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올리고피리디닐메틸렌아미노피리딘올과 금속 착화물의 합성, 분석 및 열분해 특성 연구

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Synthesis, Characterization, and Thermal Degradation of Oligo-2-[(pyridin-4-yl-)methyleneamino]pyridine-3-ol and Oligomer-Metal Complexes

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Abstract : This study examined the oxidative polycondensation reaction of 2-[(pyridin-4-yl-) methyleneamino] pyridine-3-ol (2-PMAP) using air O_2 and NaOCl oxidants at various temperatures and times in aqueous alkaline and acidic media. Under these reactions, the optimum reaction conditions using air O_2 and NaOCl oxidants were determined for 2-PMAP. The number-average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) values of O-2-PMAP synthesized in aqueous alkaline media were found to be 960, 1230, and 1.281 g mol^{-1}, using NaOCl, and 1030, 1520, and 1.476 g mol^{-1}, using air O_2, respectively. At the optimum reaction conditions, the yield of O-2-PMAP in aqueous alkaline media was 92.50% and 85.70% for air O_2 and NaOCl oxidants, respectively. The yield of O-2-PMAP in aqueous acidic media was 88.5% and 88.0% for NaOCl and air O_2 oxidants, respectively. O-2-PMAP was characterized by ^1H-, ^{13}C-NMR, FT-IR, UV-vis, SEC, and elemental analysis. TGA-DTA analysis revealed O-2-PMAP and its oligomer metal complex compounds, such as Co^{+2}, Ni^{+2}, and Cu^{+2}, to be stable against thermal decomposition and their weight losses at 1000 ℃ were found to be 73.0, 58.0, 53.5%, and 50.0%, respectively. In addition, the antimicrobial activities of the monomer and oligomer were tested against *E. Coli* (ATCC 25922), *E. Faecelis* (ATCC 29212), *P. Auroginasa* (ATCC 27853), and *S. Aureus* (ATCC 25923).

Keywords : oligo-2-[(pyridin-4-yl-)methyleneamino]pyridine-3-ol, thermal analysis, oxidative polycondensation, oligomer-metal complexes, Antimicrobial activity.

Introduction

Oligophenols including conjugated bonding and hydroxyl group have been studied for more than 60 years and they have been used in various fields. They have useful properties such as paramagnetism, semi-conductivity, and resisting to high energy. Because of these properties, they are used to prepare composites having high resistance at high temperature, thermo-stabilisators, graphite materials, and epoxy oligomer and block copolymers, photo-resists, materials which are antistatic and enduring to flame.[1-10] By adding of other functional groups to these compounds, they can be profited to new useful properties. Schiff based polymers had been demonstrated anti-microbial activities against various bacteria, yeast, and fungus. Oligophenols which have a lot of functional groups may be used for cleaning poisonous heavy metals in the industrial waste waters. Therefore, the synthesis of oligomer-metal complex compounds is very important to analytical and environmental chemistry. It seemed advant-ageous to attempt to design and prepare a polymer-based chelating ligand, which would be able to form complexes with a variety of transition metals and therefore have a large range of applications.[11]

In this paper, we have investigated the effects of different

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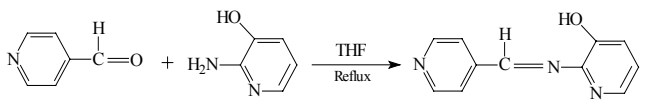
parameters such as temperature, reaction time, initial concentrations of NaOCl, HCl and alkaline for the preparation of oligo-2-[(pyridin-4-yl-) methyleneamino]pyridine-3-ol and then we determined optimum reaction conditions with oxidative polycondensation reaction for the yield of O-2-PMAP. The O-2-PMAP was characterized by FT-IR, UV-Vis, ^{1}H-, ^{13}C-NMR, elemental analysis and size exclusion chromatography (SEC) techniques. Futhermore, oligomer-metal complex compounds were synthesized from the reactions of O-2-PMAP with Co (II), Ni (II), and Cu (II) acetates. Also, thermal stabilities of O-2-PMAP and oligomer-metal complex compounds were studied by TGA-DTA techniques. Antimicrobial tests of O-4-PMAP were investigated against *S. Aureus* (ATCC 25923), *E. Faecelis* (ATCC 29212), *E.Coli* (ATCC 25922) and *P. Auroginasa* (ATCC 27853).

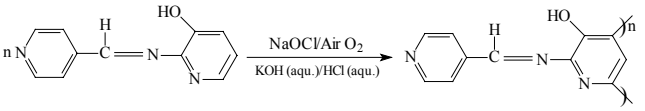
Experimental

Materials. 4-Pyridinecarbaldehyde (4-PCA), 2-amino-3-hydroxy-pyridine, methanol, ethanol, benzene, acetone, acetonitrile, toluene, heptane, hexane, 1-butanol, isoamyl alcohol, methyl acetate, ethyl acetate, dioxane, CH_2Cl_2, $CHCl_3$, CCl_4, tetrahydrofurane (THF), *N, N'*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), H_2SO_4, NaOH, KOH, hydrochloric acid (HCl, 37%), $Cu(CH_3COO)_2H_2O$, $Co(CH_3COO)_24H_2O$ and $Ni(CH_3COO)_2\ 4H_2O$ were supplied from Merck Chemical Co. (Germany) and they were used as received. Sodium hypochloride (NaOCl), (30%, aqueous solution) was supplied from Paksoy Co. (Turkey). 2-[(Pyridin-4-yl-)methyleneamino]pyridine-3-ol synthesized from condensation reaction of 4-pyridinecarbaldehyde with 2-amino-3-hydroxy-pyridine.

Syntheses of 2-[(pyridin-4-yl-) methyleneamino]pyridine-3-ol (2-PMAP) Schiff Base. 4-PCA (2.675 g, 0.025 mol) and 2-amino-3-hydroxy-pyridine (2.750 g, 0.025 mol) were dissolved in THF (50 mL) and placed into a 50 mL two-necked round-bottom flask (Scheme 1). It was fitted with a condenser and thermometer. The mixture was stirred magnetically on a water bath at 70 ℃ for 3 h. Then, the product was recrystallized in THF and it was dried in an oven at 105 ℃ (m.p.:203 ℃; yield 96%).



Scheme 1. Synthesis of 2-[(pyridin-4-yl-)methyleneamino] pyridine-3-ol.



Scheme 2. Synthesis of oligo-2-[(pyridin-4-yl-)methylene-amino] pyridine-3-ol.

Calcd. for 2-PMAP: C, 66.33; H, 4.52; N, 21.11. Found: C, 66.00; H, 4.22; N, 20.85. FT-IR (KBr; cm^{-1}): ν (CH=N) 1604 s; ν (C-O) 1286 s; ν (C=C) 1574, 1492 s; ν (aromatic C-H) 3033 s; ν (Ar-OH) 3379 s; ν (C-N=C) 1382 s. ^{1}H-NMR (DMSO): δ ppm, 10.10 (s, 1H, OH); 8.67 (s, 1H, CH=N); 6.92 (d, 1H, Ar-Ha); 6.40 (m, 1H, Ar-Hb); 7.75 (d, 1H, Ar-Hc); 7.35 (d, 2H, Ar-Hdd'); 8.50 (d, 2H, Ar-Hee'). ^{13}C-NMR (DMSO): ppm, 149.85 (C1-ipso), 123.39 (C2), 119.50 (C3), 140.35 (C4), 150.51(C5-ipso), 168.30 (C6), 135.46 (C7-ipso), 122.44 (C8), 150.67 (C9).

Synthesis of O-2-PMAP with NaOCl and air O_2 in Aqueous Alkaline Medium. O-2-PMAP was synthesized through oxidative polycondensation of 2-[(pyridin-4-yl-) methyleneamino] pyridine-3-ol with aqueous solutions of NaOCl (30%) and air O_2, respectively.[12] The 2-PMAP (0.2985 g, 1.5×10^{-3} mol) was dissolved in an aqueous solution of KOH (10%, 0.084 g, 1.5×10^{-3} mol) and placed into a 50 mL three-necked round-bottom flask (Scheme 2). It was fitted with a condenser, thermometer, stirrer and an addition funnel containing NaOCl. After heating to 40 ℃, NaOCl was added drop by drop over about 30 min. The reaction mixtures were stirred at the various temperatures and durations (Table 1). The air O_2 was passed into an aqueous solution of KOH (20%) before being sent through the reaction tube to prevent water loss in the reaction mixture and to neutralize CO_2 in the air. The reaction mixtures were cooled to room temperature, and then 1.5×10^{-3} mol HCl (37%) was added. The mixture was filtered and washed in 25 mL of hot water for three times and then dried in an oven at 110 ℃. The unreacted monomer was extracted by THF from the product.

Calcd. for O-2-PMAP : C, 67.00; H, 3.55; N, 21.32. Found: C, 66.20; H, 3.72; N, 20.90. FT-IR (KBr, cm^{-1}): ν (O-H) 3321 s; ν (C-H aryl) 3030 m; ν (C=N) 1632 s; ν (aromatic, C-O) 1261 s; ν (C-N=C) 1372 s; ν (aromatic, C=C) 1572, 1487 m. ^{1}H-NMR (DMSO): δ ppm, 10.28 (s, 1H, OH); 8.79 (s, 1H, CH=N); 7.30 (d, 1H, Ar-Ha in terminal position); 7.37 (m, 1H, Ar-Hb); 7.41 (d, 1H, Ar-Hc, in terminal position); 7.81 (d, 2H, Ar-Hdd'); 8.50 (d, 2H, Ar-Hee'). ^{13}C-NMR (DMSO): ppm, 150.40 (C1-ipso), 123.79 (C2), 115.43(C3), 146.51 (C4), 151.65(C5-ipso), 176.34 123.79 (C6), 137.12 (C7-ipso), 123.25 (C8), 152.76 (C9), 127.61 (new peak of C-C coupling system).

Table 1. The Oxidative Polycondensation of 2-[(pyridin-4-yl-)methyleneamino]pyridine-3-ol Using NaOCl (Sample number: 1-21) and Air O_2 (Sample number: 22-35) in an Aqueous Alkaline

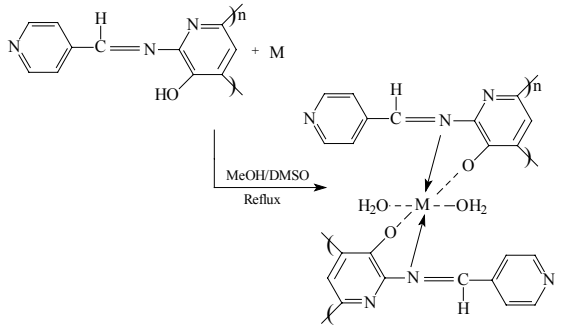
Sample number	$[2-PMAP]_0$ (mol L^{-1})	$[KOH]_0$ (mol L^{-1})	$[NaOCl]_0$ (mol L^{-1})/ Air O_2 (L/h)	Temp. (℃)	Time (h)	Yield of O-2-PMAP (%)
1	0.05	0.05	0.05	40	5	65.70
2	0.05	0.05	0.05	50	5	72.00
3	0.05	0.05	0.05	60	5	66.70
4	0.05	0.05	0.,05	70	5	64.00
5	0.05	0.05	0.05	80	5	61.30
6	0.05	0.05	0.05	90	5	32.00
7	0.05	0.05	0.10	50	5	64.30
8	0.05	0.10	0.10	50	5	85.70
9	0.05	0.10	0.15	50	5	69.30
10	0.05	0.10	0.05	50	5	81.00
11	0.05	0.15	0,05	50	5	59.00
12	0.05	0.15	0.10	50	5	63.70
13	0.05	0.15	0.15	50	5	43.70
14	0.05	0.05	0.15	50	5	68.30
15	0.05	0.15	0.20	50	5	34.30
16	0.05	0.20	0.15	50	5	79.70
17	0.05	0.20	0.20	50	5	83.00
18	0.05	0.10	0.10	50	1	76.00
19	0.05	0.10	0.10	50	3	80.30
20	0.05	0.10	0.10	50	10	56.50
21	0.05	0.10	0.10	50	20	45.50
22	0.034	0.034	8.5	40	5	58.50
23	0.034	0.034	8.5	50	5	92.50
24	0.034	0.034	8.5	60	5	78.00
25	0.034	0.034	8.5	70	5	69.50
26	0.034	0.034	8.5	80	5	63.00
27	0.034	0.034	8.5	90	5	59.50
28	0.034	0.068	8.5	50	5	31.50
29	0.034	0.072	8.5	50	5	37.00
30	0.068	0.068	8.5	50	5	52.75
31	0.068	0.072	8.5	50	5	36.75
32	0.072	0.072	8.5	50	5	54.17
33	0.034	0.034	8.5	50	1	64.00
34	0.034	0.034	8.5	50	3	60.00
35	0.034	0.034	8.5	50	10	43.00

Synthesis of O-2-PMAP with NaOCl and Air O_2 in Aqueous Acidic Medium. O-2-PMAP was synthesized through oxidative polycondensation of 2-[(pyridin-4-yl-) methyleneamino] pyridine-3-ol with aqueous solutions of NaOCl (30%) and air O_2, respectively.[12] The 2-PMAP (0.2985 g, 1.5×10^{-3} mol) was dissolved in an aqueous solution of HCl (0.084 g, 1.5×10^{-3} mol) and placed into a 50 mL three-necked round-bottom flask (Scheme 2). It was fitted with a condenser, thermometer, stirrer and an addition funnel containing NaOCl. After heating to 40 ℃, NaOCl was added drop by drop over about 30 min. The reaction mixtures were stirred at the various temperatures and durations (Table 2). The air O_2 was passed into an aqueous solution of KOH (20%) before being sent through the reaction tube to prevent water loss in the reaction mixture and to neutralize CO_2 in the air. The reaction mixtures were cooled to room temperature, and then 1.5×10^{-3} mol KOH (10%) was added. The mixture was filtered and washed in 25 mL of hot water for three times and then dried in an oven at 110 ℃. The unreacted monomer was extracted by THF from the product.

Syntheses of Oligo-2-[(pyridin-4-yl-)methyleneamino]pyridine-3-ol-metal Complexes. Cobalt (II) Complex: A solution of $Co(AcO)_2 4H_2O$ (0.300 g, 1.21×10^{-3} mol) in methanol (10 mL) was added to a solution of O-2-PMAP (0.500 g, 2.5×10^{-3} mol/unit) in DMSO (20 mL). The mixture was stirred and heated at 70 ℃ for 5 h (Scheme 3). The precipitated complex was filtered, washed with cold methanol/DMSO and then dried in vacuum oven (yield 63%).

Table 2. The Oxidative Polycondensation of 2-[(pyridin-4-yl-)methyleneamino]pyridine-3-ol Using Air NaOCl (Sample number: 1–18) and Air O_2 (Sample number: 19-32) in an Aqueous Acidic

Sample number	$[2-PMAP]_0$ (mol L^{-1})	$[HCl]_0$ (mol L^{-1})	$[NaOCl]_0$ (mol L^{-1})/ Air O_2 (L/h)	Temp. (℃)	Time (h)	Yield of O−2−PMAP (%)
1	0.05	0.10	0.05	40	5	58.70
2	0.05	0.10	0.05	50	5	68.50
3	0.05	0.10	0.05	60	5	47.00
4	0.05	0.10	0.05	70	5	42.00
5	0.05	0.10	0.05	80	5	40.00
6	0.05	0.10	0.05	90	5	35.00
7	0.05	0.10	0.10	50	5	79.50
8	0.05	010	0.15	50	5	73.00
9	0.05	0.15	0.10	50	5	87.50
10	0.05	0.20	0.10	50	5	78.50
11	0.05	0.10	0.20	50	5	43.00
12	0.05	0.20	0.15	50	5	76.00
13	0.05	0.15	0.10	50	5	88.50
14	0.05	0.15	0.20	50	5	41.00
15	0.05	0.15	0.05	50	1	70.00
16	0.05	0.15	0.05	50	3	74.50
17	0.05	0.15	0.05	50	10	39.50
18	0.05	0.15	0.05	50	20	37.50
19	0.034	0.068	8.5	40	5	76.00
20	0.034	0.068	8.5	50	5	88.00
21	0.034	0.068	8.5	60	5	48.50
22	0.034	0.068	8.5	70	5	34.50
23	0.034	0.068	8.5	80	5	26.50
24	0.068	0.068	8.5	50	5	60.75
25	0.068	0.072	8.5	50	5	54.00
26	0.034	0.072	8.5	50	5	60.00
27	0.072	0.068	8.5	50	5	51.00
28	0.072	0.072	8.5	50	5	56.20
29	0.034	0.034	8.5	50	3	74.00
30	0.034	0.034	8.5	50	7	53.00
31	0.034	0.034	8.5	50	10	41.00
32	0.034	0.034	8.5	50	20	32.00



Scheme 3. Synthesis of oligo−2−[(pyridin−4−yl−)methylene−amino]pyridine−3−ol−metal complex compounds.

Calcd. for O−2−PMAP−Co: M, 23.03. Found: M, 22.45. UV−Vis (λ_{max}): 209, 237, 278, 335 and 380 nm. FT−IR (KBr, cm^{-1}): ν (O−H) 3381 s, ν (C−H aryl) 3055 m, ν (C=N) 1636 s, ν (aromatic, C−O) 1272 s, ν (aromatic, C=C) 1546, 1528, 1495 m, ν (M−O) 559 s, ν (M−N) 655 s.

Nickel (II) Complex: A solution of $Ni(AcO)_2 4H_2O$ (0.300 g, 1.21×10^{-3} mol) in methanol (10 mL) was added to a solution of O−2−PMAP (0.500 g, 2.5×10^{-3} mol/unit) in DMSO (20 mL). The mixture was stirred and heated at 70 ℃ for 5 h (Scheme 3). The precipitated complex was filtered, washed with cold methanol/DMSO and then dried in vacuum oven (yield 59%).

Calcd. for O−2−PMAP−Ni: M, 22.66. Found: M, 22.00. UV−Vis (λ_{max}): 208, 237, 281, 341 and 388 nm. FT−IR (KBr, cm^{-1}): ν (O−H) 3370 s, ν (C−H aryl) 3048 m, ν (C=N) 1608 s, ν (aromatic, C−O) 1258 s, ν (aromatic, C=C) 1561, 1542, 1491 m, ν (M−O) 534 s, ν (M−N) 633 s.

Copper (II) Complex: A solution of $Cu(AcO)_2 H_2O$ (0.250 g, 1.25×10^{-3} mol) in methanol (5 mL) was added to a solution

of O-2-PMAP (0.500 g, 2.5×10^{-3} mol/ unit) in DMSO (20 mL). The mixture was stirred and heated at 70 ℃ for 5 h (Scheme 3). The precipitated complex was filtered, washed with cold methanol/DMSO and then dried in vacuum oven (yield 62%).

Calcd. for O-2-PMAP-Cu: M, 24.39. Found: M, 23.70. UV-Vis (λ_{max}): 206, 238, 280, 341 and 384 nm. FT-IR (KBr, cm^{-1}): ν (O-H) 3366 s, ν (C-H aryl) 3090 m, ν (C=N) 1616 s, ν (aromatic, C-O) 1265 s, ν (aromatic, C=C) 1542, 1521, 1470 m, ν (M-O) 577 s, ν (M-N) 641 s.

Preparation of Microbial Cultures. Preparation of Test Microorganism and Test Compounds: *E. Coli* (ATCC 25922), *E. Faecelis* (ATCC 29212), *P. Auroginasa* (ATCC 27853) and *S. Aureus* (ATCC 25923) were used as the test organisms in an antimicrobial study. The testing bacteria were supplied from Refik Saydam Hıfzısıhha Institute (Ankara, Turkey). The bacteria strains were inoculated into nutrient broth (Difco) incubated for 24 h. Using the Disc Diffusion method, the sterile Mueller Hinton Agar (Oxoid) was inoculated with the test microorganisms.[17] The compounds were dissolved at a concentration of 25 mg/mL in order to obtain a final concentration of 1 mg/0.1 mL. In all, two different concentrations of the drug were prepared (1 mg/1 mL and 0.1 mg/1 mL) for the microbiological assays and absorbed on sterile paper antibiotic discs, which were placed in wells (6 mm diameter) cut in the agar media. The plates were incubated at 32 ℃ (24 h). The resulting inhibition zones on the plates were measured after 48 h.

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 2-PMAP, O-2-PMAP, O-2-PMAP-Co, O-2-PMAP-Ni and O-2-PMAP-Cu were determined by using DMSO. 2-PMAP and O-2-PMAP HPMDAP and OHPMDAP were characterized by using ^{1}H and ^{13}C-NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) and recorded by using deuterated DMSO-d_6 as a solvent at 25 ℃. Tetramethylsilane was used as internal standard. Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis. The TGA-DTA measurements were made between 20-1000 ℃ (in N_2, rate 10 ℃/min). The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) were determined by size exclusion chromatography (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/Methanol (4/1, v/v; 0.4 mL min^{-1}), polystyrene standards. A refractive index detector was used to analyze the product at 25 ℃.

Results and Discussion

Investigation of Synthetic Conditions of O-2-PMAP. The conditions of oxidative polycondensation reaction of 2-PMAP with NaOCl in aqueous alkaline medium are given in Table 1. The oxidative polycondensation reaction of 2-PMAP was immediately formed phenoxy radicals in an aqueous alkaline solution and the solution turned into brown by adding oxidants such as NaOCl and air O_2. When $[KOH]_0=[NaOCl]_0=$ 0.1 mol/L and $[2\text{-PMAP}]_0=0.05$ mol/L, the yield of O-2-PMAP was 85.70% by NaOCl at 50 ℃ for 5 h. When $[2\text{-PMAP}]_0=[KOH]_0=[NaOCl]_0=0.05$ mol/L, the yield of O-2-PMAP was 66.70% by NaOCl at 60 ℃ for 5 h. The yield of O-2-PMAP increased from 64.30% to 85.70%, when the concentration of KOH was increased under the same conditions. The activity of salicylaldehyde is known to be relatively higher than 2-hydroxy-1-naphtaldehyde in oxidative polycondensation.[13] The conditions of oxidative polycondensation reaction of 2-PMAP with air O_2 in aqueous alkaline medium are given in Table 1. The yield of O-2-PMAP was 62.80% at the reaction conditions such as $[2\text{-PMAP}]_0=[KOH]_0=0.034$ mol/L and air O_2 8.5 L/h, at 50 ℃ for 5 h. The yield of O-2-PMAP was 78.0% at the reaction conditions such as $[2\text{-PMAP}]_0=[KOH]_0=0.034$ mol/L and air O_2 8.5 L/h, at 60 ℃ for 5 h. The reason may be depolymerization to monomer of oligomer at high temperatures.

The conditions of oxidative polycondensation reaction of 2-PMAP with NaOCl in aqueous acidic medium are given in Table 2. The oxidative polycondensation reaction of 2-PMAP was immediately formed phenoxy radicals in an aqueous acidic solution and the solution turned into brown by adding oxidants such as NaOCl and air O_2. When $[2\text{-PMAP}]_0=0.05$ mol/L, $[HCl]_0=0.15$ mol/L and $[NaOCl]_0=0.1$ mol/L, the yield of O-2-PMAP was 88.50% by NaOCl at 50 ℃ for 5 h. When $[2\text{-PMAP}]_0=0.05$ mol/L, $[HCl]_0=0.1$ mol/L and $[NaOCl]_0=$ 0.2 mol/L, the yield of O-2-PMAP was 43.0% by NaOCl at 50 ℃ for 5 h. The yield of O-2-PMAP increased from 79.50% to 87.50, when the concentration of HCl was increased under the same conditions. According to the results, the yield O-2-PMAP was affected by increasing both HCl and KOH concentrations. Because of electron-donor effect of azomethine group, 2-[(pyridin-4-yl-) methyleneamino] pyridine-3-ol has oxidized both in alkaline and acidic medium by air O_2 and NaOCl. In these reactions, because of formation of phenoxy radicals of 2-[(pyridin-4-yl-)methylene-amino]pyridine-3-ol compound, solution medium was turned

into brown. The oxidative polycondensation of 2-[(pyridin-4-yl-)methyleneamino]pyridine-3-ol was formed in an aqueous alkaline at 40-90 ℃ by effect of NaOCl and air O_2. At this process, air O_2 oxidant was more reactive than NaOCl.

The conditions of oxidative polycondensation reaction of 2-PMAP with air O_2 in aqueous acidic medium are given in Table 2. The yield of O-2-PMAP was 88.0% at the reaction conditions such as $[2\text{-PMAP}]_0$=0.034, $[HCl]_0$=0.068 mol/L and air O_2 8.5 L/h, at 50 ℃ for 5 h. The yield of O-2-PMAP was 60.0% at the reaction conditions such as $[2\text{-PMAP}]_0$=0.034, $[HCl]_0$=0.072 mol/L and air O_2 8.5 L/h, at 50 ℃ for 5 h. The reason may be depolymerization to monomer of oligomer at high concentration of HCl.

Solubility. The oxidative polycondensation product of 2-PMAP with NaOCl and air O_2 in aqueous alkaline and acidic medium was black solid powders. O-2-PMAP was soluble in conc.H_2SO_4, DMF and DMSO. O-2-PMAP was insoluble in toluene, acetone, methyl acetate, ethyl acetate, dioxane, benzene, methanol, ethanol, 1-butanol, isoamyl alcohol, and chlorinated solvents such as CH_2Cl_2, $CHCl_3$ and CCl_4 but it was poorly soluble in THF and acetonitrile. O-2-PMAP was insoluble in aliphatic hydrocarbons such as heptane and hexane. O-2-PMAP with Co^{+2}, Ni^{+2} and Cu^{+2} acetates was insoluble in water at room temperature. The new oligomer-metal complexes were soluble in DMSO.

Structure of O-2-PMAP. According to SEC chromatograms, the values of number-average molecular weight (M_n) and weight-average molecular weight (M_w) of O-2-PMAP were calculated according to a polystyrene standard calibration curve and are given in Table 3. According to the SEC analysis, the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) values of O-2-PMAP synthesized in an aqueous acidic medium were found to be 840, 1300 and 1.548 g mol^{-1}, using air O_2, and 2770, 3440 and 1.242 g mol^{-1}, using NaOCl, respectively. These values of O-2-PMAP synthesized in an aqueous acidic medium were higher than alkaline medium (see Table 3).

The biologic activities of 2-PMAP and O-2-PMAP were examined against *E. Coli* (ATCC 25922), *E. Faecelis* (ATCC 29212), *P. Auroginasa* (ATCC 27853) and *S. Aureus* (ATCC 25923) microorganisms. The lowest concentration (0.1 mg/1 mL) had little effect while the compounds were slightly effective (inhibition zone is not shown) and they have not demonstrated to any activities for these compounds. But, 2-PMAP and O-2-PMAP demonstrated slightly the biologic activity at the high concentrations (1 mg/1 mL). Both 2-PMAP and O-2-PMAP showed very little antibacterial activity against *E. Coli* (ATCC 25922), *E. Faecelis* (ATCC 29212), *P. Auroginasa* (ATCC 27853) and *S. Aureus* (ATCC 25923) microorganisms. The inhibition zones (mm) of 2-PMAP and O-2-PMAP were measured as 2, 3; 4, 6; 3, 5; 2 and 1, for *E. Coli* (ATCC 25922), *E. Faecelis* (ATCC 29212), *P. Auroginasa* (ATCC 27853) and *S. Aureus* (ATCC 25923) bacteria, respectively.

At the FT-IR spectrum of 2-PMAP, the characteristic bands of the functional groups were observed: Phenyl-OH group at 3379 cm^{-1}, aromatic -CH groups at 3033 cm^{-1}, azomethine (-CH=N) group at 1604 cm^{-1}, -C-N=C group at 1382 cm^{-1} and -C=C double bonds at 1574, 1492 cm^{-1}. At the FT-IR spectrum of O-2-PMAP, the characteristic peaks of the functional groups were observed: Phenyl-OH

Table 3. The Number Average Molecular Weight (M_n), Weight Average Molecular Weight (M_w), Polydispersity Index (PDI) and % Values of Oxidative Polycondensation Products of O-2-PMAP

Compounds	Total			Molecular weight distribution parameters											
				Fraction I				Fraction II				Fraction III			
	M_n	M_w	PDI	M_n	M_w	PDI	%	M_n	M_w	PDI	%	M_n	M_w	PDI	%
O-2-PMAP[a]	830	1335	1.608	1850	2230	1.205	96	3300	8000	2.424	4	-	-	-	-
O-2-PMAP[a]	960	1230	1.281	1530	2130	1.392	88	2580	6500	2.519	12	-	-	-	-
O-2-PMAP[a]	780	950	1.218	1520	1860	1.227	85	1940	3390	1.747	10	17150	18300	1.067	5
O-2-PMAP[a]	900	1200	1.333	1250	1820	1.457	95	12750	14000	1.098	5	-	-	-	-
O-2-PMAP[a]	800	1270	1.588	1530	2130	1.397	90	2540	6200	2.441	10	-	-	-	-
O-2-PMAP[a]	1030	1520	1.476	1850	2230	1.203	85	3250	7660	2.352	15	-	-	-	-
O-2-PMAP[b]	2460	3560	1.447	1240	1450	1.169	75	15950	24100	1.511	25	-	-	-	-
O-2-PMAP[b]	950	1550	1.632	1720	1980	1.153	96	3440	13100	3.808	10	-	-	-	-
O-2-PMAP[b]	2770	3440	1.242	1400	1900	1.357	90	42600	51400	1.206	10	-	-	-	-
O-2-PMAP[b]	12000	15200	1.267	1700	2300	1.353	65	65800	82500	1.254	35	-	-	-	-
O-2-PMAP[b]	840	1300	1.548	1570	2140	1.361	90	2650	7000	2.642	10	-	-	-	-
O-2-PMAP[b]	900	1280	1.422	1440	2100	1.460	95	8000	11300	1.413	5	-	-	-	-

[a]Table 1, Sample No: 2, 10, 17, 21, 23 and 33. [b]Table 2, Sample No: 9, 10, 13, 18, 20, 29.

group at 3321 cm^{-1}, aromatic −CH groups at 3030 cm^{-1}, azomethine (−CH=N) group at 1632 cm^{-1}, −C−N=C at 1372 cm^{-1} and –C=C double bonds at 1572, 1487 cm^{-1}.

The electronic spectra of 2−PMAP and O−2−PMAP were recorded in DMSO. The λ_{max} values of 2−PMAP was observed in 204, 243, 279, 308 and 325 nm. K band belong to –OH and azomethine groups of 2−PMAP was observed in 243 and 325 nm, respectively. B and R bands of 2−PMAP were observed in 279 and 308 nm. R band of CH=N group of 2−PMAP was observed in 325 nm. The same bands were observed in 209, 245, 288, 320 and 345 nm at the UV−vis spectrum of O−2−PMAP. K bands belong to −OH and azomethine groups of O−2−PMAP were observed in 245 and 320 nm, respectively. R band of CH=N group of O−2−PMAP was observed in 345 nm. In the oligomer−metal complexes, the low intensity bands in the 450−550 nm range are consistent with d→ d transitions of the metal ions.

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 ^{1}H−NMR techniques. Thermogravimetric analyses had been made for all the synthesized polymers in order to study their thermal behaviors.[14]

In order to identify the structures of 2−PMAP and O−2−PMAP, the ^{1}H− and ^{13}C−NMR spectra were recorded in DMSO−d_6 and are given in Figures 1 and 2, respectively. The signals of −OH and −CH=N groups of 2−PMAP and O−2−PMAP were observed in 10.10, 8.67, and 10.28 and 8.79 ppm, respectively. The ^{1}H− and ^{13}C−NMR spectra showed the formation of oligomeric macromolecules from 2−PMAP unit by the polymerization at the *ortho* and *para* positions according to −OH group. The reaction mechanism on the coupling selectivity has been studied by Kaya *et al.* and three possible reaction mechanisms for the C−C coupling selectivity have been proposed as literature.[15] The peak values for C2 and C4 observed in 123.39 and 140.35 ppm in the monomer and 123.79 and 146.51 ppm in the oligomer, respectively. 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. The phenyl rings in the oligomer appears to be linked primarily at *ortho* and *para* positions. On the other hand, the new peak was observed in 127.61 ppm in the ^{13}C−NMR. This peak is not present in the case of monomer. At the spectra of oligomer this new peak has assigned to C−C coupling system (Scheme 4). Chemical shift values of carbon atoms of azomethine groups of monomer and oligomer shifted from 168.30 to 176.34 ppm, respectively. The ^{13}C−NMR spectrum of O−2−MPIMP has been demonstrated C−C coupling systems. Schiff base monomer and dimer interconversion combinations of radical units are proposed as literature.[16]

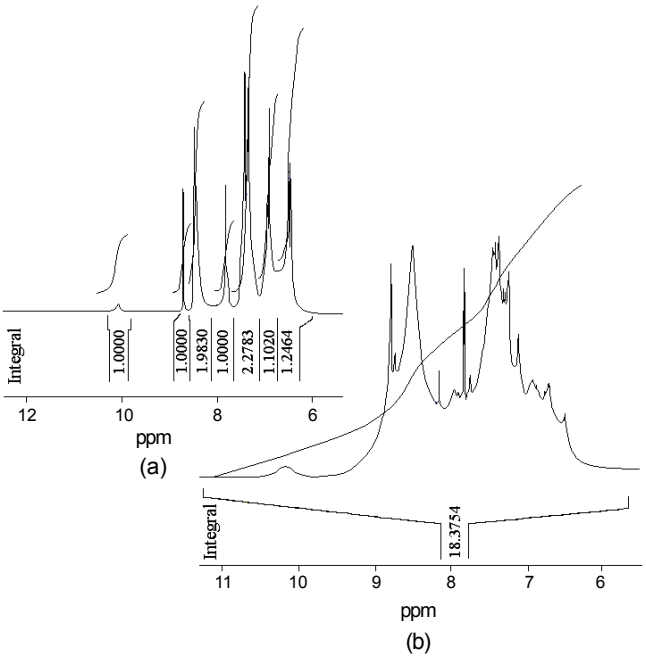


Figure 1. ^{1}H−NMR spectrum of 2−PMAP (a) and O−2−PMAP (b).

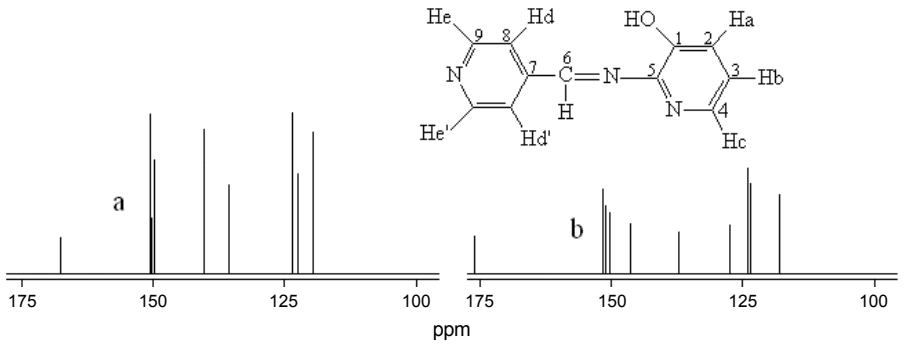
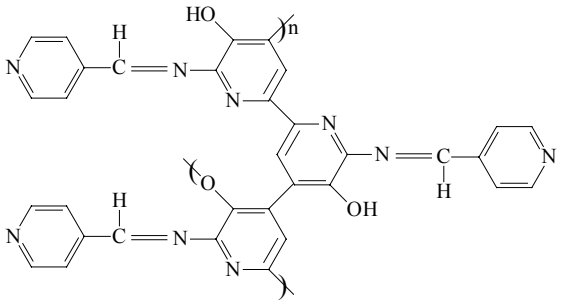


Figure 2. ^{13}C−NMR spectrum of 2−PMAP (a) and O−2−PMAP (b).

Thermal Analyses of O-2-PMAP and Its Oligomer-Metal Complexes. TGA-DTG-DTA traces of O-2-PMAP, O-2-PMAP-Cu, O-2-PMAP-Ni and O-2-PMAP-Co compounds were measured under an N_2 atmosphere in the temperature ranges of 20-1000 ℃ for their investigation of thermal stability. O-2-PMAP started to degradation at 203 ℃. The respective weight loss of O-2-PMAP was found to be 73% at 1000 ℃. 50% of O-2-PMAP's mass were lost at 720 ℃. The total weight of O-2-PMAP was lost between 225-675 ℃.



Scheme 4. The structure of oligo-2-[(pyridin-4-yl-) methyl-eneamino]pyridine-3-ol.

TGA-DTG-DTA curves of O-2-PMAP, O-2-PMAP-Co, O-2-PMAP-Ni and O-2-PMAP-Cu compounds are given in Figures 3, 4, 5 and 6. The carbonaceous residues of O-2-PMAP-Co, O-2-PMAP-Ni and O-2-PMAP-Cu compounds were found to be 42.0, 46.5 and 50.0% at 1000 ℃, respectively. 50% of weights of O-2-PMAP-Co, O-2-PMAP-Ni and O-2-PMAP-Cu were lost at 636, 832 and 1000 ℃, respectively. The total weights of them were lost between 230-800 ℃. Metal complexes of O-2-PMAP were demonstrated higher thermal stable than oligomer. The initial degradation temperatures of O-2-PMAP-Cu, O-2-PMAP-Ni and O-2-PMAP-Co were found to be 226, 229 and 200 ℃, respectively. According to these parameters, Cu^{+2} complex was showed more stable than Co^{+2} and Ni^{+2} complexes. Total weight loses of Cu^{+2}, Ni^{+2} and Co^{+2} complexes of O-2-PMAP were 50.0, 53.5 and 58.0%, respectively, at 1000 ℃. Exothermic process of Cu^{+2}, Ni^{+2} and Co^{+2} complexes of O-2PMAP started between 200-850 ℃ and T_{max} values were 600, 586 and 628 ℃, respectively. Thermal degradation of O-2-PMAP while complexes delineated the order as follows: $Cu^{+2} > Ni^{+2} > Co^{+2}$. The presence of water can be seen in TGA

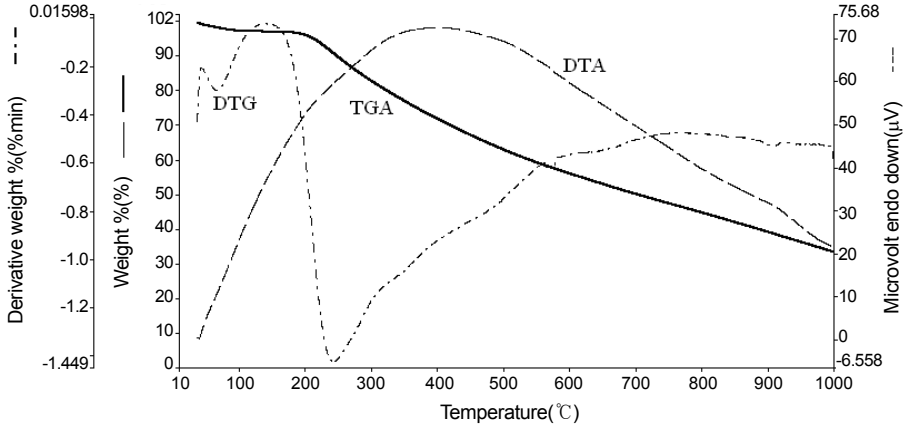


Figure 3. TGA-DTG-DTA curves of O-2-PMAP.

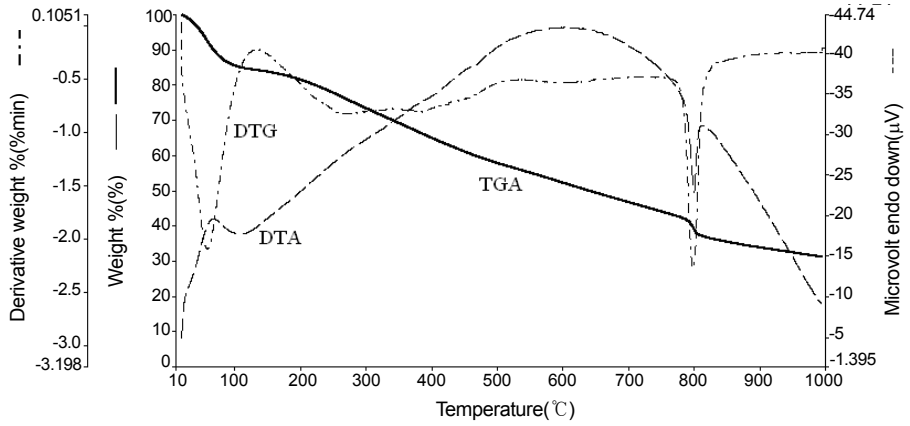


Figure 4. TGA-DTG-DTA curves of O-2-PMAP-Co complexes.

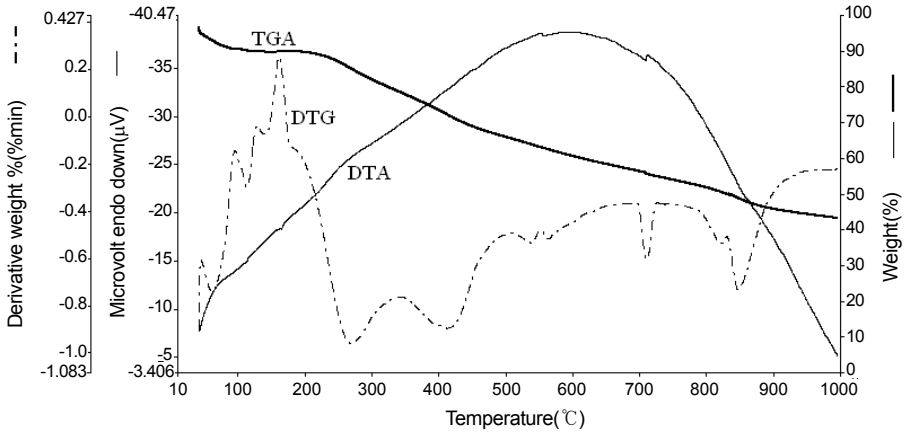


Figure 5. TGA−DTG−DTA curves of O−2−PMAP−Ni complexes.

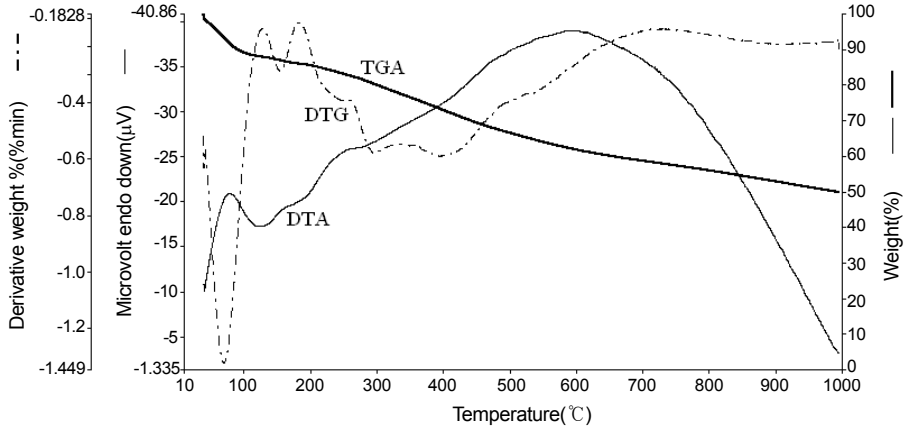


Figure 6. TGA−DTG−DTA curves of O−2−PMAP−Cu complexes.

curves of oligomer−metal complex compounds (Figures 4−6), showing between 2−8% wt losses in the 100−175 ℃ range and corresponding to the loss of water of crystallization (50−150 ℃) and coordination water (150−200 ℃).[17]

Conclusions

According to SEC analyses, the M_n, M_w and PDI values of O−2−PMAP were found to be 2460, 3560 g mol^{-1} and 1.447 and 900, 1280 g mol^{-1} and 1.422, for NaOCl and air O_2 oxidants, respectively. According to these values, molecular weight values of O−2−PMAP were higher for NaOCl oxidant. The yields of O−2−PMAP were found to be 85.7, 92.5, 88.5 and 88.0% by NaOCl and air O_2 oxidants in an aqueous alkaline and acidic medium, respectively. Both NaOCl and air O_2 demonstrated higher activity at the synthesis of O−2−PMAP. According to TG analyses, O−2−PMAP and its oligomer−metal complex compounds shown to be stable through to temperature and thermal decomposition. O−2−PMAP, O−2−PMAP−Co, O−2−PMAP−Ni and O−2−PMAP−Cu complex compounds lost about 68.0, 58.0, 53.5 and 50.0% of weights at 1000 ℃, respectively. According to these results, the highest residue was observed at the O−2−PMAP−Cu complex compound. That is, O−2−PMAP−Cu compound has higher thermal stability than O−2−PMAP−Co and O−2−PMAP−Ni compounds. 2−PMAP and O−2−PMAP have not demonstrated to any biologic activity against *E. Coli* (ATCC 25922), *E. Faecelis* (ATCC 29212), *P. Auroginasa* (ATCC 27853) and *S. Aureus* (ATCC 25923).

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