

Synthesis and Characterization of Oligo-2-Hydroxy-1-Naphthaldehyde and Its Schiff Base Oligomers

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ABSTRACT: In this study, oligo-2-hydroxy-1-naphthaldehyde (OHNA) was synthesized from the oxidative polycondensation of 2-hydroxy-1-naphthaldehyde (HNA) with air oxygen, NaOCl, and H₂O₂ in an aqueous alkaline medium at 50–95°C. We determined the products and the oxidative polycondensation reaction conditions of HNA with oxidants such as air oxygen, NaOCl, and H₂O₂. In these reactions, H₂O₂ was more active than air oxygen and NaOCl and their optimum reaction conditions were studied. The products were characterized by ¹H-NMR, FTIR, UV-visible, and elemental analysis. The respective number-average molecular weight, mass-average molecular weight, and polydispersity index values of OHNA and its Schiff base oligomers (compounds 1, 2, and 3) were found to be 500 g mol⁻¹, 1880 g mol⁻¹, and 3.75 for OHNA; 670 g mol⁻¹, 2490 g mol⁻¹, and 3.71 for compound 1; 390 g mol⁻¹, 1080 g mol⁻¹, and 2.77 for compound 2; and 320 g mol⁻¹, 670 g mol⁻¹, and 1.85 for compound 3. At the optimum reaction conditions, the yields

of the reaction products were found to be 77.0% O₂, 78.0% H₂O₂, and 75.4% NaOCl. About 80% of the HNA was converted into OHNA. In addition, new Schiff based oligomers were synthesized from the condensation reaction of OHNA with *p*-aminophenol, triethyleneglycol bis(4-aminophenyl ether), and aniline and their structures and properties were determined. Thermogravimetric and dynamic thermal analyses showed OHNA and its Schiff base oligomers to be stable against thermooxidative decomposition. The weight losses of OHNA and its Schiff base oligomer compounds 1, 2, and 3 were found to be 5% at 175, 225, 190, and 230°C, respectively; 50% at 900, 590, 650, and 620°C, respectively; and 60, 80, 85, and 82%, respectively, at 1000°C. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 442–450, 2003

Key words: oligo-2-hydroxy-1-naphthaldehyde; oxidative polycondensation; Schiff base oligomer

INTRODUCTION

The oligophenols and their derivatives have been used in various fields, because of their electron structure properties. They have useful properties such as paramagnetism, semiconductivity, the ability to be made into electrochemical cells, and resistance to high energy. Because of these properties, oligophenols were used to prepare inhibitors with resistance at high temperature, thermostabilizations,^{1,2} graphite materials,³ epoxy oligomer and block copolymers,^{4,5} adhesives,⁶ photoresists,⁷ and antistatic materials.⁸ The halogen and sulfur derivatives of oligophenols were used to prepare composite materials resistant to specific detergents such as lead collecting battery cathodes.^{9–14} Nowadays, despite these advantages, the field of bifunctional oligophenols is limited. The Schiff bases derived from 2-hydroxy-1-naphthaldehyde (HNA) are well known polydentate ligands, which coordinate in deprotonated or neutral forms. Oligomer-metal complex compounds of oligo-2-hydroxy-1-naphthalde-

hyde (OHNA) and its Schiff base oligomers can be formed from metal salts. Therefore, they can be used to remove heavy metals from industrial wastewaters.

This article investigates the effects of different parameters such as the temperature, flow rate of air oxygen, and the beginning concentration of HNA, NaOCl, H₂O₂, and alkalines on oligo-2-hydroxy-1-naphthaldehyde (OHNA). New Schiff base oligomers were synthesized from OHNA with *p*-aminophenol, triethyleneglycol bis(4-aminophenyl ether), and aniline. Then, OHNA and its Schiff base oligomers were characterized by using FTIR, UV-visible (UV-vis), ¹H-NMR, elemental analysis, thermogravimetric and dynamic thermal analyses (TG-DTA), and high pressure liquid chromatography (HPLC) techniques.

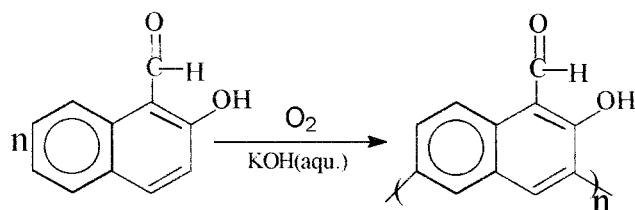
EXPERIMENTAL

Materials

Chromatographic grade HNA, *p*-aminophenol, aniline, triethyleneglycol bis(4-aminophenyl ether), 1,4-dioxane, ethanol, benzene, acetone, ethyl acetate, pyridine, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO), H₂O₂ (%35), H₂SO₄, and toluene were supplied by Merck Chemical Co. and used as received. Hydrochloric acid (HCl,

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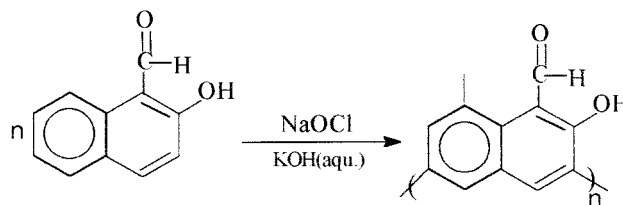


Scheme 1 The synthesis of HNA via oxidative polycondensation of HNA with air oxygen in an aqueous alkaline medium.

37%) was supplied by Merck, and KOH and sodium hypochloride (NaOCl, 34% solution in water) were procured from Paksoy.

Oxidative polycondensation of HNA with air oxygen in aqueous alkaline medium

HNA (4.3 g, 0.025 mol) was dissolved in an aqueous solution of KOH (10%, 0.025 mol) and placed in a 50-mL three-necked round-bottomed flask.¹⁰ The flask was fitted with a condenser, thermometer, and stirrer; and a glass tube was placed over the condenser for sending air oxygen. The reaction mixture was stirred at 70°C for 50 h (Scheme 1). The air oxygen was passed at a rate of 8.5 L/h during the course of the reaction. To prevent water loss in the reaction mixture and unneutralize CO₂ in air with KOH, the air oxygen was passed through 200 mL of an aqueous solution of KOH (20%) before sending it into the reaction mixture. The mixture was neutralized with 3 mL of HCl (37%) at room temperature. Unreacted HNA was removed by washing it with water. The crude product was separated into two fractions according to their solubility differences in water. The first fraction (OHNA-I) was insoluble in water, and the second fraction (OHNA-II) was soluble in water. The reaction product (first fraction) was washed with water (50 mL × 3), filtered, and dried in an oven at 105°C (3.31 g, 77% yield, black solid, mp >350°C; see Table I). ANAL.



Scheme 2 The synthesis of OHNA via oxidative polycondensation of HNA with NaOCl.

Calcd for OHNA: C, 78.10%; H, 2.95%. Found: C, 77.47%; H, 3.05%. FTIR (KBr) ν (cm⁻¹): 3429 (s, O—H), 3026 (m, C—H, aryl), 2932, 2863 (m, C—H, aldehyde), 1711 (s, C=O), 1608 (s, C=C), 1280, 1230 (s, Ar—O). ¹H-NMR (DMSO, δ): 12.04 (s, 1H, OH), 10.85 (s, 1H, CHO), 6.40–8.69 (m, 18H, Ar—H).

Oxidative polycondensation of HNA with NaOCl

In this procedure, OHNA was synthesized from an oxidative polycondensation reaction of HNA with a solution of NaOCl (34%) in water.¹⁰ The HNA (4.3 g, 0.025 mol) was dissolved in an aqueous solution of KOH (10%, 0.025 mol) and placed into a 50-mL three-necked round-bottomed flask fitted with a condenser, thermometer, stirrer, and an additional funnel containing NaOCl. After heating to 40 °C, NaOCl was added dropwise over about 20 min. The reaction mixture was stirred at 70°C for 25 h (Scheme 2). Then, the mixture was neutralized with 3 mL of HCl (37%) at room temperature. Following neutralization, the unreacted HNA was removed by washing it with water. The crude product was separated into two fractions according to their solubility differences in water. The first fraction (OHNA-I) was insoluble in water, and the second fraction (OHNA-II) was soluble in water. The crude product was washed with water (50 mL × 3), filtered, and dried in an oven at 105°C (2.67 g, 67% yield; see Table II).

TABLE I
Oxidative Polycondensation of 2-Hydroxy-1-naphthaldehyde with Air Oxygen in Aqueous KOH

Sample No.	[HNA] ₀ (mol/L)	[KOH] ₀ (mol/L)	V _{air} (L/h)	T (°C)	Time (h)	Conversion of HNA, (%)	Reaction Products (%)	
							OHNA-I	OHNA-II
1	1.29	1.29	8.5	50	5	20.7	12.9	7.8
2	1.29	1.29	8.5	60	5	23.0	15.1	7.9
3	1.29	1.29	8.5	70	5	26.2	17.8	8.4
4	1.29	1.29	8.5	70	10	43.7	37.5	6.2
5	1.29	3.87	8.5	70	10	48.8	43.8	5.0
6	1.29	1.29	8.5	70	25	66.8	54.3	12.5
7	1.29	1.29	8.5	70	50	77.0	62.0	15.0
8	1.29	1.29	8.5	80	5	28.1	17.2	10.9
9	1.29	1.29	8.5	90	5	31.1	19.5	11.6
10	1.29	1.29	8.5	95	5	35.2	21.4	13.8
11	1.29	1.29	8.5	50	5	20.7	12.9	7.8
12	1.29	2.58	8.5	95	10	53.6	35.2	18.4

TABLE II
Oxidative Polycondensation of 2-Hydroxy-1-Naphthaldehyde with NaOCl in Aqueous KOH

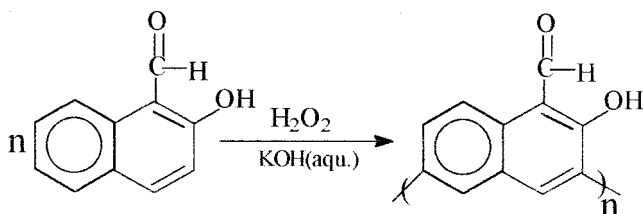
Sample No.	[HNA] ₀ (mol/L)	[KOH] ₀ (mol/L)	[NaOCl] ₀ (mol/L)	T (°C)	Time (h)	Conversion of HNA (%)	Reaction Products (%)	
							OHNA-I	OHNA-II
1	1.05	1.05	1.05	50	5	19.3	12.8	6.5
2	1.05	1.05	1.05	60	5	22.0	15.3	7.7
3	1.05	1.05	1.05	70	5	36.8	28.0	8.8
4	1.05	1.05	1.05	80	5	39.6	30.6	9.0
5	1.05	1.05	1.05	90	5	42.8	36.3	6.5
6	1.05	1.05	1.05	95	5	50.3	46.7	3.6
7	1.05	1.05	1.05	70	25	67.0	56.8	10.2
8	1.05	1.05	3.15	70	10	58.9	48.4	10.5
9	1.05	1.05	2.10	70	5	41.3	26.4	14.9
10	1.05	1.05	2.10	70	25	47.4	35.1	12.3
11	1.05	1.05	2.10	95	25	75.4	57.1	18.3
12	1.05	1.05	3.15	70	5	53.3	37.6	15.7

Oxidative polycondensation of HNA with H₂O₂

OHNA was synthesized from oxidative polycondensation of HNA with a solution of H₂O₂ (35%) in water. The HNA (4.3 g, 0.025 mol) was dissolved in an aqueous solution of KOH (10%, 0.025 mol) and placed into a 50-mL three-necked round-bottomed flask fitted with a condenser, thermometer, stirrer, and an additional funnel containing H₂O₂. After heating to 50°C, H₂O₂ was added dropwise over about 30 min. The reaction mixture was stirred at 90°C for 4 h (Scheme 3). The mixture was neutralized with 3 mL of HCl (37%) at room temperature. Then, the unreacted HNA was removed by washing it with water. The crude product was separated into two fractions according to their solubility differences in water. The first fraction (OHNA-I) was insoluble in water, and the second fraction (OHNA-II) was soluble in water. The crude product was washed with water (50 mL × 3), filtered, and dried in an oven at 105°C (2.80 g, 65% yield; see Table III).

Synthesis of Schiff base oligomers of OHNA

OHNA-I (first fraction, insoluble in water; 3.380 g, 0.02 mol/U) and triethyleneglycol bis(4-aminophenyl ether) (3.320 g, 0.01 mol) were dissolved in THF (50 mL) and placed into a 50-mL two-necked round-bottomed flask (Scheme 4).¹¹ The flask was fitted with a condenser and thermometer. The mixture was stirred



Scheme 3 The synthesis of OHNA via oxidative polycondensation of HNA with H₂O₂.

magnetically in a water bath at 90°C for 18 h. Then, THF was distilled out of this condensation product and dried in an oven at 105°C (mp >320°C, 2.21 g, 45% yield). ANAL. Calcd for compound 1: C, 75.70%; H, 4.73%; N, 4.41%. Found: C, 71.56%; H, 4.96%; N, 3.35%. IR (KBr) ν (cm⁻¹): 3435 (s, O—H), 3080 (m, C—H, aryl), 2927, 2876 (s, C—H, aliphatic), 1612 (s, C=N), 1600 (s, C=C), 1244, 1172, 1050 (C—O—C). ¹H-NMR (DMSO, δ): 9.02 (s, 1H, —CH=N—); 6.54–8.11 (m, 26H, Ar—H), 3.96 (t, 4H, ArOCH₂, ³J_{HH} = 5 ppm), 3.71 (m, 4H, ArOCH₂CH₂, ³J_{HH} = 5 ppm), 3.64 (t, 4H, OCH₂, ³J_{HH} = 5 ppm).

For the synthesis of compound 2, OHNA-I (first fraction, insoluble in water; 3.380 g, 0.020 mol/U) and *p*-aminophenol (2.180 g, 0.020 mol) were dissolved in THF and placed into a 50-mL two-necked round-bottomed flask (Scheme 5). The flask was fitted with a condenser and thermometer. The mixture was stirred magnetically in a water bath at 90°C for 18 h. Then, the THF was distilled out of the condensation product and dried in an oven at 105°C (mp >310°C, 2.21 g, 70% yield). ANAL. Calcd for compound 2: C, 78.46%; H, 3.84%; N, 5.38%. Found: C, 77.04%; H, 4.01%; N, 5.20%. FTIR (KBr) ν (cm⁻¹): 3450–3425 (O—H), 3085 (m, C—H, aryl), 1605 (s, C=N), 1600, 1495 (C=C). ¹H-NMR (DMSO, δ): 9.02 (s, 1H, —CH=N—), 10.15 (s, 2H, —OH), 6.64–8.30 (m, 22H, Ar—H).

OHNA-I (first fraction, insoluble in water; 3.380 g, 0.020 mol/U) and aniline (1.860 g, 0.020 mol) were dissolved in THF and placed into a 50-mL two-necked round-bottomed flask (Scheme 6). It was fitted with a condenser and thermometer. The mixture was stirred magnetically in a water bath at 90°C for 18 h. Then, the THF and unreacted aniline were distilled to separate them from the condensation product and dried in an oven at 105°C (mp >300°C, 2.25 g, 70% yield). ANAL. Calcd for compound 3: C, 83.61%; H, 4.10%; N, 5.74%. Found: C, 82.75%; H, 4.25%; N, 5.68%. FTIR (KBr) ν (cm⁻¹): 3440–3415 (O—H), 3080 (C—H, aryl), 1618 (s, C=N), 1580–1600, 1480–1493, 1452–1455, 1385–1396

TABLE III
Oxidative Polycondensation of 2-Hydroxy-1-Naphthaldehyde with H₂O₂ in Aqueous KOH

Sample No.	[HNA] ₀ (mol/L)	[KOH] ₀ (mol/L)	[H ₂ O ₂] ₀ (mol/L)	T (°C)	Time (h)	Conversion of HNA (%)	Reaction Products (%)	
							OHNA-I	OHNA-II
1	1.05	1.05	1.05	60	4	36.5	26.3	10.2
2	1.05	1.05	1.05	65	4	40.1	32.0	8.1
3	1.05	1.05	1.05	70	4	47.6	40.4	7.2
4	1.05	1.05	1.05	75	4	51.2	43.2	8.0
5	1.05	1.05	1.05	80	4	54.0	45.0	9.0
6	1.05	1.05	1.05	85	4	60.3	52.0	8.3
7	1.05	1.05	2.10	90	15	78.0	63.0	15.0
8	1.05	1.05	1.05	90	4	65.4	55.1	10.3

(C=C). ¹H-NMR (DMSO, δ): 9.05 (s, 1H, —CH=N—), 10.10 (s, 1H, —OH), 6.60–8.35 (m, 22H, Ar—H).

refractometric detector at 25°C was used to analyze the product.

Characterization techniques

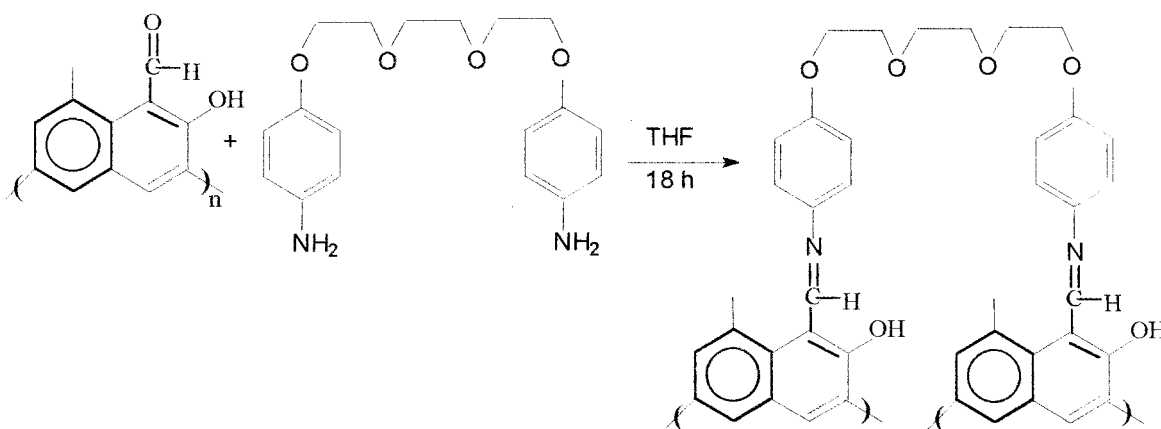
The IR and UV-vis spectra were measured with Shimadzu FTIR 8300 and UV-160 instruments, respectively. Elemental analysis was carried out with a Carlo Erba 1106. The FTIR spectra were recorded using KBr disks (4000–400 cm⁻¹). The UV-vis spectra of OHNA and compounds 1, 2, and 3 were determined by using THF. OHNA and its Schiff base oligomers were characterized by using ¹H-NMR spectra (Bruker DPX FT-NMR spectrometer operating at 400 MHz), and they were recorded at 25°C by using deuterated DMSO (DMSO-*d*₆) as the solvent. Tetramethyl silane was used as an internal standard. Thermal data were obtained by using STA 409C NETZSCH-Geratebau GmbH Thermal Analysis equipment. The TG-DTA measurements were taken between 20 and 1000°C in air at a rate of 10°C/min. The number-average molecular weight (*M_n*), weight-average molecular weight (*M_w*), and polydispersity index (PDI) were determined by HPLC (Kovo Co.). For HPLC investigations we used an SGX (100 Å, 7-nm diameter loading material) with a 3.3-mm i.d., 150-mm column with DMF (0.2 mL/min) as the eluent and polystyrene standards. A

RESULTS AND DISCUSSION

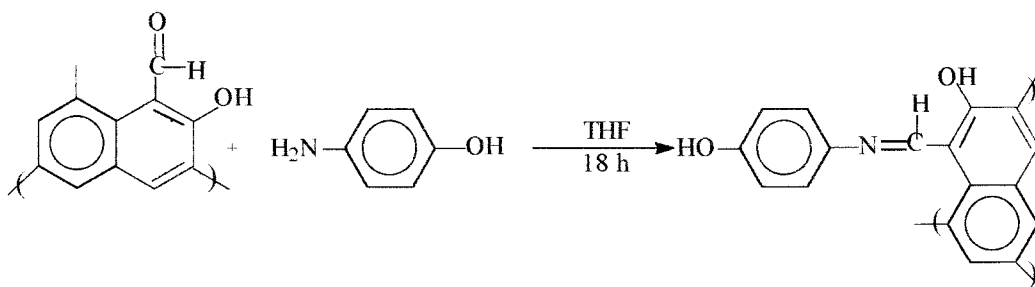
Investigation of synthesis conditions of OHNA

The conditions for the oxidative polycondensation reaction of HNA with an O₂ solution in an aqueous alkaline environment are given in Table I. The oxidative polycondensation reaction of HNA was not observed in the THF and acetic acid medium. HNA was soluble in aqueous KOH, but no reaction was observed when it was heated at 80°C for 2 h. However, the oxidative polycondensation reaction of HNA was immediate in an aqueous alkaline solution, and the solution was turned dark brown by adding oxidants such as NaOCl, H₂O₂, and air oxygen. When the original concentrations of HNA ([HNA]₀) and KOH ([KOH]₀) were 1.29 mol/L, the conversion of HNA oligomer by air oxygen at 70°C for 5 h was 26.2% (see Table I).

As seen in Table I, in these reactions, the yield of oligomer depends on temperature and time factors. For the air oxygen oxidant, the maximum yield (62.0%) of OHNA-I formed at high concentrations of HNA (1.29 mol/L) at 70°C for 50 h. The yield of



Scheme 4 The synthesis of compound 1.



Scheme 5 The synthesis of compound 2.

OHNA-I increased from 43.7 to 48.8% in the case of a $3x[\text{HNA}]_0$ of HNA under the same conditions (Table I). In addition, the yield of oligomer was affected when the rate of air passing through the reaction mixture was increased. HNA is known to be relatively less active than phenols in oxidative polycondensation.¹³

The conditions of the oxidative polycondensation reaction of HNA with 34% NaOCl solution in an aqueous alkaline medium are given in Table II. The conversion of HNA was 75.4% at optimum conditions such as $[\text{HNA}]_0$ and $[\text{KOH}]_0$ values of 1.05 mol/L and a $[\text{NaOCl}]_0$ value of 2.10 mol/L at 95°C for 25 h. The product yields of OHNA-I and OHNA-II were 57.1 and 18.3%, respectively. In Table II, under the same conditions, the yield of OHNA-I was higher than OHNA-II. The various conditions of OHNA are given for the NaOCl oxidant in Table II. The conditions of the oxidative polycondensation reaction of HNA with a 35% H_2O_2 solution in an aqueous alkaline medium are given in Table III. The conversion of HNA was 78.0% at optimum conditions such as $[\text{HNA}]_0$ and $[\text{KOH}]_0$ values of 1.05 mol/L and a $[\text{H}_2\text{O}_2]_0$ value of 2.10 mol/L at 90°C for 15 h. The product yields of OHNA-I and OHNA-II were 63.0 and 15.0%, respectively. Observe in Table III that the yield of OHNA-I was higher than OHNA-II under the same conditions. The various conditions are given for OHNA in Table III.

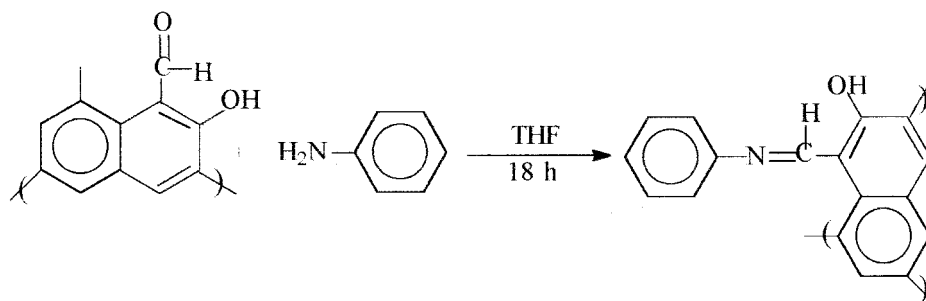
Solubility

The oxidative polycondensation products of HNA with air oxygen, H_2O_2 , and NaOCl in an aqueous

alkaline environment were black solid powders. The first fraction (OHNA-I) and the second fraction (OHNA-II) were soluble in aqueous NaOH, H_2SO_4 , pyridine, TMF, DMF, DMSO, and 1,4-dioxane. However, the first fraction (OHNA-I) was poorly soluble in acetone, ethyl acetate, and toluene. It was insoluble in water and chlorinated solvents such as CHCl_3 and CCl_4 , but it was insoluble in aliphatic solvents such as *n*-hexane and *n*-heptane. Compounds 1, 2, and 3 were soluble in THF, DMF, DMSO, and 1,4-dioxane. However, they were poorly soluble in CHCl_3 , CCl_4 , and toluene.

Structure of OHNA

According to the molecular weight distribution (Fig. 1, curve 3), the M_n , M_w , and PDI values of OHNA-I were 500 g mol^{-1} , 1880 g mol^{-1} , and 3.75, respectively, for the NaOCl oxidant. Three peaks were observed in the molecular weight distribution of OHNA-I as shown by curve 3 (Fig. 1). Sixty percent of the mass of OHNA-I was low molecular weight ($M_n = 350 \text{ g mol}^{-1}$, $M_w = 430 \text{ g mol}^{-1}$, PDI = 1.23), but 40% of its weight was high molecular weight (first fraction: $M_n = 5850 \text{ g mol}^{-1}$, $M_w = 6000 \text{ g mol}^{-1}$, PDI = 1.20; second fraction: $M_n = 2360 \text{ g mol}^{-1}$, $M_w = 3000 \text{ g mol}^{-1}$, PDI = 1.27). The M_n , M_w , and PDI values of OHNA-I were found to be 500 g mol^{-1} , 1720 g mol^{-1} , and 3.44, respectively, for the air oxygen oxidant (Fig. 1, curve 2). In the molecular weight distribution of OHNA-I shown by curve 2, three peaks were observed. Seventy-two percent of the mass of OHNA-I was low molecular weight ($M_n = 370 \text{ g mol}^{-1}$, $M_w =$



Scheme 6 The synthesis of compound 3.

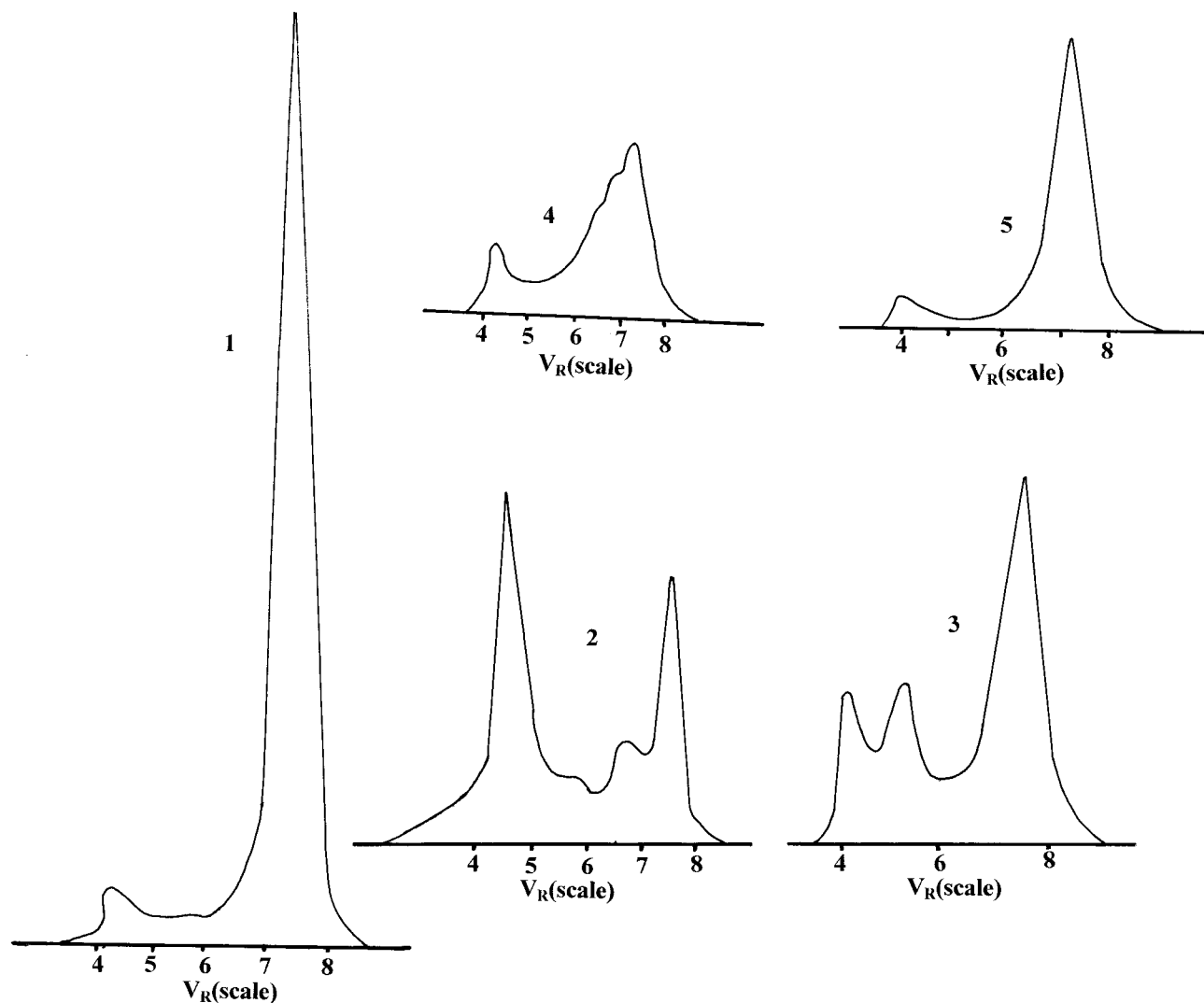


Figure 1 The molecular weight distribution curves of the condensation product of OHNA with NaOCl as the catalyst (curve 3), OHNA with air O₂ as the catalyst (curve 2), and compounds 1 (curve 4), 2 (curve 5), and 3 (curve 1).

450 g mol⁻¹, PDI = 1.22), but 38% of its weight was high molecular weight (first fraction: $M_n = 5820$ g mol⁻¹, $M_w = 6190$ g mol⁻¹, PDI = 1.06; second fraction: $M_n = 2520$ g mol⁻¹, $M_w = 2550$ g mol⁻¹, PDI = 1.01).

The M_n , M_w , and PDI values of compound 1 were found to be 670 g mol⁻¹, 2490 g mol⁻¹, and 3.71, respectively. Two peaks were observed in the molecular weight distribution of compound 1 (Fig. 1, curve 4). Sixty-eight percent of the mass of compound 1 was low molecular weight ($M_n = 480$ g mol⁻¹, $M_w = 680$ g mol⁻¹, PDI = 1.42), but 32% of its weight was high molecular weight ($M_n = 4590$ g mol⁻¹, $M_w = 6500$ g mol⁻¹, PDI = 1.42). The M_n , M_w , and PDI values of compound 2 were found to be 390 g mol⁻¹, 1080 g mol⁻¹, and 2.77, respectively. In the molecular weight distribution of compound 2 shown by curve 5 in Figure 1, two peaks were observed. Ninety percent of the mass of compound 2 was low molecular weight ($M_n =$

350 g mol⁻¹, $M_w = 440$ g mol⁻¹, PDI = 1.26), but 10% of its weight was high molecular weight ($M_n = 5850$ g mol⁻¹, $M_w = 6300$ g mol⁻¹, PDI = 1.08). The M_n , M_w , and PDI values of compound 3 were ascertained to be 320 g mol⁻¹, 670 g mol⁻¹, and 1.85, respectively. Two peaks were observed in the molecular weight distribution of compound 3 (Fig. 1, curve 1). Ninety-two percent of the mass of compound 3 was low molecular weight ($M_n = 300$ g mol⁻¹, $M_w = 340$ g mol⁻¹, PDI = 1.13), but 8% of its weight was high molecular weight ($M_n = 3990$ g mol⁻¹, $M_w = 4800$ g mol⁻¹, PDI = 1.20; see Table IV).

The oxidative polycondensation product of HNA was completely soluble in aqueous NaOH. The oligomer was again precipitated when it was neutralized with CO₂. These properties showed that phenolic hydroxy (—OH) groups are present in the structure of the oligomer according to the FTIR and ¹H-NMR analyses. The Schiff bases of HNA with aromatic amines,

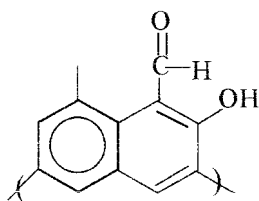
TABLE IV
Number Average Molecular Weight (M_n), Mass-Average Molecular Weight (M_w), Polydispersity Index (PDI), and Yield (%) of OHNA-I (NaOCl), OHNA-I (Air O₂), and Compounds 1, 2, and 3

Oligomers	M_n	M_w	PDI	Fraction I				Fraction II				Fraction III			
				M_n	M_w	PDI	Yield (%)	M_n	M_w	PDI	Yield (%)	M_n	M_w	PDI	Yield (%)
OHNA-I (NaOCl)	500	1880	3.75	5850	6000	1.20	20	2360	3000	1.27	20	350	430	1.23	60
OHNA-I (air O ₂)	500	1720	3.44	5820	6190	1.06	18	2520	2550	1.01	10	370	450	1.22	72
Compounds 1	670	2490	3.71	4590	6500	1.42	32	480	680	1.42	68	—	—	—	—
Compounds 2	390	1080	2.77	5850	6300	1.08	10	350	440	1.26	90	—	—	—	—
Compounds 3	320	670	1.85	3990	4800	1.20	8	300	340	1.13	92	—	—	—	—

such as aniline, and *p*-aminophenol were insoluble in ethanol.

High intensive K, less intensive B, and less intensive R bands were observed at 247, 260, and 294 nm, respectively, from the UV-vis spectra of HNA and its oligomer. The R band of the CHO group of the oligomer was observed in a lower field (bathochromic), such as 71 nm, than the same band of HNA. The difference in the visible region (400–740 nm) of the spectrum between HNA and its oligomer depends on the shifting of the B band. The mesomeric and inductive effects of the OH and CHO groups of the monomer and oligomer showed structural similarity. As a result, the UV-vis spectra of the oligomers synthesized from HNA in air O₂ and NaOCl environments were similar.

When the FTIR spectra of HNA and its oligomers are compared, both have similar bands. In the structures of the oligomers, the vibration bands of phenol OH groups were intense and wide bands at 3458 cm⁻¹ whereas the CHO band was observed at 1644 cm⁻¹. As a shoulder of the OH band, the weak vibration bands of the aldehyde C—H and aromatic C—H groups were observed at 2888–2935 and 3074 cm⁻¹, respectively. In the spectra of OHNA-I, which was synthesized from the oxidative polycondensation reaction of HNA with NaOCl, the band of the carboxylic acid group was observed at 1660 cm⁻¹. The ¹H-NMR and FTIR results showed the formation of oligomeric macromolecules from the HNA unit by the polymerization at the C₃, C₆, and C₈ positions (Scheme 7). In order to identify the structures of OHNA and its Schiff base oligomers, the ¹H-NMR spectra were recorded in DMSO-*d*₆.



Scheme 7 The structure of the HNA unit.

Structure of Schiff base derivatives of OHNA

The condensation products of OHNA with aniline, *p*-aminophenol, and triethyleneglycol bis(4-aminophenyl ether) were all dark black powders that were insoluble in ethanol. They have higher softening (glass-transition) temperatures than OHNA. These oligomers are infusible at 128°C like OHNA.

It is presumed that polymeric Schiff bases can only be prepared from the condensation of aromatic anilines with electron-acceptor substituents. Some fundamental differences were observed in the UV-vis spectra of Schiff bases formed from the condensation of HNA with aniline and *p*-aminophenol. The K band of the Schiff base oligomers was divided into two peaks (247 and 270 nm). The reason for this is the conjugation between the benzene ring and the nonbonding electrons of nitrogen in the azomethine group. The B and R bands of the CH=N groups were observed at 294, 370 and 294, and 341 nm in the spectra of compounds 1, 2, and 3, respectively. After the oxidative polycondensation reaction, the benzene band of the electron acceptors, such as CHO and NH₂, turned into the electron-donor phenylazomethine. Similarly, the UV-vis spectra of compounds 1, 2, and 3, which were synthesized by an oxidative polycondensation reaction in air oxygen, were identical to the UV-vis spectra of oligomers obtained by the condensation of OHNA-I with triethyleneglycol bis(4-aminophenyl ether), *p*-aminophenol, and aniline.

The CH=N absorption bands were observed at 1612, 1605, and 1618 cm⁻¹ for compounds 1, 2, and 3, respectively. The stretching frequencies observed at 2745, 2750, and 2700 cm⁻¹ for compounds 1, 2, and 3, respectively, show the presence of O—H ··· N intramolecular hydrogen bonds.

Thermal analyses of OHNA and its Schiff base oligomers

The TG analyses of our prepared OHNA and its Schiff base oligomers were performed under an air atmosphere in a temperature range of 20–1000°C in order to investigate the thermal stability. Figure 2 shows the

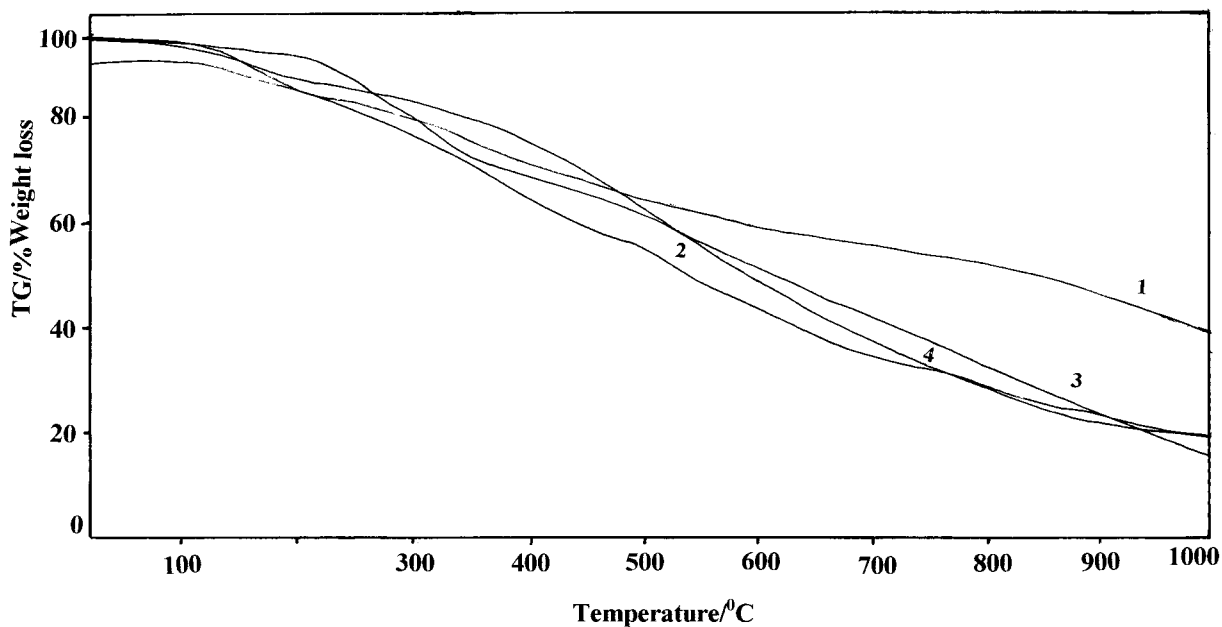


Figure 2 The TG curves of OHNA (curve 1) and its Schiff base oligomer compounds 1 (curve 2), 2 (curve 3), and 3 (curve 4).

TG curves for OHNA and its Schiff base oligomers. According to the TG curves, OHNA and its Schiff base oligomers (compounds 1, 2, and 3) started to degrade at 128, 185, 130, and 162°C, respectively (Fig. 2). OHNA and compounds 1, 2, and 3 lost 5 mass % at 175, 225, 190, and 230°C, respectively, and lost 50 mass % at 900, 590, 650, and 620°C, respectively. The weight losses of OHNA and compounds 1, 2, and 3 were

found to be 60, 80, 85, and 82%, respectively, at 1000°C.

The DTA of OHNA and the Schiff base oligomers were conducted under an air atmosphere in a temperature range of 20–1000°C in order to investigate the thermal stability (Fig. 3). Figure 3 shows the DTA curves for OHNA and its Schiff base oligomers. The maximum temperature values of OHNA and com-

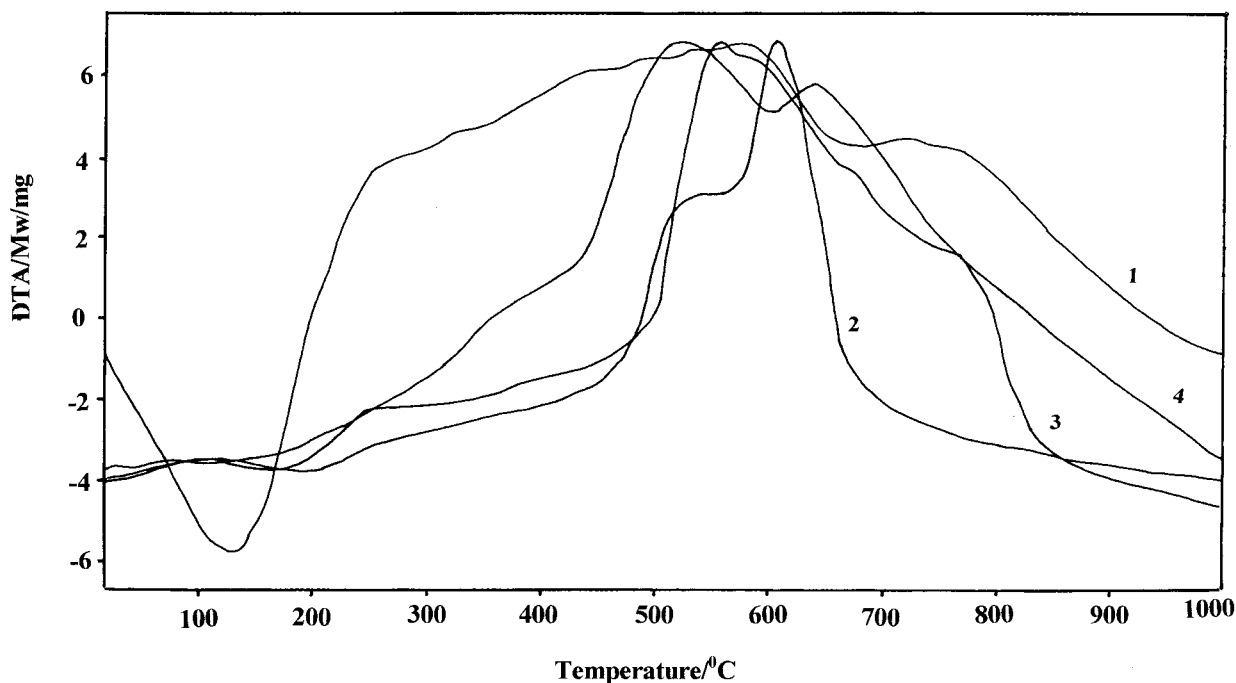


Figure 3 The DTA curves of OHNA (curve 1) and its Schiff base oligomer compounds 1 (curve 2), 2 (curve 3), and 3 (curve 4).

pounds 1–3 were 577, 605, 637, and 555°C, respectively. According to the DT and TG analyses, OHNA and the three compounds were stable against temperature and thermooxidative decomposition.

CONCLUSION

The optimum conditions of the oxidative polycondensation reaction of HNA with air oxygen, H₂O₂, and NaOCl were determined and new synthesis methods for OHNA were described. We synthesized the condensation products of OHNA and its Schiff base oligomers with aniline, *p*-aminophenol, and triethyleneglycol bis(4-aminophenyl ether) and ascertained their structure and chemical and physical properties. In this reaction, H₂O₂ was more active than O₂ and NaOCl and about 80% of the HNA was converted to OHNA. The M_n values of OHNA synthesized with NaOCl and O₂ were found to be 500 and 1880 g mol⁻¹, respectively, and the M_w values were 500 and 1720 g mol⁻¹, respectively. According to the TG analyses, OHNA and its Schiff base oligomers were resistant against thermooxidative degradation. Their carbonaceous residue values were 40, 20, 15, and 18%, respectively, at 1000°C.

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