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Syntheses and characterizations of multifunctional polyphenols derived from dihydroxyphenylene-based Schiff bases

Summary — Schiff base compounds were synthesized by condensation reaction of 1,4-diaminobenzene, naphthalene-1,5-diamine and 2,6-dichlorobenzene-1,4-diamine compounds with 2,4-dihydroxybenzaldehyde. The obtained Schiff bases were converted to their polyphenol derivatives by oxidative polycondensation. Sodium hypochlorite and air were used as the oxidants. Experimental parameters such as temperature, reaction time and oxidant concentration were varied to determine the optimum oxidative polycondensation conditions. The structures of all compounds were confirmed by FT-IR, UV-Vis and ^{1}H- and ^{13}C NMR analyses. In addition, thermal properties of the Schiff bases and the corresponding polymers were determined by TG-DTA, DSC and DMA techniques. Photoluminescence properties of the synthesized compounds were determined in DMF solutions. Electrochemical characterizations were made by cyclic voltammetry measurements. Solid state conductivities of the polymers were determined by four point probe technique using an electrometer. The number average and weight average molecular weights and polydispersity index values of the synthesized compounds were determined by the size exclusion chromatography.

Keywords: poly(imine)s, oxidative polycondensation, optimum reaction conditions.

SYNTEZA I CHARAKTERYSTYKA MULTIFUNKCJONALNYCH POLIFENOLI OTRZYMYWANYCH Z DIHYDROKSYFENYLENOWYCH ZASAD SCHIFFA

Streszczenie — W reakcji kondensacji 1,4-diaminobenzenu, 1,5-diaminonaftalenu lub 1,4-diamino-2,6-dichlorobenzenu z 2,4-dihydroksybenzaldehydem syntezowano zasady Schiffa. Otrzymane związki poddano polikondensacji utleniającej z udziałem podchloranu(I) sodu lub powietrza jako czynników utleniających, uzyskując pochodne polifenolowe. Optymalizowano warunki polikondensacji prowadząc reakcję w różnych: czasie i temperaturze. Strukturę otrzymanych pochodnych potwierdzono metodami FT-IR, UV-Vis, ^{1}H NMR i ^{13}C NMR. Właściwości termiczne wytworzonych monomerów i odpowiadających im polimerów określano za pomocą technik TG-DTA, DSC oraz DMA. Oceniano też zdolność do fluorescencji otrzymanych związków rozpuszczonych w DMF. Przeprowadzono pomiary metodą woltametrii cyklicznej wyznaczając właściwości elektrochemiczne. Za pomocą chromatografii żelowej określano liczbowo średni i wagowo średni ciężar cząsteczkowy wytworzonych związków oraz stopień polidyspersji.

Słowa kluczowe: poliimidy, polikondensacja utleniająca, optymalne warunki reakcji.

INTRODUCTION

Poly(imine)s (PIs) with a system of conjugated bonds in their main chain have been attracted the attention of researchers due to their importance in many aspects [1, 2]. Poly(imine)s or poly(Schiff-base)s with aromatic backbones were considered as high performance polymers due to their high thermal stability, excellent mechanical strength, and good optoelectronic properties. In recent years, PIs have also been explored for applications in organic electronics, such as light-emitting materials, pH sensors, and metal-collecting polymers [3—5]. Additionally, optical and semiconducting properties of these polymers have been also widely investigated for many years because of photo- and electroluminescence at a wavelength dependent on chemical structure as well as interesting non-linear optical (NLO) properties of Schiff-bases in their polymeric form [6, 7]. The conducti-

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[*)] Corresponding author; e-mail: kayaismet@hotmail.com vity values of aromatic poly(imine)s were increased by doping with iodine. Due to this property, PIs used in light emitting diodes, polymer lasers and photovoltaic cells have been investigated for over ten years [8—10].

Oligophenols and their azomethine derivatives had been previously synthesized by oxidative polycondensation (OP) method and their several useful properties reported in the literature [11]. Coupling selectivity of the Schiff base substituted oligophenols were also studied and two coupling mechanisms for this class of PIs were described including C-O-C and C-C couplings [12]. The effect of the coupling rate on thermal stability has been investigated and it was found that increasing C-O-C coupling rate also decreased the thermal stability of the oligophenol. However, there is still a need for further studies with a variation of substituents to determine the common factors affecting the properties of this class of PIs.

In this work, we have synthesized Schiff base monomers with phenyl, chlorophenyl and naphthyl groups. The Schiff bases were converted to their polyphenol species *via* OP. The electrical, electrochemical, optical, fluorescence and thermal properties of all polymers were investigated. The obtained polymers were found to be semi-conductive materials whose conductivities could be increased by iodine doping. Especially, the conductivity of poly{4,4'-[1,4-phenylene-bis(nitrilomethylidene)]dibenzene-1,3-diol} highly increased with doping that made the polymer good candidate for gas sensing applications against electro-acceptor gases like iodine. Optical and electrochemical band gap measurements showed that the novel polymers have lower band gaps than their Schiff base monomers due to their polyconjugated structures.

EXPERIMENTAL

Materials

2,4-Dihydroxybenzaldehyde (DHB), 1,4-diaminobenzene (DAB) and 2,6-dichloro-1,4-aminobenzene (DCDAB) were supplied from Fluka; 1,5-diaminonaphthalene (DAN), potassium hydroxide, hydrochloric acid, 30 % aqueous solution sodium hypochlorite, ethanol, ethyl acetate, $CHCl_3$, DMSO, DMF, THF, acetonitrile and acetone were supplied from Merck Chemical Co. and they were used as received.

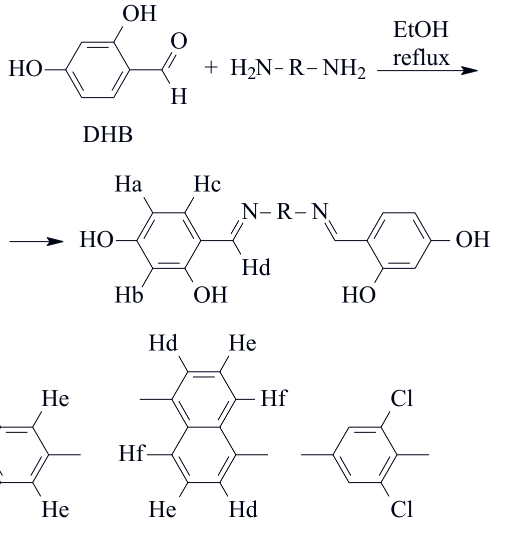
Syntheses of the Schiff bases

Schiff bases abbreviated as 4,4'-[1,4-phenylene-bis(nitrilomethylidene)]dibenzene-1,3-diol abbreviated as M1, 4-4'-[naphthalene-1,5-di bis(nitrilomethylidene)]dibenzene-1,3-diol (M2) and 4,4'-[(2,6-dichloro-1,4-phenylene)bis(nitrilomethylidene)]dibenzene-1,3-diol (M3) were synthesized by the condensation reactions of 2,4-dihydroxybenzaldehyde with 1,4-diaminobenzene, naphthalene-1, 5-diamine and 2, 6-dichloro-1,4-aminobenzene, respectively. Reactions were performed as follows:

Synthesis of M1: DHB (0.276 g, 0.002 mol) was placed into a 100 cm^3 three-necked round-bottom flask which was fitted with condenser, thermometer and magnetic stirrer. 20 cm^3 of ethanol was added into the flask and reaction mixture was heated up to 75 °C. DAB (0.108 g, 0.001 mol) in 20 cm^3 in ethanol was added and the reaction maintained for 3 h under reflux.

Synthesis of M2: DHB (0.276 g, 0.002 mol) was placed into a 100 cm^3 three-necked round-bottom flask which was fitted with condenser, thermometer and magnetic stirrer. 20 cm^3 of ethanol was added into the flask and reaction mixture was heated up to 75 °C. DAN (0.158 g, 0.001 mol) in ethanol was added in the reaction maintained for 4 h under reflux.

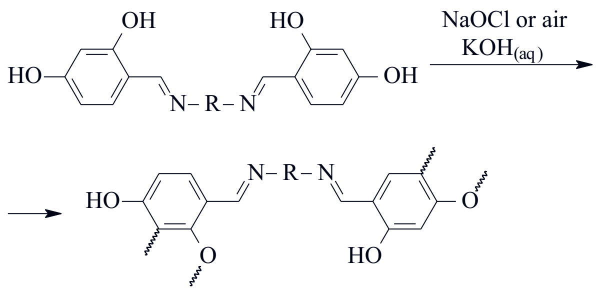
Synthesis of M3: DHB (0.276 g, 0.002 mol) was placed into a 100 cm^3 three-necked round-bottom flask which was fitted with condenser, thermometer and magnetic stirrer. 20 cm^3 of ethanol was added into the flask and reaction mixture was heated up to 75 °C. DCDAB (0.177 g, 0.001 mol) in ethanol was added in the reaction maintained for three days under reflux. The reaction mixtures were filtered and dried in a vacuum desiccator (yields: 83, 82 and 80 % for M1, M2 and M3, respectively). Schiff base reactions are shown in Scheme A.



Scheme A. Syntheses of Schiff bases abbreviated as M1, M2 and M3

The oxidative polycondensation of monomers

The synthesized Schiff bases were converted into their polymer derivatives through oxidative polycondensation in an aqueous alkaline medium using NaOCl (30 %, in



Scheme B. Syntheses of the poly(imine)s

the various concentrations) and air as the oxidant [13]. Reactions were carried out in 100 cm^3 three-necked round-bottom flasks fitted with condenser, thermometer and magnetic stirrer. The optimum reaction conditions for all polymerizations were determined between 40 and 90 °C. The oxidative polycondensation reaction mechanism is shown in Scheme B.

The oxidative polycondensation of monomers using NaOCl

Poly(4,4′-[1,4-phenylene-bis(nitrilomethylidene)]dibenzene-1,3-diol) (P1), poly{4,4′-[naphthalene-1,5-di-bis(nitrilomethylidene)]dibenzene-1,3-diol) (P2) and poly(4,4′-[(2,6-dichloro-1,4-phenylene)bis(nitrilomethylidene)]dibenzene-1,3-diol} (P3) were synthesized through oxidative polycondensation of M1 (0.087 g), M2 (0.099 g) and M3 (0.104 g) using aqueous solution of NaOCl (30 %, in the various concentrations, see Table 1). Monomers (2.5×10^{-4} mol), were dissolved in an aqueous solution of KOH (0.1 mol) and placed into a 100 cm^3 three-necked round-bottom flask. This flask was fitted with a condenser, thermometer, stirrer and an addition funnel containing NaOCl (Table 1). When the thermometer a predetermined temperature, NaOCl was added drop wise into the flask. After the reaction was completed, solutions were cooled to room temperature. Then, HCl (0.1 mol) was added to end the reaction ended. Mineral salts were separated from the reaction product by washing with water (3 × 50 cm^3), filtered and then dried in the vacuum oven at 60 °C. The product in the form of black powder was obtained.

T a b l e 1. The conditions of oxidative polycondensation of the monomers with NaOCl oxidant in an aqueous KOH

Run	Time h	Temperature, °C	[NaOCl]·10^{-3} mol/dm^3	Yields, %		
				P1	P2	P3
1	1	40	5.0	32	37	74
2	1	50	5.0	58	47	80
3	1	60	5.0	51	58	62
4	1	70	5.0	40	65	48
5	1	80	5.0	30	74	41
6	1	90	5.0	22	50	37
7	3	50	5.0	40	—	—
8	1	50	10.0	33	—	—
9	3	80	4.0	—	30	—
10	3	80	10.0	—	43	—
11	3	50	2.5	—	—	57
12	3	50	5.0	—	—	68

[M1] = [M2] = [M3] = $5 \cdot 10^{-3}$ mol/dm^3, [KOH] = 0.2 mol/dm^3.

The oxidative polycondensation of monomers using air

M1 (0.087 g), M2 (0.099 g) or M3 (0.104 g) were dissolved in aqueous solution of KOH (0.1 mol) and placed into a 100 cm^3 three-necked round-bottom flask. This flask was fitted with a condenser, thermometer, stirrer and addition funnel and an air inlet tube above condenser. The reaction mixtures were heated at various temperatures and times (Table 2). The air was passed at a rate of 8.5 dm^3/h during the course of the reaction. After the reaction was completed, the solutions were cooled to room temperature and then HCl (0.1 mol) was added to the reaction mixture. Mineral salts were separated from the reaction product by washing with water (3 × 50 cm^3), filtered and then dried in the vacuum oven at 60 °C. The products in the form of black powder were obtained.

T a b l e 2. The conditions of oxidative polycondensation of the monomers with air oxidant in an aqueous KOH

Run	Time, h	Temperature, °C	Yields, (%)		
			P1	P2	P3
1	1	40	35	22	61
2	1	50	45	32	82
3	1	60	50	47	70
4	1	70	75	53	55
5	1	80	66	75	43
6	1	90	60	59	39
7	3	70	40	—	—
8	3	80	—	68	—
9	3	50	—	—	62

[M1] = [M2] = [M3] = $2.5 \cdot 10^{-3}$ mol/dm^3 [KOH] = 0.2 mol/dm^3.

Methods of testing

— The solubility tests were done in different solvents using 1 mg samples and 1 cm^3 solvent at 25 °C.

— The Fourier Transform infrared and ultraviolet-visible spectra were measured by Perkin Elmer FT-IR Spectrum one and Specord 210 Plus, respectively. The FT-IR spectra were recorded using universal ATR sampling accessory (4000—550 cm^{-1}).

— ^1H- and ^{13}C NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) were also recorded by using deuterated DMSO-d_6 as a solvent at 25 °C. The tetramethylsilane was used as internal standard.

— Thermal date were obtained using a Perkin Elmer Diamond Thermal Analysis system. TG-DTA measurements were made between 20 and 1000 °C (in N_2, rate 10 deg /min).

— DSC analyses were carried out by using Perkin Elmer Pyris Sapphire DSC. DSC measurements were made between 20 and 420 °C (in N_2, rate 20 deg/min).

— Dynamical mechanical analysis (DMA) of P1 was carried out by a Perkin Elmer Pyris Diamond DMA 115V. Measurement was carried out in the range of 20—300 °C with 1 Hz frequency using single-cantilever technique. Sample was prepared as follows: 0.5 g of the polymer was placed into the titanium clamp (supplied from Triton Technology Ltd., United Kingdom) then closed on both sides by clamping.

— The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (*PDI*) were determined by size exclusion chromatography (SEC) techniques with Shimadzu Co. apparatus. For SEC investigations a SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. x 300 mm column was used DMF as eluent (0.4 cm^3/min) and polystyrene standards.

— A refractive index detector (RID) were used to analyze the products at 25 °C.

— A Shimadzu RF-5301PC spectrofluorophotometer was used in fluorescence measurements [12, 13]. Emission and excitation spectra of the synthesized monomers and polymers were obtained in DMF solution. Measurements were made in a wide concentration range between 3.125 and 100 mg/dm^3 to determine the optimal fluorescence concentrations. Slit width in all measurements was 3 nm.

— Ultraviolet-visible (UV-Vis) spectra of compounds were measured by Specord 210 Plus. The absorption spectra were recorded using DMSO at 25 °C. The optical band gaps (E_g) were calculated from their absorption edges.

— Cyclic voltammetry (CV) measurements were carried out with a CHI 660 C Electrochemical Analyzer (CH Instruments, Texas, USA) at a potential scan rate of 20 mV/s. All the experiments were performed in a dry box filled with argon 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^+) was measured in acetonitrile solution of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as 0.39 V with respect to Ag wire. The voltammetric measurements were carried out in acetonitrile for the Schiff bases and acetonitrile/DMSO mixture (v/v:5/1) for the polymers. The HOMO-LUMO energy levels and electrochemical band gaps (E'_g) were calculated from oxidation and reduction peak potentials [14].

— Conductivities of the synthesized polymers were measured on a Keithley 2400 Electrometer. The pellets were pressed on a hydraulic press, providing a pressure 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 [15]. Measurements were carried out for 24 h in air atmosphere after doping the pellets with I_2 in desiccator.

RESULTS AND DISCUSSION

Solubilities of the compounds

The synthesized compounds M1, M2 and M3 are respectively orange, light brown and yellow colored-powder whereas their polymer derivatives are black colored. The solubility test results are shown in Table 3. All the compounds were soluble in highly polar solvents like DMSO and DMF. Monomers and P3 were completely soluble in THF while P1 and P2 were semi-soluble in THF. Moreover, the monomers were partly soluble in ethanol, ethyl acetate and acetone. M3 is semi-soluble in chloroform while the rest of the compounds were insoluble. Monomers were completely soluble in acetonitrile contrary to the polymers in soluble this solvent.

Structures of the compounds

The FT-IR spectral data are summarized in Table 4. As it can be seen, the structures of the synthesized Schiff bases are confirmed by the growth of the imine (CH=N) peaks with disappearance of the $-NH_2$ bands and the

T a b l e 3. Solubility tests of the synthesized compounds

Solvents / Compounds	DMSO	DMF	Ethanol	Ethyl acetate	THF	Chloroform	Acetonitrile	Acetone
M1	+	+	⊥	⊥	+	-	+	⊥
M2	+	+	⊥	⊥	+	-	+	⊥
M3	+	+	⊥	⊥	+	⊥	+	⊥
P1	+	+	-	-	⊥	-	-	-
P2	+	+	-	-	⊥	-	-	-
P3	+	+	-	-	+	-	-	-

+: Soluble, ⊥: partially soluble, -: insoluble.

C=O absorption of the aldehyde (DHB) used in the condensation reactions. Imine stretch vibration is shown at 1606, 1609 and 1615 cm^{-1} for M1, M2 and M3, respectively. O-H stretching band of phenolic groups is also observed in the range of 3300—3200 cm^{-1} for M1, M2 and M3. The peaks in the FT-IR spectra of the polymers the peaks also broaden because of the polyconjugated structures.

Table 4. FT-IR spectral data of the synthesized compounds

Compounds	Functional groups, cm^{-1}			
	-OH	Ar-C-H	C=N	C=C (aromatic)
M1	3300	3020	1606	1547—1498
M2	3360	3015	1609	1591—1480
M3	3220	3030	1615	1576—1479
P1	3300	3020	1602	1510
P2	3360	3015	1606	1513—1462
P3	3220	3030	1615	1576—1429

^{1}H NMR spectra of M1 are shown in Fig. 1. As it can be seen two hydroxyl (-OH) peaks of M1 are present at 13.66 and 10.30 ppm, respectively. The structure is also confirmed by imine protons (C<u>H</u>=N) of M1 observed at 8.86 ppm, also confirm the structures. The peaks of Ha, Hb, Hc and Hd protons of phenyl groups can be found at 7.46, 6.43, 6.32 and 7.45 ppm, respectively. ^{1}H NMR spectra of P1 which was synthesized by oxidative polycondensation of M1, are shown in Fig. 2. As it is observed, hydroxyl peak in the *ortho* position disappeared after oxidative polycondensation and the intensities of phenyl Ha and Hb proton peaks are decreased.

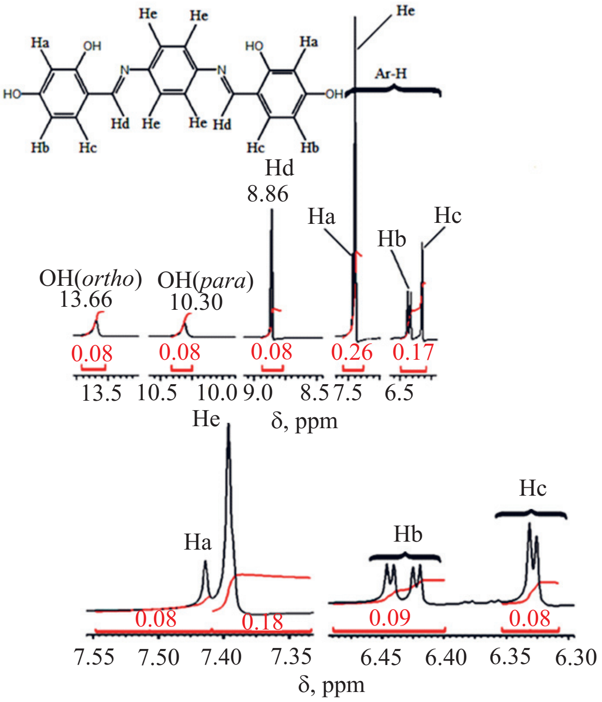


Fig. 1. ^{1}H NMR spectra of M1

^{1}H NMR data of M2 are shown in Table 5. Two hydroxyl (-OH) peaks are observed at 13.56 and 10.40 ppm, respectively. Imine protons (C<u>H</u>=N) of M2 which are found at 8.87 ppm, also confirm the structure. The peaks of Ha, Hb, Hc, Hd, He and Hf protons of aromatic groups can be observed at 6.43, 6.50, 7.45, 7.57, 7.64 and 8.08 ppm, respectively. After oxidative polycondensation, of monomer M2 hydroxyl peak in the *ortho* position was disappeared. Phenyl groups Ha and Hb proton peak integrals were also reduced.

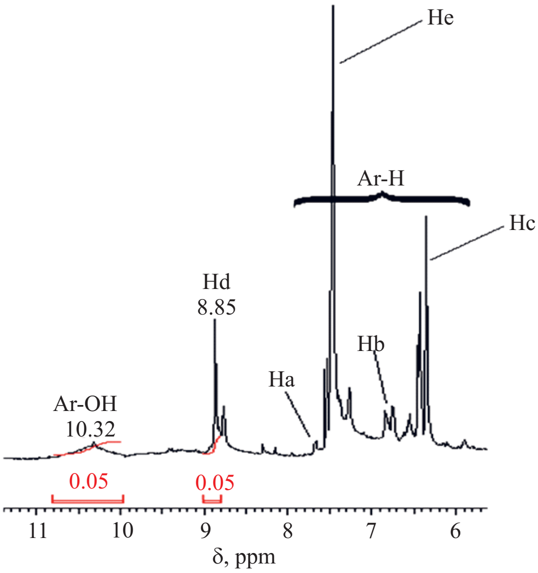


Fig. 2. ^{1}H NMR spectra of P1

^{1}H NMR data for M3 are shown in Table 5. Two hydroxyl (-OH) peaks can be seen at 13.30 and 10.30 ppm, respectively. The structure is also confirmed by the signal of imine protons (C<u>H</u>=N) of M3 which appear at 8.90 ppm. Aromatic proton peaks are observed at 6.18—7.71 ppm and the intensities of signals corresponding to the peaks in *ortho* position of phenyl groups are decreased after oxidative polycondensation. Consequently, these monomers were polymerized with C-C and C-O-C coupling *via* oxidative polycondensation. Because of the resonance forms of phenoxy radical with possible coupling site at *ortho* and *para* positions to the hydroxyl group as well as at oxygen atom, the combinations of C-O-C and C-C linkages are formed [13].

^{13}C NMR spectra of M1 and P1 are also shown in Figs. 3 and 4. After polymerization of M1 or M2, new peaks were observed at 115 and 108 ppm, corresponding to C-C and C-O-C coupling, respectively. After polymerization of M3, a new peak was appeared at 118 ppm. Which can be assigned to C-C coupling. ^{13}C NMR data of polymers are given in Table 5.

T a b l e 5. NMR analyses data of the synthesized compounds

Compounds	Spectral data (δ ppm)
M1	^{1}H NMR (DMSO): δ ppm, 8.86 (s, 2H, –CH=N–); 10.30 (s, 2H, –OH$_{para}$); 13.66 (s, 2H, –OH$_{orto}$); 7.46 (s, 2H, Ar–Ha), 6.43 (dd, 2H, Ar–Hb); 6.32 (d, 2H, Ar–Hc); 7.45 (s, 4H, Ar–Hd). ^{13}C NMR (DMSO): ppm, 102.40 (C1-H), 162.01 (C2-*ipso*–OH), 107.93 (C3–H), 112.14 (C4-H), 134.43 (C5–*ipso*), 162.48 (C6-*ipso*-OH), 163.04 (C7–H), 146.10 (C8-*ipso*), 122.10 (C9-H)
M2	^{1}H NMR (DMSO): δ ppm, 8.87 (s, 2H, –CH=N–); 10.40 (s, 2H, –OH$_{para}$); 13.56 (s, 2H, –OH$_{orto}$); 6.43 (s, 2H, Ar–Ha), 6.50 (d, 2H, Ar–Hb); 7.45 (d, 2H, Ar–Hc); 7.57 (d, 1H, Ar–Hd); 7.64 (t, 2H, Ar–He); 8.08 (d, 2H, Ar–Hf). ^{13}C NMR (DMSO): ppm, 102.43 (C1-H), 162.55 (C2-*ipso*–OH), 108.12 (C3–H), 134.56 (C4-H), 112.48 (C5–*ipso*), 162.97 (C6-*ipso*-OH), 163.52 (C7–H), 145.56 114.84 (C8-*ipso*), 126.74 (C9–H), 128.51 (C10), 120.60 (C11–H). 114.84 (C12-*ipso*)
M3	^{1}H NMR (DMSO): δ ppm, 8.90 (s, –CH=N–); 10.30 (s, 2H, –OH$_{para}$); 13.30 (s, 2H, –OH$_{orto}$); 7.71—6.18 (m, Ar-H). ^{13}C NMR (DMSO): ppm, 102.36 (C1-H), 162.10 (C2-*ipso*–OH), 107.81 (C3–H), 137.43 (C4-H), 112.11 (C5–*ipso*), 160.69 (C6-*ipso*-OH), 162.46 (C7-H), 133.15 (C8-*ipso*), 121.06 (C9–H), 139.69 (C10-*ipso*), 134.16 (C11-*ipso*)
P1	^{1}H NMR (DMSO): δ ppm, 8.84 (s, –CH=N–); 10.32 (s, 2H, –OH$_{para}$); 7.78-6.21 (m, Ar–H). ^{13}C NMR (DMSO): ppm, 102.55 (C1-H), 161.92 (C2-*ipso*–OH), 108.07 (C3–H), 111.97 (C4-H), 132.80 (C5–*ipso*), 163.14 (C6-*ipso*-OH), 165.16 (C7-H), 134.53 (C8–*ipso*), 122.11 (C9-H), 115.21 (new peak)
P2	^{1}H NMR (DMSO): δ ppm, 8.90 (s, –CH=N–); 10.53 (s, –OH$_{para}$); 8.19—6.25 (m, Ar–H). ^{13}C NMR (DMSO): ppm, 102.44 (C1-H), 163.01 (C2-*ipso*-OH), 108.29 (C3–H), 134.69 (C4-H), 112.26 (C5–*ipso*), 163.52 (C6-*ipso*-OH), 165.21 (C7-H), 145.69 (C8-*ipso*), 126.76 (C9–H), 128.44 126.76 (C10-H), 120.71 (C11–H), 115.20 (C12-*ipso*), 108.66 (new peak)
P3	^{1}H NMR (DMSO): δ ppm, 8.90 (s, –CH=N–); 10.35 (s, 2H, –OH$_{para}$); 13.93 (s, 2H, –OH$_{orto}$); 7.80—6.27 (m, Ar-H). ^{13}C NMR (DMSO): ppm, 102.35 (C1-H), 158.75 (C2-*ipso*–OH), 108.02 (C3–H), 134.35 (C4-H), 117.86 (C5–ipso), 160.50 (C6-*ipso*-OH), 162.62 (C7-H), 128.15 (C8-*ipso*), 124.07 (C9–H), 140.25 (C10-*ipso*), 135.20 (C11-*ipso*), 118.12 (new peak)

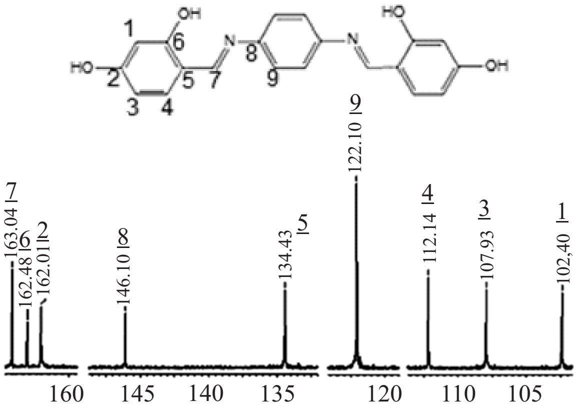


Fig. 3. ^{13}C NMR spectra of M1

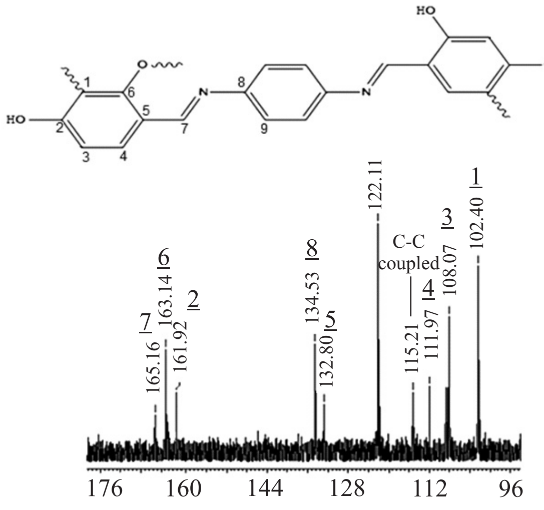


Fig. 4. ^{13}C NMR spectra of P1

The values of number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (*PDI)* determined for the polymers P1, P2 and P3 by SEC measured using RI detectors are given in Table 6. As can be seen for all the polymers, three fractions were obtained. The synthesized polyimines have quite high molecular weights indicating nearly 37—45 repeated units. The obtained results confirm the polymer structures. SEC measurements of P1 and P3 were made from run 2 products (see Table 1). SEC measurement of P2 was made from run 5 product (see Table 1).

Optical and electrochemical properties

UV-Vis spectra for all synthesized compounds were obtained in DMSO in the wavelength range of 255—700 nm. The UV-Vis spectra of M1 and their polymer are shown in Fig. 5. According to these spectra, R bands of the polymers expand in a broader range of wavelength than the monomers. The same is also true for other synthesized compounds. From the UV-Vis spectra of the syn-

T a b l e 6. Molecular weight distribution parameters of the synthesized polymers

Compounds	Total			Fraction I				Fraction II				Fraction III			
	M_w	M_n	PDI	M_w	M_n	PDI	%	M_w	M_n	PDI	%	M_w	M_n	PDI	%
P1	15 000	16 000	1.06	21 000	20 000	1.05	53	18 000	17 200	1.04	14	7 200	6 300	1.14	33
P2	13 700	15 600	1.21	20 000	17 600	1.13	61	15 400	14 400	1.06	16	4 200	3 100	1.35	23
P3	14 100	13 000	1.10	17 300	16 100	1.07	70	13 200	12 100	1.09	12	3 600	3 300	1.09	18

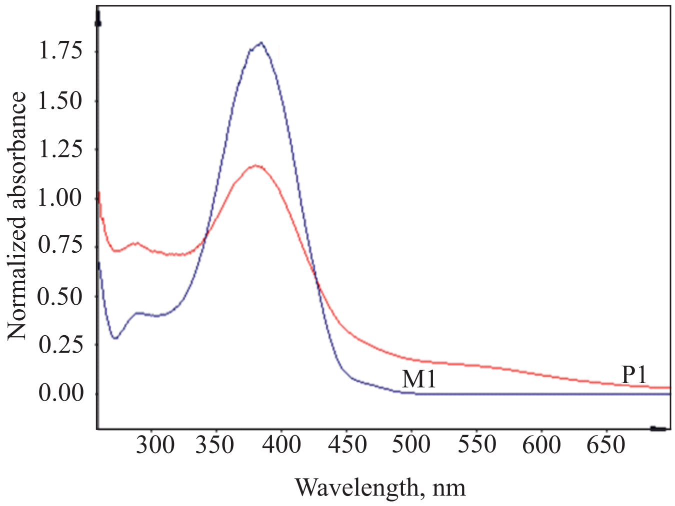


Fig. 5. Normalized absorption spectra of M1 and P1

thesized compounds, optical band gap values could be obtained by using the following equation according to as the literature [16].

$$E_g = 1242/\lambda_{onset} \tag{1}$$

T a b l e 7. Electrochemical and optical band gap values of the synthesized compounds

Compounds	a)LUMO, eV	b)HOMO, eV	c)E_g	d)E'_g
M1	-3.27	-5.59	2.66	2.32
M2	-2.89	-5.97	2.72	3.08
M3	-2.76	-5.80	2.75	3.04
P1	-3.41	-5.34	2.48	1.93
P2	-3.24	-5.67	2.59	2.43
P3	-2.79	-5.39	2.62	2.60

[a] Highest occupied molecular orbital, [b] Lowest unoccupied molecular orbital, [c] Optical band gap, [d] Electrochemical band gap.

λ_{onset} is the onset wavelength which can be determined by intersection of two tangents on the absorption edges. λ_{onset} also indicates the electronic transition start wavelength. The calculated optical band gap values are shown in Table 7. As can be observed, the synthesized polyimine have lower optical band gaps than their Schiff base monomers. This is because of the polyconjugated structures of the polymers which increase HOMO and decrease LUMO energy levels resulting in lower band gaps. Moreover, when comparing the optical band gap values the following order is obtained: M3<M2<M1<P3<P2<P1.

According to the cyclic voltammetry (CV) measurements, the calculated HOMO-LUMO energy levels and the electrochemical band gaps (E'_g) were calculated and are shown in Table 7. These data were estimated by using the oxidation (E_{ox}) and reduction (E_{red}) peak potentials. The calculations were made by using the following equations [17, 18].

$$E_{HOMO} = -(4.39+E_{ox}) \tag{2}$$

$$E_{LUMO} = -(4.39+E_{red}) \tag{3}$$

$$E'_g = E_{LUMO}-E_{HOMO} \tag{4}$$

The calculated electrochemical band gaps agree with the optical band gap values; as a result of the polyconjugated structure the polymers have lower band gaps. The obtained results show that the order of the electrochemical band gap values of the synthesized compounds is as follows M3<M2<M1<P3< P2<P1, which is a not different from the optical band gaps order.

Electrical conductivity

Electrical conductivities of the synthesized polyimines were determined and their changes related to doping time with iodine are shown in Fig. 6. As can be observed that the undoped P1 has higher electrical conductivity, that P2 ($5 \cdot 10^{-11}$ and $6.9 \cdot 10^{-12}$ S cm^{-1}, respectively). However, after a long time iodine doping (96 h) the conductivities increased by 2260 and 82 times of their initial values for P1 and P2. The conductivity of P3 could not be determined, because of an electronegative group on its structure. When these types groups on the structure take part of *ortho* and *para* positions, electron density is sub-

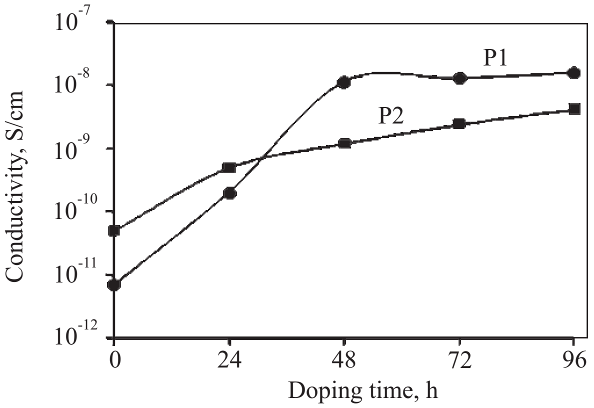
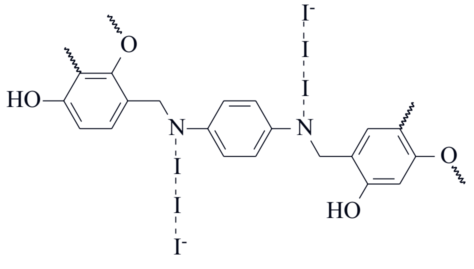


Fig. 6. Electrical conductivity changes of the I_2-doped and undoped polymers vs. doping time at 25 °C



Scheme C. Schematic illustration of conductivity measurement and possible doping reaction of P1 stantially reduced. Doping mechanism of imine polymers has been previously studied and presented in the literature. Doping mechanism of P1 is shown in Scheme C. According to the proposed mechanism, nitrogen is a very electronegative element and is capable to coordinate an iodine molecule. As a result, a charge-transfer complex between imine compound and dopant iodine is formed and a considerable increase in conductivity can be observed [19, 20]. Therefore the synthesized P1 and P2 can be used as semi-conductive materials in electronic or opto-electronic studies after a long time iodine doping.

Fluorescence characteristics

Fluorescence studies of the synthesized compounds were carried out in DMF solutions. Measurements were made for various concentrations to determine the optimal ones. Fig. 7 shows the excitation and emission spectra of M1, M2, M3, P1, P2 and P3 in DMF. These figures also indicate concentration-fluorescence intensity relationships of the compounds. The obtained results from Fig. 7 are also given in Table 8. As seen in Fig. 7, P2 in

Table 8. Fluorescence spectral data of the compounds synthesized with optimum concentrations in DMF solvent

Compounds	Concentration mg/cm^3	$^{a)}\lambda_{Ex}$	$^{b)}\lambda_{Em}$	$^{c)}\lambda_{max\ (Ex)}$	$^{d)}\lambda_{max\ (Em)}$	$^{e)}I_{Ex}$	$^{f)}I_{Em}$
M1	0.2	460	510	460	510	248	246
M2	0.2	440	506	441	506	250	253
M3	0.1	430	520	424	524	143	134
P1	0.05	440	508	438	508	33	34
P2	0.05	350	380	350	380	563	486
P3	0.1	408	560	486	560	86	82

a) Excitation wavelength for emission, b) Emission wavelength for excitation, c) Maximum excitation wavelength, d) Maximum emission wavelength, e) Maximum excitation intensity, f) Maximum emission intensity.

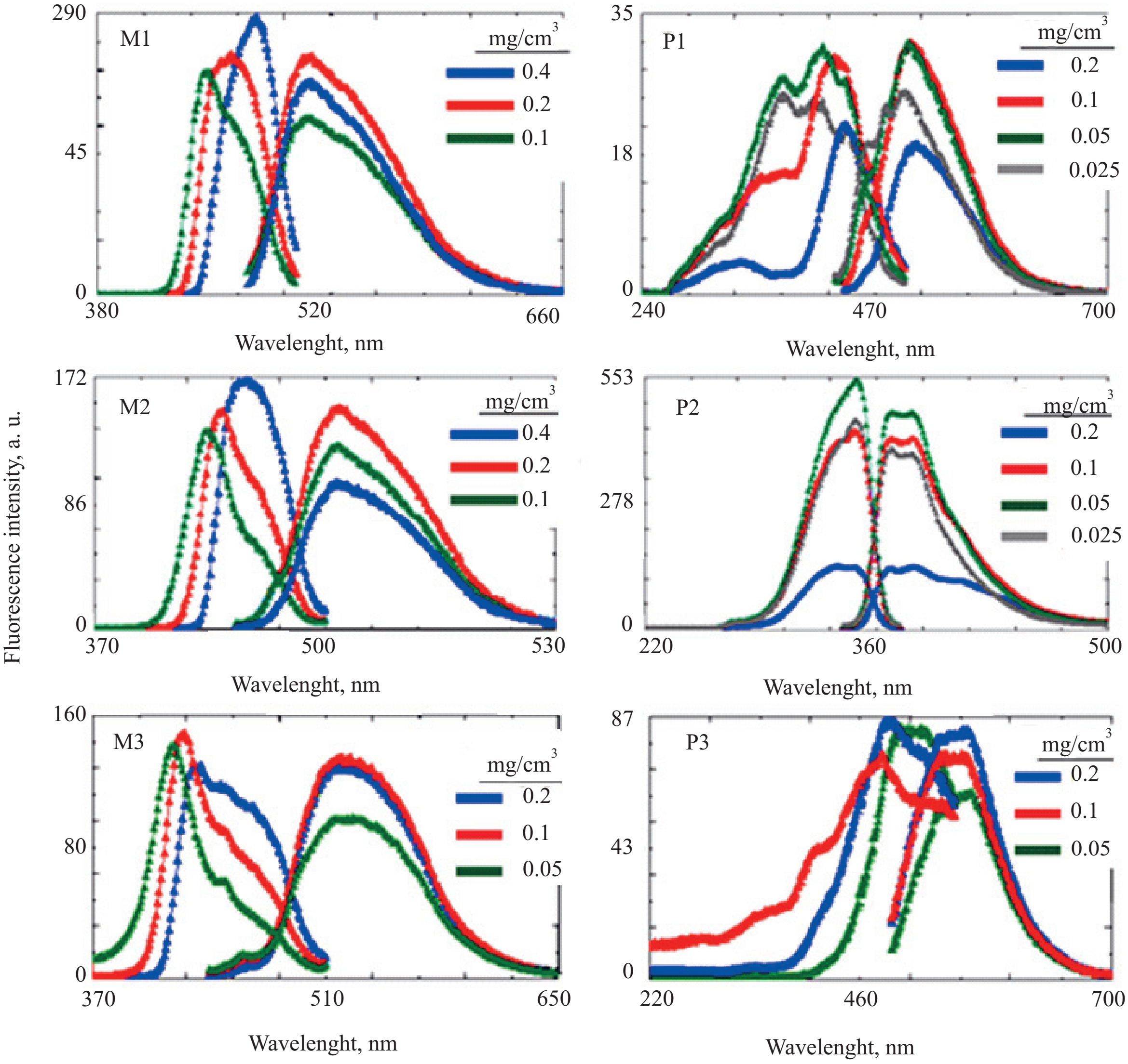


Fig. 7. Emission and excitation spectra of various concentrated solutions of M1, M2, M3, P1, P2 and P3 in DMF

DMF solutions shows higher fluorescence intensity than other compounds. Also, P2 displays the highest change in fluorescence yield with an increase of solution concentration. M3 has higher fluorescence intensity than its polymers, because of electronegative chlorine atoms in the structure of molecule. These compounds can be used as metal ion sensors. With an increased number of aromatic rings, higher fluorescence intensity of the compounds is observed.

Thermal analysis

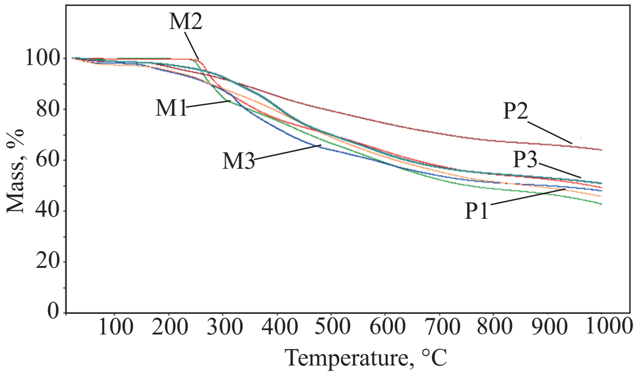


Fig. 8. TGA curves of the synthesized compounds

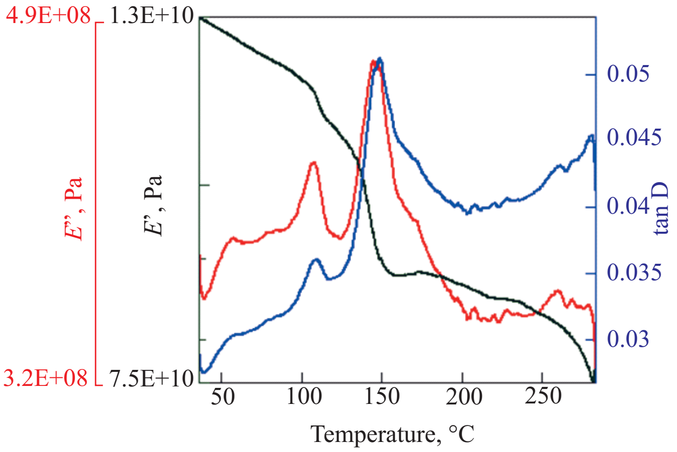


Fig. 9. DMA curves of P1

TGA-DTA, DTG, DMA and DSC thermal degradation data are summarized in Table 9. TGA curves of the synthesized compounds are also shown in Fig. 8. According to the TGA results, the initial degradation temperature (T_{on}) of M1 is higher than thise of polymer P1 due to C-O-C coupling, whereas P3 has higher T_{on} value than its monomer since in this case oxidative polycondensation reaction does not result in C-O-C coupling [21]. The char values (%) of the polymers are also higher than those of the Schiff bases. According to the obtained results the Schiff bases thermally degrade in one step while their polymers undergo degradation in three steps. Nearly 3.2 % of weight loss of P1 observed in the range of 30—160 °C can be attributed to the removal of absorbed and hydrate water as well as about, 1.5 % of weight loss of P2 in the temperatures between 30 and 150 °C and nearly 2.0 % of weight loss of P3 between in 30 and 140 °C [22]. The initial degradation temperatures (°C) and chars values (%) are 243 and 43 for M1; 253 and 49 for M2; 289 and 48 for M3; 228 and 49 for P1; 263 and 64 for P2; 298 and 51 for P3, respectively. According to the DSC measurements, glass transition temperatures (T_g) of P1, P2 and P3 were calculated as 108, 163, 200 °C, respectively. DMA curve of the synthesized P1 is also given in Fig. 9. According to the DMA data, the glass transition temperature (T_g) of P1 was calculated as 148 °C.

CONCLUSIONS

The structures of the synthesized compounds were characterized by FT-IR, UV-vis, NMR, and SEC techniques. The solubility tests indicated that the synthesized polyphenols are soluble in polar organic solvents like DMSO and DMF. According to the optical and electrochemical analyses, the synthesized polymers have lower band gaps than Schiff bases. Electrical conductivity measurements showed that the conductivity of the polymers could be increased by doping with iodine. This increase in the conductivity was higher in the case of P1 since M1 polymerized to the greater degree than M2. The conduc-

Table 9. Thermal degradation data of the synthesized compounds

Compounds	a) T_{on} °C	b) T_{max}, °C	$T_{20\%}$, 20 % weight loss, °C	$T_{50\%}$, 50 % weight loss, °C	% Char at 1000 °C	DTA, °C		DSC		DMA
						endo	exo	c) T_g, °C	d) ΔC_p, J/g °C	c) T_g, °C
M1	243	266	345	753	43	262, 482	-	-	-	-
M2	253	275	364	975	49	267, 471	-	-	-	-
M3	289	328	344	888	48	473	317	-	-	-
P1	228	271, 428	428	875	49	267, 471	-	108	9.946	148
P2	263	213, 380, 570	532	-	64	472	-	163	0.207	-
P3	298	400, 574	420	-	51	468	-	203	0.237	-

a) The onset temperature, b) Maximum weight temperature, c) Glass transition temperature, d) Change of specific heat during glass transition.

tivities of P3 were not measured since it contains electronegative chlorine atom. Fluorescence spectra of the synthesized compounds were obtained in DMF and the highest fluorescence intensity was observed for P2. Thermal degradation characteristics were also studied. According to the obtained results the Schiff bases M1 and M2 are more thermally stable than their polymers due to the presence of etheric bonds in the latter. Glass transition temperatures of P1, P2 and P3 were determined by DSC as 108, 163 and 200 °C, respectively, while T_g value of P1 determined from by DMA curve was 148 °C, because of the good thermal stability the synthesized Schiff base polymers can be promising candidates for aerospace applications. Moreover, due to heaving semi-conductive structures, they could also be used in electronic, optoelectronic, electro-active and photovoltaic applications.

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