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Synthesis, Characterization, Optimization Reaction Conditions, and Molecular Weight Distribution of Poly(4-(4-nitrobenzylideneamino)phenol)

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ABSTRACT

In this study, the conditions of oxidative polycondensation reaction of 4-(4-nitrobenzylideneamino)phenol (4-NBAP) were studied using oxidants such as air (O_2), H_2O_2 , and NaOCl in an aqueous alkaline medium of 50-90°C. Poly(4-(4-nitrobenzylideneamino)phenol) (P-4-NBAP) was characterized by ^{1}H and ^{13}C NMR, FTIR, UV-vis, size exclusion chromatography (SEC), and elemental analysis techniques. The solubility of oligomer was investigated by using organic solvents such as dimethylformamide, tetrahydrofurane, dimethylsulfoxide, methanol, ethanol, $CHCl_3$, CCl_4, toluene, acetonitrile, ethyl acetate. According to air (O_2) oxidant (flow rate 8.5 L/h), the conversion of (4-NBAP) was 50.83% in optimum conditions such as $[4\text{-NBAP}]_o = [KOH]_o = 0.05$ mol/L at 60°C for 10 h. According to the SEC analysis, the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of P-4-NBAP were found to be 11109, 12886 g mol^{-1} and 1.160 using air (O_2); 17517, 23402 g mol^{-1} and 1.336 using NaOCl; and 8960, 10653 g mol^{-1} and 1.189 using H_2O_2, respectively. Also, thermogravimetric analysis showed poly(4-(4-nitrobenzylideneamino)phenol) is stable against thermal decomposition. The weight loss of P-4-NBAP was found to be 49.23% at 1000°C.

Key Words:

air(O_2);
H_2O_2;
NaOCl;
poly(4-(4-nitrobenzylideneamino)phenol);
oxidative polycondensation;
thermal analysis;
Schiff base.

INTRODUCTION

The oxidative polycondensation method is simply the reaction of compounds including -OH groups and active functional groups (-NH_2, -CHO, -COOH) in their structure with the oxidants like NaOCl, H_2O_2 and air (O_2) in the aqueous alkaline or acidic media. The main advantage of oxidative polycondensation method is the use of easily found, cheap, and simple structured oxidants. Many studies on oxidative polymerization and reaction mechanisms of

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polyphenols have been reported [1]. Schiff base substituted oligomers or polymers which included azomethine (–CH=N–) and active hydroxyl (–OH) groups have been used in various fields such as electrochemical cell and materials resistant to high energy due to their useful properties such as paramagnetism and semi-conductivity,. Because of these properties, they were used to prepare composites with resistance to high temperature, thermo-stabilisatiors, graphite materials, epoxy oligomer and block copolymers, and photo resists and antistatic materials [2–9]. The halogen derivatives of oligophenols were used to prepare composite materials such as lead-storing battery cathodes which are enduring to flame and specific detergents [10]. These compounds profited from new properties in their structures adding to other functional groups. These types of Schiff base oligomers or polymers can be demonstrated as having anti-microbial properties against some bacteria [11].

All azomethine polymers show a remarkable thermal stability. Non-conjugated polymers are white or cream in color and have thermal stabilities of about 300°C in N_2 and 250°C in air atmosphere. Aromatic azomethine polymers are yellow ,orange, red, brown, and black colored products, with thermal stabilities up to 500-550°C in N_2 and 430-480°C in air atmosphere. They are also resistant to radiation and their stability is shown to be independent from dose rate and nature of the ionizing radiation [12].

In this paper, we have investigated the effects of different parameters such as temperature, time, and initial concentration of NaOCl and H_2O_2 and alkaline for the synthesis of poly(4-(4-nitrobenzylideneamino) phenol) (P-4-NBAP). The structures of 4-(4-nitrobenzylideneamino) phenol (4-NBAP) and P-4-NBAP were characterized by using FTIR, UV-vis, ^{1}H NMR, ^{13}C NMR, and elemental analysis techniques. TGA and DTA analyses of 4-NBAP and P-4-NBAP were measured at the N_2 atmosphere. Also, molecular weight distribution of P-4-NBAP was determined by SEC technique.

MATERIALS AND METHODS

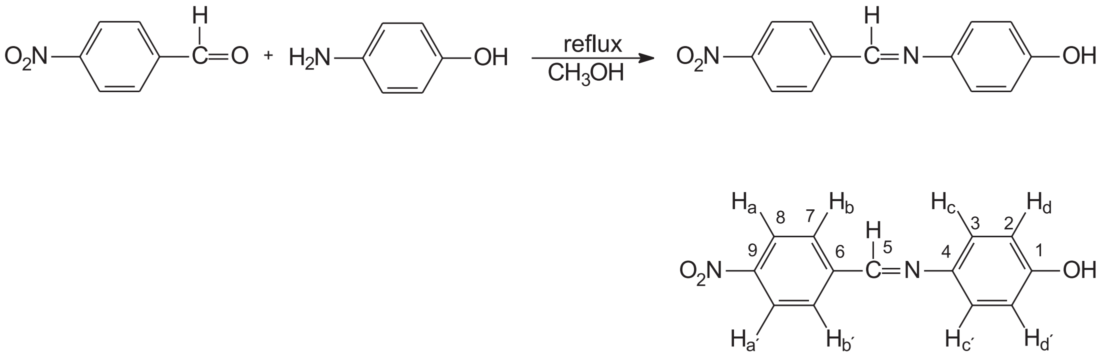
Materials

4-nitrobenzaldehyde, 4-aminophenol, 1,4-dioxane, methanol, ethanol, acetonitrile, toluene, acetone, ethyl acetate, heptane, hexane, CCl_4, $CHCl_3$, tetrahydrofurane (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO), H_2SO_4, KOH, hydrochloric acid (HCl) (37 wt %) and H_2O_2 (30% aqueous solution) were supplied from Merck and they were used as received. Sodium hypochloride (NaOCl 30% aqueous solution) was supplied from Paksoy Chemical Co. (Turkey). 4-(4-nitrobenzylideneamino) phenol (4-NBAP) was synthesized by condensation reaction to 4-nitrobenzaldehyde with 4-aminophenol and recrystallizied in methanol.

Synthesis of 4-(4-nitrobenzylideneamino)phenol and Poly(4-(4-nitrobenzylideneamino)phenol)

Synthesis of 4-(4-nitrobenzylideneamino)phenol

4-(4-nitrobenzylideneamino)phenol (4-NBAP) was prepared by the condensation of 4-nitrobenzaldehyde (3.775 g, 0.025 mol) with 4-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 I). The precipitated 4-NBAP was filtered, recrystallized from methanol and dried in a vacuum desiccator



Scheme I. Synthesis of 4-(4-nitrobenzylideneamino) phenol.

(yield: 89.8% and mp: 176°C).

Anal. calcd. for 4-NBAP: C, 64.46; H, 4.13; N, 11.57; Found: C, 64.00; H, 3.95; N, 11.00; UV-Vis (λ_{max}) : 230, 260, 322 and 377 nm; FTIR (KBr, cm^{-1}) : ν (O–H) 3439 s, ν (C–H phenyl) 3062 m, ν (C=N) 1623 s, ν (C=C phenyl) 1596, 1575, 1506 s and ν (C–O) 1261 s; ^{1}H NMR (DMSO): δ *ppm*, 9.66 (s, 1H, –OH), 8.75 (s, 1H, –CH=N–), 8.30 (d, 2H, Ar-Haa'), 8.10 (d, 2H, Ar-Hbb'), 7.29 (d, 2H, Ar-Hcc'), 6.82 (d, 2H, Ar-Hdd'); ^{13}C NMR (DMSO): δ ppm, 157.96 (C1-ipso), 116.52 (C2-H), 123.80 (C3-H), 142.35 (C4-ipso), 149.04 (C5-H), 142.83 (C6-ipso), 129.75 (C7-H), 124.62 (C8-H), 155.34 (C9-ipso).

Synthesis of Poly(4-(4-nitrobenzylideneamino)phenol) with air (O_2)

4-NBAP (0.242 g, 0.001 mol) was dissolved in an aqueous solution of KOH (10 wt %) (0.112 g, 0.002 mol) and placed into a (50 mL) three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and an addition of glass tubing over the condenser for sending air (O_2). The reaction mixture was stirred at the different temperatures and times (Table 1). The air (O_2) was passed in at a rate of 8.5 L/h during the course of the reaction. In order not to have water loss in the reaction mixture and to deneutralize the CO_2 of the air (O_2) to KOH, air (O_2) was passed into 200 mL of an aqueous solution of KOH (20 wt %) before sending to reaction vessel (Scheme II) [13]. The mixture was neutralized with 0.174 mL HCl (37 wt %) at room temperature. The mixture was then filtered and washed with hot water (25 mL × 3) for separating from mineral salts and unreacted monomer and then dried in an oven at 110°C.

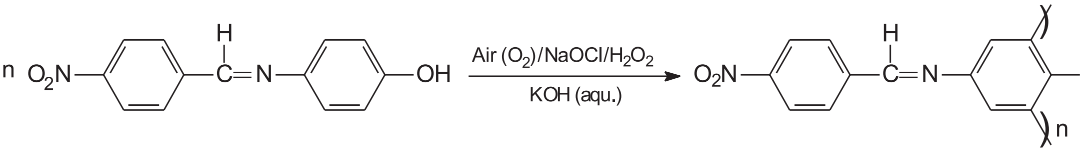
Synthesis of Poly(4-(4-nitrobenzylideneamino)phenol) with NaOCl

P-4-NBAP was synthesized through oxidative polycondensation of 4-(4-nitrobenzylideneamino) phenol in a aqueous solution of NaOCl (30 wt %). 4-NBAP (0.242 g, 0.001 mol) was dissolved in an aqueous solution of KOH (10 wt %, 0.112 g, 0.002 mol) and placed into a (50 mL) three-necked round bottom flask (Scheme II). It was fitted with a condenser, thermometer, stirrer and an addition of a funnel containing NaOCl. After heating to 40°C, NaOCl was added drop wise for about 20 min. The reaction mixture was stirred at the different temperatures and time intervals (Table 2) [13]. The mixture was then neutralized with 0.174 mL HCl (37 wt %) at room temperature and the above mentioned processes were repeated.

Anal. calcd. for P-4-NBAP: C, 65.00; H, 3.33; N, 11.67; Found: C, 64.60; H, 3.45; N, 12.00; UV-Vis (λ_{max}): 225, 259 and 385 nm; FTIR (KBr, cm^{-1}): ν (O–H) 3321 s, ν (C–H aryl) 3074 m, ν (C=N) 1619 s, ν (C=C phenyl) 1594, 1509 s and ν (C–O) 1340 s; ^{1}H NMR (DMSO): δ *ppm*, 9.58 (s, 1H, –OH); 8.62 (s, 1H, –CH=N–); 7.70 (d, 2H, Ar-Haa'); 7.55 (d, 2H, Ar-Hbb'); 6.64 (s, 2H, Ar-Hcc'); ^{13}C NMR (DMSO): δ ppm, 189.95 (C1-ipso), 133.50 (C2-ipso), 122.67 (C3-H), 142.10 (C4-ipso), 152.25 (C5-H), 144.45 (C6-ipso), 132.35 (C7-H), 130.50 (C8-H), 160.84 (C9-ipso).

Synthesis of Poly(4-(4-nitrobenzylideneamino) phenol) with H_2O_2

P-4-NBAP was synthesized through oxidative polycondensation of 4-NBAP with a solution in water of H_2O_2 (30%). 4-NBAP (0.242 g, 0.001 mol) Was dissolved in an aqueous solution of KOH (10 wt %, 0.112 g, 0.002 mol) and placed into a (50 mL) three-necked round-bottom flask (Scheme II). It was fitted with a condenser, thermometer, stirrer and an addition of a funnel containing H_2O_2. After heating at 40°C for 30 min, H_2O_2 was added drop wise for about 20 min. The reaction mixture was heated at the different temperatures and time intervals (Table 3) [13]. The mixture was then neutralized with 0.174 mL



Scheme II. Synthesis of oligo(4-(4-nitrobenzylideneamino)phenol).

HCl (37 wt %) at room temperature and the above mentioned processes were repeated.

Solubility and Characterization Techniques

While, 4-NBAP was orange color, crystal form, and completely soluble in organic solvents such as methanol, ethanol, THF, acetone, 1,4-dioxane, ethyl acetate, DMF, and DMSO; it was only partially soluble in toluene and chloroform; and insoluble in heptane and hexane. P-4-NBAP was dark brown, powder form, and completely soluble in organic solvents such as DMF and DMSO but insoluble in methanol, ethanol, acetonitrile, ethyl acetate, $CHCl_3$, 1,4-dioxane, heptane, and hexane.

The infrared and ultraviolet-visible spectra were measured by a Perkin Elmer FTIR BX and a Shimadzu UV-1208, respectively. Elemental analysis was carried out with a Carlo Erba 1106. The FTIR spectra were recorded using KBr disc (4000–350 cm^{-1}). The UV-vis spectra of 4-NBAP and P-4-NBAP were recorded by using methanol. 4-NBAP and P-4-NBAP were characterized by using ^1H NMR and ^{13}C NMR spectra (Bruker Avance DPX-400 and 100.6 MHz, respectively) recorded at 25°C by using deuteriated DMSO as a solvent and TMS as an internal standard. Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis System. The TG-DTA measurements were made between 20-1000°C (in N_2 and rate 10°C/min). The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) were determined by the Shimadzue size exclusion chromatography (SEC) instrument. For SEC investigations we used an SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. x 300 mm column; eluent: DMF/methanol (v/v, 4/1, 0.4 mL/min), polystyrene standards. A refractive index detector (at 25°C) was used to analyze the product.

RESULTS and DISCUSSION

The Investigation of Synthesis Conditions of P-4-NBAP

4-NBAP was oxidized by the alkaline medium using air(O_2), H_2O_2, and NaOCl. When it interacts with oxidants such as air(O_2), H_2O_2, and NaOCl; it immediately precipitates brown phenoxy radicals with adding of the alkaline. The converted product of 4-NBAP solution was 50.83 wt % using the air(O_2) medium for 10 h at 60°C. The various conditions for preparing P-4-NBAP are given in Table 1. It can be

Table 1. The parameters of oxidative polycondensation reaction of 4-(4-nitrobenzylideneamino) phenol with air O_2 in aqueous KOH.

Sample No.	Temperature (°C)	Time (h)	$[4\text{-NBAP}]_o$ (mol/L)	$[KOH]_o$ (mol/L)	Air (O_2) (L/h)	Conversion of 4-NBAP (%)
1	50	5	0.05	0.05	8.5	46.29
2	60	5	0.05	0.05	8.5	48.25
3	70	5	0.05	0.05	8.5	37.19
4	80	5	0.05	0.05	8.5	35.53
5	90	5	0.05	0.05	8.5	32.64
6	60	10	0.05	0.05	8.5	50.83
7	60	15	0.05	0.05	8.5	46.28
8	60	20	0.05	0.05	8.5	35.61
9	60	25	0.05	0.05	8.5	29.74
10	60	10	0.05	0.10	8.5	26.86
11	60	10	0.05	0.15	8.5	22.72
12	60	10	0.05	0.20	8.5	10.33
13	60	10	0.05	0.25	8.5	6.61

seen in Table 1 that the converted products decreased with increasing temperature. The conversion of 4-NBAP was 50.83% at optimum conditions such as $[\text{4-NBAP}]_o$ = 0.05, $[\text{KOH}]_o$ = 0.05 mol/L at 60°C for 10 h. The conversion of 4-NBAP was 46.280% in reaction conditions such as $[\text{4-NBAP}]_o$ = 0.05, $[\text{KOH}]_o$ = 0.05 mol/L at 60°C for 15 h. H_2O_2 As oxidant demonstrated less activity than air(O_2) and NaOCl at the conversion of 4-NBAP to polymer.

For NaOCl 30 wt % solution in an aqueous alkaline medium, the conditions of oxidative polycondensation reaction of 4-NBAP are given in Table 2. The conversion of 4-NBAP was 52.89% at optimum conditions such as $[\text{4-NBAP}]_o$ = 0.05, $[\text{KOH}]_o$ = 0.10, and $[\text{NaOCl}]_o$ = 0.12 mol/L at 80°C for 10 h. The conversion of 4-NBAP was 50.91% in the reaction conditions such as $[\text{4-NBAP}]_o$ = 0.05, $[\text{KOH}]_o$ = 0.15, and $[\text{NaOCl}]_o$ = 0.12 mol/L at 80°C for 10 h. In the same conditions, when the molar amount of alkaline increased in the solution medium, the total yield of conversion of 4-NBAP was found to be 35.54% (Table 2).

The conditions of the oxidative polycondensation reaction of 4-NBAP are given in Table 3, for H_2O_2 solution 30% in an aqueous alkaline medium. The conversion of 4-NBAP was 22.31% in the optimum conditions such as $[\text{4-NBAP}]_o$ = 0.05, $[\text{KOH}]_o$ = 0.10, and $[H_2O_2]_o$ = 0.58 mol/L, at 70°C for 10 h. The conversion of 4-NBAP was 7.04% in the reaction conditions such as $[\text{4-NBAP}]_o$ = 0.05, $[\text{KOH}]_o$ = 0.10, and $[H_2O_2]_o$ = 0.58 mol/L at 70°C for 20 h. While the conversion of 4-NBAP to oligomer was 14.87% at 50°C for 5 h, its conversion was 13.64% at 90°C for 5 h. The reason for this condition may be the oligomer's depolymerization to monomer at high temperatures. As may be seen from Tables 1, 2, and 3 in these reactions the yield of the polymer formation is depended on temperature, initial concentration of monomers, and time.

Structure of P-4-NBAP

The SEC analyses of P-4-NBAP were performed at

Table 2. The parameters of oxidative polycondensation reaction of 4-(4-nitrobenzylideneamino)phenol with NaOCl in aqueous KOH.

Sample No.	Temperature (°C)	Time (h)	$[\text{4-NBAP}]_o$ (mol/L)	$[\text{KOH}]_o$ (mol/L)	$[\text{NaOCl}]_o$ (mol/L)	Conversion of 4-NBAP (%)
1	50	5	0.05	0.10	0.12	20.66
2	60	5	0.05	0.10	0.12	28.93
3	70	5	0.05	0.10	0.12	35.54
4	80	5	0.05	0.10	0.12	49.54
5	90	5	0.05	0.10	0.12	46.28
6	80	10	0.05	0.10	0.12	52.89
7	80	15	0.05	0.10	0.12	48.34
8	80	20	0.05	0.10	0.12	45.45
9	80	25	0.05	0.10	0.12	42.56
10	80	10	0.05	0.15	0.12	50.91
11	80	10	0.05	0.20	0.12	45.95
12	80	10	0.05	0.25	0.12	40.18
13	80	10	0.05	0.30	0.12	35.54
14	80	10	0.05	0.25	0.18	42.02
15	80	10	0.05	0.25	0.24	38.35
16	80	10	0.05	0.25	0.30	35.41
17	80	10	0.05	0.25	0.36	33.80

Table 3. The parameters of oxidative polycondensation reaction of 4-(4-nitrobenzylideneamino)phenol with H_2O_2 in aqueous KOH.

Sample No.	Temperature (°C)	Time (h)	$[4\text{-NBAP}]_o$ (mol/L)	$[KOH]_o$ (mol/L)	$[NaOCl]_o$ (mol/L)	Conversion of 4-NBAP (%)
1	50	5	0.05	0.10	0.58	14.87
2	60	5	0.05	0.10	0.58	16.12
3	70	5	0.05	0.10	0.58	19.42
4	80	5	0.05	0.10	0.58	18.60
5	90	5	0.05	0.10	0.58	13.64
6	70	10	0.05	0.10	0.58	22.31
7	70	15	0.05	0.10	0.58	16.22
8	70	20	0.05	0.10	0.58	7.04
9	70	25	0.05	0.10	0.58	4.13
10	70	5	0.05	0.15	0.58	21.90
11	70	5	0.05	0.20	0.58	18.51
12	70	5	0.05	0.25	0.58	15.29
13	70	5	0.05	0.30	0.58	14.46

30°C using DMF/Methanol (v/v, 4/1) as eluent at a flow rate of 0.4 mL/min. For the oxidant H_2O_2 the values of M_n, M_w and PDI for P-4-NBAP were found to be 8960, 10653 g mol^{-1}, and 1.189, respectively. Three peaks were observed in the chromatogram of P-4-NBAP. 45 wt % of the mass of P-4-NBAP was of low molecular weight (M_n= 2462, M_w= 3348 g mol^{-1}, and PDI= 1.360), but 55 wt % of its weight was of high molecular weight (first fraction (25 wt %): M_n= 79796, M_w= 93102 g mol^{-1}, and PDI= 1.167; second fraction (30%): M_n= 19410, M_w= 23925 g mol^{-1}, and PDI= 1.232).

For the oxidant air(O_2) the values of M_n, M_w and PDI for P-4-NBAP were found to be 11109, 12886 g mol^{-1}, and 1.160, respectively. Three peaks were observed in the chromatogram of P-4-NBAP. 35 wt % of the mass of P-4-NBAP was of low molecular weight (M_n= 1876, M_w= 2256 g mol^{-1}, and PDI= 1.203), but 65 wt % of its weight was of high molecular weight (first fraction (35 wt %): M_n= 74138, M_w= 86489 g mol^{-1}, and PDI= 1.166; second fraction (30 wt %): M_n= 22414, M_w= 25327 g mol^{-1}, and PDI= 1.130).

For the oxidant NaOCl the values of Mn, M_w and PDI for P-4-NBAP were found to be 17517, 23402 g mol^{-1} and 1.336, respectively. Three peaks were observed in the chromatogram of P-4-NBAP. 25 wt % of the mass of P-4-NBAP was of low molecular weight (M_n= 2926, M_w= 3789 g mol^{-1}, and PDI= 1.295), but 75 wt % of its weight was of high molecular weight (first fraction (45 wt %): M_n= 101654, M_w= 137161 g mol^{-1}, and PDI= 1.349; second fraction (30 wt %): M_n= 20252, M_w= 25119 g mol^{-1}, and PDI= 1.240). The increasing of polymerization time, temperatures and oxidant concentrations increased the molecular weight and MWD of P-4-NBAP.

The UV-vis spectra of 4-NBAP and P-4-NBAP were similar to one another. However, in the spectra of 4-NBAP the K bands of phenol and C_6H_5–N= were observed at 230 and 260 nm, respectively. The benzene band of 4-NBAP and strength R band of –CH=N– groups were observed at 260 and 377 nm, respectively. In UV-Vis spectra of P-4-NBAP the K and R bands were observed at 225 and 259 nm, respectively [6].

FTIR spectra of the oxidative polycondensation product of 4-NBAP are only different in the reduction of band strength and numbers from the FTIR spectrum of monomer. In the FTIR spectra, the bands of –OH

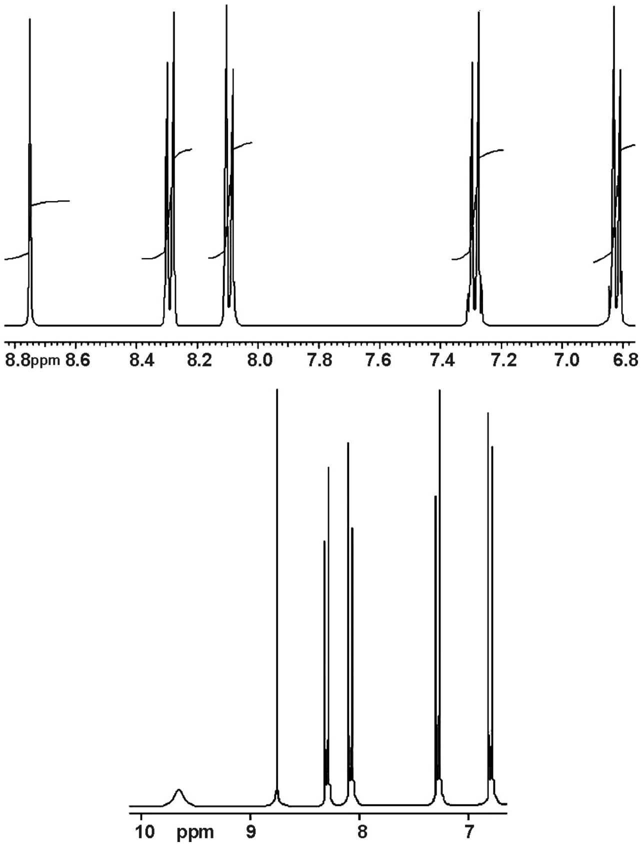


Figure 1. ^{1}H NMR Spectrum of 4-(4-nitrobenzylideneamino)phenol.

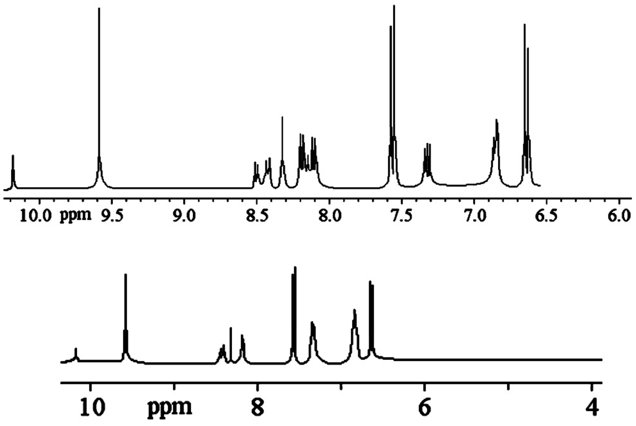


Figure 3. ^{1}H NMR Spectrum of poly(4-(4-nitrobenzylideneamino)phenol).

and –CH=N groups for 4-NBAP were observed at 3439 and 3321 and for P-4-NBAP at 1623 and 1619 cm^{-1}, respectively.

^{1}H and ^{13}C NMR Spectra of monomer and polymer were recorded in DMSO-d_6 to identify their structures (Figures 1, 2, 3, and 4). In the ^{1}H NMR spectra, the signals of –OH and –CH=N groups of 4-NBAP were observed at 9.66 and 8.75 ppm for and P-4-NBAP at 9.58 and 8.62 ppm, respectively. According to ^{13}C NMR spectrum, the peak values of ortho carbons of the monomer and the polymer are observed in 116.52 and 133.50 ppm, respectively. It is seen that, for the polymer this value was shifted downfield. Although the hydroxyl groups are involved in the formation of free radicals leading to polymer formation, they do not appear to be involved in bond formation. Thus the phenyl rings in the polymer appears to be linked primarily at ortho positions. The reaction mechanism on the coupling selectivity has been studied by Kaya and co-workers [6]. According to ^{1}H and ^{13}C NMR spectral data of the P-4-NBAP, polymer's chemical formula is shown in Scheme III.

Thermal Analysis of Monomer and Polymer

The TGA and DTA curves of monomer and polymer are given in Figures 5 and 6, respectively. The initial degradation temperature and 58.73% weight loss of 4-NBAP was found to be 216 and 1000°C, respectively. The endothermic processes of 4-NBAP was observed

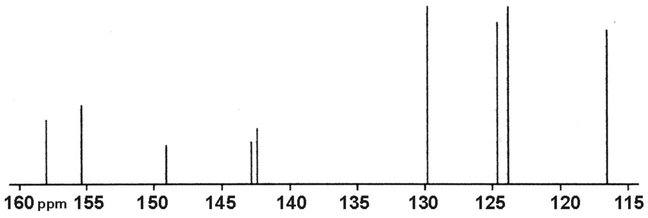


Figure 2. ^{13}C NMR Spectrum of 4-(4-nitrobenzylideneamino)phenol.

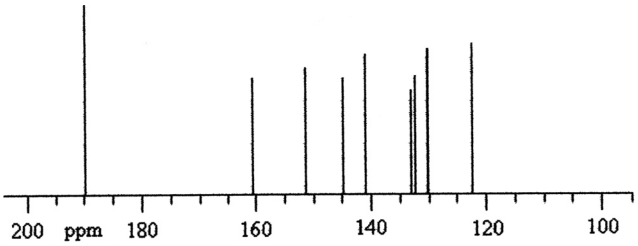
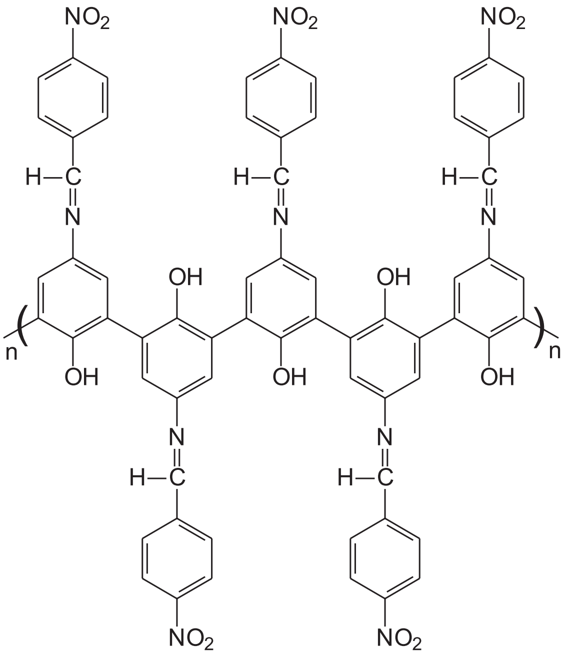


Figure 4. ^{13}C NMR Spectrum of poly(4-(4-nitrobenzylideneamino)phenol).



Scheme III. The structure of oligo(4-(4-nitrobenzylideneamino) phenol).

at 252°C. According to DTA curve, exothermic processes and T_{max} value of 4-NBAP observed at 176°C and 700°C, respectively. The 50% weight loss of 4-NBAP was observed at 655°C. Thermal decomposition of monomer was formed in three steps. The first step was at 215-290°C and the weight loss was found to be 29%. The second step was at 295-400°C and the weight loss was found to be 9.45%. The third step was at 400-1000°C and the weight loss was found to be 19.64%. The initial degradation temperature and 49.23% weight losses of P-4-NBAP were found to be at 295 and 1000°C, respectively.

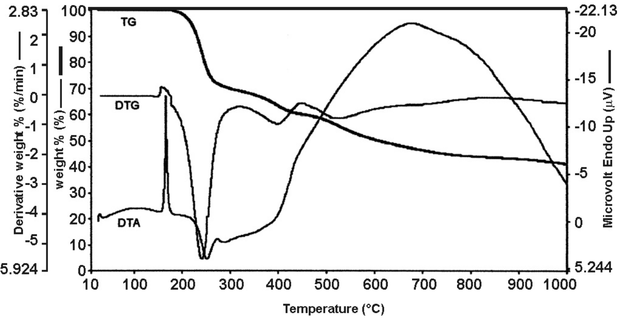


Figure 5. TGA-DTA Curves of 4-(4-nitrobenzylideneamino)phenol.

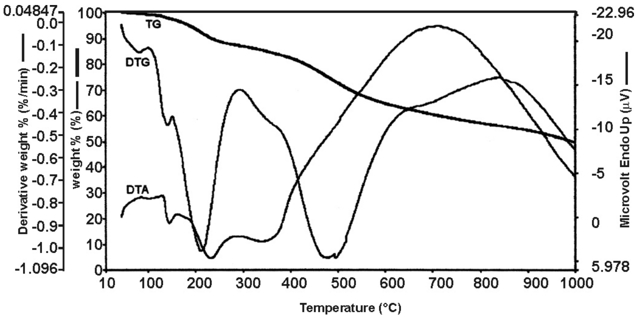


Figure 6. TGA-DTA Curves of poly(4-(4-nitrobenzylideneamino)phenol).

This polymer formed carbines residue at a high amount (about 50%) at 1000°C. Because of the long conjugated band systems, the polymer demonstrated higher resistance against high temperature than the monomer. The water presence is also seen in TG curves of polymer compound (Figure 6) which was appeared until 10.43% weight lost at 100-215°C range and required crystallization water removal.

CONCLUSIONS

4-(4-nitrobenzylideneamino) phenol with a Schiff base substitute was converted to polymer by oxidants such as air(O_2), H_2O_2, and NaOCl in an aqueous alkaline medium. The amount of converting of 4-NBAP to polymer was found to be 20.66-42.56% at 50–80°C for 5-25 h, bound to an initial amount of NaOCl. The 4-NBAP was converted to polymer at the various temperatures for 5–25 h by using oxidants such as air(O_2), H_2O_2, and NaOCl. Using H_2O_2 oxidant, the amount of P-4-NBAP was found to be 21.90% at 70°C for 5 h. At the oxidative polycondensation reaction of 4-NBAP, the oxidants NaOCl and air(O_2) demonstrated higher activity than H_2O_2. The maximum converting of monomer to polymer, with air(O_2) was found to be 50.83%. The ^{1}H and ^{13}C NMR spectral analyses have demonstrated that the ortho-carbons of the phenol ring unite with each other during the formation of polymer from the oxidative polycondensation of 4-NBAP. Thermal analysis results have been demonstrated sufficiently resistant to the thermal decomposition of the synthesized Schiff base substitute oligomer or polymer.

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