

Synthesis and Characterization of the Polyaminophenol Derivatives Containing Thiophene in Side Chain: Thermal Degradation, Electrical Conductivity, Optical-Electrochemical, and Fluorescent Properties

İsmet Kaya, Aysel Aydın

Department of Chemistry, Çanakkale Onsekiz Mart University, Faculty of Sciences and Arts, 17020, Çanakkale, Turkey

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ABSTRACT: Novel polyaminophenols, poly-2-[3-thienylmethylene]aminophenol (P-2,3-TP), poly-3-[3-thienylmethylene]aminophenol (P-3,3-TP) and poly-4-[3-thienylmethylene]amino phenol (P-4,3-TP), were synthesized by oxidative polycondensation reaction. Metal complexes of P-2,3-TP were also obtained. The structures of synthesized compounds were confirmed by FT-IR, UV-vis, ^1H NMR, and ^{13}C NMR techniques. The characterization was made by TG-DTA, DSC, and gel permeation chromatography (GPC) analyses in addition to solubility tests. Electrical conductivities of polymers were measured by four-point probe tech-

nique. Fluorescence measurements were carried out in various solutions and optimum concentrations and maximal intensities were determined. The new synthesized polyaminophenols are good candidates for electronic, opto-electronic, and photovoltaic applications due to polyconjugated structures. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3028–3040, 2011

Key words: polymer-metal complexes; fluorescence; Schiff base substituted polyaminophenols; oxidative polymerization; cyclic voltammetry

INTRODUCTION

Schiff base substituted polyaminophenols have been widely investigated due to their interesting their optical and electrochemical, conductivity, thermal stability^{1–3} and antimicrobial properties.⁴ These materials are an attractive class of high-performance polymers that exhibit interesting properties which are associated mainly with their conjugated backbone. They present good thermal stability,⁵ mechanical strength,⁶ nonlinear optical properties,⁷ the ability to form metal chelates,⁸ semiconducting properties,⁹ environmental stability and fiber-forming properties.¹⁰ When these polymers were heated, mesophases could be formed.¹¹ For this reason, they have high melting points and low solubilities and this limits their characterization. Polyazomethines are usually synthesized via the condensation reaction of amines with aldehydes.^{12,13} They have been known as thermally resistant materials.^{14–16} Up till

now, these classes of polymers have attracted much more attention because of their useful properties and wide application fields. For the first time, polyazomethines were prepared by Adams et al.¹⁷ Polyazomethines including conjugated bonding and active hydroxyl group have been studied for more than 60 years and they have been used in various fields due to useful properties such as paramagnetism, semi conductivity, electrochemical cell, and resisting 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.¹⁸ Two novel functional conjugated poly-Schiff bases containing triphenylamine unite were synthesized by Niu et al. and its the optical, and electrochemical properties were studied by the UV-vis, photoluminescence spectrum and cyclic voltammetry technology.¹⁹ Kaya et al. have been studied thermal and conductivity properties of oligo/polyphenols and their metal complexes. Antimicrobial properties of them were also studied. For example, antimicrobial activities of oligo-*N*-2-aminopyridinylsalicylaldimine, oligo-2-[(thien-2-yl-methylene)]aminophenol and their metal complexes was investigated by Kaya et al.^{20,21} Conjugated polymers can be used as light-emitting

Correspondence to: İ Kaya (kayaismet@hotmail.com).

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diodes, polymer lasers, and photovoltaic cells.²² Conjugated polyazomethines have been recognized as a new class of materials for organic light emission devices (OLED)s.²³ The electronic and optoelectronic properties of these materials depends on polymer chain structure containing donor or acceptor side groups such as heteroatoms or rings (pyridine, furan, or thiophene) with heteroatoms. Also, electronic and optoelectronic properties of these polymers depend on the π -electron delocalization connected with chain planarity. A decrease of planarity lowers the HOMO level but raises the LUMO level and leads to a wider band gap.^{23–26}

In this study, novel polyaminophenols substituted were synthesized and with their various properties were investigated. Electrical properties of doped and undoped the polyaminophenols were also determined by four-point probe technique using an electrometer.

EXPERIMENTAL

Materials

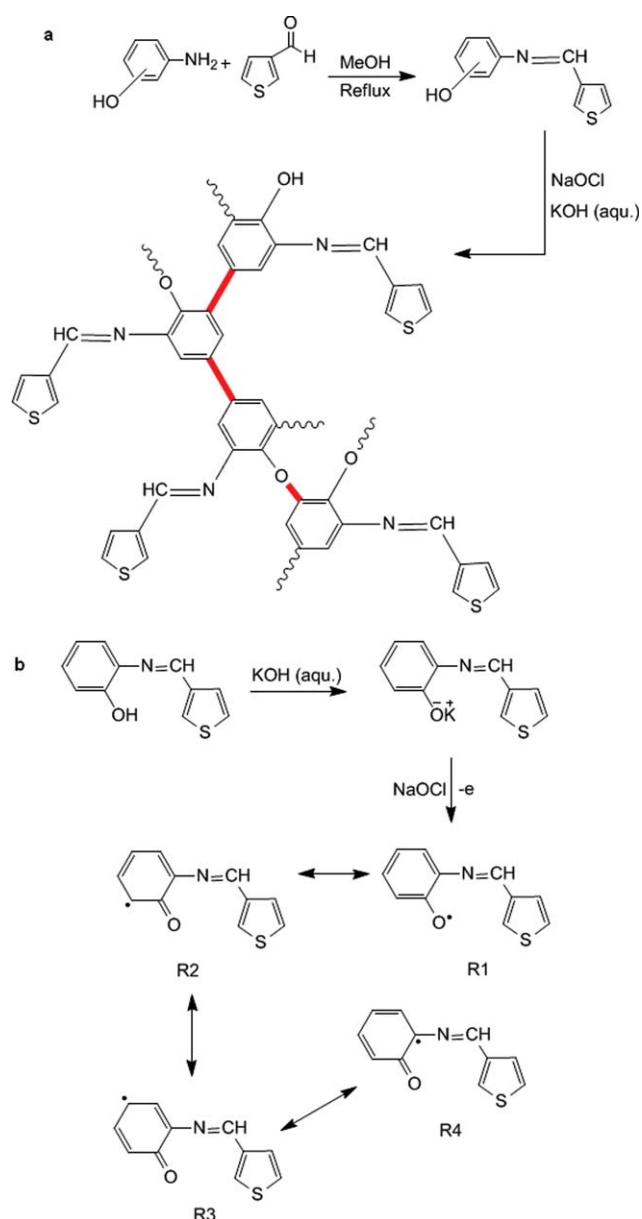
Thiophene-3-carboxyaldehyde, 2-aminophenol, 3-aminophenol, 4-aminophenol, methanol, acetonitrile, toluene, acetone, ethyl acetate, heptane, CHCl_3 , tetrahydrofuran (THF), dimethylsulfoxide (DMSO), H_2SO_4 (98%), KOH and hydrochloric acid (HCl, 37%), Cu $(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, Co $(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, Zn $(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Cd $(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Ni $(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were supplied from Merck Chemical Co. (Germany). Sodium hypochlorite (NaOCl), (30% aqueous solution) was supplied from Paksoy Chemical Co. (Turkey). Thiophene-3-carboxyaldehyde, 2-aminophenol, 3-aminophenol, and 4-aminophenol are used as received.

Syntheses of the aminophenol Schiff bases

2-[3-thienylmethylene]aminophenol (2,3-TP), 3-[3-thienylmethylene]aminophenol (3,3-TP) and 4-[3-thienylmethylene]aminophenol (4,3-TP) were prepared by the condensation reactions of thiophene-3-carboxyaldehyde (1.22 g, 0.01 mol) with 2-aminophenol (1.37 g, 0.01 mol), 3-aminophenol (1.37 g, 0.01 mol), and 4-aminophenol (1.37 g, 0.01 mol) in 25 mL methanol achieved by boiling the mixture under reflux for 3 h at 70°C (Scheme 1). The obtained Schiff bases were filtered, recrystallized from methanol and dried in vacuum oven at 60°C (The yields of Schiff bases \approx 70–75%).

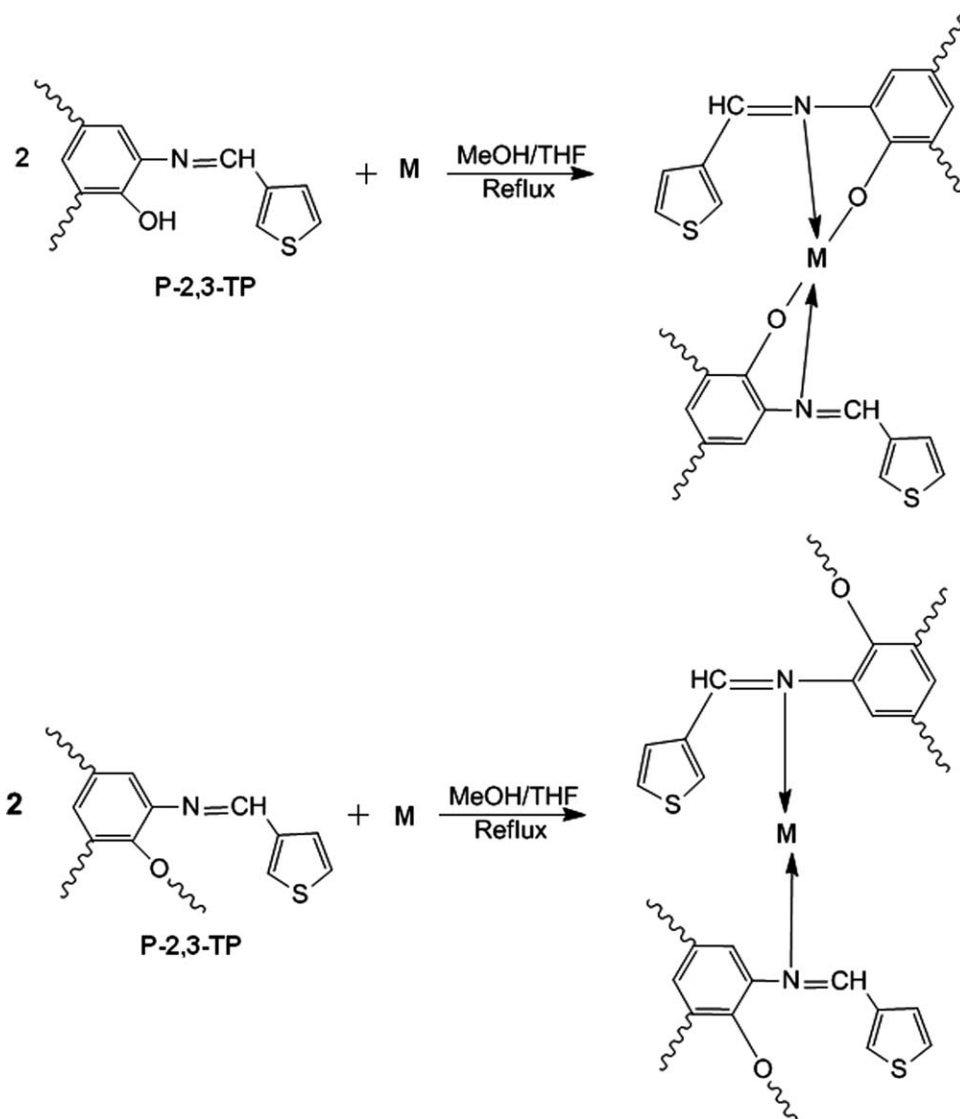
Syntheses of the polyaminophenols

Polyaminophenols (PAPs) (P-2,3-TP, P-3,3-TP and P-4,3-TP) were synthesized through oxidative polycondensation²⁷ of 2,3-TP, 3,3-TP and 4,3-TP in an aque-



Scheme 1 Syntheses of the PAPs (P-2,3-TP, P-3,3-TP and P-4,3-TP) (a) and polymerization mechanism of the PAPs (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

ous alkaline medium by NaOCl as oxidant (30%), respectively. Schiff bases (0.203 g, 0.001 mol) were separately dissolved in an aqueous solution of KOH (10%, 0.001 mol) and placed into a 50-mL three-necked round-bottom flask (Scheme 1). It was fitted with a condenser, thermometer, stirrer and an addition funnel containing NaOCl. Reactions were maintained under reflux for 5 h and the reaction mixtures were cooled at the room temperature and then 0.001 mol HCl (37%) was added. For the separation of mineral salts and unreacted monomers, the mixture was filtered and washed with hot water (3×10 mL for each polymer) and then dried in a vacuum oven at 60°C.



Scheme 2 Synthesis of poly-2-[3-thienylmethylene]aminophenol-metal complexes.

Syntheses of poly-2-[3-thienylmethylene]aminophenol (P-2,3-TP)-metal complexes

Solutions of Cu (CH₃COO)₂ · H₂O, Co (CH₃COO)₂ · 4H₂O, Zn (CH₃COO)₂ · 2H₂O, Cd (CH₃COO)₂ · 2H₂O, Ni (CH₃COO)₂ · 4H₂O and UO₂(NO₃)₂ · 6H₂O (1 mmol) in MeOH (10 mL) were added to a solution of P-2,3-TP (2 mmol/unit) in THF (20 mL). The mixture was stirred and heated at 70°C for 5 h (Scheme 2). The precipitated complexes were filtered, washed with cold MeOH/THF (1 : 1) and then dried in a vacuum oven at 60°C.

Electrochemical properties

Cyclic voltammetry (CV) measurements were carried out with a CHI 660 C Electrochemical Analyzer (CH Instruments, TX) at a potential scan rate of 25 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⁺) measured in acetonitrile solution of 0.1M tetrabutylammonium hexafluorophosphate (TBAPF₆) and was 0.39 V with respect to Ag wire. The voltammetric measurements were carried out in acetonitrile for the Schiff bases, acetonitrile/DMSO mixture (v/v : 10/1) for the polymers and polymer-metal complexes. The HOMO-LUMO energy levels and electrochemical band gaps (E_g') were calculated from oxidation and reduction onset values.²⁸

Electrical properties

The conductivities of synthesized polymers were measured on a Keithley 2400 Electrometer. The

TABLE I
Solubility Test Results of the Compounds Synthesized

Compounds	MeOH	ACN	Toluene	Acetone	Ethyl acetate	Heptane	CHCl ₃	THF	DMSO	H ₂ SO ₄
2,3-TP	+	+	⊥	+	+	---	+	+	+	+
3,3-TP	⊥	⊥	---	+	⊥	---	---	+	+	+
4,3-TP	⊥	⊥	---	+	+	---	---	+	+	+
P-2,3-TP	⊥	⊥	⊥	⊥	⊥	---	⊥	⊥	+	+
P-3,3-TP	⊥	⊥	---	⊥	---	---	---	⊥	+	+
P-4,3-TP	⊥	---	---	---	---	---	---	---	+	+
P-2,3-TP-Zn	⊥	+	---	⊥	---	⊥	⊥	⊥	+	+
P-2,3-TP-Cd	+	⊥	---	---	---	---	⊥	---	+	⊥
P-2,3-TP-Ni	+	⊥	⊥	⊥	⊥	---	⊥	⊥	+	⊥
P-2,3-TP-Co	⊥	⊥	⊥	⊥	⊥	---	---	⊥	+	+
P-2,3-TP-U	⊥	⊥	---	⊥	---	---	⊥	⊥	⊥	⊥
P-2,3-TP-Cu	⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥

MeOH, methanol; CAN, acetonitrile; CHCl₃, chloroform; THF, tetrahydrofuran; DMSO, dimethylsulfoxide; H₂SO₄, sulphuric acid; +, soluble; ⊥, partially soluble, -, insoluble.

pellets were pressed on hydraulic press developing up to 1687.2 kg/cm². Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in desiccator.²⁹

Optical properties

The optical band gaps (E_g) of monomer, polymer and polymer-metal complexes were calculated from their absorption edges. Ultraviolet-visible (UV-vis) spectra were measured by Perkin-Elmer Lambda 25. The absorption spectra of the compounds were recorded by using DMSO at 25°C.

Fluorescence measurements

A Shimadzu RF-5301PC spectrofluorophotometer was used in fluorescence measurements. Emission and excitation spectra of compounds were obtained in DMSO solutions with the different concentration (mg L⁻¹). The optimal emission and excitation wavelengths in each compound were determined. Also, optimizations of the concentrations to obtain maximal emission intensity values were investigated in DMSO for each compound.

Solubility and characterization techniques

While 2,3-TP was yellow color in crystal form and was completely soluble in organic solvents such as methanol, acetone, acetonitrile, THF, ethyl acetate, chloroform, H₂SO₄ and DMSO but it was partly soluble in toluene. 2,3-TP was only insoluble in heptane. P-2,3-TP was dark brown in powder form and was completely soluble in solvents such as H₂SO₄ and DMSO. P-2,3-TP was partly soluble in methanol, acetonitrile, toluene, acetone, ethyl acetate, chloroform, and THF. P-2,3-TP was only insoluble in

heptane as its monomer. Solubility test results of the other compounds are given in Table I.

The infrared and UV-vis spectra were measured by Perkin-Elmer FT-IR Spectrum One and Perkin-Elmer Lambda 25, respectively. UV-vis spectra of compounds were recorded by using DMSO. The aminophenol derivatives were characterized by using ¹H NMR and ¹³C NMR spectra (Bruker Avance DPX-400 and 100.6 MHz, respectively) recorded at 25°C by using deuterated DMSO as a solvent. Tetramethylsilane was used as internal standard. Thermal data were obtained by using Perkin-Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between 20 and 1000°C (in N₂, rate 10°C/min). DSC analyses of polyaminophenols were carried out by using Perkin-Elmer Pyris Sapphire DSC. DSC measurements were made between 35 and 420°C (in N₂, rate 10°C/min). The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) were determined by using GPC/Multi-Angle Light Scattering technique (GPC/MALS) with a Macherey-Nagel GmbH and Co. (Germany) (100 Å and 7 nm diameter loading material) 7.7 mm i.d. × 300 mm columns, DMF/MeOH eluent (0.4 mL min⁻¹, v/v, 4/1), and a refractive index detector at 30°C (Shimadzu Co. Japan).

RESULTS AND DISCUSSION

Structures of the APs and PAPs

FT-IR data of monomer, polymer and polymer-metal complexes are given in Table II, respectively. The hydroxyl and azomethine bands of 2,3-TP and P-2,3-TP were observed 3298 and 1615; 3228 and 1607 cm⁻¹, respectively. IR spectra of polymers show a red shift vibration bands in comparison to their corresponding monomers. as shown this figure. In

TABLE II
FT-IR Spectral Data of 2,3-TP, P-2,3-TP, 3,3-TP, P-3,3-TP, 4,3-TP, P-4,3-TP and P-2,3-TP's Metal Complexes

Compounds	Wave number (cm ⁻¹)						Metal-O	Metal-N
	—OH	—CH=N	—C—S	—C=C	—C—O			
2,3-TP	3298	1615	750	1595, 1580, 1524	1217	—	—	
P-2,3-TP	3228	1607	745	1565, 1512, 1497	1223	—	—	
3,3-TP	3185	1615	774	1590, 1505, 1444	1236	—	—	
P-3,3-TP	3190	1608	771	1588, 1504, 1428	1234	—	—	
4,3-TP	3265	1611	774	1585, 1519, 1501	1233	—	—	
P-4,3-TP	3165	1595	799	1555, 1499, 1444	1219	—	—	
P-2,3-TP-Cu	3266	1595	747	1524, 1440, 1418	1255	547	625	
P-2,3-TP-Zn	3009	1591	753	1540, 1446, 1406	1231	552	612	
P-2,3-TP-Cd	3136	1581	747	1531, 1436, 1408	1204	542	613	
P-2,3-TP-U	3098	1607	747	1518, 1488, 1459	1282	570	683	
P-2,3-TP-Co	3317	1581	748	1559, 1532, 1497	1249	583	665	
P-2,3-TP-Ni	3098	1586	738	1516, 1507, 1413	1253	546	675	

addition, the absorption bands of the metal-oxygen (M-O) and the metal-nitrogen (M-N) linkages were appeared in range of 542–583 cm⁻¹ and 612–683 cm⁻¹, respectively. The absorption bands range of C-S stretch vibrations were observed between 738 and 799 cm⁻¹. A detailed FT-IR data of the other compounds are given in Table II.

To identify the structures of monomer and polymer, the ¹H NMR and ¹³C NMR spectra were recorded in DMSO-d₆. ¹H NMR and ¹³C NMR spectral data of the some synthesized compounds are given in Table III. According to obtained ¹H NMR spectral data of 2,3-TP and P-2,3-TP, the signals of phenolic —OH and —CH=N groups were observed in 9.93 and 8.68 ppm and 10.02 and 9.20 ppm, respectively. The NMR spectral data results of P-2,3-TP confirm formation of polymer units. Phenols having azomethine group were polymerized, and the results are reported in the literature.^{21,27,28} As examined these spectral data, it is understood that 2,3-TP was polymerized mainly by C—O and/or C—C coupling mechanism. The coupling ratios (C—O and/or C—C) using the integration ratio of imine and —OH

protons can be determined from the ¹H NMR spectra.³⁰ The ¹H NMR results show that the polymerization of 2,3-TP mainly proceeds via *ortho* and *para* positions of phenolic —OH group. According to ¹H NMR spectral data of phenolic —OH group of P-3,3-TP completely disappeared because polymerization proceed via C—O coupling.

Optical and electrochemical properties

The UV-vis spectroscopic studies were carried out in DMSO solutions of all compounds obtained. The UV-vis spectra of the synthesized compounds are shown in Figure 1. According to these spectra, a red shift occurs at the absorption edges of the synthesized polymers as compared to their corresponding monomers. This is because of the polyconjugated structures of the polymers. This polyconjugation increases HOMO and decreases LUMO energy levels resulting lower band gaps. The optical band gaps (E_g) of monomers, polymers and P-2,3-TP's metal complexes were determined as in the literature²¹ and given in Table IV. These results show that the synthesized polymers

TABLE III
The NMR Data of 2,3-TP, 4,3-TP, P-2,3-TP, and P-3,3-TP

Compounds	Spectral data (δ ppm)
2,3-TP	¹ H-NMR (DMSO-d ₆): 9.93 (s, 1H, —OH), 8.68 (s, 1H, —CH=N—), 7.81 (s, 1H, Ar-Ha), 7.69 (d, 1H, Ar-Hb), 7.02 (d, 1H, Ar-Hc), 7.25 (d, 1H, Ar-Hd), 7.19 (t, 1H, Ar-He), 6.90 (t, 1H, Ar-Hf), 7.39 (d, 1H, Ar-Hg). ¹³ C-NMR (DMSO-d ₆): 151.59 (C1-ipso-OH), 115.25 (C2-H), 127.13 (C3-H), 120.33 (C4-H), 116.05 (C5-H), 135.95 (C6-ipso), 152.37 (C7-H), 140.81 (C8-ipso), 125.95 (C9-H), 128.93 (C10-H), 130.88(C11-H).
4,3-TP	¹ H-NMR (DMSO-d ₆): 9.42 (s, 1H, —OH), 8.56 (s, 1H, —CH=N—), 8.04 (s, 1H, Ar-Ha), 7.58 (d, 1H, Ar-Hb), 7.13 (d, 1H, Ar-Hg, Hd), 6.78 (d, 1H, Ar-Hf, He, Hc). ¹³ C-NMR (DMSO-d ₆): 126.10 (C1, C5-H), 116.40 (C2, C4-H), 152.59 (C3-ipso-OH), 141.66 (C6-ipso), 156.75 (C7-H), 143.53 (C8-ipso), 122.90 (C9-H), 128.08 (C10-H), 131.08 (C11-H).
P-2,3-TP	¹ H-NMR (DMSO-d ₆): 10.02 (s, 1H, —OH), 9.20 (s, 1H, —CH=N—), 8.79 (s, 1H, Ar-Ha), 8.61 (d, 1H, Ar-Hb), 7.62 (d, 1H, Ar-He), 7.33 (d, 1H, Ar-Hc), 6.88 (d, 1H, Ar-Hd).
P-3,3-TP	¹ H-NMR (DMSO-d ₆): 9.06 (s, 1H, —CH=N—), 8.67 (s, 1H, Ar-Ha), 8.51 (d, 1H, Ar-Hb), 7.58 (d, 1H, Ar-He), 7.25 (d, 1H, Ar-Hc), 6.56 (s, 1H, Ar-Hd).

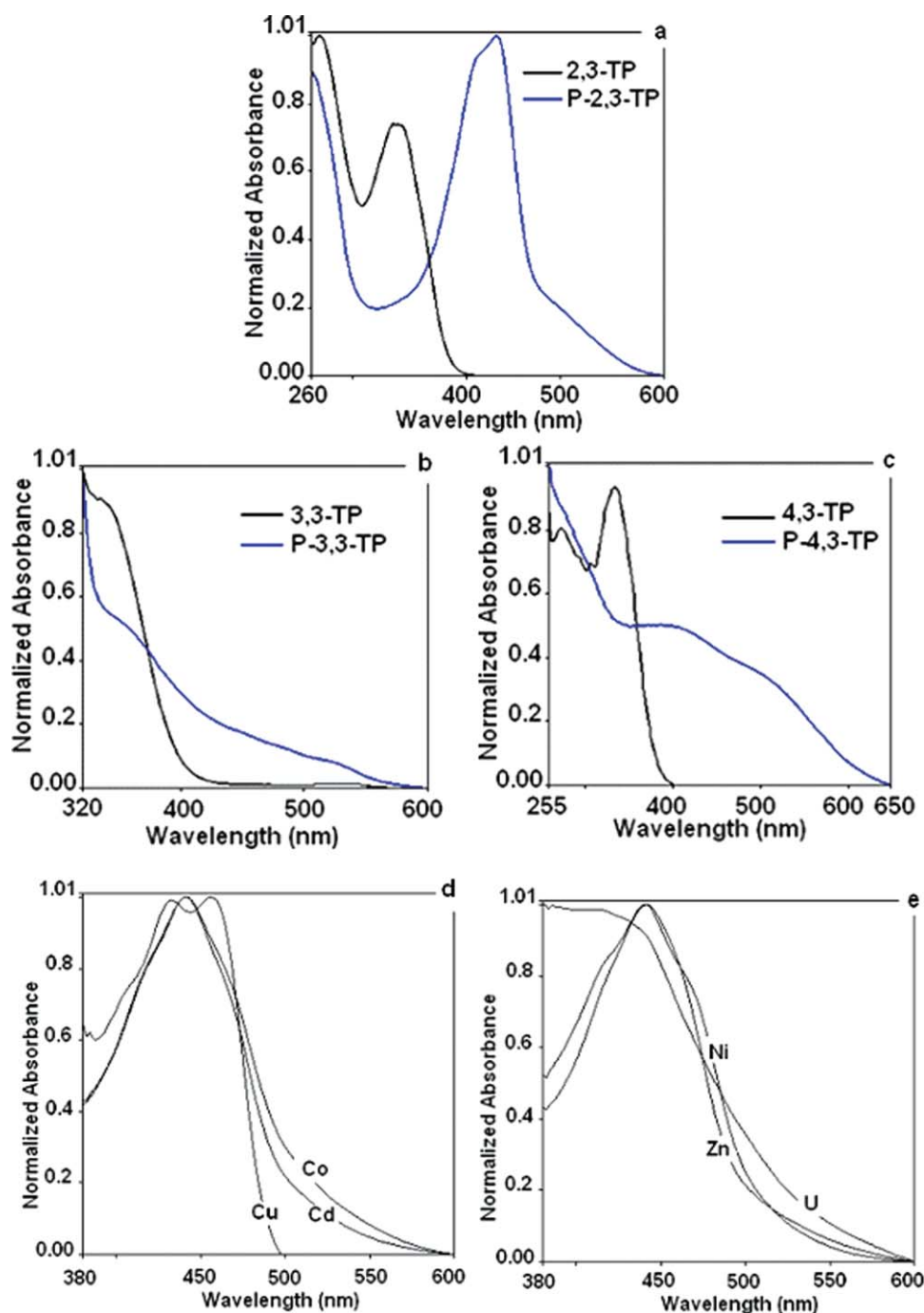


Figure 1 Absorption spectra of 2,3-TP and P-2,3-TP (a), 3,3-TP and P-3,3-TP (b), 4,3-TP and P-4,3-TP (c), P-2,3-TP's metal complexes (d) and (e). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

have lower optical band gaps as expected. It is seen from Figure 1, the red shifting of the $-\text{CH}=\text{N}-$ bands of the polymers demonstrate the formation of the polymeric conjugate π -system. The optical band gaps can be different from the electrochemical band gaps calculated, in some cases. It is important to realize that there should be a difference which can be explained by the dissimilar nature of the measurements where different energy processes contribute to band gap estimation.²⁹

According to the cyclic voltammetry (CV) measurements, HOMO-LUMO energy levels and the electrochemical band gaps (E_g') of compounds were calculated and given in Table IV. These data were estimated by using the oxidation onset (E_{ox}) and reduction onset (E_{red}) values. The calculations were made by using the following equations³⁰:

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

TABLE IV
Electrochemical and Optical Parameters of the Compounds Synthesized

Compounds	λ_{\max}^a (nm)	HOMO ^b (eV)	LUMO ^c (eV)	E_g^d (eV)	$E_g'^e$ (eV)
2,3-TP	396	-6.31	-3.09	3.14	3.22
P-2,3-TP	564	-5.11	-3.38	2.20	1.73
3,3-TP	405	-5.28	-2.66	3.07	2.62
P-3,3-TP	568	-5.29	-3.26	2.19	2.03
4,3-TP	383	-5.43	-3.17	3.24	2.32
P-4,3-TP	621	5.64	-3.30	2.00	2.34
P-2,3-TP-Cd	529	-4.39	-2.97	2.35	1.42
P-2,3-TP-Co	562	-5.66	-3.31	2.21	2.35
P-2,3-TP-Cu	492	-5.52	-3.27	2.52	2.25
P-2,3-TP-Ni	527	-5.74	-3.34	2.36	2.40
P-2,3-TP-U	565	-5.17	-3.53	2.20	1.64
P-2,3-TP-Zn	559	-5.20	-2.83	2.22	2.37

^a Maximum wavelength.

^b Highest occupied molecular orbital.

^c Lowest unoccupied molecular orbital.

^d Optical band gap.

^e Electrochemical band gap.

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

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

The obtained results indicate that after polymerization, HOMO energy levels increase, while LUMO energy levels decrease. Therefore, 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. Cyclic voltammograms of the monomers, polymers, and metal complexes are given in Figure 2. According to the electrochemical analysis results, the order of the electrochemical band gap values of the polymers changes as follows: P-2,3-TP < P-3,3-TP < P-4,3-TP. However, the order of the optical band gaps of the polymers is different and is as follows: P-4,3-TP < P-3,3-TP \approx P-2,3-TP. The order of the electrochemical band gap values of the polymer-metal complexes changes as follows: P-2,3-TP-Cd < P-2,3-TP-U < P-2,3-TP-Cu < P-2,3-TP-Co < P-2,3-TP-Zn < P-2,3-TP-Ni. However, the order of the optical band gaps of the polymer-metal complexes were different and as follows: P-2,3-TP-U < P-2,3-TP-Co < P-2,3-TP-Zn < P-2,3-TP-Cd < P-2,3-TP-Ni < P-2,3-TP-Cu. As seen in Table IV the optical band gaps are slightly higher than those of the electrochemical ones. These results are in agreement with the literature data.³¹

GPC analysis

The number-average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) values of the PAPs were calculated using RI detector from GPC measurements.

Obtained GPC results show that the total values the molecular weight of P-4,3-TP is higher than the total molecular weights of P-2,3-TP and P-3,3-TP. The M_n , M_w , and PDI values of P-2,3-TP, P-3,3-TP and P-4,3-TP were found to be 16,450 g mol⁻¹, 18,800 g mol⁻¹ and 1.143; 10,700 g mol⁻¹, 13,750 g mol⁻¹ and 1.285; 34,800 g mol⁻¹, 37,500 g mol⁻¹ and 1.078, respectively. As seen these results, in contrast to the other monomers, 4,3-TP is easily polymerized even at low temperatures. This suggests that the radicalic stability of the growing polymer chains of 4,3-TP is kept for a longer time. As a result, a longer polymer chain is obtained for P-4,3-TP during the polymerization. These results also agree with the solubility tests. P-2,3-TP and P-3,3-TP have low molecular weights. The low molecular weight of compounds obtained consistent with their better solubility. Polymers were soluble in common organic solvents such as acetonitrile, acetone and THF. P-4,3-TP has lower solubility due to its high-molecular weighted structures.³²

Fluorescence

Fluorescence measurements of the synthesized materials are carried out using DMSO. The fluorescence intensity values in DMSO with the different concentrations (mg L⁻¹) are seen in Table V. As seen in Figure 3, the PAPs had quite higher fluorescence intensities when they compared with their monomers. This is probably because of the polyconjugated structures of the PAPs. The results show that the order of the fluorescence intensities of the polymers is different and is as follows: P-4,3-TP < P-2,3-TP < P-3,3-TP. To obtain maximal fluorescence intensity in DMSO should be used the different concentrations of the synthesized compounds. Fluorescence

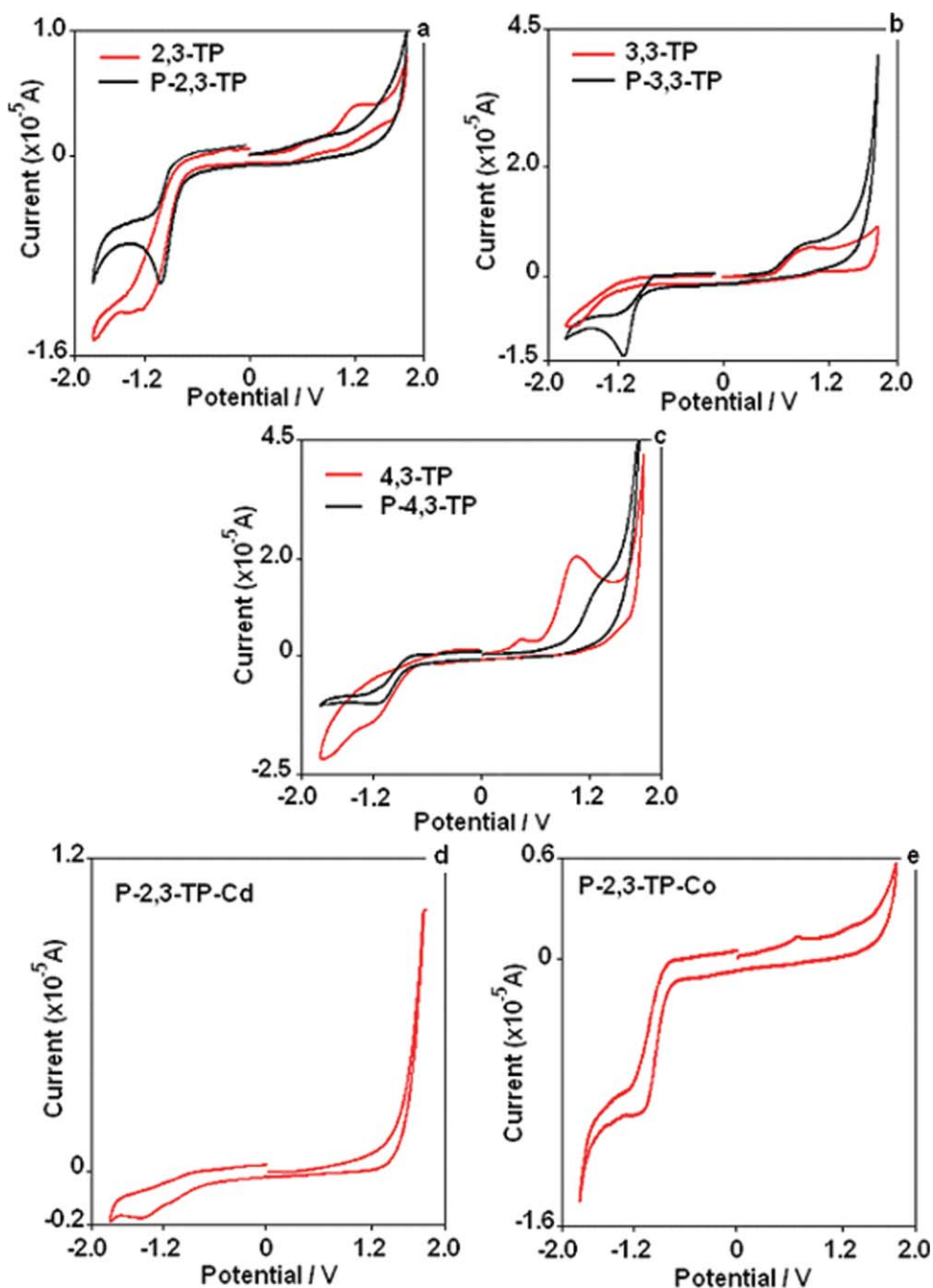


Figure 2 Cyclic voltammograms of 2,3-TP and P-2,3-TP (a), 3,3-TP and P-3,3-TP (b), 4,3-TP and P-4,3-TP (c), P-2,3-TP-Cd (d), P-2,3-TP-Co (e), P-2,3-TP-Cu (f), P-2,3-TP-U (g), P-2,3-TP-Ni (h), P-2,3-TP-Zn (i). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

data and the concentrations are also summarized in Table V. As seen in Table V, exception of P-2,3-TP-Cd the other synthesized materials have a bit high Stoke's shift values ($\Delta\lambda_{ST}$). Stoke's shift is an important value for a fluorescence sensor. The higher Stoke's shift value supplies very low background signals and resultantly allow the usage of the material in construction of a fluorescence sensor.³³ A series of Schiff bases and some chelate-structured polymer models have been presented as

possible ion-selective sensors depending on quenching of the fluorescence intensity values when exposed to corresponding ion like Fe (II), Cu (II), etc.^{34–36} Additionally, P-2,3-TP-Zn has high fluorescence intensity and it can give a selective-sensitive response against Zn^{+2} ion. Moreover, the order of the fluorescence intensities of the polymer-metal complexes is different and is as follows: P-2,3-TP-Cu < P-2,3-TP-Co < P-2,3-TP-Ni < P-2,3-TP-U < P-2,3-TP-Cd < P-2,3-TP-Zn.

TABLE V
Fluorescence spectral data of the compounds synthesized

Compounds	$\lambda_{\text{Ex}}^{\text{a}}$	$\lambda_{\text{Em}}^{\text{b}}$	$\lambda_{\text{max}}(\text{Ex})^{\text{c}}$	$\lambda_{\text{max}}(\text{Em})^{\text{d}}$	I_{Ex}^{e}	I_{Em}^{f}	$\Delta\lambda_{\text{ST}}^{\text{g}}$	Conc. (mg L ⁻¹) ^h
2,3-TP	404	497	404	490	77	78	86	100
3,3-TP	306	444	301	433	53	53	132	50
4,3-TP	311	386	295	374	104	88	79	6.25
P-2,3-TP	304	359	298	350	189	189	52	6.25
P-3,3-TP	552	558	535	562	1120	1050	27	100
P-4,3-TP	335	386	345	374	33	40	29	0.781
P-2,3-TP-Zn	273	380	272	376	632	659	104	50
P-2,3-TP-U	508	553	508	555	327	334	47	100
P-2,3-TP-Cd	508	526	507	526	480	480	19	100
P-2,3-TP-Cu	317	364	296	353	71	58	57	25
P-2,3-TP-Ni	295	354	294	349	141	140	55	50
P-2,3-TP-Co	295	353	293	351	127	127	58	12.5

^a Excitation wavelength for emission.

^b Emission wavelength for excitation.

^c Maximum emission wavelength.

^d Maximum excitation wavelength.

^e Maximum excitation intensity.

^f Maximum emission intensity.

^g Stoke's shift.

^h Concentration (mg L⁻¹), DMSO was used as organic solvent.

The optimization of the concentrations to obtain maximal emission intensity is also investigated in DMSO because of all of the compounds are completely soluble in DMSO. The obtained results show that the synthesized materials have the maximum fluorescence intensity in the concentration range of 0.781–100 mg L⁻¹. However, the optimal fluores-

cence concentration of P-4,3-TP is quite lower than the other compounds.

Thermal analysis

Thermal degradation results of compounds are given in Table VI. TGA and DTG curves of the

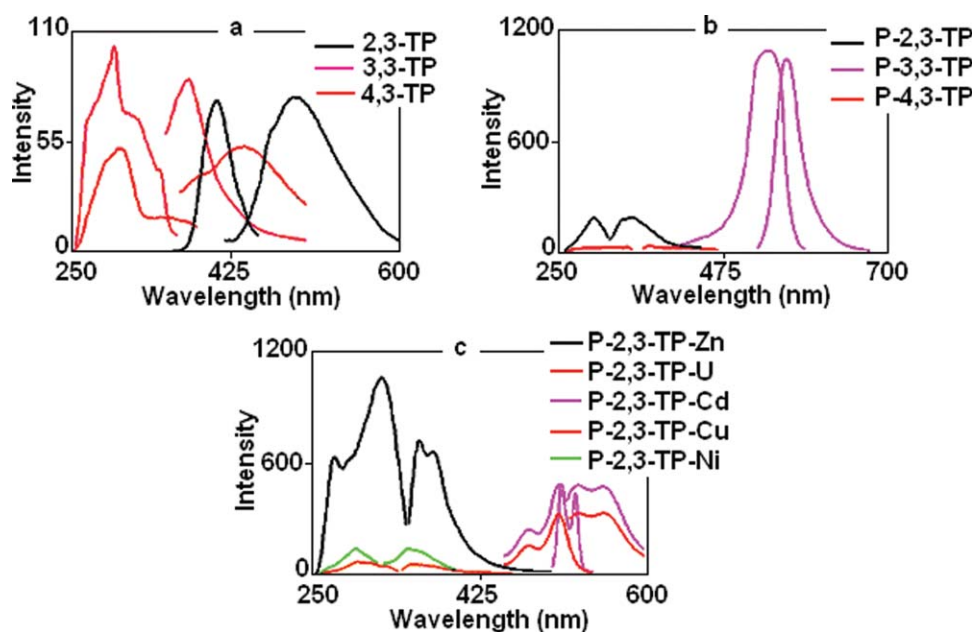


Figure 3 Emission and excitation spectra of 2,3-TP, 3,3-TP and 4,3-TP (a), P-2,3-TP, P-3,3-TP and P-4,3-TP (b), P-2,3-TP-Zn, P-2,3-TP-U, P-2,3-TP-Cd, P-2,3-TP-Cu and P-2,3-TP-Ni (c) in DMSO. Conditions: Slit: λ_{Ex} 5nm, λ_{Em} 5nm; concentration of the compounds (mg L⁻¹): 100, 50, 6.25, 6.25, 100, 0.781, 50, 100, 100, 25, 50 for 2,3-TP, 3,3TP, 4,3-TP, P-2,3-TP, P-3,3-TP, P-4,3-TP, P-2,3-TP-Zn, P-2,3-TP-U, P-2,3-TP-Cd, P-2,3-TP-Cu, P-2,3-TP-Ni, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VI
Thermal Degradation Values of the Compounds Synthesized

Compounds	T_{on}^{a}	$T_{\text{max}}^{\text{b}}$	20% weight losses	50% weight losses	% Char at 1000°C	DTA Endo	DSC	
							T_g^{c} (°C)	ΔC_p^{d} (J/g °C)
P-2,3-TP	200	232, 547	352	–	55.33	–	173	0.462
P-3,3-TP	255	272, 449	331	991	50.55	272	198	0.047
P-4,3-TP	269	312, 409	552	–	62.28	–	223	0.067
P-2,3-TP-Cd	247	280, 579	266	481	7.70	239, 290, 586	–	–
P-2,3-TP-Co	177	280, 551, 817	294	723	28.58	491	–	–
P-2,3-TP-Cu	197	228, 870	225	668	36.26	112, 227, 495	–	–
P-2,3-TP-Ni	311	90, 330, 398	313	450	51.12	97, 340, 482	–	–
P-2,3-TP-Zn	209	241	225	248	21.93	248, 493	–	–
P-2,3-TP-U	134	178, 326	287	–	68.74	–	–	–

^a The onset temperature.

^b Maximum temperature.

^c Glass transition temperature.

^d Change of specific heat during glass transition.

synthesized polymers and their metal complexes are also shown in Figures 4(a,b) and 5(a,b) respectively. According to the TGA results, the initial degradation temperature (T_{on}) of P-2,3-TP is lower than P-4,3-TP and P-3,3-TP. This is probably because of formation of C—O—C etheric bond during the oxidative polycondensation. This weak bond is easily broken at moderate temperatures and this results in thermally as unstable polymer. Additionally, P-4,3-TP has the highest molecular weight among polymers and its C—O coupling rate is relatively low, as explained above. The higher C—C coupling rate and molecular weight are responsible for higher thermal stability of P-4,3-TP. On the other hand, TGA results show that the synthesized polymers lost about 50–60% of their weights at 1000°C, while P-2,3-TP, P-3,3-TP, and P-4,3-TP lost 55.33%, 50.55%, and 62.28% of their weights, respectively. According to the TGA results, the initial degradation temperatures of P-2,3-TP-U and P-2,3-TP-Co is lower than the polymers. Moreover, P-2,3-TP-U has the highest carbene residue when polymer–metal complexes are heated until 1000°C. In the range of 30–300°C for all the compounds occurred

definite weight missing. This event probably originates from adsorbed and coordination water in the Co, Cu, Cd, U, Zn, and Ni-polymer complexes at different values and quantities. These values are to be found as 13.98%, 24.52%, 6.80%, 6.7%, 6.35%, 8.25%, 18.25%, and 10.00% for P-2,3-TP, P-3,3-TP, P-4,3-TP, P-2,3-TP-Cd, P-2,3-TP-Co, P-2,3-TP-Cu, P-2,3-TP-Ni, and P-2,3-TP-U. Theoretically the calculated these values are different for polymer–metal complexes as follows: 6.57%, 13.56%, 13.56%, 7.16%, 3.73%, and 14.46% for P-2,3-TP-Cd, P-2,3-TP-Co, P-2,3-TP-Ni, P-2,3-TP-Zn, P-2,3-TP-Cu, and P-2,3-TP-U. In this dehydration process, the ease of adsorbed water desolvation ($20^\circ\text{C} \leq T \leq 96^\circ\text{C}$) in these complexes suggests the weak interaction of water.³⁷ Temperature ranges reported^{38–40} for the release of coordinated water molecules in some complexes (Fe, Ni, etc.). From DTA analysis results of the polymers and polymer–metal complexes are not observed any exothermic peaks. Also, the some polymer–metal complexes have not endothermic peaks. However, more sensitive measurements were carried out by DSC method to determine the exothermic and endothermic events for the polymers and

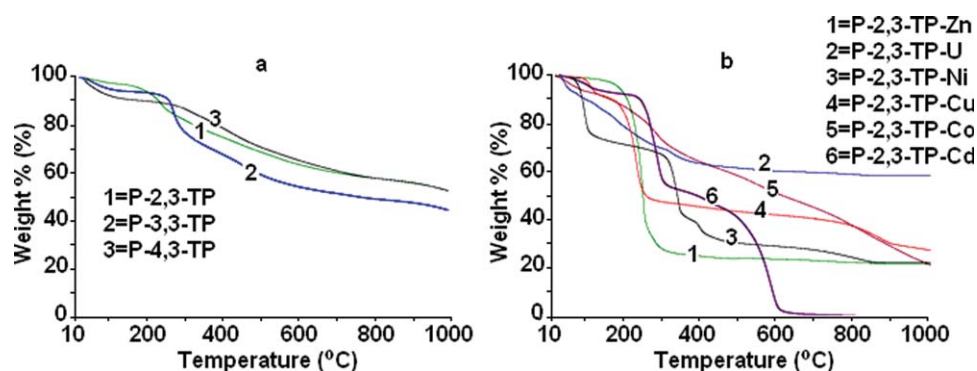


Figure 4 TGA curves of the polymers (a) and polymer-metal complexes (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

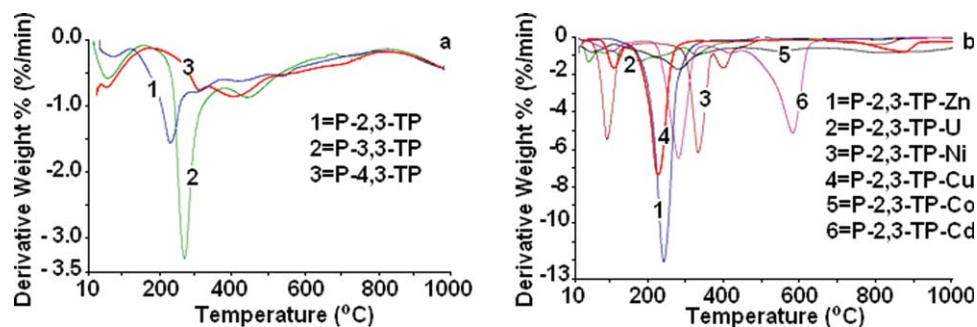


Figure 5 DTG curves of the polymers (a) and polymer-metal complexes (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wide endo and exo peaks were obtained with no definite melting peaks. The glass transition temperatures (T_g) and changes of specific heat during glass transition (ΔC_p) of P-2,3-TP, P-3,3-TP and P-3,3-TP were calculated from the DSC traces and given in Table VI. T_g values of P-2,3-TP, P-3,3-TP and P-3,3-TP were found as 173, 198, and 223°C, respectively.

Electrical conductivities

Electrical conductivities of the synthesized PAPs and the changes of these values related to doping time with iodine are determined and shown in Figure 6. As seen in Figure 6, at the undoped states of the polymers P-4,3-TP has a bit high conductivity whereas P-2,3-TP and P-3,3-TP have lower conductivities. This results in higher conductivity, and consequently due to having lower band gap P-2,3-TP has higher conductivity than the other polymers. However, it's seen in the doping state conductivities that the maximal conductivity increase and maximal final conductivity can be obtained for P-2,3-TP. This is possibly from $-\text{OH}$ group on *ortho* positions of P-2,3-TP and imine ($\text{CH}=\text{N}$) bond coordinated with an iodine molecule. Additionally, the electron pairs on $-\text{OH}$ group takes part to conjugation in polymer

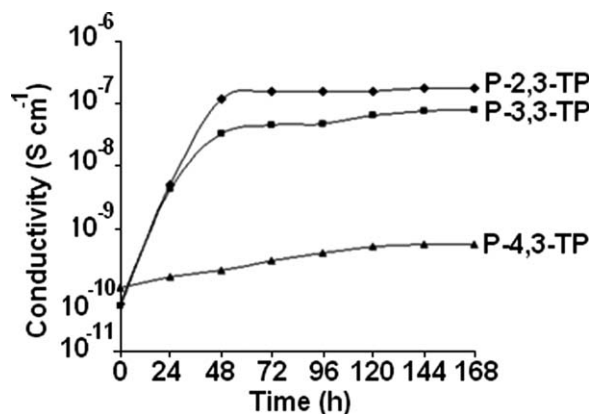
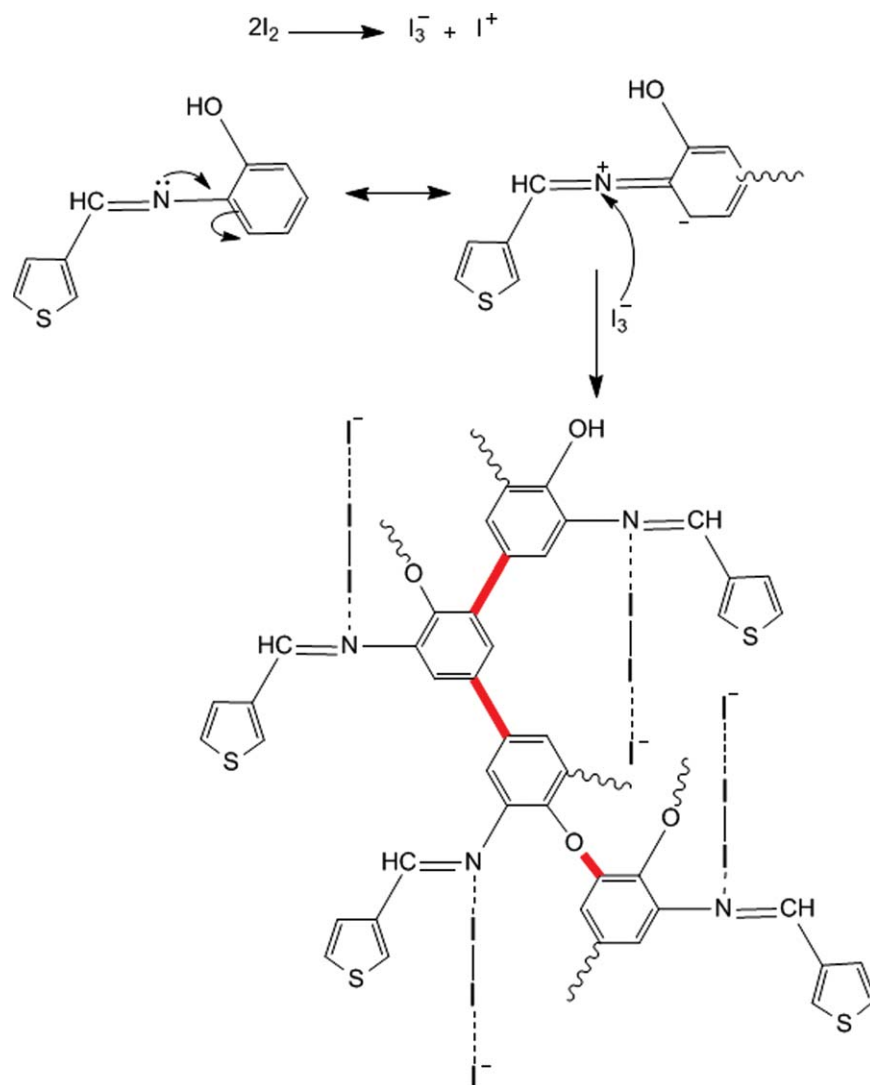


Figure 6 Electrical conductivity changes of the I_2 -doped polymers at 25°C.

chain. Consequently, the electrical conductivity of P-2,3-TP is the highest than the other polymers. Moreover, the little significant difference in conductivities of P-2,3-TP and P-3,3-TP was observed. P-4,3-TP has the lowest conductivity because of $-\text{OH}$ groups are on *para* positions. This is probably from distant locations of $-\text{OH}$ groups and imine ($\text{CH}=\text{N}$) bond. Diaz et al. suggested the doping mechanism of Schiff base polymers.³⁰ According to doping 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.⁴¹ As a result the synthesized polyaminophenols, especially P-2,3-TP and P-3,3-TP can be used as semiconductive materials in electronic or opto-electronic studies after a long time iodine doping. Conductivity measurements of imine polymers have been previously studied and a considerable increase was reported when they doped with iodine.⁴² This procedure produces a lot of application fields for conducting polymers. With these properties conducting polymers are used in gas sensing materials against several kinds of electro-donor (such as CO , CO_2 , NH_3 , H_2S , etc.) and electro-acceptor (such as I_2 and NO_2) gases.^{43–46} These studies show that the doping level and electrical conductivities of a conducting polymer can be changed considerable by doping with chemical vapors. The sensing process of the conductive/semiconductive polymers generally depends on the electron transferring mechanism from the analytes.⁴⁵ Coordination of iodine during P-2,3-TP doping is as follow at Scheme 3. On the nitrogen atom coordination of iodine ions with Schiff base polymers and pyridine solutions had been suggested at the literatures⁴⁷ as follows:

CONCLUSIONS

Novel Schiff bases and Schiff base substituted polyaminophenol derivatives containing thiophene in the side chain were synthesized by condensation reaction



Scheme 3 Coordination of iodine ions during P-2,3-TP doping. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of thiophene-3-carboxaldehyde with aromatic 2-, 3-, 4-aminophenols. The oxidative polycondensation of 2,3-TP, 3,3-TP and 4,3-TP was carried out in an aqueous alkaline medium by NaOCl oxidant (30%). The synthesized PAPs have quite higher fluorescence intensities than their monomer models. Specially, P-3,3-TP can be a promising spectrofluorometric ion sensor because of the highly fluorescence intensity. According to the optical and electrochemical analyses the synthesized polymers have quite low band gaps compared to their monomers. P-2,3-TP has the lowest band gap and resultantly the highest conductivity. Thermal degradation characteristics were also determined. According to thermal analyses results initial degradation temperatures of the polymers were quite high in the range of 200–267°C. P-4,3-TP is more stable of the synthesized polymers. The initial degradation temperature (T_{on}) of metal complexes are generally very well as P-2,3-TP-Ni, P-2,3-TP-Zn, and

P-2,3-TP-Cu. Moreover, in this study, we aim to introduce sequences of polyaminophenols with -OH group substitute on *ortho*, *meta* or *para* positions, Schiff bases and polymer-metal complexes for various properties such as optical, electrochemical, conductivity and fluorescent, etc.

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