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Effect of triphenylamine as electron-donor evenly spaced in 2, 4, 6 and 8 thiophene units of the main chain: synthesis and properties

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Abstract Several poly(thiophene) derivatives containing triphenylamine (TPA) as electron-donor were synthesized by chemical homopolymerization in $CHCl_3$ media using $FeCl_3$ as oxidizing agent. Monomers containing TPA bonded by imine groups to terminal thiophene, bithiophene, terthiophene units allows polymerization to be performed in conditions similar to thiophene. TPA units are regularly spaced in 2, 4, 6 and 8 thiophenyl units in the main chain. TPA electron-donor effect on the polymers chains, as compared to poly(thiophene) was studied. Polymers, labeled as poly(TPA-Th), poly(TPA-biTh) and poly(TPA-Terth) were characterized by ^{1}H-NMR, FT-IR and UV–visible spectroscopy, elemental analysis, thermal stability (TGA) intrinsic viscosity, differential scanning calorimetry (DSC) and electrochemically using cyclic voltammetry (CV). The characterizations are consistent with the proposed structures. The polymers exhibited different optical absorption.

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They exhibited low intrinsic viscosity, a different effective conjugation and high thermal stability. Moreover, the polymers displayed two redox processes with a redox potential lower than that of poly(thiophene). Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO) and optical band gap (E_g) were measured and the obtained values were compared with those of poly(thiophene). The effect of the presence of TPA units in the thiophenyl chains on HOMO, LUMO, band gap, redox potential and on TGA is reported. To complete the series, HOMO/LUMO levels and band gap of a polymer containing TPA with 8 thiophenyl units in the chain were determined using theoretical calculations. The results proved that, with respect to poly(thiophene), it is possible to decrease HOMO and LUMO without changing the band gap, projecting itself as a potential polymer to be studied in organic photocells.

Introduction

Organic hole-transport materials have been studied in devices such as light-emitting diodes and solar cells [1]. Triphenylamine (TPA) possesses redox activity and fluorescence and, due to nitrogen oxidizability, the molecule is a good charge carrier [2]. Furthermore, TPA is an electron-rich molecule and small molecules and polymers containing TPA segments exhibit high photoluminescence and photocatalytic properties [3, 4]. Since the phenyl rings of TPA are not coplanar, a higher solubility should be expected. Furthermore, the presence of a nitrogen redox site, change the electronic and redox properties of TPA, which is useful for the development of novel optoelectronic devices [5]. TPA in the core of small molecules bonded to thienylenevinylene, indanedione, dicyanovinyl moieties have been studied in solar cells [6]. Another report has utilized TPA as luminescent material in organic light-emitting diodes [7]. TPA-based small molecules, with electron-donor architecture, are being studied in sensitized solar cells [8–10]. Other polymers with TPA units have been also reported, the polymers showed strong fluorescence in solid state and can be used as non-doped emitter to fabricate emitting diodes [11]. Polyacetylenes carrying triphenylamine moieties have been reported with electrochromism properties and high thermal stability in presence of air [12]. Hyperbranched oligomers with TPA segments were synthesized and intramolecular charge transfer was found in its excited state [13].

Few polymers containing triphenylamine and imine moieties have been reported. Poly-Schiff base with triphenylamine in the main chain showed semiconductor properties [14]. Niu et al. [15] have reported two conjugated hole transport polyazomethine, the synthesis was performed by reaction between 4,4′-bisamino triphenylamine and dialdehydes. The polymers have non-crystalline structure, heat resistance stability and hole transport ability. Other poly-Schiff bases were synthesized from 4,4′-bisaminotriphenylamine for use in organic electronic devices [16]. Sek et al. [17] reported a series of poly-Schiff bases synthesized at high temperature by polycondensation of diformyl-TPA with various aromatic diamines. The obtained blue light-emitting polymers exhibited high band gap. Conjugated poly-Schiff bases can be synthesized by reacting two co-monomers, aromatic

diamines and aromatic dialdehydes [14, 17–19]. Other synthesis methods consist in introducing the imine group in monomers containing thiophene or pyrrole in the terminal units, then, polymerization takes place by an oxidative condensation mechanism. In this type of reaction the monomer is oxidized with an oxidizing agent or electrochemically at the surface of an inert electrode [20–23]. Poly-Schiff bases synthesized by oxidative mechanism of monomers containing TPA segments has been recently reported and studied in a double-layered organic solar cell with 0.43 % efficiency [24].

The goal of this paper is the synthesis of several poly-Schiff bases containing TPA regularly spaced in 2, 4 and 6 thiophene units. To complete the series, theoretical calculations of a polymer containing TPA with 8 thiophenyl units in the main chain were carried out. Synthesized polymers were characterized by spectroscopy, elemental analysis, cyclic voltammetry, viscosity, TGA, differential scanning calorimetry (DSC) and physical properties such as HOMO, LUMO and optical band gap were assessed and compared with those of poly(thiophene). The TPA electron-donor effect on the polymeric chain is discussed.

Experimental

Measurements

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a JASCO FT-IR 4200 spectrometer. Nuclear Magnetic Resonance (NMR) spectra were recorded using tetramethyl silane as internal reference on a 400 MHz Bruker spectrometer. Elemental analyses were conducted on an EA-1108 Fisons Elemental Analyzer. UV–Vis spectra were run on a Perkin–Elmer Lambda 35UV/VIS spectrometer. The spectra of 100 mg L^{-1} polymers solution was run in chloroform (CHCl$_3$). TGA measurements were performed using a thermo-microbalance Netzsch TG 209 F1 Iris. Samples (ca. 5 mg) were placed into alumina pans and heated under nitrogen (20 mL min^{-1}) from 30 to 1,000 °C at 10 °C min^{-1} to obtain the corresponding thermal decomposition profile. Prior to measurements, samples were dried under reduced pressure in a vacuum oven. Calorimetric behavior was studied by DSC using a Netzsch DSC 204 F1 Phoenix differential scanning calorimeter. Samples (ca. 5 mg) were placed into aluminum pans and heated under nitrogen (250 mL min^{-1}) from 0 to 200 °C at 10 °C min^{-1} heating rate. To minimize differences in the thermal history of the samples, the corresponding thermograms were run considering decomposition temperatures determined by TGA, according to the following temperature program: heating up to 200 °C (dynamic stage), isothermal stage at 200 °C (static), cooling until room temperature (dynamic, quenching step) and heating up to 300 °C (dynamic). Prior to measurements, samples were dried under reduced pressure into a vacuum oven. Electro-polymerization was performed using a standard three-electrode cell. The working electrode was a 0.2-cm^2 platinum disk while a Pt wire was the counter electrode. Ag/AgCl was used as reference electrode. Unless otherwise stated, all potentials quoted in the current work are referred to this reference electrode. Monomers were electropolymerized from a

0.1 mg mL^{-1} monomer solution in anhydrous CH$_3$CN using 0.1 M tetrabutylam-monium hexafluorophosphate (TBAPF$_6$) as supporting electrolyte. Cyclic voltam-mograms were recorded at 50 mV s^{-1} scan rate.

Some theoretical calculations were performed on poly(TPA-quarterTh). The Gaussian 03 computational package [25] was used to perform ground-state and transition-state geometry optimization calculations employing Becke's three-parameter hybrid exchange functional and the Lee [26], Yang [27], Parr [28] non-local correlation functional B3LYP [26–28], and in addition, a 6-31G* basis set was used for S, C, N, O, and H atoms [29].

Reagents

Aniline, *p*-fluoro-nitrobenzene, CsF, DMSO, Pd/C 10 %, hydrazine monohydrate, thiophene-2-carboxaldehyde; 2,2′-bithiophene-5-carboxaldehyde, TBAPF6, ben-zene, *p*-toluenesulfonic acid and CH$_3$CN were purchased from Sigma-Aldrich. FeCl$_3$, CHCl$_3$, CH$_2$Cl$_2$ were from Merck. Prior to use CHCl$_3$, CH$_2$Cl$_2$ and DMF were dried over CaCl$_2$ and molecular sieves 4 Å pellets, and distilled.

Synthesis

4,4′-Bis amino-triphenylamine

To a 250-mL round-bottom flask, equipped with a reflux condenser, 4.3 g 4,4′-bisdinitro-triphenylamine, 140 mL ethanol, and 210 mg 10 % Pd/C catalyst were added. The mixture was stirred, brought to boil and then 4.2 g hydrazine monohydrate was slowly added and subsequently refluxed for 215 min (checked by TLC, line spotted using acetone and eluted with ether). The warm mixture was filtered using a Buchner funnel and the filtrate concentrated by evaporation until ca. 40 % of the total volume remains. The mixture was next cooled at room temperature (90 min), filtered using a Buchner funnel and the resulting solid washed with mother liquor and finally with a little volume of cold ethanol. 4,4′-Bis amino-triphenyl-amine was oven dried at 50 °C for 2 h. Yield, 2.08 g (59 %). mp = 177 °C (decomposed). ^{1}H-NMR (DMSO-d6): monosubstituted phenyl ring, t(1H, 6.69 ppm), t(2H, 7.08 ppm), d(2H, 6.76 ppm), *p*-disubstituted two rings; d(4H, 6.65 ppm), d(4H, 6.87 ppm), s(4H, 4.60 ppm, correspond to the 4 hydrogens of the primary amines). Elemental analysis: C 78.89; H 6.43; N 15.41; ration mol/mol found C/N 18/3.01; C/H 18/18.0. FT-IR (KBr): vNH$_2$ at 3,418, 3,339 and 3,204 cm^{-1}, vCH at 3,050 and 3,030 cm^{-1}, vC $=$ C at 1,618, 1,603 and 1,494 cm^{-1}, vCN at 1,330 cm^{-1}, γCH (para-di-substitution pattern) at 828 cm^{-1}, γCH (mono-substitution pattern) at 754 and 694 cm^{-1}.

2,2′:5′,2″-Terthiophene-5-carboxaldehyde

In a 10-mL beaker 0.3 mL (3.89 mmol) of dried dimethylformamide was poured; the beaker was immersed into a 0–5 °C ice/salt water bath and, under vigorous stirring, 0.3 mL (3.21 mmol) POCl$_3$ were added. The mixture was transferred to a

25-mL round-bottom flask containing 0.6 g (2.42 mmol) 2,2′:5′,2″-terthiophene dissolved in 6 mL of dried CH_2Cl_2. The mixture was stirred at room temperature for 3 h and then refluxed for 15 min, filtered under vacuum and the collected solid washed with cold CH_2Cl_2. The precipitate was purified by adding 2 mL 1 M NaOH under stirring and the mixture filtered under vacuum. The solid was washed with 3 mL of 1 M NaOH and then with plenty of water. The obtained yellow solid was oven dried at 50 °C for 5 h. Yield, 0.24 g (36.4 %). ^{1}H-NMR (DMSO-d_6): s(1H, 9.9 ppm, CHO), d(1H, 8.0 ppm), m(3H, 7.6 ppm), d,d(1H, 7.4 ppm), d(1H, 7.3 ppm), d(1H, 7.1 ppm). Elemental analysis: C 56.6; H 2.1; S 32.4; O 8.9 % (by difference), found mol/mol ratio C/H 13/6; C/S 13/2.8, C/O 13/1.4. mp 138–139 °C. FT-IR (KBr): vCH at 3,096 cm^{-1}, vCHO at 1,651 cm^{-1}, vC=C at 1,459 cm^{-1}, CH at 1,020 cm^{-1}.

Monomers synthesis

The following monomers were synthesized.

N,N′-Bis(thien-2-yl methylene)-4,4′-diamino triphenylamine, labeled as TPA-Th

0.60 g 4,4′-bis amino-triphenylamine, 30 mL benzene and 80 mg p-toluenesulfonic acid as catalyst were added into a 50-mL round-bottom flask fitted with a Dean-stark trap and reflux condenser. The mixture was heated and then 0.51 g of thiophene-2-carboxaldehyde dissolved in 12 mL benzene was added under stirring. The mixture was refluxed for 30 min (checked by TLC, eluted with CHCl$_3$). The hot mixture was filtered and the solvent removed from the filtrate. The residue was dissolved in the minimum possible amount of hot benzene and the resulting black solid was precipitated by adding n-hexane. The supernatant was poured into a flask and the solvent wholly removed. The obtained yellow solid was dissolved in the minimum amount of acetone and the monomer precipitated by adding water. The yellow solid was separated by vacuum filtration and finally air dried. Yield, 0.25 g (33 %). ^{1}H-NMR (DMSO-d_6): m(3H, 7.08 ppm), t(2H, 7.35 ppm), d(4H, 7.05 ppm), d(4H, 7.25 ppm), Imine s (2H, 8.82 ppm), d(2H, 7.65 ppm), t(2H, 7.25 ppm), d(2H, 7.80 ppm). Elemental analysis: C 72.4; H 5.4; N 9.0; S 13.0 %. Found mol/mol ration C/N 28/2.98; C/H 28/25, C/S 28/1.9. mp 74–75 °C. FT-IR (KBr): vCH at 3,070 and 3,025 cm^{-1}, vCH=N at 1,614 cm^{-1}, vC=C at 1,593 and 1,494 cm^{-1}, vCN at 1,315 cm^{-1}, γCH (para-di-substitution pattern) at 843 cm^{-1}, γCH (benzene ring mono-substitution pattern) at 754 and 694 cm^{-1}; γCH (thiophene ring mono-substitution pattern) at 708 cm^{-1}.

N,N′-Bis((2,2′-bithien-5yl)methylene) 4,4′diaminotriphenylamine, labeled as TPA-biTh

0.41 g (1.48 mmol) 4,4′-bis aminotriphenylamine was dissolved in a 50-mL flask with 16 mL of hot benzene and then 0.08 g (0.42 mmol) of p-toluenesulfonic acid monohydrate was added. The mixture was stirred and 0.60 g (3.09 mmol) of 2,2′-bithiophene-5-carboxaldehyde dissolved in 9 mL benzene was added. The mixture

was refluxed for 1 h and then vacuum filtered while hot. The insoluble solid (catalyst) was washed with benzene and then both the filtrate and washings were joined and the volume reduced down to 5 mL on a hot plate under stirring. Next, with a Pasteur pipette, they were transferred to a beaker containing 50 mL ethyl ether and stirred and allowed to stand for 2.5 h. The obtained brick color solid was then vacuum filtered and oven dried at 45 °C. Yield, 0.22 g (23.6 %). ^{1}H-NMR (DMSO-d$_6$): Imine s(2H, 8.79 ppm), d(4H, 7.60 ppm), d(2H, 7.49 ppm), m(8H, 7.35 ppm), d(2H, 7.15 ppm), m(7H, 7.06 ppm). Elemental analysis: C 68.01; H 3.0; N 6.8; S 19.3 %. Found mol/mol ration C/N 36/3.09; C/H 36/19.0, C/S 32/3.83. mp 74–75 °C. FT-IR (KBr): vCH at 3,060 cm^{-1}, vCH=N at 1,607 cm^{-1}, vC=C at 1,494 cm^{-1}, 1,453 cm-1, vCN at 1,300 cm-1, γCH (para-di-substitution pattern) at 833 cm^{-1}, γCH (benzene ring mono-substitution pattern) at 750 and 670 cm^{-1}.

N,N′-Bis((2,2′:5′,2″-terthien 5-yl)methylene) 4,4′diamino triphenylamine, labeled as TPA-terTh

25 mg (0.1 mmol) 4,4′-bis aminotriphenylamine was dissolved in a 50-mL flask with 3 mL benzene and 4 drops of glacial acetic acid added as catalyst. The solution was heated under stirring for 5 min and 49 mg (0.18 mmol) of 2,2′:5′,2″-terthiophene-5-carboxaldehyde, dissolved in 10 mL benzene, was slowly added. The reaction mixture was refluxed for 20 h, the volume reduced down to 3 mL and finally left aside at room temperature for 30 min. The solid precipitate was separated by vacuum filtration and washed with cold benzene. The product was oven dried at 45 °C for 4 h. Yield, 0.024 g (30.30 %). ^{1}H-NMR (CDCl3): imine s(2H, 9.9 ppm), m(13H, 7.2 ppm), m(14H, 7.1 ppm). Elemental analysis: C 67.5; H 3.5; N 5.8; S 25.0 %. Found mol/mol ration C/N 44/3.2; C/H 44/27.1, C/S 44/6.1. mp 217–218 °C. FT-IR (KBr): vCH at 3,060 cm^{-1}, 2,921 cm^{-1}, vCH=N at 1,603 cm^{-1}, vC=C at 1,494, 1,459 cm^{-1}, γCH (para-di-substitution pattern) at 843 cm^{-1}.

Polymers synthesis

Poly(TPA-Th) synthesis

Into a 50-mL round-bottom flask, fitted with reflux condenser, 600 mg of monomer and 16 mL of dried CHCl$_3$ were placed. Subsequently, the supernatant of a mixture prepared by adding 0.20 g of anhydrous FeCl$_3$ to 8 mL dried CHCl$_3$ was added. The mixture was warmed for 24 min, (checked by TLC, eluted with CHCl$_3$) and then filtered utilizing a Buchner funnel. The final product was thoroughly washed with CHCl$_3$ and then oven dried at 30 °C. Yield, 90 mg (15 % yield). Theoretical empirical formula: C$_{28}$H$_{19}$N$_3$S$_2$; Elemental analysis: C 55.8; H 3.5; N 7.4; S 10.6 %. Found mol/mol ration C/N 28/3.2; C/H 28/20.9; C/S 28/1.99.

Poly(TPA-biTh) synthesis

Into a 100-mL round-bottom flask, 29 mL of dried CHCl$_3$ were cooled in an ice-salt water bath at 0–5 °C. 410 mg (0.65 mmol) of monomer was added, the mixture

stirred until total monomer dissolution and then, the flask was immersed into the ice-salt water bath at 0–5 °C and, under stirring, the supernatant of a suspension obtained by adding 0.50 g (3.08 mmol) of anhydrous FeCl$_3$ into 14 mL of dried CHCl$_3$, was added. The mixture was stirred for 20 min, vacuum filtered and the obtained purple solid washed with methanol. The polymer was oven dried at 40 °C for 2 h. Yield, 103 mg (25 %). theoretical empirical formula C$_{36}$H$_{23}$N$_3$S$_4$; Elemental analysis: C 47.50; H 2.85; N 5.18; S 13.75 %. Found mol/mol ration C/N 36/3.3; C/H 36/26.0, C/S 36/3.9.

Poly(TPA-terTh) synthesis

15 mL of dried CHCl$_3$ in a 50-mL round-bottom flask was cooled in an ice-salt water bath at 0–5 °C for 30 min and then 0.20 g (0.25 mmol) of monomer was added. Once the monomer is wholly dissolved, the supernatant of a mixture prepared by adding 0.20 g (1.23 mmol) of anhydrous FeCl$_3$ to 8 mL dried CHCl$_3$. was added. The mixture was stirred during 20 min at 0–5 °C, filtered and the obtained polymer washed with plenty of cold methanol. The product was oven dried at 40 °C during 3 h. Yield, 0.07 g (35 %). Theoretical empirical formula C$_{44}$H$_{27}$N$_3$S$_6$; Elemental analysis: C 67.49; H 3.46; N 5.75; S 23.85 %. Found mol/mol ration C/N 44/3.2; C/H 44/27, C/S 44/5.8.

Results and discussion

4,4′-Bisdinitro-triphenylamine was synthesized according to Liou et al. [30], then the dinitro compound was reduced using hydrazine and 10 % Pd/carbon as catalyst to obtain 4,4′-bis amino-triphenylamine, Fig. 1.

TPA-Th, TPA-biTh and TPA-terTh monomers were synthesized by condensation between 4,4′-bis amino-triphenylamine and two moles of the following reagents: thiophene-2-carboxaldehyde, 2,2′-bithiophene-5-carboxaldehyde and 2,2′:5′,2″-terthiophene-5-carboxaldehyde, respectively, using a catalyst in benzene medium.

The polymers were synthesized using FeCl$_3$ in dried chloroform as oxidant. Monomers and polymers route of synthesis, along with their structure, are shown in Fig. 2.

Monomers yields are low (24–33 %) due to losses that occur by the formation of a difficult-to-break adduct with the catalyst which, in addition, proved to be insoluble in the reaction medium. Monomers characterization by FT-IR and ^{1}H-NMR spectroscopy and elemental analysis agrees well with the thought structure. Polymers synthesis was complicated because the monomer fails to polymerize in the
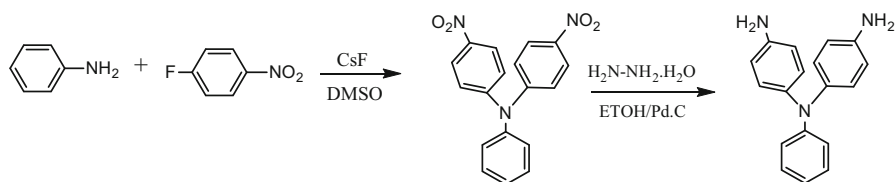

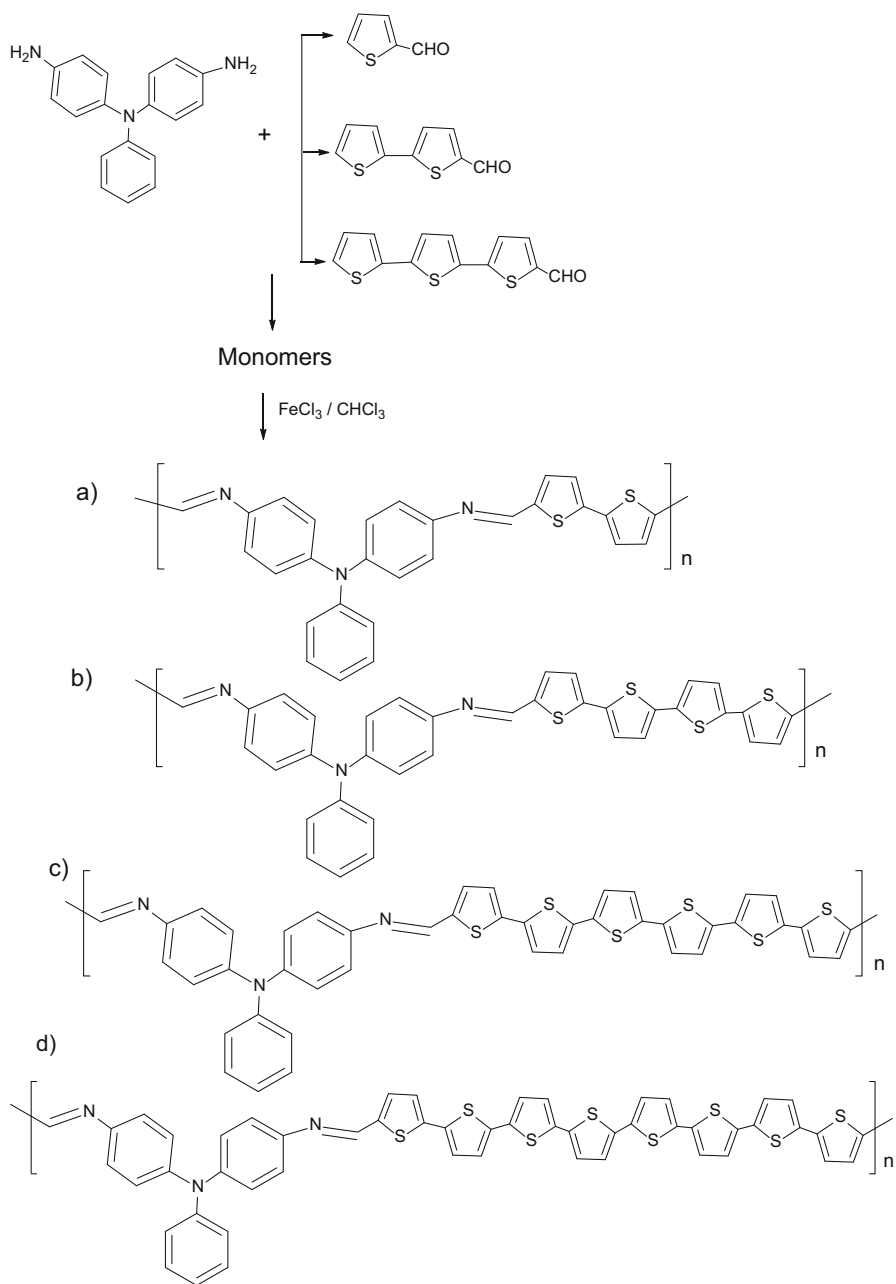**Fig. 1** Scheme of 4,4′-bis amino-triphenylamine synthesis

Fig. 2 Synthesis routes and polymer structure of (a) poly(TPA-Th); (b) poly(TPA-biTh); (c) poly(TPA-terTh); (d) poly(TPA-quatTh)

presence of small amounts of water and, moreover, after prolonged polymerization time in the presence of FeCl$_3$, cleavage of the imine bonds occurs. Optimal times of syntheses are given in experimental.

Characterization of polymers

Figure 3 exhibits polymers FT-IR spectra, which proved to be quite similar. The most important bands correspond to the imine group at 1,609, 1,643 and 1,634 cm^{-1} in poly(TPA-Th), poly(TPA-biTh) and poly (TPA-terTh), respectively; aromatic C–H bonds at 3,030, 3,065 and 3,074 cm^{-1} in poly (TPA-Th), poly(TPA-biTh) and poly(TPA-terTh), respectively; aromatic C=C at 1,580, 1,494 cm^{-1} in poly(TPA-Th), 1,589 and 1,493 cm^{-1} in poly(TPA-biTh), and 1,589, 1,489 cm^{-1} in poly (TPA-terTh); thiophene rings out-of-plane deformation bands are observed at 694, 699 and 699 cm^{-1} in poly(TPA-Th), poly TPA-biTh) and poly(TPA-terTh, respectively.

Polymers elemental analysis and theoretical empirical formula are included in polymer synthesis section. Found C/H, C/N and C/S ratios agree well with the empirical formulas and polymeric structures. The presence of the imine group (–CH=N) in the polymers was confirmed by ^{1}H-NMR spectroscopy. Figure 4 shows the spectra and the prominent peaks associated to imine groups that appear in the
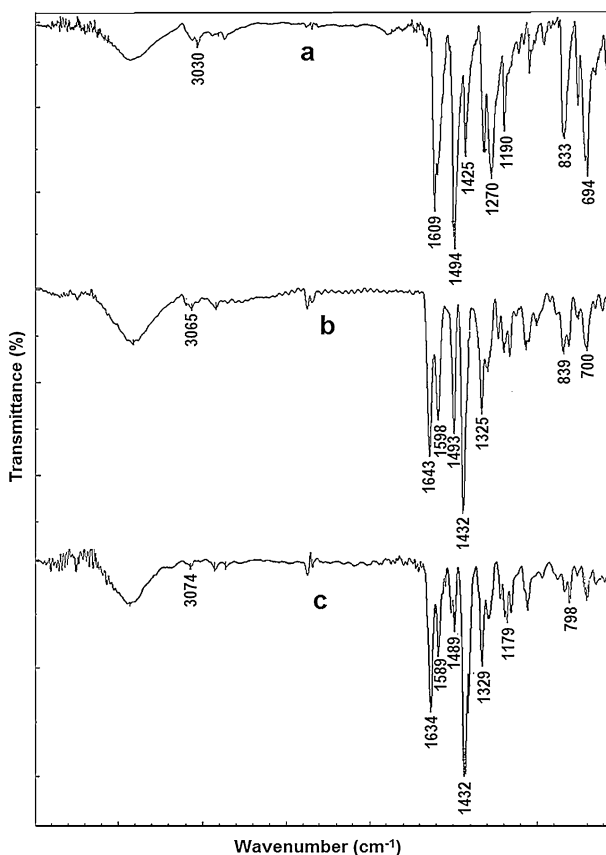

Fig. 3 FT-IR spectra of polymers (*a*) poly(TPA-Th, (*b*) poly(TPA-biTH), (*c*) poly(TPA-terTh)
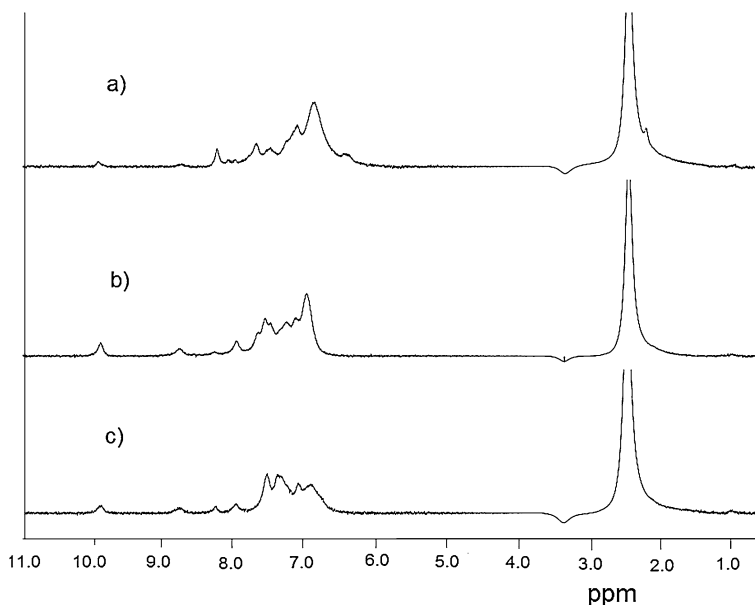
Fig. 4 ¹H-NMR spectra of (*a*) poly(TPA-Th), (*b*) poly(TPA-biTh), (*c*) poly(TPA-terTh) in DMSO-d6

range 9.5–10 ppm. Other peaks between 8.5 and 6.5 ppm are associated to aromatic C–H. The peaks at 2.6 ppm correspond to the deuterated solvent. Due to polymers low solubility in the deuterated solvent, spectra were vertically expanded and to display aromatic hydrogen, water molecule peaks that appeared at 3.4 ppm had to be removed.

Optical properties

The polymers exhibit different optical absorptions. Fig. 5 shows the results, a set of absorption maxima are observed: at 290 and 380 nm for poly(TPA-Th), 358 nm for poly(TPA-biTh) and 371 nm for poly(TPA-terTh) corresponding to $\pi–\pi^*$ and $n–\pi^*$ transitions [31]. Figure 5d exhibits the absorption spectra of poly(thiophene), synthesized under the same conditions used for the other polymers. It is noteworthy that the transitions appeared with maximum absorption at 440 nm. Polymers hypsochromic shift reflects a decrease of the conjugation length in the skeleton with regard to poly(thiophene) chains. The lower polymer conjugation is due to (1) a low molecular size since all three polymers present low intrinsic viscosity, and (2) the presence of TPA and imine groups in the chains; TPA has a tetrahedral geometry and imine groups a *trans* one, both groups prevent a more effective delocalization.

The absorption spectra correspond either to polymers of low molecular size or to oligomers, the intrinsic viscosity was 0.05, 0.05, 0.09 dL/g for poly(TPA-Th), poly(TPA-biTh) and poly(TPA-terTh), respectively. The higher conjugation belongs to poly (TPA-terTh) since the $\pi–\pi^*$ and $n–\pi^*$ transitions in its absorption spectrum has a bathochromic shift with respect to poly(TPA-Th) and poly
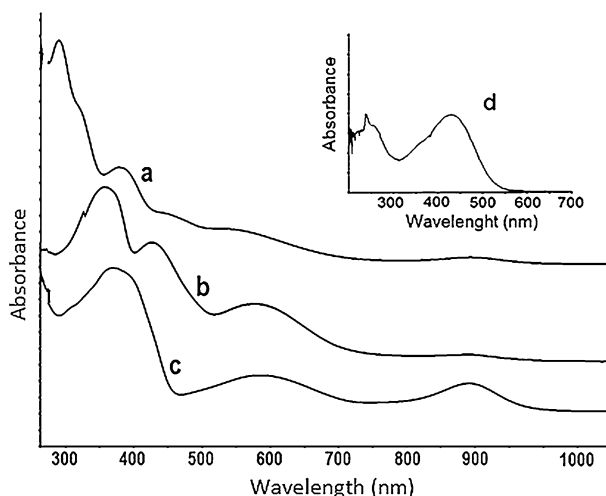
Fig. 5 Optical absorption spectra of (*a*) poly(TPA-Th), (*b*) poly(TPA-biTh), (*c*) poly(TPA-terTh), (*d*) poly(thiophene)

(TPA-biTh). The higher conjugation of poly(TPA-terTh) is consistent with the increased viscosity and, structurally, with the largest number of thiophenyl units in the skeleton; indeed poly(TPA-terTh) presents 6 thiophenyl units in the main chain, on the other hand, poly(TPA-biTh) and poly(TPA-Th) exhibit, respectively, 4 and 2 conjugated thiophenyl units in the skeleton. We believe polymers low molecular size is rather related to short polymerization times.

Furthermore, poly(TPA-terTh) and poly(TPA-biTh) exhibit maximum absorption at 584 and 576 nm, respectively, while in poly(TPA-Th) the same absorption appears as a shoulder at 550 nm and is shifted toward shorter wavelengths. Besides, poly (TPA-biTh) displays an additional absorption at 415 nm. Those transitions of lower energy can be attributed to species with different chains length in the polymers that possess different effective conjugation lengths. Roncali et al. [32] and Ribeiro et al. [33] have reported similar results with polymers of different chain lengths and low molecular size obtained by fractionation of polymers obtained from terthiophene.

The absorption spectra correspond to neutral polymers, i.e., in reduced (undoped) state [34] since no low transition energy associated to bipolarons appear. Maximum absorptions at 889 nm are ascribed to a very low polaron population, which is more significant in poly (TPA-terTh). Carrier bands usually embrace the entire optical spectrum from 700 nm to near infrared [33, 34] and it has been demonstrated that poly(thiophene) doping starts with the transformation of the longest conjugation segments [34, 35]; this is consistent with the higher absorption intensity observed at 889 nm in the polymer with the greatest number of thiophenyl units in the main chain, i.e., poly(TPA-terTh).

Physical properties

An approximation of the Tauc equation [36, 37], with data obtained by UV–Vis spectrometry, was employed for optical band gap (E_g) measurements.

$$A = B\left(hv - E_g\right)^{1/2}/hv$$

where A is absorbance, B material constant, h Planck constant and v frequency. If $A = 0$, $hv = E_g$. Table 1 shows the E_g obtained for the polymers. It is seen that the three synthesized polymers exhibit E_g higher than poly(thiophene) band gap, revealing that the TPA units in the polymer chains increase the band gap. Regarding poly(TPA-quatTh), theoretical E_g, HOMO and LUMO were calculated, E_g found was 2.33 eV while that of poly(thiophene) was 2.30 eV. The similarity of the results showed that 8 units of conjugate thiophenyl in a polymer chain alternated with one electron-donor group (TPA) are sufficient to obtain an E_g similar to that of poly(thiophene). However, poly(TPA-quatTh) HOMO and LUMO theoretical results were different from those of poly(thiophene) (Table 1). HOMO and LUMO values for poly(TPA-quatTh) were −4.67 and −2.24 eV, respectively, whereas for poly(thiophene) were −5.45 and −3.29 eV. These results demonstrated that TPA electron-donor effect on the chains attached to 8 thiophenyl units allows increasing HOMO and LUMO 0.78 and 1.05 eV, respectively, as compared to poly(thiophene).

HOMO values can be inferred from the cyclic voltammograms (Fig. 6) and were calculated from the first peak of the corresponding redox wave (E_1ox vs. Ag/AgCl) [38], according to the following equation.

$$E(\text{HOMO}) = -(E_1\text{ox} + 4.7)\ \text{eV}$$

Comparing the HOMO energy levels, it can be noted that they increase in the following order: poly(TPA-Th) < poly(TPA-biTh) < poly(TPA-terTh) = poly(thiophene) < poly(TPA-quatTh) and this order is related to the increasing number of thiophenyl units in the polymeric chain. LUMO also increases as thiophenyl units in the chains do. Furthermore, HOMO of poly(TPA-terTh) containing 6 thiophenyl units in the main chain is similar to that of poly(thiophene); and poly(TPA-Th), poly(TPA-biTh) containing 2, 4 thiophenyl units in the main chain has a HOMO smaller than poly(thiophene).

Table 1 Polymers physical properties

Polymer	HOMO (eV)	LUMO[c] (eV)	Optical E_g (eV)
Poly(TPA-Th)	−5.65	−3.01	2.64
Poly(TPA-biTh)	−5.55	−2.73	2.82
Poly(TPA-terTh)	−5.45	−2.75	2.70
Poly(TPA-quatTh)	−4.67[a]	−2.24[a]	2.33[a]
Poly(thiophene)	−5.45[b]	−3.29[b]	2.30

[a] From theoretical calculations

[b] From reference 35

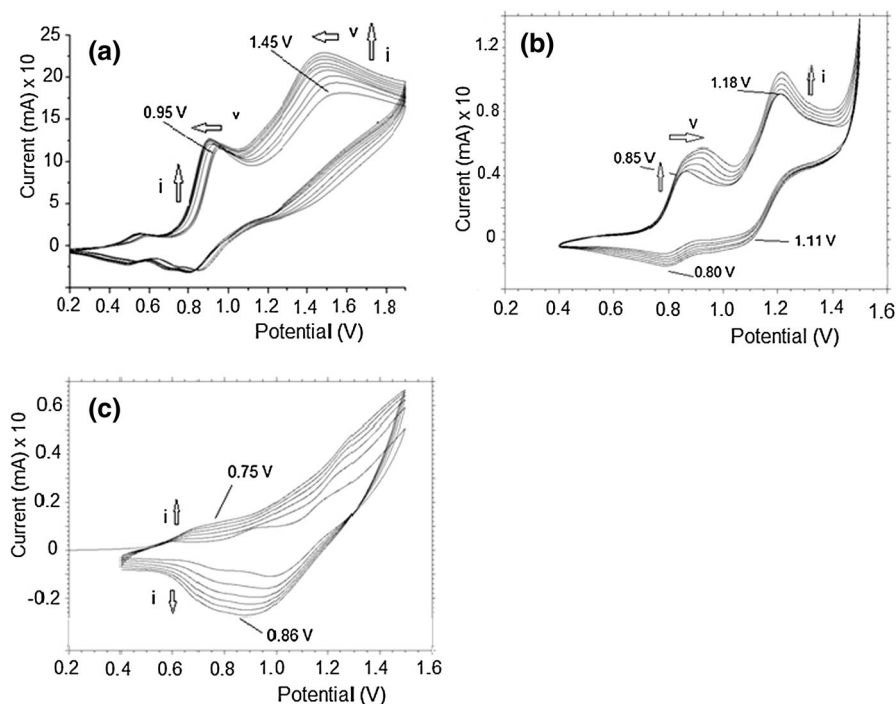[c] LUMO values were calculated from HOMO and E_g

Fig. 6 Cyclic voltammograms of **a** TPA-Th; **b** TPA-biTh and **c** TPA-terTh in dried CH_3CN and 0.1 M $TBAPF_6$ supporting electrolyte

Poly(TPA-quatTh) containing 8 thiophenyl units in the chain exhibited a HOMO higher than poly(thiophene). Synthesis of poly(TPA-quatTh) is in progress in our laboratory.

Polymers cyclic voltammograms exhibit two main redox curves. It is seen that as the number of cycles increases so does the current, reflecting the semiconductor properties of the materials. These voltammograms are typical of doped polymers. Poly(TPA-Th) showed a shift of its oxidation potential to lower values with increasing number of cycles providing further evidence of an autocatalytic mechanism [39]. In contrast, poly(TPA-biTh) oxidation potential shifts toward anodic potential as the number of cycles increases, indicating an energy increase for the oxidation of the polymer owing to the presence of polymer-oxidized species.

The onset of monomers oxidation was found to occur at ca. 0.75, 0.77 and 0.6 V and the first oxidation peak at 0.95, 0.85 and 0.75 V for poly(TPA-Th), poly(TPA-biTh) and poly(TPA-terTh), respectively. The values are slightly similar to those of thiophene derivatives bonded to electron-donor groups [40, 41]. In TPA-terTh the position of the oxidation second peak is not clear, in the case of the second oxidation peak at 1.45, 1.18 V in the TPA-Th, TPA-biTh that appear as a wide wave in Fig. 6a, b, corresponds to chains whose structure contains dications of different conjugation lengths [42]. Different conjugation lengths in poly(thiophene) electropolymerized from thiophene was reported by Link et al. [39].

Poly(TPA-Th), poly(TPA-biTh) and poly(TPA-terTh) containing, respectively, 2, 4 and 6 thiophenyl units in its polymeric backbone, revealed that the gradual increase of thiophene units, provokes a gradual decrease of oxidation potentials, Fig. 6. Consequently, TPA electron-donor effect decreases polymers oxidation potential in polymers electrochemically synthesized. This decrease is greater as the number of thiophenyl units in the chain increases; however, the reduction potential of poly(TPA-Th) and poly(TPA-terTh) are alike.

TGA and DSC studies

Figure 7 exhibits thermal decomposition profiles obtained by TGA for selected examples of the studied polymers. In all cases, the obtained residual weight was higher than 30 % at 1,000 °C, indicating high thermal stability. The TGA profiles were also used as reference to set the temperature ranges for DSC since the obtention of information from the corresponding thermograms requires thermal stability of the samples.

Different temperatures are used to represent the extent of the thermal decomposition in a polymer sample, e.g., T_{50}, the temperature at which the weight reaches 50 % of the original weight. From the decomposition profiles shown in Fig. 7, T_{50} was determined and the obtained values were 925, 840 and 825 °C for poly(TPA-bith), poly(TPA-Terth) and poly(TPA-Th), respectively. From the differential thermograms, maximum decomposition temperatures (T_{max}) 476.9, 498.2 and 518.3 °C, respectively, were obtained. These values confirm the good thermal stability suggested by the residual weight.

Figure 8 shows thermograms obtained for poly(TPA-bith), poly(TPA-Terth) and poly(TPA-Th). With the exception of an unclear signal for poly(TPA-bith), glass transition signals were not observed. This process represents a sudden change in the mobility of the chain segments of a macromolecule in the amorphous phase, which should be prevented by the presence of C=N bonds and bulky aromatic groups. Moreover, endothermic signals were observed at about 200 °C, results that can be related to decomposition process experienced by the polymer samples. This behavior was previously observed by TGA: in all the cases, the initial

Fig. 7 Thermal decomposition profiles obtained by TGA of (a) poly(TPA-bith) (dotted line), (b) poly(TPA-terth) (line) and (c) poly(TPA-Th) (dashed line)
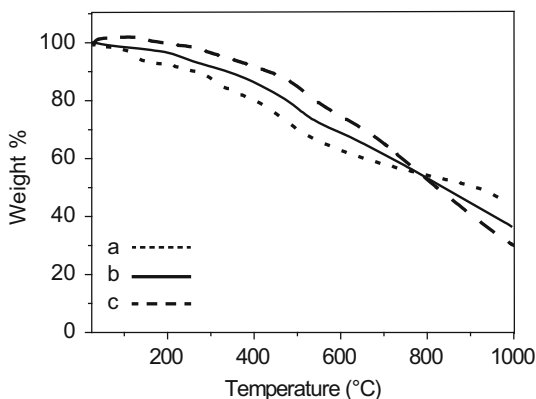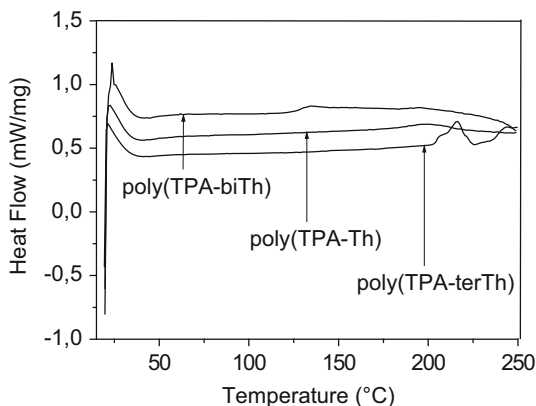
Fig. 8 Polymers DSC thermograms

decomposition temperature is about 200 °C (Fig. 7). The endothermic signal observed is a very small peak, comparable with glass transition signals, indicating a small initial decomposition.

Conclusions

Various poly-Schiff bases containing TPA and 2, 4 and 6 units of thiophenyl in the main chain were synthesized and characterized. Polymers characterization by FT-IR and ^{1}H-NMR spectroscopy and elemental analysis agree well with the thought structures. The obtained polymers were of low viscosity, almost neutral and with a very low population of charge carriers. TPA units in the chains affect polymers properties as compared to poly(thiophene), namely decreases the oxidation potential while HOMO, LUMO and band gap can be modified. When TPA is incorporated into 8 thiophene units, the HOMO and LUMO can be increased, without band gap modification, with respect to poly(thiophene) HOMO and LUMO. Poly(TPA-Th), poly(TPA-biTh) and poly(TPA-terTh) have HOMO values that allow polymers to be studied in organic photocells. The polymers exhibited high thermal stability with the exception of poly(TPA-biTh), they showed no glass transition temperature.

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