Synthesis, Characterization, and Antimicrobial Properties of Oligo-4-[(pyridine-3-yl-methylene) amino] Phenol

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ABSTRACT: The oxidative polycondensation reaction conditions of 4-[(pyridine-3-yl-methylene) amino]phenol (4-PMAP) were studied using H₂O₂, atmospheric O₂, and NaOCl oxidants in an aqueous alkaline medium between 30°C and 90°C. Synthesized oligo-4-[(pyridine-3-yl-methylene) amino] phenol (O-4-PMAP) was characterized by ¹H-, ¹³C NMR, FTIR, UV-vis, size exclusion chromatography (SEC), and elemental analysis techniques. The yield of O-4-PMAP was found to be 32% (for H₂O₂ oxidant), 68% (for atmospheric O₂ oxidant), and 82% (for NaOCl oxidant). According to the SEC analysis, the number-average molecular weight, weight-average molecular weight, and polydispersity index values of O-4-PMAP was found to be 5767, 6646 g mol⁻¹, and 1.152, respectively, using

 $\rm H_2O_2$, and 4540, 5139 g mol⁻¹, and 1.132, respectively, using atmospheric $\rm O_2$, and 9037, 9235 g mol⁻¹, and 1.022, using NaOCl, respectively. According to TG and DSC analyses, O-4-PMAP was more stable than 4-PMAP against thermal decomposition. The weight loss of O-4-PMAP was found to be 94.80% at 1000°C. Also, antimicrobial activities of the oligomer were tested against *B. cereus*, *L. monocytogenes*, *B. megaterium*, *B. subtilis*, *E. coli*, *Str. thermophilus*, *M. smegmatis*, *B. brevis*, *E. aeroginesa*, *P. vulgaris*, *M. luteus*, *S. aureus*, and *B. jeoreseens*. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3327–3333, 2006

Key words: polycondensation; polyaromatics; thermal and antimicrobial properties

INTRODUCTION

There are some typical synthetic methods for oligophenols. The first oxidative polymerization represents nucleophilic substitution of halogenated aromatic compounds by metal phenolates and other catalytic oxidative polymerization of phenols. The other method is the oxidative polycondensation of Schiff base monomers including phenol. There are some significant advantages of this method because of the use of oxidants such as NaOCl, H₂O₂, and atmospheric O₂. For example, these type of oxidants are cheap and easy to provide. Phenols and Schiff base substitute phenols were polymerized to a simple form by using these oxidants.

The oligophenols and their derivatives which included azomethine (—CH=N) and active hydroxyl (—OH) groups have been used in various fields. They have useful properties such as paramagnetism and semiconducting, and are used as an electrochemical cell. Because of these properties, they are used to prepare composites having resistance to high temperature and graphite materials, epoxy oligomer and block copolymer adhesives, photo resists, and antistatic materials.^{2–7} The halogen and sulfur derivatives of oligophe-

nols were used to prepare the composite materials having endurance to flame and specific detergents such as lead storing battery cathodes. These compounds can gain new properties when other functional groups are added to their structures. Also, these type of oligomers can be used as an antimicrobial agent.

Oligo-4-[(pyridine-3-yl-methylene) amino] phenol (O-4-PMAP) is produced via C—C coupling. The reaction mechanism on the coupling selectivity has been studied by Kaya and coworkers and three possible reaction mechanisms for the C—C coupling selectivity have been proposed in literature. ^{9,10} Regioselectivity of coupling was found in the polymerization of some specific phenol with Schiff base substitute. ^{11–14}

In this article, we have investigated the effects of different parameters such as temperature, time, and initial concentrations of NaOCl and H₂O₂ for the synthesis of O-4-PMAP in the alkaline medium. 4-PMAP and O-4-PMAP were characterized using FTIR, UV-vis, ¹H-¹³C NMR, elemental analysis, TG-DSC, and SEC techniques. Also, antimicrobial activities of O-4-PMAP were tested against 13 types of microorganisms.

MATERIALS AND METHODS

Materials

3-Pyridinecarbaldehyde (3-PCA), 4-aminophenol, 1,4-dioxane, methanol, ethanol, 1-butanol, acetonitrile,

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Scheme 1

benzene, toluene, acetone, ethyl acetate, heptane, CCl₄, CHCl₃, THF, DMF, DMSO, H₂SO₄, NaOH, KOH, H₂O₂ (30% aqueous solution), and hydrochloric acid (HCl, 37%) were supplied from Merck Chemical Co. (Germany) and they were used as received. Sodium hypo chloride (NaOCl), (30% aqueous solution) was supplied from Paksoy Chemical Co. (Turkey). 4-[(Pyridine-3-yl-methylene) amino] phenol (4-PMAP) was synthesized by condensation reaction of 3-PCA with 4-aminophenol and was recrystallized in methanol.

Preparation of 4-[(pyridine-3-yl-methylene) amino] phenol

4-PMAP was prepared by the condensation of 3-PCA (0.469 mL, 0.009 mol) with 4-aminophenol (0.535 g, 0.009 mol) in methanol (25 mL), achieved by boiling the mixture under reflux for 2 h at 70°C (Scheme 1). The precipitated 4-PMAP was filtered, recrystallized from methanol, and dried in a vacuum desiccator (yield, 85%).

Anal. calcd for 4-PMAP: C, 72.73; H, 5.05; N, 14.14. Found: C, 71.88; H, 5.85; N, 13.75. UV–vis (λ_{max}): 229, 243, 282, and 350 nm. FTIR (KBr, cm⁻¹): v (O—H) 3439 s, v (C—H phenyl) 3100 m, v (C=N) 1609 s, v (C=C phenyl) 1571, 1561, 1420 s, v (C—O) 1297 s. ¹H NMR (DMSO): δ (ppm) 8.70 (s, 1H, —CH=N—); 9.59 (s, 1H, —OH); 7.26 (dd, 2H, Ar-Haa'), 6.84 (dd, 2H, Ar-Hbb'), 8.69 (d, 1H, Ar-Hc), 7.53 (t, 1H, Ar-Hd), 8.25 (d, 1H, Ar-He), 9.02 (s, 1H, Ar-Hf). ¹³C NMR (DMSO): ppm, 155.16 (C1-ipso), 116.21 (C2, C6-H), 123.17 (C3, C5-H), 142.66 (C4-ipso), 157.17 (C7-H), 124.44 (C8-ipso), 134.97 (C9-H), 132.43(C10-H), 151.82 (C11-H), 150.51 (C12-H).

Synthesis of oligo-4-[(pyridine-3-yl-methylene) amino] phenol by using NaOCl, H_2O_2 , and atmospheric O_2 as oxidant¹¹

O-4-PMAP was synthesized through oxidative polycondensation of 4-PMAP with aqueous solutions of NaOCl (30%) and H₂O₂ (30%) and atmospheric O₂. The 4-PMAP (0.198 g, 0.001 mol) was dissolved in an aqueous solution of KOH (10%, 0.056 g, 0.001 mol) and placed into a 50-mL three-necked round-bottom flask (Scheme 2). It was fitted with a condenser, thermometer, stirrer and a funnel containing NaOCl or H_2O_2 . After heating to 30°C, NaOCl or H₂O₂ was added dropwise for about 20 min. However, for atmospheric O₂ oxidant was added to glass tubing over condenser. The reaction mixtures were stirred at various temperatures and times (Table I, II, and III, respectively). To prevent water loss in the reaction mixture and unneutralizing the CO_2 of atmospheric O_2 to KOH atmospheric O_2 passed into an aqueous solution of KOH (%20) before being sent through the reaction tube (Scheme 2). The reaction mixtures were cooled to room temperature and then 0.087 mL HCl (37%) was added. Unreacted monomer was separated from the reaction product by washing with methanol. The mixtures were filtered and washed with hot water (3 \times 25 mL) for separating from mineral salts and then dried in the oven at 110°C.

Anal. calcd for O-4-PMAP: C, 73.47; H, 4.08; N, 14.29. Found: C, 73.00; H, 4.70; N, 14.40. UV–vis (λ_{max}): 214, 229, 242, 263, 353, and 489. FTIR (KBr, cm⁻¹): v (O—H) 3394 s, v (C—H phenyl) 3080 m, v (C=N) 1617 s, v (C=C phenyl) 1603, 1577, 1494 s, v (C—O) 1281 s. ¹H NMR (DMSO): δ (ppm) 8.65 (s, 1H, —CH=N—); 9.50 (s, 1H, —OH); 7.22 (dd, 2H, Ar-Haa'), 8.60 (d, 1H, Ar-Hc) 7.50 (t, 1H, Ar-Hd) 8.24 (d, 1H, Ar-He) 9.00 (s, 1H,

TABLE I
The Oxidative Polycondensation Reaction Parameters of 4-[(Pyridine-3-yl-methylene) amino] Phenol with NaOCl in Aqueous KOH

Sample no.	[4-PMAP] ₀ (mol L ⁻¹)	[KOH] ₀ (mol L ⁻¹)	[NaOCl] ₀ (mol L ⁻¹)	Temp. (°C)	Time (h)	Yield of O-4-PMAP (%)
1	0.38	0.38	0.38	30	5	69
2	0.38	0.38	0.38	40	5	77
3	0.38	0.38	0.38	50	5	82
4	0.38	0.38	0.38	60	5	70
5	0.38	0.38	0.38	70	5	53
6	0.38	0.38	0.38	80	5	36
7	0.38	0.38	0.38	90	5	25
8	0.38	0.38	0.38	90	10	47
9	0.38	0.38	0.38	90	15	31
10	0.38	0.38	0.38	90	25	20
11	0.38	0.38	0.76	50	5	4
12	0.38	0.38	0.76	60	5	6
13	0.38	0.38	0.76	70	5	13
14	0.38	0.38	0.76	80	5	38
15	0.38	0.38	0.76	90	5	16
16	0.38	0.38	0.76	80	10	32
17	0.38	0.38	0.76	80	15	23
18	0.38	0.38	0.76	80	25	17

Ar-Hf). ¹³C NMR (DMSO): ppm, 161.85 (C1-ipso), 118.45 (C2, C6-ipso), 128.40 (C3, C5-H), 149.90 (C4-ipso), 162.40 (C7-H), 124.70 (C8-ipso), 135.21 (C9-H), 133.70 (C10-H), 153.03 (C11-H), 151.75 (C12-H).

Preparation of microbial cultures

Bacillus megaterium DSM 32, Bacillus subtilis IMG 22, Bacillus brevis FMC 32, E. coli DM, Str. thermophilus, M. smegmatis, M. luteus, E. Aeroginesa CCM 2531, P. vulgaris DSM 50,071, S. Aureus COWAN 1, L. monocytogenes SCOTT A, B. cereus, and B. jeoreseens, and yeast were used as the test organisms in an antimicrobial study.

There are some applications of these bacteria such as molecular biology, non-pathogenic microorganism, modern biological engineering and gram positive. The bacteria and yeast strains were inoculated into nutrient broth (Difco) and malt extract broth (Difco) and incubated for 24 and 48 h, respectively. Using the disc diffusion method, the sterile Mueller Hinton agar (Oxoid) for bacteria and Sabouraud dextrose agar for yeast were separately inoculated with the test microorganisms. 15,16 The compound was dissolved in DMSO as 50 $\mu g/disc$ solutions 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

TABLE II
The Oxidative Polycondensation Reaction Parameters of 4-[(Phenylimino) methyl] Phenol with H₂O₂ in Aqueous KOH

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			•		-		
2 0.38 0.38 0.38 40 5 21 3 0.38 0.38 0.38 50 5 32 4 0.38 0.38 0.38 60 5 27 5 0.38 0.38 0.38 70 5 26 6 0.38 0.38 0.38 80 5 8 7 0.38 0.38 0.38 90 5 5 8 0.38 0.38 0.38 50 10 25 9 0.38 0.38 0.38 50 15 18 10 0.38 0.38 0.38 50 25 11 11 0.38 0.38 0.76 50 5 7 12 0.38 0.38 0.76 50 5 17 14 0.38 0.38 0.76 70 5 16 15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76	_			$[H_2O_2]_0$ (mol L ⁻¹)	Temp. (°C)		Yield of O-4-PMAP (%)
3 0.38 0.38 0.38 50 5 32 4 0.38 0.38 0.38 60 5 27 5 0.38 0.38 0.38 70 5 26 6 0.38 0.38 0.38 80 5 8 7 0.38 0.38 0.38 90 5 5 8 0.38 0.38 0.38 50 10 25 9 0.38 0.38 0.38 50 15 18 10 0.38 0.38 0.38 50 25 11 11 0.38 0.38 0.76 50 5 7 12 0.38 0.38 0.76 60 5 11 13 0.38 0.38 0.76 70 5 17 14 0.38 0.38 0.76 90 5 10 15 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76	1	0.38	0.38	0.38	30	5	18
4 0.38 0.38 0.38 60 5 27 5 0.38 0.38 0.38 70 5 26 6 0.38 0.38 0.38 80 5 8 7 0.38 0.38 0.38 90 5 5 8 0.38 0.38 0.38 50 10 25 9 0.38 0.38 0.38 50 15 18 10 0.38 0.38 0.38 50 25 11 11 0.38 0.38 0.76 50 5 7 12 0.38 0.38 0.76 60 5 11 13 0.38 0.38 0.76 70 5 17 14 0.38 0.38 0.76 80 5 16 15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76	2	0.38	0.38	0.38	40	5	21
5 0.38 0.38 0.38 70 5 26 6 0.38 0.38 0.38 80 5 8 7 0.38 0.38 0.38 90 5 5 8 0.38 0.38 0.38 50 10 25 9 0.38 0.38 0.38 50 15 18 10 0.38 0.38 0.38 50 25 11 11 0.38 0.38 0.76 50 5 7 12 0.38 0.38 0.76 60 5 11 13 0.38 0.38 0.76 70 5 17 14 0.38 0.38 0.76 80 5 16 15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76 70 15 6	3	0.38	0.38	0.38	50	5	32
6 0.38 0.38 0.38 80 5 8 7 0.38 0.38 0.38 90 5 5 8 0.38 0.38 0.38 50 10 25 9 0.38 0.38 0.38 50 15 18 10 0.38 0.38 0.38 50 25 11 11 0.38 0.38 0.76 50 5 7 12 0.38 0.38 0.76 60 5 11 13 0.38 0.38 0.76 70 5 17 14 0.38 0.38 0.76 80 5 16 15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76 70 15 6	4	0.38	0.38	0.38	60	5	27
7 0.38 0.38 0.38 90 5 5 8 0.38 0.38 0.38 50 10 25 9 0.38 0.38 0.38 50 15 18 10 0.38 0.38 0.38 50 25 11 11 0.38 0.38 0.76 50 5 7 12 0.38 0.38 0.76 60 5 11 13 0.38 0.38 0.76 70 5 17 14 0.38 0.38 0.76 80 5 16 15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76 70 15 6	5	0.38	0.38	0.38	70	5	26
8 0.38 0.38 0.38 50 10 25 9 0.38 0.38 0.38 50 15 18 10 0.38 0.38 0.38 50 25 11 11 0.38 0.38 0.76 50 5 7 12 0.38 0.38 0.76 60 5 11 13 0.38 0.38 0.76 70 5 17 14 0.38 0.38 0.76 80 5 16 15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76 70 15 6	6	0.38	0.38	0.38	80	5	8
9 0.38 0.38 0.38 50 15 18 10 0.38 0.38 0.38 50 25 11 11 0.38 0.38 0.76 50 5 7 12 0.38 0.38 0.76 60 5 11 13 0.38 0.38 0.76 70 5 17 14 0.38 0.38 0.76 80 5 16 15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76 70 15 6	7	0.38	0.38	0.38	90	5	5
10 0.38 0.38 0.38 50 25 11 11 0.38 0.38 0.76 50 5 7 12 0.38 0.38 0.76 60 5 11 13 0.38 0.38 0.76 70 5 17 14 0.38 0.38 0.76 80 5 16 15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76 70 15 6	8	0.38	0.38	0.38	50	10	25
11 0.38 0.38 0.76 50 5 7 12 0.38 0.38 0.76 60 5 11 13 0.38 0.38 0.76 70 5 17 14 0.38 0.38 0.76 80 5 16 15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76 70 15 6	9	0.38	0.38	0.38	50	15	18
12 0.38 0.38 0.76 60 5 11 13 0.38 0.38 0.76 70 5 17 14 0.38 0.38 0.76 80 5 16 15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76 70 15 6	10	0.38	0.38	0.38	50	25	11
13 0.38 0.38 0.76 70 5 17 14 0.38 0.38 0.76 80 5 16 15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76 70 15 6	11	0.38	0.38	0.76	50	5	7
14 0.38 0.38 0.76 80 5 16 15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76 70 15 6	12	0.38	0.38	0.76	60	5	11
15 0.38 0.38 0.76 90 5 10 16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76 70 15 6	13	0.38	0.38	0.76	70	5	17
16 0.38 0.38 0.76 70 10 12 17 0.38 0.38 0.76 70 15 6	14	0.38	0.38	0.76	80	5	16
17 0.38 0.38 0.76 70 15 6	15	0.38	0.38	0.76	90	5	10
	16	0.38	0.38	0.76	70	10	12
18 0.38 0.38 0.76 70 25 4	17	0.38	0.38	0.76	70	15	6
	18	0.38	0.38	0.76	70	25	4

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TABLE III
The Oxidative Polycondensation Reaction Parameters of 4-[(Pyridine-3-yl-methylene)
amino] Phenol under Atmospheric O ₂ in Aqueous KOH

Sample no.	[4-PMAP] ₀ (mol L ⁻¹)	[KOH] ₀ (mol L ⁻¹)	Atm. O_2 (L h^{-1})	Temp. (°C)	Time (h)	Yield of O-4-PMAP (%)
1	0.38	0.38	8.5	50	3	44
2	0.38	0.38	8.5	60	3	68
3	0.38	0.38	8.5	70	3	62
4	0.38	0.38	8.5	80	3	55
5	0.38	0.38	8.5	90	3	47
6	0.38	0.38	8.5	60	1	33
7	0.38	0.38	8.5	30	3	36
8	0.38	0.38	8.5	40	3	41
9	0.38	0.38	8.5	60	5	46
10	0.38	0.38	8.5	60	10	43
11	0.38	0.38	8.5	60	15	41
12	0.38	0.38	8.5	60	25	39

32°C for bacteria (18–24 h) and at 25°C for yeast (72 h). The resulting inhibition zones on the plates were measured after 48 h. The control samples were only absorbed in DMSO. The data reported in Table IV are the average data of three experiments.

Characterization techniques

The infrared and UV-vis spectra were measured by PerkinElmer FTIR BX and UV-1208 Shimadzu, respectively. Elemental analysis was carried out with a Carlo Erba 1106. The FTIR spectra were recorded using KBr disc (4000–350 cm⁻¹). UV-vis spectra of 4-PMAP and O-4-PMAP were determined by using ethanol and DMSO, respectively. 4-PMAP and O-4-PMAP were characterized by using ¹H- and ¹³C NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) and recorded at 25°C by using

TABLE IV
Antimicrobial Activity of Oligo-4-[(phenylimino) methyl] Phenol^a

Microorganism (Inhibition zone) ^b	O-4-PMAP
(Hillibition zone)	0-4-1 MAI
B. cereus	11
B megaterium	_c
E. coli	_c
L. monocytogenes	10
B. subtilis	32
Str.thermophilus	34
M. smegmatis	14
B. brevis	16
E. aeroginesa	13
P. vurgaris	15
M. luteus	16
S. aureus	23
B. jeoreseens	17

^a Compound conc., 50 μg/disc.

deuterated DMSO-d₆ as solvent. TMS was used as internal standard. Thermal data were obtained by using STA 409 C NETZSCH-Geratebau GmbH thermal analysis equipment. TG-DSC measurements were made between 20 and 1000°C (in N₂; rate, 10°C /min). SEC analyses were performed at 30°C using DMF as eluent at a flow rate of 0.4 mL/min. A refractive index detector was used as a detector. The instrument (Shimadzu 10AVp series HPLC-SEC system) was calibrated with a mixture of polystyrene standards (Polymer Laboratories; the peak molecular weights, Mp, between 162 and 19,880) using GPC software for the determination of the molecular weight (M_n) , weight-average molecular weight (M_w) , and polydispersity index (PDI), of the polymer samples. For SEC investigations, 3.3 mm i.d. \times 300 mm columns (100 Å and 7.7 nm diameter loading material) were used (Macherey-Nagel GmbH and Co.).

RESULTS AND DISCUSSION

The investigation of synthesis conditions of O-4-PMAP

The alkaline solution of [(pyridine-3-yl-methylene) amino] phenol interacted with oxidants such as atmospheric O₂, H₂O₂, and NaOCl and immediately precipitated phenoxy radicals with brown adding. The oxidative polycondensation reaction conditions of O-4-PMAP synthesized with 30% NaOCl solution in aqueous alkaline medium are given in Table I. The yield of O-4-PMAP was 70.0% for NaOCl oxidant for 5 h at 60°C. It is seen that in Table I, the amount of products decreased with increasing temperature. At the same conditions, when molar amount of NaOCl increased in two coating dependence on 4-PMAP, total yield changed from 70.0% to 6.0% (see Table I). The yield of O-4-PMAP was 82.0% at optimum conditions such as $[4-PMAP]_0 = [KOH]_0 = [NaOCl]_0 = 0.38 \text{ mol/L}, at$ 50°C for 5 h. The yield of O-4-PMAP was 20.0% at the other reaction conditions such as $[4-PMAP]_0 = [KOH]_0$ $= [NaOCl]_0 = 0.38 \text{ mol/L at } 90^{\circ}\text{C for } 25 \text{ h.}$

^b Including disc diameter of 86 mm.

^c Compound has not any activity against the microorganism.

The oxidative polycondensation reaction conditions of 4-PMAP with 30% $\rm H_2O_2$ solution in aqueous alkaline medium are given in Table II. The yield of O-4-PMAP was 32.0% at optimum conditions such as [4-PMAP]₀ = [KOH]₀ = [$\rm H_2O_2$]₀ = 0.38 mol/L, at 50°C for 5 h. The yield of O-4-PMAP was 5.0% at the reaction conditions such as [4-PMAP]₀ = [KOH]₀ = [$\rm H_2O_2$]₀ = 0.38 mol/L at 90°C for 5 h. From these values, it was found that an increase in reaction temperature decreased their yields.

The oxidative polycondensation reaction conditions of 4-PMAP with atmospheric O_2 solution in aqueous alkaline medium are given in Table III. In the oxidative polycondensation reaction of 4-PMAP, when atmospheric O_2 passed at 8.5 L h^{-2} rate into the reaction medium at 50°C , the yield of product was 44.0%. The yield of O-4-PMAP was 68.0% at optimum conditions such as $[4\text{-PMAP}]_0 = [\text{KOH}]_0 = 0.38 \text{ mol/L}$ at 60°C for 3 h. At the same conditions, when reaction temperatures increased, total yield decreased (see Table III).

The polymerization of 4-PMAP was influenced under the above-mentioned conditions such as temperature, time, and initial concentration of NaOCl and $\rm H_2O_2$, oxidants. It is seen that from Tables I, II, and III, the yields of these reactions were dependent upon temperature, time, and initial concentrations of oxidants. When oxidative polycondensation reaction time increased, the yield of oligomer decreased at the same conditions. The reason of these is conversion from oligomer to monomer at higher reaction times (see Tables I, II, and III). NaOCl and atmospheric $\rm O_2$ oxidants were more active than $\rm H_2O_2$ for the conversion of 4-PMAP at the same conditions.

Solubility

O-4-PMAP was a dark brown powder and it was completely soluble in organic solvents such as DMF, THF, DMSO, aqueous alkaline solution and conc. H₂SO₄. O-4-PMAP was insoluble in heptane, acetonitrile, benzene, toluene, ethyl acetate, CHCl₃, CCl₄, methanol, 1-butanol, ethanol and 1,4-dioxane and acetone.

Structure of O-4-PMAP

SEC chromatograms of O-4-PMAP are given in Figure 1. With H_2O_2 oxidant, M_n , M_w , and PDI values of O-4-PMAP were found to be 5767, 6646 g mol⁻¹ and 1.152, respectively, [Fig. 1 (a)]. Two peaks were observed in the chromatogram of O-4-PMAP. Sixty-five percent of the mass of O-4-PMAP was of low molecular weight ($M_n = 1369$, $M_w = 1726$ g mol⁻¹, PDI = 1.261) but 35% was of high molecular weight ($M_n = 30,413$, $M_w = 34,772$ g mol⁻¹, PDI = 1.143). With atmospheric O_2 oxidant, M_n , M_w and PDI values of O-4-PMAP were found to be 4540, 5139 g mol⁻¹, and 1.132, respectively, [Fig. 1 (b)]. Two peaks were observed in the chromatogram of

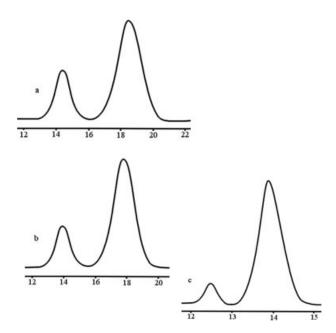


Figure 1 The chromatographic curves of the oxidative polycondensation product of 4-[(pyridine-3-yl-methylene) amino]phenol: (a) H_2O_2 as oxidant, (b) atmospheric O_2 as oxidant, (c) NaOCl as oxidant.

O-4-PMAP. Seventy-five percent of the mass of O-4-PMAP was of low molecular weight ($M_n = 1687$, $M_w = 2239$ g mol⁻¹, PDI = 1.328) but 25% was of high molecular weight ($M_n = 31,261$, $M_w = 34,397$ g mol⁻¹, PDI = 1.100). With NaOCl oxidant, M_n , M_w , and PDI values of O-4-PMAP were found to be 9037, 9235 g mol⁻¹, and 1.022, respectively, [Fig. 1 (c)]. Two peaks were observed in the chromatogram of O-4-PMAP. Ninety percent of the mass of O-4-PMAP was of low molecular weight ($M_n = 15,303$, $M_w = 15,312$ g mol⁻¹, PDI = 1.000) but 10% was of high molecular weight ($M_n = 43,021$, $M_w = 46,880$ g mol⁻¹, PDI = 1.090).

The UV–vis spectra of O-4-PMAP and 4-PMAP were similar. However, in the spectra of 4-PMAP, K bands of phenol and C_6H_5 —N= were observed at 229 and 243 nm, respectively. Benzene band of 4-PMAP and strength R band of —CH=N— groups were observed in 282 and 350 nm, respectively. λ_{max} values of O-4-PMAP were observed at 214, 229, 242, 263, 353, and 489 nm. In the UV–vis spectra of O-4-PMAP, K and R bands were observed at 229 and 353 nm, respectively.

Characteristic peaks of functional groups were observed in the FTIR spectra of 4-PMAP and O-4-PMAP: phenyl —OH, —CH=N and —C—O groups, 3439, 1609, and 1297 cm⁻¹; 3428, 1619, and 1281 cm⁻¹, respectively. To identify the structures of monomer and oligomer, the ¹H NMR spectra were recorded in DMSO-*d*₆. In the ¹H NMR spectra of 4-PMAP and O-4-PMAP, the signals of —OH and —CH=N groups were observed at 9.59 and 8.70 ppm and 9.50 and 8.65 ppm, respectively. The FTIR spectral data and the results of the ¹H- and ¹³C-NMR spectra of the O-4-

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PMAP confirm together. 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. In addition, infrared studies revealed no ether linkage (C—O—C) in the polymer structure, i.e., any peak observed in 1244, 1172, and 1050 cm⁻¹ regions. Thus the phenyl rings in the polymer appear to be linked primarily at ortho positions.

Thermal analyses of oligo-4-[(pyridine-3-yl-methylene) amino] phenol

Thermal TG-DSC curves of monomer and oligomer were given in Figures 2 and 3. The initial degradation temperature, 50% and 94.80% weight loss of O-4-PMAP was found to be 195, 425, and 1000°C, respectively. This oligomer formed carbines residue at low amount such as 5.20% at 1000°C. Compared with monomer, oligomer demonstrated higher resistance against high temperature because of long conjugated band systems. The initial degradation temperature and 99.00% weight loss of 4-PMAP was found to be 95 and 1000°C, respectively. According to TG analysis, O-4-PMAP was more stable than monomer through temperature and thermal decomposition. The presence of water is also evidenced in TGA curves of monomer and oligomer (Figs. 2 and 3) which showed until 3% weight losses in the 50–150°C assigned both adsorption (50-100°C) and crystallization water (100-150°C) removal. According to DSC curve of monomer, endothermic processes observed in 225°C. $T_{\rm max}$ value of O-4-PMAP observed in 450°C.

Study of antimicrobial activities of oligomer

The biological activities of O-4-PMAP were tested against different microorganisms by using DMSO as solvent and the data reported in Table IV. The sample concentration was $50 \, \mu g$. It has been suggested that the O-4-PMAP with the N and O donor system might in-

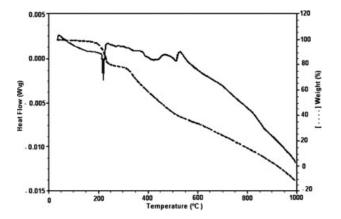


Figure 2 TG-DSC curves of 4-[(pyridine-3-yl-methylene) amino]phenol.

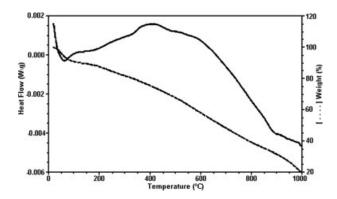


Figure 3 TG-DSC curves of oligo-4-[(pyridine-3-yl-methylene) amino]phenol.

hibit enzyme production because enzymes that require free hydroxyl groups for their activity appear to the especially susceptible to deactivation by the ions of the O-4-PMAP. The variation in the effectiveness of different biradical agents against different organisms¹⁷ depends on the impermeability of the cell. The hydrocarbon acts as a lipophilic group 18 to drive the compound through the semi permeable membrane of the cell. O-4-PMAP demonstrated the highest biologic activity, against 11 types of microorganisms. O-4-PMAP has not demonstrated any activity against B megaterium and E. coli. These results indicate that it is very important to synthesize Schiff base substitute oligomers to prepare new active agents. Antimicrobial properties of oligoortho-azomethinephenol and some of its oligomermetal complexes had been investigated by I. Kaya and coworkers and they too had observed similar results. 19

CONCLUSIONS

Oligo-4-[(pyridine-3-yl-methylene) amino]phenol was synthesized by oxidants such as atmospheric O_2 , H_2O_2 and NaOCl in aqueous alkaline medium. The yield of O-4-PMAP was found to be 82% when NaOCl was used as oxidant. The M_n , M_w and PDI values of 4-PMAP were found to be 5767, 6646 g mol^{-1} , and 1.152, respectively, using H₂O₂, and 4540, 5139 g mol⁻¹, and 1.132 respectively, using atmospheric O₂ and 9037, 9235 g mol^{-1} , and 1.022, respectively. In the oxidative polycondensation reaction of 4-PMAP, H₂O₂ oxidant was demonstrated to be less active than NaOCl and atmospheric O₂ oxidants. It is determined that enough resistance against thermal degradation of synthesized 4-[(pyridine-3-yl-methylene) amino]phenol. The carbines residue of this oligomer was formed at low amount (5.20%) at 1000°C. Also, O-4-PMAP was demonstrated the highest biologic activity against 11 types of microorganisms.

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