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Synthesis, characterization and optimum reaction conditions of oligo-2-amino-3-hydroxypyridine and its Schiff base oligomer

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Abstract

The oxidative polycondensation reaction conditions of 2-amino-3-hydroxypyridine (AHP) and 2-[benzilydeneimino] pyridine-3-ol (BIP) were studied by oxidants such as with air O_2, NaOCl and H_2O_2. Oligo-2-amino-3-hydroxypyridine (OAHP) was synthesized from the oxidative polycondensation of AHP with air O_2, NaOCl and H_2O_2 in an aqueous acidic and alkaline medium at 30–90 °C. BIP was synthesized from condensation of 2-amino-3-hydroxypyridine with benzaldehyde. Oligo-2-[benzilydeneimino] pyridine-3-ol (OBIP) was synthesized from the oxidative polycondensation of BIP with air O_2, NaOCl and H_2O_2 in an aqueous alkaline medium at 40–90 °C. About 95% BIP was converted to OBIP. The number average molecular weight, (M_n) weight average molecular weight (M_w) and polydispersity index (PDI) values of OAHP and OBIP (for air O_2 oxidant) were found to be 1433, 1912 g mol^{-1}, 1.33 and 2637, 5106 g mol^{-1} and 1.94, respectively. At the optimum reaction conditions, the yield of OAHP was found to be 86.0% (for air O_2 oxidant), 43.0% (for H_2O_2 oxidant) and 85.0% (for NaOCl oxidant). At the optimum reaction conditions, the yield of OBIP was found to be 91.0% (for air O_2 oxidant), 92.0% (for H_2O_2 oxidant) and 95.0% (for NaOCl oxidant). The OHAP and OBIP were characterized by FT-IR, UV–Vis, ^1H and ^{13}C-NMR elemental analysis. TG and DTA analyses were shown to be unstable of OAHP and OBIP against thermo-oxidative decomposition. According to TG analyses, the weight loss of OAHP and OBIP was found to be 97.35 and 96.60% at 520 and 685 °C, respectively.

Keywords: Oligo-2-amino-3-hydroxypyridine; Oxidative polycondensation; Oligo-2-[benzilydeneimino] pyridine-3-ol

1. Introduction

Polymer–Schiff bases including conjugated bonding and active hydroxyl group have been studied for more than 60 years and they have been used in various fields. They have useful properties such as paramagnetizm, semi conductivity, electrochemical cell and resisting to high energy. Because of these properties, they are used to prepare composites having high resistance at high temperature, thermo-stabilisatiors, graphite materials, and epoxy oligomer and block copolymers, photo resists, materials, which are antistatic and enduring to flame [1–9]. By adding of other functional groups to these compounds, they can be profited new useful properties. Oligophenols, which have a lot of functionality groups may be used for cleaning of poisonous heavy metals in the industrial waste waters. Therefore, the synthesis of oligomer–metal complexes is very important at analytic and environmental chemistry. It seemed advantageous to attempt to design and prepare a polymer-bound chelating ligand, which would be able to form complexes with a variety of transition metals and, therefore, have a large range of applications. Also, coordination compounds of salicylaldehyde's Schiff base have been proven to be an excellent model system to study the enzymatic reactions of pyridoxal phosphate. Both of these systems are effectively catalyzing transamination and racemization reaction [10].

In this paper, we investigated the effects of different parameters such as temperature, times and initial concentration of NaOCl, H_2O_2 and alkaline for the preparation of oligo-2-amino-3-hydroxypyridine (OAHP) and oligo-2-[benzilydeneimino] pyridine -3-ol (OBIP) and then we determined optimum reaction conditions with oxidative polycondensation methods for AHP and BIP. OAHP and OBIP were characterized by using FT-1R, UV-Vis, ^1H and ^{13}C-NMR, elemental analysis and size exclusion chromatography (SEC) techniques. Also, thermal stabilities of OAHP and OBIP were studied by TG-DTA techniques.

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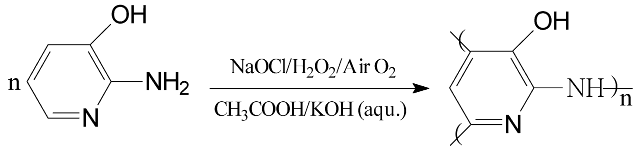


Scheme 1.

2. Materials and methods

2.1. Materials

2-Amino-3-hydroxypyridine (AHP), benzaldehyde (BA), 1, 4-dioxane, methanol, ethanol, benzene, toluene, acetone, ethyl acetate, *n*-heptane, *n*-hexane, pyridine, $CHCl_3$, CCl_4, tetrahydrofurane, THF, dimethylformamide, DMF, dimethylsulfoxide, DMSO, H_2SO_4, toluene, H_2O_2 (30%, aqueous solution), NaOH, KOH, hydrochloric acid (HCl, 37%) and acetic acid (glacial) were supplied from Merck Chemical Co. as chromatographic grade and they were used as received. Sodiumhypochloride (NaOCl), (30%, aqueous solution) was supplied from Paksoy Co. (Turkey). 2-[Benzilydeneimino] pyridine-3-ol (BIP) was synthesized from condensation reaction of AHP with benzaldehyde.

2.2. The oxidative polycondensation of AHP using NaOCl [11]

OAHP was synthesized through oxidative polycondensation of 2-amino-3-hydroxypyridine using aqueous solution of NaOCl (0.3546 ml, 30%). The 2-amino-3-hydroxypyridine (0.200 g, 0.0018 mol) was dissolved in an aqueous solution of acetic acid (10%, 0.5 ml) or KOH (10%) (0.100 g, 0.0018 mol) and placed into a 50 ml three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and an addition to funnel containing NaOCl. At 25 °C, NaOCl was added drop wise over about 20 min. The reaction mixture was stirred between 30 and 70 °C for 1–5 h (Scheme 1, Table 1). The mixture was neutralized with KOH or acetic acid (10%). Unreacted monomer extracted by using ethanol. Then, mineral salt were separated from the reaction product by washing with water (50 ml × 3), and filtered and then dried in the oven at 105 °C. The product was brown solid.

2.3. Oxidative polycondensation of AHP using H_2O_2

AHP (0.200 g, 0.0018 mol) was dissolved in an aqueous solution of KOH (0.100, 0.0018 mol) and placed into a 50 ml three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and addition funnel containing H_2O_2. The H_2O_2 (0.1567 ml 30%) was added drop wise over of reaction mixtures at 25 °C and about at 20 min. The reaction mixture was stirred at the various temperatures for 5–10 h (Scheme 1, Table 2). Then 0.188 ml of HCl (37%) was added to the reaction mixture. Unreacted monomer extracted by using ethanol. Then, mineral salt were separated from the reaction product by washing with water (50 ml × 3), and filtered and then dried in the oven at 105 °C. The product was brown solid.

2.4. Oxidative polycondensation of AHP using air O_2

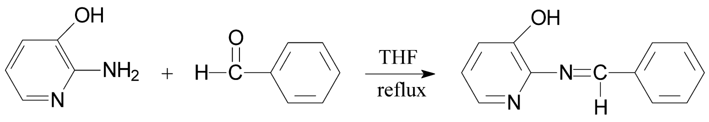
AHP (0.200 g, 0.0018 mol) was dissolved in an aqueous solution of KOH (10%) (0.100 g, 0.0018 mol) and placed into a 50 ml three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and addition to placed glass tubing over condenser for sending air oxygen. The reaction mixture was heated at the various temperatures and times (Table 3). The air was passed into rate $8.5\ l\ h^{-1}$ during the course of the reaction. In order not to have water loss in the reaction mixture and to unneutralize to CO_2 of air oxygen to KOH, air oxygen passed into an aqueous solution of KOH (20%) before sending reaction tubing (Scheme 1). It was cooled to room temperature and then 0.169 ml of HCl (37%) was added to the reaction mixture. Unreacted

Table 1
The oxidative polycondensation of 2-amino-3-hydroxy pyridine with NaOCl in an aqueous KOH and acidic medium

Sample no.	$[AHP]_0$ (mol l^{-1})	$[CH_3COOH]_0$ (mol l^{-1})	[KOH] (mol l^{-1})	$[NaOCl]_0$ (mol l^{-1})	Temperature (°C)	Time (h)	Conversion of AHP (%)
1	0.72	0.72	–	0.72	30	1	85
2	0.72	0.72	–	0.72	40	1	54
3	0.72	0.72	–	0.72	50	1	39
4	0.72	0.72	–	0.72	60	1	24
5	0.72	0.72	–	0.72	70	1	19
6	0.72	0.72	–	0.72	30	3	41
7	0.72	0.72	–	0.72	30	5	21
8	0.72	–	0.72	0.72	30	1	35
9	0.72	–	0.72	0.72	40	1	43
10	0.72	–	0.72	0.72	50	1	45
11	0.72	–	0.72	0.72	60	1	27
12	0.72	–	0.72	0.72	70	1	23
13	0.72	–	0.72	0.72	50	2	43
14	0.72	–	0.72	0.72	50	5	27

Table 2
The oxidative polycondensation of 2-amino-3-hydroxy pyridine with H_2O_2 in an aqueous KOH

Sample no.	$[AHP]_0$ (mol l^{-1})	[KOH] (mol l^{-1})	$[H_2O_2]_0$ (mol l^{-1})	Temperature (°C)	Time (h)	Conversion of AHP (%)
1	0.72	0.72	0.72	50	5	21.0
2	0.72	0.72	0.72	60	5	30.0
3	0.72	0.72	0.72	70	5	37.0
4	0.72	0.72	0.72	80	5	43.0
5	0.72	0.72	0.72	90	5	30.0
6	0.72	1.44	0.72	80	5	27.0
7	0.72	0.72	1.44	80	5	24.0
8	0.72	0.72	0.72	80	10	29.0



Scheme 2.

monomer extracted by using ethanol. Then, mineral salt were separated from the reaction product by washing with water (50 ml × 3), and filtered and then dried in the oven at 105 °C. The product was brown solid.

Anal. calcd. for OAHP: C, 55.55; H, 3.70; N, 25.93. Found: C, 54.60; H, 4.00; and N, 25.00. FT-IR (KBr; cm^{-1}): 3250 (–OH); 3331 (N–H); 1361 (C–N); 1571, 1461, 1420 (C=C); 3080 (aromatic C–H); 1210 (aromatic, C–O); 1293 (aromatic-N). UV–Vis (λ_{max}): 251, 273, 310 and 352 nm. ^{1}H NMR (DMSO): δ ppm, 10.55 (s, 1H, O*H*); 7.95 (s, 2H, N*H*$_2$); 8.99 (s, 1H, N*H*); 6.84 (s, 1H, C4–*H*); [terminal groups: 8.49 (d, 1H, C3–*H*); 7.35 (dd, 1H, C4–*H*); 8.51 (d, 1H, C5–*H*)]. ^{13}C NMR (DMSO): ppm, 135.00 (C1–*ipso*OH); 151.00 (C2–*ipso*-NH$_2$); 148.00 (C3-*ipso*); 115.00 (C4–H); 133.00 (C5-*ipso*).

2.5. Syntheses of 2-[benzilydeneimino] pyridine-3-ol (BIP) Schiff base

AHP (1.10 g, 0.01 mol) and benzaldehyde (1.06 g, 0.01 mol) were dissolved in THF (25 ml) and placed into a 50 ml two-necked round-bottom flask (Scheme 2). It was fitted with a condenser and thermometer. The mixture was stirred magnetically on a water bath at 70 °C for 2 h. Then, THF and unreacted benzaldehyde were distilled from the condensation product and then, the precipitated BIP was filtered and recrystalizied from THF and was dried in an oven at 105 °C (82%, yield).

Anal. calcd. for BIP: C, 72.73; H, 5.05; N, 14.14. Found: C, 73.40; H, 5.25; N, 13.85. FT-IR (KBr; cm^{-1}): ν (C–N) 1338 s; ν (C–C) 1517–1573 s; ν (aromatic C–H) 3250–3100 s; ν (CH=N) 1620 s; ν (Ar-OH) 3418 s; ν (olefinic –CH) 2920 s. UV–Vis (λ_{max}) : 256, 275, 305 and 358 nm. ^{1}H NMR (DMSO): δ ppm, 10.45 (s, 1H, O*H*); 9.05 (s, 1H, C*H*=N); 6.25–7.85 (m, 8H, Ar-H). ^{13}C NMR (DMSO): ppm, 148.60 (C1–*ipso*-OH), 124.80 (C2–H), 123.70 (C3–H), 141.80 (C4–H), 163.80 (C5-*ipso*), 160.10 (C6–H), 133.80 (C7-*ipso*), 129.20 (C8–H), 128.90 (C9–H), 131.10 (C10–H).

2.6. The synthesis of oligo-2-[benzilydeneimino] pyridine-3-ol using NaOCl [12]

OBIP was synthesized through oxidative polycondensation of BIP with solution in water of NaOCl (30%). The BIP (0.200 g, 0.001 mol) was dissolved in an aqueous solution of KOH (0.056 g, 0.001 mol) and placed into a 50 ml three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and an addition to funnel containing NaOCl. After heating at 50 °C for 30 min, NaOCl was added drop wise over about 20 min. The reaction mixture was heated at the various temperatures and times (Table 4). The

Table 3
The oxidative polycondensation of 2-amino-3-hydroxy pyridine with air O_2 in an aqueous KOH

Sample no.	$[AHP]_0$ (mol l^{-1})	[KOH] (mol l^{-1})	Air O_2 (l h^{-1})	Temperature (°C)	Time (h)	Conversion of AHP (%)
1	0.72	0.72	8.5	50	5	51.0
2	0.72	0.72	8.5	60	5	60.0
3	0.72	0.72	8.5	70	5	66.0
4	0.72	0.72	8.5	80	5	86.0
5	0.72	0.72	8.5	90	5	63.0
6	0.72	1.44	8.5	80	5	71.0
7	0.72	0.72	8.5	80	10	52.0

Table 4
The oxidative polycondensation of 2-benzilydeneiminopyridine-3-ol with NaOCl in an aqueous KOH

Sample no.	$[BIP]_0$ (mol l^{-1})	[KOH] (mol l^{-1})	$[NaOCl]_0$ (mol l^{-1})	Temperature (°C)	Time (h)	Conversion of BIP %
1	0.40	0.40	0.40	40	1	57.0
2	0.40	0.40	0.40	50	1	62.0
3	0.40	0.40	0.40	60	1	66.0
4	0.40	0.40	0.40	70	1	67.0
5	0.40	0.40	0.40	80	1	86.0
6	0.40	0.40	0.40	90	1	88.0
7	0.40	0.80	0.40	90	1	61.0
8	0.40	0.40	0.80	90	1	95.0
9	0.40	0.80	0.80	90	1	50.0
10	0.40	0.40	0.40	90	2	81.0
11	0.40	0.40	0.40	90	5	79.0
12	0.40	0.40	0.40	90	10	53.0

Table 5
The oxidative polycondensation of 2-(benzilydeneimino) pyridine-3-ol with H_2O_2 in an aqueous KOH

Sample no.	$[BİP]_0$ (mol l^{-1})	[KOH] (mol l^{-1})	$[H_2O_2]_0$ (mol l^{-1})	Temperature (°C)	Time (h)	Conversion of BIP (%)
1	0.40	0.40	0.40	50	5	57.0
2	0.40	0.40	0.40	60	5	85.0
3	0.40	0.40	0.40	70	5	92.0
4	0.40	0.40	0.40	80	5	55.0
5	0.40	0.40	0.40	90	5	52.0
6	0.40	0.40	0.40	70	2	57.0
7	0.40	0.40	0.40	70	10	70.0

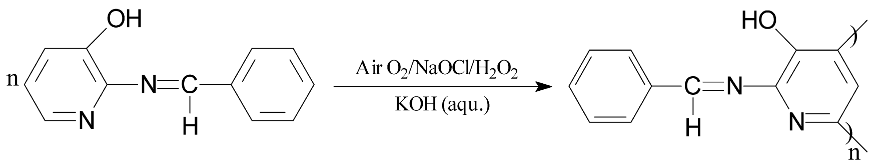
Table 6
The oxidative polycondensation of 2-benzilydeneiminopyridine-3-ol with air O_2 in an aqueous KOH

Sample no.	$[BİP]_0$ (mol l^{-1})	[KOH] (mol l^{-1})	Air O_2, (l h^{-1})	Temperature (°C)	Time (h)	Conversion of BIP (%)
1	0.40	0.40	8.5	50	5	68.0
2	0.40	0.40	8.5	60	5	74.0
3	0.40	0.40	8.5	70	5	82.0
4	0.40	0.40	8.5	80	5	91.0
5	0.40	0.40	8.5	90	5	43.0

mixture was neutralized with 0.188 ml HCl (37%) at room temperature (Scheme 3). The mixture was filtered and washed with hot water for separating from mineral salts and dried in the oven at 110 °C. The product was black solid.

2.7. The synthesis of oligo-2-[benzilydeneimino] pyridine-3-ol using H_2O_2 [12]

OBIP was synthesized through oxidative polycondensation of BIP with solution in water of H_2O_2 (30%). The BIP (0.200 g, 0.001 mol) was dissolved in an aqueous solution of KOH (0.056 g, 0.001 mol) and placed into a 50 ml three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and an addition to funnel containing H_2O_2. After heating at 40 °C for 30 min, H_2O_2 was added drop wise over about 20 min. The reaction mixture was heated at the various temperatures and times (Table 5). The mixture was neutralized with 0.188 ml HCl (37%) at room temperature (Scheme 3). The mixture was filtered and washed with hot water for separating from mineral salts and dried in the oven at 110 °C. The product was black solid.



Scheme 3.

2.8. The synthesis of oligo-2-[benzilydeneimino] pyridine-3-ol using air oxygen [12]

BIP (0.200 g, 0.001 mol) was dissolved in an aqueous solution of KOH (0.056 g, 0.001 mol) and placed into a 50 ml three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and addition to placed glass tubing over condenser for sending air oxygen. The reaction mixture was heated at the various temperatures (Table 6). The air was passed into rate 8.5 l h^{-1} during the course of the reaction. In order not to have water loss in the reaction mixture and to unneutralize to CO_2 of air oxygen to KOH, air oxygen passed into an aqueous solution of KOH (20%) before sending reaction tubing (Scheme 3). It was cooled to room temperature and then 0.188 ml of HCl (37%) was added to the reaction mixture. The mixture was filtered and washed with hot water for separating from mineral salts and dried in the oven at 110 °C. The product was black solid.

Anal. calcd. for OBIP: C, 73.47; H, 4.08; N, 14.29. Found: C, 74.10; H, 4.20; N, 13.95. FT-IR (KBr, cm^{-1}): ν (O–H) 3395 s, ν (C–H aryl) 3080 m, ν (C–H alifatic) 2920 s, ν (C=N) 1630 s, ν (aromatic, C=N) 1375 s, ν (aromatic, C–O) 1299 s, ν (–C=N–C) 1284 s, ν (aromatic, C=C) 1603, 1577, 1494 m. UV–Vis (λ_{max}) : 258, 279, 318 and 370 nm. ^{1}H NMR (DMSO): δ ppm, 11.64 (s, 1H, O*H*); 13.85 (s, 1H, COO*H*); 9.15 (s, 1H, C*H*=N); 6.33–7.96 (m, 6H, Ar-*H*). ^{13}C NMR (DMSO): ppm, 143.80 (C1–*ipso*-OH), 131.40 (C2-*ipso*), 121.40 (C3–H), 147.90 (C4-*ipso*), 164.50 (C5-*ipso*), 160.10 (C6–H), 133.50 (C7-*ipso*), 129.00 (C8–H), 128.55 (C9–H), 131.00 (C10–H).

2.9. Characterization techniques

The infrared and ultraviolet–visible spectra were measured by Perkin–Elmer BX II and Shimadzu UV-1208, respectively. Elemental analysis was carried out with a Carlo Erba 1106. The FT-IR spectra were recorded using KBr disc (4000–350 cm^{-1}). UV–Vis spectra of OAHP, BIP and OBIP were determined by using THF. OAHP, BIP and OBIP were characterized by using a ^{1}H and ^{13}C NMR spectra (Bruker DPX FT NMR spectrometer operating at 400 and 100.6 MHz, respectively) and were recorded at 25 °C by using deuterated DMSO as solvent. TMS was used as internal standard. Thermal data were obtained by using STA 409C NETZSCH-Geratebau GmbH Thermal Analysis. TG-DTA measurements were made between 20 and 1000 °C (in air, rate 10 °C min^{-1}). The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined by SEC of Shimadzu Co. For SEC investigations were used a SGX (100 Å and 7 nm diameter loading material) 7.7 mm i.d.x 300 mm columns; eluent: DMF (0.4 ml min^{-1}), polystyrene standards. A refractive index detector (RID) (at 25 °C) was used to analyze the product.

3. Results and discussion

3.1. The investigation of synthesis conditions of OAHP and OBIP

The conditions for oxidative polycondensation reaction of AHP with NaOCl solution in aqueous acidic and alkaline medium are given in Table 1. The oxidative polycondensation reaction of AHP immediately formed in an aqueous acidic and alkaline solutions and solution turned into brown by adding oxidants such as NaOCl, air O_2 and H_2O_2 were present. When $[AHP]_0 = [CH_3COOH]_0 = [NaOCl]_0 = 0.72$ mol l^{-1}, the conversion of AHP oligomer was 85.0% at 30 °C for 1 h. When $[AHP]_0 = [KOH]_0 = [NaOCl]_0 = 0.72$ mol l^{-1}, the conversion of AHP oligomer was 45.0% at 50 °C for 1 h. According to acidic medium, the conversion of AHP oligomer was less at the alkaline medium (see Table 1).

The maximum yield (43.0%) of OAHP formed at the concentrations of AHP (0.72 mol l^{-1}), H_2O_2 (0.72 mol l^{-1}) and KOH (0.72 mol l^{-1}), at 80 °C for 5 h. The yield of OAHP decreased from 43.0 to 24.0%, when increased concentration of H_2O_2 from 0.72 to 1.44 mol l^{-1} under the same conditions (Table 2). Also, the yield of oligomer was affected by increasing the concentration of KOH. AHPs know relatively less active than phenols in oxidative polycondensation. As is seen in Table 2, oligomer of AHP formed in the presence of H_2O_2 at the various initial concentration, temperatures and times.

The maximum conversion (86.0%) of OAHP formed at the concentrations of AHP (0.72 mol l^{-1}) and KOH (0.72 mol l^{-1}), at 80 °C for 5 h. The yield of OAHP increased from 66.0 to 86.0%, when increased temperature of the reaction from 70 to 80 °C under the same conditions (Table 3). Also, the conversion of AHP was affected by increasing the concentration of KOH. As is seen in Table 3, the product of AHP formed in the presence of at the various initial concentration, temperatures and times.

However, the oxidative polycondensation reaction of BIP immediately was formed in an aqueous alkaline solution and the solution turned into brown by adding oxidants such as NaOCl, H_2O_2 and air oxygen. When $[BIP]_0 = [KOH]_0 = [NaOCl]_0 = 0.40$ mol l^{-1}, the conversion of BIP to oligomer by NaOCl at 90 °C for 1 h was 88.0% (see Table 4). When $[BIP]_0 = [KOH]_0 = 0.40$ mol l^{-1} and $[NaOCl]_0 = 0.80$, the conversion of BIP to oligomer by NaOCl at 90 °C for 1 h was 95.0%. The yield of OBIP decreased from 88.0 to 53.0%, when increased times of the reaction from 1 to 10 h under the same conditions. The reason of this may be depolymerisation to monomer of oligomer at high times. Also, the conversion of BIP was affected by increasing the concentration of KOH.

The conditions of oxidative polycondensation reaction of BIP with 30% H_2O_2 solution in aqueous alkaline medium are given in Table 5. The conversion of BIP was 92.0% at optimum conditions such as $[BIP]_0 = [KOH]_0 = [H_2O_2]_0 = 0.40$ mol l^{-1}, at 70 °C for 5 h. The conversion of

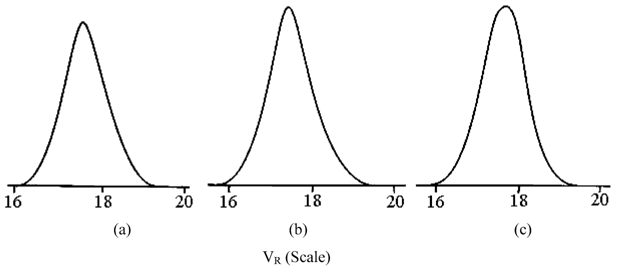


Fig. 1. The SEC analyses curves of the condensation product of (1) AHP, (a), (air oxygen, as oxidant) (b) (NaOCl, as oxidant) and (c) (H_2O_2, as oxidant).

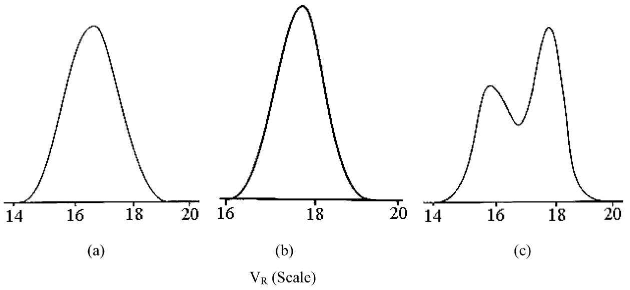
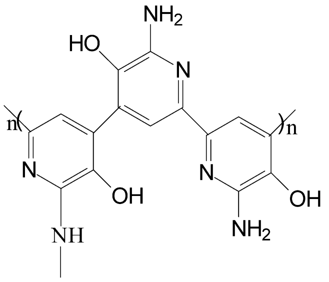


Fig. 2. The SEC analyses curves of the condensation product of (a) (air oxygen, as oxidant), (b) (H_2O_2, as oxidant) and (c) (NaOCl, as oxidant).

BIP was 70.0% at the reaction conditions such as $[BIP]_0 = [KOH]_0 = [H_2O_2]_0 = 0.40$ mol l^{-1} at 70 °C for 10 h. BIP is known relatively higher active than oligo-2-hydroxy-1-naftaldehyde (OHNA) in oxidative polycondensation [13].

The conditions of oxidative polycondensation reaction of BIP with air oxygen in aqueous alkaline medium are given in Table 6. The conversion of BIP was 91.0% at optimum conditions such as $[BIP]_0 = [KOH]_0 = 0.40$ mol l^{-1} and air O_2 8.5 l h^{-1}, at 80 °C for 5 h. The conversion of BIP was 43% at the reaction conditions such as $[BIP]_0 = [KOH]_0 = 0.40$ mol l^{-1} and air O_2 8.5 l h^{-1}, at 90 °C for 5 h. The reason of this may be depolymerisation to monomer of oligomer at high temperatures.

Because of electron-donor effect of 2-amino-3-hydroxypyridine has oxidized at alkaline and acidic medium by air oxygen, H_2O_2 and NaOCl. In this reaction, medium was brown, because of 2-amino-3-hydroxypyridine–phenoxy radicals. At this process, air oxygen was more reactive than NaOCl and H_2O_2. The oxidative polycondensation of BIP was formed in an aqueous alkaline at 40–90 °C by effect of NaOCl, air oxygen and H_2O_2. At this process, NaOCl was more reactive than air oxygen and H_2O_2.



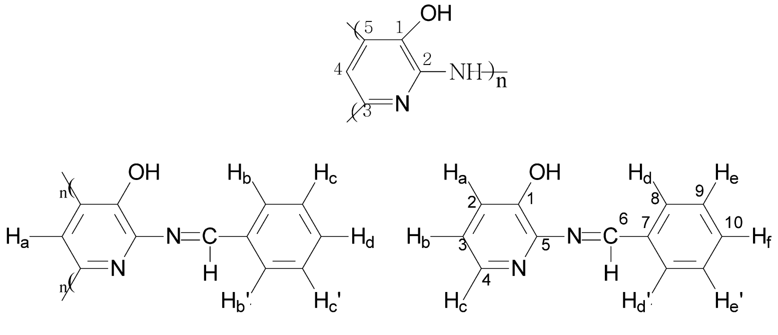
Scheme 5. The structure of OHAP.

3.2. Solubility

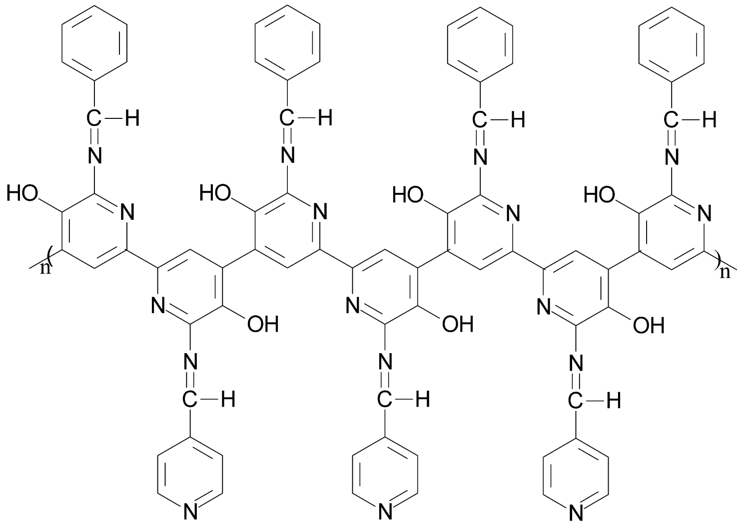
The oxidative polycondensation products that synthesized using oxidants such as air O_2, H_2O_2 and NaOCl in aqueous acidic and alkaline medium were brown solid powders. OAHP was soluble in conc. H_2SO_4, THF, DMF, DMSO and aqueous solution of NaOH. However, OAHP was any unsoluble in organic solvents such as *n*-hexane, *n*-heptane, toluene, benzene, acetone, ethyl acetate, 1,4-dioxane, methanol, ethanol, pyridine, $CHCl_3$ and CCl_4. The oxidative polycondensation products that synthesized using oxidants such as air O_2, H_2O_2 and NaOCl in aqueous alkaline medium were black and brown solid powders. The OBIP was soluble in common organic solvents such as DMSO, conc. H_2SO_4 and aqueous solution of NaOH, DMF, THF and pyridine. However, OBIP was partly soluble in methanol and ethanol. But, OBIP was any unsoluble in organic solvents such as *n*-hexane, *n*-heptane, toluene, benzene, acetone, ethyl acetate, 1,4-dioxane, $CHCl_3$ and CCl_4.

3.3. Structure of OAHP and OBIP

SEC analysis chromatograms of OAHP are given in Fig. 1. The number average molecular weight (M_n), weight average molecular weight (M_w) and PDI values of OAHP (as oxidant, air O_2) were found to be 1433, 1912 g mol^{-1} and 1.333, respectively. The M_n, M_w and PDI values of



Scheme 4.



Scheme 6. The structure of OBIP.

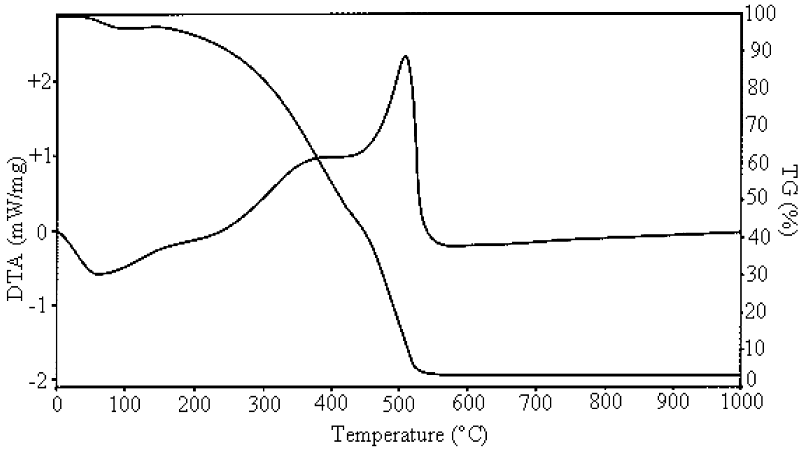


Fig. 3. DTA–TG curves of OAHP.

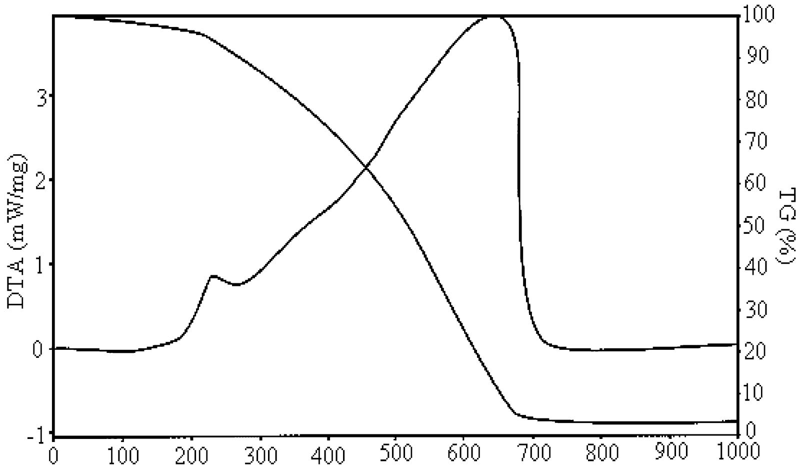


Fig. 4. DTA–TG curves of OBIP.

OAHP (as oxidant, NaOCl) were found to be 1580, 2263 g mol^{-1} and 1.432, respectively. The M_n, M_w and PDI values of OAHP (as oxidant, H_2O_2) were found to be 1462, 1907 g mol^{-1} and 1.304, respectively.

SEC analysis chromatograms of OBIP are given in Fig. 2. The M_n, M_w and PDI values of OBIP (as oxidant, air O_2) were found to be 2637, 5106 g mol^{-1} and 1.936, respectively. The M_n, M_w and PDI values of OBIP (as oxidant, H_2O_2) were found to be 2313, 3806 g mol^{-1} and 1.645, respectively. The M_n, M_w and PDI values of OBIP (as oxidant, NaOCl) were found to be 1180, 1930 g mol^{-1} and 1.64, respectively. According to SEC analysis, two peaks were observed in chromatogram of OBIP. Forty-five percent of OBIP's weight was low molecular weight ($M_n = 1254$ g mol^{-1}, $M_w = 1382$ g mol^{-1} and PDI = 1.102) but 55% of its weight was high molecular weight ($M_n = 3623$ g mol^{-1}, $M_w = 4084$ g mol^{-1} and PDI = 1.127).

At the FT-IR spectra of the OHAP, the characteristic peaks of the functional groups were observed: Phenyl–OH group at 3250 cm^{-1}, aromatic –CH groups at 3080 cm^{-1}, –NH bonding at 3331 cm^{-1} and –C=C double bond at 1571, 1461, 1420 and 1368 cm^{-1}, respectively, The characteristic peaks clearly show the binding of functional groups of the synthesized products. At the FT-IR spectrum of OBIP, the characteristic peaks of the functional groups were observed: Phenyl–OH group at 3395 cm^{-1}, aromatic –CH groups at 3080 cm^{-1}, azomethine (–CH=N) group at 1630 cm^{-1}, and –C=C double bonds at 1603, 1577, 1494 cm^{-1}, –C=N–C group at 1284 cm^{-1} and –COOH group at 1680 cm^{-1}. A part of the azomethine (–CH=N) group oxidized to carboxylic group (–COOH) during the polycondensation reaction. Thus, reaction product which is OBIP, involves 2-[benzilydeneimino] pyridine azomethine and carboxyl (–COOH) (10%) groups. The signal of proton of carboxyl (–COOH) group observed in 13.85 ppm at the ^{1}H NMR spectrum.

The electronic spectra of AHP, OAHP and BIP and OBIP were recorded in THF. At the UV–Vis spectrum of AHP, the bands were observed in 248, 268, 298 and 314 nm. K bands belong to –OH, pyridine and py–CH=N– groups were observed in 248, 268 and 298 nm, respectively. R band of $-NH_2$ group was observed in 314 nm. At the UV–Vis spectrum of OAHP, the bands were observed in 251, 273, 310 and 352 nm. K bands belong to –OH, pyridine and py–CH=N– groups were observed in 251, 273 and 310 nm, respectively. R bands of CH=N group were observed in 352 nm. At the UV–Vis spectrum of BIP, the bands were observed the same bands in 256, 275, 305 and 358 nm. K bands belong to –OH, benzene and py–CH=N– groups were observed in 256, 275 and 305 nm, respectively. R band of $-NH_2$ group was observed in 358 nm. At the UV–Vis spectrum of OBIP, the bands were observed the same bands in 258, 279, 318 and 370 nm. K bands belong to –OH, benzene and py–CH=N– groups were observed in 258, 279 and 318 nm, respectively. R bands of CH=N group were observed in 370 nm.

In order to identify the structures of OAHP and OBIP,

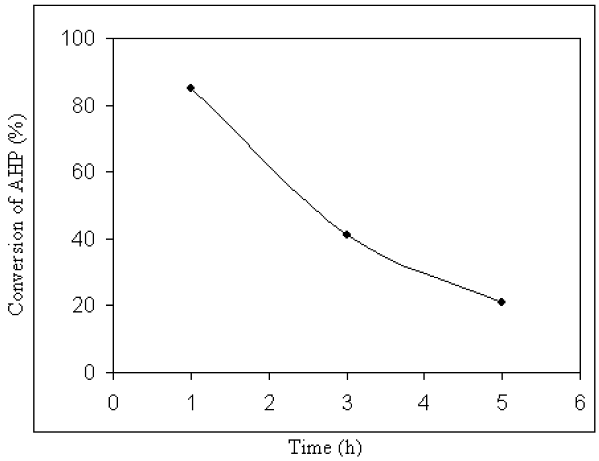


Fig. 6. According to times, % conversion of AHP with NaOCl oxidant at the oxidative polycondensation reaction at the acidic medium.

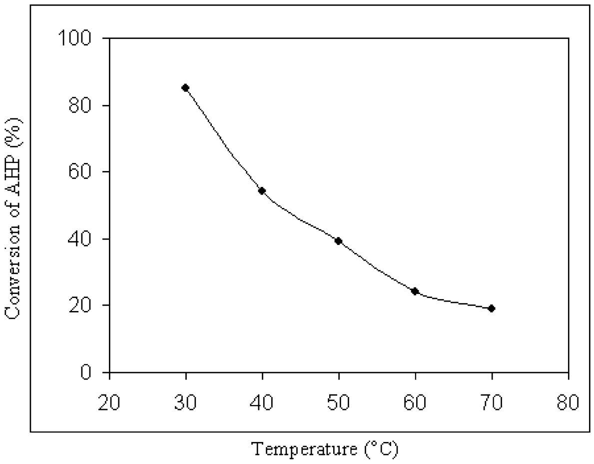


Fig. 5. According to temperature, % conversion of AHP with NaOCl oxidant at the oxidative polycondensation reaction at the acidic medium.

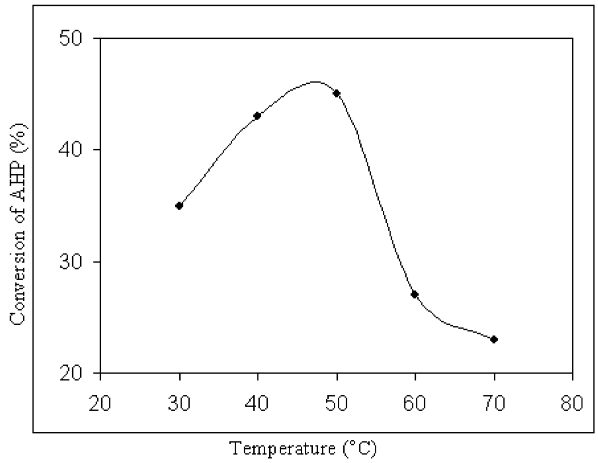


Fig. 7. According to temperature, % conversion of AHP with NaOCl oxidant at the oxidative polycondensation reaction at the alkaline medium.

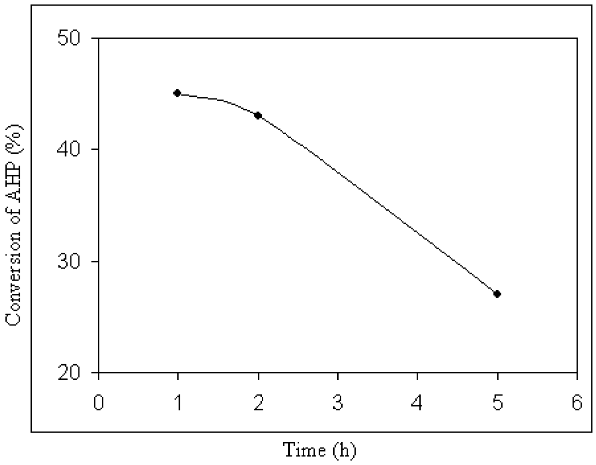


Fig. 8. According to times, % conversion of AHP with NaOCl oxidant at the oxidative polycondensation reaction at the alkaline medium.

the ^1H and ^{13}C NMR spectra were recorded in MSO-d_6. The FT-IR spectral data of the OAHP and OBIP confirm the results of the ^1H and ^{13}C NMR spectra. The ^1H and ^{13}C NMR and FT-IR results showed the formation of oligomeric macromolecules from AHP unit by the polymerization at the *ortho*, *para* and amine positions according to –OH group (Scheme 4). The ^1H and ^{13}C NMR and FT-IR results showed the formation of oligomeric macromolecules from BIP unit by the polymerization at the *ortho* and *para* positions according to –OH group (Scheme 4).

According to spectral and SEC analyses, OAHP's formula is given as follows (Scheme 5).

According to spectral and SEC analyses, OBIP's formula is given as follows (Scheme 6).

Polymers with azomethine structure containing 1,5-naphthyl or 1,4-phenyl moieties had been synthesized through polycondensation of some dialdehydes with diamines. Both monomers and polymers had been characterized by FT-IR and ^1H NMR techniques. Thermogravimetric analyses had been made for all the synthesized polymers in order to study their thermal behaviors [14].

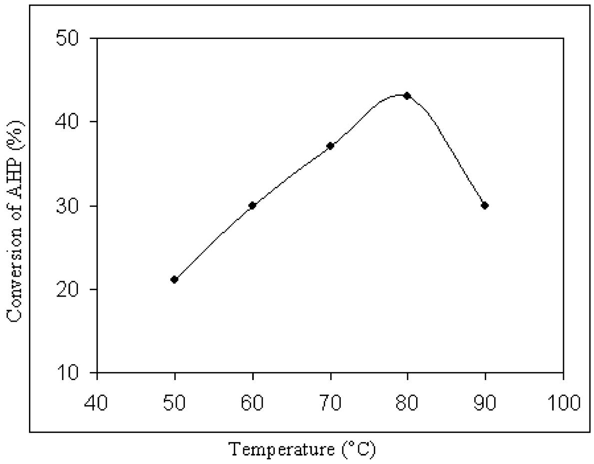


Fig. 9. According to temperatures, % conversion of AHP with H_2O_2 oxidant at the oxidative polycondensation reaction.

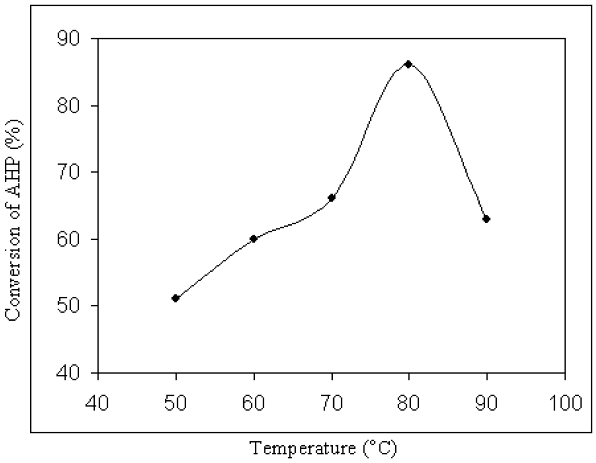


Fig. 10. According to temperatures, % conversion of AHP with air O_2 oxidant at the oxidative polycondensation reaction at the alkaline medium.

3.4. Thermal analyses of OAHP and OBIP

TGA and DTA curves of OAHP and OBIP were measured under an air atmosphere in the temperature ranges of 20–1000 °C, for investigate thermal stability. Figs. 3 and 4 shows the TG and DTA tracings for the OAHP and OBIP, respectively. OAHP and OBIP started to degradation at 180 and 220 °C, respectively. The TG data indicate that the OAHP and OBIP decomposed at low temperatures. 50% of mass of OAHP and OBIP was lost at 410 and 525 °C, respectively. OBIP demonstrated more resistance than OAHP against temperature at the same condition. The respective weight loss of OAHP and OBIP was found 97.35 and 96.60% at 520 and 685 °C, respectively. The exothermic processes of OAHP and OBIP are seen in Figs. 3 and 4. The exothermic peaks of OAHP and OBIP were observed in

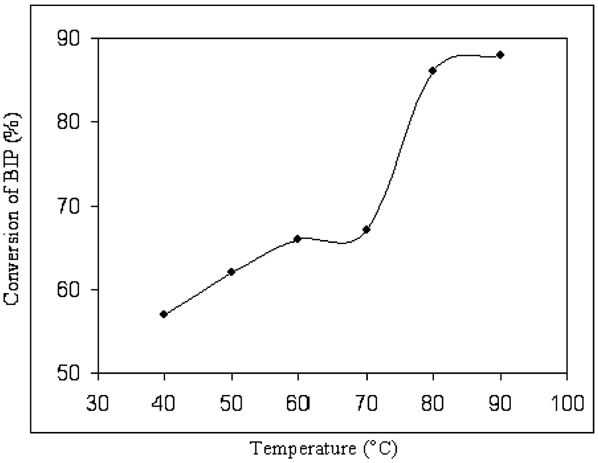


Fig. 11. According to temperatures, % conversion of BIP with NaOCl oxidant at the oxidative polycondensation reaction at the alkaline medium.

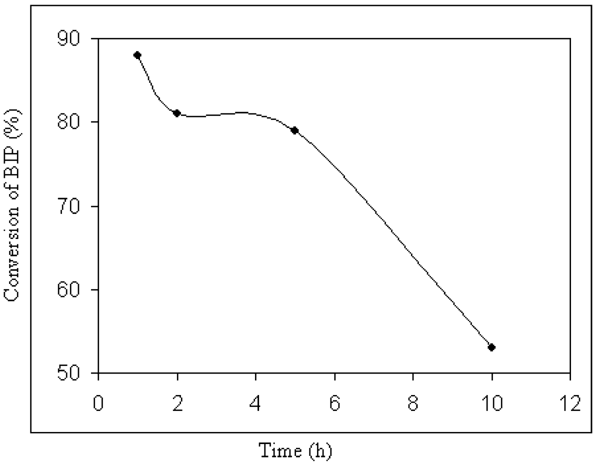


Fig. 12. According to times, % conversion of BIP with NaOCl oxidant at the oxidative polycondensation reaction at the alkaline medium.

510; 230 and 648 °C, respectively. According to DTA and TG analyses, OAHP and OBIP were observed to be unstable through to temperature and thermo-oxidative decomposition. Because OAHP and OBIP break up to the high a rate between 200 and 550 °C and 230–650 °C, respectively. İ. Kaya and co-workers had been made thermal analyses all of the synthesized Schiff base oligomers in order to study their thermal behaviors [11–13]. Thermal stabilities of pyridine ring Schiff base oligomers [11,15] were lower than oligophenols [9,13].

3.5. Kinetics study of AHP and BIP

The polymerization of AHP under the mentioned condition is influenced, as expected, by the effected temperatures and times at the air O_2, NaOCl and H_2O_2 oxidants (see Figs. 5–10). The polymerization of BIP under the mentioned condition is influenced, as expected, by the effected temperatures and times at the air O_2, NaOCl and H_2O_2 oxidants (see Figs. 11–15). It is seen that Figs. 5–15, % the effects of the reaction times and temperatures on the yield for the AHP and BIP were investigated. According to selected oxidants, the % conversion of AHP and BIP affected from temperatures, times and beginning concentration of oxidants.

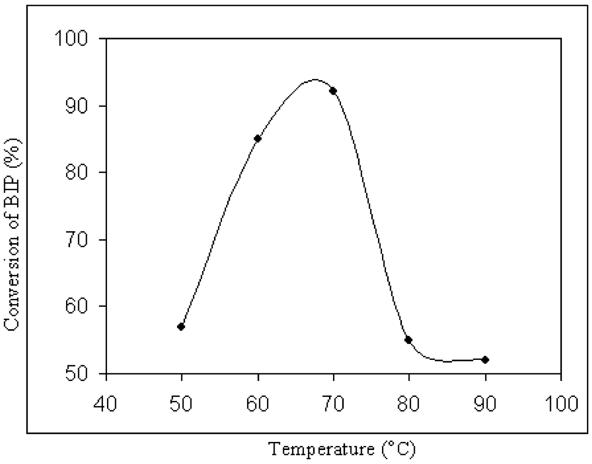


Fig. 13. According to temperatures, % conversion of AHP with H_2O_2 oxidant at the oxidative polycondensation reaction at the alkaline medium.

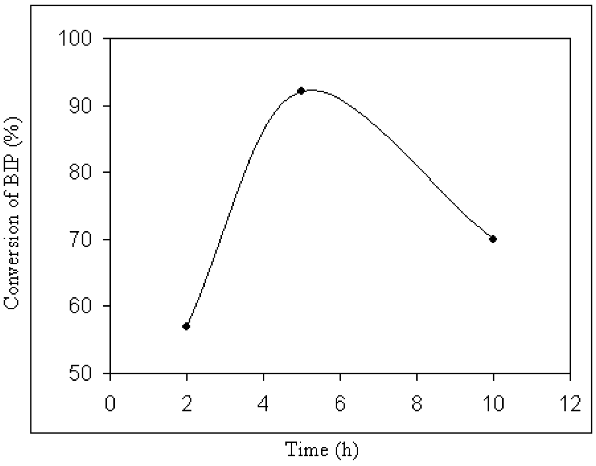


Fig. 14. According to times, % conversion of BIP with H_2O_2 oxidant at the oxidative polycondensation reaction at the alkaline medium.

4. Conclusion

According to chemical and spectral analyses, synthesized oligo-2-amino-3-hydroxypyridine (OAHP) and oligo-2-[benzilydeneimino] pyridine-3-ol (OBIP) macromolecules were appointed to formation from units bonding with *o*-and *p*-carbons of pyridine and azomethinephenol, according to –OH groups. According to SEC analyses, the M_n, M_w and PDI values of OAHP (as oxidant, NaOCl) and OBIP (as oxidant, H_2O_2) were found to be 1580, 2263 g mol^{-1} and 1.432 and 2313, 3806 g mol^{-1} and 1.645, respectively. According to these values, 86.0% and 95.0% of AHP and BIP turned into OAHP and OBIP. The % conversions of

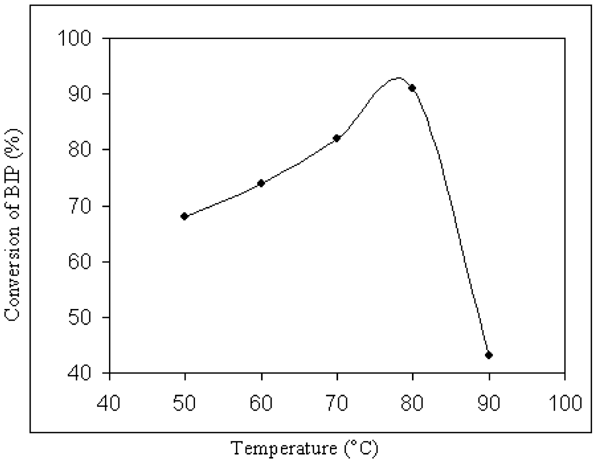


Fig. 15. According to temperatures, % conversion of BIP with air O_2 oxidant at the oxidative polycondensation reaction at the alkaline medium.

AHP and BIP were affected from temperatures, times and the initial concentration of oxidants such as NaOCl and H_2O_2. NaOCl and air oxygen demonstrated higher activity than H_2O_2 for OAHP. NaOCl demonstrated higher activity than air oxygen and H_2O_2 for OBIP. The results of DTA and TG analyses of OAHP and OBIP were demonstrated to be unstable of their, through to temperature and thermo-oxidative decomposition. The most a part of weights of OAHP and OBIP were lost at 520 and 685 °C, respectively.

References

[1] Seriven EF. Chem Soc Rev 1983;12:129.
[2] Vaidya EI. J Am Chem Soc, Polym Prep 1986;27:101.
[3] Balto BA. J Macromol Sci, Chem 1980;A14:107.
[4] Cosellato U, Vigato PA, Vidali M. J Coord Chem Rev 1977;23:31.
[5] Walter CI, Anderson HL, Sanders JK. J Chem Soc Commun 1964;4:58.
[6] Sahni KS, Reedijk J. Coord Chem Rev 1984;9:1.
[7] Kaya İ, Vilayetoğlu AR, Topak H. J Appl Polym Sci 2002;85(9):2004.
[8] Patel MN, Patıl SH. J Macromol Sci, Chem 1981;A16(8):1429.
[9] Kaya İ, Vilayetoğlu AR, Mart H. Polymer 2001;42(11):4859.
[10] Williams RJP. Biochem.Soc. Trans. 1990;18:689.
[11] Kaya İ, Koyuncu S. Polymer 2003;44(24):7299.
[12] Kaya İ, Demir HÖ, Vilayetoğlu AR. Synth Met 2002;126(2,3):183.
[13] Kaya İ, Senol D. J Appl Polym Sci 2003;90(2):442.
[14] Catanescu O, Grigoras M, Colotin G, Dobreanu A, Hurduc N, Simionescu CI. Eur Polym J 2001;37(11):2213.
[15] Kaya İ, Cihangiroğlu N. J Polym Res 2004; in press.