals of –OH and –CH=N groups were observed at 10.15 and 8.45 ppm and at 9.80 and 9.34 ppm, respectively. The FT-IR and ^{1}H-NMR spectral data were compatible. According to spectral and SEC analyses, O-4-PIMP's

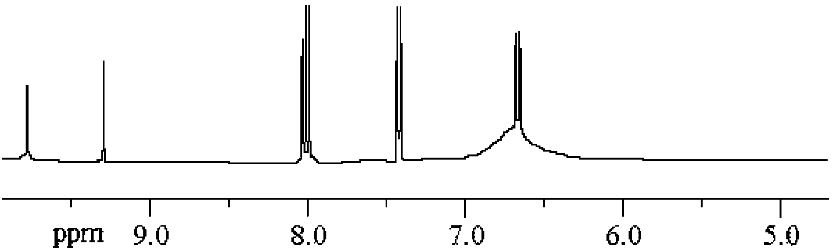


Figure 2. ^{1}H-NMR spectrum of oligo-4-[(phenyl imino) methyl] phenol.

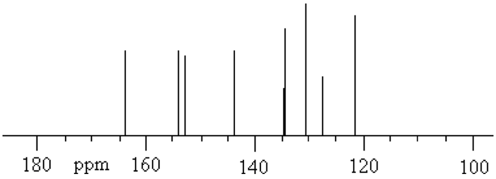
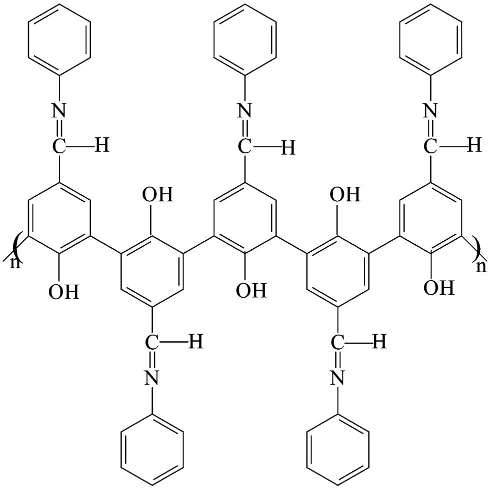


Figure 3. ^{13}C-NMR spectrum of oligo-4-[(phenyl imino) methyl] phenol.

formula is as shown in Scheme 4. Cross-linking in polymer structure is expected because the *ortho* and the *para* positions in the corresponding monomer structure are unsubstituted. ^{13}C-NMR studies of O-4-PIMP indicated that the linkage between any two adjacent phenyl rings is largely at *ortho* positions. However, this type of linkage may strain the polymer backbone in such a manner that the phenyl rings are out of plane with respect to the adjacent rings. The NMR peak values for C2 and C6 were observed at 118.45 and 144.00 ppm for the monomer and the oligomer, respectively. On the other hand, if the monomers were linked at *meta* positions on the ring, the peaks for C3 and C5 should shift downfield, and there was no significant shift in the peak positions for C3 and C5 of oligomer.

Thermal Analysis

Thermal data for the monomer and the oligomer were obtained in N_2 and are given in Figures 4 and 5, respectively. For 4-PIMP the initial



Scheme 4. Structure of O-4-PIMP.

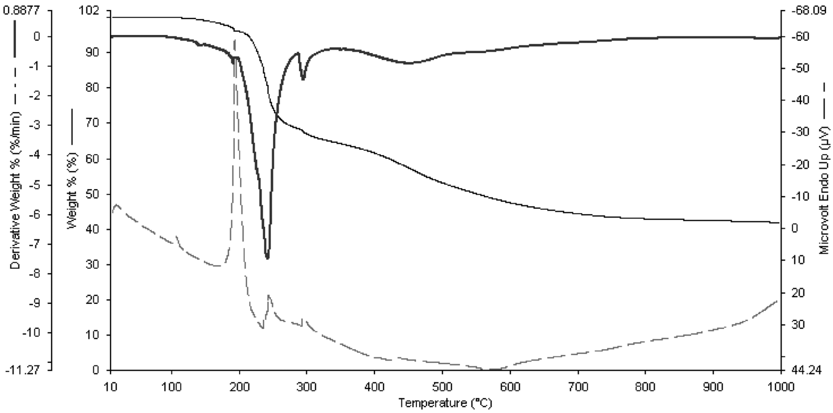


Figure 4. TG-DTG-DTA curves of 4-[(phenyl imino) methyl] phenol.

degradation temperature was 198°C; 50.0% and 57.6% weight losses were found at 530°C and 1000°C, respectively.

The largest weight loss was observed at 200–300°C from–the TGA curve. According to TG analyses, it can be understood that 4-PIMP and O-4-PIMP are relatively stable to thermal decomposition. According to DTA analysis, some exothermic processes occurred at 195° and 247°C. The exothermic processes of 4-PIMP were observed at 198°C.

For O-4-PIMP, the initial degradation temperature was found to be 254°C; 46.6% weight loss was found at 1000°C. From the DTGA curve, the highest weight loss was observed at 250–400°C. The presence of water can be seen in TGA (Figure 5), showing 7.47% weight losses in

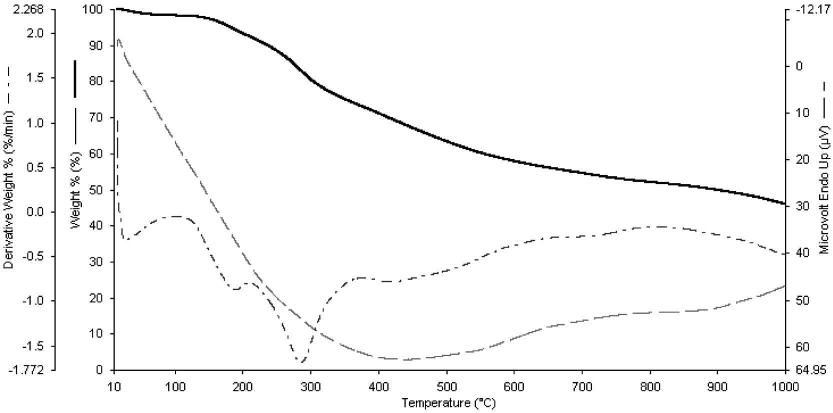


Figure 5. TG-DTG-DTA curves of oligo-4-[(phenyl imino) methyl] phenol.

Table VI. Thermal decomposition values of some monomer and oligomer compounds

Compounds	T_{on}[a]	50% weight losses	% Carbon residue at 1000°C
4-PIMP	198	530	42.38
O-4-PIMP[b]	240	540	24.00
O-4-PIMP[c]	278	550	34.00
O-4-PIMP[d]	280	475	36.00
O-4-PIMP[e]	254	—	53.41
O-4-PIMP[f]	289	435	40.00
B-3′-HA[g]	85	529	3.00
O-B-3′-HA[h]	120	830	40.54
4-HPIMN[i]	287	334	28.02
O-4-HPIMN[j]	250	570	44.22

[a] The onset temperature. 4-HPIMN = 2-[(4-hydroxyphenyl) imino methyl]-1-naphtol. O-4-HPIMN = oligo-2-[(4-hydroxyphenyl) imino methyl]-1-naphtol.
[b] Table I, Sample no. 9.
[c] Table III, Sample no. 13.
[d] Table III, Sample no. 16.
[e] Table II, Sample no. 10.
[f] Table IV, Sample no. 9.
[g] Ref. 14.
[h] Ref. 14.
[i] Ref. 16.
[j] Ref. 16.

the 100°–175°C range, corresponding to the loss of water of crystallization (50°–150°C) and coordination water (150°–200°C).[16] Previously, the initial degradation temperature of benzylidene-3′-hydroxyaniline and oligo-benzylidene-3′-hydroxyaniline was found to be 185° and 120°C, respectively.[14] According to the current data, 4-PIMP and O-4-PIMP were more stable against thermal and thermo-oxidative decomposition than benzylidene-3′-hydroxyaniline (B-3′-HA) and oligo-benzylidene-3′-hydroxyaniline (O-B-3′-HA). For comparison, thermal data of 4-PIMP, O-4-PIMP, and some other monomer and oligomer compounds are given in Table VI.

CONCLUSION

In this study it was seen that 4-[(phenylimino) methyl] phenol was not converted to oligomers in acidic media with oxidants such as air oxygen, NaOCl, and H_2O_2, but 4-[(phenylimino) methyl] phenol with Schiff's base substituent was converted with these oxidants in aqueous alkaline and neutral media. The conversion of 4-PIMP to oligomer was found to be 44%, 65%, and 75% for air O_2, H_2O_2, and NaOCl oxidants, respectively. For the oxidative polycondensation reaction of 4-PIMP, air O_2 demonstrated less activity than NaOCl and H_2O_2. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) values of O-4-PIMP were found to be 8215, 17789 $g\,mol^{-1}$, and 2.165, 5268, 10320 $g\,mol^{-1}$, and 1.959, and 4800, 5260 $g\,mol^{-1}$, and 1.096, using NaOCl, air O_2, and H_2O_2 oxidants, respectively. Spectral analyses such as UV-vis, FT-IR, and ^{1}H and ^{13}C-NMR have demonstrated that oligomers were formed from the oxidative condensation of 4-PIMP through the *ortho*-carbons of phenol rings. This Schiff's base and its oligomer were found to have good resistance against thermal degradation.

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