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Synthesis, Characterization, and Optimum Reaction Conditions of Oligo-Benzylidene-3'-Hydroxyaniline

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In this study, the oxidative polycondensation reactions of benzylidene-3'-hydroxyaniline (B-3'-HA) with air, H₂O₂, and NaOCl were studied in an aqueous alkaline medium at 40–90 °C. Oligobenzylidene-3'-hydroxyaniline (O-B-3'-HA) was characterized by ¹H-NMR, ¹³C-NMR, FT-IR, UV-Vis, size exclusion chromatography (SEC), and elemental analysis. With NaOCl oxidant, the conversion of B-3'-HA was 98.0% under optimum conditions such as [B-3'-HA]₀ = [NaOCl]₀ = [KOH]₀ = 0.1015 mol/L at 50 °C for 5 h. H₂O₂ was less active than O₂ and NaOCl. According to the SEC analysis, the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) values were found to be 2640 g mol⁻¹, 5130 g mol⁻¹, and 1.942 using NaOCl, and 1960 g mol⁻¹, 3170 g mol⁻¹, and 1.615 using air, and 2370 g mol⁻¹, 4720 g mol⁻¹, and 1.990 using H₂O₂, respectively. Thermal analyses indicate that O-B-3'-HA is stable against thermo-oxidative decomposition.

Keywords: Oxidative polycondensation; Oligo-benzylidene-3'-hydroxyaniline; Thermal analysis; Air oxidation; NaOCl; H₂O₂

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INTRODUCTION

Oligophenols and their derivatives are used in various fields. They are paramagnetic and semiconductive, and because of these properties, they are used to prepare composites that resist high temperature, thermal stabilizers and graphite materials, epoxy adhesives, photoresists, and antistatic materials^[1-10]. Halogen and sulfur derivatives of oligophenols are used to prepare flame-retardant composite materials and lead storage batteries^[9]. These compounds benefited from structural variations that improved their properties.

In this article, I have synthesized for the first time oligo-benzylidene-3'-hydroxyaniline by oxidative polycondensation reaction and investigated the effects of different parameters such as temperature, reaction time, and initial concentrations of NaOCl, H₂O₂, and caustic. The monomer and the oligomer were characterized by FT-IR, UV-Vis, ¹H and ¹³C-NMR, elemental analysis, TGA, DTA, and size exclusion chromatography (SEC) techniques.

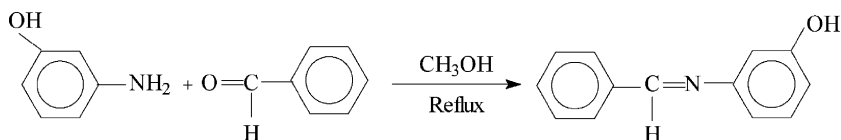
EXPERIMENTAL

Materials

Benzaldehyde (BA), 3-aminophenol, 1, 4-dioxane, methanol, ethanol, 1-buanol, benzene, toluene, acetone, ethyl acetate, tetrahydrofuran (THF), N, N'-dimethylformamide (DMF), dimethylsulfoxide (DMSO), H₂SO₄, pyridine, CCl₄, CHCl₃, n-heptane, n-hexane, acetonitrile, NaOH, KOH, H₂O₂ (30% aqueous solution), and hydrochloric acid (HCl, 37%) were obtained from Merck Chemical Co. (all chromatographic grade), and they were used as received. Sodium hypochlorite (NaOCl) (30% aqueous solution) was supplied by Paksoy Chem. Co. (Turkey).

Preparation of Benzylidene-3'-Hydroxyaniline (B-3'-HA)

B-3'-HA was prepared by the condensation of benzaldehyde (2.650 g, 0.025 mol) and 3-aminophenol (2.725 g, 0.025 mol) in methanol (50 mL), achieved by boiling the mixture under reflux for 2 h at 70°C (Scheme 1).



SCHEME 1 Benzylidene-3'-hydroxyaniline (B-3'-HA).

The precipitated B-3'-HA was filtered, recrystallized from methanol, and dried in a vacuum desiccator (yield 90%).

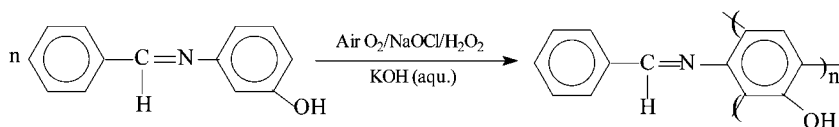
- Analysis calculated for B-3'-HA: C, 79.19; H, 5.58; N, 7.11. Found: C, 78.80; H, 6.00; N, 6.95.
- UV-Vis (λ_{\max}): 226, 265, 300, and 348 nm.
- FT-IR (KBr, cm^{-1}): $\nu(\text{O-H})$ 3400 s, $\nu(\text{C-H aryl})$ 3019 m, $\nu(\text{C=N})$ 1621 s, $\nu(\text{aromatic=C})$ 1508, 1496, 1446, 1422 s, $\nu(\text{C-O})$ 1227 s, $\nu(\text{C-H aliphatic})$ 2886 s.
- $^1\text{H-NMR}$ (DMSO): δ ppm, 8.90 (s, 1H, $-\text{CH=N-}$); 9.75 (s, 1H, $-\text{OH}$); 6.80 (d, 1H, Ar-Ha), 7.15 (dd, 1H, Ar-Hb), 6.75 (d, 1H, Ar-Hc), 6.70 (s, 1H, Ar-Ha'), 7.65 (d, 2H, Ar-Hdd'), 7.30 (m, 3H, Ar-Hee'f).
- $^{13}\text{C-NMR}$ (DMSO): ppm, 160.00 (C1-*ipso*-OH), 114.40 (C2-H), 131.50 (C3-H), 114.90 (C4-H), 155.00 (C5-*ipso*), 110.00 (C6-H), 160.30 (C7-H), 134.00 (C8-*ipso*), 129.20 (C9-H), 128.90 (C10-H), 131.10 (C11-H).

Synthesis of Oligo-Benzylidene-3'-Hydroxyaniline (O-B-3'-HA) with Air

B-3'-HA (3.94 g, 0.02 mol) was dissolved in an aqueous solution of KOH (10%) (1.12 g, 0.02 mol) and placed in a 100 mL three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer, and adapter to place glass tubing over the condenser for sending air. The reaction mixture was stirred at various temperatures and times (Table I). Air was introduced at a rate of 8.5 L/h during the course of the reaction. In order to avoid water loss in the reaction mixture and to remove CO_2 , the air was bubbled through 200 mL of an aqueous solution of KOH (20%) before being fed into the reaction vessel (Scheme 2). After the

TABLE I Oxidative polycondensation reaction parameters of benzylidene-3'-hydroxyaniline with air in aqueous KOH

Sample no.	Temp., °C	Time, h	[B-3'-HA] ₀ , mol/L	[KOH] ₀ , mol/L	Air O ₂ , L/h	Conversion of B-3'-HA, %
1	50	5	0.25	0.25	8.5	60.0
2	60	5	0.25	0.25	8.5	65.0
3	70	5	0.25	0.25	8.5	68.0
4	80	5	0.25	0.25	8.5	78.0
5	90	5	0.25	0.25	8.5	92.0
6	90	5	0.25	0.50	8.5	85.0
7	90	10	0.25	0.25	8.5	82.0
8	90	25	0.25	0.25	8.5	70.0



SCHEME 2 Oligo-benzylidene-3'-hydroxyaniline (O-B-3'-HA).

reaction, the mixture was neutralized with 1.67 ml HCl (37%) at room temperature. The mixture was filtered and washed with hot water (50 mL \times 3) to separate the mineral salts and unreacted monomer and then dried in an oven at 110°C.

- Analysis calculated for O-B-3'-HA: C, 80.00; H, 4.62; N, 7.18. Found: C, 79.36; H, 5.00; N, 6.77.
- UV-Vis (λ_{max}): 227, 264, 300, and 351 nm.
- FT-IR (KBr, cm^{-1}): $\nu(\text{O-H})$ 3435 s, $\nu(\text{C-H aryl})$ 3035 m, $\nu(\text{C-H aliphatic})$ 2917 s, $\nu(\text{C=N})$ 1612 s, $\nu(\text{C=C})$ 1594, 1512, 1496, 1450, 1422, s $\nu(\text{C-O})$ 1235 s.
- $^1\text{H-NMR}$ (DMSO): δ ppm, 9.02 (s, 1H, $-\text{CH}=\text{N}-$); 10.00 (s, 1H, $-\text{OH}$); 7.55 (s, 1H, Ar-Ha); 7.63 (d, 2H, Ar-Hbb'); 7.30 (m, 3H, Ar-Hcc'd).
- $^{13}\text{C-NMR}$ (DMSO): ppm, 154.40 (C1-*ipso*-OH), 126.75 (C2-*ipso*), 128.00 (C3-H), 125.00 (C4-*ipso*), 151.35 (C5-*ipso*), 118.35 (C6-*ipso*), 160.10 (C7-H), 133.80 (C8-*ipso*), 129.15 (C9-H), 128.85 (C10-H), 131.00 (C11-H).

Synthesis of O-B-3'-HA with NaOCl

O-B-3'-HA was next synthesized through oxidative polycondensation of benzylidene-3'-hydroxyaniline with an aqueous solution of NaOCl (30%). The 3-HPBA (3.94 g, 0.02 mol) was dissolved in an aqueous solution of KOH (10%, 1.12 g, 0.02 mol) and placed in a 50 mL three-necked round-bottom flask (Scheme 2). It was fitted with a condenser, thermometer, stirrer, and an adapter connected to a funnel containing NaOCl. After heating to 30°C, NaOCl was added dropwise over about 20 min. The reaction mixture was stirred at various temperatures and times (Table II). The mixture was neutralized with 1.67 mL HCl (37%) at room temperature. The mixture was filtered and washed with hot water (50 mL \times 3) to separate out the mineral salts and unreacted monomer and then dried in an oven at 110°C.

Synthesis of O-3-HPBA with H_2O_2

O-B-3'-HA was also synthesized through oxidative polycondensation of B-3'-HA with H_2O_2 . The B-3'-HA (3.94 g, 0.02 mol) was dissolved in an

TABLE II Oxidative polycondensation reaction parameters of benzylidene-3'-hydroxyaniline with NaOCl in aqueous KOH

Sample no.	Temp., °C	Time, h	[B-3'-HA] ₀ , mol/L	[KOH] ₀ , mol/L	[NaOCl] ₀ , mol/L	Conservation of B-3'-HA, %
1	40	2	0.1015	0.1015	0.1015	85.0
2	50	2	0.1015	0.1015	0.1015	94.0
3	60	2	0.1015	0.1015	0.1015	83.0
4	70	2	0.1015	0.1015	0.1015	68.0
5	80	2	0.1015	0.1015	0.1015	64.0
6	90	2	0.1015	0.1015	0.1015	61.0
7	70	5	0.1015	0.1015	0.1015	90.0
8	50	2	0.1015	0.2030	0.1015	84.0
9	50	2	0.1015	0.1015	0.2030	86.0
10	50	5	0.1015	0.1015	0.1015	98.0
11	50	10	0.1015	0.1015	0.1015	83.0
12	50	25	0.1015	0.1015	0.1015	80.0

aqueous solution of KOH (10%, 1.12 g, 0.02 mol) and placed in a 50 mL three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer, and an adapter connected to a funnel containing H₂O₂ (30% in water). After heating at 50°C for 30 min., H₂O₂ was added dropwise over about 20 min. The reaction mixture was heated at various temperatures and times (Table III). The mixture was neutralized with 1.67 mL HCl (37%) at room temperature (Scheme 2). It was filtered and

TABLE III Oxidative polycondensation reaction parameters of benzylidene-3'-hydroxyaniline with H₂O₂ in aqueous KOH

Sample no.	Temp., °C	Time, h	[B-3'-HA] ₀ , mol/L	[KOH] ₀ , mol/L	[H ₂ O ₂] ₀ , mol/L	Conservation of B-3'-HA, %
1	60	2	0.25	0.25	0.25	42.0
2	70	2	0.25	0.25	0.25	60.0
3	80	2	0.25	0.25	0.25	75.0
4	90	2	0.25	0.25	0.25	62.0
5	80	2	0.25	0.50	0.25	78.0
6	80	2	0.25	0.25	0.50	70.0
7	80	5	0.25	0.50	0.25	73.0
8	80	10	0.25	0.50	0.25	70.0
9	80	25	0.25	0.50	0.25	65.0

washed with hot water (50 mL \times 3) to separate out mineral salts and unreacted monomer and then dried in an oven at 110°C.

Characterization Techniques

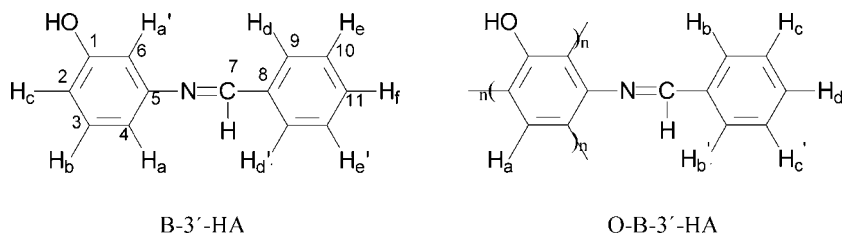
Fourier transform-infrared (FT-IR) and UV-Vis spectra were recorded on a Perkin-Elmer FT-IR BX II and Shimadzu UV-1208, respectively. Elemental analysis was carried out with a Carlo Erba 1106 instrument. The FT-IR spectra were recorded using KBr discs (4000–350 cm^{-1}). UV-Vis spectra of B-3'-HA and O-B-3'-HA were obtained in tetrahydrofuran (THF) solutions. The ^1H and ^{13}C -NMR (nuclear magnetic resonance) spectra were taken on a Bruker DPX FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively, at 25°C, using deuterate dimethylsulfoxide (DMSO) as solvent. Trimethylsilyl (TMS) was used as the internal standard. Thermal data were obtained by using a STA 409 C NETZSCH-Geratebau GmbH thermal analyzer. The thermogravimetric measurements were made between 20 and 1100°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 SEC. Shimadzu equipment was used, with SGX columns (100 Å and 7 nm diameter loading material, 3.3 mm i.d. \times 300 mm length), dimethylformamide (DMF) eluent (0.4 mL/min), and polystyrene standards. A refractive index detector (at 25°C) was used to analyze the product.

RESULTS AND DISCUSSION

Investigation of Synthesis Conditions of O-B-3'-HA

B-3'-HA is not normally oxidized at the neutral aqueous and organic media by oxygen, H_2O_2 , and NaOCl. When alkaline, B-3'-HA interacts with oxidizers such as air oxygen, H_2O_2 , and NaOCl and immediately generates phenoxy radicals, which gives a brown color. The conversion of B-3'-HA was 92.0% under optimum conditions such as $[\text{B-3'-HA}]_0 = [\text{KOH}]_0 = 0.25 \text{ mol/L}$ at 90°C for 5 h. In comparison, the conversion of B-3'-HA was 60.0% when $[\text{B-3'-HA}]_0 = [\text{KOH}]_0 = 0.25 \text{ mol/L}$ at 50°C for 5 h, and the conversion was 85% when $[\text{B-3'-HA}]_0 = 0.25 \text{ mol/L}$, $[\text{KOH}]_0 = 0.50 \text{ mol/L}$ at 90°C for 5 h. The various reaction conditions for O-B-3'-HA are summarized in Table I. For the oligomer formation of B-3'-HA, air and NaOCl was demonstrated to have higher activities than H_2O_2 .

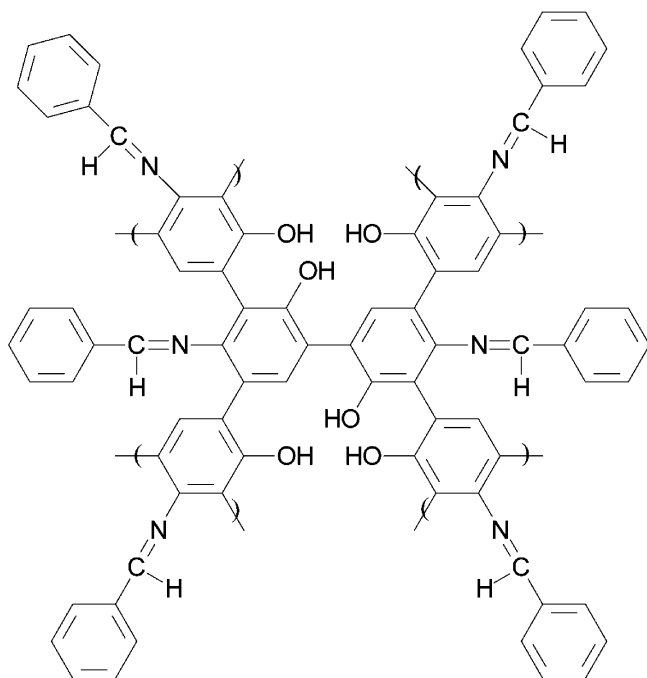
The reaction conditions for oxidative polycondensation reaction of B-3'-HA with 30% NaOCl solution in aqueous alkaline medium are given in Table II. The conversion of B-3'-HA was 98.0% under optimum conditions such as $[\text{B-3'-HA}]_0 = [\text{KOH}]_0 = [\text{NaOCl}]_0 = 0.1015 \text{ mol/L}$,



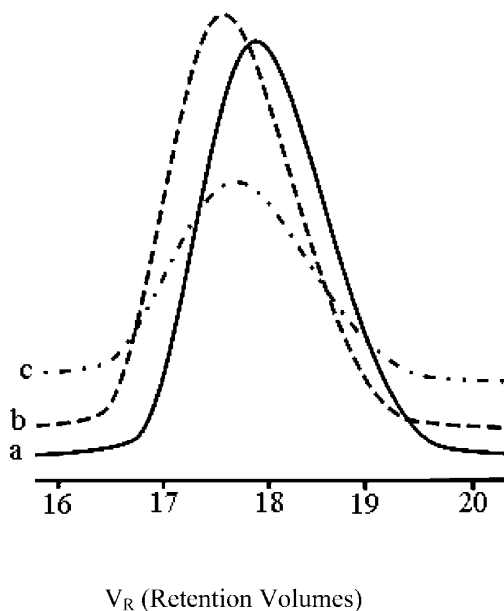
SCHEME 3 B-3'-HA and OB-3'-HA.

at 50°C for 5 h. The conversion of B-3'-HA was 80.0% when $[B-3'-HA]_0 = [KOH]_0 = [NaOCl]_0 = 0.1015 \text{ mol/L}$ at 50°C for 25 h. When the reaction time increased under the same reaction conditions, the conversion decreased. Moreover, when the alkaline concentration increased, the total yield was 86.0% (see Table II).

The conditions for the same reaction with 30% H_2O_2 solution in aqueous medium are given in Table III. The conversion of B-3'-HA was



SCHEME 4 Structure of O-B-3'-HA.



Molecular weight distribution (according to Polystyrene standards)

FIGURE 1 SEC curves of O-B-3'-HA: a), air as catalyst; b), NaOCl as catalyst; and c), H_2O_2 as catalyst.

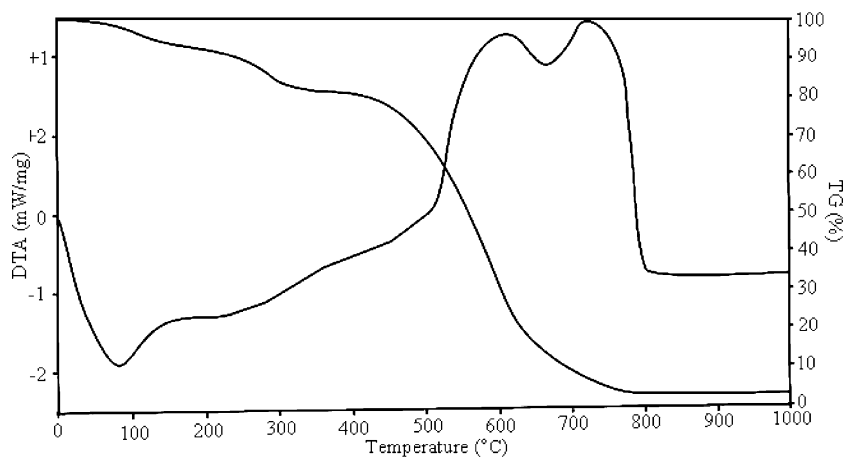


FIGURE 2 DTA and TGA curves of benzylidene-3'-hydroxyaniline.

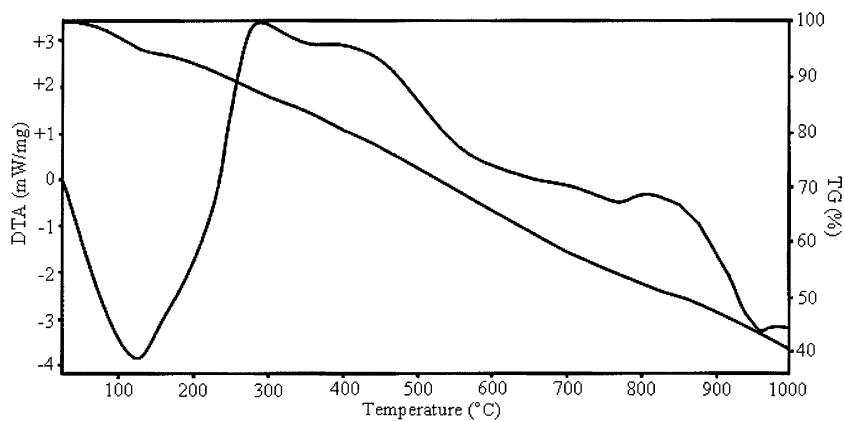


FIGURE 3 DTA and TGA curves of oligo-benzylidene-3'-hydroxyaniline.

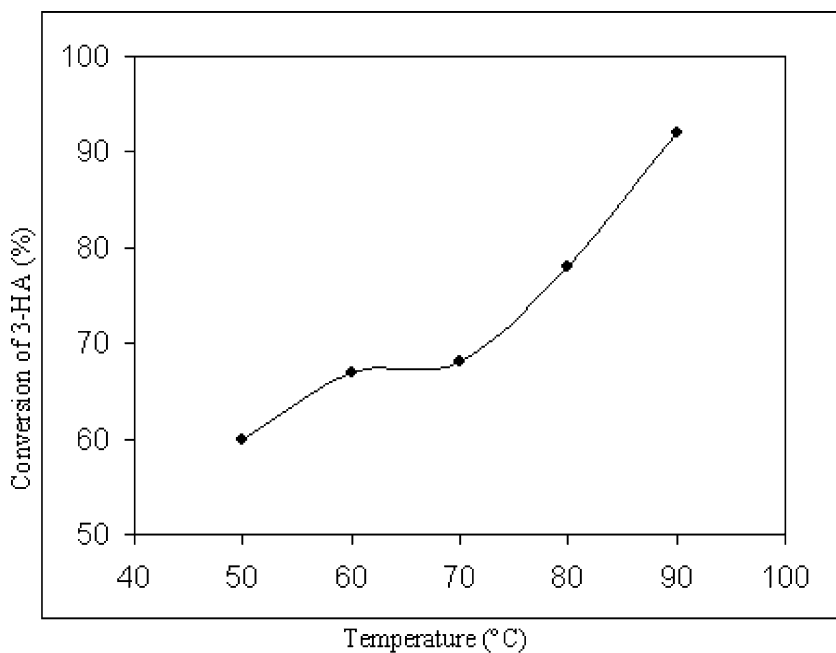


FIGURE 4 Percent conversion versus temperature for the oxidative polycondensation of B-3'-HA with air oxidant in the alkaline medium.

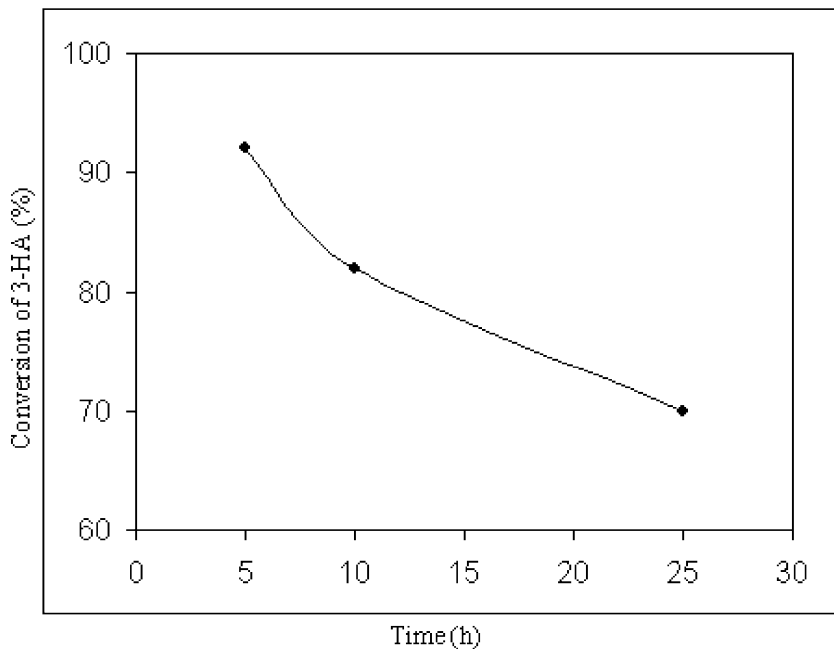


FIGURE 5 Percent conversion versus time for the oxidative polycondensation of B-3'-HA with air oxidant in the alkaline medium.

75.0% under optimum reaction conditions such as $[B-3'-HA]_0 = [KOH]_0 = [H_2O_2]_0 = 0.25$ mol/L, at 80°C for 2 h. In comparison, the conversion was 65.0% when $[B-3'-HA]_0 = [H_2O_2]_0 = 0.25$ mol/L and $[KOH]_0 = 0.50$ mol/L at 80°C for 25 h. The conversion was 75.0% at 80°C for 2 h and 62.0% at 90°C for 2 h. The reason for the low conversion may be depolymerization to monomer at high temperatures. As seen from Tables I–III, the yield of the oligomer depended on temperature, times, and initial concentrations of oxidants.

Solubility

O-B-3'-HA is dark brown in the form powder and is completely soluble in organic solvents such as DMF, THF, DMSO, acetone, aqueous alkaline pyridine, and concentrated H_2SO_4 . It is partly soluble in methanol, 1-butanol, ethanol and $CHCl_3$. O-B-3'-HA is insoluble in n-heptane, n-hexane, toluene, benzene, acetonitrile, ethyl acetate, CCl_4 and 1, 4-dioxane.

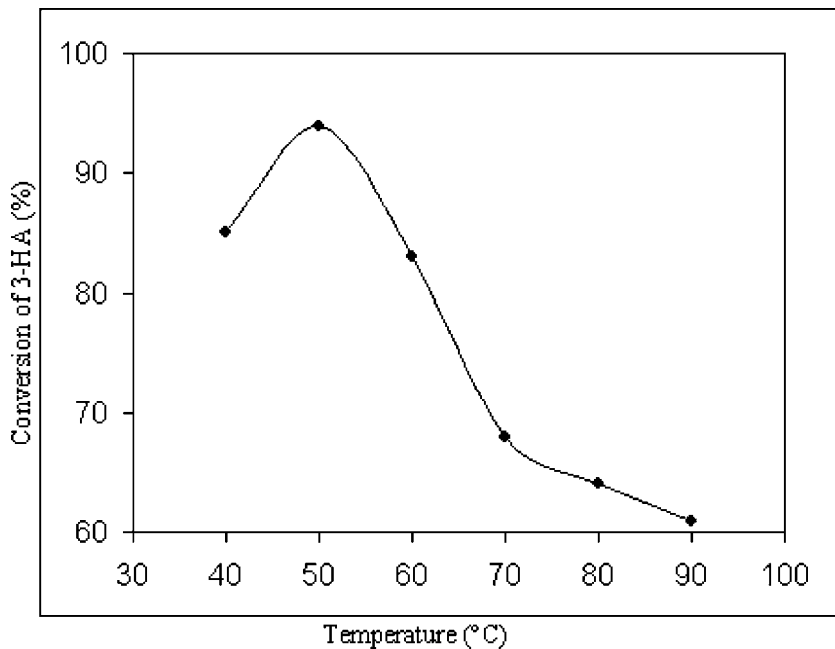


FIGURE 6 Percent conversion versus temperature for the oxidative polycondensation of B-3'-HA with NaOCl oxidant in the alkaline medium.

Structure of O-B-3'-HA

SEC analysis confirmed that B-3'-HA was converted to its oligomer. In the case of air oxidation, M_n , M_w , and PDI of O-B-3'-HA were found to be 1960 g mol^{-1} , 3170 g mol^{-1} , and 1.615, respectively. In the case of NaOCl oxidant, M_n , M_w and PDI values were 2640 g mol^{-1} , 5130 g mol^{-1} , and 1.942, respectively. In the case of H_2O_2 oxidant, M_n , M_w and PDI values were found to be 2370 g mol^{-1} , 4720 g mol^{-1} , and 1.990, respectively. According to 18.00, 17.50 and 17.80 retention volume values, molecular weight changes calculated to be 3170, 5130 and 4720 g mol^{-1} , respectively.

The UV-Vis spectra of B-3'-HA and O-B-3'-HA were similar to each other. In the spectrum of B-3'-HA, K bands of phenol and $\text{C}_6\text{H}_5\text{-N=}$ were observed at 226 and 265 nm, respectively. Benzene band of B-3'-HA and R band of -CH=N- groups were observed at 300 and 348 nm, respectively. For O-B-3'-HA, K and R bands were observed at 227 and 264 and 351 nm, respectively.

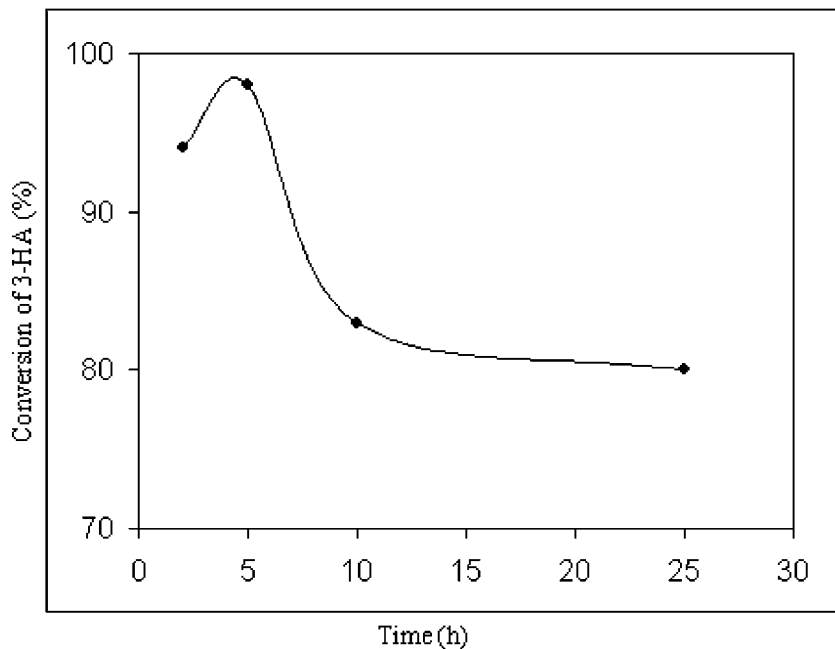


FIGURE 7 Percent conversion versus time for the oxidative polycondensation of B-3'-HA with NaOCl oxidant in the alkaline medium.

In the FT-IR spectrum of O-B-3'-HA, bands of hydroxyl ($-\text{OH}$) and azomethine ($-\text{CH}=\text{N}$) groups were observed at 3435 cm^{-1} and 1612 cm^{-1} , respectively. The ^1H and ^{13}C -NMR spectra provided more definitive structure determination. The NMR results showed the formation of oligomeric macromolecules from the B-3'-HA residue via the polymerization on C_2 , C_4 , and C_6 positions (Scheme 3).

FT-IR spectrum for O-B-3'-HA confirmed the ^1H and ^{13}C -NMR results. From spectral and SEC data, an empirical structure can be given for O-B-3'-HA (Scheme 4):

Thermal Analysis of Oligo-Benzylidene-3'-Hydroxyaniline

The TGA curves of monomer and oligomer are given in Figures 2 and 3. The initial degradation temperatures of B-3'-HA and O-B-3'-HA started at 85 and 120°C , respectively, and 50% weight loss at 529 and 830°C , respectively. Total weight loss of B-3'-HA and O-B-3'-HA was found to be 97.0% and 59.46% at 1000°C , respectively. For this oligomer,

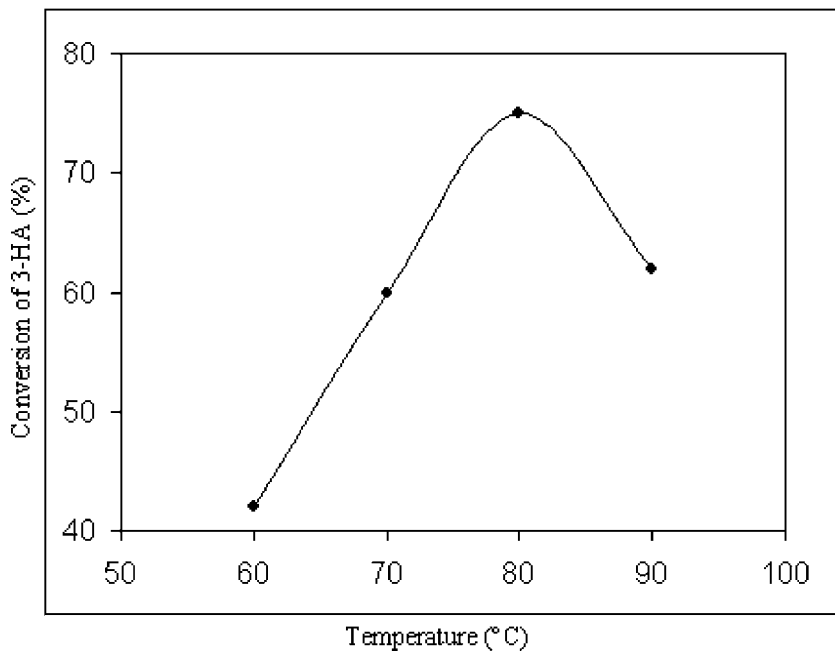


FIGURE 8 Percent conversion versus temperature for the oxidative polycondensation of B-3'-HA with H₂O₂ oxidant in the alkaline medium.

carbonaceous residues were formed at a high amount (40.54%) at 1000°C, but the monomer did not form carbonaceous residues at 1000°C. Because of the conjugated carbons, the oligomer demonstrated higher resistance against high temperature, in contrast to the monomer. Thus, O-B-3'-HA lost 28.0% of its mass at 500°C, whereas B-3'-HA lost 32.5% of its mass at 500°C. Note that because of fast scan rates (10°C/min), the weight loss data represent relative numbers and are not meant to be interpreted on the basis of their absolute values.

The DTA analyses of B-3'-HA and O-B-3'-HA were measured in air at ambient pressure in the temperature range 20–1000°C in order to investigate the thermal stability. Figures 2 and 3 show the DTA traces for B-3'-HA and O-B-3'-HA. Endothermic peaks at around 100°C are due to evaporation of absorbed water. T_{\max} values for B-3'-HA were observed at 611°C and 725°C; for O-B-3'-HA they were observed at 291°C and 800°C. According to DTA and TGA, as far as thermo-oxidative decomposition is concerned, O-B-3'-HA has better thermal stability than the monomer.

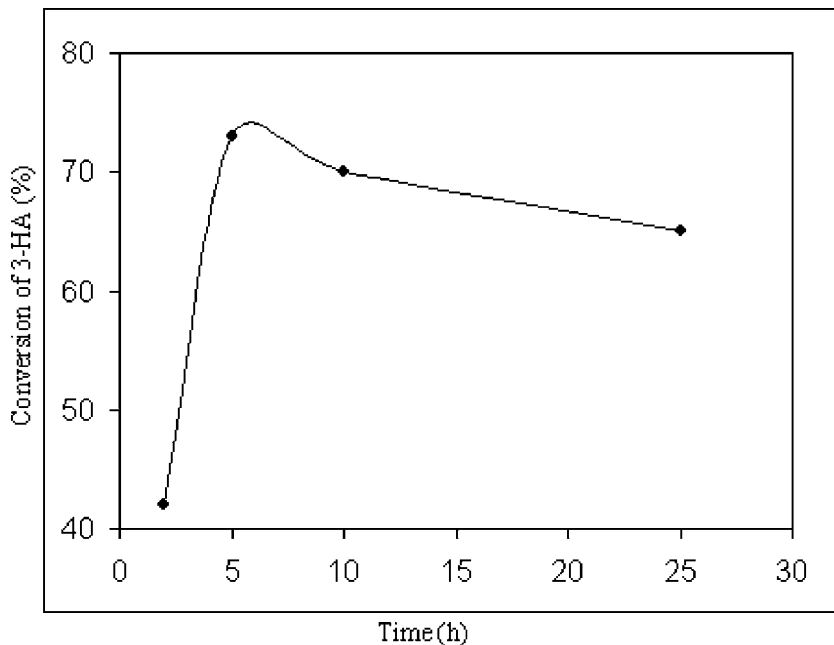


FIGURE 9 Percent conversion versus time for the oxidative polycondensation of B-3'-HA with H_2O_2 oxidant in the alkaline medium.

A Kinetic Study of B-3'-HA

Polymerization of B-3'-HA under the aforementioned conditions is influenced, as expected, by the reaction temperatures and the time of reaction with NaOCl and air (Figures 4–9). Thus, the data in Figures 4–9 permit the percent conversion of B-3'-HA to be investigated. The percent conversion of B-3'-HA is affected by reaction temperature and times, depending on the oxidant used.

CONCLUSION

B-3'-HA has been converted to oligomers by oxidants such as air, H_2O_2 , and NaOCl in an aqueous alkaline medium. Conversion was found to be 42–98% for reactions carried out at 0–90°C for 2–25 h. This is an oxidative polycondensation reaction, and H_2O_2 was demonstrated to have less activity than air and NaOCl. The conversion for air was found to be 92% and for NaOCl 98.0%. M_n , M_w , and PDI values of

O-B-3'-HA were found to be 2640 g mol^{-1} , 5130 g mol^{-1} , and 1.942, respectively. Chemical and spectral analyses, such as UV-Vis, FT-IR, ^1H - and ^{13}C -NMR, indicated bond formation between *ortho* and *para* carbons of the phenol ring during oligomer formation. The oligomer degrades at higher temperatures than the monomer; the oligomer and the monomer lost half of their weights at 564 and 852°C , respectively. Thermal stability of the oligomer was also higher than that of the monomer. The oligomer was found to have good resistance against thermo-oxidative degradation.

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