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ORIGINAL PAPER

Synthesis and characterization of novel polythiophenes bearing oligo(ethylene glycol) segments and azobenzene units

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Abstract New copolymers of thiophenes containing azobenzene moieties in the side chain, 3-((((((4-phenyl)azo)phenoxy)ethyl)triethoxy)oxy)-4-methylthiophene/3-methyltetra (oxyethylene)oxy-4-methylthiophene (**CP1**) and 3-((((((4-phenyl) azo)phenoxy)ethyl) triethoxy) oxy)-4-methylthiophene/3-dodecylthiophene (**CP2**), were synthesized from 3-bromo-4-methylthiophene. These copolymers were characterized by ^{1}H-NMR spectroscopy, and their thermal, optical, and electrochemical properties were determined by thermogravimetric analysis, differential scanning calorimetry, absorption spectroscopy, and cyclic voltammetry. **CP1** possesses higher degree of conjugation and azobenzene content than **CP2**, and its structure is more regio-regular. Besides, **CP1** exhibited a higher glass transition temperature ($T_g = 35$ °C, $T_5 = 225$ °C) and a lower thermal stability than **CP2** ($T_g = 13$ °C, $T_5 = 307$ °C). Both copolymers showed a similar solvatochromic behavior when they were dissolved in chloroform and mixtures chloroform:methanol.

Keywords Polythiophene · Azobenzene · Optical properties

Introduction

Polythiophene (**PT**) has been considered one of the most promising electroconducting polymers due to its high stability, ease of structural modification, and controllable electrochemical behavior. At the beginning, the application of this polymer was very limited due to its insolubility in many organic solvents and due to its extended π-conjugated structure. In order to resolve this problem, thiophenes containing alkyl chains have been used as monomers. This new kind of 3-substituted

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thiophenes produces processable conducting polymers, whose electronic properties can be modified allowing us to characterize them by chemical and physical methods [1]. The stability of the poly(3-alkylthiophenes) in the doped state can be achieved by releasing the alkyl crowding along the backbone or by introducing alcoxy groups. A monomer bearing two methylene groups between the thiophene unit and the first oxygen atom, or with two ether functions, allows the obtention of highly stable polymers at normal conditions [2, 3]. For some polythiophenes, interesting thermochromic [4, 5], ionochromic [4, 5], photochromic [6], piezochromic [7], and biochromic [8] properties have been reported in literature. These color changes are usually due to a twisting of the polymer backbone or conformational changes, which modify significantly the effective conjugation length. This phenomenon is always associated with a shift of the absorption bands in the UV–vis region [9]. The increase of this effective degree of conjugation improves remarkably the electrochemical properties and conductivity of these polymers. If the side chain of the polymer has a strong donor effect and enters into conjugation with its backbone, a significant modification of the thermal and optical properties of such polymers takes place [10]. Several studies about the conformational changes in polythiophenes, possessing photochromic moieties in the side chain, have been reported in [6, 11]. One of these photochromic groups is azobenzene, which causes changes in the absorption spectra of these polymers because of its *trans–cis* photoisomerization [12]. Azobenzene can modify significantly the conformation of the conjugated polymer backbone [6, 13], giving rise to thermochromic [6, 12] and photochromic effects [14–17], as well as changes in the conductivity [18, 19] and anisotropy of polythiophenes [20].

The chromic properties of substituted polythiophenes make them an excellent choice for the elaboration of light emitting diodes [21], gas sensors [22–24], biomedical applications [25], metallic ions sensors [26, 27], and biosensors [28–30]. The main aim of this study is the synthesis and characterization of new copolymers of azobenzene-substituted polythiophenes with 3-methyl-4-(tetraethoxy)oxythiophene and 3-dodecylthiophene, respectively, as well as the study of the effect of these co-monomers on the properties of the obtained copolymers. Among the substituted polythiophenes, which have been used as sensing materials, poly(3-dodecyl thiophene) is one of the most technologically promising polymers due to its ease of synthesis, low cost, versatile processability, and electrical conductivity [30]. In this article, we report the synthesis and characterization of a series of polymers containing azobenzene moieties linked to the polythiophene backbone via a well-defined oligo(ethylene glycol) spacer.

Experimental

Apparatus

^{1}H- and ^{13}C-NMR spectra of the intermediates, monomers, and polymers were recorded in a Bruker Avance 400 Spectrometer, operating at 400 and 100 MHz, respectively. Thermal properties of the polymers were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was conducted on a Hi-Res TGA 2950 Instrument (from 25 to 550 °C) and DSC on a DSC 2910 TA instrument (from −75 to 200 °C), in both cases with a heating rate of 5 °C/min T_5 (5% weight loss temperature), T_g (glass transition temperature), and T_s (softening point) were determined. Absorption spectra of the polymers in solution and casted film were carried out on a Varian Cary 1 Bio UV/vis Spectrophotometer model 8452A. Molecular weights of the polymers were determined by Gel Permeation Chromatography (GPC), using a Waters 2695 Instrument connected to a Diffraction Index Detector Waters 2414. Measurements were carried out using THF as solvent and a polystyrene standard. For cyclic voltammetry, an Autolab PGSTAT100 potentiostat was employed. All experiments were carried out in a three-electrode undivided cell, using tetrahydrofurane (THF) as solvent, $LiClO_4$ as supporting electrolyte, Ag–AgCl as reference electrode, a platinum disc with a surface area of 0.0314 cm^2 as the working electrode, and a platinum wire as auxiliary electrode.

Chemicals

Tetra(ethylene glycol), 3-bromo-4-methylthiophene, 3-dodecylthiophene, and other chemicals used in the synthesis of the monomers and polymers were purchased from Aldrich and used as received. Chloroform was distilled over calcium hydride (CaH_2) to remove traces of water.

3-methyl-4-(tetraethoxy)thiophene (**1**) (see Fig. 1) was synthesized using a procedure similar to that reported in [6]. Tetra(ethylene glycol) (20.43 g, 105 mmol) and Na (0.70 g, 30 mmol) were reacted for 3 h under nitrogen atmosphere to give the corresponding alcoxide. Afterward, a mixture of 3-bromo-4-methylthiophene (2.01 g, 11.4 mmol), CuBr (1.96 g, 13.6 mmol) was prepared; NMP (12 mL) was added and the reaction mixture was heated at 110 °C for 36 h. Then, it was cooled to room temperature, filtered, and the filtrates were extracted with diethyl ether, dried with $MgSO_4$, and concentrated under reduced pressure. Finally, the product was purified by column chromatography, using ethyl acetate as eluent to give a light yellow oil (1.39 g, 4.78 mmol). Yield: 42%. ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm) (Scheme 1, R = OH): 6.81 (s, 1H, H^1), 6.16 (s, 1H, H^2), 4.11 (t, 2H, tioph–O–CH_2), 3.84–3.87 (t, 2H, tioph–CH_2–$\mathit{CH_2}$–O), 3.66–3.75 (m, 10H, all other OCH_2), 3.58 (t, 2H, $\mathit{CH_2}$–OH), 2.88 (OH), 2.09 (s, 3H, CH_3–tioph). ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): 155.96 (1C, Cd), 129.29 (1C, Cc), 120.10 (1C, Ca), 96.74 (1C, Cb), 72.71, 70.99, 70.79, 70.74, 70.44, 69.85, 69.75, 61.85 (8C, all OCH_2), 12.89 (1C, CH_3–tioph).

3-methyltetra(oxyethylene)oxy-4-methylthiophene (**2**) was obtained from **1** (Fig. 1) following a similar method as that reported in [5]. **1** (0.130 g, 0.45 mmol) was added to a solution of KOH (0.126 g, 2.24 mmol) dissolved in DMSO (7 mL); the mixture was reacted for 1 h at room temperature to form the corresponding alcoxide. Methyl iodide (0.573 g, 4.03 mmol) was added and the reaction mixture was stirred for 24 h. Afterward, it was filtered and poured into water to remove DMSO; the product was extracted with dichloromethane. The organic phase was dried with $MgSO_4$ and concentrated at reduced pressure. The resulting product was

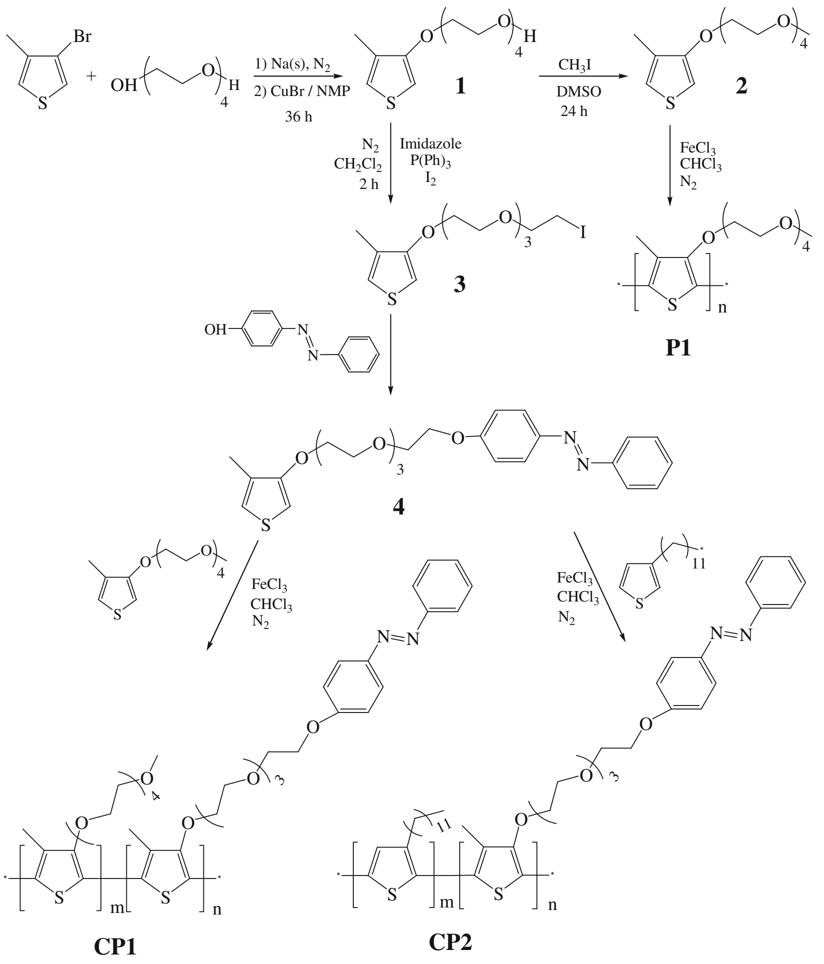
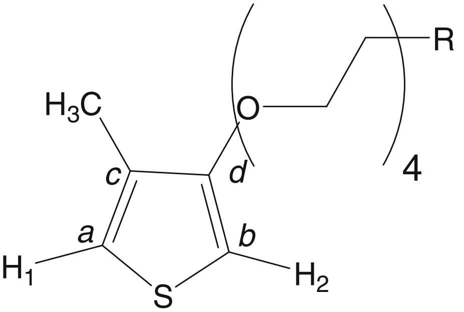


Fig. 1 Synthesis of polymer **P1**, and copolymers **CP1** and **CP2**

Scheme 1 Assignment of the signals for compounds **1**, **2** and **3**

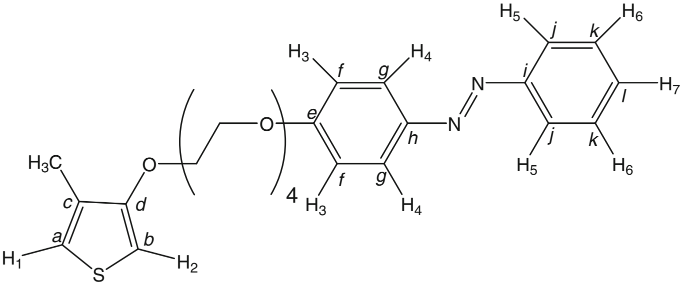


purified by flash column chromatography, using ethyl acetate as eluent. The pure product was a yellow oil (0.91 g, 0.3 mmol). Yield: 67%. ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm) (Scheme 1, R = OCH_3): 6.80 (s, 1H, H^1), 6.15 (s, 1H, H^2), 4.08 (t, 2H, tioph–O–CH_2), 3.84 (t, 2H, tioph–CH_2–$\mathit{CH_2}$–O), 3.72 (t, 2H, OCH_2), 3.62–3.68 (m, 8H, all other OCH_2), 3.53 (t, 2H, $\mathit{CH_2}$–OCH_3), 3.36 (s, 3H, O–CH_3), 2.08 (s, 3H, tioph–CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): 155.99 (1C, Cd), 129.27 (1C, Cc), 120.03 (1C, Ca), 96.63 (1C, Cb), 72.03, 70.99, 70.77, 70.62, 70.62, 69.81, 69.73 (8C, all OCH_2), 59.14 (1C, OCH_3), 12.86 (CH_3–tioph).

Poly(3-methyltetra(oxyethylene)oxy-4-methylthiophene) (***P1***) (Fig. 1) was obtained from **2** according to a similar procedure reported in [5]. A solution of $FeCl_3$ (0.128 g, 0.789 mmol) in $CHCl_3$ (5 mL) was prepared; then, **2** (0.06 g, 0.197 mmol) in $CHCl_3$ (1 mL) was added dropwise under inert atmosphere. The reaction mixture was stirred for 24 h at room temperature; then the solution was poured into methanol (200 mL) to precipitate the product. The resulting polythiophene **P1** was isolated by filtration, washed with methanol, and dried; then it was reduced in an ammonium hydroxide solution. The polymer was obtained as a dark purple powder. Yield: 85%. M_w = 196,800 g/mol, M_n = 183,200 g/mol, PD = 1.1 (from GPC).

3-(((2-iodoethyl)triethoxy)oxy)-4-methylthiophene (**3**) was obtained from **1** (see Fig. 1) using a similar procedure to that described by Lange and Gottardo [31]. First, CH_2Cl_2 (5 mL), triphenylphosphine (0.393 g, 1.5 mmol), imidazole (0.102 g, 1.5 mmol), and iodine (0.381 g, 1.5 mmol) were mixed in a bottom round flask under argon atmosphere. Then, a solution of **1** (0.290 g, 1 mmol) in anhydrous CH_2Cl_2 (1 mL) was added. The solution was stirred for 3 h; the crude product was washed with water to remove salts formed during the reaction, dried with $MgSO_4$, and concentrated under vacuum. Finally, this compound was purified by flash column chromatography, using a mixture ethyl acetate–hexane 80:20 as eluent. The pure product was obtained as a light yellow oil (0.284 g, 0.72 mmol). Yield: 72%. ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm) (Scheme 1, R = I): 6.81 (s, 1H, H^1), 6.17 (s, 1H, H^2), 4.09–4.11 (t, 2H, tioph–O–$\mathit{CH_2}$), 3.85 (t, 2H, tioph–O–CH_2–$\mathit{CH_2}$), 3.72–3.76 (m, 4H, OCH_2), 3.66–3.69 (m, 6H, all other OCH_2), 3.25 (t, 2H, CH_2–I), 2.10 (s, 3H, tioph–CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): 156.0 (1C, Cd), 129.28 (1C, Cc), 120.07 (1C, Ca), 96.68 (1C, Cb), 72.11, 71.04, 70.88, 70.78, 70.36, 69.85, 69.77 (7C, all OCH_2), 12.91 (1C, tioph–CH_3), 3.12 (1C, CH_2–I).

3-((((((4-phenyl)azo)phenoxy)ethyl)triethoxy)oxy)-4-methylthiophene (**4**) (Fig. 1; Scheme 2) was obtained according to the method reported in [6]. 4-hydroxyazobenzene (0.149 g, 0.75 mmol) and **3** (0.211 g, 0.53 mmol) were dissolved in dry acetone (6 mL). Then, K_2CO_3 (0.164 g, 1.19 mmol) and KI (0.01 g, 0.06 mmol) were added to the solution. The reaction mixture was heated to reflux for 48 h. with vigorous stirring. Then, the solution was cooled to room temperature, and the compound was separated by filtration, dissolved in CH_2Cl_2 and washed with water, to remove the remaining salts. The resulting product was purified by column chromatography, using ethyl acetate–hexane 50:50 as eluent. The pure product was obtained as a dark orange oil (0.22 g, 0.47 mmol). Yield: 89%. ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm) (Scheme 2): 7.90 (dd, 4H, H^4 and H^5, J_1 = 10.76 Hz, J_2 = 8.19 Hz), 7.44–7.53 (m, 3H, H^6 and H^7), 7.04 (d, 2H, H^3, J = 9.02 Hz), 6.82 (s, 1H, H^2), 6.16 (s, 1H, H^1), 4.21 (t, 2H, CH_2–O–phenyl), 4.09 (t, 2H, tioph–O–CH_2),



Scheme 2 Assignment of the signals for compound **4**

3.86–3.91 (m, 4H, OCH_2), 3.70–3.76 (m, 8H, all other OCH_2), 2.10 (s, 3H, tioph–CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): 156.05 (1C, Ce), 152.92 (1C, Ci), 147.25 (1C, Ch), 130.57 (1C, Cl), 129.34 (1C, Cc), 129.22 (2C, Cj), 124.90 (2C, Cg), 122.75 (2C, Ck), 120.13 (1C, Ca), 115.02 (2C, Cf), 96.73 (1C, Cb), 71.08, 70.90, 70.88, 69.89, 69.81, 67.90 (8C, all OCH_2), 12.93(1C, tioph–CH_3).

Copolymer of 3-((((((4-phenyl)azo)phenoxy)ethyl)triethoxy)oxy)-4-methylthiophene and 3-methyltetra(oxyethylene)oxy-4-methylthiophene (***CP1***) (Fig. 1). A solution of $FeCl_3$ (0.248 g, 1.53 mmol) in $CHCl_3$ (3 mL) was prepared. Another solution of **4** (0.6 g, 0.127 mmol) dissolved in $CHCl_3$ (1 mL) and **2** (0.78 g, 0.255 mmol) dissolved in $CHCl_3$ (1 mL) were added dropwise to the $FeCl_3$ solution. The reaction mixture was reacted for 24 h at room temperature; then the resulting solution was poured into methanol (200 mL) to precipitate the polymer. The crude product was separated by filtration, washed with methanol, and dried. A black copolymer was obtained. Yield: 82%. $M_w = 49{,}100$ g/mol, $M_n = 17{,}970$ g/mol, PD = 2.7 (from GPC).

Copolymer of 3-((((((4-phenyl)azo)phenoxy)ethyl)triethoxy)oxy)-4-methylthiophene and 3-dodecylthiophene (***CP2***) (Fig. 1) A solution of $FeCl_3$ (0.25 g, 1.53 mmol) in dry $CHCl_3$ (3 mL) was prepared under inert atmosphere. **4** (0.6 g, 0.127 mmol) dissolved in $CHCl_3$ (1 mL) and 3-dodecylthiophene (0.65 g, 0.255 mmol) in $CHCl_3$ (1 mL) were added dropwise to the $FeCl_3$ solution. The reaction mixture was reacted for 24 h at room temperature; then the solution was poured into methanol (200 mL) to precipitate the polymer. The resulting product was separated by filtration, washed with methanol, and dried. A dark brown copolymer was obtained. Yield: 80%. $M_w = 73{,}900$ g/mol, $M_n = 23{,}200$ g/mol, PD = 3.2 (from GPC).

Results and discussion

^{1}H-NMR spectra of the polymers

The ^{1}H-NMR spectrum of **P1** is shown in Fig. 2. As can see, there are two signals at 2.3 and 2 ppm due to the protons of the methyl groups linked to the thiophene rings. Besides, five more signals at 3.36 ppm (terminal –OCH_3) and 3.54–4.02 ppm (all

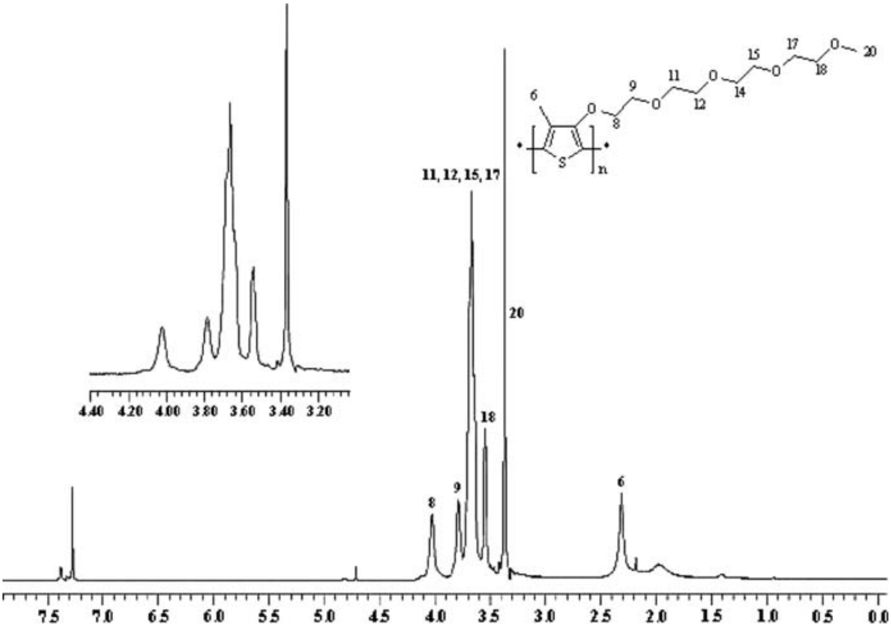


Fig. 2 ^{1}H-NMR spectrum of polymer **P1** in $CDCl_3$ solution

OCH_2 present in the side chains) can also be observed. The intense signal at 2.3 ppm reveals a highly regio-regular substitution pattern along the polymer backbone, whereas the weak signal at 2 ppm indicates the presence of traces of non-regio-regular parts or defaults [4]. According to the intensity ratio of both signals in the spectrum, **P1** has a head-to-tail content of about 85%.

^{1}H-NMR spectrum of **CP1** (Fig. 3) shows also a broad signal at 2.31 ppm due to the protons of the methyl groups present in the thiophene rings, as well as a weak signal at 2.19 ppm due to head-to-head defaults. The intensities ratio between these both signals revealed that **CP1** possesses also a head-to-tail content of about 85%. Signals between 3.3 and 4.3 ppm (from **b** to **f**) are attributed to the protons of the OCH_2 groups of the oligo(ethylene glycol) segments present in both repeat units. The signals **c**, **d**, and **e** are due to the protons of the azobenzene unit. A percentage of copolymerization about 40% was calculated, according to the intensities ratio of the signals at 7 ppm (**c**) and 3.35 ppm (**b**). Figure 4 shows the ^{1}H-NMR spectrum of **CP2**. Here, we can observe two signals at 2.80 and 2.57 ppm, due to the α-CH_2 protons present in the alkyl chain of the 3-dodecylthiophene moieties (**c**). The first signal at 2.80 ppm is related to a head-to-tail coupling, whereas the second one at 2.57 ppm arises from head-to-head defaults. A comparison between both signals, revealed that **CP2** possesses head-to-tail 3-dodecylthiophene content of about 80%. On the other hand, a head-to-tail content of about 80% was estimated for the azobenzene-substituted polythiophene, when the intensity ratio was calculated for the signals that appear at 2.18 and 2.30 ppm. A copolymerization percentage was calculated by comparing the intensities of the signals at 7.85 ppm (**g**) and 2.80 ppm

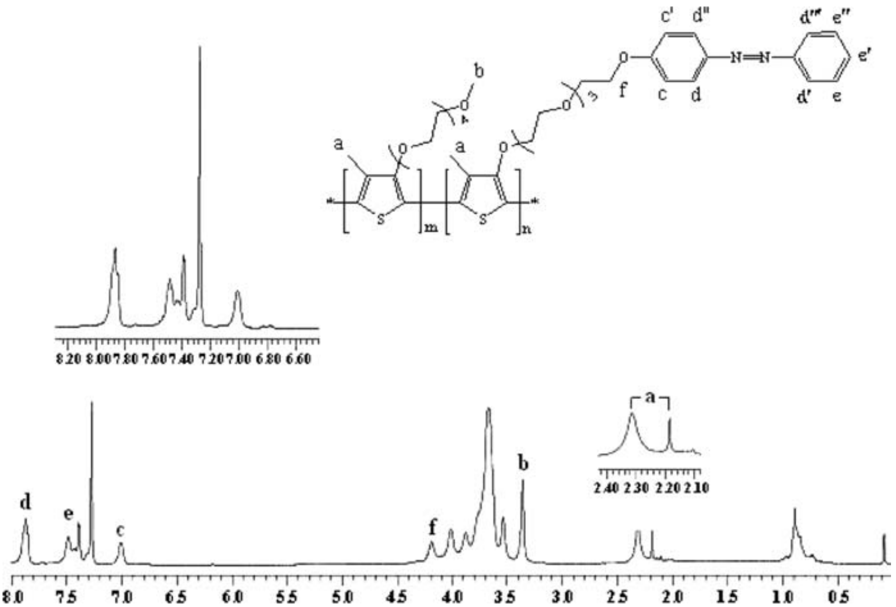


Fig. 3 ^{1}H-NMR spectrum of copolymer CP1 in $CDCl_3$ solution

(**c**). Therefore, **CP2** has a less regio-regular structure and a lower content of azobenzene-substituted thiophene units (12%) than its homologue **CP1** (40%).

Optical properties of the polymers

The absorption spectra of **P1** are shown Fig. 5. As we can notice, this polymer exhibits a maximum absorption band in $CHCl_3$ solution at $\lambda = 423$ nm (Fig. 5A), which is attributed to the polythiophene backbone [15]. Since a twisting of the conjugated polymer backbone provokes a decrease in the effective conjugation length [29], and taking into account that the resulting solution is yellow, we can conclude that this polymer in $CHCl_3$ solution adopts a non-planar conformation. This effect has been previously reported in the literature for similar polymers [4]. On the other hand, the spectrum of **P1** in acetone solution (Fig. 5B) shows this absorption band at $\lambda = 424$ nm, due to the presence of twisted conformation sequences in the polythiophene backbone, followed by an additional well-structured band centered at $\lambda_{max} = 559$ nm. This band, which has a vibronic fine structure, can be attributed to nearly planar or planar-conjugated sequences [4]. The simultaneous presence of two absorption bands reveals the coexistence of two different conformations along the polymer backbone [4]. Indeed, when **P1** is dissolved in acetone, the resulting solution is yellow, but after shaking, it becomes violet.

In contrast, when a poor solvent as chloroform-methanol 10:90 is used, the resulting solution is totally violet. Figure 5C shows the UV–vis spectrum of **P1** in this medium; as we can see, it is very similar to that recorded in acetone solution. Indeed, we can observe a less intense absorption band at $\lambda = 425$ nm, followed by a

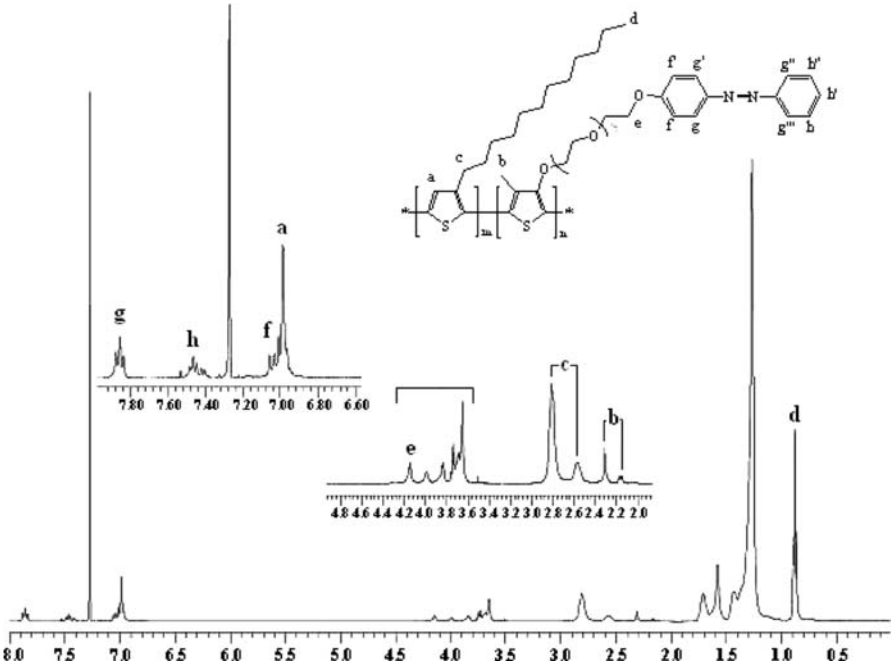
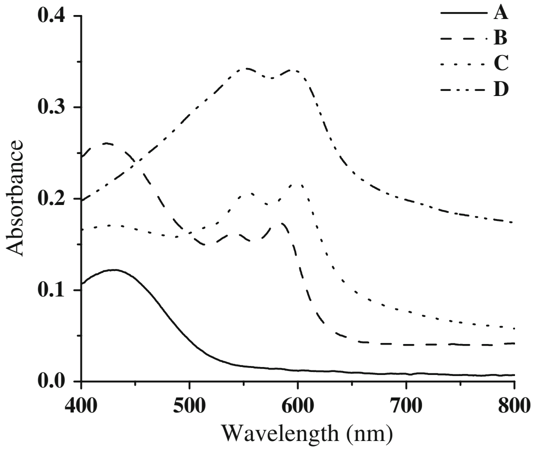


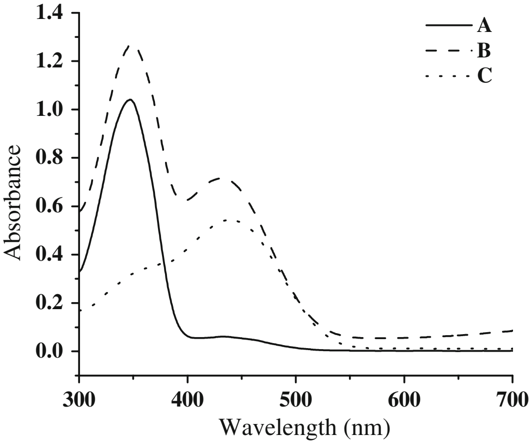
Fig. 4 ^{1}H-NMR spectrum of copolymer **CP2** in $CDCl_3$ solution

Fig. 5 UV–vis absorption spectra of **P1**: (*A*) in $CHCl_3$ solution, (*B*) in acetone solution, (*C*) in chloroform-methanol 10:90 solution, and (*D*) in solid state, at room temperature



second band centered at $\lambda_{max} = 573$ nm. However, the absorption band related to a less conjugated backbone conformation ($\lambda = 425$ nm) (Fig. 5C) is very discrete compared to that observed at $\lambda = 428$ nm in acetone solution (Fig. 5B). This means that a poor solvent favors a mostly planar conformation of the polymer backbone. In casted film, **P1** (Fig. 5D) exhibited only one absorption band centered at $\lambda = 575$ nm related to a planar-conjugated backbone. It is worth to note that this

Fig. 6 UV–vis absorption spectra in $CHCl_3$ solution at room temperature of: (*A*) azobenzene-containing monomer (**4**), (*B*) **CP1**, and (*C*) **CP2**



polymer adopts a very planar conformation in the solid state. The dark violet color of this polymer film is an additional proof of its high conjugation degree.

Figure 6 shows the absorption spectra of monomer **4** (Fig. 6A) and copolymers **CP1** (Fig. 6B) and **CP2** (Fig. 6C) in $CHCl_3$ solution. As we can see, **4** exhibits a broad absorption band at $\lambda = 347$ nm followed by discrete band at $\lambda = 440$ nm. These absorption bands are due to π–π* and n–π* transitions of the azobenzene unit, respectively [6]. On the other hand, **CP1** and **CP2** show almost the same absorption band around $\lambda = 348$ nm. Such band is associated to the π–π* transition of azobenzene, which is more intense for **CP1** [6]. These copolymers exhibit also an intense maximum absorption band at $\lambda = 432$ for **CP1** and $\lambda = 441$ nm for **CP2**, which is attributed to the polythiophene backbone bearing a non-planar conformation. The higher intensity of the absorption band of **CP1** at $\lambda = 348$ nm, compared to that of **CP2** confirmed that **CP1** possesses higher azobenzene content [12]. These results match well with those previously obtained by ^{1}H-NMR spectra, which predicted 40% content of thiophene bearing azobenzene for **CP1** (Fig. 3) and only 12% for **CP2** (Fig. 4).

As other azobenzene-substituted polythiophenes reported in [6], **CP1** and **CP2** exhibited solvatochromism, when they were dissolved in good and bad solvents. Figures 7 and 8 show the absorption spectra in $CHCl_3$, chloroform-methanol and in the solid state of **CP1** and **CP2**, respectively. In $CHCl_3$ solution (Fig. 7A), the absorption spectrum of **CP1** shows a broad band at $\lambda = 348$ nm due to the π–π* transition of azobenzene moieties, followed by a less intense band around $\lambda = 442$ nm, associated to the polythiophene backbone bearing a non-planar conformation. As in $CHCl_3$ solution, in chloroform:methanol 20:80 (Fig. 7B) this polymer shows the band at $\lambda = 348$ nm followed by a shoulder at $\lambda = 442$ nm and a maximum absorption band centered at $\lambda_{max} = 575$ nm. This absorption band has a vibronic fine structure and can be attributed to a planar-conjugated polythiophene backbone. According to these results, in $CHCl_3$ solution, a twisted conformation of the polythiophene backbone is significantly favored, whereas in chloroform-methanol solution a mostly planar conformation of the polymer backbone predominates.

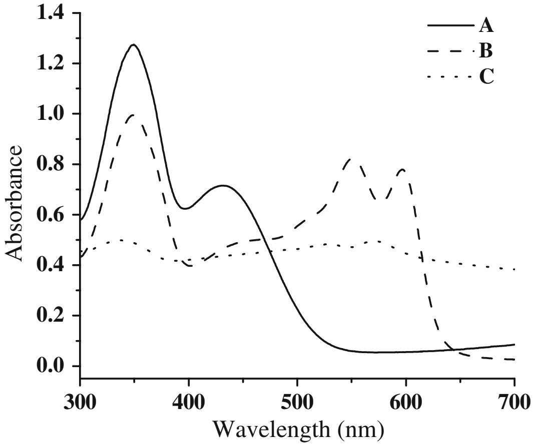


Fig. 7 UV–vis spectra of copolymer **CP1**: (*A*) in $CHCl_3$ solution, (*B*) in chloroform–methanol 20:80 solution, and (*C*) in solid state, at room temperature

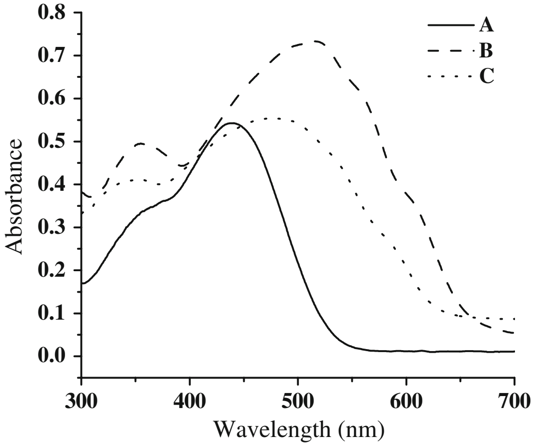


Fig. 8 UV–vis spectra of copolymer **CP2**: (*A*) in $CHCl_3$ solution, (*B*) in chloroform–methanol 20:80 solution, and (*C*) in solid state, at room temperature

Indeed, the $CHCl_3$ solution of **CP1** is yellow and in chloroform–methanol 20:80 it turns violet. The absorption spectrum of **CP1** in the solid state is shown in Fig. 7C. In casted film, this copolymer exhibits a similar behavior to that observed in chloroform–methanol 20:80. Nevertheless, the absorption band at $\lambda = 442$ nm related to a less conjugated polythiophene sequences is not observed. Instead, three bands appear at $\lambda = 337$ nm, $\lambda = 528$ nm, and $\lambda = 571$ nm, revealing the presence of the azobenzene units and a highly conjugated polymer backbone bearing a nearly planar conformation, respectively.

The absorption spectra of **CP2** in $CHCl_3$ solution (A) chloroform–methanol 20:80 solution (B), and in the solid state (C) are shown in Fig. 8. The absorption spectrum of **CP2** in $CHCl_3$ exhibited a maximum absorption band at $\lambda_{\max} =$ 437 nm due to the non-planar sequences present in the copolymer backbone, preceded by a shoulder at $\lambda = 350$ nm, coming from the π to π^* transition of the azobenzene units. In chloroform:methanol 20:80 and in the solid state, we can also observe the characteristic band of the π–π^* transition of the azobenzene units around $\lambda = 350$ nm (less intense), followed by a broad absorption band at $\lambda_{max} = 517$ nm (chloroform:methanol 20:80), due to the conjugated sequences of the polythiophene backbone with two shoulders at $\lambda = 565$ nm and $\lambda = 610$ nm. Similarly, the absorption spectrum of **CP2** in film showed a broad band at $\lambda_{max} = 488$ nm in film with two shoulders at $\lambda = 538$ nm and $\lambda = 584$ nm. The red-shifted shoulders observed in both spectra (8B and 8C) can be probably due to the formation of intermolecular J-aggregates between azobenzene units of neighbor polymer chains [32]. On the other hand, **CP2** exhibited solvatochromic effects as **CP1**, so that when this copolymer is dissolved in a poor solvent, the resulting solution is light violet. Since **CP1** exhibited a more red-shifted absorption band than **CP2** due to its more planar backbone conformation, we can affirm that **CP1** possesses a more regio-regular structure and a higher degree of conjugation.

Thermal and electrochemical properties of the polymers

T_g (glass transition temperature), T_5 (5% weight loss temperature), and T_s (softening point) of all polymers and copolymers were determined by TGA and DSC. As it could be expected, **CP1** ($T_g = 35$ °C) and **CP2** ($T_g = 13$ °C) exhibited higher glass transition temperatures than **P1** ($T_g = -64$ °C). This can be explained in terms of the rigidity of the polymer structure, which is enhanced by the presence of the azobenzene units. **CP1** has a superior T_g value than its homologue **CP2**, due to its higher content of azobenzene-containing thiophene. On the other hand **P1**, **CP1** and **CP2** exhibit T_5 (5% weight loss temperature) values of 400, 225, and 307 °C, respectively. These copolymers showed drastic degradation beyond 250 °C and are thermally less stable than **P1**, due to the presence of azobenzene moieties. It is very well known that in azobenzene, the N=N bond is very labile and decomposes very easily at high temperatures. Since **CP2** has a lower content of azobenzene, it showed better thermal stability than **CP1**.

Voltammograms of **CP1** and **CP2** (not shown) exhibit a similar behavior, showing an irreversible potential shoulder at 1.6 V. **CP2** shows a higher current density than **CP1**, because this copolymer is sterically less hindered because of its lower azobenzene content. This allows **CP2** to have a more efficient incorporation of the doping anion.

Conclusion

^{1}H-NMR and absorption spectroscopies showed that **CP1** has higher azobenzene content and a more regio-regular structure than **CP2**. **CP1** exhibits a higher T_g value than its homologue **CP2**, due to its higher azobenzene content, which increases the rigidity of this copolymer. However, **CP1** showed a lower thermal stability since the N=N bond decomposes easily at high temperatures. Both copolymers exhibited solvatochromic effects; in chloroform, the solution is yellow because it favors a twisted conformation of the polymer backbone. In contrast, in a bad solvent such as chloroform–methanol 20:80, a mostly planar conformation of the polymer backbone is favored, so that the solution turns violet. Since **CP2** has a less effective conjugation length than **CP1**, it is less sensitive to solvatochromic effects. The higher current density of **CP2** shows that this copolymer has a more efficient incorporation of the doping anion.

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