ISMET KAYA[1)*)], ALI BILICI[2)]

Syntheses, structures, electric conduction, electrochemical properties and antimicrobial activity of azomethine monomer and oligomer based on 4-hydroxybenzaldehyde and 2-aminopyridine

Summary — The effects of temperature (50—80 $^{\circ}$C), reaction time (up to 15 h) as well as type and concentration of oxidizing agent (NaOCl, air O_2, H_2O_2) on the course of oxidative polymerization of 4-[(pyridin-2-yl-imino)methyl]phenol (4-PIMP) in aqueous alkaline medium, and on the yield of the oligomers formed (O-4-PIMP) were investigated. The optimal conditions of the process have been found. Reaction products were characterized using the following methods: ^{1}H NMR, ^{13}C NMR, FT-IR, UV-VIS, gel permeation chromatography and thermal analyses TG-DTA. M_n values of O-4-PIMP are in the range 1250—4450. The oligomer shows better thermal stability than the monomer. On the basis of voltammetric measurements' results the electrochemical properties of 4-PIMP and O-4-PIMP were characterized in detail, including an effect of iodine doping of O-4-PIMP on the electric conduction. The comparison of antibacterial activity of 4-PIMP and O-4-PIMP against 8 bacterial strains has been done.

Key words: 4-[(pyridin-2-yl-imino)methyl]phenol, oligomers, oxidative polymerization, electrochemical properties, antibacterial activity.

OTRZYMYWANIE, STRUKTURA, PRZEWODNICTWO ELEKTRYCZNE, WŁAŚCIWOŚCI ELEKTROCHEMICZNE ORAZ DZIAŁANIE PRZECIWBAKTERYJNE ZAWIERAJĄCYCH UGRUPOWANIE AZOMETINOWE MONOMERU I OLIGOMERU NA PODSTAWIE 4-HYDROKSYBENZALDEHYDU I 2-AMINOPIRYDYNY

Streszczenie — Zbadano wpływ temperatury (50—80 $^{\circ}$C), czasu trwania (do 15 h) oraz rodzaju (NaOCl, tlen powietrza, H_2O_2) i stężenia czynnika utleniającego na przebieg utleniającej polimeryzacji 4-[(pirydyn-2-ylo-imino)metylo]fenolu (4-PIMP) w wodnym środowisku zasadowym na wydajność powstających oligomerów (O-4-PIMP), określając optymalne warunki tego procesu (tabele 1 i 2). Produkty charakteryzowano metodami ^{1}H NMR, ^{13}C NMR, FT-IR, UV-VIS, chromatografii żelowej, analizy termicznej (TG-DTA) (rys. 1—5 i 7, tabela 3). Wartości $\overline{M}_n$ O-4-PIMP mieszczą się w przedziale 1250—4450; oligomer odznacza się lepszą odpornością cieplną niż monomer. Na podstawie wyników pomiarów woltametrycznych szczegółowo scharakteryzowano elektrochemiczne właściwości 4-PIMP i O-4-PIMP, w tym wpływ domieszkowania jodem O-4-PIMP na przewodnictwo elektryczne (rys. 6 i 8). Porównano przeciwbakteryjne działanie 4-PIMP i O-4-PIMP w stosunku do 8 szczepów bakterii (tabela 8).

Słowa kluczowe: 4-[(pirydyn-2-ylo-imino)metylo]fenol, oligomery, polimeryzacja utleniająca, właściwości elektrochemiczne, działanie przeciwbakteryjne.

The Schiff base polymers including conjugated bonds and active hydroxyl (-OH) and azomethine (-CH=N) groups have aroused researchers' interest last decade [1]. These type polymers have based used in various fields because of useful properties such as paramagnetism, semiconductivity, electrochemical properties and resistance to high energy [2, 3]. Because of these properties, they are used to prepare composites having high resistance at high temperature, being thermally stable, in graphite materials, epoxy oligomers and block copolymers, photoresists, materials which are antistatic or flame retarded [4—8]. By introducing of other functional groups to these compounds, they can be enriched with new useful properties. Schiff base polymers have shown antimicrobial activity against various bacteria, yeast and fungi [9, 10]. Oligophenols which have a lot of functional groups may be used for cleaning of the industrial waste waters from harmful heavy metals. Therefore, the synthesis of oligomer-metal complexes is very important for analytical and environmental chemistry. It seemed advantageous to attempt to design and prepare polymer bounded chelating ligands, which would be able to form complexes with a variety of transition metals and therefore having wide range of applications [11].

[1)] Çanakkale Onsekiz Mart University, Faculty of Sciences and Arts, Department of Chemistry, 17020, Çanakkale, Turkey.
[2)] Ankara University, Faculty of Science, Department of Chemistry, Tandoğan, Ankara, Turkey.
[*)] Author for correspondence; e-mail: kayaismet@hotmail.com

In the oxidative polymerization of phenol derivatives, it is known that two types of the linkage between the monomer units, the C-C and C-O-C bonds, can be formed during the polymerization. The reaction mechanism and the coupling selectivity have been studied by Kobayashi *et al.* and three possible reaction mechanisms for the C-C coupling selectivity had been proposed [12]. Regioselectivity of coupling was found in the polymerization of oligophenol [13] and polyazomethine [14].

In this paper, the synthesis of oligo-4-[(pyridin-2-yl--imino)methyl]phenol (O-4-PIMP) was investigated and the effects of different parameters such as temperature, initial concentrations of NaOCl and the presence of alkaline medium were studied. O-4-PIMP was characterized by using FT-IR, UV-VIS, ^{1}H NMR, ^{13}C NMR, elemental analysis, TG-DTA, as well as AC conduction measure and SEC techniques. The electrochemical (E'_g) and optical band gaps (E_g) of monomer and oligomer were determined using cyclic voltammetry (CV) and UV-VIS measurements, respectively. The antimicrobial activity of monomer and oligomer has been also studied.

EXPERIMENTAL

Materials

4-Hydroxybenzaldehyde (4-HB), 2-aminopyridine, dioxane, methanol, ethanol, 1-butanol, acetonitrile, benzene, toluene, acetone, ethyl acetate, heptane, CCl_4, $CHCl_3$, tetrahydrofurane (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO), H_2SO_4 (98 %), NaOH, KOH and hydrochloric acid (HCl, 37 %) were supplied from Merck Chemical Co. (Germany) and were used as received. Sodium hypochlorite (NaOCl, 30 % aqueous solution) was supplied by Paksoy Chemical Co. (Turkey).

Methods of preparation

Preparation of 4-[(pyridin-2-yl-imino)methyl]phenol

4-[(Pyridin-2-yl-imino)methyl]phenol (4-PIMP) was prepared by the condensation of 4-hydroxybenzaldehyde (25 mmol) with 2-aminopyridine (25 mmol) in methanol (15 ml) by keeping the boiling mixture under reflux for 3 h [Eq. (1)].

$$HO-\langle\rangle-CHO + H_2N-\langle\rangle_N \xrightarrow{-H_2O}$$

$$\longrightarrow HO-\langle\rangle-CH=N-\langle\rangle_N \tag{1}$$
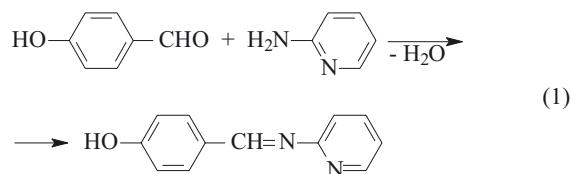
The precipitated 4-PIMP was filtered, recrystallized from methanol and dried in vacuum desiccators (yield 92 %). Characterization of the products by elemental analysis, UV-VIS, FT-IR, ^{1}H NMR and ^{13}C NMR methods gave the following results:

Calculate for 4-PIMP: C, 72.73; H, 5.05; N, 14.14; found: C, 72.58; H, 4.95; N, 13.85.

UV-VIS (λ_{max}): 208, 221, 285 and 334 nm, respectively.

FT-IR (cm^{-1}): ν (O-H) 3200 s, ν (C-H phenyl) 3016 m, ν (C=N) 1615 s, ν (C=C phenyl) 1594, 1508, 1498 s, ν (C-O) 1293 s.

^{1}H NMR (DMSO): δ ppm, 8.98 (s, 1H, -CH=N-); 9.93 (s, 1H, -OH); 6.93 (d, 2H, Ar-Haa' and d, 1H, Ar-Hc); 7.77 (d, 2H, Ar-Hbb'); 7.36 (t, 1H, Ar-Hd); 6.47 (t, 1H, Ar-He), 8.64 (d, 1H, Ar-Hf).
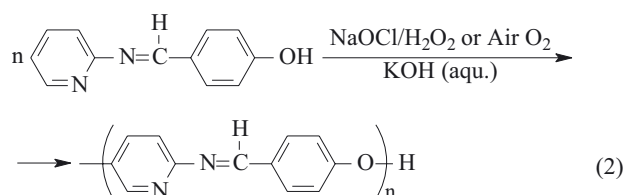
^{13}C NMR (DMSO): ppm, 159.92 (C1-*ipso*), 108.69 (C2, 6-H), 132.65 (C3, 5-H), 128.85 (C4-*ipso*), 191.66 (C7-H),

$$HO-\langle\rangle-CH=N-\langle\rangle He \tag{I}$$
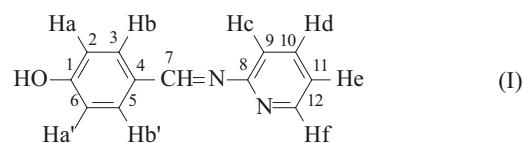
163.75 (C8-*ipso*), 116.32 (C9-H), 137.74 (C10-H), 112.48 (C11-H), 147.80 (C12-H) [see Formula (I)].

Oxidative polymerization of 4-PIMP

O-4-PIMP was synthesized through oxidative polymerization of 4-PIMP in KOH solution with aqueous solutions of NaOCl (30 %), H_2O_2 (30 %) or air O_2 [15]:

$$n\langle\rangle-N=C-\langle\rangle-OH \xrightarrow[KOH (aqu.)]{NaOCl/H_2O_2 \text{ or Air } O_2}$$

$$\longrightarrow \left[\langle\rangle-N=C-\langle\rangle-O\right]_n H \tag{2}$$

The 4-PIMP (0.198 g, 0.001 mol) was dissolved in an aqueous solution of KOH (10 %, 0.001 mol) and placed into a 50-ml three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and an additional funnel in case of use of NaOCl or H_2O_2 systems. After heating to 40 ^{o}C, the oxidizer was added drop by drop during about 20 min. The reaction mixtures were stirred at the various temperatures and durations. In the oxidizing reaction with O_2, an air O_2 was passed into an aqueous solution of KOH (20 %) before being sent through the reaction tube (to prevent water loss from the reaction mixture and to neutralize CO_2 in the air). The reaction mixture was cooled to room temperature, and then 0.001 mol HCl (37 %) was added. For the separation of mineral salt and unreacted monomer, the mixture was filtered, washed with hot water (3 × 25 ml) and then dried in an oven at 110 ^{o}C. The results of O-4-PIMP analyses are:

Calculate for O-4-PIMP: C, 73.74; H, 4.08; N, 14.29; found: C, 73.10; H, 4.20; N, 14.15.

UV-VIS (λ_{max}): 210, 274 and 355.

FT-IR (cm^{-1}): ν (O-H) 3380 s, ν (C-H phenyl) 3030 m, ν (C=N) 1630 s, ν (C=C phenyl) 1590, 1502, 1498 s, ν (C-O) 1280 s.

^{1}H NMR (DMSO): δ ppm, 9.80 (s, 1H, -CH=N-); 10.70 (s, 1H, -OH); 6.95 (proton at the terminal position, d, 2H, Ar-Haa′); 7.08 (d, 1H, Ar-Hc); 7.78 (d, 2H, Ar-Hbb′); 7.38 (t, 1H, Ar-Hd); 6.66 (t, 1H, Ar-He); 9.75 (d, 1H, Ar-Hf); 7.90 (new peak).

^{13}C NMR (DMSO): ppm, 164.14 (C1-*ipso*), 113.93 (C2, 6-H) (new peaks: 129.04 and 136.04), 132.52 (C3, 5-H), 129.04 (C4-*ipso*), 191.45 (C7-H), 161.82 (C8-*ipso*), 116.37 (C9-H), 144.52 (C10-H), 115.87 (C11-H), 152.12 (C12-H).

Methods of characterization

Physicochemical properties

O-4-PIMP was dark brown at powder form and it was completely soluble in DMF, DMSO and aqueous alkaline or concentrated H_2SO_4 solutions but it was insoluble in heptane, acetone, THF, hexane, benzene, toluene, acetonitrile, methanol, ethanol, CH_2Cl_2, CCl_4 or dioxane.

The infrared spectra were obtained using Perkin-Elmer FT-IR equipment with ATR attachment (4000—550 cm^{-1}).

Elemental analysis was carried out using a "Carlo Erba 1106" apparatus.

UV-VIS spectra of 4-PIMP and O-4-PIMP were registered using methanol and DMSO, respectively.

These substances were characterized also by ^{1}H NMR and ^{13}C NMR methods ("Bruker Avance DPX-400" and 100.6 MHz, respectively). Spectra were recorded at 25 ^{o}C, using deuterated DMSO as a solvent. Tetramethylsilane was used as internal standard.

Thermal data obtained using Perkin Elmer Diamond Thermal Analysis. TG-DTA measurements were made in the range of 20—1000 ^{o}C (in N_2, rate 10 ^{o}C/min).

Size Exclusion Chromatography (SEC) analyses were performed at 25 ^{o}C using DMF/methanol (4/1 v/v) as eluent at a flow rate of 0.4 ml/min. A refractive index detector was used. The instrument (Shimadzu 10AVp series HPLC-SEC system) was calibrated using a mixture of polystyrene standards (Polymer Laboratories; the peak molecular weights, M_p, between 162 and 60 450), using SEC software for the determination M_n, M_w and polydispersity indexes (*PDI*) of the polymer samples. For SEC investigations a Macherey-Nagel GmbH & Co. equipment (100 Å and 7.7 nm diameter loading material) 3.3 mm i.d. x 300 mm columns was used.

Electrical and electrochemical properties

Cyclic voltammetry (CV) measurements were carried out using a CH instruments "660B 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-wave potential ($E^{1/2}$) of (Fc/Fc$^+$) measured in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) acetonitrile solution is

0.39 V *vs.* Ag wire or 0.38 V *vs.* supported calomel electrolyte (SCE). The voltammetric measurements were carried out for monomer and oligomer in acetonitrile and DMSO solutions, respectively [16, 17]. The electrochemical HOMO and LUMO energy gaps (E_g) were calculated from oxidation and reduction onset values.

Conductivity was measured using a Keithley "2400 Electrometer". The pellets were pressed in hydraulic press with load up to 1687.2 kg/cm^2. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in a desiccator [7].

Optical properties

The optical band gaps (E_g) of monomer and oligomer compounds were calculated from their absorption edges. Ultraviolet-visible (UV-VIS) spectra were measured using Perkin Elmer "Lambda 25" apparatus. The absorption spectra of monomer and oligomer were recorded using methanol and DMSO solutions, respectively, at 25 ^{o}C.

Preparation of test microorganisms and tested compounds

Escherichia coli ATCC 25922, *Staphylococcus aureus* ATCC 29213, *Pseudomonas aeruginosa* ATCC 27853, *Bacillus cereus* England 1988, *Listeria monocytogenes* NCTC 2167, *Enterococcus faecalis* ATCC 8043, *Vibrio cholerae* 0139 NCTC12946, and *Bacillus subtilis* ATCC 6633 were used as the test organisms in an antimicrobial study. The testing bacteria were supplied by Refik Saydam Hifzisihha Institute (Ankara, Turkey). The bacteria strains were inoculated into nutrient medium ("Difco") and incubated for 24 h. Using the Disc Diffusion method, the sterile Mueller Hinton Agar ("Oxoid") was inoculated with the test microorganisms [18]. The tested compounds were dissolved in DMSO at a concentration of 10 mg/ml in order to obtain a final concentration of 1 mg/0.1 ml. Three different concentrations of the drug were prepared (1 mg/0.1 ml, 0.1 mg/0.1 ml, and 0.01 mg/0.1 ml) for the microbiological tests and the were absorbed on sterile paper antibiotic discs, which were placed in wells (6 mm of diameter) cut in the agar media. The plates were incubated at 32 ^{o}C (for 24 h). The resulting inhibition zones on the plates were measured after 48 h. The control samples were absorbed only in DMSO.

RESULTS AND DISCUSSION

Determination of optimal oxidative polymerization conditions of 4-PIMP

The parameters of oxidative polymerization of 4-PIMP with 30 % NaOCl solution in aqueous alkaline medium are given in Table 1. So, the yield of O-4-PIMP increased with the increasing temperature (except for the highest one, *i.e.*, 90 ^{o}C). At the same conditions (time, temperature), when molar amount of NaOCl increased

twice, the yield increased from 68 % to 91 % (see Table 1, samples 12 and 14). The maximal conversion of 4-PIMP (97 %, sample 6) was reached in the following conditions: $[4\text{-PIMP}]_0 = [KOH]_0 = 0.075$ mol/L and $[NaOCl]_0 = 0.211$ mol/L, at 80 °C for 6 h. Reaction time prolongation to 15 h, when the other condition were kept the same, caused decrease in 4-PIMP conversion to 20 %.

T a b l e 1. Oxidative polymerizations of 4-[(pyridine-2-yl-imi-no)methyl]phenol[*] with NaOCl in an aqueous KOH

Sample No.	Temp. °C	Time h	$[KOH]_0$ mol/L	$[NaOCl]_0$ mol/L	The yield of O-4-PIMP, %
1	50	3	0.075	0.211	89
2	60	3	0.075	0.211	92
3	70	3	0.075	0.211	95
4	80	3	0.075	0.211	96
5	90	3	0.075	0.211	90
6	80	6	0.075	0.211	97
7	80	9	0.075	0.211	94
8	80	12	0.075	0.211	91
9	80	15	0.075	0.211	90
10	80	6	0.150	0.211	81
11	80	6	0.225	0.211	74
12	80	6	0.300	0.211	68
13	80	6	0.075	0.316	99
14	80	6	0.075	0.422	91
15	80	6	0.075	0.528	90

[*] Monomer concentration used in reactions was 0.075 mol L^{-1}.

T a b l e 2. Oxidative polymerizations of 4-[(pyridine-2-yl-imi-no)methyl]phenol[*] in an aqueous KOH with air O_2 passing with constant rate 8.5 L/h

Sample No.	Temp., °C	Time h	$[KOH]_0$ mol/L	The yield of O-4-PIMP, %
1	50	3	0.075	78
2	60	3	0.075	85
3	70	3	0.075	89
4	80	3	0.075	86
5	90	3	0.075	77
6	70	6	0.075	91
7	70	9	0.075	94
8	70	12	0.075	86
9	70	15	0.075	85
10	70	9	0.150	76
11	70	9	0.225	65
12	70	9	0.300	53

[*] Monomer concentration used in reactions was 0.075 mol L^{-1}.

Table 2 presents similar data concerning the use of air O_2, passing with constant rate 8.5 L/h, as an oxidizing agent in the oxidative polymerization discussed. The maximal yield of O-4-PIMP in this case was 94 % at optimum reactivity conditions, namely $[4\text{-PIMP}]_0 = [KOH]_0 = 0.075$ mol/L, temp. 70 °C, time 9 h (sample 7). For the same time and temperature conditions, 100 % increase in KOH concentration caused decrease in yield to 76 % (sample 10).

From the comparison of the data presented in Table 1 and 2 it results that both NaOCl and air O_2 are good oxidants in oxidative polymerization of 4-PIMP.

Structure of O-4-PIMP

The values of number-average molecular weight and weight-average molecular weight of O-4-PIMP determined by SEC method are given in Table 3. So, the highest molecular weights were obtained when NaOCl was used as an oxidizer. The same time this oxidizer let obtain relatively narrow molecular weight distribution (small PDI values). Because of the higher molecular weight, together with the broadening of polydispersity, NMR analyses failed to give valuable information for the characterization of these compounds. However, SEC analysis shows that new oligomer was formed with small part of fractions of higher molecular weights. At the same time, the molecular weights measured by SEC based on PS standards, should be estimated as the minimal ones because of the highly branched or comb-like structures of the obtained oligoazomethine.

The UV-VIS spectra of O-4-PIMP and 4-PIMP are similar one to another. However, in the spectra of 4-PIMP, K bands of phenol and C_6H_5-N= were observed at 208 nm and 221 nm, respectively, benzene band of 4-PIMP and strength R band of -C=N- groups — at 285 nm and 334 nm, respectively, while in the UV-VIS spectra of O-4-PIMP K and R bands were observed at 274 and 355 nm, respectively, and shifting of -CH=N-band from 334 nm (monomer) to 355 nm (oligomer) has
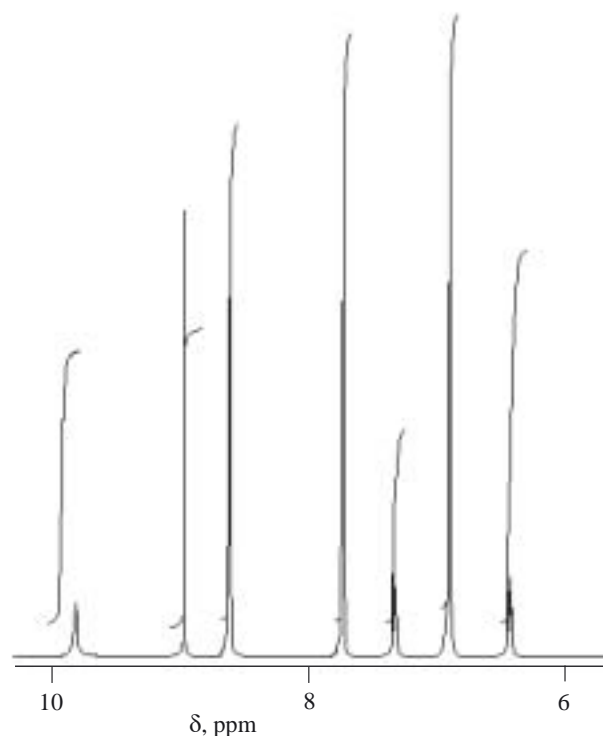

Fig. 1. ^1H NMR spectrum of 4-PIMP

T a b l e 3. Effect of oxidizing agent type on the number average molecular weight, weight average molecular weight, polydispersity index (*PDI*) and parts of fractions in the products of oxidative polymerization of O-4-PIMP[*]

Product	Molecular weight distribution parameters															
	total			fraction I			part %	fraction II			part %	fraction III			part %
	M_n	M_w	*PDI*	M_n	M_w	*PDI*		M_n	M_w	*PDI*		M_n	M_w	*PDI*	
O-4-PIMP[1)]	1250	1750	1.400	2000	2400	1.200	84	2700	3000	1.111	4	16 500	25 450	1.542	12
O-4-PIMP[2)]	4450	5200	1.169	850	900	1.059	40	2000	2200	1.100	25	35 700	41 650	1.167	35
O-4-PIMP[3)]	1800	1950	1.083	2700	2900	1.074	95	19 850	21 600	1.088	5	—	—	—	—

[*] Type of oxidizer: 1 — air O_2, 2 — NaOCl, 3 — H_2O_2.
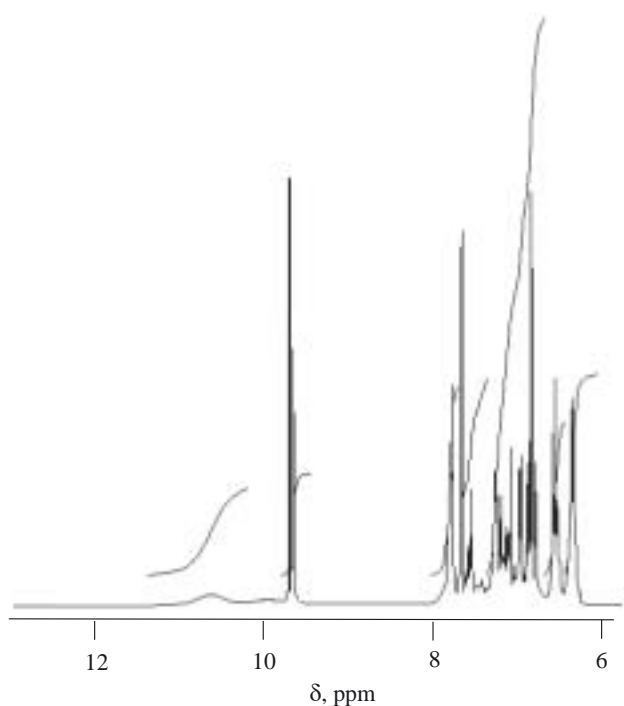
Fig. 2. ^1H NMR spectrum O-4-PIMP
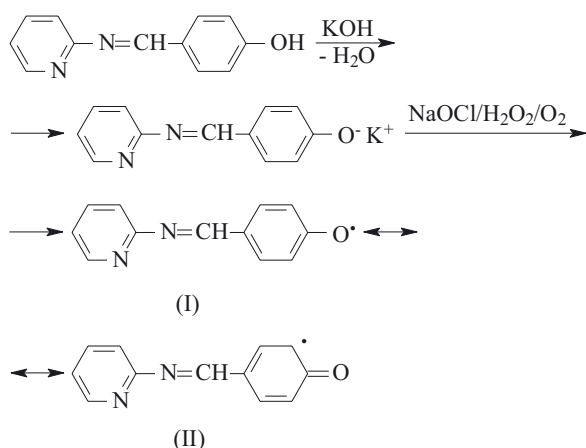
Scheme A. Radical units formation

Schemes B1 and B2. Interconversions of radical units (I) and (II) from scheme A [15]

demonstrated the formation of conjugated π-system at the structure of oligomer.

FT-IR spectra of the second fractions of oxidative polymerization product of 4-[(pyridine-2-yl-imino)me-thyl]phenol differ only by reduction of band strength and peak numbers in comparison with FT-IR spectra of 4-PIMP and O-4-PIMP. In these two last spectra bands of OH and -CH=N groups were observed at 3200, 1615 cm^{-1}, and 3380, 1630 respectively.

In order to identify the structures of monomer and oligomer, the ^{1}H NMR and ^{13}C NMR spectra were recorded. At the ^{1}H NMR spectra of 4-PIMP (Fig. 1) and O-4-PIMP (Fig. 2) the signals of -OH and -CH=N groups were observed at 9.93, 8.98 ppm and 10.70, 9.80 ppm respectively.

The FT-IR, ^{1}H NMR and ^{13}C NMR spectra of O-4-PIMP have confirmed the oligomer formation. The reaction mechanism and the coupling selectivity have been studied by us [15] and three possible reaction mechanisms for the C-C coupling selectivity have been proposed according to the literature [12, 19] namely; (i) coupling of Schiff base substituted free phenoxy radicals resulting from one-electron-oxidation of 4-[(pyridine-2-yl-imino)methyl]phenol and other Schiff base monomers, (ii) coupling of phenoxy radicals coordinated to each other in *ortho* or *para* positions by using oxidants (such as NaOCl, H$_2$O$_2$ or air O$_2$) and (iii) coupling through phenoxy anion formed by using KOH. Monomer and dimer interconversion combinations of radical units and formation of radical units are proposed in [15] (see Schemes A and B).

At the ^{1}H NMR spectra of O-4-PIMP (Fig. 2), small signal of -OH observed at 10.67 ppm demonstrates the formation of C-C and C-O-C coupling systems. According to ^{1}H NMR spectra of O-4-PIMP, the ratios of C-C and C-O-C coupling systems were determined from proton integration of -OH peak and they were found to be 87 % (C-C) and 13 % (C-O-C). In ^{13}C NMR spectra the

peak values for C2,6 were observed at 108.69 ppm in the monomer and 129.04 and 136.04 ppm (new peaks) in the oligomer, respectively (Fig. 3). The shifting of this value of oligomer demonstrated the formation of conjugated π-system.

Thermal stability of 4-PIMP and O-4-PIMP

Thermal TG-DTA curves of monomer and oligomer ware given in Figs. 4 and 5. The initial, 50 % and 97.87 % weight loss degradation temperatures of 4-PIMP were found to be 165 °C, 253 °C and 1000 °C, respectively. The initial, 50 % and 51.62 % degradation temperatures weight loss of O-4-PIMP were found to be 201 °C, 815 °C and 1000 °C, respectively. This oligomer formed carbonized residue at high amount (48.38 % at 1000 °C).
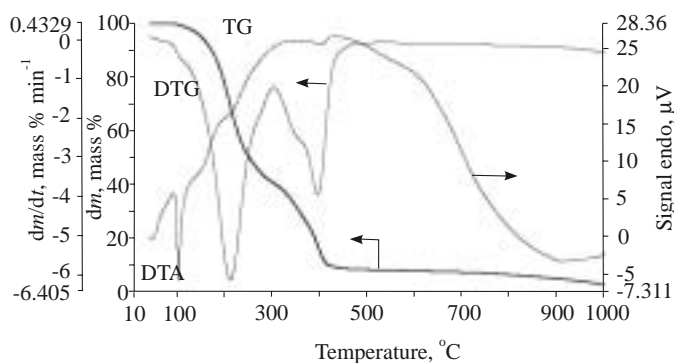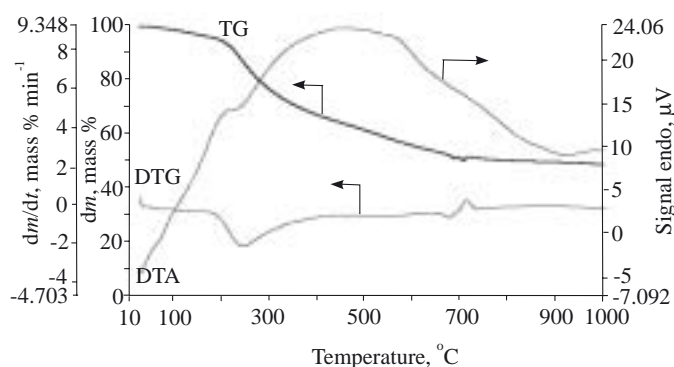

Fig. 4. TG-DTG-DTA curves of 4-PIMP
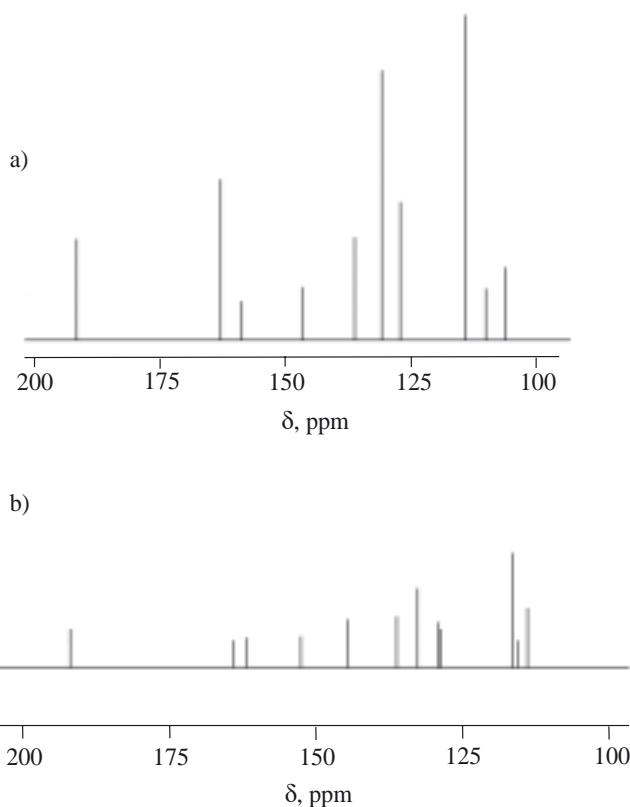

Fig. 5. TG-DTG-DTA curves O-4-PIMP

Fig. 3. ^{13}C NMR spectrum of 4-PIMP (a) and O-4-PIMP (b)

Because of formation of long conjugated bonds systems in the structure of oligomer, it demonstrated higher resistance to high temperature in comparison to monomer. According to DTG curves of 4-PIMP and O-4-PIMP, T_{max} values were observed at 210 °C, 393 °C and 241 °C, respectively. According to DTA curves of 4-PIMP, endothermic peaks were observed at 99 °C and 420 °C. The data published recently on good thermal stability of polyketanils (polymers containing, as O-4-PIMP, N=C groups) [20] confirm our results.

Electrochemical, electrical and optical properties of 4-PIMP and O-4-PIMP

The HOMO, LUMO and electrochemical energy gaps (E'_g) were calculated from oxidation and reduction onset values and for 4-PIMP and O-4-PIMP were found to be -5.78, -5.57 (HOMO); -2.60, -2.79 (LUMO) and 3.18, 2.78 eV (E'_g), respectively.

The cyclic voltammograms of O-4-PIMP (Fig. 6, curve 2) displayed two irreversible peaks — cathodal and anodal ones. The cathodal peak (E_{pc}) which occured -1.6 V was assigned to the reduction of the azomethine group, while the anodal peak (E_{pa}) occurred 1.3 V might be corresponded to oxidation of OH groups. Similarly, the cyclic voltammograms of 4-PIMP displayed two irreversible peaks (Fig. 6, curve 1): the cathodal peak which occurred at E_{pc} = -2.0 was assigned to the reduction of the azomethine group while the anodal occurred at E_{pa} = 1.65 V might be corresponded to oxidation of OH groups. With an increase in the electron-withdrawing
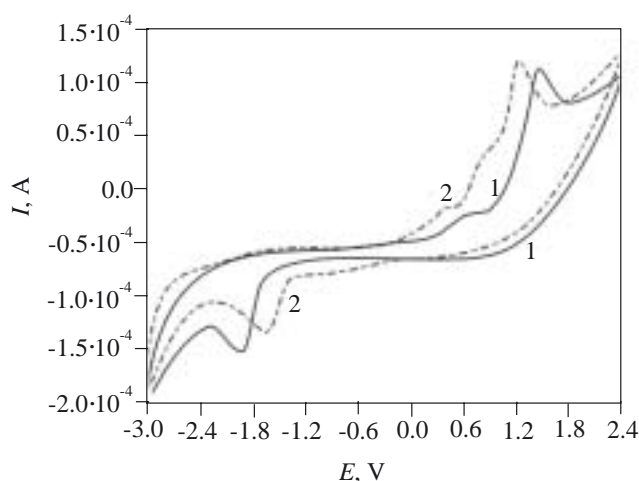
Fig. 6. Cyclic voltammograms of 4-PIMP (1) and O-4-PIMP (2), measured vs. Ag/AgCl

power of the substituent groups, the E_{pa} values in the range +1.30 to 1.65 V are shifted anodally indicating their difficulty in oxidation. Electrochemical investigation of the free ligands showed some cathodal and anodal irreversible peaks due to interconversions *via* electron transfer [21].

From the absorption spectra of 4-PIMP and O-4-PIMP (Fig. 7) λ_{max} (nm) and E_g (eV) values of 4-PIMP and O-4-PIMP were found to be 287, 290 nm and 3.82, 3.60 nm respectively.

When doped with iodine, the conductivity of O-4-PIMP could be substantially increased. Figure 8 shows the doping results for O-4-PIMP with iodine for the various times at 25 °C. Although the structure of different O-4-PIMP differs, little difference in conductivity was observed. For doping of O-4-PIMP with iodine, the conductivity first increased significantly with dop-
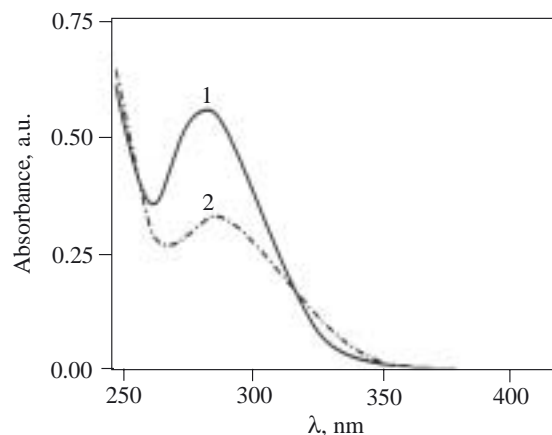
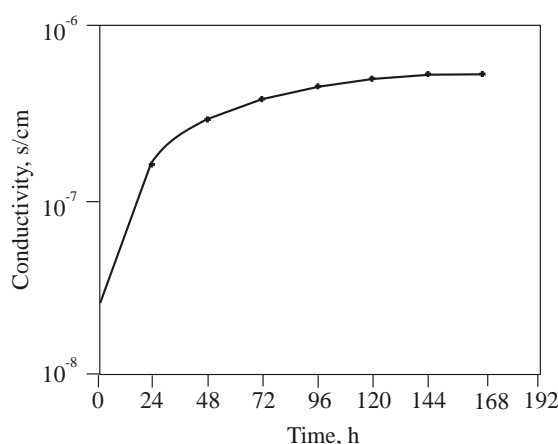*Fig. 7. Absorption spectra of 4-PIMP (1) and O-4-PIMP (2)*

Fig. 8. Electrical conductivity of I$_2$-doped O-4-PIMP vs. doping time at 25 °C

ing time (for about 48—60 h), then tends to level-off. The maximal (or saturated) conductivity shown in Fig. 8 was 5.40 · 10^{-7} S/cm. The increasing conductivity could indicate that a charge-transfer complex between O-4-PIMP and dopant iodine is continuously formed. Consequently, Fig. 8 not only shows the conductivity/doping time relationship but also indicates how quickly the doping reaction runs. The experiments showed that a long 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
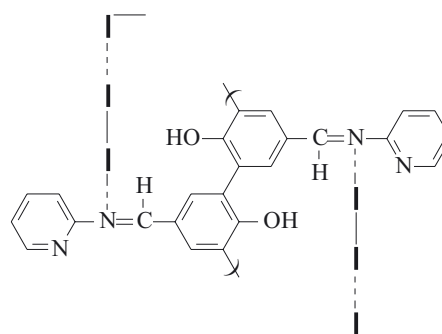
Scheme C. Coordination of iodine during O-4-PIMP doping

T a b l e 4. Antimicrobial activity of 4-[(pyridine-2-yl-imino)methyl]phenol and its oligomer

Bacteria	Inhibition zones					
	4-PIMP			O-4-PIMP		
	0.1 mg/0.1 ml	0.01 mg/0.1 ml	0.001 mg/0.1 ml	0.1 mg/0.1 ml	0.01 mg/0.1 ml	0.001 mg/0.1 ml
Bacillus subtilis ATCC 6633	5	3	—	5	—	—
Listeria monocytogenes NCTC 2167	4	3	1	8	5	4
Enterococcus faecalis	4	—	—	3	2	—
Bacillus cereus England 1988	2	—	—	6	—	—
Vibrio cholerae 0139 NCTC 12946	4	—	—	4	—	—
Pseudomonas aeruginosa	3	5	3	4	4	—
Staphylococcus aureus	3	—	—	—	—	—
E. Coli	4	2	—	4	3	2

the influence of doping conditions, the conductivity of doped O-4-PIMP has been related with doping extend.

Diaz *et al*. had been suggested the conductivity mechanisms of Schiff base polymers doped with iodine [7]. Nitrogen is a very electronegative element and it is capable to coordinate a iodine molecule. Coordination of iodine on the nitrogen atom of Schiff base polymers in pyridine solution had been suggested in the literatures as follows [22, 23] (Scheme C).

The increasing conjugation length in the compounds may lead to higher conductivity [24]. Figure 8 illustrates the effect of doping time on electrical conductivity of I_2 — doped O-4-PIMP.

Antimicrobial activity of 4-PIMP and O-4-PIMP

Bactericidal activity of the monomer and oligomer are given in Table 4. It has been suggested than the monomer and oligomer with N and O donor system might inhibit enzymes' activity because enzymes require free hydroxyl groups for their activity [25]. The variation in the effectiveness of different bi-radical agents against different organisms depends on the impermeability of the cell [26]. In this study 4-PIMP and O-4-PIMP at high concentrations (0.1 mg/0.1 ml) demonstrated the highest biological activity, and affected eight and seven types of microorganisms, respectively. At their lowest concentration (0.001 mg/0.1 ml) they showed little effect. Both 4-PIMP and O-4-PIMP showed good antibacterial activity against *Listeria monocytogenes*, *Enterococcus faecalis*, *Bacillus cereus*, *Vibrio cholerae* and *Pseudomonas aeruginosa*. The oligomer showed no activity against *Pseudomonas aeruginosa* in all the concentrations tested.

CONCLUSION

Oxidative polymerizations of 4-PIMP were performed at various temperatures and times, using different oxidant agents, namely air O_2, NaOCl or H_2O_2. Colored (ranging from light brown to black) oligoazomethine products were obtained. The major feature of the synthesized oligoazomethine is its good solubility in organic solvents (DMSO, DMF, DMAc, partially in methanol, ethanol and ethyl acetate) what distinguished majority of them from aromatic polyazomethine or poly(Schiff base)s which are insoluble. This opens possibilities of various applications *e.g.* as electroactive and photoactive materials. Oligoazomethines can be easily prepared by oxidative polymerization without special reaction conditions such as high temperature or use of special catalysts. The results of this study show that synthesized oligomers are an interesting class of conjugated compounds which structures and electronic properties can be regulated in a wide range by using different oxidative reagents. The antimicrobial activity of monomer and oligomer against selected bacteria were found.

REFERENCES

1. El-Shekeil A. G., Al-Yusufy F. A., Saknidy S.: *Polym. Intern.* 1997, **42**, 39.
2. Suh S. C., Shim S. C.: *Synth. Metals* 2000, **114** (1), 91.
3. Mamedov B. A., Vidadi Y. A., Alieva D. N., Ragimov A. V.: *Polym. Intern.* 1997, **43** (2), 126.
4. Grigoras M., Catanescu C. O.: *J. Macromol. Sci. Part C — Polym. Rev.* 2004, **C44** (2), 131.
5. Ragimov A. V., Mamedov B. A., Gasanova S. G.: *Polym. Intern.* 1997, **43** (4), 343.
6. Baughman R. H., Bredas J. L., Chance R. R., Elsenbaumer R. L., Shacklette L. W.: *Chem. Rev.* 1982, **82**, 209.
7. Diaz F. R., Moreno J., Tagle L. H., East G. A., Radic D.: *Synth. Met.* 1999, **100** (2), 187.
8. Aly K. I., Khalaf A. A.: *J. Appl. Polym. Sci.* 2000, **77**, 1218.
9. Kaya I., Vilayetoğlu A. R., Topak H. J.: *J. Appl. Polym. Sci.* 2002, **85**, 2004.
10. Kaya I., Demir H. Ö., Vilayetoğlu A. R.: *Synth. Met.* 2002, **126** (2—3), 183.
11. Kaya I., Gül M.: *Europ. Polym. J.* 2004, **40**, 2025.

12. Kobayashi S., Higashimura H.: *Prog. Polym. Sci.* 2003, **28**, 1015.
13. Patel M. N., Patil S. H.: *J. Macromol. Sci. Chem.* 1981, **A16**, 1429.
14. Kaya I.: *J. Polym. Res.* 2004, **11** (3), 175.
15. Kaya I., Bilici A.: *Synth. Met.* 2006, **156** (9—10), 736.
16. Li Y., Cao Y., Gao J., Wang D., Yu G., Heeger A. J.: *Synth. Met.* 1999, **99**, 243.
17. Colladet K., Nicolas M., Goris L., Lutsen L., Vanderzande D.: *Thin Solid Films* 2004, **451—452**, 7.
18. Collins C. H., Lyne P. A., Grange J. M.: "Microbiological Methods", 3rd Ed., Butterworths, Canada 1989, p. 410.
19. Ayyagari M. S., Marx K. A., Tripathy S. K., Akkara J. A., Kaplan D. L.: *Macromolecules* 1995, **28**, 5192.
20. Iwan A., Sęk D.: *Polimery* 2005, **50**, 581.
21. Kadish K. M.: "Electrochemical and Spectrochemical Studies of Biological Redox Components", ACS, Washington 1982.
22. Tassaing T., Besnard M.: *J. Phys. Chem. A* 1997, **101**, 2803.
23. Satoh N., Nakashima T., Yamamoto K.: *J. Am. Chem. Soc.* 2005, **127**, 13 030.
24. Sari N.: *J. Macromol. Sci., Part A: Pure Appl. Chem.* 2006, **43**, 1609.
25. Lawrence P. G., Harold P. L., Francis O. G.: *Antibiot. Chemother.* 1980, **5**, 1597.
26. Rich S., Horsfall J. G.: *Phytopathology* 1952, **42**, 457.