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ORIGINAL ARTICLE

Synthesis, Characterization and Fluorescence Quantum Yields of Thermally Resisted Shinning Polymers Containing Thiophene and Azomethine Units

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Abstract

Poly(azomethine)s containing thiophene with bridges pyridine, sulphur and oxygen were synthesized in two steps. Before, thiophene centric dialdehyde (DIAL-Th) compound was synthesized via elimination reaction of 4-hydroxy benzaldehyde with thiophene bromide. Then, poly(azomethine)s containing thiophene (PAZ-Th) unit were synthesized from condensation reactions of DIAL-Th with pyridine-3,5-diamine, 4,4′-thiodianiline and 4,4′-oxydianiline. The obtained dialdehyde and poly(azomethine-thiophene)s were ratified by fourier-transform infrared spectroscopy (FT-IR), ultraviolet–visible spectroscopy (UV-Vis), hydrogen and carbon nuclear magnetic resonance spectroscopy (^{1}H-^{13}C-NMR) measurements. The some properties of poly(azomethine-thiophene)s were investigated such as optic, electronic, surface and thermal. Electrochemical and fluorescence properties of compounds were made by cyclic voltammetry (CV) and fluorescence analysis, respectively. According to fluorescence measurement, PAZ-Th-1 was interestingly demonstrated five different colors in DMF solution. Blue, green, yellow, orange and red were observed at 420, 440, 480, 500 and 520 nm, respectively, in this solution. The fluorescence quantum yields of PAZ-Th-1 were found to be 4.0, 15.0, 18.0, 6.4 and 6.2% at 420, 440, 480, 500 and 520 nm, respectively. According to thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses, T_{onset} and glass transition temperature of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were found as 256, 248, 224 °C and 162, 176, 137 °C, respectively. Also, surface analyses of synthesized poly(azomethine-thiophene)s were photographed by scanning electron microscope (SEM) at room temperature.

Keywords Poly(azomethine)s · Multichromic properties · Thermal resistance · Fluorescence quantum yield

Introduction

Thiophene has specific aromatic compound with containing five-carbureted aromatic structure and hetero sulphur atom also it is obtained quite easily from ingenuous products especially coal or petroleum. Name of thiophene that coalescence of the ion (sulphur) and phaino (shinning) is cited from Grek language. It is substantially important for pharmacological products [1]. Poly(thiophene)s have sequacious π-conjugated polymeric chain, high useful modification, applicable electrical and optical especially thermo/photo/piezo/biochromic properties for emission and conductive materials [2–9]. Likewise, they are useful candidate light emitting diodes, gas sensors, biomedical materials [10–20].

Azomethines have obtained from condensation reactions of aldehyde and primer amine compounds. Their macro covalent dynamic molecules are called as poly(azomethine)s and poly(imine)s. Poly(azomethine)s and derivatives are constantly used design of new materials owing to π conjugations between carbon and nitrogen atoms. They are generally applicable compounds for electro-photoactive and aerospace materials, light emitting diodes, dye-sensitized solar cells, electrochemical sensors and perovskite photovoltaics [21–25]. Poly(pyridine)s are also sort of aromatic poly(azomethine) due to containing imine bond on the aromatic rings. They have high quantum yields with certain derivatives especially ruthenium complexes and use light emitters in light-emitting electrochemical cells, light-triggered drug release and imaging of live cell and pH-responsive luminescence [26–28].

Before we synthesized dialdehyde (DIAL-Th) with thiophene centric from elimination reaction of 4-hydroxybenzaldehyde

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with 2,5-dibromothiophene. Then, three different poly(azomethine-thiophene)s abbreviated as PAZ-Th-1, PAZ-Th-2, PAZ-Th-3 and containing thiophene unit were synthesized from condensation reactions of DIAL-Th with pyridine-3,5-diamine, 4,4′-thiodianiline and 4,4′-oxydianiline, respectively. All purely synthesized compounds were structurally characterized with FT-IR, UV-Vis, ^{1}H and ^{13}C NMR and CV measurements. Thermal, surface and fluorescence properties of poly(azomethine-thiophene)s were examined by TG-DTA and DSC, SEM and fluorescence (FL) analyses. Photochromic properties and fluorescence quantum yields were interpreted at different wavelength in DMF and EtOH solutions.

Experimental

Chemicals

4-hydroxybenzaldehyde, 2,5-dibromothiophene, pyridine-3,5-diamine, 4,4′-thiodianiline, 4,4′-oxydianiline were supplied from Sigma Aldrich Chem. Co. (Germany). Tetrahydrofuran (THF), dimethylformamide (DMF), methanol (MeOH), ethanol (EtOH), acetonitrile were supplied from Merck Chem. Co. (Germany). All chemical compounds and solvents were used without purification.

Synthesis of Dialdehyde

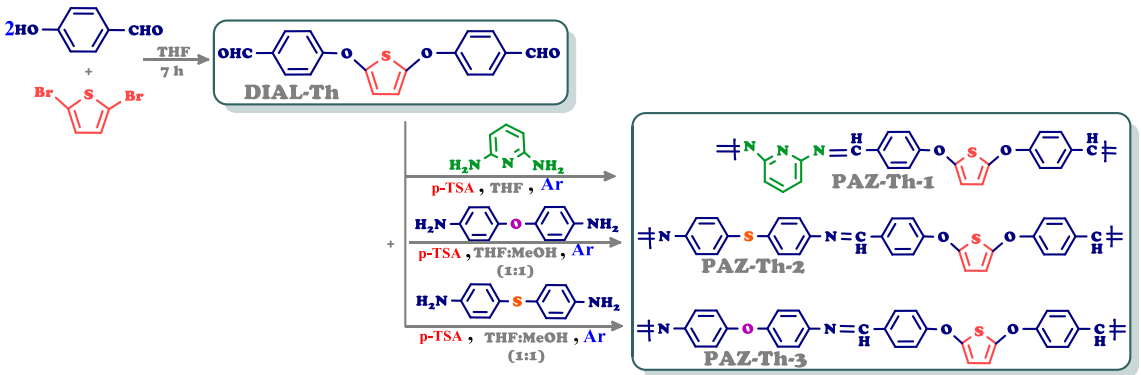
Dialdehyde containing thiophene unit were synthesized according to the procedure presented in Scheme 1. 4-hydroxybenzaldehyde (2.44 g, 0.02 mol) was dissolved in 30 mL of THF in a 250 mL three-necked flask equipped with a condenser and magnetic stir bar. Anhydrous sodium carbonate (2.653 g, 0.025 mol) was added to the flask. 2,5-dibromothiophene (9.680 g, 0.04 mol) was dissolved in 50 mL THF and added to the reaction mixture under argon atmosphere. The mixture was heated for 7 h at 110 °C under continuous stirring. After cooling, the product was poured into 250 mL cold water and ice (approximately 0–5 °C). The precipitate was washed with 3 × 250 mL water for separating mineral salts [29]. Then, dialdehyde was filtered, dried and finally recrystallized in methanol. The yield of dialdehyde was found to be 65%.

For DIAL-Th, ^{1}H NMR (DMS-$_{d6}$, δ, ppm): 10.56 (s, 2H,-CHO), 6.65 (s, 2H, Ha), 6.91 (d, 2H, Hb), 7.73 (d, 2H,-Hc). ^{13}C NMR (DMS-$_{d6}$, δ, ppm): 116.26 (C1-H), 150.19 (C2-ipso), 153.70 (C3-ipso), 128.87 (C4-H), 132.52 (C5-H), 125.97 (C6-ipso), 191.34 (C7-H).

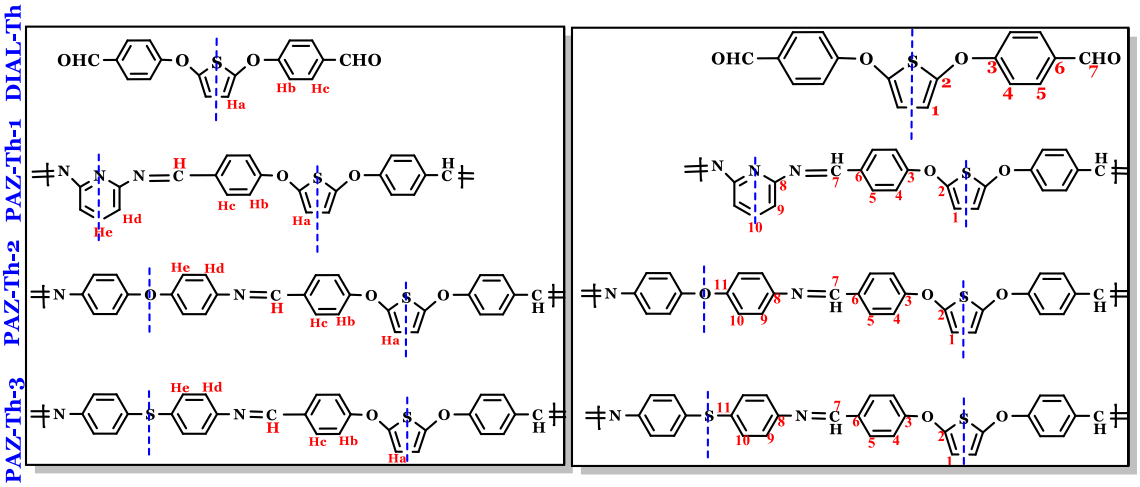
Syntheses of Poly(azomethine-thiophene)s

0.02 mol DIAL-Th was dissolved in THF (30 mL) at three different bottom flask and then 0.02 mol pyridine-3,5-diamine (10 mL THF); 0.02 mol 4,4′-thiodianiline (10 mL THF:MeOH (1:1) solution mixture); 0.02 mol 4,4′-oxydianiline (10 mL THF:MeOH (1:1) solution mixture) were separately added to initialize reaction bottom flasks. Reaction systems were contained 250 mL three-necked round bottom flask equipped with a reflux condenser, a gas inlet-outlet, a Dean-Stark trap and a magnetic stirrer. Also, 2 mL of toluene (in order to remove water as an azeotropic mixture) and *p*-toluene sulfonic acid (*p*-TSA) (4 mg) as catalyst were added to each other reaction mixtures and purged with a stream of argon (Scheme 1) as in literature [30]. Reaction mixtures were stirred for 2 h at room temperature and 60 °C 7 h under argon atmosphere. After cooling at room temperature, PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were precipitated into cold methanol, washed with methanol at room temperature to remove unreacted monomers and dried at 40 o C for 24 h in a vacuum oven. The yields of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were found to be 68, 70 and 75%, respectively. The structures of dialdehyde and poly(azomethine-thiophene)s are given in Scheme 2.

For PAZ-Th-1, ^{1}H NMR (DMS-$_{d6}$, δ, ppm): 6.55 (d, 2H, Ha), 6.89 (d, 2H, Hb), 7.75 (d, 2H,-Hc), 7.23 (s, 1H,-Hd), 9.70 (s, 2H,-He), 8.30 (s, 1H,-CH=N), 4.69 (s, terminal NH_2), 9.91 (s, 1H,terminal-CHO). ^{13}C NMR (DMS-$_{d6}$, δ, ppm): 116.18 (C1-H), 150.03 (C2-ipso), 153.78 (C3-ipso), 128.82 (C4-H),



Scheme 1 Synthesis procedures of poly(azomethine-thiophene)s.



Scheme 2 The structures of dialdehyde and poly(azomethine-thiophene)s.

129.53 (C5-H), 126.05 (C6-ipso), 163.82 (C7-H), 143.75 (C8-ipso), 132.04 (C9-H), 132.53 (C10-H) and 191.37 (terminal -CHO). For PAZ-Th-2, ^{1}H NMR (DMS-$_{d6}$, δ, ppm): 6.69 (d, 2H, Ha), 7.02 (d, 2H, Hb), 7.76 (d, 2H,-Hc), 6.88 (d, 2H,-Hd), 7.24 (d, 2H,-He), 8.46 (s, 1H,-CH=N), 4.94 (s, terminal NH_2), 10.08 (s, 1H,terminal-CHO). ^{13}C NMR (DMS-$_{d6}$, δ, ppm): 115.77 (C1-H), 147.79 (C2-ipso), 155.14 (C3-ipso), 128.05 (C4-H), 131.46 (C5-H), 131.76 (C6-ipso), 161.84 (C7-H), 146.57 (C8-ipso), 119.61 (C9-H), 122.75 (C10-H), 159.76 (C11-ipso) and 191.36 (terminal -CHO). For PAZ-Th-3, ^{1}H NMR (DMS-$_{d6}$, δ, ppm): 6.61 (d, 2H, Ha), 7.20 (d, 2H, Hb), 7.75 (d, 2H,-Hc), 6.86 (d, 2H,-Hd), 7.33 (d, 2H,-He), 8.44 (s, 1H,-CH=N), 5.47 (s, terminal NH_2), 9.76 (s, 1H,terminal-CHO). ^{13}C NMR (DMS-$_{d6}$, δ, ppm): 116.12 (C1-H), 151.62 (C2-ipso), 159.82 (C3-ipso), 127.82 (C4-H), 131.14 (C5-H), 136.43 (C6-ipso), 163.60 (C7-H), 150.26 (C8-ipso), 122.35 (C9-H), 132.42 (C10-H), 160.79 (C11-ipso) and 191.34 (terminal -CHO).

Characterization Techniques

AnalytikJena Specord 210 Plus double beam spectrophotometer (260–800 nm) was used for analysis of Ultraviolet-Visible absorption curve and calculations of the synthesized compounds. Required solutions of synthesized products were arranged as 5×10^{-4} M in DMF at room temperature. PerkinElmer FT-IR-FIR Spectrum (4000–650 cm^{-1}) was used for analysis of Fourier transform infrared (FT-IR) spectra of synthesized products. ^{13}C and ^{1}H NMR spectra were obtained by Agilent 600 MHz Premium COMPACT NMR Magnet as use solvent DMSO-$_{d6}$ at room temperature. Fluorescence spectra of compounds were analyzed by Shimadzu RF-5301PC spectrofluorofotometer. Emission spectra of the compounds were obtained in DMF and EtOH solutions at 0.025 mg mL^{-1} and 0.05 mg mL^{-1} concentrations, respectively. Thermogravimetric-differential thermal analysis (TG-DTA) measurements were realized in PerkinElmer Diamond thermal analysis instrument between 20 and 1000 °C at heating rate 10 °C min^{-1} under nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis were obtained from heating the poly(azomethine-thiophene)s between 25 and 450 °C at heating rate 10 °C min^{-1} under nitrogen purging by PerkinElmer Pyris Sapphire instrument. The ceramic and aluminum capsules were used for the analyses of TGA and DSC, respectively. The amount of each sample was weighed as about 10 mg. Gel permeation chromatography-light scattering (GPC-LS) instrument of Malvern Viscotek GPC Dual 270 max system was used for determination number average molecular weight (M_n) and weight average molecular weight (M_w), Z-average molecular weight (M_z), the peak molecular weight (M_p) and polydispersity index (PDI) values of poly(azomethine-thiophene)s. For GPC investigations a medium 300 × 8.00 mm dual column light scattering detector (LSD) and a refractive index detector (RID) were used to analyze the products at 55 °C. LiBr (40 mM) was added to the DMF mobile phase to dissociate molecular aggregates of polymers during GPC analysis. Poly(styrene) was used as calibration standard and Mp values were between 1250 and 60,000 Da. Jeol JSM-7100F (Japan) Scotty instrument was used for displayed SEM images of obtained poly(azomethine-thiophene)s. The coating process was used to create a thin gold/palladium film onto the poly(azomethine-thiophene)s for increase of surface conductivity of samples.

Cyclic voltammetry (CV) measurements were performed using a CH instruments 660C model electrochemical workstation. The electrochemical cell consists of an Ag wire pseudo-reference electrode (RE), Pt wire as counter electrode (CE), and platinum working electrode (WE) immersed in 0.1 M tetrabutylammonium hexafluorophosphate (TBA-HFP) as the supporting electrolyte. The experiments were carried out in acetonitrile/DMSO (4/1, *v*/v) solvent mixture under argon atmosphere. The scan rate was 100 mV/s at room

temperature. The potentials were calibrated to the ferrocene redox couple ($E^{1/2}$) (Fc/Fc^+) 0.39 V versus Ag/Ag^+. All reported potentials were given versus Ag/Ag^+.

Results and Discussion

Spectral Analyses of Synthesized Compounds

Fourier transforms infrared (FT-IR) spectroscopic analysis and obtained curves of synthesized compounds are demonstrated in Fig. 1. According to first FT-IR spectra incident to DIAL-Th, the stretching vibrations of -C=O, -C=C, Ar-CH, -CHO, -C-O and -C-S (in thiophene ring) groups were observed at 1663, 1589, 3044, 2879, 1214 and 701 cm^{-1} [31]. The stretching vibrations of azomethine (-CH=N-) groups of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were observed at 1596, 1624 and 1621 cm^{-1}, respectively. Aromatic C-H stretching vibration of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were observed at 3060, 3056 and 3067 cm^{-1}, respectively. The observations of imine peaks have demonstrated formation of PAZ-Th compounds. The stretching vibration of C=C and C-S functional groups of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were observed at 1574, 1590, 1586 cm^{-1}; 718, 727 and 723 cm^{-1}, respectively [32]. The stretching vibration bands of terminal -C=O and terminal $-NH_2$ groups of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were observed at 1666, 1669, 1672 cm^{-1}; 3381, 3365 and 3367 cm^{-1}, respectively.

According to ^1H NMR spectra of DIAL-Th, the signals of aldehyde, thiophene (Ha) and aromatic (Hb, Hc) protons were observed at 10.56, 6.65 and 6.91, 7.73 ppm, respectively. ^1H and ^{13}C NMR spectra of PAZ-Th-3 are shown in Fig. 2. The signals of aldehyde carbon (-CHO), C1, C2-ipso, C3-ipso, C4, C5 and C6-ipso were observed at 191.34, 116.26, 150.19, 153.70, 128.87, 132.52 and 125.97, respectively. According to ^1H-NMR spectra, the signals of azomethine (-CH=N-) protons of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were observed at 8.30, 8.46 and 8.44 ppm, respectively. According to ^{13}C-NMR spectra, the signals of azomethine (-CH=N-) carbon atoms PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were observed at 163.82, 161.84 and 163.60 ppm, respectively. Also, the thiophene and aromatic proton signals of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were observed between 6.55 and 9.70–6.89; 6.69 and 7.76–6.88; 6.61 and 7.75–6.86 ppm, respectively. The thiophene and aromatic carbon atom signals of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were observed between 116.18–150.03 and 153.78–126.05; 115.77–147.79 and 159.76–119.61; 116.12–151.62 and 160.79–122.35 ppm, respectively [33]. The signals of terminal aldehyde and amine protons of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were observed at 9.91 and

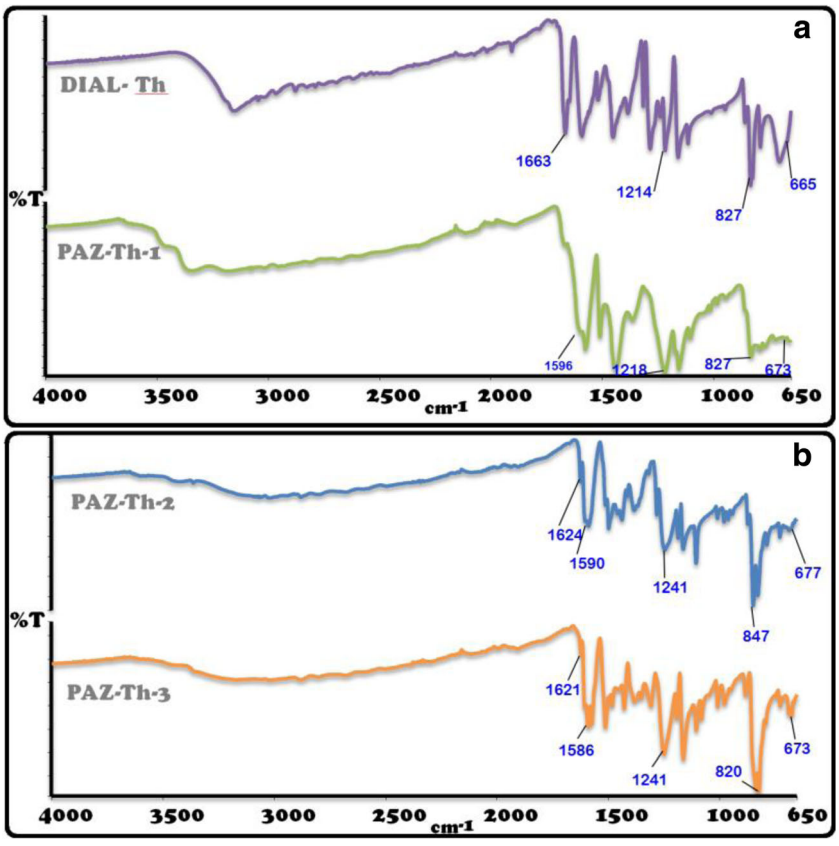


Fig. 1 FT-IR spectra of dialdehyde (DIAL-Th) and PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 poly(azomethine-thiophene)s between 4000 and 650 cm^{-1}

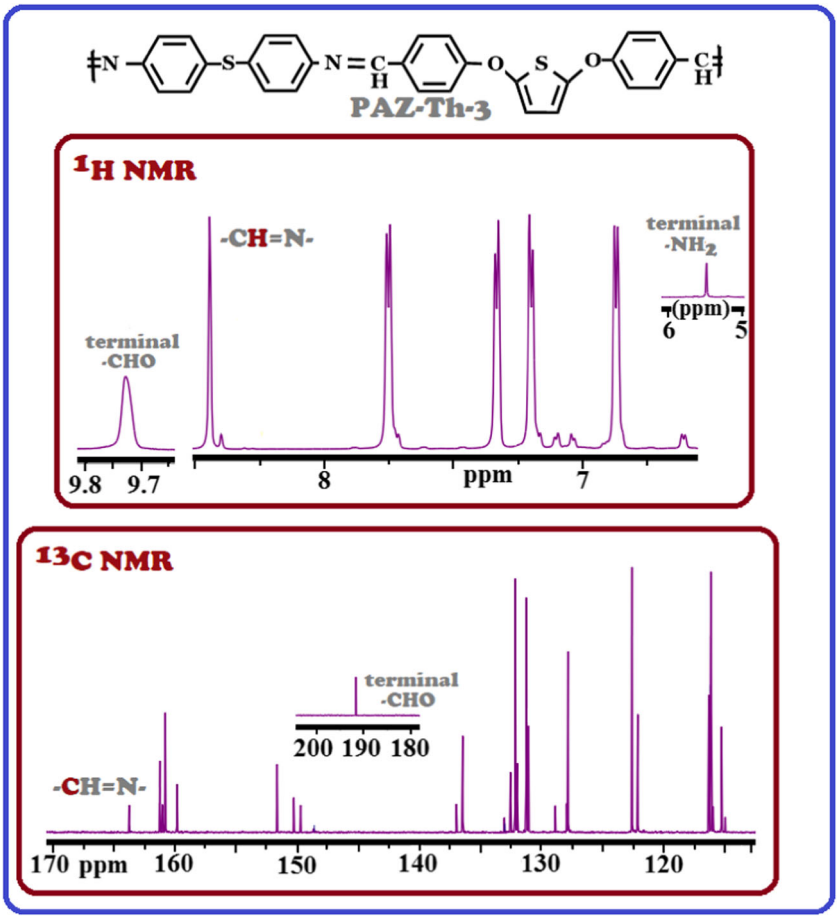


Fig. 2 ^{1}H -^{13}C NMR spectra of synthesized PAZ-Th-3 poly(azomethine-thiophene)

4.69 ppm; 10.08 and 4.94; 9.76 and 5.47 ppm, respectively. Terminal aldehyde carbon atom signals of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were observed at 191.37, 191.36 and 191.34 ppm, respectively. All these results were verified the structures of synthesized compounds.

UV-Vis spectra and data of synthesized compounds are given in Fig. 3 and Table 1. According to UV-Vis spectra of DIAL-Th, absorption band were observed at 266 and 286 nm due to $\pi \rightarrow \pi^*$ electronic transition of benzene and thiophene rings, respectively. According to UV-Vis spectra of PAZ-Th-1, the first absorption band was observed at 270 and 287 nm due to $\pi \rightarrow \pi^*$ electronic transition of benzene and thiophene rings, respectively. The second absorption band was observed at 324 and 422 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transition of azomethine bonds on polymeric chain, respectively. The thirty absorption band was observed at 449 nm due to $n \rightarrow \pi^*$ electronic transition of azomethine bonds in pyridine rings. According to UV-Vis spectra of PAZ-Th-2,

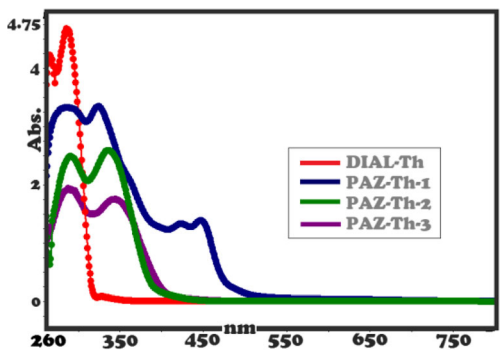


Fig. 3 UV-Vis analysis spectra of dialdehyde (DIAL-Th) and PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 poly(azomethine-thiophene)s in DMF (5×10^{-4} M)

Table 1 UV-Vis analysis results of DIAL-Th and poly(azomethine-thiophene)s

Compound	[a]λ_{max}(nm)	λ_{onset} (nm)	[b]E_g (eV)
DIAL-Th	266, 286	320	3.88
PAZ-Th-1	270, 287, 324, 422, 449	522	2.38
PAZ-Th-2	264, 288, 335, 375	410	3.03
PAZ-Th-3	264, 289, 345,370	415	2.99

[a] Absorbance wavelength

[b] Optical band gap

the first absorption band was observed at 264 and 288 nm due to π → π* electronic transition of overlapped benzene and thiophene rings, respectively. The second absorption band was observed at 335 and 375 nm due to π → π* and n → π* electronic transition of azomethine bonds, respectively. According to UV-Vis spectra of PAZ-Th-3, the first absorption band was observed at 264 and 289 nm due to π → π* electronic transition of benzene and thiophene rings. The second absorption band was observed at 345 and 370 nm due to π → π* and n → π* electronic transition of azomethine bonds, respectively. Also, λ_{onset} and optical band gaps of DIAL-Th, PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were calculated to be 320, 522,410, 415 nm and 3.88, 2.38, 3.03, 2.99 eV, respectively. The similar optical band gap results were found between 2.79–3.04 eV for poly(azomethine-ether)s containing mesitylene unit in literature [34]. The π → π* electronic transitions of bithiophenes substituted with alkyl and alkoxy groups were observed between 280 and 320 nm [35].

Electrochemical Properties

Cyclic voltammetric (CV) analysis curves and calculated data of DIAL-Th and PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 are shown in Fig. 4 and Table 2, respectively. Electrochemical band gap (E'_g), highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values of compounds were calculated from CV measurements. The HOMO, LUMO and E'_g values of DIAL-Th, PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were calculated to be −6.06, −5.57, −5.92, −6.04 eV; −3.10, −2.68, −3.03, −3.04 eV and 2.96, 2.88, 2.88 and 3.00 eV, respectively. Both optical band gap (E_g) and electrochemical band gap (E'_g) values of DIAL-Th were higher than poly(azomethine-thiophene)s. Electrochemical band gap values of poly(azomethine)s containing carboxyl and hydroxyl units were given between 2.36–2.70 eV

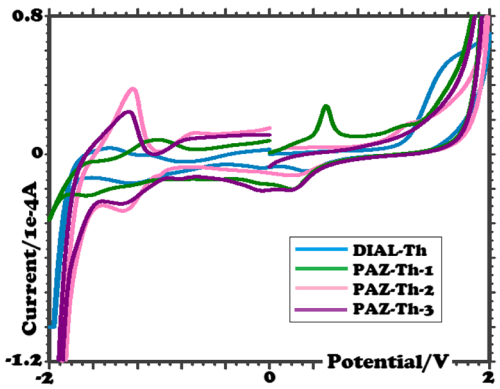


Fig. 4 Cyclic voltammetric curves of dialdehyde (DIAL-Th) and PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 poly(azomethine-thiophene)s (scan rate 100 mV s^{-1})

Table 2 Electrochemical analysis results of DIAL-Th and poly(azomethine-thiophene)s

Compound	E_{ox} (V)	$E_{red.}$ (V)	[a]HOMO (eV)	[b]LUMO (eV)	[c]E'_g (eV)
DIAL-Th	1.670	−1.289	−6.06	−3.10	2.96
PAZ-Th-1	1.180	−1.708	−5.57	−2.68	2.88
PAZ-Th-2	1.528	−1.354	−5.92	−3.03	2.88
PAZ-Th-3	1.651	−1.347	−6.04	−3.04	3.00

[a] Highest occupied molecular orbital

[b] Lowest unoccupied molecular orbital

[c] Electrochemical band gap

in literature [36]. The $E_{ox.}$ and $E_{red.}$ values of poly(azomethine-thiophene)s were found between 1.180–1.651 V and − 1.347-(−1.708) V, respectively.

Molecular Weight Distributions

Weight-average molecular weight (M_w), number-average molecular weight (M_n), Z-average molecular weight (M_z), peak molecular weight (M_p), polydispersity (PDI) of poly(azomethine-thiophene)s were calculated by Gel Permeation Chromatography-Light Scattering (GPC-LS) analysis. M_w and M_n values of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were found as 17,450, 15,600, 5400 Da and 15,200, 13,100, 5050 Da, respectively. M_z and M_p values of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were calculated as 20,000, 18,700, 5800 Da and 14,350, 10,000, 5100 Da and also PDI values of polymers 1.15, 1.19, 1.07, respectively.

Fluorescence and Quantum Yields of Obtained Compounds

Fluorescence and multichromic changes in DMF and EtOH solutions of synthesized compounds are shown in Figs. 5 and 6. Fluorescence quantum yields of synthesized compounds were calculated at different wavelength as in literature [37–39]. Fluorescein was dissolved in 0.1 M NaOH and it was used as a standard for all the measurements [37]. Because of having maximum FL intensities, ideal solution concentrations were determined as 0.025 mg mL^{-1} and 0.05 mg mL^{-1} for DMF and EtOH. Also, they are excited different wavelength. Different colors were observed at the various wavelengths by DMF and EtOH solutions of compounds. Fluorescence measurement was taken by adding one drop of standard solvent to the solution in DMF. Excitation and emission slit width values were determined to be 5 nm for both poly(azomethine-thiophene)s and the standard. Peak area was calculated from the graphs taken after the fluorescence measurement induced by the same excitation for poly(azomethine-thiophene)s. In the same exothermic substance, the absorbance value was observed in the UV-vis

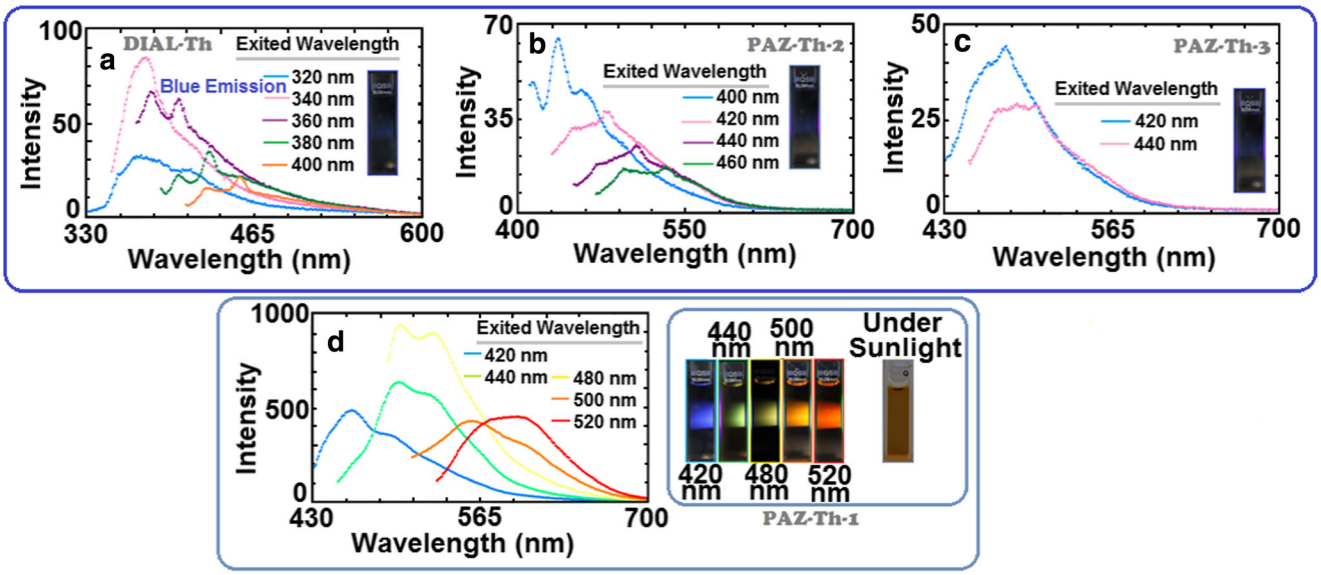


Fig. 5 FL spectra of synthesized compounds in DMF solutions (concentration: 0.025 mg mL^{-1}, slit width: λ_{Ex} 5 nm, λ_{Em} 5 nm) a-Blue emission spectra of DIAL-Th excited at the different wavelength, b-Blue emission spectra of PAZ-Th-2 excited at the different wavelength, c-Blue emission spectra of PAZ-Th-3 excited at the different wavelength, d-Blue emission spectra (excited at 420 nm), green emission (excited at 440 nm), yellow emission spectra (excited at 480 nm, slit width: λ_{Ex} 3 nm, λ_{Em} 3 nm), orange emission spectra (excited at 500 nm), red emission spectra (excited at 520 nm) of PAZ-Th-1 and under sunlight

spectrum. Fluorescence Quantum yields of poly(azomethine-thiophene)s were calculated as the following Eq. (1).

$$Q_{MX} = Q_{YS}\left[\frac{A_x}{A_s}\right]x\left[\frac{f_s}{f_x}\right]x\left[\frac{\eta_x}{\eta_s}\right] \quad (1)$$

where Q_{MX} is quantum yield of compound, Q_{YS} is quantum yield of fluorescein standard (0.79), A_X is area of the compound whose calculate quantum yield, A_S is area of fluorescein standard (22.36), f_s ($1–10^{-D}$, D: The absorbance value of the standard measured in UV–Vis 0.1506), f_x ($1–10^{-D}$ D: Absorbance value of the measured substance in UV–Vis, η_x is the refractive index of DMF (1.43) and ethanol (1.36), η_s is refractive index of the fluorescein standard solvent [40].

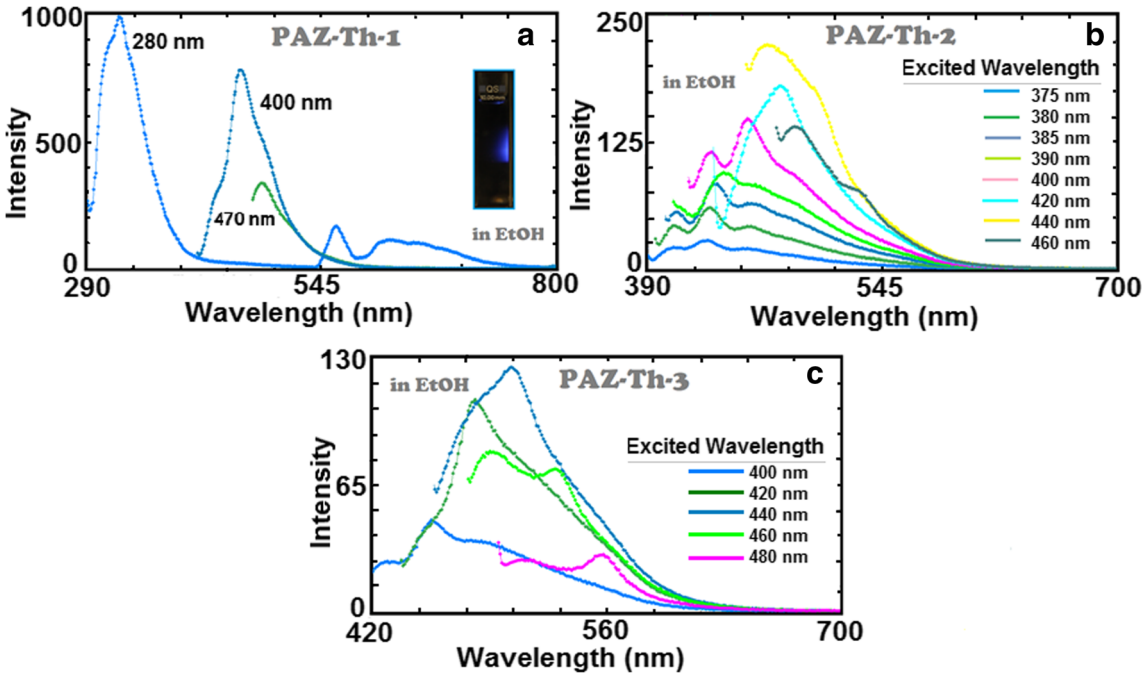


Fig. 6 FL spectra of compounds in EtOH solutions (concentration: 0.05 mg mL^{-1}, slit width: λ_{Ex} 5 nm, λ_{Em} 5 nm) a- Blue emission spectra of PAZ-Th-1 excited at the different wavelength b- Emission spectra of PAZ-Th-2 excited at the different wavelength c- Emission spectra of PAZ-Th-3 excited at the different wavelength

According to fluorescence spectra of DIAL-Th, blue emission was observed at 320, 340, 360, 380 and 400 nm in 0.025 mg mL^{-1} concentrated DMF solution (Fig. 5a). The fluorescence quantum yields of DIAL-Th were calculated to be 1.2, 1.5, 1.4, 0.8 and 0.62% at 320, 340, 360, 380 and 400 nm, respectively. According to fluorescence spectra of PAZ-Th-1, blue, green, yellow, orange, red emissions were observed at 420, 440, 480, 500, 520 nm, respectively (Fig. 5d). The fluorescence quantum yields of PAZ-Th-1 were calculated to be 4.0, 15.0, 18.0, 6.4, 6.2%, respectively, for these wavelengths. The solution in DMF of PAZ-Th-1 was brown under sunlight. According to all these photochemical analysis, PAZ-Th-1 was having excellent photochromic properties and it could use to be photoactive materials. According to fluorescence spectra of PAZ-Th-2, blue emissions were observed at 400, 420, 440, 460 nm and fluorescence quantum yields were calculated to be 1.1, 0.9, 0.7, 0.6%, respectively (Fig. 5b). According to fluorescence spectra of PAZ-Th-3, blue emissions were observed at 420, 440 nm and also fluorescence quantum yields were calculated to be 1.0 and 0.8%, respectively (Fig. 5c). All these results were obtained in DMF solutions and 0.025 mg mL^{-1} concentration [41, 42]. Fluorescence properties of PAZ-Th-2 and PAZ-Th-3 were observed to be less than PAZ-Th-1.

According to fluorescence spectra of PAZ-Th-1 in Fig. 6a, blue emission was observed at 280, 400, 470 nm and also their quantum yields were calculated to be 8.0, 1.6 and 7.7%, respectively. According to fluorescence spectra of PAZ-Th-2, no emission color was observed at 375, 380, 385, 390, 400, 420, 440 and 460 nm (Fig. 6b). The fluorescence quantum yields were calculated to be 1.0, 1.5, 3.2, 3.8, 5.6, 5.8, 6.4 and 2.0%, respectively, at the same wavelengths. According to fluorescence spectra of PAZ-Th-3, no emission color was observed at 400, 420, 440, 460,480 nm (Fig. 6c). The fluorescence quantum yields were calculated as 1.6, 4.7, 2.0, 2.4 and 1.1%, respectively, at the same wavelengths. All these results were obtained in EtOH solutions at 0.05 mg mL^{-1} concentration. According to all FL spectra, data and calculations, PAZ-Th-1 is so specifically compound as fluorescence fields because of containing pyridine and thiophene chromophores on poly(azomethine-thiophene) backbone at the same time.

Thermal Properties

The TG-DTA and DSC analyses of compounds were shown in Figs. 7 and 8, respectively. According to TG measurements, the starting degradation temperature (T_{onset}) values of DIAL-Th, PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were calculated to be 162, 256, 248 and 224 °C, respectively. Total % char values of DIAL-Th, PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were found as 0.69, 44.56, 50.71 and 4.57%, respectively, at 1000 °C. According to these values, the thermal stabilities of poly(azomethine-thiophene) containing pyridine and ether units were higher than DIAL-Th and PAZ-Th-3. The moisture quantities of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were found as 5.65, 3.40 and 3.05%, respectively, until 125 °C. 20% mass losses of DIAL-Th, PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were calculated as 167, 359, 391 and 441 °C, respectively. The temperature observation of maximum mass losses (T_{max}) values of DIAL-Th, PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were found as 203; 313,726; 262, 387 and 377, 674 °C, respectively. The starting degradation temperature of poly(azomethine-thiophene) containing pyridine unite was higher than ether and sulfur bridges compounds. The thermal degradation of PAZ-Th-1 was formed at the second degradation step. The mass losses of the first and the second steps

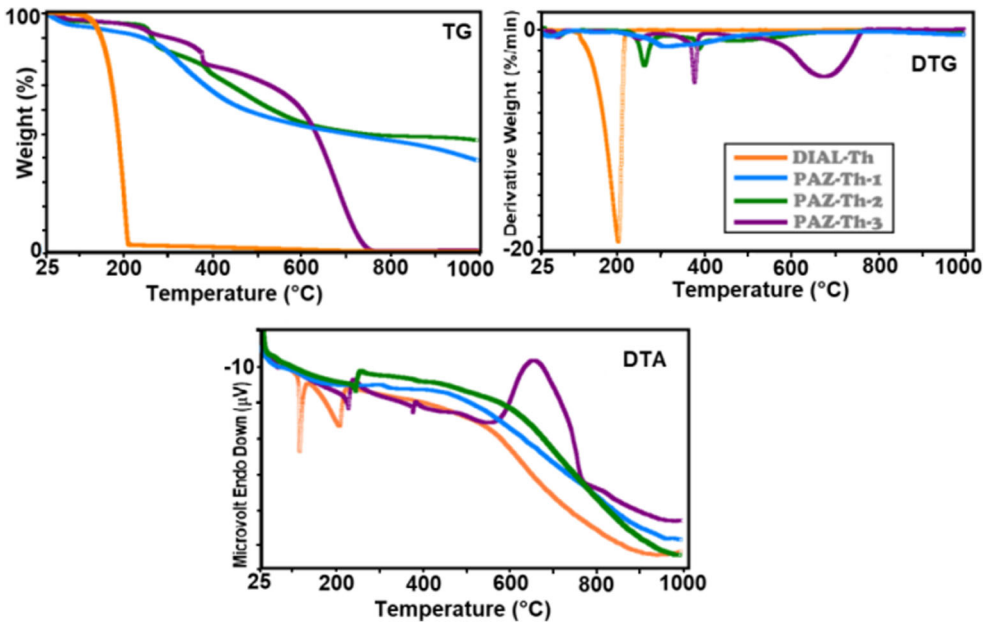


Fig. 7 TG-DTG-DTA curves of DIAL-Th, PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 poly(azomethine-thiophene)s

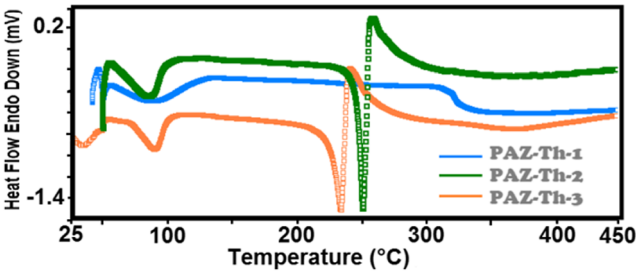


Fig. 8 DSC curves of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 poly(azomethine-thiophene)s

were 41.90 and 13.52% between 125 and 627 and 627–1000 °C, respectively. The thermal degradation of PAZ-Th-2 was formed at the second degradation step. The mass losses of the first and the second steps were 13.24 and 36.04% between 125 and 315 and 315–1000 °C, respectively. The thermal degradation of PAZ-Th-3 was formed at the second degradation steps. The mass losses of the first and the second steps were 19.36 and 76.07% between 125 and 412 and 412–1000 °C, respectively. All these results are clarified that having high onset temperature and %char values of poly(azomethine-thiophene)s. Also they were candidates for thermal resisted in material industries.

According to DSC measurements, the glass transition temperature (T_g) and ΔCp values of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were calculated as 162, 176 and 137 °C; 2.08×10^{-3} J g^{-1} $°C^{-1}$, 5.16×10^{-3} J g^{-1} $°C^{-1}$ and 2.93×10^{-3} J g^{-1} $°C^{-1}$, respectively. There are similar results for some polymer compounds in the literature [43–45]. The glass transition temperatures of polyimides containing thiophene unit were found between 157 and 220 °C [44]. Endothermic peaks were observed at DSC curves of PAZ-Th-2 and PAZ-Th-3 in 252 and 233 °C, respectively.

Surface Properties

Surface analysis of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were realized by Field Emission Scanning Electron Microscope (FE-SEM) techniques and images are given in Fig. 9. Images of PAZ-Th-1 were spongy like kashar cheese. Pore size of PAZ-Th-1 was calculated as 1.63 and 8.84 μm. PAZ-Th-2 and PAZ-Th-3 were having lamellar plaque. The molecular weight values of PAZ-Th-2 and PAZ-Th-3 to be having lamellar plaque were found lower than PAZ-Th-1. Also, Ton values of PAZ-Th-1 to be having pore structure were found higher than

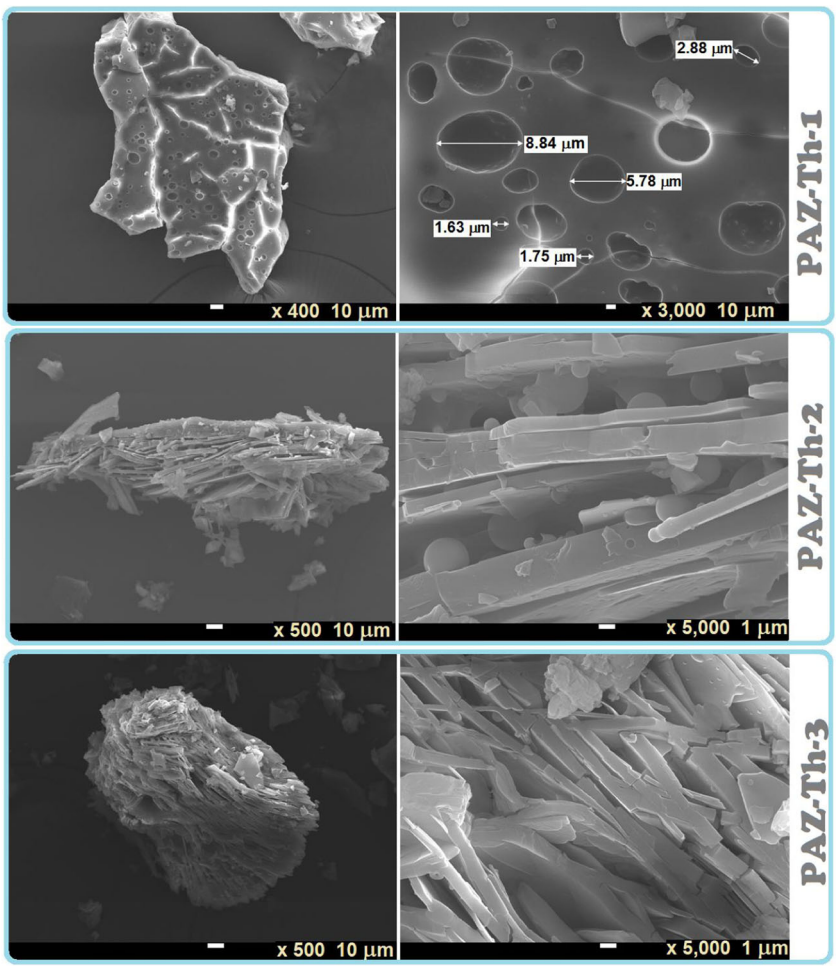


Fig. 9 SEM photograph of synthesized PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 poly(azomethine-thiophene)s

PAZ-Th-2 and PAZ-Th-3 lamellar plaque structure. Plaques of PAZ-Th-2 were having small oval particles. Similar images of poly(azomethine) were found at literatures [46, 47].

Conclusion

Consequently, poly(azomethine)s containing thiophene units were purely synthesized via condensation and elimination reactions. The structures of poly(azomethine-thiophene)s were confirmed by FT-IR, UV-Vis and ^{1}H-^{13}C-NMR measurements. Also, poly(azomethine-thiophene)s were characterized with CV, FL, TG-DTA and SEM analyses. According to FL analysis PAZ-Th-1 was observed photochromic/multichromic properties due to emit five different colors such as blue, green, yellow, orange and red at 420, 440, 480, 500 and 520 nm, respectively. The fluorescence quantum yields of PAZ-Th-1 were calculated to be 4, 15, 18, 6.4, 6.2%, respectively, when excited at same wavelength in DMF solution. In addition, PAZ-Th-1 was demonstrated monochromic property in EtOH solution, when excited at 280, 400 and 470 nm. The fluorescence quantum yields of PAZ-Th-1 were calculated to be 8.0, 1.6, and 7.7%, respectively, at the same wavelength in EtOH solution. According to thermal analysis results, onset temperatures and glass transition temperatures of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were found as 256, 248 and 224 °C and 162, 176 and 137 °C, respectively. Also, % char values of PAZ-Th-1, PAZ-Th-2 and PAZ-Th-3 were found as 44.56, 50.71 and 4.57%, respectively, at 1000 °C. All these properties of synthesized poly(azomethine-thiophene)s were suitable candidates for thermal resisted materials. Especially PAZ-Th-1 can be actively used as photovoltaic material industry due to chromic characters and good quantum yield. The thermal, surface, molecular weight and FL properties of PAZ-Th-1 were better than PAZ-Th-2 and PAZ-Th-3. To be very good of FL properties of PAZ-Th-1 has come forward from pyridine ring in the structure.

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