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Synthesis, characterization and electrochemical properties of poly-4-[1-(4-hydroxyphenyl)ethylideneamino]phenol

Summary — The polymer of 4-[1-(4-hydroxyphenyl)ethylideneamino]phenol (4-HPEAP) being a Schiff base substitute was formed with use of oxidants such as air O_2, H_2O_2 or NaOCl in an aqueous alkaline medium. The yield of polymer was found to be 95, 51 and 96 % for air O_2, H_2O_2 and NaOCl, respectively. During these polymerization reactions of 4-HPEAP, H_2O_2 demonstrated lower activity than NaOCl and air O_2. The spectral analyses results such as ^{1}H NMR and ^{13}C NMR showed that the phenol units were connected at *ortho* positions, forming the C-C coupling system. The polymer was found to show relatively high thermal stability. This polymer lost half of the weight at 230 °C. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and electrochemical energy gaps (E'_g) of 4-HPEAP and P-4-HPEAP were found to be -6.30, -6.15; -2.41, -2.57; 3.89 and 3.58 eV, respectively. According to UV-Vis measurements, the optical band gaps (E_g) of 4-HPEAP and P-4-HPEAP were found to be 3.56 and 3.47 eV, respectively.

Key words: oxidative polycondensation, poly-4-[1-(4-hydroxyphenyl)ethylideneamino] phenol, thermal analysis, conductivity, optic and electrochemical properties.

SYNTEZA, CHARAKTERYSTYKA I WŁAŚCIWOŚCI ELEKTROCHEMICZNE POLI-4-[1-(4-HYDROKSYFENYLO)ETYLIDENOAMINO]FENOLU (P-4-HPEAP)

Streszczenie — Otrzymano P-4-HPEAP na drodze utleniającej polikondensacji 4-HPEAP z alkalicznymi roztworami wodnymi zawierającymi O_2, H_2O_2 lub NaOCl w charakterze czynników utleniających. Wydajność uzyskanego polimeru wynosiła 95 % (O_2), 51 % (H_2O_2) i 96 % (NaOCl). Monomer 4-[1-(4-hydroksyfenylo)etylidenoamino]fenol (4-HPEAP) oraz polimer poddano analizie spektralnej metodami ^{1}H NMR i ^{13}C NMR. Zbadano ich stabilność cieplną (TG, DTA, DTG) oraz właściwości elektrochemiczne.

Słowa kluczowe: utleniająca polikondensacja, poli-4-[1-(4-hydroksyfenylo)etylidenoamino]fenol, analiza termiczna, przewodnictwo, właściwości optyczne i elektrochemiczne.

The oligophenols and their derivatives which included azomethine (-CH=N) and active hydroxyl (-OH) groups from an attractive class of polymers that exhibit interesting properties which are associated mainly with their conjugated backbone and the presence of imine sites. Thus, they present good thermal stability, the ability to form metal chelates, good electrical and optical properties. Because of these properties, oligophenols are used to prepare composites resistant to high temperature, graphite materials, epoxy polymers, block copolymers adhesives and antistatic materials [1—12]. These compounds can gain new properties when other functional groups are added to their structures [13]. Also, these type polymers can be used as antimicrobial agents [14, 15]. Most of these compounds exhibit an unusual adsorptive behavior with different solvents, very similar to those of molecular sieve [16—19]. They have the capability of different metal ions coordination [20, 21] and they can be used for cleaning of the industrial waste waters from poisonous heavy metals. Therefore, the syntheses of polymer-metal complexes are very important for analytic and environmental chemistry [22, 23]. It seemed advantageous to attempt to design and prepare a polymer-bound chelating ligand, which would be able to form complexes with a variety of transition metals.

There are some typical methods of oligophenols syntheses. The first oxidative polymerization represents nucleofilic substitution of halogenated aromatic compounds by metal phenolates and other catalytic oxidative polymerization of phenols [24]. The other one method is the oxidative polycondensation of Schiff base monomers including phenol. Phenols and Schiff base substitute phenols easily polymerize using oxidants. This method has significant advantages such as moderate reaction temperatures, and water as by-product. The oxidants used are cheap and of simple structures. The oxidative polymerization, therefore, is a clean and low-loading process for phenolic polymers syntheses.

In this paper, we have investigated the effects of different parameters such as temperature, reaction time, various oxidants and initial concentration of NaOCl on

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the formation of poly-4-[1-(4-hydroxyphenyl)ethylideneamino]phenol (P-4-HPEAP). We have characterized 4-[1-(4-hydroxyphenyl)ethylideneamino]phenol (4-HPEAP) and P-4-HPEAP by FT-IR, UV-Vis, ^{1}H NMR, ^{13}C NMR, elemental analysis, TG-DTA and SEC techniques. The electrical conductivity of the polymer was measured after doping with I_2. Also, electrochemical (E'_g) and optical (E_g) band gaps of the monomer and polymer were determined from cyclic voltammetry (*CV*) and UV-Vis measurements.

EXPERIMENTAL

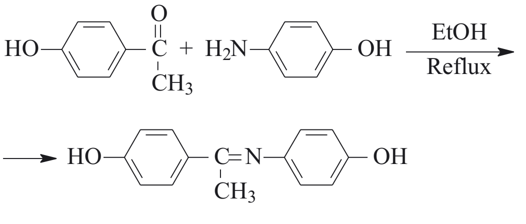
Materials

4-Hydroxyacetophenon, 4-aminophenol, dioxane, methanol, ethanol, 1-butanol, acetonitrile, benzene, toluene, acetone, ethyl acetate, heptane, CCl_4, $CHCl_3$, tetrahydrofuran (THF), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), H_2SO_4 (98 %), NaOH, KOH and HCl (37 %) were supplied by Merck Chemical Co. and were used as received.

Sodium hypochloride (NaOCl, 30 % aqueous solution) was supplied by Paksoy Chemical Co. (Turkey).

Preparation of 4-[1-(4-hydroxyphenyl)ethylideneamino]phenol (4-HPEAP)

4-[1-(4-hydroxyphenyl)ethylideneamino]phenol was prepared by the condensation of 4-hydroxyacetophenon (1.36 g, 0.01 mol) with 4-aminophenol (1.09 g, 0.01 mol) in ethanol (50 ml) by boiling of the mixture under reflux for 2 h at 70 °C (Scheme A). The precipitated 4-[1-(4-hydroxyphenyl)ethylideneamino]phenol was filtered, recrystallized from ethanol and dried in vacuum desiccators (yield 88 %).

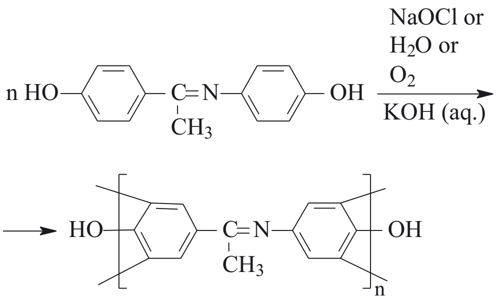


Scheme A. Synthesis of 4-[1-(4-hydroxyphenyl)ethylideneamino]phenol

Elemental analysis (Carlo Erba 1106): calculate for 4-HPEAP: C 74.01; H 5.73; N 6.17; found: C 73.90; H 5.59; N 6.05.

Syntheses of P-4-HPEAP

P-4-HPEAP was synthesized in oxidative polycondensation of 4-HPEAP with aqueous solutions of NaOCl (30 %), H_2O_2 (30 %) or air O_2 [10] (Scheme B). The 4-HPEAP (0.227 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 addition funnel containing NaOCl or H_2O_2. After heating to room temperature, NaOCl or H_2O_2 were added dropwise for about 20 min. The reaction mixtures were stirred at various temperatures and durations. In case of air O_2 use it was passed through an aqueous solution of KOH (20 %) before being sent through the reaction tube to prevent water loss in the reaction mixture and to neutralize CO_2 present in an air. The reaction mixtures were cooled to room temperature, and then 0.001 mol of HCl (37 %) was added. For the separation of mineral salts, the mixtures were filtered and washed in 25 ml of hot water three times. Unreacted monomer was separated from the reaction products by washing with ethyl acetate and then dried in an oven at 110 °C.



Scheme B. Synthesis of poly-4-[1-(4-hydroxyphenyl)ethylideneamino]phenol

Elemental analysis: calculate for P-4-HPEAP: C 74.67; H 4.89; N 6.22; found: C 74.40; H 5.20; N 6.00.

Solubility: P-4-HPEAP was dark brown at powder forms and it was completely soluble in organic solvents such as DMF, THF, DMSO, aqueous alkalies or concentrated H_2SO_4 but only partly soluble in methanol, ethanol and 1-butanol. P-4-HPEAP was insoluble in heptane, hexane, benzene, toluene, ethyl acetate, acetonitrile, $CHCl_3$, CCl_4 and dioxane. The solubility tests were done by using 1 mg sample and 1 ml solvent at 25 °C.

Method of testing

Electrical properties

Conductivity was measured using a Keithley 2400 Electrometer. The pellets were pressed in hydraulic press developing up to about $1.70 \cdot 10^3$ kg/cm^2. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in desiccators [25].

Electrochemical properties

Cyclic voltammetry (CV) measurements were carried out using 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-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 electrode (SCE). The voltammetric measurements were carried out for monomer and polymer in acetonitrile and DMSO, respectively. The HOMO and LUMO energy levels of the monomer and polymer were determined from the onset potentials of n-doping (ϕ'_n) and p-doping (ϕ'_p), respectively, as in literature [26].

Optical properties

The optical band gaps (E_g) of monomer and polymer 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 polymer were recorded with use of methanol and DMSO, respectively, at 25 °C.

Spectrometric investigations

The spectra of the products were recorded as follows. The infrared — using Perkin Elmer FT-IR Spectrum one and universal ATR sampling accessory (4000—550 cm^{-1}).

UV-Vis spectra using Perkin Elmer Lambda 25 — with use of methanol and DMSO.

^{1}H NMR and ^{13}C NMR — using Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively, and with use of deuterated DMSO-d$_6$ as a solvent, at 25 °C; tetramethylsilane was used as internal standard.

Thermal stability

Thermal data were obtained using Perkin-Elmer Diamond Thermal Analysis equipment. The TG-DTA measurements were made in the range 20—1000 °C (in N$_2$, at rate 10 °C/min).

Molecular weight determination

The number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$) and polydispersity index (*PDI*) were determined by size exclusion chromatography (SEC) technique (Shimadzu Co.). For SEC investigations there were used SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. × 300 mm columns; eluent: DMF (0.4 ml/min), polystyrene standards. A refractive index detector (at 25 °C) was used to analyze the product.

RESULTS AND DISCUSSION

Conditions of P-4-HPEAP syntheses

4-[1-(4-hydroxyphenyl)ethylideneamino]phenol not oxidized at the normal conditions at the neutral aqueous or organic medium by air O$_2$, H$_2$O$_2$ (30 % aqueous solution) or NaOCl (30 % aqueous solution). In the conditions of reactions with oxidants used the product immediately precipitated with color change (to brown) of alkaline solution. The conditions of oxidative polycondensation reaction of 4-HPEAP with 30 % NaOCl solution in aqueous alkaline medium are given in Table 1. At conditions given for series 1—5 the yields increased with increasing temperature (except for 90 °C). The highest value of the yield of 4-HPEAP was 96 % at the reaction conditions such as [KOH]$_0$ = 0.002 and [4-HPEAP]$_0$ = [NaOCl]$_0$ = 0.001 mol/L at 60 °C for 5 h (sample 15).

Table 1. Parameters of the reactions of 4-[1-(4-hydroxyphenyl)ethylideneamino]phenol oxidative polycondensation with NaOCl in aqueous KOH$^{*)}$

Sample No.	[KOH]$_0$ mol L^{-1}	[NaOCl]$_0$ mol L^{-1}	Temp. °C	Times h	Yield of P-4-HPEAP, %
1	0.001	0.001	50		76
2	0.001	0.001	60	3	83
3	0.001	0.001	70	3	85
4	0.001	0.001	80	3	86
5	0.001	0.001	90	3	79
6	0.001	0.001	80	5	91
7	0.001	0.001	80	10	88
8	0.001	0.001	80	15	81
9	0.001	0.001	80	25	80
10	0.002	0.001	50	3	91
11	0.002	0.001	60	3	94
12	0.002	0.001	70	3	90
13	0.002	0.001	80	3	86
14	0.002	0.001	90	3	79
15	0.002	0.001	60	5	96
16	0.002	0.001	60	10	93
17	0.002	0.001	60	15	88
18	0.002	0.001	60	25	85
19	0.001	0.002	50	3	86
20	0.001	0.002	60	3	90
21	0.001	0.002	70	3	84
22	0.001	0.002	80	3	80
23	0.001	0.002	90	3	80
24	0.001	0.002	60	5	90
25	0.001	0.002	60	10	93
26	0.001	0.002	60	15	90
27	0.001	0.002	60	25	90

$^{*)}$ The initial concentration of 4-HPEAP was 0.001 mol L^{-1}.

When [KOH]$_0$:[NaOCl]$_0$ molar ratio increased from 1:1 to 2:1 (series 10—18) increase in temperature caused decrease in yield from 91 to 89 % (samples 10—14), similarly as in case of reaction time prolongation (from 96 to 85 %, samples 15—18).

The reaction conditions of 4-HPEAP oxidative polycondensation with 30 % H$_2$O$_2$ solution (samples 1—17) or with air O$_2$ (samples 18—29) in an aqueous alkaline medium are given in Table 2. The yield of P-4-HPEAP was 51 % at optimum conditions such as [4-HPEAP]$_0$ = [KOH]$_0$ = [H$_2$O$_2$]$_0$ = 0.001 mol/L, at 70 °C for 5h (sample

6). At similar conditions, but when molar amount of base increased twice (samples 9—17), total yield of P-4-HPEAP changed from 51 % to 46 % (sample 15). The yield of P-4-HPEAP was only 36 % at the reaction conditions such as [4-HPEAP]$_0$ = [KOH]$_0$ = [H$_2$O$_2$]$_0$ = 0.001 mol/L at 70 °C for 15 h (sample 8). According to these values, yield of P-4-HPEAP decreased with increasing reaction time (samples 6—8).

T a b l e 2. Parameters of the reactions of 4-[1-(4-hydroxyphenyl)ethylideneamino]phenol oxidative polycondensation with H_2O_2 (1—17) and air O_2 (18—27) in aqueous KOH$^{*)}$

Sample No.	[KOH]$_0$ mol L^{-1}	[H$_2$O$_2$]$_0$, mol L^{-1} or air O$_2$, L/h	Temp. °C	Times h	Yield of P-4-HPEAP, %
1	0.001	0.001	50	3	38
2	0.001	0.001	60	3	43
3	0.001	0.001	70	3	47
4	0.001	0.001	80	3	40
5	0.001	0.001	90	3	38
6	0.001	0.001	70	5	51
7	0.001	0.001	70	10	44
8	0.001	0.001	70	15	36
9	0.002	0.001	50	3	24
10	0.002	0.001	60	3	31
11	0.002	0.001	70	3	38
12	0.002	0.001	80	3	30
13	0.002	0.001	90	3	29
14	0.002	0.001	70	5	46
15	0.002	0.001	70	10	42
16	0.002	0.001	70	15	31
17	0.002	0.001	70	25	26
18	0.001	8.5	30	3	56
19	0.001	8.5	40	3	87
20	0.001	8.5	50	3	91
21	0.001	8.5	60	3	90
22	0.001	8.5	70	3	81
23	0.001	8.5	80	3	73
24	0.001	8.5	90	3	68
25	0.001	8.5	50	1	79
26	0.001	8.5	50	5	93
27	0.001	8.5	50	10	95
28	0.001	8.5	50	15	91
29	0.001	8.5	50	25	88

$^{*)}$ See Table 1.

At the oxidative polycondensation reaction of 4-HPEAP, when air oxygen passed with 8.5 L/h rate into the reaction medium at 30 °C, the yield of product was 56 %. The yield of P-4-HPEAP was 95 % at optimum conditions such as [4-HPEAP]$_0$ = [KOH]$_0$ = 0.01 mol/L at 50 °C for 10 h (sample 27).

As it is seen from Table 1 and 2, in these reactions the yield of the polymer was dependent upon temperature, times and initial concentrations of base. At the same conditions, the yield of P-4-HPEAP with use of NaOCl or air O_2 was higher than with H_2O_2.

Structure of P-4-HPEAP

The values of number-average molecular weight ($\overline{M}_n$) and weight-average molecular weight ($\overline{M}_w$) of P-4-HPEAP were calculated from SEC chromatograms according to polystyrene standard calibration curve. They are given in Table 3. The highest $\overline{M}_n$ and $\overline{M}_w$ values of P-4-HPEAP are obtained for the samples prepared with NaOCl while the lowest in case of air O_2 use.

The UV-Vis spectra of 4-HPEAP and P-4-HPEAP were similar one to other. However, at the spectrum of 4-HPEAP, K bands of phenol and C_6H_5-N= were observed in 220 nm and 277 nm, respectively. Strength R band of -CH=N- group was observed in 335 nm. λ_{max} values of P-4-HPEAP were observed in 205, 233, 296 and 381 nm. In UV-Vis spectra of P-4-HPEAP, K and R bands were observed in 296 nm and 381 nm, respectively. The UV-Vis spectra shows specific bands for λ_{max} assigned to aromatic and azometinic π-π* transitions at about 280 and 350 nm, respectively [27]. The shifting of the -CH=N- group band from 296 nm to 381 nm has been related to the formation of the polymeric conjugated π system.

According to the FT-IR spectra, 4-HPEAP and P-4-HPEAP differ only in band strength (reduction for P-4-HPEAP) and peak numbers. At the FT-IR spectra of 4-HPEAP and P-4-HPEAP, bands of -OH and -C=N groups were observed in 3285 and 1659 cm^{-1}; 3328 and 1618 cm^{-1}, respectively. Additionally in FT-IR spectra of 4-HPEAP and P-4-HPEAP the following bonds occur: 3073m and 3075m (C-H phenyl); 2992s and 2994s (C-H aliphatic); 1602, 1576, 1509s and 1595, 1570, 1498s (C=C phenyl); 1277s and 1280s (C-O).

In order to identify the structures of monomer and polymer, the ^{1}H and ^{13}C NMR spectra were recorded (Figs. 1, 2 and Figs. 3, 4, respectively). At the ^{1}H NMR

T a b l e 3. Number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$), polydispersity index (*PDI*) and fraction part of P-4-HPEAP (%)

Compounds	Molecular weight distribution parameters														
	Total			Fraction I				Fraction II				Fraction III			
	$\overline{M}_n$	$\overline{M}_w$	PDI	$\overline{M}_n$	$\overline{M}_w$	PDI	%	$\overline{M}_n$	$\overline{M}_w$	PDI	%	$\overline{M}_n$	$\overline{M}_w$	PDI	%
P-4-HPEAP$^{1)}$	1400	1550	1.107	2000	2200	1.100	60	2700	3200	1.185	30	22500	24000	1.067	10
P-4-HPEAP$^{2)}$	5000	5470	1.094	2500	2900	1.160	15	3000	3750	1.250	30	25000	27000	1.080	55
P-4-HPEAP$^{3)}$	3000	3300	1.100	2800	3350	1.196	30	2900	3500	1.207	45	27000	29500	1.093	25

Oxidants: 1 — air O_2, 2 — NaOCl, 3 — H_2O_2.

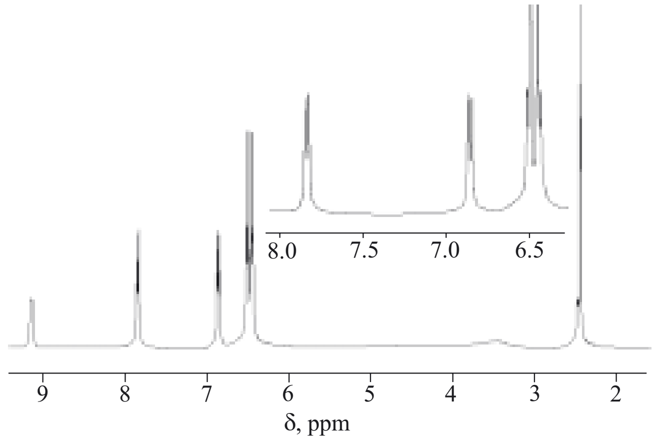


Fig. 1. ^{1}H NMR spectrum of 4-HPEAP

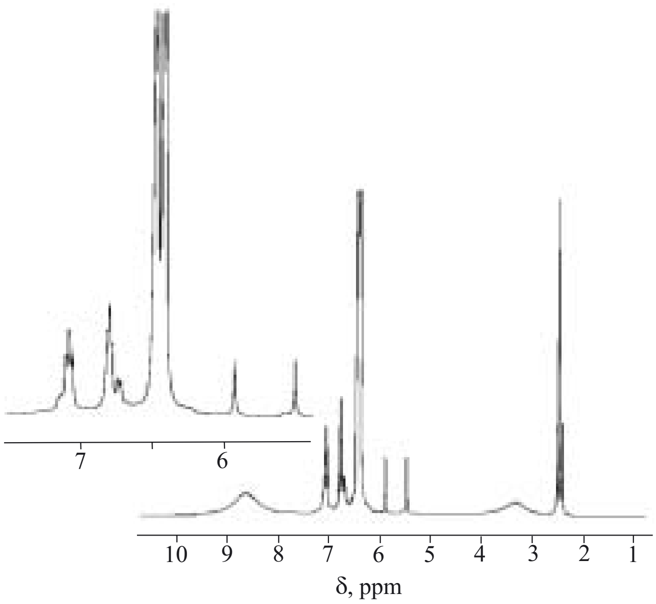


Fig. 3. ^{1}H NMR spectrum of P-4-HPEAP

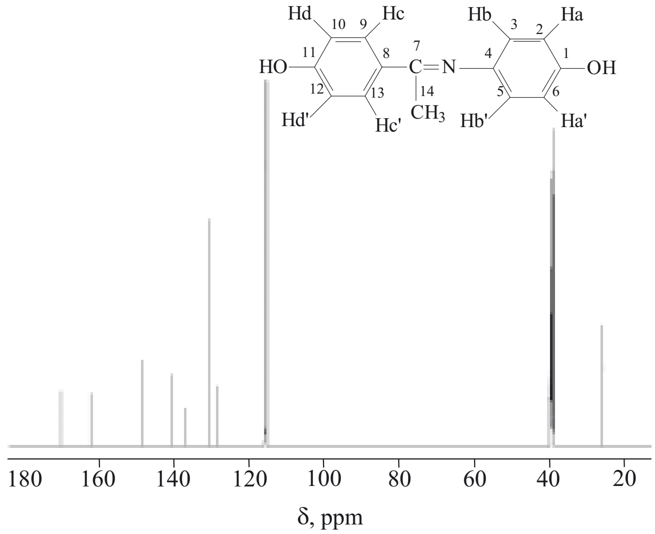


Fig. 2. ^{13}C NMR spectrum of 4-HPEAP

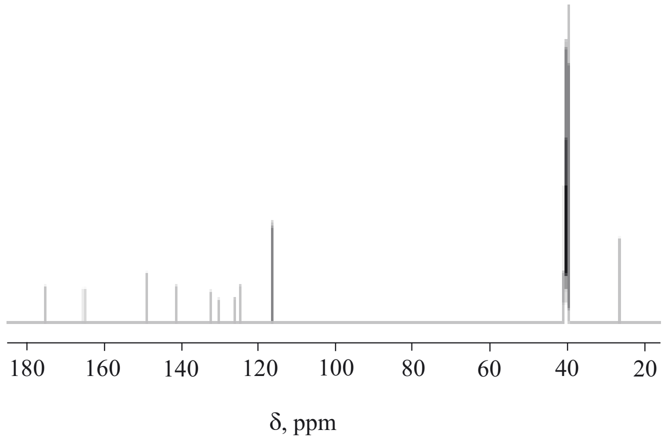


Fig. 4. ^{13}C NMR spectrum of P-4-HPEAP

spectra (Figs. 1 and 3) the chemical shift values (ppm) of -OH and aromatic and aliphatic protons were observed of 4-HPEAP: in 9.15 (s, 2H, -OH), 6.51 (d, 2H, Ar-Haa′), 6.45 (d, 2H, Ar-Hbb′), 7.83 (d, 2H, Ar-Hcc′), 6.93 (d, 2H, Ar-Hdd′), 2.50 (s, 3H, -CH_3) and of P-4-HPEAP in 8.68 (s, 2H, -OH), 5.50 (s, 2H, Ar-Hbb′), 5.92 (s, 2H, Ar-Hcc′), [terminal protons: 6.48 (d, 2H, Ar-Haa′), 6.41 (d, 2H, Ar-Hbb′), 7.10 (d, 2H, Ar-Hcc′), 6.81 (d, 2H, Ar-Hdd′)], 2.51 (s, 3H, -CH_3).

At ^{13}C NMR spectra of 4-HPEAP the following chemical shifts were observed:

148.81 (C1-ipso-OH), 115.83 (C2,6-H), 129.11 (C3,5-H), 141.01 (C4-ipso), 170.25 (C7-ipso), 137.44 (C8-ipso), 131.17 (C9,13-H), 116.06 (C10,12-H), 162.48 (C11-ipso-OH), 26.65 (C14-H_3).

While at ^{13}C NMR spectra of P-4-HPEAP bonds: 166.86 (C1, C11-ipso-OH), 116.20 (C2-6-H, terminal), 125.16 (C2-6-ipso), 129.85 (C3-H, C-5), 149.44 (C4-ipso), 175.53 (C7-ipso), 141.32 (C8-ipso), 132.58 (C9-H, C13-H), 116.45 (C10-12-H, terminal), 126.55 (C10-12-ipso), 27.40 (C14-H_3) are present.

The ^{1}H NMR and ^{13}C NMR spectra results of P-4-HPEAP confirm the formation of polymer units. Shifting to lower peak values for C2, 6 and C10, 12 demonstrated the formation of polymer units. The ^{13}C NMR spectra of P-4-HPEAP have been demonstrated C-C coupling systems. Monomer and dimer interconversion combinations of radical units are proposed in the literature [28]. The hydroxyl groups are involved in the formation of free radicals leading to polymer formation. According to ^{1}H NMR, an integral value of hydroxyl group was found to be 1.000. Thus, the phenyl rings in the polymer appear to be linked primarily both at *ortho* positions according to -OH groups of P-4-HPEAP (Scheme B).

Thermal analyses of 4-HPEAP and P-4-HPEAP

TG/DTA curves of monomer and polymer are given in Fig. 5 and Fig. 6. The initial degradation temperature and temperature of 50 % and 96.45 % weight losses of

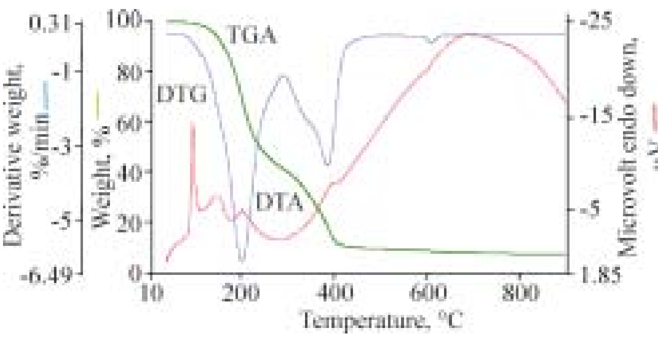


Fig. 5. TG-DTG-DTA curves of 4-HPEAP

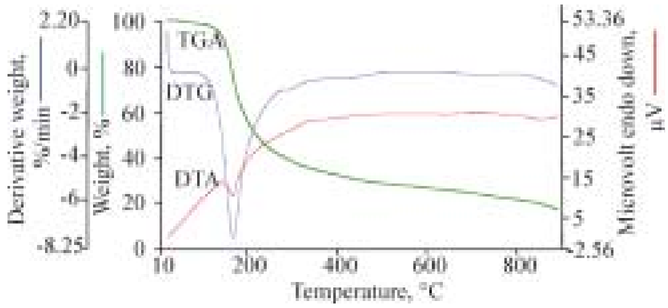


Fig. 6. TG-DTG-DTA curves of P-4-HPEAP

4-HPEAP were found to be 115, 242 and 900 °C, respectively. According to DTG curve, thermal degradation of 4-HPEAP runs in two steps. The weight loss of the first step was found to be 58.44 % at temp. range 120—295 °C. The weight loss of the second step was found to be 38.0 % at 295—900 °C. According to DTA analysis, exothermic peaks were observed at 101, 150 and 205 °C. According to DTG analysis, T_{max} values for monomer were observed at 201 and 387 °C.

The initial degradation temperature and temperature of 50 % and 83.48 % weight loss of P-4-HPEAP were found to be 151, 230 and 900 °C, respectively. Because of long conjugated bonds systems, polymer demonstrated higher resistance to high temperature than a monomer. According to TG analysis, initial degradation temperature of P-4-HPEAP was higher than of monomer and polymer was more stable than a monomer up to thermal decomposition. At temp. 900 °C the residue was formed at high amount such as 16.52 %. According to DTA analysis, the glass transition temperature (T_g) of polymer was observed at 164 °C. According to DTG analysis, T_{max} value of polymer was observed at 172 °C.

Electrochemical properties of 4-HPEAP and P-4-HPEAP

The voltammetric measurements of 4-HPEAP and P-4-HPEAP were carried out in acetonitrile and DMSO, respectively. The HOMO and LUMO energy levels and electrochemical energy gaps (E'_g) were calculated from oxidation and reduction onset values and are shown in

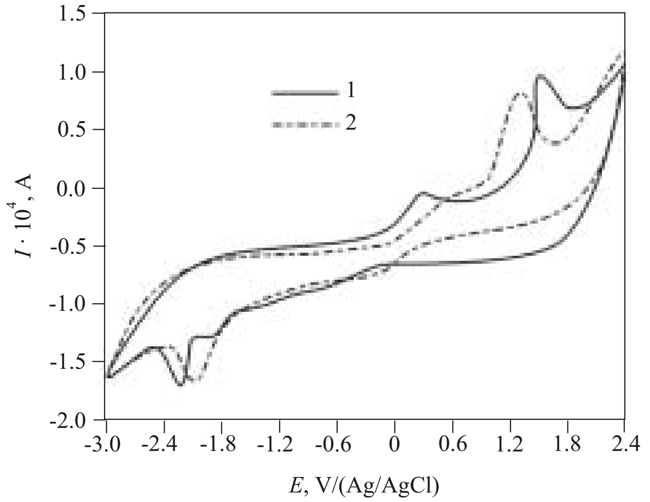


Fig. 7. Cyclic voltammograms of 4-HPEAP (1) and P-4-HPEAP (2) (cyclic voltammograms measured vs. Ag/AgCl)

Figure 7. The HOMO and LUMO energy levels and electrochemical energy gaps (E'_g) of 4-HPEAP and P-4-HPEAP were found to be -6.30, -6.15; -2.41, -2.57; 3.89 and 3.58 eV, respectively. The electrochemical analyses results for 4-HPEAP and P-4-HPEAP showed the lower band gap values of polymer with respect to monomer. Band theory is used for explanation of conductivity mechanism. According to band theory, the increase in energy level (E'_g) between full molecule orbital and empty molecule orbital can make difficult passing of electrons from full molecule orbital to empty one. In addition, electrochemical band gap values of 4-HPEAP and P-4-HPEAP were found to be 3.89 and 3.58 eV, respectively. The difference of these values is lower than difference between HOMO and LUMO energy levels of P-4-HPEAP and 4-HPEAP.

The absorption spectra of 4-HPEAP and P-4-HPEAP were recorded using methanol and DMSO at 25 °C (Fig. 8) and λ_{max} (nm) and E_g (eV) values of 4-HPEAP and P-4-HPEAP were found to be 289, 296 nm and 3.56 and

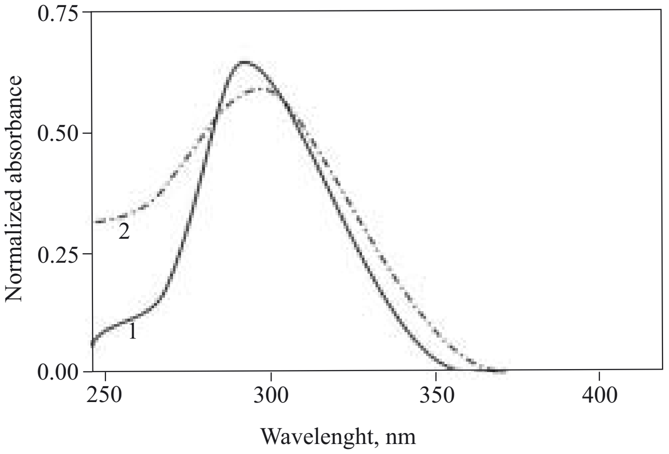


Fig. 8. Absorption spectra of 4-HPEAP (1) and P-4-HPEAP (2)

3.47, respectively. Both electrochemical energy gaps (E'_g) and optical band gap values of 4-[(2-hydroxybenzylidene)amino]benzoic acid and poly-4-[(2-hydroxybenzylidene)amino]benzoic acid had been determined by CV technique [28]. The optical band gaps value of 4-HPEAP is higher than of P-4-HPEAP. This results corresponds with electrochemical energy gaps (E'_g) value which was obtained by calculation from electrochemical oxidation and reduction potentials. The band gap value of polymer was low in the comparison with band gap of monomer.

Conductivity value before the polymer was doped with iodine was 10^{-11}—10^{-10} S/cm. When polymer was doped with iodine, conductivity could increase by about four orders of magnitude (up to 10^{-4} S/cm). Figure 9 show the results for P-4-HPEAP doped with iodine at various times at 25 °C. For the doping of P-4-HPEAP with iodine, it was found that the conductivity of P-4-HPEAP first increased greatly with doping time, but then tended to level-off. The maximal conductivity of polymer was $1.55 \cdot 10^{-7}$ S/cm. The increasing conductivity could indicate that a charge-transfer complex between P-4-HPEAP and dopant iodine was continuously formed. Consequently, Fig. 9 not only shows the conductivity/doping time dependence but also indicates how quickly the doping reaction takes place. The experiments showed that 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 conductivity of doped P-4-HPEAP has been related to doping extent. Diaz *et al.* had been suggested the conductivity mechanisms of Schiff base polymers for doping with iodine [25, 29]. Nitrogen is a very electronegative element and it is capable to coordinate an iodine molecule. Coordination of iodine during P-4-HPEAP doping is as follows (Scheme C): Sakai suggested the coordination of iodine on nitrogen atom of Schiff base polymers [30—32]. The conductivity value of P-4-HPEAP before doping with iodine was lower.

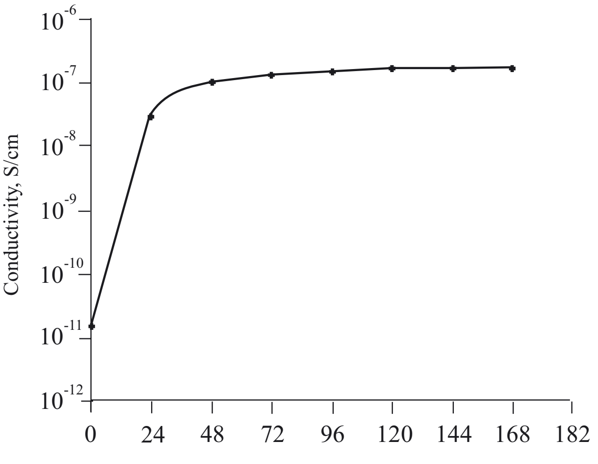
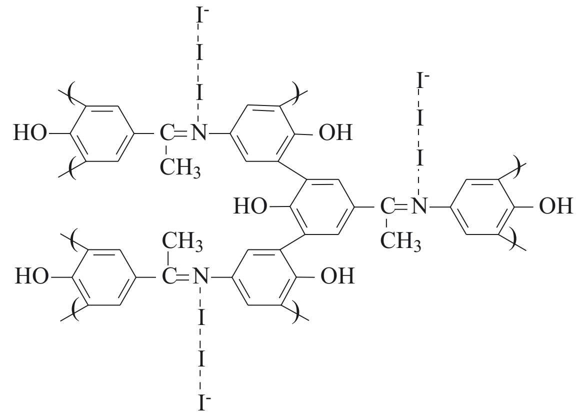


Fig. 9. Electrical conductivity of I_2-doped P-4-HPEAP vs. doping time at 25 °C



Scheme C. Coordination of iodine during P-4-HPEAP doping

CONCLUSION

The conditions of 4-[1-(4-hydroxyphenyl)ethylideneamino]phenol (4-HPEAP) oxidative polycondensation with use of such oxidants as air O_2 or H_2O_2 or NaOCl, in an aqueous alkaline medium at temp. 30—90 °C were studied. At the optimum reaction conditions, the yield of poly-4-[1-(4-hydroxyphenyl)ethylideneamino]phenol (P-4-HPEAP) was found to be 95 %, 51 % and 96 % for air O_2, H_2O_2 and NaOCl oxidants, respectively. According to the SEC analysis, the number-average molecular weight ($\overline{M}_n$), weight-average molecular weight ($\overline{M}_w$) and polydispersity index (*PDI*) values of P-4-HPEAP were found to be 3000, 3300 and 1.100, when H_2O_2 was used, 1400, 1550 and 1.107 for air O_2 and 5000, 5470 and 1.094 for NaOCl use, respectively. According to TG analyses, the weight losses of 4-HPEAP and P-4-HPEAP were found to be 96.86 % and 83.48 % at 900 °C, respectively. Also, electrical conductivity of P-4-HPEAP was measured, showing that the polymer is a typical semiconductor. The band gap value of the monomer is higher than that of the polymer.

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