

SYNTHESES AND CHARACTERIZATION OF POLY(IMINOPHENOL)S DERIVED FROM 4-BROMOBENZALDEHYDE: THERMAL, OPTICAL, ELECTROCHEMICAL AND FLUORESCENT PROPERTIES

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Abstract Schiff base monomers [2-(4-bromobenzylideneamino)phenol and 2-(4-bromobenzylideneamino)-5-methylphenol] were synthesized by the condensation reaction of 4-bromobenzaldehyde with aromatic aminophenols. Then, the monomers were converted to their polyphenol derivatives by oxidative polycondensation reactions (OP) in an aqueous alkaline medium. The structures of the synthesized compounds were characterized by solubility tests, FT-IR, NMR, TG-DTA, DSC and SEC techniques. The HOMO-LUMO energy levels and electrochemical (E_g') and optical (E_g) band gaps were calculated from cyclic voltammetry (CV) and UV-Vis measurements, respectively. Cyclic voltammetry (CV) was used to determine the electrochemical oxidation-reduction characteristics. Optical properties were investigated by UV-Vis and fluorescence analyses. Solid state electrical conductivities were measured on polymer films by four point probe technique using a Keithley 2400 electrometer. The effects of electron-donating ($-\text{CH}_3$) group at *p*-position of $-\text{NH}_2$ group in aminophenol on electrochemical and thermal properties were also discussed. Photoluminescence (PL) properties of the synthesized materials were determined in solution forms using different solvents. Fluorescence measurements were carried out in various concentrated solutions to determine the optimum concentrations to obtain the maximal PL intensities.

Keywords: Schiff base polymers; Thermal analysis; Fluorescence; Cyclic voltammetry; Conductivity.

INTRODUCTION

The poly(imine)s are an example of conjugated polymers, also known as poly(azomethines) or as Schiff base polymers. When polymers have a wholly aromatic and conjugated structure of their main chain they possess a high thermal stability, mechanical strength, environmental stability and good conducting and opto-electronic properties^[1–6]. The polyazomethines including azomethine ($-\text{CH}=\text{N}$) and active hydroxyl ($-\text{OH}$) groups have been used in various fields. They have useful properties such as paramagnetism, electrochemical cell performance and resistance to high energy. Because of these properties, they were used to prepare composites with graphite materials, epoxy oligomer and block copolymers as adhesives, photoresists and antistatic materials^[7–10]. Schiff base substituted polyphenols have been studied by Kaya and co-workers for the last decade. This class of polymers was mainly found to be electro-active as well as semi-conductive materials, and their conductivities were increased by doping with iodine^[11–14].

Oligophenols and their azomethine derivatives had been previously synthesized by oxidative polycondensation method and presented in the literature with their several useful properties^[15–17]. This method is easy to apply, environmentally harmless and uses cheap oxidants such as NaOCl, H_2O_2 and air.

Kaya and coworkers synthesized 4-fluorobenzaldehyde based Schiff base compounds, and investigated the

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effect of the substituent ($-\text{CH}_3$) as electron-donating on some physical properties^[18]. However, there is no report on investigation of the effect of methyl groups on thermal stability, optical and conductivity measurements including 4-bromobenzaldehyde and aminophenols. For this reason, 4-bromobenzaldehyde based Schiff bases were synthesized. The obtained Schiff bases were converted to their polyphenol derivatives. Then, the synthesized compounds were characterized using FT-IR, UV-Vis spectra, ^1H -NMR, ^{13}C -NMR and SEC analyses. TG-DTA technique was used to determine the stabilities of thermal degradation. DSC analyses of the polyphenols were also carried out, thus the glass transition temperatures (T_g) were determined. The fluorescence spectra of the synthesized compounds were also carried out to determine maximal emission-excitation intensities. Optical properties were determined by using UV-Vis spectra, and the optical band gaps were calculated from absorption edges. The obtained polymers were found to be semi-conductive materials whose conductivities could be increased by iodine doping, and the conductivity of P-4-BBAMP highly increased with doping that made the polymer a good candidate for gas sensing applications against electro-acceptor gases like iodine.

EXPERIMENTAL

Materials

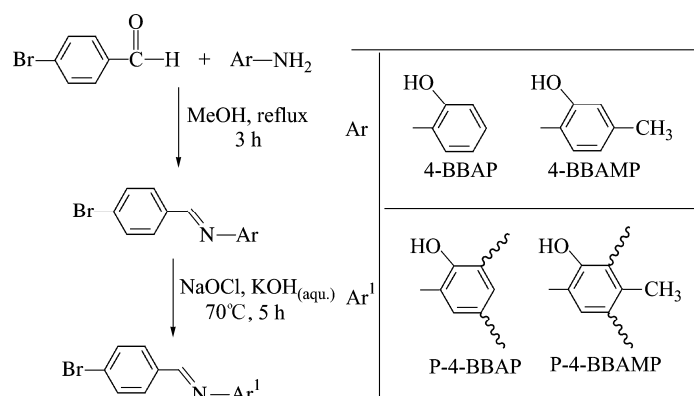
4-Bromobenzaldehyde (BBA), 2-aminophenol (AP), 2-amino-5-methylphenol (AMP), tetrabutylammonium hexafluorophosphate (TBAPF_6), dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), methanol, ethanol, acetonitrile, acetone, toluene, ethyl acetate, heptane, hexane, CCl_4 , CHCl_3 , H_2SO_4 , KOH and HCl were supplied from Merck Chemical Co. (Germany), and they were used as received. 30% aqueous solution of sodium hypochlorite, NaOCl, was supplied by Paksoy Chemical Co. (Turkey).

Syntheses of Schiff Bases

The Schiff bases (4-BBAP and 4-BBAMP) were synthesized by the condensation reaction of 4-bromobenzaldehyde with aminophenols (2-aminophenol and 2-amino-4-methylphenol). Reactions were performed as follows: 4-bromobenzaldehyde (3.700 g, 2×10^{-2} mol) was placed into a 250 mL three-necked round-bottom flask which was fitted with condenser, thermometer and magnetic stirrer. 50 mL ethanol was added into the flask, and the reaction mixture was heated to 60°C . A solution of equivalent amount of 2-aminophenol (2.18 g, 2×10^{-2} mol) or 2-amino-4-methylphenol (2.46 g, 2×10^{-2} mol) in 20 mL ethanol was added into the flask. Reactions were maintained for 3 h under reflux. The precipitated monomers were filtered, recrystallized from acetonitrile and dried in vacuum desiccators^[2] (yields: 93%, and 87% for 4-BBAP and 4-BBAMP, respectively).

Syntheses of Polyphenols

The synthesized monomers (4-BBAP and 4-BBAMP) were converted to their polyphenol derivatives *via* oxidative polycondensation reactions in an aqueous alkaline medium using NaOCl (30% in water) as reported in the literature^[6, 7]. 4-BBAP (1.104 g, 4×10^{-3} mol) or 4-BBAMP (1.160 g, 4×10^{-3} mol) were dissolved in an aqueous KOH solution (30%, 0.03 mol, 0.56 mL) and placed into a 50 mL three-necked round-bottom flask which was fitted with a condenser, a thermometer, a stirrer and an addition funnel containing NaOCl. After heating the solution to 40°C , NaOCl was added drop by drop within about 20 min. Then, the reaction mixtures were heated to 80°C , and reaction was maintained for 5 h. The reaction mixtures were cooled to room temperature and then they were neutralized with 0.03 mol HCl solution. For the separation of mineral salts, the mixture was filtered and washed in 25 mL of hot water for three times. Then, unreacted monomers were separated from the reaction products by washing with ethanol and dried in a vacuum oven at 60°C (yields: 62% and 59% for P-4-BBAP and P-4-BBAMP, respectively). All the synthesized procedures were summarized in Scheme 1.



Scheme 1 Synthesis of the monomers and their polyphenol species

Characterization Techniques

The solubility tests were done in different solvents by using 1 mg sample and 1 mL solvent at 25°C. The infrared and ultraviolet-visible spectra were measured by using a Perkin Elmer FT-IR Spectrum One Spectrometer and a Perkin-Elmer Lambda 25, respectively. The FT-IR spectra were recorded by using a 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. Tetramethylsilane was used as an internal standard. Thermal data were obtained by using a Perkin-Elmer Diamond Thermal Analysis System. TG-DTA measurements were made in the range of 20–1000°C (in N_2 , rate 10 K/min). DSC analyses were carried out by using a Perkin-Elmer Pyris Sapphire DSC. DSC measurements were made between 25°C and 420°C (in N_2 , rate 20 K/min). 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 of Shimadzu Co. For SEC investigations an SGX (10 nm and 7 nm diameter loading material) 3.3 mm i.d. $\times$ 300 mm column was used (eluent: DMF (0.4 mL/min), polystyrene standards). A refractive index detector (RID) and a UV detector were used to analyze the products at 25°C.

Optical and Electrochemical Properties

Ultraviolet-visible (UV-Vis) spectra were measured by a Perkin-Elmer Lambda 25. The absorption spectra were recorded by 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 mol/L tetrabutylammonium hexafluorophosphate (TBAPF_6) and was 0.39 V with respect to Ag wire. The voltammetric measurements were carried out in acetonitrile for the Schiff bases and in acetonitrile/DMSO mixture (5/1, V/V) for the polymers. The HOMO-LUMO energy levels and electrochemical band gaps (E_g') were calculated from oxidation and reduction peak potentials^[6].

Electrical Properties

Conductivities of the synthesized materials were measured on a Keithley 2400 Electrometer. The pellets were pressed on a hydraulic press developing 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^[19, 20]. Measurements were carried out per 24 h.

Fluorescence Measurements

A Shimadzu RF-5301PC spectrofluorophotometer was used in fluorescence measurements. Emission and excitation spectra of the synthesized compounds were obtained in solution forms in DMF and THF for the

monomers, and in DMF and DMSO for the polymers. Measurements were made in a wide concentration range of 3.125–100 mg/L to determine the optimal fluorescence concentrations. Slit width in all measurements was 3 nm.

RESULTS AND DISCUSSION

Solubility and Structure of the Compounds

The solubility test results are shown in Table 1. According to Table 1, all the synthesized compounds are soluble in highly polar solvents like DMSO, DMF and H₂SO₄. The synthesized monomers are completely soluble in CCl₄ while their polyphenols are insoluble. Moreover, the monomers are generally soluble in other common polar organic solvents like ethanol, methanol, ethyl acetate, acetonitrile, chloroform, THF and acetone. Additionally, they are soluble in some apolar solvents like toluene and CCl₄, while insoluble in hexane. However, the synthesized polyphenols are completely insoluble in all other solvents except DMSO, DMF, and H₂SO₄ because of their high molecular weight.

Table 1. Solubility test results of the synthesized compounds

Solvents	4-BBAP	4-BBAMP	P-4-BBAP	P-4-BBAMP
Methanol	+	+	⊥	⊥
Ethanol	+	+	⊥	—
THF	+	+	⊥	+
CH ₃ CN	+	+	—	⊥
Toluene	+	+	⊥	⊥
Ethylacetate	+	+	⊥	+
Chloroform	+	+	—	⊥
CCl ₄	+	+	—	—
Hexane	⊥	—	—	—
Acetone	+	+	—	⊥
DMF	+	+	+	+
DMSO	+	+	+	+
H ₂ SO ₄	+	+	+	+

+: soluble; ⊥: partially soluble; —: insoluble

FT-IR spectral data of 2-aminophenol, 4-bromobenzaldehyde, 4-BBAP and P-4-BBAP are given Fig. 1. Similarly, 2-amino-4-methylphenol, 4-BBAMP and P-4-BBAMP are given Fig. 2. As seen in Figs. 1 and 2 the structures of the synthesized monomers are confirmed by growing imine ($-\text{CH}=\text{N}$) peaks with disappearing of

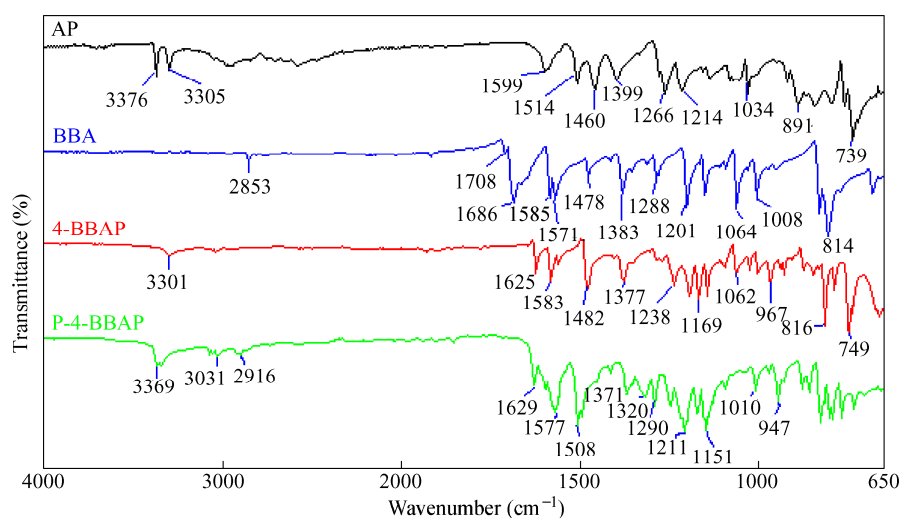


Fig. 1 FT-IR spectra of AP, BBA, 4-BBAP and P-4-BBAP

the —NH_2 peak of aminophenols and the —CHO peak of the 4-bromobenzaldehyde used in the condensation reactions. According to Fig. 1 in the spectrum of 4-bromobenzaldehyde the characteristic aldehyde (—CHO) peak is observed at 1686 cm^{-1} and the 2-aminophenol and 2-methyl-4-aminophenol —NH_2 peaks are observed at 3376 and 3369 cm^{-1} , respectively. In the spectra of 4-BBAP and 4-BBAMP the imine (—CH=N) peak is observed at 1625 and 1629 cm^{-1} , respectively. In the spectra of P-4-BBAP and P-4-BBAMP the same peak is observed at 1629 and 1627 cm^{-1} , respectively. Also, the —OH stretch of phenolic groups is observed in the range of $3301\text{--}3369\text{ cm}^{-1}$. In the spectra of polymers the peaks also broaden due to the polyconjugated structure.

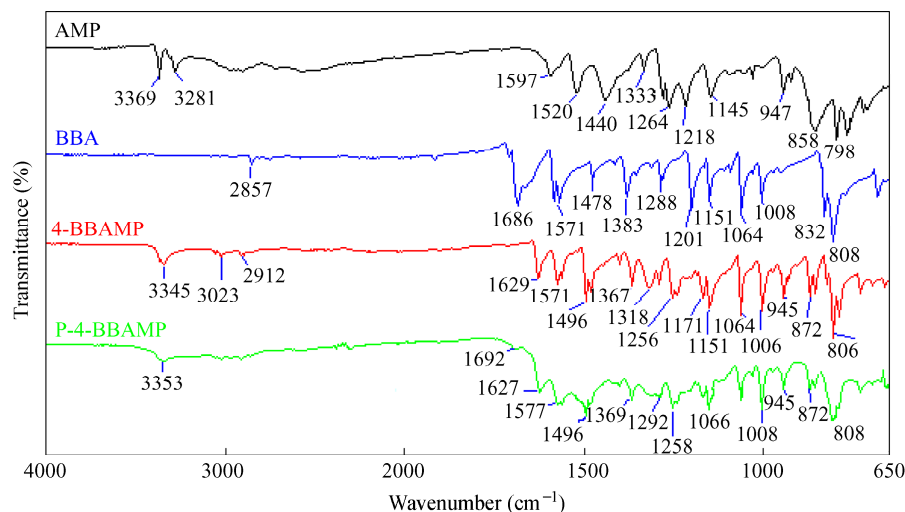


Fig. 2 FT-IR spectra of AMP, BBA, 4-BBAMP and P-4-BBAMP

$^1\text{H-NMR}$ spectra of 4-BBAP and 4-BBAMP are given in Fig. 3. Also, the same spectra of P-4-BBAP and P-4-BBAMP are given in Fig. 4. Similarly, $^{13}\text{C-NMR}$ spectra of 4-BBAMP and P-4-BBAMP are given in Figs. 5(a) and 5(b), respectively. According to Fig. 3(A) in the spectrum of 4-BBAP —OH and imine (—CH=N) peaks are observed at $\delta = 9.10$ and 8.73 , respectively. In the spectrum of 4-BBAMP the same peaks are observed at $\delta = 8.98$ and 8.73 , respectively. In the spectra of P-4-BBAP and P-4-BBAMP these peaks are observed at $\delta = 10.19$ and 8.98 and at $\delta = 8.87$ and 8.73 , respectively. Additionally, methyl (—CH_3) substituents of 4-BBAMP and P-4-BBAMP are observed at $\delta = 2.36$ and 2.26 , respectively. As a result of the polymerization broad peaks are obtained at the aromatic regions of the $^1\text{H-NMR}$ spectra of the polymers.

$^{13}\text{C-NMR}$ spectrum of 4-BBAMP (Fig. 5a) also confirms the structure by the peaks observed at $\delta = 156.5$ and 151.5 which could be attributed to the imine (—CH=N) and —OH carbons, respectively. In the spectrum of P-4-BBAMP (Fig. 5b) these peaks are observed at $\delta = 156.5$ and 151.5 , respectively. Additionally, aliphatic —CH_3 peaks of 4-BBAMP and P-4-BBAMP are observed at $\delta = 20.8$ and 20.9 , respectively. These results confirmed the proposed structures shown in Scheme 1.

According to the SEC chromatograms, the calculated number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) values of P-4-BBAP and P-4-BBAMP were obtained by using a UV detector. The M_n , M_w and PDI values of P-4-BBAP and P-4-BBAMP were found as 45000, 46200 and 1.027 and 32000, 33400 and 1.044, respectively. According to these results P-4-BBAP and P-4-BBAMP contain approximately 168–169 and 115–116 repeated units, respectively. These results indicate that P-4-BBAMP has lower molecular weights than P-4-BBAP. The synthesized compounds have single fraction. The obtained results confirm the polymer structures. According to these results, the synthesized polymers have quite high molecular weights.

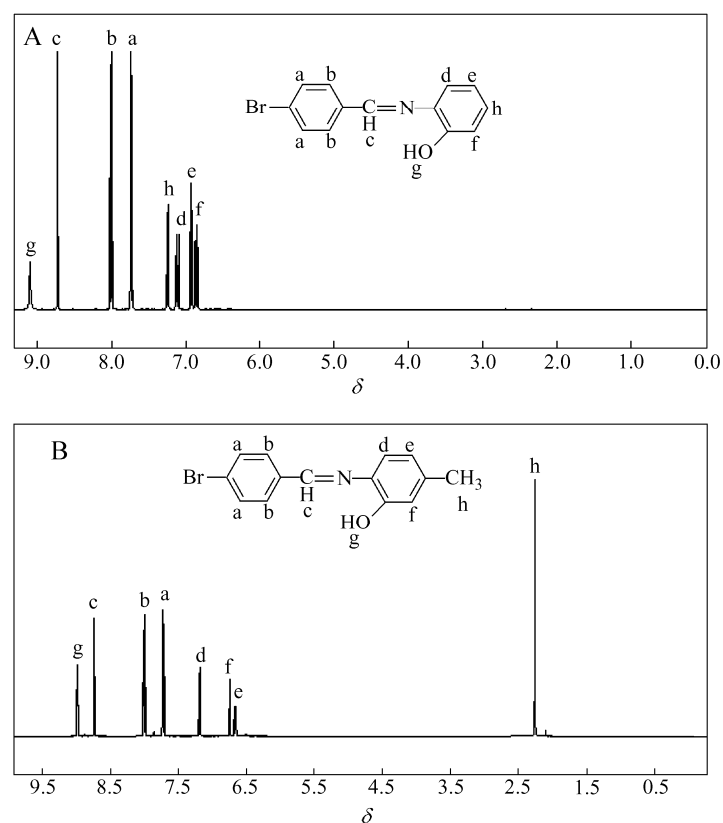


Fig. 3 ^1H -NMR spectra of 4-BBAP (A) and 4-BBAMP (B)

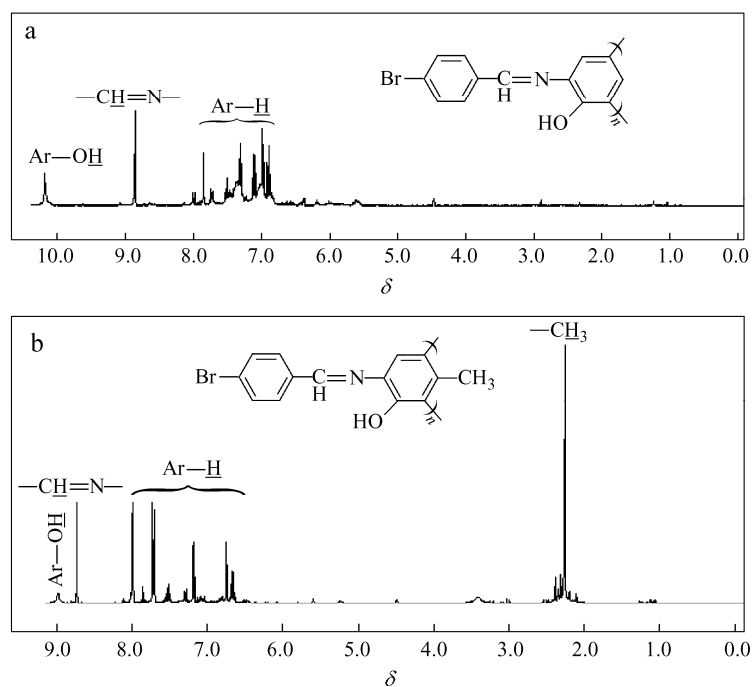


Fig. 4 ^1H -NMR spectra of P-4-BBAP (a) and P-4-BBAMP (b)

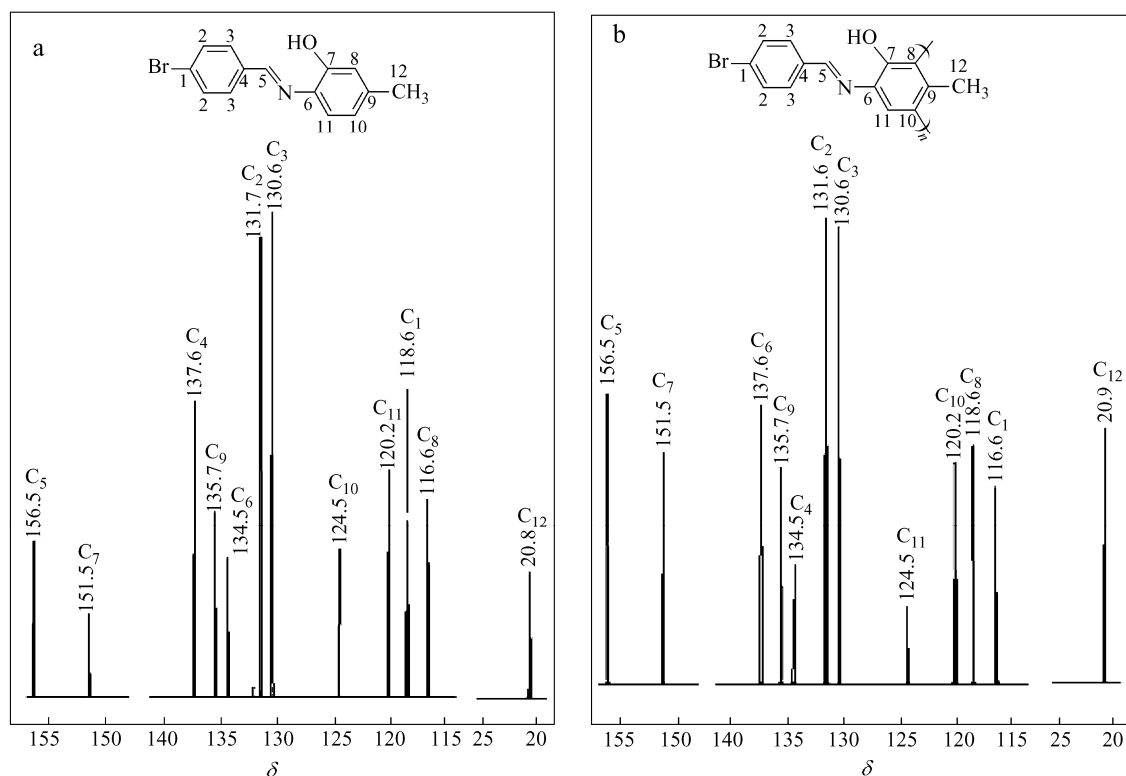


Fig. 5 ^{13}C -NMR spectra of (a) 4-BBAMP and (b) P-4-BBAMP

Optical and Electrochemical Properties

UV-Vis spectra for all synthesized compounds are obtained in DMSO in the wavelength range of 260–600 nm. The UV-Vis spectra of the synthesized compounds are shown in Fig. 6. According to these spectra, the absorption edges of the synthesized polymers shifted to higher wavelength values. This is because of the polyconjugated structures of the polymers which increase the HOMO energy level and decrease the LUMO energy level thus resulting in lower band gaps. The optical band gaps (E_g) were calculated as in the literature^[21] and are shown in Table 2. These results show that the synthesized polymers have lower optical band gaps compared to the monomers, as expected.

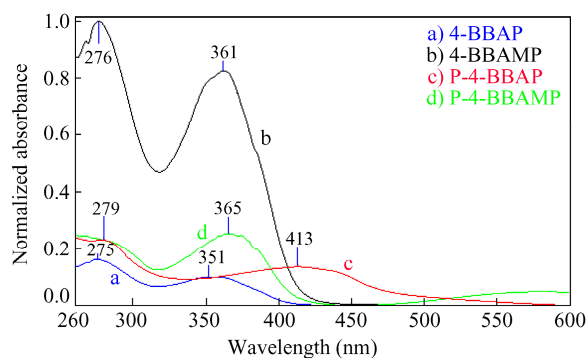


Fig. 6 UV-Vis spectra of 4-BBAP, 4-BBAMP, P-4-BBAP and P-4-BBAMP

Cyclic voltammograms of the synthesized compounds are also shown in Fig. 7. According to the cyclic voltammetry (CV) measurements, the calculated HOMO and LUMO energy levels and the electrochemical band gaps (E_g) are shown in Table 2. These data are estimated by using the oxidation (E_{ox}) and reduction (E_{red}) peak

potentials. The calculations are made by using the following equations:

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

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

$$E_g' = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (3)$$

The calculated electrochemical band gap values agree with the optical band gap ones; as a result of the polyconjugated structure the polymers have lower band gaps. However, it's observed in all CVs that the HOMO energy levels of the polymers are lower than those of the Schiff bases. As seen in Table 2, the obtained results indicate that after the polycondensation reactions, the HOMO energy levels increase while the LUMO energy levels decrease and so the electrochemical band gaps (E_g') of the polymers are lower than those of the monomers. Lower band gaps facilitate the electronic transitions between HOMO and LUMO energy levels and make the polymers more electro-conductive than the monomers. According to the electrochemical analysis results, the order of the electrochemical band gap values of the polymers changes as follows: P-4-BBAP < P-4-BBAMP < 4-BBAP < 4-BBAMP. The order of the optical band gaps of the polymers is the same.

Table 2. Electronic structure parameters of the synthesized compounds

Compounds	HOMO (eV) ^a	LUMO (eV) ^b	E_g (eV) ^c	E_g' (eV) ^d
4-BBAP	-5.88	-2.82	3.03	3.06
4-BBAMP	-5.96	-2.71	3.09	3.25
P-4-BBAP	-5.43	-2.87	2.57	2.56
P-4-BBAMP	-5.61	-2.91	2.99	2.70

^a Highest occupied molecular orbital; ^b Lowest unoccupied molecular orbital; ^c Optical band gap;

^d Electrochemical band gap

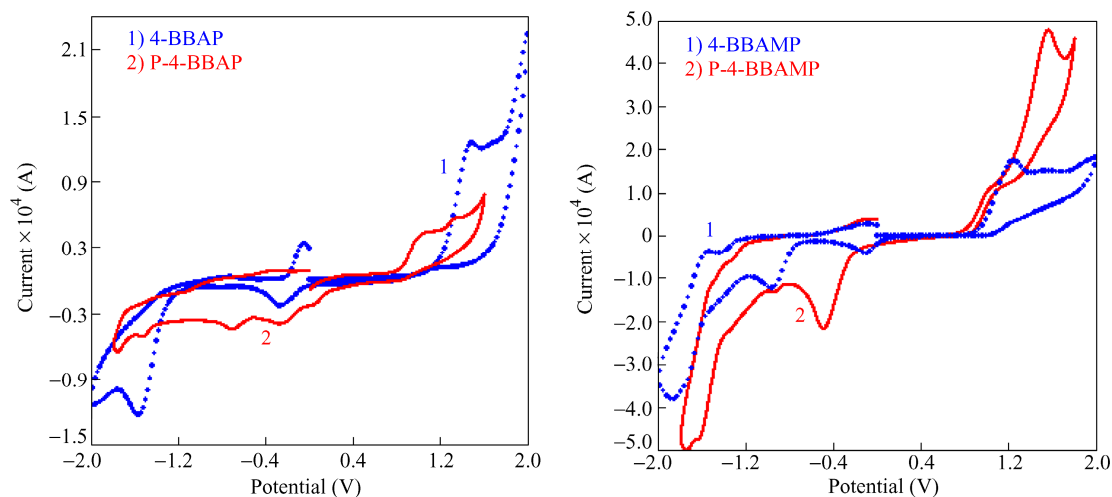


Fig. 7 Cyclic voltammograms of 4-BBAP, P-4-BBAP, 4-BBAMP and P-4-BBAMP

Electrical Conductivity

Electrical conductivities of the synthesized polyphenols and the changes of these values related to doping time with iodine are determined and shown in Table 3. As seen in Table 3, P-4-BBAP has the higher electrical conductivity than P-4-BBAMP at the undoped state, but P-4-BBAMP has higher electrical conductivity than P-BBAP at doped states. However, after long time iodine doping for 168 h the conductivities nearly increased by 563 and 3 times of their magnitudes for P-4-BBAMP and P-4-BBAP, respectively.

According to these results P-4-BBAP has approximately 1.77 times higher undoped conductivity ($11.33 \times$

10^{-10}) than P-4-BBAMP. On the other hand, after doping with iodine for 168 h the conductivity of P-4-BBAMP is approximately 104.4 times higher than that of P-4-BBAP. Doping mechanism of imine polymers has been previously studied and presented in the literature^[9]. According to the proposed mechanism nitrogen, being a very electronegative element, is capable of coordinating with 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^[22]. The synthesized P-4-BBAMP has methyl ($-\text{CH}_3$) substituent in the structure taking part of *para* position of carbon atom which is simultaneously bound with the imine nitrogen. It is known $-\text{CH}_3$ substituent as an electron-donating group partly increases the electron density of *ortho* and *para* positions of the aromatic ring. As a result, the electron density on carbon atom which is simultaneously bound with the imine nitrogen of P-4-BBAMP becomes higher than that of P-4-BBAP. This also increases the electron density on the imine nitrogen and consequently the ability of iodine doping. As a result, high rate of increase is obtained for P-4-BBAMP, while lower rate for P-4-BBAP. Total charges of imine nitrogens are also calculated by Huckel calculation method^[21] and given in Fig. 8. As a result of the calculation the charge of imine nitrogen is -0.445 for P-4-BBAMP while -0.214 for P-4-BBAP. These results support the obtained conductivity increase as mentioned above; with higher electron density P-4-BBAMP could be highly doped when exposure to iodine vapor. Consequently, the conductivity of P-4-BBAMP could be highly increased and used as a semi-conductive polymer in electronic, opto-electronic, electroactive and photovoltaic applications.

Table 3. Electrical conductivity results of I_2 -doped and undoped compounds versus doping time at 25°C

Time (h)	Conductivity $\times 10^{-10}$ (S cm^{-1})	
	P-4-BBAP	P-4-BBAMP
0	11.33	6.40
24	18.70	40
48	25.10	219
72	30.05	847
96	32.26	1538
120	33.22	2551
144	33.67	2941
168	34.48	3601

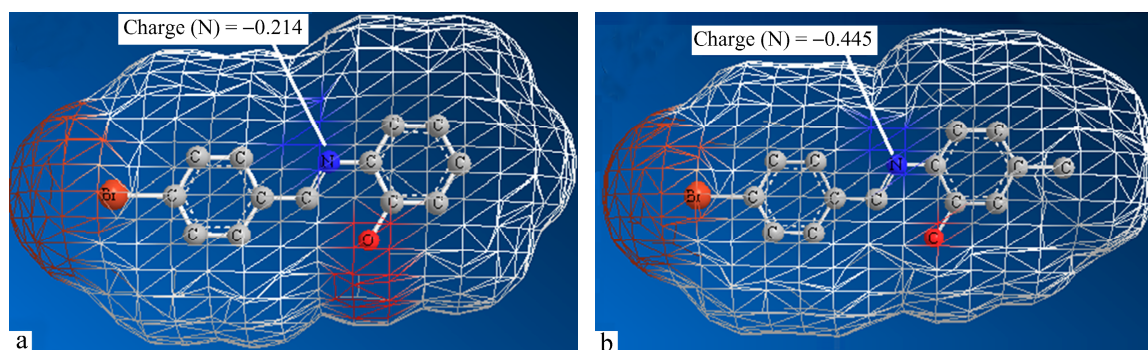


Fig. 8 Total charge density distribution views of 4-BBAP (a) and 4-4-BBAMP (b) (H atoms aren't shown.)

Fluorescence Characteristics

Fluorescence measurements of the synthesized compounds are carried out using different solvents such as THF, DMF and DMSO for the monomers and their polyphenol derivatives. Figure 9 show the excitation and emission spectra of 4-BBAP, 4-BBAMP, P-4-BBAP and P-4-BBAMP in different solvents. Figure 10 also indicates the concentration and fluorescence intensity relationships of the compounds. As seen in Fig. 9 the synthesized compounds have higher maximum emission and excitation wavelengths in THF. Measurements are made for various concentrations to determine the optimal conditions in THF. Fluorescence spectral data of the synthesized compounds at the optimum concentrations are given in Table 4. According to Table 4, the optimum

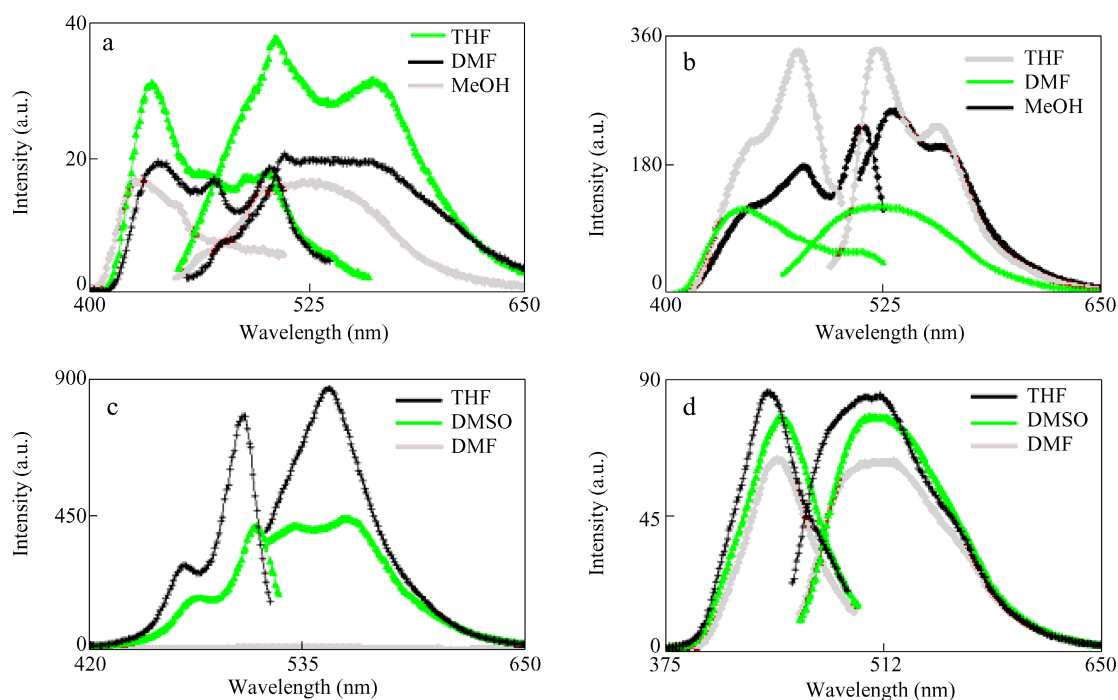


Fig. 9 Emission and excitation spectra of 4-BBAP (a), 4-BBAMP (b), P-4-BBAP (c) and P-4-BBAMP (d) in various solvents
Slit width: λ_{Ex} , 3 nm; λ_{Em} , 3 nm

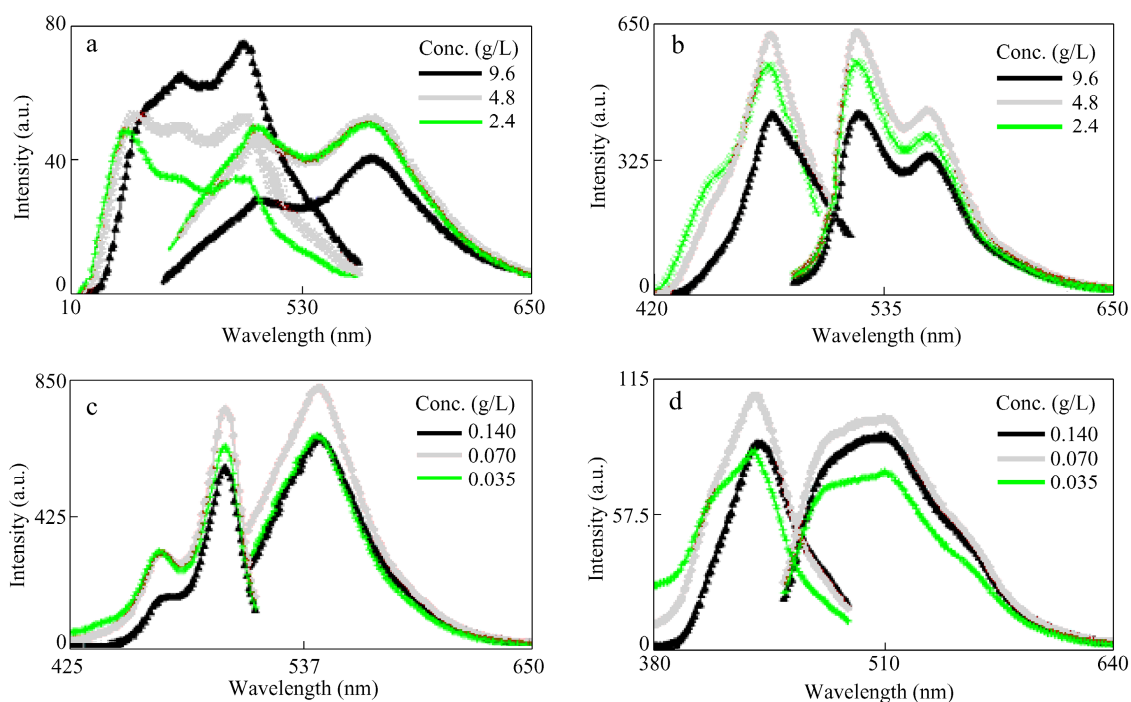


Fig. 10 Emission and excitation spectra of various concentrated solutions of 4-BBAP (a), 4-BBAMP (b), P-4-BBAP (c) and P-4-BBAMP (d) in THF
Slit width: λ_{Ex} , 3 nm; λ_{Em} , 3 nm

concentrations to obtain maximal emission-excitation intensities are 9.60 and 0.14 mg/mL for monomers and polymers, respectively. These results clearly indicate that 4-BBAMP has higher fluorescence intensity than 4-BBAP. However, P-4-BBAP has higher fluorescence intensity than P-4-BBAMP. P-4-BBAP and P-4-BBAMP give the emission peaks at 547 and 511 nm with the intensities of 667 and 92 a.u., respectively. Dye 6-carboxyrhodamine 6G and “Dye BODIPY FL” have emission peaks at 547 and 511 nm and excitation peaks at 528 and 502 nm, respectively. Fluorescence characteristics of P-4-BBAP and P-4-BBAMP resembles those of “Dye 6-Carboxyrhodamine 6G”, and “Dye BODIPY FL” presented in the literature^[23].

Table 4. Fluorescence spectral data of the synthesized compounds

Compounds	Conc. (mg/mL)	λ_{Ex} (nm) ^a	λ_{Em} (nm) ^b	$\lambda_{\text{max(Ex)}}$ (nm) ^c	$\lambda_{\text{max(Em)}}$ (nm) ^d	I_{Ex} ^e	I_{Em} ^f
4-BBAP	9.6	439	571	500	567	74	40
4-BBAMP	9.6	477	520	478	522	437	439
P-4-BBAP	0.14	501	526	500	547	575	667
P-4-BBAMP	0.14	44	501	439	511	88	92

^aExcitation wavelength for emission; ^bEmission wavelength for excitation; ^cMaximum excitation wavelength;

^dMaximum emission wavelength; ^eMaximum excitation intensity; ^fMaximum emission intensity

Thermal Analysis

TGA and DSC curves of the synthesized compounds are given in Fig. 11 and Fig. 12, respectively. The results of TGA and DSC are summarized in Table 5. According to the TGA results, the onset temperatures of the synthesized compounds are nearly the same. The initial degradation temperature and char content are 224°C and 0% for 4-BBAP, 231°C and 0% for 4-BBAMP, 170°C and 23.63% for P-4-BBAP, 174°C and 28.21% for P-4-BBAMP, respectively. These results show that P-4-BBAMP derived from 2-amino-4-methylphenol has higher char content than P-4-BBAP derived from 2-aminophenol. The chars (%) values of the polymers are also higher than those of the Schiff bases. On the other hand, P-4-BBAMP has higher onset temperatures than P-4-BBAP. According to the DSC traces, the glass transition temperatures (T_g) of P-4-BBAP and P-4-BBAMP are 206 and 171°C, respectively.

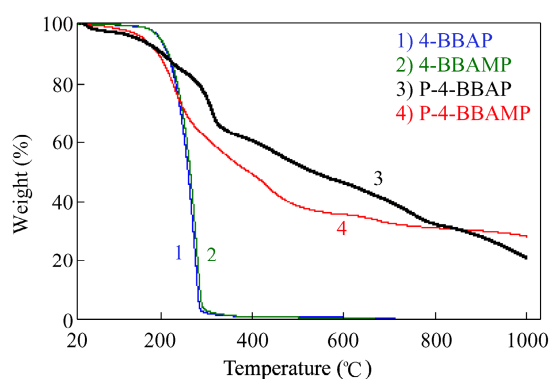


Fig. 11 TGA curves of the synthesized compounds

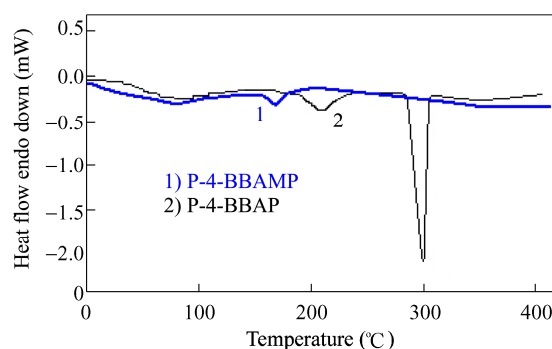


Fig. 12 DSC curves of the synthesized polymers

Table 5. Thermal degradation values of the synthesized compounds

Compounds	T_{on} (°C) ^a	T_{Wmax} (°C) ^b	T_{20} (°C) ^c	T_{50} (°C) ^f	% weight loss at 1000°C	DSC	
						T_g (°C) ^e	ΔC_p (J/(g K)) ^d
4-BBAP	224	266	232	258	—	—	—
4-BBAMP	231	270	236	265	—	—	—
P-4-BBAP	170	306, 451, 747	292	586	76.37	206	0.383
P-4-BBAMP	174	227, 431, 672	225	398	71.79	171	0.585

^aThe onset temperature; ^bMaximum weight loss temperature; ^cGlass transition temperature;

^dChange of specific heat during glass transition; ^e20% weight loss temperature; ^f50% weight loss temperature

CONCLUSIONS

Novel 4-bromobenzaldehyde based Schiff bases and their polyphenol species were synthesized by condensation and oxidative polycondensation reaction, respectively. The structures of the synthesized compounds were characterized by solubility tests, FT-IR, UV-Vis, NMR, and SEC techniques. Solubility test results indicate 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 quite low band gaps. Electrical conductivity measurements showed that the conductivity of the polymers could be increased regardably. Especially, by doping with iodine the conductivity of P-4-BBAMP highly increased. Electrical conductivity measurements show that the synthesized polymers are semi-conductors and they can be used as semi-conductive polymer in electronic, opto-electronic and photovoltaic applications. Fluorescence measurements of the synthesized compounds were obtained using different solvents such as DMF, THF and DMSO. Thermal degradation characteristics were also determined. According to the obtained results the synthesized polyphenols have higher stabilities than their Schiff base monomers. DSC analyses of the polymers showed that P-4-BBAP and P-4-BBAMP have T_g values at 206°C and 171°C, respectively. Consequently, because of the fine thermal stabilities the synthesized compounds can be promising candidates for aerospace applications and they can be used to produce temperature-stable materials.

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