Synthesis, characterization, thermal and electrochemical properties of imine polymers containing pyridine and pyrimidine units

Hatice Karaer[1), 2)], **İsmet Kaya**[1), *)], **Haluk Aydın**[2)]

DOI: dx.doi.org/10.14314/polimery.2017.170

Abstract: Schiff bases polymers were synthesized from 2-hydroxybenzaldehyde (2-HBA) *via* oxidative polymerization method in an aqueous alkaline medium in the presence of NaOCl as an oxidant. Then, these polymeric Schiff bases were prepared from the polyaldehyde by grafting each of them with different amines containing pyridine and pyrimidine groups. The structures of polymers were confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR, and UV-Vis measurements. The polymers were characterized by GPC and SEM analyses. Furthermore, their optical properties were determined by UV-Vis and fluorescence spectroscopy, their electrochemical properties by cyclic voltammetry (CV) analysis and solid state conductivity measurements by the four-point probe technique, their thermal behavior by TG, DTA, and DSC measurements. The electrical conductivity of the polymers was also measured and found that they are semiconductive. The number average molecular weight ($\overline{M}_n$), the weight average molecular weight ($\overline{M}_w$), and dispersity (*Đ*) values of the polymers were found from GPC analysis and were equal 5900, 5450 and 1.08, respectively, for poly(2-hydroxybenzaldehyde) (P-2HBA) polymer. Electrochemical energy gap (E'_g) was found by CV, whereas optical band gap (E_g) was determined by UV-Vis measurements.

Keywords: poly(imines), poly(phenoxy-imines), optical properties, thermogravimetric analysis, semiconductivity.

Synteza, charakterystyka, właściwości termiczne i elektrochemiczne polimerów iminowych zawierających jednostki pirydynowe i pirymidynowe

Streszczenie: Polizasady Schiffa zsyntetyzowano metodą polimeryzacji utleniającej 2-hydroksybenzaldehydu (2-HBA) w środowisku alkalicznym, w obecności NaOCl jako utleniacza, a następnie szczepiono otrzymany polialdehyd za pomocą amin zawierających grupy pirydynowe i pirymidynowe. Uzyskane polimery charakteryzowano metodami GPC i SEM, a ich struktury potwierdzono za pomocą spektroskopii FT-IR, ^{1}H NMR, ^{13}C NMR i UV-Vis. Właściwości optyczne polizasad Schiffa analizowano spektroskopią fluorescencyjną i UV-Vis, a właściwości termiczne określono metodami TG, DTA i DSC. Korzystając z woltamperometrii cyklicznej (CV) oraz pomiarów przewodności ciała stałego metodą czteropunktową badano właściwości elektrochemiczne otrzymanych polimerów. Pomiary te wskazują na półprzewodnikowy charakter polimerów. Stwierdzono, że wartości liczbowo średniego ciężaru cząsteczkowego ($\overline{M}_n$), wagowo średniego ciężaru cząsteczkowego ($\overline{M}_w$) i stopnia polidyspersji (*Đ*) poli(2-hydroksybenzaldehydu) (P-2HBA) wyznaczone na podstawie analizy GPC są równe, odpowiednio, 5900, 5450 oraz 1,08. Szerokość elektrochemicznej przerwy energetycznej (E'_g) oznaczono metodą CV, natomiast szerokość optycznej przerwy energetycznej (E_g) za pomocą spektroskopii UV-Vis.

Słowa kluczowe: poli(iminy), poli(fenoksy-iminy), właściwości optyczne, analiza termograwimetryczna, półprzewodnictwo.

Polymeric Schiff bases (polyimines or polyazomethines) are a class of materials containing the -CH=N- structural unit that exhibit good thermal stability and advantageous mechanical properties [1]. Polymeric Schiff bases generally show basic properties, since they have a C=N linkage in backbone. Considerable interest has been focused on this polymers due to their thermal stability, potential semiconductivity, conductivity, and non-linear optical properties [2]. Polyazomethines (PAMs) possessing p-conjugated systems have low band gaps and, con-

---

[1)] Çanakkale Onsekiz Mart University, Faculty of Sciences and Arts, Department of Chemistry, 17020, Çanakkale, Turkey.

[2)] Dicle University, Faculty of Science, Department of Chemistry, 21280, Diyarbakır, Turkey.

[*)] Author for correspondence; e-mail: kayaismet@hotmail.com

sequently, are semiconductive [3]. They were synthesized by polycondensation of dialdehydes or diketones with an aliphatic or aromatic diamine to give high molecular weight polymers [2]. Polyimines including conjugated bonding and active hydroxyl group have been studied for more than 60 years and have been used in various fields owing to their useful properties such as paramagnetism, semiconductivity, electrochemical cell, and resistivity to high energy. They are used to prepare composites with high positive temperature coefficient of resistance, thermostabilisators, graphite materials, epoxy oligomer and block copolymers, and photo resists as well as photo materials, which are antistatic and enduring to flame [4]. Schiff base substituted oligophenol derivatives are usually synthesized by oxidative polycondensation reaction of the corresponding Schiff base using cheap oxidants such as H_2O_2, NaOCl, and air [5]. The main advantage of the oxidative polycondensation method is the usage of easily available, simple and cheap structured oxidants [6]. Oxidative polymerization is one of the important green chemistry processes to prepare multifunctional polymers, and widely used to prepare different types of polymers such as polyaniline, polythiophene, polyfluorene, polypyrrole, polyphenol, polycarbazole, poly Schiff bases, and their different derivatives [7].

In this study, the oxidative polycondensation reactions of 2-hydroxybenzaldehyde, were studied by using NaOCl oxidant in an aqueous alkaline medium at 70 °C. Then, poly Schiff bases were prepared from the polyaldehyde by grafting each of them with six different amines containing pyridine and pyrimidine groups. The structures of the synthesized polymers were approved by FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy, GPC and SEM analyses, UV-Vis and fluorescence spectroscopy, CV analysis, solid state conductivity measurements, and by TG-DTA analysis.

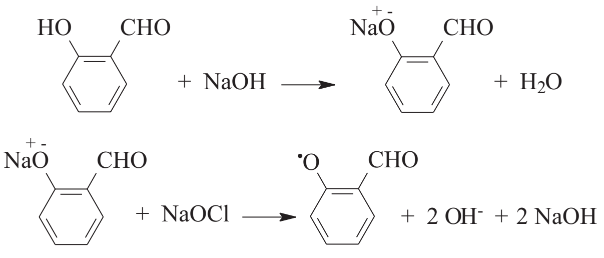
EXPERIMENTAL PART

Materials

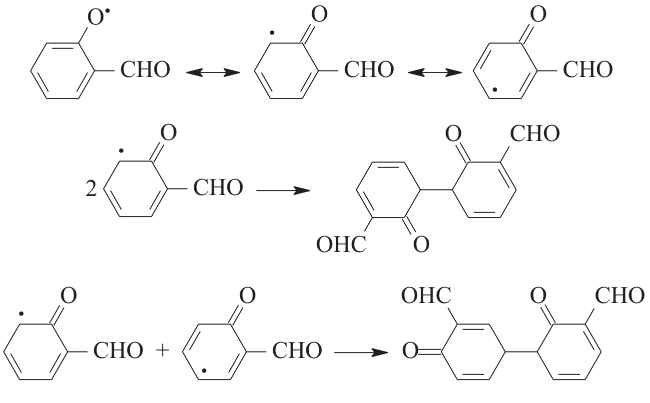
2-Hydroxybenzaldehyde (2-HBA), ethanol, KOH, and HCl were supplied by Merck Chemical Co. (Germany) and used as received. Sodium hypochlorite (30 % aqueous solution of NaOCl) was purchased by Paksoy Chemical Co. (Turkey). 2-Amino-3-methylpyridine (3MP), 2-amino-6-methylpyridine (6MP), 2-amino-4-methylpyridine (4MP), 2-amino-4,6-dimethylpyrimidine (46MP), 2,4,6-triaminopyrimidine (TAP), 2-aminopyrimidine (2AP) were supplied from Sigma-Aldrich and they used as received.

Synthesis of P-2HBA with NaOCl in an aqueous alkaline medium

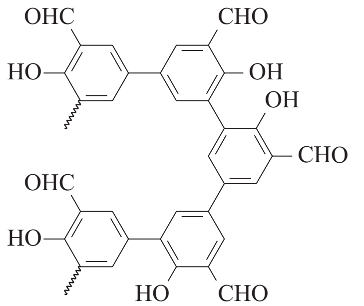
P-2HBA was synthesized through oxidative polycondensation of 2-HBA with an aqueous solution of NaOCl (30 %) as in the literature [8–11]. 2-HBA (0.001 mol) was dissolved in an aqueous solution of KOH (0.001 mol, 10 %) and placed into a 100 cm^3 three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer, and an addition funnel containing NaOCl. After heating it to 70 °C, NaOCl was added dropwise for almost 30 min. The reaction mixture was cooled to room temperature, and then 0.001 mol HCl (37 %) was added to solution. The crude product was washed with 25 cm^3 of hot water for three times for the separation from mineral salt. Synthesis reaction, resonance forms and combination of radicals, and structure of P-2HBA are shown in Schemes A–C, respectively.



Scheme A



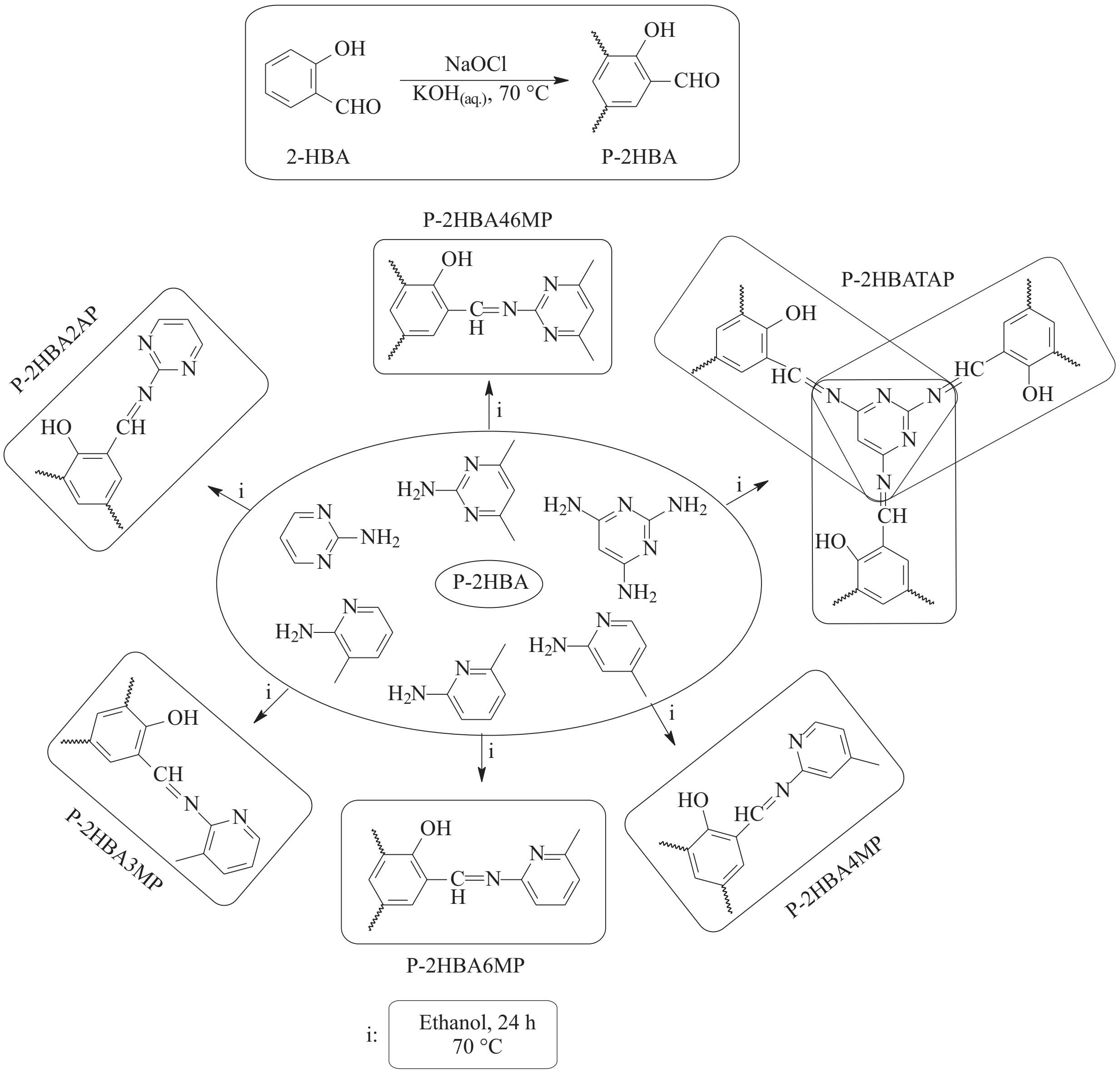
Scheme B



Scheme C

Synthesis of Schiff base polymers

The poly Schiff bases abbreviated as P-2HBA2AP, P-2HBA46MP, P-2HBATAP, P-2HBA3MP, P-2HBA4MP and P-2HBA6MP were synthesized by the condensation reaction of 2-aminopyrimidine (2AP), 2-amino-4,6-dimethylpyrimidine (46MP), 2,4,6-triaminopyrimidine (TAP), 2-amino-3-methylpyridine (3MP), 2-amino-4-methylpyridine (4MP), and 2-amino-6-methylpyridine (6MP) with poly(2-hydroxybenzaldehyde), respectively



Scheme D

(Scheme D). Poly(2-hydroxybenzaldehyde) was weighed and put into a 100 cm^3 three-neck, round bottom reaction flask separately, and then 30 cm^3 of methanol was added and it was dissolved at room temperature by continuous mixing on a hot plate magnetic stirrer under condenser. Then, amines, 3MP (1.08 g, 1 x 10^{-2} mol), 6MP (1.08 g, 1 x 10^{-2} mol), 4MP (1.08 g, 1 x 10^{-2} mol), 46MP (1.2 g, 1 x 10^{-2} mol), TAP (1.25 g, 1 x 10^{-2} mol), and 2AP (0.95 g, 1 x 10^{-2} mol) dissolved in 10 cm^3 of methanol were added into the reaction flask, and were left to form a poly Schiff base monomer at 70 °C [9]. Dark brown-black polymers were obtained at the end of the reaction.

Methods of testing

The infrared and ultraviolet–visible spectra were recorded by a PerkinElmer FT-IR Spectrum one and Analytikjena Specord 210 Plus, respectively. The FT-IR spectra were recorded using a universal ATR sampling accessory (4000–550 cm^{-1}). ^{1}H and ^{13}C NMR spectra were performed using Bruker AV400 spectrometer (T = 25 °C, solvent – deuterated DMSO-d$_6$, internal standard – tetramethylsilane). Thermal data were obtained using a PerkinElmer Diamond Thermal Analysis system. TG–DTA measurements were made under a nitrogen flow and at a heating rate of 10 °C/min from room temperature to 1000 °C. DSC analyses were carried out using a PerkinElmer Pyris Sapphire DSC. DSC measurements were made in the range 25–450 °C (in N$_2$, heating rate 10 °C/min). The number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$), and dispersity ($Đ = \overline{M}_w/\overline{M}_n$) were determined by Gel Permeation Chromatography-Light Scattering (GPC-LS) device of Malvern Viscotek GPC Dual 270 max. GPC-LS analyses were performed at 55 °C using DMF with lithium bromide (1 g/dm^3) as eluent at a flow rate of 1 cm^3/min. A medium 300 x 8.00 mm dual column was used. A refractive index detector (RID), Light Scattering Detector (LS), and polystyrene standards were used to analyze the products. Surface morphology of the polymers was determined by field emission scanning electron microscope (FE-SEM, JEOL, JSM-7100). Conductivity was measured by a Keithley 2400 Electrometer (Keithley, Ohio, USA). The pellets were pressed on hydraulic press at 1687.2 kg/cm^2. Iodine doping was performed by exposing the pellets to iodine vapor at atmospheric pressure and room temperature in a desiccator [12]. Cyclic voltammetry (CV) measurements were performed by a CHI 660C Electrochemical Analyzer (CH Instruments, Texas, USA) at a potential scan rate of 20 mV/s. All experiments were carried out 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$^+$) measured in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) acetonitrile solution is 0.39 V with respect to Ag wire. The voltammetric measurements were performed in acetonitrile [13]. An ultrasonic bath was used to dissolve the samples. The HOMO–LUMO energy levels and electrochemical band gaps (E'_g) were calculated from the reduction and oxidation peak potential and onset values. The UV-Vis spectra were recorded using MeOH as a solvent, at 25 °C. The optical band gaps (E_g) were calculated from their absorption edges [14].

RESULTS AND DISCUSSION

Structures of the compounds

The FT-IR spectrum of P-2HBA polymer was not significantly different from that of the 2-HBA monomer, as expected. FT-IR spectra of P-2HBA and 2-HBA are given in Fig. 1. However, peaks of P-2HBA polymer were broader than that of 2-HBA monomer after the polycondensation reaction owing to their polyconjugated structures. Moreover, the edged peaks of 2-HBA monomer were broader and decreased numerically because of the increase in molecular weight after polymerization reactions [15], confirming polymerization of 2-HBA. Bands in the FT-IR spectra of the polymers decreased due to their conjugated bond systems [16].

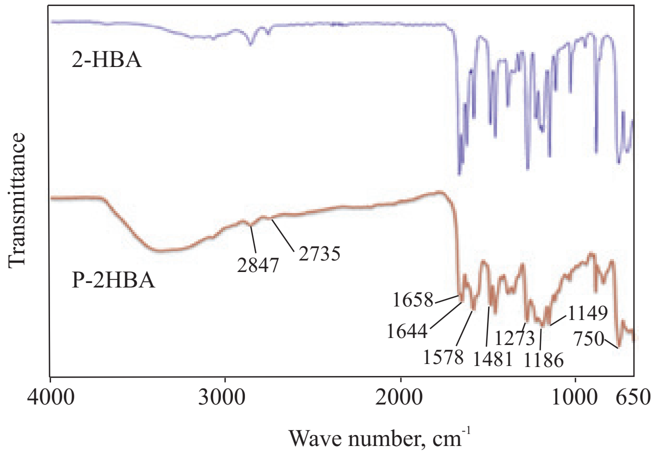


Fig. 1. FT-IR spectra of 2-HBA and P-2HBA

As seen in Fig. 1, -OH stretching band was observed at 3320 cm^{-1}, aromatic -CH peak at 3060 cm^{-1}, aldehyde -CH peak at 2847 cm^{-1} for P-2HBA polymer. The peak at 1658 cm^{-1} corresponds to -C=O stretching vibration of aldehyde for P-2HBA. Furthermore, peaks at 1450–1650 cm^{-1} were assigned to benzene cycle and C=C moiety and those at 1000–1400 cm^{-1} were attributed to C-O stretching [17]. Again, those at 1578 and 1481 cm^{-1} correspond to aromatic C=C and those at 1273 cm^{-1} were due to C-O bending vibration peaks for phenol group. Peaks of P-2HBA were broader than those of 2-HBA, implying that 2-HBA polymerized [18]. The broad peak at about 3500–3000 cm^{-1} corresponds to hydroxyl -OH stretching. Additionally, aromatic -CH stretchings were observed at 3000–2900 cm^{-1}, while aliphatic ones for methyl -CH$_3$ group were seen at 2950–2900 cm^{-1} except for -TAP and -2AP coded polymers. The peak at 1608, 1602, 1610, 1629, 1610 and 1633 cm^{-1} corresponds to -CH=N stretching vibration of imine for P-2HBA3MP, P-2HBA4MP, P-2HBA6MP, P-2HBA46MP, P-2HBATAP and P-2HBA2AP, respectively.

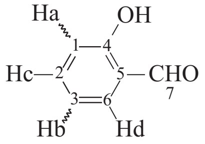
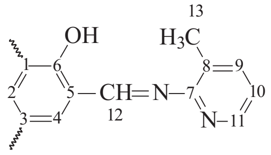
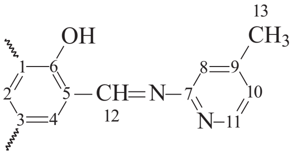
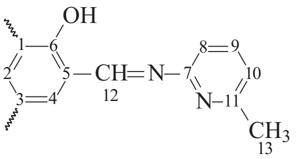
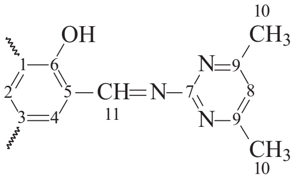
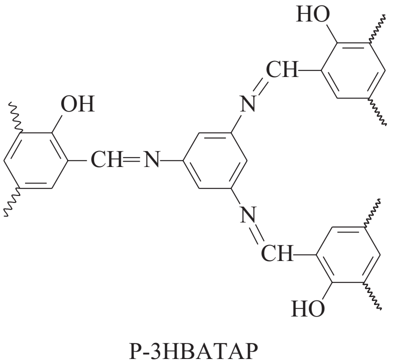
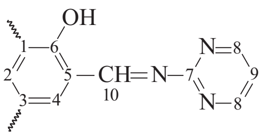
As expected, in the FT-IR spectra of the poly Schiff bases, functional groups different from P-2HBA were observed, confirming formation of the polymers. In the FT-IR spectra of poly Schiff bases, pyridine and pyrimidine groups were given separately in Fig. 2a and Fig. 2b, -3MP, -4MP and -6MP coded materials contain pyridine groups, whereas -46MP, -TAP and -2AP coded materials include pyrimidine groups.

The structures of the poly Schiff bases were confirmed by newly appeared imine -CH=N peaks, disappearing of the amine -NH$_2$ peaks and the C=O peaks of the aldehyde used in the condensation reactions. These changes are also shown in Fig. 2a and Fig. 2b.

^{1}H NMR and ^{13}C NMR data of the polymers are listed in Table 1. It is known that phenol based Schiff bases polymerize by oxidative polymerization *via* C-C *ortho* and/or *para* positions of the ring in terms of -OH or C-O-C binding *via* oxygen atom of -OH moiety (Scheme D). Integration ratio of the -OH proton at 10.80 ppm decreases compared to that of -CHO at 10.26 ppm, however, the signal does not completely disappear, indicating that -OH moiety does not lose, it remains after polymerization. This shows also that proton of -OH leaves and polymerization occurs *via* oxygen atom (10 %).

In the ^{1}H NMR spectrum of the poly Schiff base, decrease of integration ratio of the protons at *ortho* and *para* positions of the ring in terms of -OH group after polymerization shows that these protons decrease in numbers compared to the other protons in the structure [16]. It is understood from the decreasing in the integration of -OH that polymerization occurs through -C-O-C- binding, mainly C-C binding exists and it occurs at the point where -Ha proton exists. Resonances in the ^{1}H NMR spectrum of the polymer broadened after oxidative polymerization, showing that monomers repeated in the structure.

T a b l e 1. NMR spectra data of the polymers

Polymers	NMR spectra data, ppm
 P-2HBA	^{1}H NMR (DMSO-d$_6$, ppm, δ): 10.80 (s, -OH), 7.54 (d, Ar-Hd), 7.52 (t, Ar-Hb), 7.50 (d, Ar-Hc), 6.99 (d, Ar-Ha), 9.84 (s, -CHO). ^{13}C NMR (DMSO-d$_6$, ppm, δ): 119.92 (C1-ipso), 122.72 (C2-H), 117.50 (C3-ipso), 161.03 (C4-ipso), 145.87 (C5-ipso), 129.66 (C6-H), 192.22 (C7-H), 136.78, 119.62, 116.02 (new peaks, C-O-C and C-C coupling).
 P-2HBA3MP	^{1}H NMR (DMSO-d$_6$, ppm, δ): 10.26 (s, -OH), 6.80-8.33 (m, aromatic protons), 8.13 (s, -CH=N). ^{13}C NMR (DMSO-d$_6$, ppm, δ): 119.77 (C1-H), 117.09 (C2-H), 123.59 (C3-H), 116.16 (C4-H), 146.78 (C5-ipso), 145.28 (C6-ipso), 164.04 (C7-ipso), 129.38 (C8-ipso), 128.18 (C9-H), 137.42 (C10-H), 156.00 (C11-H), 161.22 (C12-H), 17.22 (C13, CH$_3$), 133.74, 139.97, 123.69 (new peaks, C-C coupling).
 P-2HBA4MP	^{1}H NMR (DMSO-d$_6$, ppm, δ): 10.54 (s, -OH), 6.55-8.50 (m, aromatic protons), 8.22 (s, -CH=N). ^{13}C NMR (DMSO-d$_6$, ppm, δ): 117.79 (C1-H), 122.54 (C2-H), 120.79 (C3-H), 136.63 (C4-H), 147.44 (C5-ipso), 157.06 (C6-ipso), 164.81 (C7-ipso), 114.35 (C8-H), 113.79 (C9-ipso), 129.63 (C10-H), 160.05 (C11-H), 161.27 (C12-H), 21.01 (-CH$_3$), 133.61 (new peak, C-C coupling).
 P-2HBA6MP	^{1}H NMR (DMSO-d$_6$, ppm, δ): 10.53 (s, -OH), 6.50-8.00 (m, aromatic protons), 8.19 (s, -CH=N). ^{13}C NMR (DMSO-d$_6$, ppm, δ): 117.24 (C1-H), 111.02 (C2-H), 119.85 (C3-H), 122.72 (C4-H), 133.67 (C5-ipso), 156.45 (C6-H), 164.41 (C7-ipso), 122.58 (C8-H), 122.58 (C9-H), 137.67 (C10-H), 159.57 (C11-ipso), 161.43 (C12-H), 24.10 (C13, -CH$_3$), 139.17 (new peak, C-C coupling).
 P-2HBA46MP	^{1}H NMR (DMSO-d$_6$, ppm, δ): 10.70 (s, -OH), 6.50-8.00 (m, aromatic protons), 8.17 (s, -CH=N).
 P-3HBATAP	^{1}H NMR (DMSO-d$_6$, ppm, δ): 10.20 (s, -OH), 5.50-7.55 (m, aromatic protons), 8.33 (s, -CH=N).
 P-2HBA2AP	^{1}H NMR (DMSO-d$_6$, ppm, δ): 10.37 (s, -OH), 6.50-7.55 (m, aromatic protons), 8.42 (s, -CH=N). ^{13}C NMR (DMSO-d$_6$, ppm, δ): 118.16 (C1-H), 129.66 (C2-H), 119.92 (C3-H), 122.42 (C4-H), 136.91 (C5-ipso), 158.06 (C6-ipso), 171.67 (C7-ipso), 166.48 (C8-H), 117.43 (C9-H), 163.89 (C10-H), 136.10 (new peak, C-C coupling).

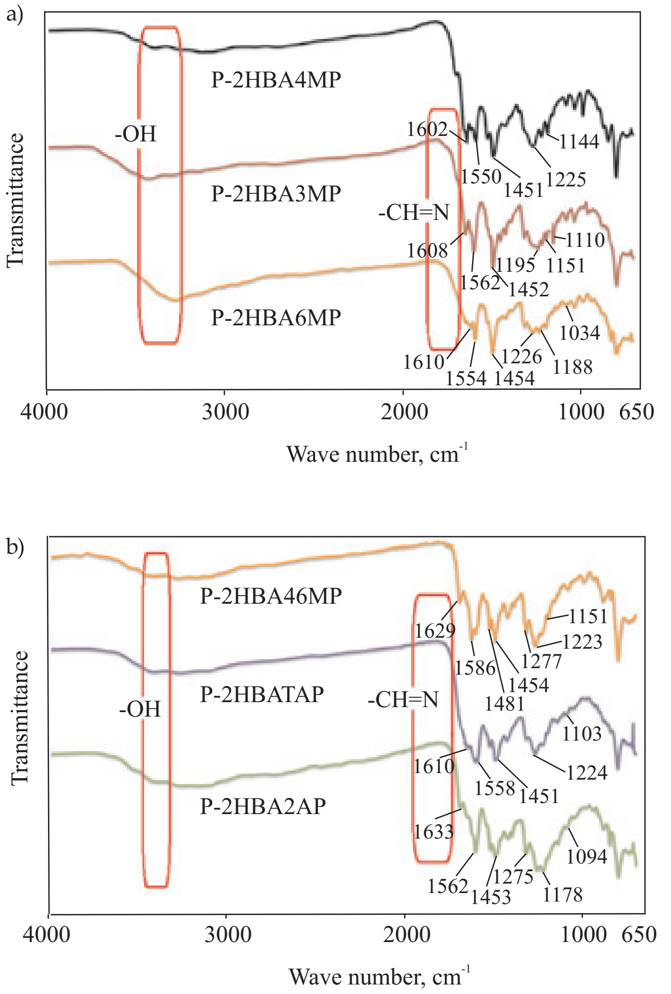


Fig. 2. FT-IR spectra of poly Schiff bases containing: a) pyridine, b) pyrimidine

Five different carbons are observed at structure of P-2HBA. In the ^{13}C NMR spectrum, decreasing of resonance intensity of C6 and appearing of a new resonance at 145.87 ppm clearly indicate that phenoxy unit, which occurred from -OH group bound to C6 (ipso-carbon), forms the polymer structure consisting of oxyphenylene units C-O-C. New signals were observed in the region of 140 to 160 ppm owing to -C-O-C- coupling, which confirm polymerization occurred *via* -OH moiety [16].

As stated in the previous studies, phenol-based monomers may be polymerized either by C-O-C binding *via* oxygen atom of -OH or by C-C coupling of monomer units with *ortho* or *para* position of the phenol in terms of -OH group [15]. The short resonances at 119.62 and 116.02 ppm obviously indicate that P-2HBA polymerizes through C1 and C3 carbons, *i.e.*, C-C binding occurs for the radical occurred at *ortho* or *para* position of phenol by distribution of the phenoxy radical to the cycle. Schemes A–C display oxidative polymerization reaction mechanism of P-2HBA. The hydroxyl, aldehyde and aromatic proton signals of P-2HBA were observed in 10.80, 9.84 and 7.54––6.99 ppm range, respectively, in the ^{1}H NMR spectrum. In the ^{13}C NMR spectra, resonances for polyaldehyde C=O and hydroxyl carbon atoms are observed at 192.22 and 161.03 ppm, respectively.

In the ^{1}H NMR spectra of poly Schiff bases, the signal of aldehyde proton (at 9.84 ppm) of P-2HBA disappears and a new signal between 8.13 and 8.42 ppm appears, indicating azomethine formation -CH=N. In the ^{13}C NMR spectra, resonances for poly Schiff bases -CH=N carbon atoms are observed between 161.22–163.89 ppm. Aliphatic -CH$_3$ carbon signals of P-2HBA3MP, P-2HBA4MP and P-2HBA6MP were observed in 17.22, 21.01 and 24.10 ppm, respectively, while in the ^{1}H NMR spectra, aliphatic -CH$_3$ protons are observed at 2.36, 2.12, 2.20 and 2.45 ppm for P-2HBA3MP, P-2HBA4MP, P-2HBA6MP and P-2HBA46MP, respectively.

According to the GPC chromatograms, the calculated number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$), and dispersity (*Đ*) values of P-2HBA3MP, P-2HBA4MP, P-2HBA6MP, P-2HBATAP, P-2HBA46MP and P-2HBA2AP were measured by RI detector, are given in Table 2. According to these results, P-2HBA, P-2HBA3MP, P-2HBA6MP, P-2HBA4MP, P-2HBA46MP, P-2HBATAP and P-2HBA2AP contain ap-

Table 2. GPC analysis results of the polymers

Compounds	Total			Molecular weight distribution parameters							
				Fraction I				Fraction II			
	$\overline{M}_w$	$\overline{M}_n$	*Đ*	$\overline{M}_w$	$\overline{M}_n$	*Đ*	%	$\overline{M}_w$	$\overline{M}_n$	*Đ*	%
P-2HBA	5900	5450	1.08	–	–	–	–	–	–	–	–
P-2HBA3MP	12350	9700	1.27	–	–	–	–	–	–	–	–
P-2HBA6MP	11370	9200	1.24	–	–	–	–	–	–	–	–
P-2HBA4MP	7800	5650	1.23	18500	13400	1.38	70	8550	6300	1.36	30
P-2HBA46MP	12450	10300	1.21	–	–	–	–	–	–	–	–
P-2HBATAP	7900	5750	1.37	17900	12800	1.40	75	9650	7500	1.29	25
P-2HBA2AP	14500	11900	1.22	–	–	–	–	–	–	–	–

$\overline{M}_n$ – number average molecular weight; $\overline{M}_w$ – weight average molecular weight; *Đ* – dispersity.

T a b l e 3. Thermal degradation values of the polymers

Compounds	T_{on} °C	T_{max} °C	T_{20} °C	T_{50} °C	carbine residue at 1000 °C, wt %	Exo / Endo	T_g, °C / ΔC_p, J/g·°C
P-2HBA	139	157, 860	333	866	39	805 / –	112 / 0.118
P-2HBA2AP	250	291, 873	752	866	10	306, 793 / 879	116 / 0.855
P-2HBA46MP	120	126, 335, 583	373	–	52	– / –	114 / 0.215
P-2HBATAP	203	235, 836, 913	324	820	4	318, 803 / –	188 / 0.321
P-2HBA3MP	145	151	143	535	36	– / –	123 / 0.044
P-2HBA6MP	135	148, 567, 953	170	660	21	– / –	118 / 0.163
P-2HBA4MP	122	146, 572, 803	171	638	37	594 / –	113 / 1.246

T_{on} – the onset temperature; T_{max} – temperature of the maxima of the peaks; T_{20} – temperature corresponding to 20 % weight loss; T_{50} – temperature corresponding to 50 % weight loss; T_g – glass transition temperature; ΔC_p – change of specific heat during glass transition.

proximately 45–49, 46–59, 44–54, 27–37, 46–55, 13–18 and 60–73 repeated units, respectively.

Thermal analysis of the polymers

TG and DSC thermograms were taken to determine the temperatures corresponding to 20 and 50 % weight losses of the polymers (T_{20}, T_{50}), the initial degradation temperatures (T_{on}), the number of decomposition steps, exothermic and endothermic peaks, glass transition temperatures (T_g), and specific heat change (ΔC_p) of monomers. The values measured from thermograms are shown in Table 3. TGA curves of the polymers are shown in Fig. 3. T_{on} of the polymers, P-2HBA, P-2HBA2AP, P-2HBA46MP, P-2HBATAP, P-2HBA3MP, P-2HBA6MP and P-2HBA4MP were found to be 139, 250, 120, 203, 145, 135 and 122 °C, respectively. T_{50} were calculated as 866, 866, 820, 535, 660 and 638 °C for P-2HBA, P-2HBA2AP, P-2HBATAP, P-2HBA3MP, P-2HBA6MP and P-2HBA4MP, respectively. The glass transition temperatures of the polymers lie between 112 and 188 °C, as observed in DSC analysis. According to the thermal analysis data, it can be said that the polymers are thermally stable.

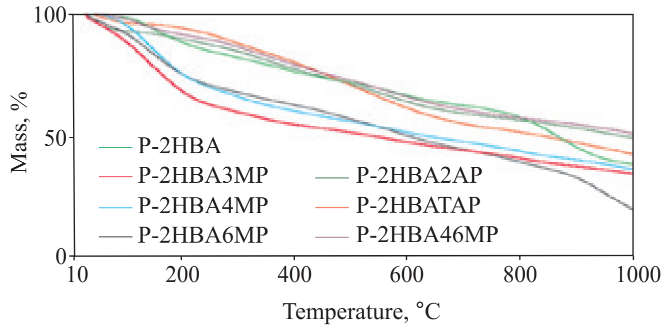


Fig. 3. TGA curves of the polymers

Electrochemical and conductivity properties of polymers

The voltammetric measurements were performed in acetonitrile. The values of electrochemical band gaps (E'_g) were given in Table 4. These data were estimated by using the oxidation onset (E_{ox}) and reduction onset (E_{red}) values, as given in Fig. 4 for the polymers. The calculations were performed by using the following equations [19]:

$$E_{HOMO} = -(4.39 + E_{ox}) \tag{1}$$

$$E_{LUMO} = -(4.39 + E_{red}) \tag{2}$$

$$E'_g = E_{LUMO} - E_{HOMO} \tag{3}$$

The HOMO–LUMO energy levels and the electrochemical band gaps were also given schematically in Fig. 5. It is seen that the electrochemical band and optical gaps values of the polymers were changed between 2.78–2.48 eV and 2.96–2.19 eV, respectively (Table 4).

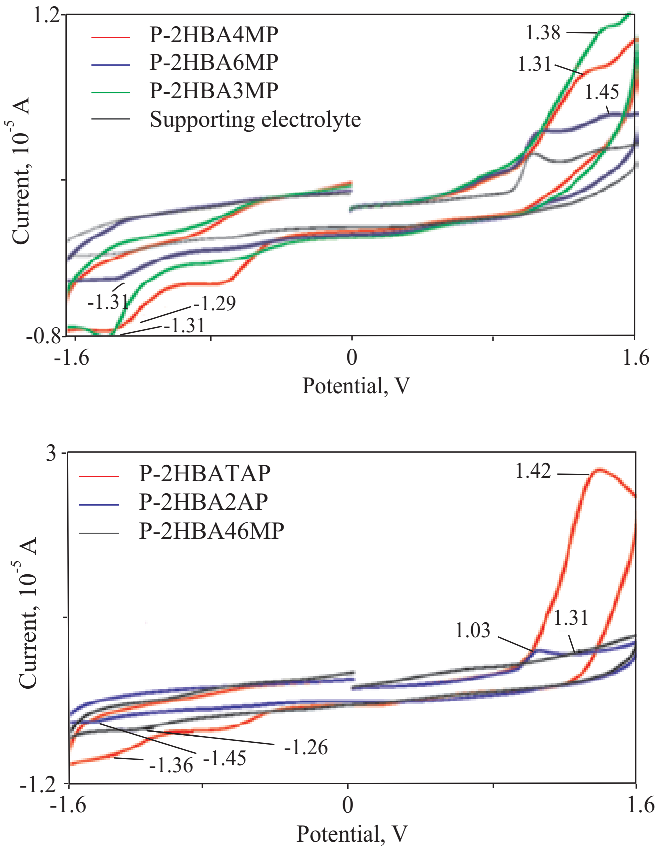


Fig. 4. Cyclic voltammograms of the polymers

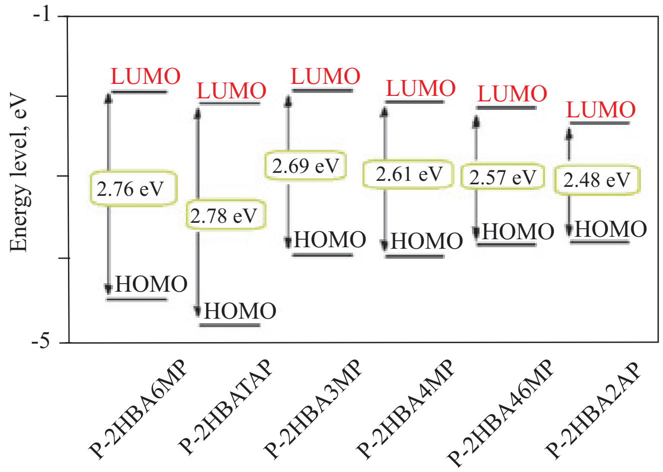


Fig. 5. HOMO–LUMO energy levels and electrochemical band gaps of the polymers

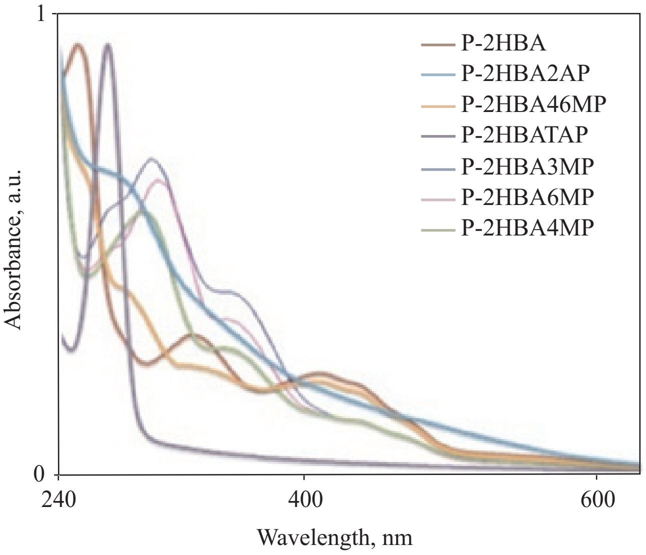


Fig. 6. UV-Vis spectra of the polymers

Table 4. Electronical structure parameters of the polymers

Compounds	HOMO[a] eV	LUMO[b] eV	E'_g [c] eV	E_g [d] eV
P-2HBA3MP	-5.77	-3.08	2.69	2.52
P-2HBA6MP	-5.84	-3.08	2.76	2.49
P-2HBA4MP	-5.71	-3.10	2.61	2.50
P-2HBA46MP	-5.70	-3.13	2.57	2.49
P-2HBATAP	-5.81	-3.03	2.78	2.96
P-2HBA2AP	-5.42	-2.94	2.48	2.19

[a] Highest occupied molecular orbital; [b] lowest unoccupied molecular orbital; [c] electrochemical band gap; [d] optical band gap.

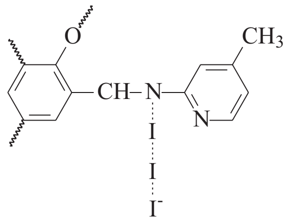
The UV-Vis spectra of the polymers were recorded using MeOH as a solvent, at 25 °C and shown in Fig. 6. Their optical band gaps (E_g) were calculated as in the literature [14] and shown in Table 4. These results clearly show that the polymers have lower optical band gaps. The optical band gaps (E_g) could be obtained by using the following equation as in the literature [14]:

$$E_g = 1242 / \lambda_{onset} \tag{4}$$

where 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. When UV spectra of the polymers in Fig. 6 are considered, the absorption bands at 250–300 nm may be assigned to $\pi''\pi^*$ electronic transitions in the aromatic ring and those at 295–380 nm may be assigned to $\pi''\pi^*$ electronic transitions in the azomethine group. The bands observed in the UV spectra of the polymers are in the same or close regions, implying that structure of polymers are similar and functional groups (-OH or -CH=N) have the same resonance and inductive effect [20].

For the polymers, the graph was plotted versus time regarding to the solid state conductivity values measured at air atmosphere. The measurements for the polymers were carried out in pure form and then polymers were exposed to iodine vapor in a desiccator, and the change in their conductivities versus time was measured at specific time intervals by doping. In doping process, electron emitting amine nitrogen and electron pulling iodine coordinate, and the formation of radical cation (polaron) structure in polymer chain (on amine nitrogen) are enabled. The electron vacancy formed due to this polaron facilitates the electron flow, which results in an increase in the electrical conductivity. High electron intensity allows the polymer to coordinate with iodine more, and consequently an increase at a higher level for the electron flow is obtained [13].

Electrical conductivities of the polymers and the changes of these values as a function of doping time with iodine were determined and shown in Fig. 7. Diaz *et al.* [21] suggested the doping mechanism of Schiff base polymers. According to doping mechanism, nitrogen, being a very electronegative element, is capable of coordinating with an iodine molecule (Scheme E). Consequently, a charge-transfer complex between imine compound and dopant iodine is formed and a considerable increase in conductivity can be observed [22]. However, steric hindrance of the substituents bound with the phenol ring prevents the iodine coordination and consequently could decrease the doping level of the polymer [22]. The experimental results show that a longer doping time is required to obtain the maximum conductivity [23]. According to Fig. 7, for poly(azomethine)s, the conductivities of the undoped polymers were 10^{-10} S·cm^{-1}, after 120 h doping, the conductivity of P-2HBA6MP and P-2HBA4MP was found to



Scheme E

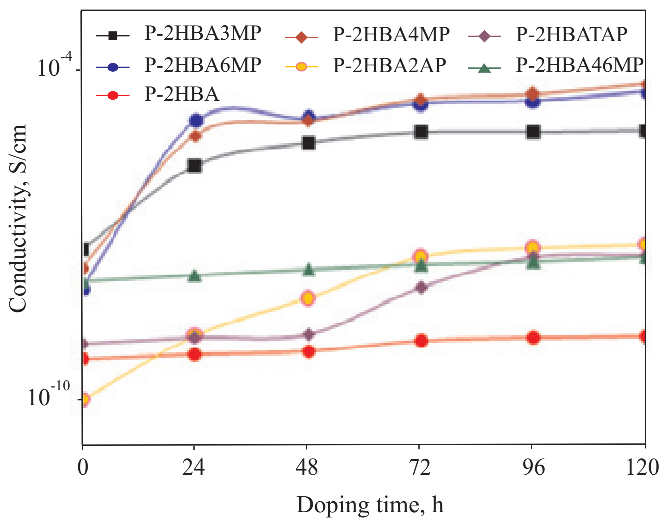


Fig. 7. Electrical conductivity changes of the I_2-doped at 25 °C

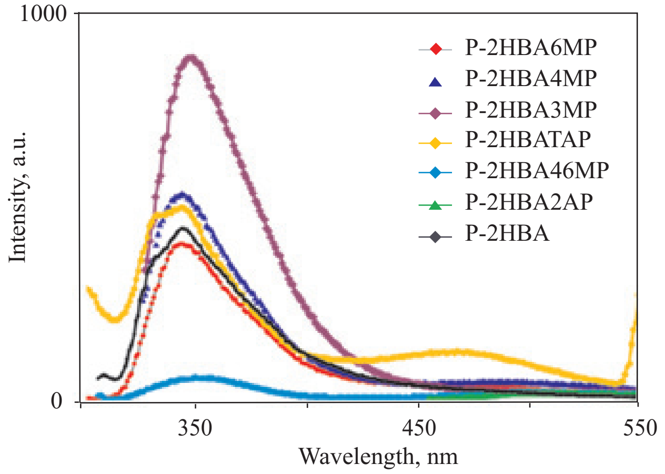


Fig. 8. Emission spectra of solutions in DMF (slit width: λ_{Ex} = 5 nm, λ_{Em} = 5 nm; concentration of the compounds: 0.001 g/dm^3)

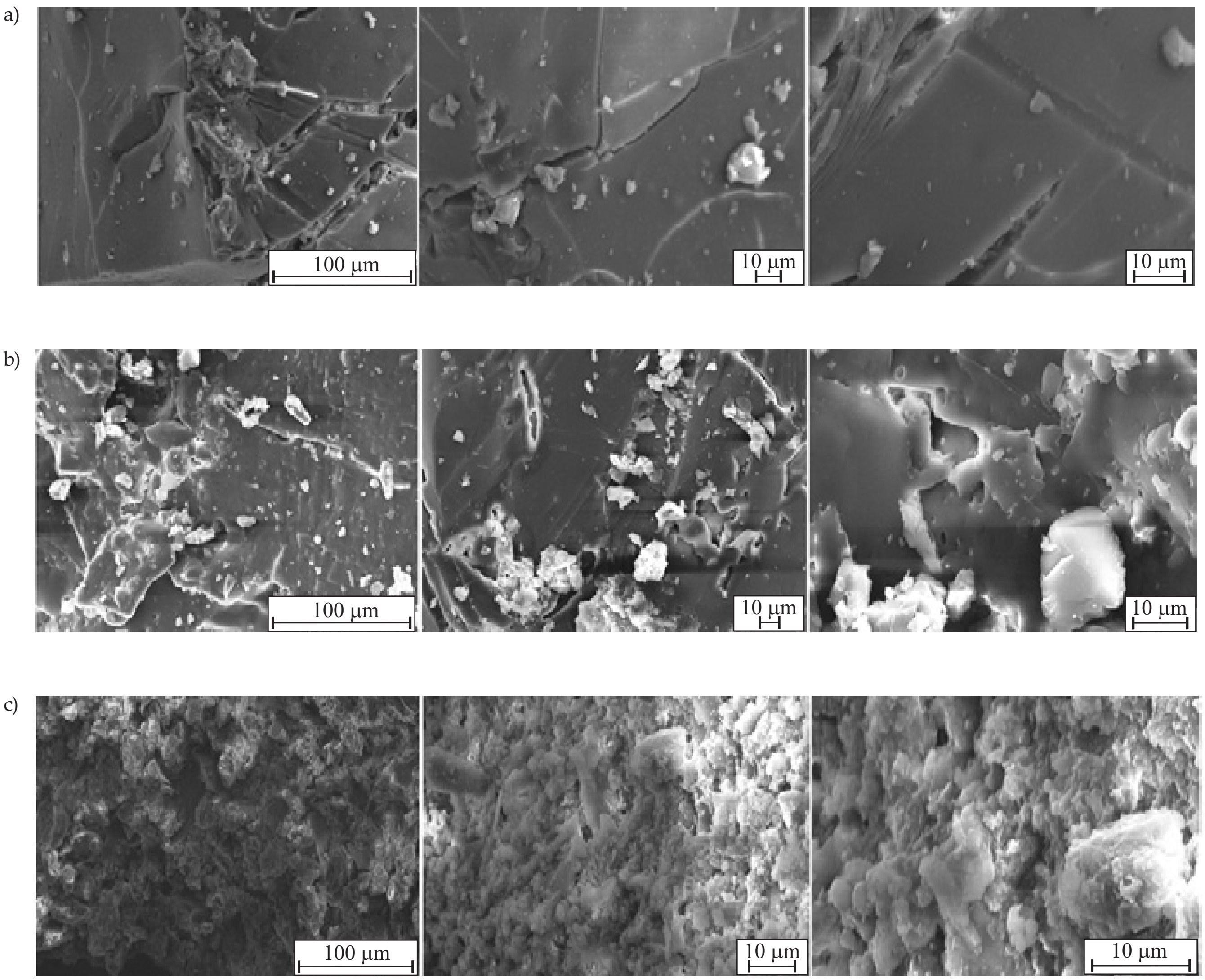


Fig. 9. SEM images of: a) P-2HBA, b) P-2HBA3MP, and c) P-2HBATAP

T a b l e 5. Fluorescence spectral data of the polymers

Compounds	λ_{Ex} a)	λ_{maxEm} b)	I_{Em} c)
P-2HBA	296	345	450
P-2HBA2AP	445	510	25
P-2HBA46MP	305	351	62
P-2HBATAP	277	344	504
P-2HBA3MP	317	348	898
P-2HBA6MP	276	343	411
P-2HBA4MP	316	344	541

a) Excitation wavelength for emission; b) emission wavelength for excitation; c) maximum emission intensity.

be around 10^{-5} S·cm^{-1} and it is better than the other polymers. Poly(azomethine)s showed semiconducting behavior, and the conductivity rapidly increased from 10^{-11} to 10^{-5} S·cm^{-1}.

A Shimadzu RF-5301PC spectrofluorophotometer was used in the fluorescence measurements. Emission and excitation spectra of the polymers were obtained in solution forms in DMF. The measurements were performed at 1 x 10^{-3} mg/dm^3 concentration. Slit width in all measurements was 5 nm. The obtained results are also summarized in Table 5. According to Table 5 and Fig. 8, out of P-2HBA series poly Schiff bases, P-2HBA3MP has maximum emission intensity, indicating that it has fluorescence characteristics while P-2HBA2AP and P-2HBA46MP have the lowest intensity and display no fluorescence characteristics.

The morphological properties of the polymers were obtained by scanning electron microscopy (FE-SEM) technique. Fig. 9 shows FE-SEM images of surface morphologies for P-2HBA, P-2HBA3MP and P-2HBATAP. According to Fig. 9 FE-SEM micrographs imply that P-2HBA (a) and P-2HBA3MP (b) have smooth structures in layers but P-2HBATAP (c) has spongy morphology.

CONCLUSION

Novel polyphenol derivatives of azomethine compounds having polyconjugated structures were synthesized by oxidative polycondensation reaction. According to ^{1}H NMR and ^{13}C NMR spectra, it was found that P-2HBA polymerized *via* C-O-C or C-C binding, however, polymerization takes place mainly *via* C-C binding. Molecular mass of P-2HBA2AP was the highest in terms of GPC analysis. Since the other poly Schiff bases contain methylene moieties, binding was less due to steric hindrance. According to TG and DTA analysis, P-2HBA46MP had the highest thermal stability. Considering DSC analysis, ΔC_p (thermal capacity) value of P-2HBA3MP was the lowest, implying that amount of energy required to soften the polymer was also the lowest. The value of optical band gap (E_g) was in agreement with that of electrochemical band gap calculated by CV (E'_g). Furthermore, optical band gap decreased by increasing of conjugation. The low values of electrochemical and optical band gaps show that the polymers have polyconjugated structure. Conductivities of the polymers are in the range of 10^{-8}–10^{-11} S·cm^{-1} and they can be made semiconductor by iodine doping. Conductivity measurements clearly indicated that the polymers are semiconductor. Compounds containing pyridine and pyrimidine moieties have important applications such as solar cell. Thus, future studies may be on the use of these polymers as solar cell and opto-electronic.

REFERENCES

[1] Adams R., Bullock R.E., Wilson W.C.: *Journal of the American Chemical Society* **1923**, *45*, 521. http://dx.doi.org/10.1021/ja01655a032

[2] Nishat N., Khan S.A., Rasool R., Parveen S.: *Journal of Inorganic and Organometallic Polymers and Materials* **2011**, *21*, 673. http://dx.doi.org/10.1007/s10904-011-9457-y

[3] Yıldırım M., Kaya İ.: *Polymer* **2009**, *50*, 5653. http://dx.doi.org/10.1016/j.polymer.2009.06.053

[4] Kaya İ., Aydın A.: *Polymers for Advanced Technologies* **2009**, *21*, 337. http://dx.doi.org/10.1002/pat.1433

[5] Kaya İ., Yıldırım M., Aydın A., Şenol D.: *Reactive and Functional Polymers* **2010**, *70*, 815. http://dx.doi.org/10.1016/j.reactfunctpolym.2010.07.013

[6] Mart H., Yürük H., Saçak M. *et al.*: *Polymer Degradation and Stability* **2004**, *83*, 395. http://dx.doi.org/10.1016/j.polymdegradstab.2003.08.003

[7] Bilici A., Kaya İ., Yıldırım M.: *European Polymer Journal* **2011**, *47*, 1005. http://dx.doi.org/10.1016/j.eurpolymj.2011.02.019

[8] Kaya İ., Koça S.: *Polymer* **2004**, *45*, 1743. http://dx.doi.org/10.1016/j.polymer.2004.01.035

[9] Doğan F., Kaya İ., Bilici A.: *Synthetic Metals* **2011**, *161*, 79. http://dx.doi.org/10.1016/j.synthmet.2010.11.001

[10] Bilici A., Doğan F., Yıldırım M., Kaya İ.: *Materials Chemistry and Physics* **2013**, *140*, 66. http://dx.doi.org/10.1016/j.matchemphys.2013.02.066

[11] Kaya İ., Vilayetoğlu A.R., Mart H.: *Polymer* **2001**, *42*, 4859. http://dx.doi.org/10.1016/S0032-3861(00)00883-1

[12] Kaya İ., Yıldırım M.: *Journal of Applied Polymer Science* **2007**, *106*, 2282. http://dx.doi.org/10.1002/app.26939

[13] Kaya İ., Yıldırım M.: *European Polymer Journal* **2007**, *43*, 127. http://dx.doi.org/10.1016/j.eurpolymj.2006.10.014

[14] Colladet K., Nicolas M., Goris L. *et al.*: *Thin Solid Films* **2004**, *451*, 7. http://dx.doi.org/10.1016/j.tsf.2003.10.085

[15] Özbülbül A.: "Synthesis and Characterization of New Type Oligomer Schiff Bases with Based Oligophenol" Master thesis, Institute of Science and Technology, Çukuova University, Adana, Turkey, 2006, p. 108.

[16] Karakaplan M., Demetgül C., Serin S.: *Journal of Macromolecular Science, Part A* **2008**, *45*, 406. http://dx.doi.org/10.1080/10601320801947197

[17] Erdik E.: "Spectroscopic Methods in Organic Chemistry", 5th ed., Gazi Press, Ankara 2008, p. 531.

[18] Çıtakoğlu N.: "Synthesis and Characterization of Imine Polymers Containing Aliphatic Methylsilane Group" Master thesis, Institute of Science and Technology, Çanakkale Onsekiz Mart University, Çanakkale, Turkey, 2012, p. 82.

[19] Cernini R., Li X-C., Spencer G.W.C. *et al.*: *Synthetic Metals* **1997**, *84*, 359. http://dx.doi.org/10.1016/S0379-6779(97)80781-3

[20] Cazacu M., Marcu M., Vlad A. *et al.*: *Journal of Organometallic Chemistry* **2004**, *689*, 3005. http://dx.doi.org/10.1016/j.jorganchem.2004.05.051

[21] Diaz F.R., Moreno J., Tagle L.H. *et al.*: *Synthetic Metals* **1999**, *100*, 187. http://dx.doi.org/10.1016/S0379-6779(98)01484-2

[22] Kaya İ., Yıldırım M.: *Synthetic Metals* **2009**, *159*, 1572. http://dx.doi.org/10.1016/j.synthmet.2009.04.019

[23] Kaya İ., Yıldırım M.: *Journal of Applied Polymer Science* **2008**, *110*, 539. http://dx.doi.org/10.1002/app.28632

Received 25 IV 2016.

Politechnika Krakowska i Firma FAMPUR w Bydgoszczy

zapraszają do udziału

w Konferencji Naukowo-Technicznej „Poliuretany 2017 – materiały przyjazne dla człowieka i środowiska"

Ustroń, 8–11 października 2017 r.

Tematyka konferencji:

- nowe surowce poliolowe i izocyjanianowe
- substancje spieniające nowej generacji
- katalizatory i inne substancje pomocnicze
- nowoczesne rozwiązania technologiczne
- poliuretany wytwarzane metodami bezizocyjanianowymi
- modyfikacja kompozycji PUR
- struktura, właściwości, zastosowanie różnych materiałów PUR
- zagospodarowanie odpadów
- maszyny i urządzenia do wytwarzania i przetwórstwa PUR
- zagadnienia prawne dotyczące przetwórstwa PUR

Patronat medialny: Czasopismo „Polimery"

Miejsce konferencji: Hotel „Muflon", 43-450 Ustroń, ul. Sanatoryjna 32

Terminy: Zgłoszenie udziału w konferencji z prezentacją oraz przesłanie streszczenia (maks. 100 słów) – 31 marca 2017 r.
Zgłoszenie udziału w konferencji bez prezentacji – 31 lipca 2017 r.
Przesłanie pełnego tekstu wystąpienia do materiałów konferencyjnych – 31 sierpnia 2017 r.

Zgłoszenia oraz teksty i prezentacje do materiałów konferencyjnych należy kierować na poliuretany2017@chemia.pk.edu.pl lub listownie na adres: Leonard Szczepkowski, FAMPUR Adam Przekurat, ul. Wojciecha Gersona 40/30, 85-305 Bydgoszcz z dopiskiem: Poliuretany 2017.

Opłata konferencyjna:
Uczestnicy z prezentacją: 1000 zł + 23 % VAT (pok. 2–3 os.), 1150 zł + 23 % VAT (pok. 1 os.).
Uczestnicy bez prezentacji: 1200 zł + 23 % VAT (pok. 2–3 os.), 1350 zł + 23 % VAT (pok. 1 os.).
Wszyscy uczestnicy po 31 lipca 2017 r.: 1300 zł + 23 % VAT (pok. 2–3 os.), 1450 zł + 23 % VAT (pok. 1 os.).
Opłata obejmuje: materiały konferencyjne, noclegi, wyżywienie i udział w imprezach towarzyszących.
Opłatę konferencyjną w odpowiedniej wysokości należy przelać na rachunek: FAMPUR Adam Przekurat, ul. Wojciecha Gersona 40/30, 85-305 Bydgoszcz, Bank Zachodni WBK S.A. Wrocław; 3 O/Bydgoszcz
Nr rachunku: 18 1090 1896 0000 0001 2037 7409
Tytuł: imię i nazwisko uczestnika z dopiskiem „konferencja/PUR2017"