



Synthesis, Characterization, Thermal Properties and Conductivity of Oligo-4-[(2-methoxyphenylimino)methyl]phenol

Ismet Kaya* and Semra Koça

Department of Chemistry, Faculty of Sciences and Arts
Çanakkale Onsekiz Mart University, TR-17020, Çanakkale, Turkey

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ABSTRACT

The oxidative polycondensation reaction conditions of 4-[(2-methoxyphenylimino)methyl]phenol (2-MPIMP) were studied by using oxidants such as air and NaOCl in an aqueous alkaline medium between 50°C and 90°C. The structures of synthesized monomer and oligomer were confirmed by FTIR, UV-vis, ¹H NMR, ¹³C NMR and elemental analysis. The characterization was afforded by TGA-DTA, size exclusion chromatography (SEC) and solubility tests. At optimum reaction conditions, the yield of oligo-4-[(2-methoxyphenylimino)methyl]phenol (O-2-MPIMP) was found to be 38.72% and 72.21% by air and NaOCl oxidants, respectively. 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-MPIMP were respectively found to be 1400, 2350 g.mol⁻¹, and 1.679 using air and 1650, 2350 g.mol⁻¹, and 1.424 using NaOCl. TGA-DTA analyses of O-2-MPIMP were shown to be a stable compound against thermal decomposition. The weight losses of 2-MPIMP and O-2-MPIMP were found to be 57.09% and 59.11% at 1000°C, respectively. Also, electrical conductivity of the O-2-MPIMP was measured, showing that the oligomer was a semiconductor. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of monomer and oligomer were determined from the onset potentials for n-doping and p-doping, respectively. Optical band gaps (E_g) of 2-MPIMP and O-2-MPIMP were calculated from UV-vis measurements.

Key Words:

oxidative polycondensation;
oligo-4-[(2-methoxyphenylimino)
methyl]phenol;
thermal analysis;
conductivity and band gap.

INTRODUCTION

Polymers are useful materials in fabrication, flexibility, chemical inertness as well as being light in weights. Polymers with highly conjugated chains have attracted much attention in the last few years because they are materials of academic interest and also they are investigated as the materials of

electronics [1,2], opto-electronics [3,4] and photonics [5]. In addition, electrically conducting polymers have a wide variety of applications ranking from electrode materials [6], microelectronic devices [7], catalysts for photo-electrochemical processes [8], organic batteries [9] to electrochemical display devices

(*) To whom correspondence to be addressed.
E-mail: kayaismet@hotmail.com

[10]. The oxidative polycondensation method is simply the reaction of compounds including $-OH$ groups and active functional groups ($-NH_2$, $-CHO$, $-COOH$) in their structure with the oxidants as $NaOCl$, H_2O_2 , and air in the aqueous alkaline and acidic medium [11]. Another class of this family is that of polyimines (PIs), which are also known as polymeric Schiff bases, polymers that are synthesized by a polycondensation reaction between an amine and hydrazine with an aldehyde or diketone [12]. Because of the properties based on their electronic structure, oligophenols and their derivatives have been used in various fields. They have paramagnetism, semi-conductivity, electrochemical cell and resistance to high energy. Therefore, they have been used to prepare composites with resistance to high temperature and graphite materials, epoxy oligomer and block copolymers, adhesives, photoresists and antistatic materials [13-19]. Schiff based derivatives of oligophenols have antimicrobial properties [20,21]. In addition, the conductivity and electrochemical properties of some poly(Schiff) bases and their metal complexes have been studied by Kaya et al. [22,23].

In this article, we have investigated the effects of different parameters such as temperature, the reaction time and the concentration of oxidants as $NaOCl$ for O-2-MPIMP in alkaline medium. Also, these effects on the physical and chemical properties of methoxy group of azomethine oligomer were investigated. 2-MPIMP and O-2-MPIMP were characterized by using FTIR, UV-vis, 1H NMR, ^{13}C NMR and SEC techniques. In addition, thermal stabilities of 2-MPIMP and O-2-MPIMP were measured by TG-DTA tech-

niques. The electrical conductivity of monomer and oligomer were measured by doping with I_2 , using a four-point probe technique at room temperature and atmospheric pressure. At the end of the doping with I_2 an important increase was attained on the conductivity of 2-MPIMP and O-2-MPIMP. Finally, electrochemical properties of 2-MPIMP and O-2-MPIMP were determined by cyclic voltammetry. HOMO, LUMO and electrochemical energy gaps (E'_g) were calculated from the oxidation and reduction onset values. Also, optical (E_g) energy gaps of the monomer and oligomer were determined from their absorption edges at UV-vis measurements.

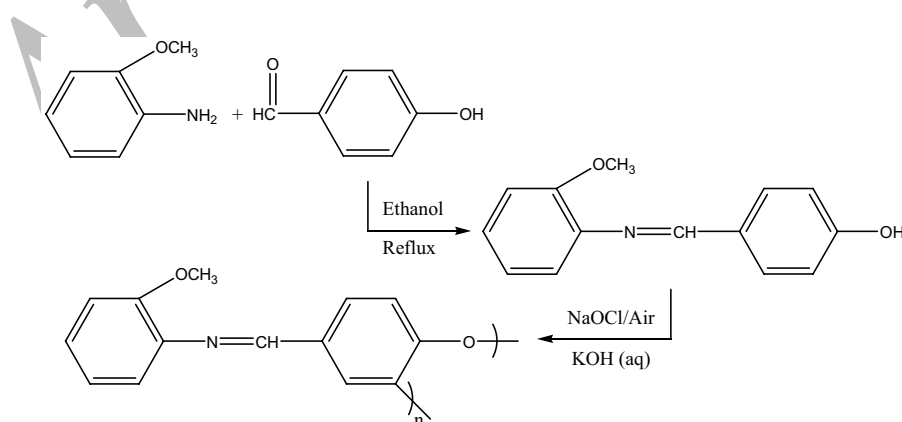
EXPERIMENTAL

Materials

All solvents and reagents were supplied from Merck Chemical Co. and they were used as received. Sodium hypochlorite ($NaOCl$), (30% aqueous solution) was supplied from Paksoy Chemical Co. (Turkey). The chemical 4-[(2-methoxyphenylimino)methyl]phenol was synthesized from the condensation reaction of *o*-anisidine with *p*-hydroxybenzaldehyde.

Preparation of 4-[(2-Methoxyphenylimino)methyl]phenol (2-MPIMP)

2-MPIMP was prepared by the condensation of *o*-anisidine (1.23 g, 0.01 mol) with *p*-hydroxybenzaldehyde (1.22 g, 0.01 mol) in ethanol (30 mL) achieved by boiling the mixture under reflux for 2 h at $70^\circ C$ (Scheme I). The precipitated 2-MPIMP was filtered,



Scheme I. Synthesis of 4-[(2-methoxyphenylimino)methyl]phenol (2-MPIMP) and oligo-4-[(2-methoxyphenylimino)methyl]phenol (O-2-MPIMP).

recrystallized from ethanol and dried in vacuum desiccators (yield 86%).

Calcd. for 2-MPIMP: C, 74.01; H, 5.73; N, 6.17. Found: C, 73.85; H, 5.62; N, 6.03. UV-vis (λ_{\max}): 206, 220, 281, and 324 nm. FTIR (cm^{-1}): $\nu(\text{O-H})$ 3150 s, $\nu(\text{C-H phenyl})$ 3009 m, $\nu(\text{C-H aliphatic})$ 2936 s, $\nu(\text{C=N})$ 1604 s, $\nu(\text{OCH}_3)$ 1150 s, $\nu(\text{C=C phenyl})$ 1582, 1517, 1492 s, $\nu(\text{C-O})$ 1251 s. $^1\text{H NMR}$ (DMSO): δ , ppm, 10.21 (s, 1H, -OH), 8.37 (s, 1H, -CH=N-), 7.33 (d, 2H), 7.82 (d, 2H, Ar-Hbb'), 6.93-7.00 (m, 5H, Ar-Haa', Ar-Hc, Ar-Hd and Ar-He), 7.14 (t, 1H, Ar-Hf), 3.77 (s, 3H, -OCH₃). $^{13}\text{C NMR}$ (DMSO): δ , ppm, 160.90 (C1-ipso), 116.15 (C2), 131.12 (C3), 128.23 (C4-ipso), 161.11 (C5), 142.46 (C6-ipso), 152.33 (C7-ipso), 112.32 (C8), 126.35 (C9), 121.34 (C10), 120.66 (C11), 55.83 (C12).

Synthesis of Oligo-4[(2-methoxyphenylimino)methyl]phenol (O-2-MPIMP) with NaOCl and Air in Aqueous Alkaline Medium

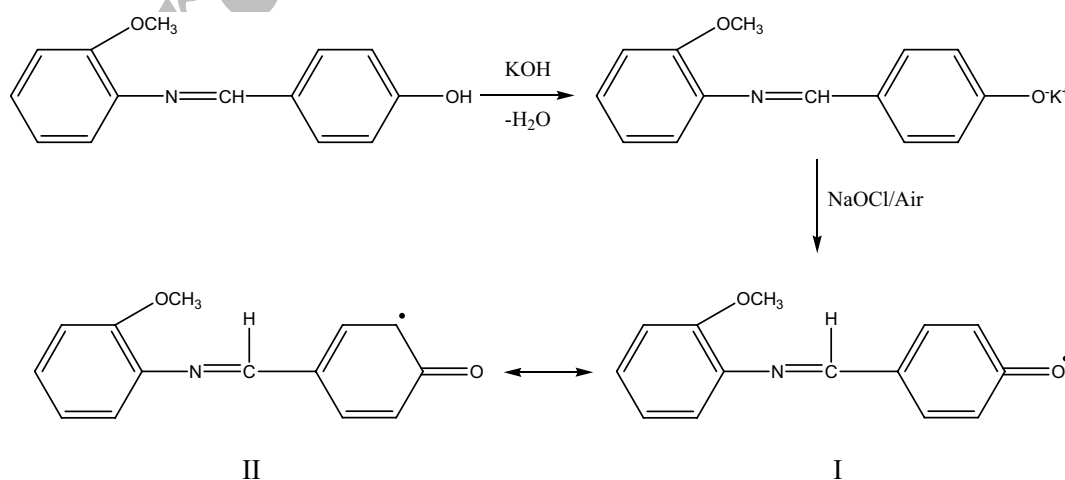
O-2-MPIMP was synthesized through oxidative polycondensation of 2-MPIMP solution of NaOCl (30%) and air oxidants [20], respectively (Scheme II). 2-MPIMP (0.227 g, 0.001 mol) was dissolved in an aqueous solution of KOH (0.056 g, 0.001 mol) and placed into a 50-mL three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and a funnel containing NaOCl. After heating to room temperature, NaOCl was added dropwise over about 30 min and the mixture was heated between 50°C and 90°C. The reaction mixtures were stirred at various temperatures and durations (Table 1). Air passed into

an aqueous solution of KOH (20%) before passing through the reaction tube to prevent water loss in the reaction mixture and to remove CO₂ (Scheme I). The mixture was neutralized with 0.001 mol HCl (37%) at room temperature. Unreacted monomer was separated from the reaction products by washing with ethanol. The mixture was filtered and washed with hot water (3 × 25 mL) to remove mineral salts and then dried in an oven at 105°C.

Calcd. for O-2-MPIMP: C, 74.67; H, 4.89; N, 6.22. Found: C, 74.00; H, 4.45; N, 6.00. UV-vis (λ_{\max}): 208, 278, and 380. FTIR (cm^{-1}): $\nu(\text{O-H})$ 3303 s, $\nu(\text{C-H phenyl})$ 3068 m, $\nu(\text{C-H aliphatic})$ 2942 s, $\nu(\text{C=N})$ 1580 s, $\nu(\text{OCH}_3)$ 1085 s, $\nu(\text{C=C phenyl})$ 1508, 1482, 1463 s, $\nu(\text{C-O})$ 1244 s. $^1\text{H NMR}$ (DMSO): δ , ppm, 9.98 (s, 1H, -OH), 8.97 (s, 1H, -CH=N-), 6.70-7.75 (m, 5H, aromatic protons), 3.94 (s, 3H, -OCH₃). $^{13}\text{C NMR}$ (DMSO): δ , ppm, 157.17 (C1-ipso), 95.90 (C2-ipso), 127.50 (C3), 130.03 (C4-ipso), 179.71 (C5), 147.16 (C6-ipso), 152.55 (C7-ipso), 112.53 (C8), 126.33 (C9), 124.05 (C10), 121.31 (C11), 56.30 (C12), 117.83 (new peak of C-C coupling system).

Electrochemical Properties

Cyclic voltammetry (CV) measurements were carried out with a CH instruments 660C Electrochemical Analyzer at a potential scan rate of 20 mV/s. All the experiments were performed in dry box under Ar atmosphere at room temperature. The electrochemical potential of Ag was calibrated with respect to the ferrocene/ferrocenium (Fc/Fc⁺) couple. The half-



Scheme II. The reaction mechanism of phenoxy radical formation.

Table 1. The oxidative polycondensation reaction parameters of (2-MPIMP)^a with NaOCl (samples no 1-15) and air (samples no 16-25) in aqueous KOH.

Sample no	Temperature (°C)	Time (h)	[2-MPIMP] ₀ (mol/L)	[KOH] ₀ (mol/L)	[NaOCl] ₀ (mol/L)	Yield of O-2-MPIMP (%)
1	50	3	0.05	0.05	0.15	23
2	60	3	0.05	0.05	0.15	32
3	70	3	0.05	0.05	0.15	26
4	80	3	0.05	0.05	0.15	22
5	90	3	0.05	0.05	0.15	13
6	60	5	0.05	0.05	0.15	41
7	60	10	0.05	0.05	0.15	48
8	60	15	0.05	0.05	0.15	66
9	60	20	0.05	0.05	0.15	56
10	60	15	0.05	0.075	0.15	18
11	60	15	0.05	0.100	0.15	16
12	60	15	0.05	0.125	0.15	14
13	60	15	0.05	0.075	0.225	57
14	60	15	0.05	0.05	0.300	72
15	60	15	0.05	0.075	0.375	67
16	50	3	0.05	0.01	8.5	24
17	60	3	0.05	0.01	8.5	23
18	70	3	0.05	0.01	8.5	22
19	80	3	0.05	0.01	8.5	20
20	90	3	0.05	0.01	8.5	20
21	50	5	0.05	0.01	8.5	30
22	50	10	0.05	0.01	8.5	34
23	50	15	0.05	0.01	8.5	39
24	50	20	0.05	0.01	8.5	26
25	50	15	0.05	0.01	8.5	35

a = The initial concentration of 2-MPIMP was used as 0.05 mol.L⁻¹.

wave potential ($E^{1/2}$) of (Fc/Fc⁺) measured in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) acetonitrile solution is 0.39 V vs. Ag wire or 0.38 V vs. supporting calomel electrode (SCE). The voltammetric measurements were carried out for 2-MPIMP and O-2-MPIMP in acetonitrile and DMSO, respectively. The HOMO and LUMO energy levels of 2-MPIMP and O-2-MPIMP were determined from the onset potentials of the n-doping (ϕ'_n) and p-doping (ϕ'_p), respectively, as in literature [24].

Optical Properties

The optical band gaps (E_g) of monomer and oligomer compounds were calculated from their absorption edges. Ultraviolet-visible spectra were measured by a

Perkin Elmer Lambda 25 spectrophotometer. The absorption spectra of monomer and oligomer were recorded at 25°C by using methanol (MeOH) and DMSO, respectively.

Electrical Properties

Conductivity was measured on a Keithley 2400 Electrometer. The pellets were pressed on hydraulic press developing up to 1687.2 kg/cm². Iodine doping was carried out by the exposure of the pellets to iodine vapour at atmospheric pressure and room temperature in a desiccator [23].

Solubility and Characterization Techniques

O-2-MPIMP was a dark brown powder and it was

completely soluble in organic solvents such as DMF, THF, DMSO, aqueous alkaline and concentrated H_2SO_4 but it was partly soluble in toluene, ethanol. 2-MPIMP was only completely soluble in DMF but it was insoluble in methanol, ethanol, THF, acetone, chloroform. The solubility tests were performed by using 1 mg sample and 1 mL solvent at 25°C. The infrared spectra were measured by a Perkin Elmer FTIR instrument. The FTIR spectra were recorded using ATR attachment ($4000-550\text{ cm}^{-1}$). UV-vis spectra of 2-MPIMP and O-2-MPIMP were determined by using MeOH and DMSO, respectively. Elemental analysis was carried out with a Carlo Erba 1106 Elemental Analyzer. 2-MPIMP and O-2-MPIMP were characterized by using 1H NMR and ^{13}C NMR spectra (Bruker AC FT NMR spectrometer operating at 400 and 100.6 MHz, respectively) and were recorded using deuterated DMSO- d_6 as a solvent at 25°C. Tetramethylsilane was used as internal standard. Thermal data were obtained by using a Perkin-Elmer Diamond Thermal Analysis system (USA). The TGA-DTA measurements were made between 15-1000°C (in N_2 , 10°C/min). The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) values were determined by size exclusion chromatography (SEC) techniques of the Shimadzu Co. For SEC investigations we used an SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. × 300 mm column; eluent: DMF/MeOH (v/v, 4/1, 0.4 mL/min), polystyrene standards. A refractive index detector was used to analyze the product at 25°C.

RESULTS AND DISCUSSION

Synthetic Conditions of O-2-MPIMP

2-MPIMP was not oxidized in normal condition of neutral aqueous and organic medium by air and NaOCl (30% aqueous solution), because when 2-MPIMP interacted by oxidants such as air and NaOCl, it immediately precipitated the phenoxy radicals, producing brown colouration when added to alkaline solution. The reaction conditions of oxidative polycondensation of 2-MPIMP with 30% NaOCl solution in aqueous alkaline medium are given in Table 1 (samples no 1-15). The yield of O-2-MPIMP was 32%

in NaOCl medium for 3 h at 60°C (sample no 2). The yield of O-2-MPIMP was 66% in reaction conditions such as $[KOH]_0 = [2-MPIMP] = 0.05\text{ mol/L}$ $[NaOCl]_0 = 0.15\text{ mol/L}$ at 60°C for 15 h (sample no 8). Under similar conditions (except for KOH), the yield of O-2-MPIMP was 72% (sample no 14). When the amount of KOH in molar units increased to twice amount, total yield of O-2-MPIMP dropped from 66% (sample no 8) to 16% (sample no 11). That is, the increase in the amount of KOH lowered the yield of O-2-MPIMP. The increase in the amount of NaOCl, however, increased O-2-MPIMP yield as reported in Table 1. In addition, when the temperature raised from 50°C to 90°C the yield of O-2-MPIMP was reduced to 13% (sample no 5) from the earlier 23% (sample no 1). The oxidative polycondensation reaction of 2-MPIMP with air oxidant in an aqueous alkaline medium is given in Table 1 (samples no 16-25). In oxidative polycondensation reaction of 2-MPIMP when air passed with rate of 8.5 L/h into the reaction medium at 50°C for 3 h, the yield of product was 24% (sample no 16). The yield of O-2-MPIMP was 39% at optimum conditions such as $[2-MPIMP]_0 = 0.05$ $[KOH]_0 = 0.01\text{ mol/L}$ and 8.5 $L\cdot h^{-1}$ rate at 50°C for 15 h (sample no 23). As it is seen from Table 1, the yield of the oligomer in these reactions was dependent upon temperature, reaction time and initial concentrations of alkaline and the oxidants. Under the same conditions, the yield of O-2-MPIMP with NaOCl oxidant was higher than air.

Structure of O-2-MPIMP

According to SEC chromatograms, the values of number average molecular weight (M_n) and weight average molecular weight (M_w) of O-2-MPIMP were calculated according to a polystyrene standard calibration curve and are given in Table 2. It is seen that, three fractions are observed in oligomer treated by air and NaOCl oxidants. A high fraction of products had a small molecular weight distribution. As it is reported in Table 2, with increase in reaction time the values of M_n and M_w of the oligomer increased as well.

The UV-vis spectra of both 2-MPIMP and O-2-MPIMP were similar. However, in the spectra of 2-MPIMP, strong K band of phenol was observed in 206 nm. Benzene band of 2-MPIMP was in 220 nm and R bands were in 281 nm and 324 nm. R band at

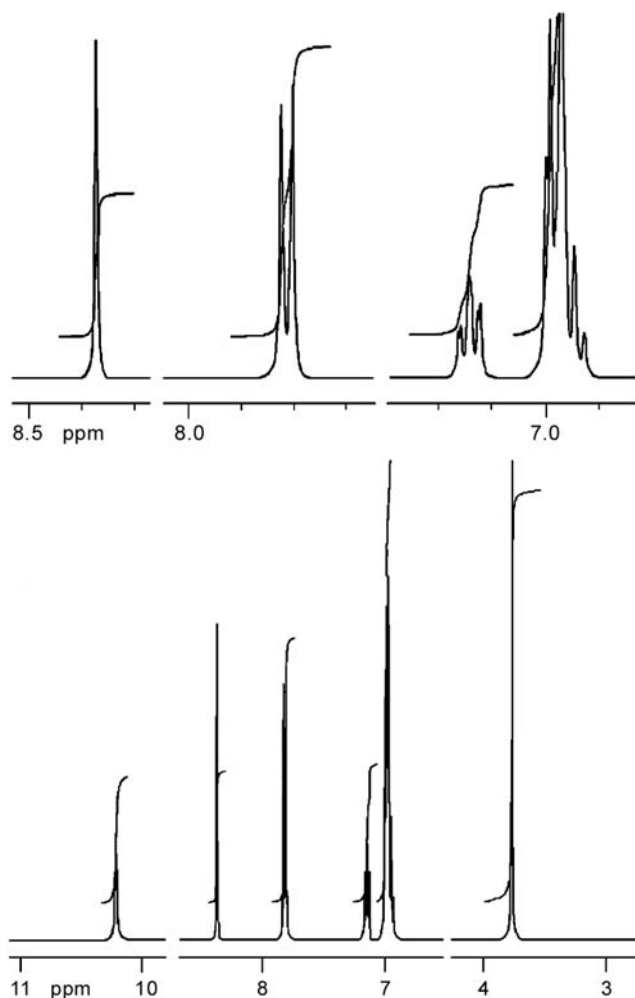


Figure 1. ^1H NMR spectra of 2-MPIMP.

324 nm explains $-\text{CH}=\text{N}-$ group. λ_{max} values of O-2-MPIMP were observed at 208, 278 and 380 nm. According to UV-vis spectra of O-2-MPIMP K, B, and R bands were observed in 208, 278 and 380 nm, respectively. Because of the conjugated band systems,

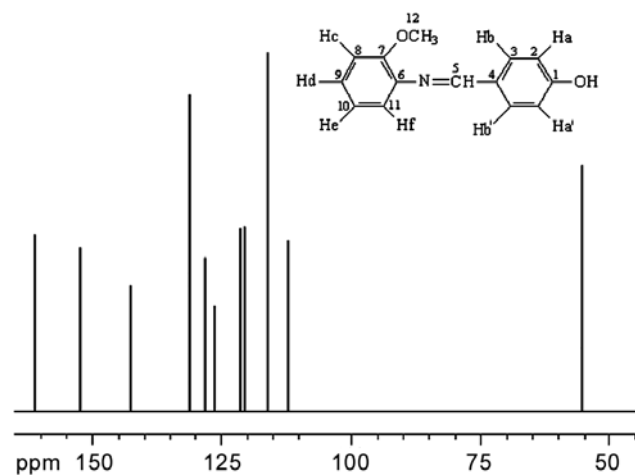


Figure 2. ^{13}C NMR spectrum of 2-MPIMP.

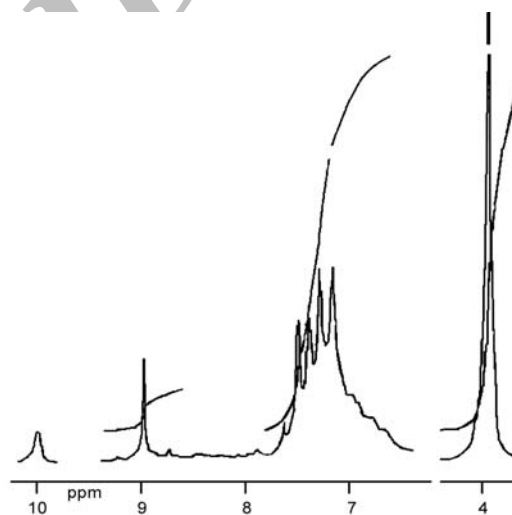


Figure 3. ^1H NMR spectrum of O-2-MPIMP.

azomethine group of oligomer shifted to higher field. The FTIR spectra of 2-MPIMP oxidative polycondensation products are only different by reduction of

Table 2. The number average molecular weight (M_n), weight average molecular weight (M_w), polydispersity index (PDI) and percentage values of O-2-MPIMP.

Oligomer	Molecular weight distributions															
	Total			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-MPIMP ^a	1640	2350	1.433	1300	1400	1.077	80	3000	4900	1.633	10	35800	54300	1.517	10	
O-2-MPIMP ^b	750	1050	1.400	1100	1650	1.500	94	7500	11100	1.480	4	43800	57500	1.313	2	
O-2-MPIMP ^c	1400	2350	1.679	700	950	1.367	82	1260	1900	1.508	6	29700	50800	1.710	12	

a = NaOCl oxidant (20 h, 60°C), b = NaOCl oxidant (3 h, 90°C), and c = Air oxidant.

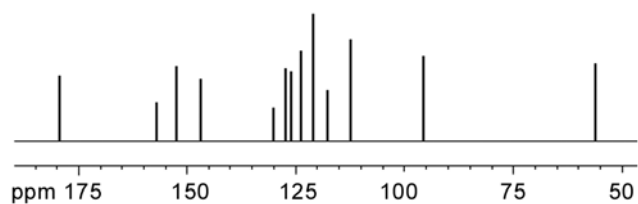
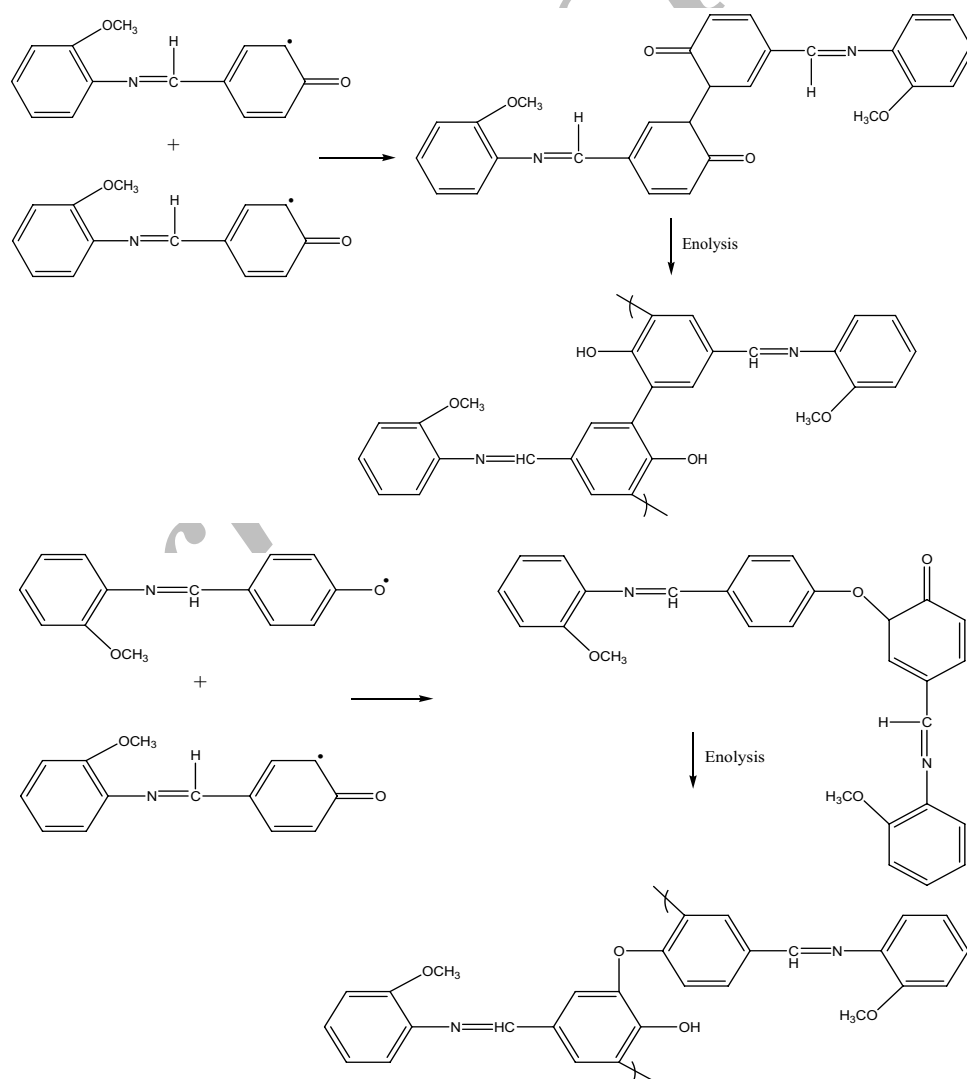


Figure 4. ^{13}C NMR spectrum of O-2-MPIMP.

band strength and peak numbers from the spectra of 2-MPIMP. At the FTIR spectra of 2-MPIMP and O-2-MPIMP bands of $-\text{OH}$, $-\text{CH}=\text{N}$ and aliphatic $-\text{CH}_3$ groups were observed at 3150 , 1604 and 2936 cm^{-1} ; 3303 , 1580 and 2942 cm^{-1} , respectively. In order to identify the structures of monomer and oligomer, the ^1H NMR spectra were recorded in $\text{DMSO-}d_6$.

^1H NMR and ^{13}C NMR spectra of the 2-MPIMP and O-2-MPIMP are given in Figures 1, 2, 3 and 4, respectively. At the ^1H NMR spectra of 2-MPIMP and O-2-MPIMP, the signals of $-\text{OH}$ and $-\text{CH}=\text{N}$ groups were observed at 10.21 and 8.37 ppm , and 9.98 and 8.97 ppm , respectively. According to ^{13}C NMR spectra, the peak values for C1, C2 and C5 observed at 160.90 , 116.15 and 161.11 ppm in the monomer and 157.17 , 95.90 and 179.71 ppm in the oligomer, respectively. As it is seen in Figure 3, because of C-C coupling system a new peak was observed at 117.83 ppm . The ^{13}C NMR spectrum of O-2-MPIMP has shown C-C and C-O coupling systems. The phenyl rings in the oligomer appear to be linked primarily at *ortho* and oxyphenylene positions. The reaction mechanism on the coupling selectivity



Scheme III. The reaction mechanism of oligomer formation.

has been studied by Kaya et al. and two possible reaction mechanisms (Scheme II) for the C-C and C-O couplings have been proposed [22]. Interconversion combinations of radical units and formation of dimer, trimer, tetramer and pentamer units are proposed as follows (Scheme III). The SEC spectral data and the results of FTIR, ^1H NMR and ^{13}C NMR spectra of O-2-MPIMP have supported each other.

Thermal Analyses of 2-MPIMP and O-2-MPIMP

TG-DTG-DTA curves of monomer and oligomer are given in Figures 5 and 6. The initial degradation temperature, 50% weight loss of 2-MPIMP and oligomer were found to be 205°C and 573°C, respectively. According to DTG curve, thermal degradation of 2-MPIMP was completed in two steps. Degradation formed in the first step as 29.41% at the temperatures between 90-328°C. The second step of degradation formed as 27.66% at the temperatures between 328-1000°C. T_{max} values of 2-MPIMP were observed in 227°C and 407°C. According to DTA analysis, two exothermic peaks were observed at 216°C and 389°C. Also two endothermic peaks were observed at 183 and 254°C. The initial degradation temperature, 50% and 59.11% weight loss of O-2-MPIMP found to be 240°C, 544°C, and 1000°C, respectively. According to DTG curve, T_{max} value of O-2-MPIMP was observed at 314°C. Because of long conjugated band systems, oligomer demonstrated higher resistance against high temperature than monomer and it was more stable than monomer against temperature and thermal decomposition. The high thermal stability of O-2-MPIMP demonstrated to be formed by more C-C than C-O coupling systems.

The voltammetric measurements of 2-MPIMP and

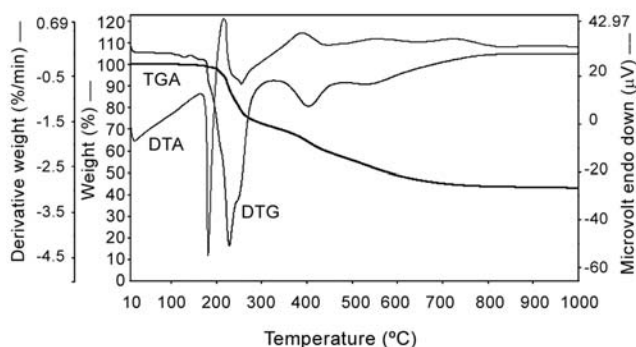


Figure 5. TG-DTG-DTA curves of 2-MPIMP.

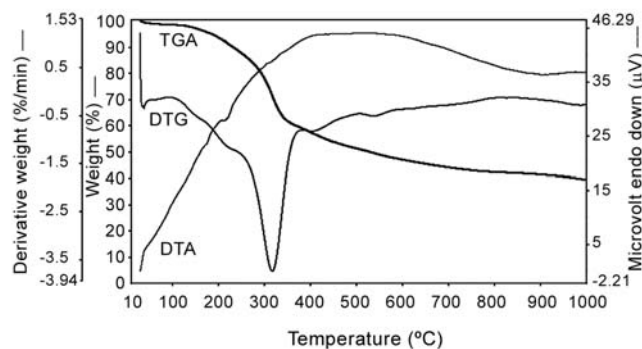


Figure 6. TG-DTG-DTA curves of O-2-MPIMP.

O-2-MPIMP were carried out in acetonitrile and DMSO, respectively. The HOMO and LUMO energy levels of 2-MPIMP and O-2-MPIMP were determined from the onset potentials of the n -doping (ϕ_n') and p -doping (ϕ_p'), respectively (Figure 7). The HOMO and LUMO energy levels and electrochemical band gaps [24] (E_g'), ($E_g' = \Delta\phi = \phi_p' - \phi_n'$) of 2-MPIMP and O-2-MPIMP were found to be -5.11, -5.09; -2.74, -2.92; 2.37 and 2.17 eV, respectively. Similar results were observed in oligo-2-[(4-chlorophenyl)iminomethylene]phenol and its some oligomer-metal complexes [23].

The absorption spectra of 2-MPIMP and O-2-MPIMP were recorded by using MeOH and DMSO at 25°C (Figure 8) and λ_{max} and E_g values of 2-MPIMP and O-2-MPIMP were found to be 324 nm, 380 nm, and 3.22 eV and 2.50 eV, respectively. Due to more extended conjugation, compared with the monomer,

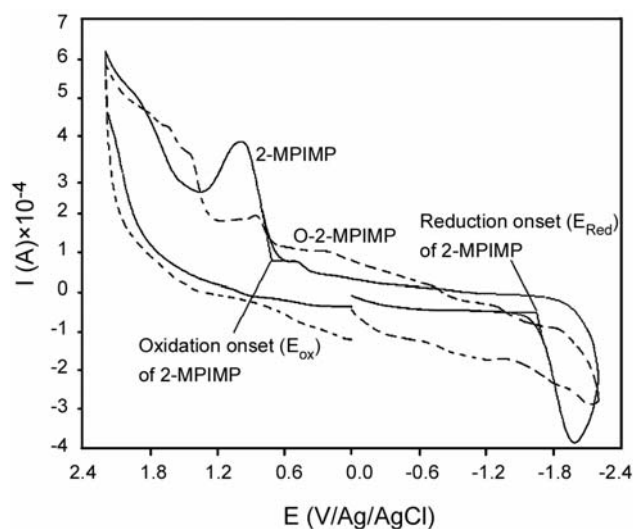


Figure 7. Cyclic voltammograms of monomer and oligomer.

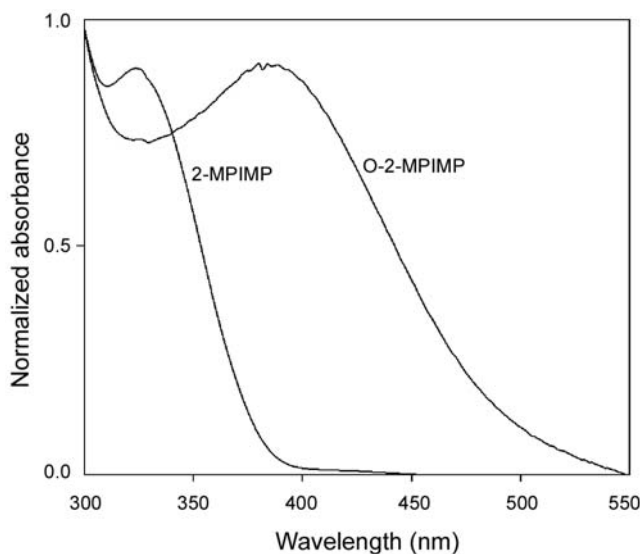


Figure 8. Absorption spectra of monomer and oligomer.

the absorption band of oligomer broadened and highly shifted to low energy range. Figure 8 shows that the absorption maximum (λ_{\max}) of oligomer and exhibited 56 nm red shifted as compared to monomer. While the optical band gap value of oligo-2-[(4-chlorophenyl)iminomethylene]phenol was found to be 3.10 eV [23], this value of O-2-MPIMP was 2.50 eV. This change has been due to the structures of oligomers.

The conductivity values of monomer and oligomer were 10^{-10} - 10^{-9} S/cm after being doped with iodine. When doped with iodine, their conductivities could be increased by about five orders of magnitude (up to 10^{-4} S/cm). Figure 9 shows the results of 2-MPIMP and O-2-MPIMP doped with iodine at various time lengths at 25°C. In doping of 2-MPIMP and O-2-MPIMP with iodine, the conductivities of 2-MPIMP

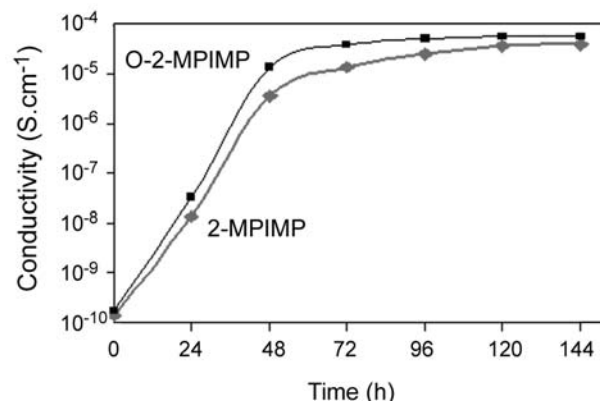
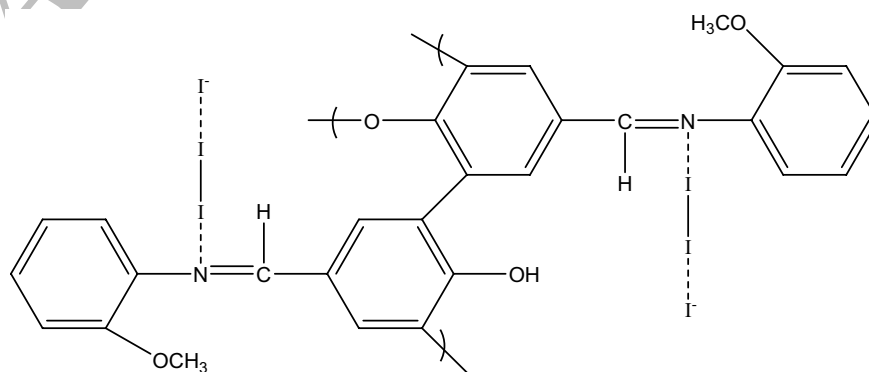


Figure 9. Electrical conductivity of I₂-doped monomer and oligomer vs. doping time at 25°C.

and O-2-MPIMP first increase greatly with doping time, but then tends to level-off. The maximal conductivities of monomer and oligomer were 3.84×10^{-5} S/cm and 5.86×10^{-5} S/cm (Figure 9). The increase in conductivity could indicate that a charge-transfer complex between 2-MPIMP and O-2-MPIMP and dopant iodine was continuously formed.

Consequently, Figure 9 not only shows the conductivity/doping time relationship but also indicates how quickly the doping reaction takes place. The experimental results showed that a longer doping time is needed to obtain the maximal conductivity. As a result, the conductivity/doping time curve varies with doping conditions. In order to exclude the influence of doping conditions, the conductivities of doped monomer and oligomer have been related with doping extent (Figure 9). Diaz et al. have suggested the conductivity mechanisms of Schiff base oligomer and polymer for doping with iodine [1]. Nitrogen is a very electronegative element and it is capable of coordinat-



Scheme IV. Coordination of iodine during O-2-MPIMP doping.

ing with iodine molecule. On the nitrogen atom coordination of iodine with Schiff base oligomer and/or polymer and pyridine compounds there is a suggested mechanism available in the literature (Scheme IV) [17,23].

CONCLUSION

Oligo-4-[(2-methoxyphenylimino)methyl]phenol with Schiff base substitute has been synthesized by oxidants such as air and NaOCl in an aqueous alkaline medium. The yield of O-2-MPIMP was found to be 38.72% and 72.21% for air and NaOCl oxidants, respectively. At the oxidative polycondensation reaction of 2-MPIMP, NaOCl demonstrated higher activity than air. FTIR, ^1H NMR and ^{13}C NMR data have all demonstrated *ortho*-carbons and phenolic -OH group of phenol rings forming an oligomer during oxidative polycondensation of 2-MPIMP. Thermal analysis results have demonstrated to be enough resistant against thermal degradation of synthesized oligomer. The carbines residue of O-2-MPIMP was found in high amount of 40.89% at 1000°C. Properties of monomer and oligomer with potential low-band gap characteristics were determined. The band gap value of monomer was higher than oligomer. This is a result of the azomethine group that is an electron-donor. This increases the HOMO more than the LUMO and therefore lowers the band gap. The observed band gaps are sufficiently low to make this oligomer highly promising for photovoltaic applications. These types of molecules can be utilized as organic electroluminescent devices (OELD) in organic electronic technologies.

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