

Synthesis, Characterization, and Thermal Degradation of Oligo-2-(morpholinoiminomethyl)phenol and Its Pb(II) Complex Compound

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ABSTRACT: The oxidative polycondensation reaction conditions of 2-(morpholinoiminomethyl)phenol were studied with H₂O₂, air O₂, and sodium hypochloride (NaOCl) oxidants in an aqueous alkaline medium between 40 and 90°C. The structure of oligo-2-(morpholinoiminomethyl)phenol was characterized with ¹H- and ¹³C-NMR, Fourier transform infrared, ultraviolet-visible, size exclusion chromatography, and elemental analysis techniques. Under the optimum reaction conditions, the yield of oligo-2-(morpholinoiminomethyl)phenol was 28% for the H₂O₂ oxidant, 12% for the air O₂ oxidant, and 58% for the NaOCl oxidant. According to the size exclusion chromatography analysis, the number-average molecular weight, weight-average

molecular weight, and polydispersity index of oligo-2-(morpholinoiminomethyl)phenol were 2420 g/mol, 2740 g/mol, and 1.187 with H₂O₂, 1425 g/mol, 2060 g/mol, and 1.446 with air O₂, and 1309 g/mol, 1401 g/mol, and 1.070 with NaOCl, respectively. Thermogravimetry/dynamic thermal analysis showed that the oligo-2-(morpholinoiminomethyl)phenol-lead complex compound was more stable than 2-(morpholinoiminomethyl)phenol and oligo-2-(morpholinoiminomethyl)phenol against thermal degradation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3795–3804, 2006

Key words: polycondensation; synthesis; thermal properties

INTRODUCTION

Polyazomethine polymers attracted attention in the early 1960s¹ as promising conducting and semiconducting materials. Polyazomethines, which include azomethine (—CH=N) and active hydroxyl (—OH) groups, have been used in various fields. They have useful properties, such as paramagnetism, electrochemical cells, and resistance to high energy. Because of these properties, they have been used to prepare composites with resistance to high temperatures, graphite materials, epoxy oligomer and block copolymer adhesives, photoresists, and antistatic materials.^{2–8} The halogen and sulfur derivatives of oligophenols have been used to prepare composite materials enduring flame and specific detergents such as lead-storage battery cathodes.⁹ These compounds profit from new properties added to their structures by other functional groups. Because of the azomethine (—C=N) and hydroxyl (—OH) groups, these types of oligomers can be used as antimicrobial agents.¹⁰ Also, because of these groups, azomethine polymers

have the ability to coordinate with different metal ions. For this reason, they can be used to clean poisonous heavy metals in industrial wastewater. Therefore, the synthesis of oligomer-metal complexes is very important in analytical and environmental chemistry. It seems advantageous to attempt to design and prepare a polymer-bound chelating ligand that would be able to form complexes with a variety of transition metals and therefore have a large range of applications.¹¹

In this article, we investigate the effects of different parameters, such as the temperature, time, and initial concentrations of sodium hypochloride (NaOCl) and H₂O₂, on 2-(morpholinoiminomethyl)phenols in an aqueous alkaline medium. 2-(Morpholinoiminomethyl)phenol (2-MIMP) and oligo-2-(morpholinoiminomethyl)phenol (O-2-MIMP) have been characterized with Fourier transform infrared (FTIR), ultraviolet-visible (UV-vis), ¹H- and ¹³C-NMR, elemental analysis, thermogravimetry (TG)/dynamic thermal analysis (DTA), and size exclusion chromatography (SEC) techniques.

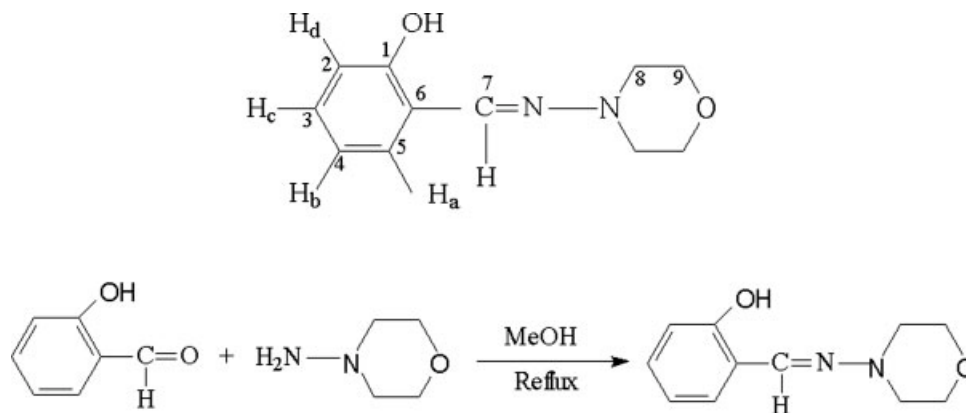
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EXPERIMENTAL

Materials

Aminomorpholin, salicylaldehyde, methanol, ethanol, benzene, toluene, acetone, ethyl acetate, hexane,



Scheme 1

CH_2Cl_2 , CCl_4 , CHCl_3 , tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), H_2SO_4 (98%), NaOH, KOH, H_2O_2 (30% aqueous solution), hydrochloric acid (HCl; 37%), and $\text{Pb}(\text{AcO})_2 \cdot 3\text{H}_2\text{O}$ were supplied by Merck Chemical Co. (chromatographic-grade) and were used as received. NaOCl (30% aqueous solution) was supplied by Paksoy Chemical Co. (Turkey). 2-MIMP was synthesized to allow the condensation reaction of salicylaldehyde with aminomorpholin, and it recrystallized in methanol.

Preparation of 2-MIMP

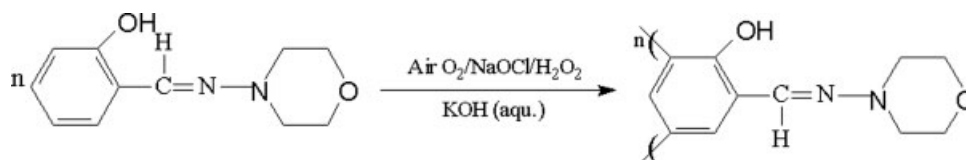
Aminomorpholin (0.535 g, 0.009 mol) was dissolved in methanol (15 mL), and then salicylaldehyde (0.469 mL, 0.009 mol) was added to this solution. The resulting mixture was refluxed and stirred at 70°C for 3 h (Scheme 1). The reaction mixture was cooled to room temperature and washed with cool ethanol. The product was recrystallized from methanol to give Schiff base 2-MIMP in an 85% yield as a yellow, crystalline solid.

ANAL. Calcd for 2-MIMP: C, 64.08%; H, 6.80%; N, 13.59%. Found: C, 63.63%; H, 6.75%; N, 13.55%. UV-vis [maximum wavelength (λ_{max}): 230, 255, 290, 345 nm. FTIR (KBr, cm^{-1}): ν (O—H) 3360 s, ν (C—H aliphatic) 2959 s, ν (C=N) 1601 s, ν (=N—N) 1516 s, ν (C=C phenyl) 1454, 1400 s, ν (CH₂—N) 2846 s, ν (C—O) 1278 s, ν (for morpholine ring —C—O—C) 1245, 1172 s. $^1\text{H-NMR}$ (DMSO, δ , ppm): 7.95 (s, 1H, —CH=N—), 11.27 (s, 1H, —OH), 7.35 (d, 1H, Ar—H_a), 6.82 (m, 2H, Ar—H_bH_d), 7.18 (m, 1H, Ar—H_c), 3.05 (t, 2H, N—CH₂), 3.72 (t, 2H, O—CH₂).

$^{13}\text{C-NMR}$ (DMSO, ppm): 157.09 (C1-ipso), 116.43 (C2-H), 129.87 (C3-H), 119.99 (C4-H), 129.63 (C5-H), 119.56 (C6-ipso), 140.05 (C7-H), 51.95 (C8-H₂), 65.90 (C9-H₂).

Synthesis of O-2-MIMP with NaOCl, H₂O₂, and air O₂ as oxidants in an aqueous alkaline medium

O-2-MIMP was synthesized through the oxidative polycondensation of 2-MIMP with aqueous solutions of NaOCl (30%), H₂O₂ (30%), and air O₂ oxidants.¹² 2-MIMP (0.206 g, 0.001 mol) was dissolved in an aqueous solution of KOH (10%, 0.056 g, 0.001 mol) and placed in a 50-mL, three-necked, round-bottom flask (Scheme 2). It was fitted with a condenser, thermometer, stirrer, and addition funnel containing NaOCl or H₂O₂. After heating to 30°C , NaOCl and H₂O₂ were added dropwise over about 20 min. However, the air O₂ oxidant was added to glass tubing over the condenser. The reaction mixtures were stirred at various temperatures and times (Tables I–III). Air O₂ passed into an aqueous solution of KOH (20%) before being sent through the reaction tube to prevent water loss in the reaction mixture and the neutralization of CO₂ in air to KOH. The reaction mixtures were cooled to room temperature, and then 0.001 mol of HCl (37%) was added. The unreacted monomer was separated from the reaction product via washing with CHCl_3 . The mixture was filtered and washed with hot water (3×25 mL) to separate it from mineral salts and then was dried in an oven at 110°C .



Scheme 2

TABLE I
Oxidative Polycondensation Reaction Parameters of 2-MIMP with NaOCl
in Aqueous KOH

Sample	[2-MIMP] ₀ (mol/L)	[KOH] ₀ (mol/L)	[NaOCl] ₀ (mol/L)	Temperature (°C)	Time (h)	Yield of O-2-MIMP (%)
1	0.2	0.2	0.2	40	3	47
2	0.2	0.2	0.2	50	3	58
3	0.2	0.2	0.2	60	3	39
4	0.2	0.2	0.2	70	3	36
5	0.2	0.2	0.2	80	3	29
6	0.2	0.2	0.2	90	3	27
7	0.2	0.2	0.2	50	5	44
8	0.2	0.2	0.2	50	10	40
9	0.2	0.2	0.2	50	15	38
10	0.2	0.2	0.2	50	25	31
11	0.2	0.2	0.4	40	3	18
12	0.2	0.2	0.4	50	3	22
13	0.2	0.2	0.4	60	3	26
14	0.2	0.2	0.4	70	3	14
15	0.2	0.2	0.4	80	3	8
16	0.2	0.2	0.4	90	3	7
17	0.2	0.2	0.4	60	1	11
18	0.2	0.2	0.4	60	5	14
19	0.2	0.2	0.4	60	10	12
20	0.2	0.2	0.4	60	15	6
21	0.2	0.2	0.4	60	25	6
22	0.2	0.4	0.2	40	3	34
23	0.2	0.4	0.2	50	3	36
24	0.2	0.4	0.2	60	3	42
25	0.2	0.4	0.2	70	3	56
26	0.2	0.4	0.2	80	3	44
27	0.2	0.4	0.2	90	3	43
28	0.2	0.4	0.2	70	1	39
29	0.2	0.4	0.2	70	5	43
30	0.2	0.4	0.2	70	10	42
31	0.2	0.4	0.2	70	15	41
32	0.2	0.4	0.2	70	25	38

ANAL. Calcd for O-2-MIMP: C, 64.71%; H, 5.88%; N, 13.73%. Found: C, 63.71%; H, 6.68%; N, 11.62%. UV-vis (λ_{\max}): 240, 260, 329, 392. FTIR (KBr, cm^{-1}): ν (O—H) 3448 s, ν (C—H aliphatic) 2963 s, ν (C—H phenyl) 3075 m, ν (C=N) 1620 s, ν (=N—N) 1598 s, ν (C=C phenyl) 1481, 1450 s, ν (CH₂—N) 2856 s, ν (C—O—C) 1272 s. ¹H-NMR (DMSO, δ , ppm): 8.01 (s, 1H, —CH=N—), 11.87 (s, 1H, —OH), 6.90 (m, 1H, Ar—Ha), 7.90 (m, 1H, Ar—Hc), 1.07 (t, 2H,

N—CH₂), 3.46 (t, 2H, O—CH₂). ¹³C-NMR (DMSO, ppm): 161.10 (C1-ipso), 119.39 (C2-ipso), 130.55 (C3-H), 126.15 (C4-ipso), 130.05 (C5-H), 119.97 (C6-ipso), 142.38 (C7-H), 51.86 (C8-H₂), 65.84 (C9-H₂).

Synthesis of the O-2-MIMP/Pb(II) metal complex

A solution of Pb(AcO)₂ · 3H₂O (0.001 mol, 0.379 g) in methanol (10 mL) was added to a solution of O-2-

TABLE II
Oxidative Polycondensation Reaction Parameters of 2-MIMP with Air O₂
in Aqueous KOH

Sample	[2-MIMP] ₀ (mol/L)	[KOH] ₀ (mol/L)	Air O ₂ (L/h)	Temperature (°C)	Time (h)	Yield of O-2-MIMP (%)
1	0.2	0.2	8.5	60	3	6
2	0.2	0.2	8.5	70	3	8
3	0.2	0.2	8.5	80	3	9
4	0.2	0.2	8.5	90	3	6
5	0.2	0.2	8.5	70	5	10
6	0.2	0.2	8.5	70	10	12
7	0.2	0.2	8.5	70	15	10
8	0.2	0.2	8.5	70	25	7

TABLE III
Oxidative Polycondensation Reaction Parameters of 2-MIMP with H₂O₂
in Aqueous KOH

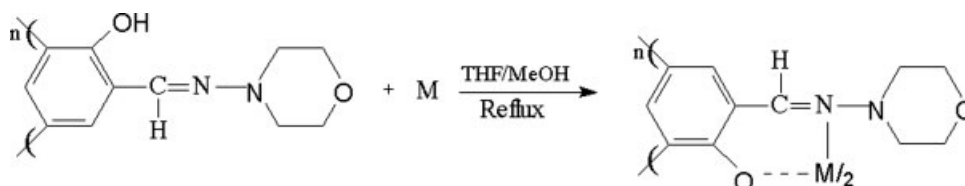
Sample	[2-MIMP] ₀ (mol/L)	[KOH] ₀ (mol/L)	[H ₂ O ₂] ₀ (mol/L)	Temperature (°C)	Time (h)	Yield of O-2-MIMP (%)
1	0.2	0.2	0.2	40	3	11
2	0.2	0.2	0.2	50	3	16
3	0.2	0.2	0.2	60	3	22
4	0.2	0.2	0.2	70	3	28
5	0.2	0.2	0.2	80	3	24
6	0.2	0.2	0.2	90	3	19
7	0.2	0.2	0.2	70	1	26
8	0.2	0.2	0.2	70	5	26
9	0.2	0.2	0.2	70	10	24
10	0.2	0.2	0.2	70	15	21
11	0.2	0.2	0.2	70	25	13
12	0.2	0.2	0.4	40	3	6
13	0.2	0.2	0.4	50	3	7
14	0.2	0.2	0.4	60	3	9
15	0.2	0.2	0.4	70	3	12
16	0.2	0.2	0.4	80	3	10
17	0.2	0.2	0.4	90	3	10
18	0.2	0.2	0.4	70	1	7
19	0.2	0.2	0.4	70	5	8
20	0.2	0.2	0.4	70	10	6
21	0.2	0.2	0.4	70	15	6
22	0.2	0.2	0.4	70	25	3
23	0.2	0.4	0.2	40	3	22
24	0.2	0.4	0.2	50	3	24
25	0.2	0.4	0.2	60	3	16
26	0.2	0.4	0.2	70	3	11
27	0.2	0.4	0.2	80	3	10
28	0.2	0.4	0.2	90	3	9
29	0.2	0.4	0.2	50	1	18
30	0.2	0.4	0.2	50	5	12
31	0.2	0.4	0.2	50	10	11
32	0.2	0.4	0.2	50	15	9
33	0.2	0.4	0.2	50	25	6

MIMP (0.002 mol/unit, 0.408 g) in THF (20 mL). The mixture was stirred and heated at 70°C for 5 h (Scheme 3). The precipitated complex was filtered, washed with cold methanol/THF (1 : 1), and then dried in a vacuum oven (90%, > 250°C).

ANAL. Calcd for O-2-MIMP/Pb: C, 32.10%; H, 2.92%; N, 6.81%; M, 50.39%. Found: C, 31.80%; H, 3.25%; N, 7.00%; M, 40.28%. FTIR (KBr, cm⁻¹): ν (O—H) 3510 s, ν (C—H aryl) 3030 m, ν (C=N) 1649 s, ν (aromatic, C—O—C) 1050 s, ν (aromatic, C=C) 1561, 1410 m, ν (M—O) 618 s, ν (M—N) 663 s.

Characterization techniques

The IR and UV-vis spectra were measured with a PerkinElmer (Germany) FTIR BX and a Shimadzu (Japan) UV-1208, respectively. Elemental analysis was carried out with a Carlo Erba (Italy) 1106. The FTIR spectra were recorded with KBr discs (4000–350 cm⁻¹). UV-vis spectra of 2-MIMP and O-2-MIMP were recorded with DMSO. 2-MIMP and O-2-MIMP were characterized with ¹H- and ¹³C-NMR spectra with a Bruker (Germany) AC FT NMR spectrometer operating at 400 and 100.6 MHz,



Scheme 3

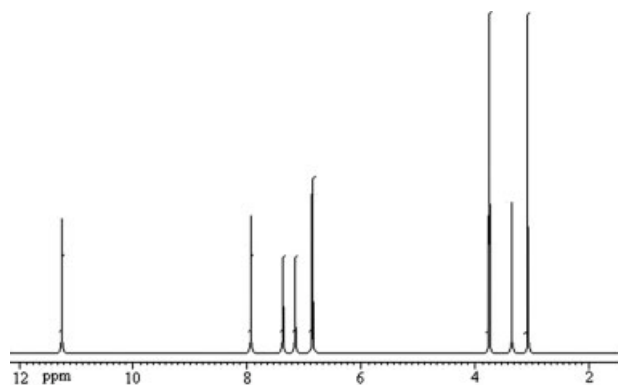


Figure 1 ^1H -NMR spectrum of 2-MIMP.

respectively, and recorded at 25°C with deuterated DMSO as a solvent. Tetramethylsilane was used as the internal standard. Thermal data were obtained with a PerkinElmer Diamond thermal analyzer. TG-DTA measurements were made between 20 and 800°C (in N_2 at a rate of 10°C/min). SEC analyses were performed at 30°C with DMF/methanol (4/1 v/v) as the eluent at a flow rate of 0.4 mL/min. A refractive-index detector was used as a detector. The instrument (10AVp series high-performance liquid chromatography/size exclusion chromatography system, Shimadzu, Japan) was calibrated with a mixture of polystyrene standards (Polymer Laboratories; the peak molecular weights were between 162 and 19,880) with gel permeation chromatography software for the determination of the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) of the polymer samples. For SEC investigations (100-Å and 7.7-nm-diameter loading material, Macherey-Nagel GmbH & Co., Germany), 3.3-mm-i.d., 300-mm columns were used. Metal analysis was determined by the complexometric titration method.

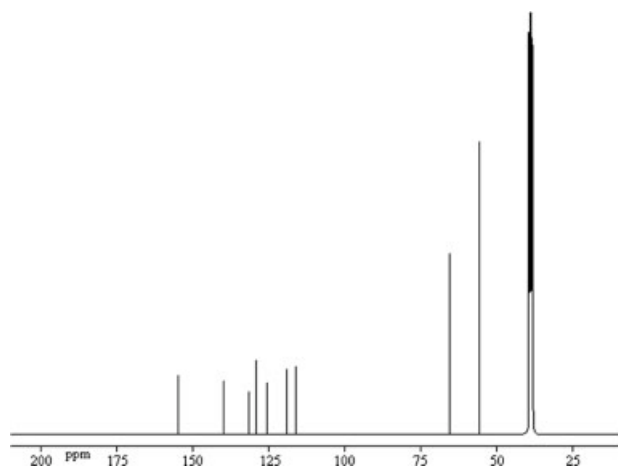


Figure 2 ^{13}C -NMR spectrum of 2-MIMP.

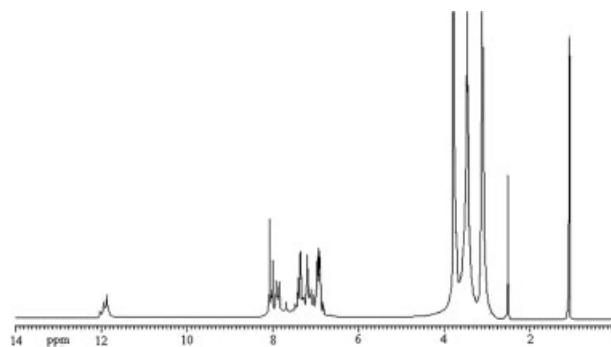


Figure 3 ^1H -NMR spectrum of O-2-MIMP.

RESULTS AND DISCUSSION

Synthesis of O-2-MIMP

The optimum reaction conditions of 2-MIMP were investigated in an aqueous alkaline medium with air O_2 , H_2O_2 , and NaOCl as oxidants. When 2-MIMP interacted with these oxidants in an aqueous alkaline medium, brown phenoxy radicals immediately precipitated in the solution medium. The oxidative polycondensation reaction conditions of 2-MIMP with a 30% NaOCl solution in an aqueous alkaline medium are given in Table I. The conversion to the oligomer of the 2-MIMP solution was 58.0% for the NaOCl oxidant for 3 h at 50°C. Table I shows that the yield of the oligomer decreased with increasing temperature and reaction time. Under the same conditions, when the molar amount of NaOCl was doubled, the total yield of O-2-MIMP changed from 58.0 to 22.0%. The yield of O-2-MIMP was 31.0% with $[\text{2-MIMP}]_0 = [\text{KOH}]_0 = [\text{NaOCl}]_0 = 0.2$ mol/L at 50°C for 25 h. The conversion of 2-MIMP to the oligomer decreased with an increase in the oligomerization time under the same conditions. The rea-

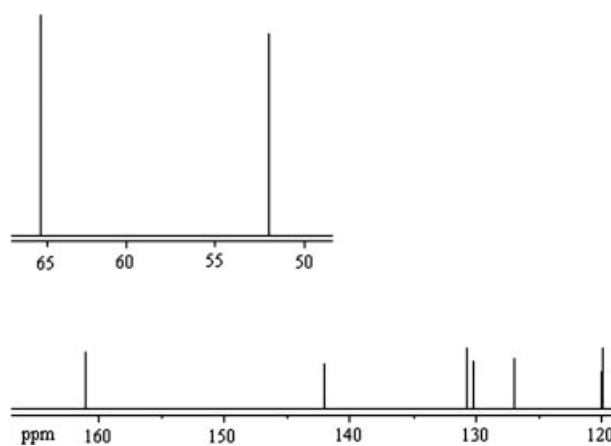
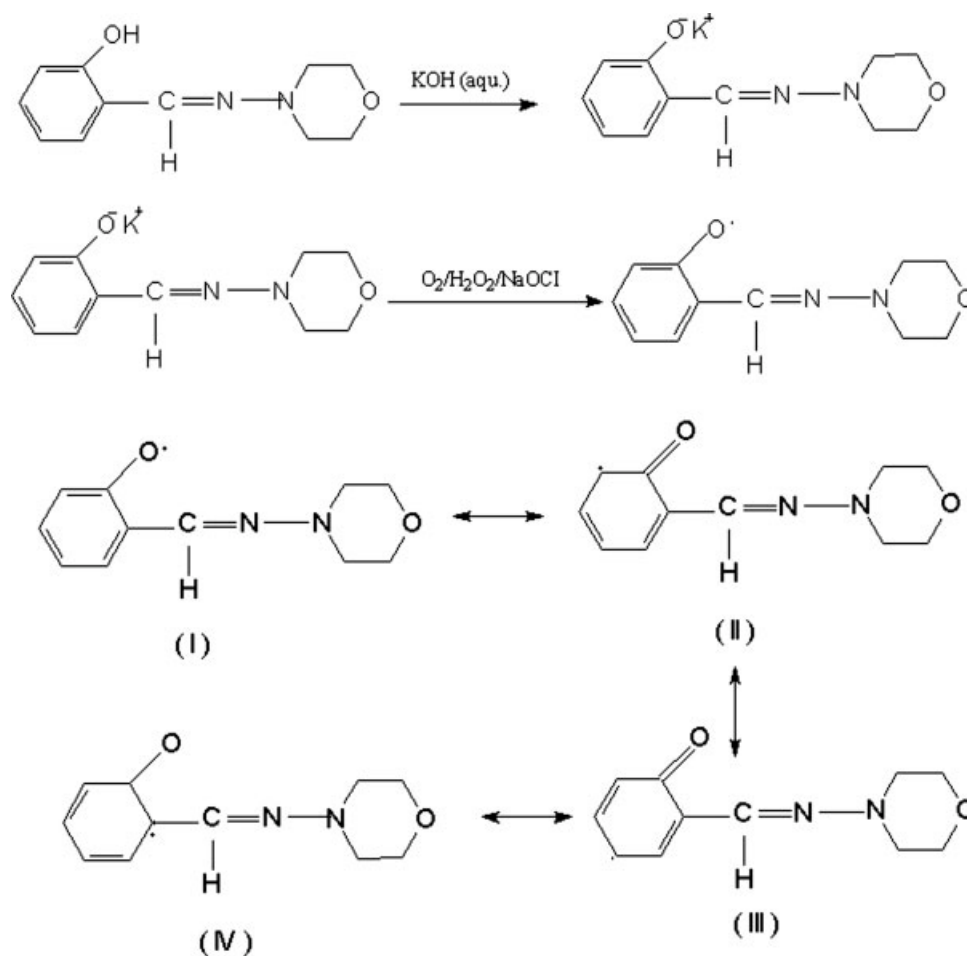


Figure 4 ^{13}C -NMR spectrum of O-2-MIMP.



Scheme 4

son for this may be the conversion from the oligomer to the monomer at the high reaction times.

The oxidative polycondensation reaction conditions of 2-MIMP with air O_2 in an aqueous alkaline medium are given in Table II. The conversion of 2-MIMP was 12.00% with $[\text{2-MIMP}]_0 = [\text{KOH}]_0 = 0.2 \text{ mol/L}$ and air O_2 (flow rate = 8.5 L/h) at 70°C for 10 h. Under the same conditions, when the temperatures and reaction times were increased, the total yield of O-2-MIMP decreased. When the reaction temperatures increased from 70 to 90°C , the yield changed from 8 to 6%. When the temperature was over 70°C , the conversion decreased slightly. Warm heating is of possible benefit to chain propagation for obtaining higher conversions, but higher temperatures usually result in deactivated species in azomethine polymerizations. It is possible that chain transfer takes place more easily at higher temperatures.

The oxidative polycondensation reaction conditions of 2-MIMP with a 30% H_2O_2 solution in an aqueous alkaline medium are given in Table III. The conversion of 2-MIMP was 28.0% under the optimum conditions of $[\text{2-MIMP}]_0 = [\text{KOH}]_0 = [\text{H}_2\text{O}_2]_0 = 0.20 \text{ mol/L}$ at 70°C for 3 h. The conversion of 2-MIMP was

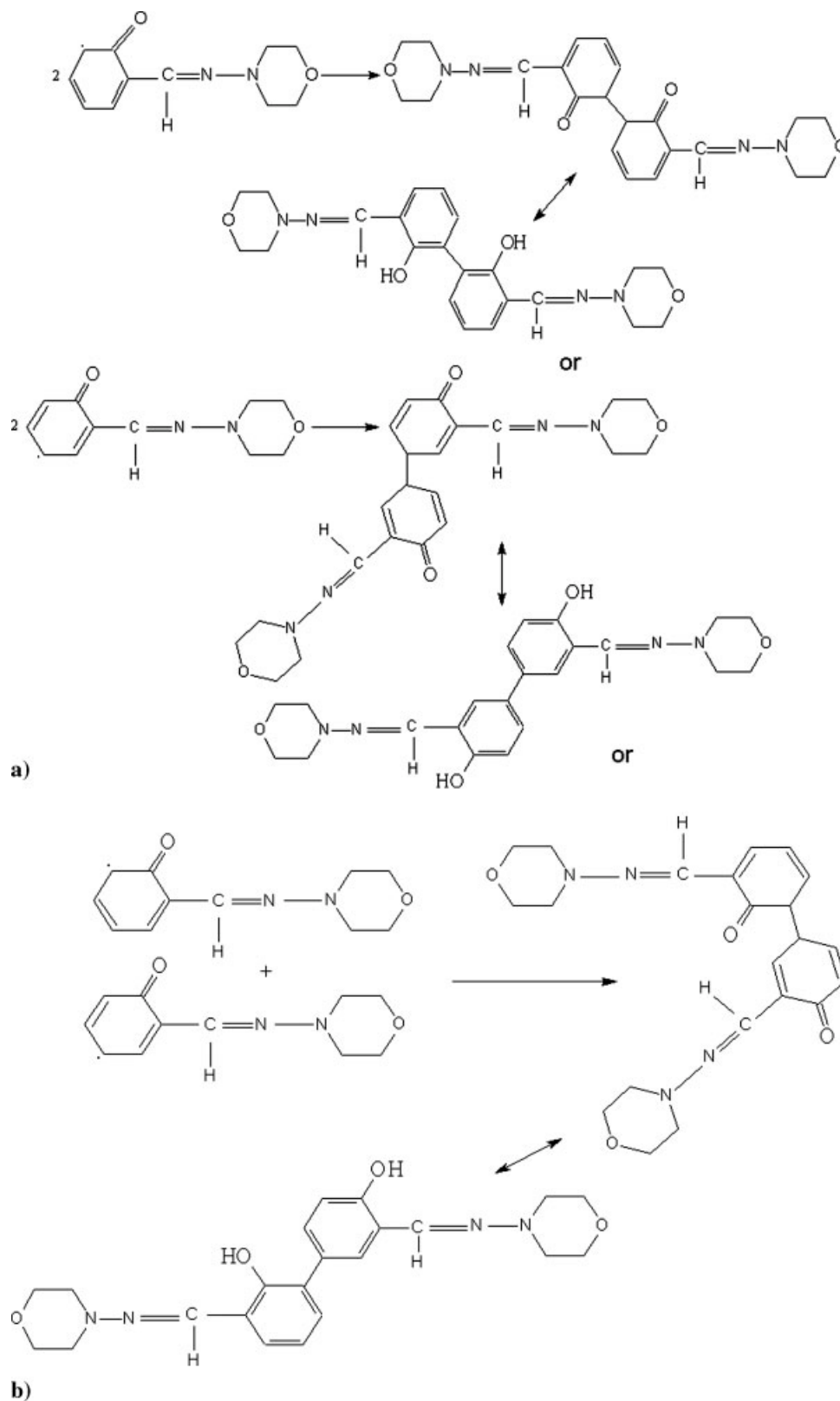
26.0% with $[\text{2-MIMP}]_0 = [\text{KOH}]_0 = [\text{H}_2\text{O}_2]_0 = 0.20 \text{ mol/L}$ at 70°C for 1 h. According to these values, increasing the reaction time reduced the yields of the oligomer. As shown in Tables I–III, the yields of these reactions were dependent on the temperature, time, and initial concentrations of the oxidants. NaOCl was a better oxidant than air O_2 and H_2O_2 under the same conditions for the conversion of 2-MIMP.

Solubility

O-2-MIMP was a brown powder and was completely soluble in organic solvents such as DMF, THF, DMSO, methanol, and ethanol. O-2-MIMP was insoluble in hexane, benzene, toluene, CH_2Cl_2 , CHCl_3 , CCl_4 , and acetone but was partly soluble in ethyl acetate. O-2-MIMP/Pb was insoluble in hexane, benzene, toluene, DMSO, THF, DMF, CH_2Cl_2 , CHCl_3 , CCl_4 , methanol, ethanol, and acetone.

Structure of O-2-MIMP

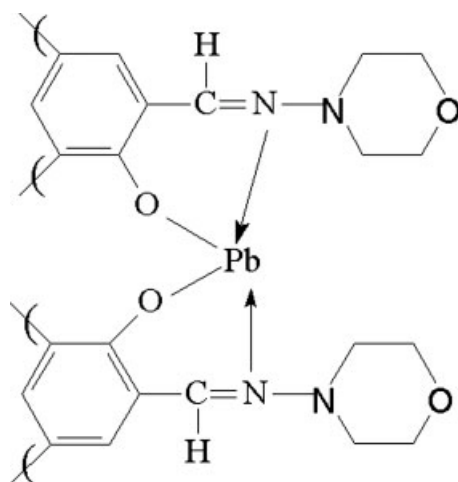
SEC analyses of O-2-MIMP were performed at 30°C with DMF/methanol (4/1 v/v) as the eluent at a



Scheme 5

flow rate of 0.4 mL/min. With the oxidant H_2O_2 , M_n , M_w , and PDI of O-2-MIMP were 2420 g/mol, 2740 g/mol, and 1.187, respectively. When air O_2 was used as the oxidant, M_n , M_w , and PDI of

O-2-MIMP were 1425 g/mol, 2060 g/mol, and 1.446, respectively. Two peaks were observed in the chromatogram of O-2-MIMP; 75% of the mass of O-2-MIMP was low-molecular-weight ($M_n = 1687$,



Scheme 6

$M_w = 2239$ g/mol, PDI = 1.328), but 25% of its weight was high-molecular-weight ($M_n = 31261$, $M_w = 34397$ g/mol, PDI = 1.100). With the oxidant NaOCl, M_n , M_w , and PDI of O-2-MIMP were 1309 g/mol, 1401 g/mol, and 1.070, respectively.

The UV-vis spectra of 2-MIMP, O-2-MIMP, and the O-2-MIMP/Pb complex compound were measured with DMSO as the solvent. In the spectra of 2-MIMP, K bands of phenol and $C_6H_5-N=$ were observed at 230 and 255 nm, respectively. The benzene band of 2-MIMP and the strength R band of $-CH=N-$ groups were observed at 290 and 345 nm, respectively. The λ_{max} values of O-2-MIMP were observed at 240, 260, 329, and 392 nm. In UV-vis spectra of O-2-MIMP, K and R bands were observed at 240 and 392 nm, respectively.

The FTIR spectra of the oxidative polycondensation product of 2-MIMP were only different in the reduction of the band strength and numbers from

the FTIR spectra of 2-MIMP. In the FTIR spectra of 2-MIMP and O-2-MIMP, bands of $-OH$ and $-CH=N$ groups were observed at 3360 and 1601 cm^{-1} and at 3448 and 1620 cm^{-1} , respectively. To identify the structures of the monomer and oligomer, the 1H -NMR spectra were recorded in $DMSO-d_6$. 1H - and ^{13}C -NMR spectra of the monomer are given in Figures 1 and 2, respectively. In the 1H -NMR spectra of 2-MIMP and O-2-MIMP, the signals of $-OH$ and $-CH=N$ groups were observed at 11.27 and 7.95 ppm and at 11.87 and 8.01 ppm, respectively. According to the FTIR spectral data and the results of the 1H - and ^{13}C -NMR spectra, the phenyl rings in the polymer were linked primarily at the ortho and para positions.

Other phenol derivatives have also been polymerized, and the results have been reported in the literature.^{6,9,13} Crosslinking in a polymer structure is expected in those cases in which the ortho and para positions in the corresponding monomer structure are unsubstituted. ^{13}C -NMR studies of O-2-MIMP indicate that the linkage between any two adjacent phenyl rings is largely at the ortho and para positions (Figs. 3 and 4). However, this type of linkage may strain the polymer backbone in such a manner that the phenyl rings are out of plane with respect to the adjacent rings. The peak values for C2 and C4 can be observed at 116.43 and 119.99 ppm for the monomer and at 119.39 and 126.15 ppm for the polymer, respectively. These values are in agreement with the theoretically calculated peak positions for ortho and para linkages on the ring. On the other hand, if the monomer were linked at meta positions on the ring, the peaks for C3 and C5 should shift downfield. There was no significant change in the peak positions for C3 and C5 of the oligomer. Although the hydroxyl groups are involved in the

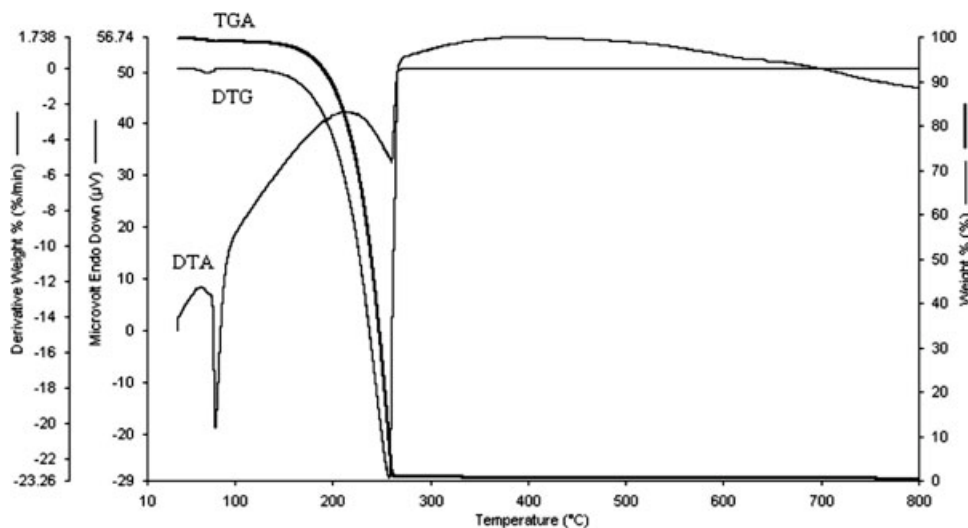


Figure 5 TGA-DTG-DTA curves of 2-MIMP.

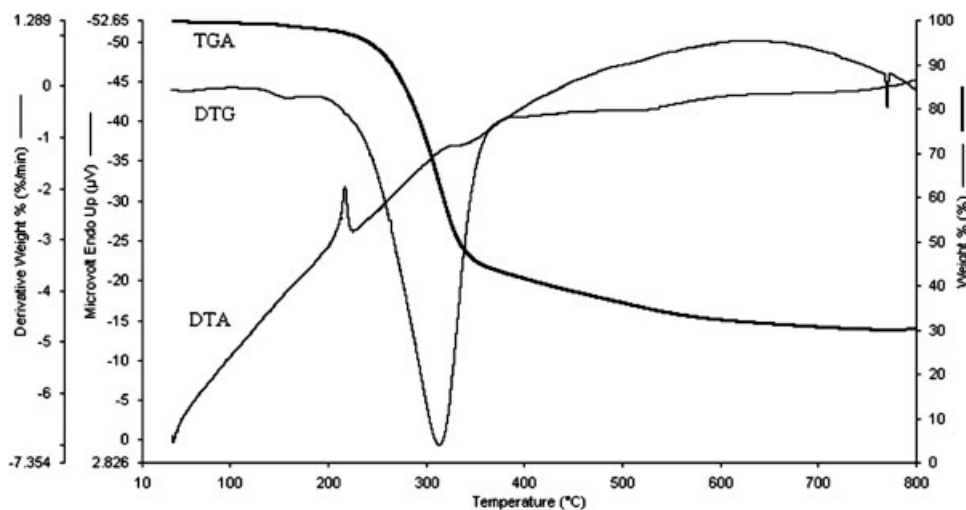


Figure 6 TGA-DTG-DTA curves of O-2-MIMP.

formation of free radicals leading to polymer formation, they do not appear to be involved in bond formation. Thus, the phenyl rings in the polymer appear to be linked primarily at the ortho and para positions. The reaction mechanism for the coupling selectivity was studied by Kaya and coworkers,⁹ and three possible reaction mechanisms for the C—C coupling selectivity have been proposed, as shown in Scheme 4.

The ¹³C-NMR spectrum of O-2-MIMP showed C—C coupling systems. Monomer and dimer inter-conversion combinations of radical units are proposed in Scheme 5.

Metal complex compounds of this oligomer were not formed from selected metal salts such as Co(AcO)₂ · 4H₂O, Ni(AcO)₂ · 4H₂O, Cu(AcO)₂ · 4H₂O, 3FeSO₄ · 7H₂O, ZnCl₂, Hg(NO₃)₂ · H₂O, MnSO₄ · H₂O, MgSO₄ · 7H₂O, and Cd(AcO)₂ · 2H₂O. The

complex compound of this oligomer was formed only with Pb(AcO)₂ · 3H₂O. For this reason, this oligomer can be selective for the Pb(II) ion. In the FTIR spectra of O-2-MIMP/Pb, bands of OH, —CH=N, M—O, and M—N groups were observed at 3510, 1649, 618, and 663 cm⁻¹, respectively.

The stretching bands of the —OH group and —CH=N group shifted to 3510 and 1649 cm⁻¹, respectively, as a result of coordination of the azomethine nitrogen atom with the Pb(II) ion. The —CH=N vibration shifted to a lower frequency in the complexes by 29 cm⁻¹, suggesting the involvement of nitrogen in the coordination.⁹ The structure of the oligomer/Pb(II) complex compound is shown in Scheme 6.

A new Pb(II)-selective electrode has been developed, based on a bis(acetylacetonate)-*p*-phenylenediamine-lead(II) {[LPb(NO₃)₂]H₂O} complex ionophore

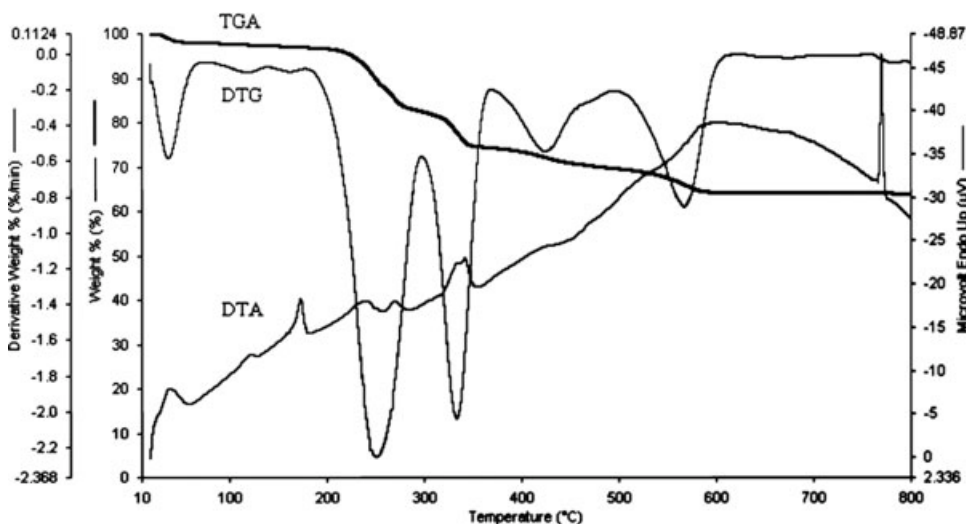


Figure 7 TGA-DTG-DTA curves of the O-2-MIMP/Pb complex compound.

as a sensing material, dioctylphthalate as a solvent mediator, and poly(vinyl chloride) as a matrix.¹⁴

Thermal analyses

The thermal degradations of the monomer, oligomer, and oligomer–metal complex were studied with TG–DTA in the medium N₂, and the curves of these analyses are given in Figures 5–7, respectively. The initial degradation temperature and 100.00% weight loss of 2-MIMP were found at 208 and 300°C, respectively. The initial degradation temperature and 69.83% weight loss of O-2-MIMP were found at 264 and 800°C, respectively. This oligomer formed a carbene residue in a high amount (30.17%) at 800°C. Because of long conjugated band systems, the oligomer demonstrated higher resistance against high temperatures than the monomer. The high thermal stability of O-2-MIMP demonstrated the formation of a C–C coupling system. The initial degradation temperature and 36.22% weight loss of the O-2-MIMP/Pb complex compound were found at 229 and 800°C, respectively. The differential thermogravimetry (DTG) curve of the O-2-MIMP/Pb complex compound shows that the thermal degradation of the O-2-MIMP/Pb complex compound occurred in four steps. In the first step, the highest weight loss was observed between 210 and 300°C, and the second, third, and fourth steps were observed at 300–380, 380–500, and 500–620°C, respectively. According to thermogravimetric analysis (TGA), the O-2-MIMP/Pb complex compound was more stable than 2-MIMP and O-2-MIMP against temperature and thermal decomposition. According to the TG curve, the high thermal stability of the O-2-MIMP/Pb oligomer complex compound may indicate the formation of metal–oxygen valance and a metal–nitrogen coordination bond between the oligomer and metal ion. The presence of water can also be seen in the TG curve of the oligomer–metal complex compound (Fig. 7), which appeared until a 4 wt % loss in the 50–190°C range.

CONCLUSIONS

2-MIMP was converted to the oligomer by the oxidation of air O₂, H₂O₂, and NaOCl in an aqueous alkaline medium. The yield of O-2-MIMP was 58% with the NaOCl oxidant. The M_n , M_w , and PDI values of 2-MIMP were 2420 g/mol, 2740 g/mol, and 1.187, respectively, with H₂O₂; 1425 g/mol, 2060 g/mol, and 1.446, respectively, with air O₂; and 1309 g/mol, 1401 g/mol, and 1.070, respectively, with NaOCl. In the oxidative polycondensation reaction of 2-MIMP, air O₂ demonstrated less activity than the NaOCl and H₂O₂ oxidants. Spectral analyses, such as UV–vis, FTIR, and ¹H- and ¹³C-NMR, demonstrated the formation of oligomers from ortho and para carbons of the phenol ring through the oxidative polycondensation of 2-MIMP. According to TG–DTA analyses, 2-MIMP and O-2-MIMP had less stability than the oligomer–metal complex compound against thermal degradation.

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