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Synthesis, characterization and optical studies of conjugated Schiff base polymer containing thieno[3,2-*b*]thiophene and 1,2,4-triazole groups

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ABSTRACT

A conjugated polyschiff base (poly(*N*-thieno[3,2-*b*]thiophen-2-yl)methylene)-1*H*-1,2,4-triazol-5-amine) poly(TTMA)) was synthesized by condensation polymerization between thieno[3,2-*b*]thiophene-2,5-dicarboxaldehyde and 3,5-diamino-1,2,4-triazole. The poly(TTMA) was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR spectra and thermal analysis. The number average molecular weight (*Mn*) and polydispersity index of the poly(TTMA) were determined by gel permeation chromatography (GPC). In addition, the optical properties of the poly(TTMA) solutions were investigated at different molarities. The band gap E_g value of the poly(TTMA) decreased with the increasing molarity. The absorption band edge values of the poly(TTMA) decreased as the molarity increased. The average transmittance values of the poly(TTMA) increased with the increasing molarity and the highest values of molar extinction coefficient also were found in the near ultraviolet region. Its values decreased with the increasing molarity. These results showed that the poly(TTMA) can be used for the fabrication of many optoelectronic devices due to its suitable optical properties and low optical band gap.

1. Introduction

In recent years, conjugated polymers have been studied by a number of researchers and a great variety of structures have been obtained [1–5]. The Schiff base polymers have an important place in this group. They have attracted attention because of their electrical and optoelectronic properties as well as their biological activities [6–11]. Conjugated polymers are commonly used in electronic circuit elements production such as conductive coatings, photoreceptors, photodiodes, solar cells, ion exchangers, accumulators, sensors, electro chromic devices, rechargeable batteries, thin film transistors and light emitting diodes [12–16]. Therefore, syntheses of novel derived conjugated polymers are very important in developing of technological applications. Besides, the synthesized polymers including substituted triazole rings have been favorable portions to high performance electrical memory polymers [17–19]. Moreover, the polymers having thieno[3,2-*b*]thiophene structure are also easily available as attractive candidates for building organic semiconductors. Iain Meager et al. reported formation of a thieno [3,2-*b*]thiophene is indigo and they obtained a series of alternating thieno [3,2-*b*] thiophene-based copolymers. These new polymers having low band gap showed properties of semiconducting polymers used for OFET [20]. Wu et al. also designed organic semiconductors of thieno[3,2-*b*]thiophene bridged isoindigo and they successfully produced novel oligomers which displayed p-channel FET behaviours. These oligomers had also good air stabilities at high temperatures [21]. Encouraged by these successful efforts, we aimed both to synthesize novel conjugated polymer containing thiophene and triazole moieties and to investigate optical properties and optoelectronic parameters of newly synthesized polymer.

In this work, the new conjugated polymer was synthesized by the polycondensation method of thieno [3,2-*b*] thiophene-2,5-dicarboxyaldehyde and 3,5-diamino-1,2,4-triazole. The spectroscopic analysis of the synthesized conjugated polyschiff base was carried out by ^{1}H NMR, ^{13}C NMR, FT-IR, GPC and thermal analysis method. Polymeric conductivity values were calculated by measuring the reflectance, permeability and absorption values at different concentrations in the UV–Vis spectrophotometer. The optical properties of the new conjugated poly(TTMA) were investigated such as band gap, absorbance band edge, direct transition,

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indirect transition, forbidden indirect transition, refractive index and change of molar absorption coefficient values according to concentration.

2. Experimental

2.1. Starting materials

Thieno[3,2-*b*]thiophene-2,5-dicarboxyaldehyde and 3,5-diamino-1,2,4-triazole) were purchased as chemical reactive from Sigma Aldrich. Dimethylformamide, ethanol and glacial acetic acid were also supplied as solvents from Merck (Darmstadt, Germany). These materials were performed without purification.

2.2. Equipment

The infrared spectra were obtained by a Perkin Elmer Precisely Spectrum one spectrometer using an ATR head in the range of 4.000–600 cm^{-1}.^{1}H and ^{13}C NMR spectra were recorded in deuterated DMSO-d6 at 400 MHz and 100 MHz. Molecular weight and PDI of the polymer were determined by gel permeation chromatography (GPC) using Agilent 1100 Series, equipped with refractive index detector. The polymer was dissolved in DMF in an ultrasonic bath and then the solution was prepared by filtration through a 40 μm pore diameter teflon filter. Ultraviolet–visible (UV–vis) spectra were recorded by Shimadzu model UV-1800 Spectrophotometer in the wavelength between 1100 and 190 nm at room temperature. The measurements were carried out in DMF solution. TGA measurement was performed using Perkin Elmer Pyris 1 in the range of 20–900 °C with heating rate of 10 °C min^{-1} under N_2 atmosphere.

2.3. Synthesis and characterization of poly(N-thieno[3,2-b] thiophen-2-yl)methylene)-1H-1,2,4-triazol-5-amine) poly(TTMA)

The thieno[3,2-*b*]thiophene-2,5-dicarboxaldehyde (0.196 g, 0.5 mmol) was dissolved in dimethylformamide (10 ml). The 3,5-diamino-1,2,4-triazole (0.099 g, 0.5 mmol) was added to the reaction pot and the solution was mixed at about 85 °C for 24 h. During the reaction, the a few drops of glacial acetic acid were added to the reaction medium. Then the poly(TTMA) was precipitated with water. The obtained poly(TTMA) was dried under vacuum at about 50 °C. Yield: 65%. Colour: orange. FT-IR (ν, cm^{-1}): 3236 (-NH stretching), 1641 (-N=CH stretching), 1577 (C=N stretching in triazole ring), 1441, 1377 (C-S stretching in thieno[3,2-*b*]thiophene ring). ^{1}H NMR (400 MHz, DMSO-d6) (δ, ppm): 12.15 (-NH in triazole ring, s, 1H), 10.03 (H atom of aldehyde at the end of the polymer chains), 9.16 (-N=C<u>H</u>, s, 1H), 8.44–7.53 (-C<u>H</u> in thieno [3,2-b] thiophene, m, 2H), 6.16 (NH_2 atoms at the end of the polymer chains s, 2H), ^{13}C NMR (100 MHz, DMSO-d6) (δ, ppm):185.76 (<u>C</u> atoms of aldehyde at the end of the polymer chains), 163.66 (-N=<u>C</u>H), 156.85, 154.77, (C atoms of triazole ring), 147.93, 144.96, 131.74, 127.64 (C atoms of thieno [3,2-b] thiophene ring).

3. Results and discussion

3.1. Synthesis and characterization

Poly(TTMA) was synthesized by polycondensation of thieno[3, 2-*b*]thiophene-2,5-dicarboxaldehyde and 3,5-diamino-1,2,4-triazole in Scheme 1.

The poly(TTMA) was characterized using FT-IR, ^{1}H NMR, ^{13}C NMR, GPC and TGA analysis. FT-IR spectra of the poly(TTMA), thieno [3, 2-*b*]thiophene-2,5-dicarboxaldehyde and 3,5-diamino-1,2,4-triazole were comparatively shown in Fig. 1. Distinctive carbonyl (-C=O) band of thieno[3,2-*b*]thiophene-2,5-dicarboxaldehyde and amine (-NH_2) stretch vibration of 3,5-diamino-1,2,4-triazole were seen at 1651, 3387 and 3304 cm^{-1}, respectively. After polymerization, these bands of aldehyde and amine vanished and imine peak was observed at 1641 cm^{-1}. Furthermore, when the triazole's peaks shifted to 1631 and 1595 cm^{-1}, the new peaks for poly(TTMA) formed, as shown Fig. 1. These data were referred to formation of the polymer structure.

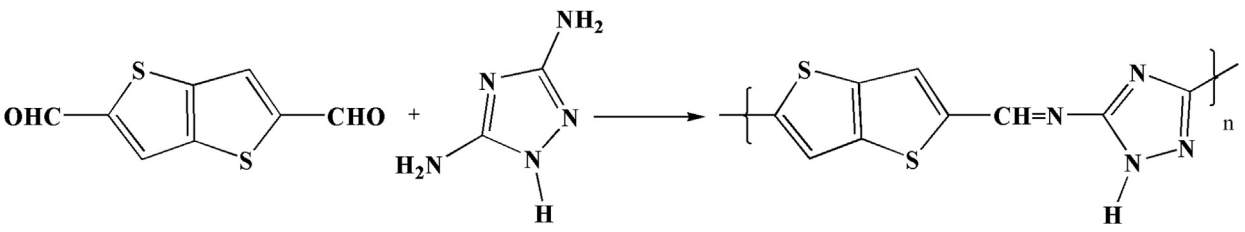
^{1}H NMR spectrum of poly(TTMA) was presented in Fig. 2. The imine proton, CH protons of thieno[3, 2-b] thiophene and the NH proton of 1,2,4-triazole were seen at 9.16, 8.44–7.53 and 12.15 ppm, respectively. Imine, thieno[3,2-*b*]thiophene ring and 1,2,4 triazole ring carbon peaks were distinctively observed at 163.66, 147.93–127.64 and 156.85, 154.77 ppm in ^{13}C NMR spectrum, respectively (see the Supporting Information). *Mn* value of polymer was calculated as 1.706 *via* GPC. PDI value was determined as 1.13.

TGA thermogram of poly(TTMA) was given in Fig. 3. Onset temperature (T_{on}) was determined as 296 °C. The poly(TTMA) left 13% waste at 950 °C and 50% weight loss was also observed at 609 °C. These results indicated that poly(TTMA) was a thermally stable polymer due to polyconjugated structure. Additionally, the poly(TTMA) demonstrated a linear decrease on weight losses as temperature increased. The synthesized poly(TTMA) had high onset temperature and waste in comparison with polyschiff base [22]. The results of TGA thermogram were summarized in Table 1.

3.2. Optical properties

To investigate optical properties, transmittance (T), reflection (R) and absorbance (A) values of the poly(TTMA) were recorded at room temperature as a function of wavelength at different concentrations. The graph plotted against the wavelength of the permeability was given in Fig. 4a and the concentration decreased in the transmittance (T) as shown Fig. 4a. The transmittance spectrum of the poly(TTMA) exhibited a band shoulder between 450 and 525 nm, and it showed the band gap of the poly(TTMA).

In Fig. 4a, the poly(TTMA) is transparent in the near invisible region (NIR). Furthermore, increasing transmittance values were observed with the decreasing molarity. In the same graph, the transmittance increased to 520 nm. The solution of the poly(TTMA) at 0.55 mM has the highest transmittance in three concentrations. The average transmittance (T_{avg}) values of the poly(TTMA) at 0.55,



Scheme 1. Synthesis of the poly(TTMA).