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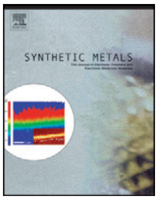

Synthesis and characterization of novel polythiophenes bearing oligo (ethylene glycol) spacers and crown ethers

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ABSTRACT

Two novel thiophene containing monomers (**TM**): 3-methyltetra(oxyethylene)oxy-4-methylthiophene (**TM1**) and 3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene (**TM2**) were synthesized and characterized. Both monomers were polymerized in the presence of $FeCl_3$ to give the corresponding copolymer (**CPT1**). **TM2** was also copolymerized in the presence of 3-dodecylthiophene to lead a second copolymer (**CPT2**). On the other hand, **TM1** and **TM2** were homopolymerized under the same reaction conditions to give poly[3-methyltetra(oxyethylene)oxy-4-methylthiophene] (**PT1**) and poly[3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene] (**PT2**), where the former was used as reference compound. Solvatochromic and thermochromic behaviors of these polymers were investigated. All polymers exhibited solvatochromism; in a mixture of chloroform–methanol 20:80, **CPT1** gives a violet solution and its polymer backbone adopts a planar conformation. By contrast, in chloroform **CPT1** adopts a twisted conformation, giving an orange solution. This copolymer exhibits also an extended conjugation length in the solid state at room temperature (dark red) and a less conjugated conformation after heating (yellow). **CPT2** shows a similar thermochromic behavior as **CPT1** in chloroform, but in the solid state its color changes from dark red to orange.

1. Introduction

Polythiophene (**PT**) is one of the most promising electroconducting polymers due to its high stability, ease of structural modification and controllable electrochemical behavior. For some time, its applications were limited by its insolubility in many organic solvents, due to its strong π-conjugated structure. To resolve this problem, alkyl chains were added in position 3 of the thiophene unit, in order to obtain monomers able to produce soluble polymers. This new kind of poly(3-alkylthiophene)s are processable conducting polymers, whose electronic properties can be modified, allowing their full characterization by chemical and physical methods [1]. The stability of poly(3-alkylthiophenes) in the doped state can be achieved by releasing the side alkyl chains crowding along the backbone or by introducing alkoxy groups. A monomer containing two methylene groups between the thiophene ring and the first oxygen atom, allows to obtain highly stable polymers [2,3].

For some polythiophenes, interesting thermochromic [4–6], ionochromic [5–7], photochromic [8], piezochromic [9] and biochromic [10] properties have been reported in literature. These color changes are due to transitions from a planar to a twisted conformation of the polymer backbone and viceversa, leading to a modification of the effective conjugation length, which produces a shift of the absorption bands in their UV–vis spectra [11]. In polymers bearing alkoxy groups, the lone pairs of the oxygen atom enter into conjugation with the polymer backbone, thereby inducing a planar conformation [12]. The augment of the effective degree of conjugation improves significantly the electronic mobility and conductivity in the polymers.

The chromic properties of substituted polythiophenes make them an excellent choice for light emitting diodes [13], gas sensors [14–16], biomedical applications [17], metal ions sensors [18,19], and biosensors [20–23]. Because of their potential medical and industrial applications in the elaboration of electrochemical ion sensors, crown-ether functionalized conducting polymers based on polythiophene and polypyrrole have been prepared, in order to get a controlled electrochemical response to alkali metal ions [23–28]. Crown ethers are a unique category of ionic scavengers, whose recognition properties derive from the heteroatoms present in the molecule and the overall structure. Incorporation of crown ethers into polymers allows the easy handling, recycling and adaptation of this important set of complexant agents to continuous processes [29].

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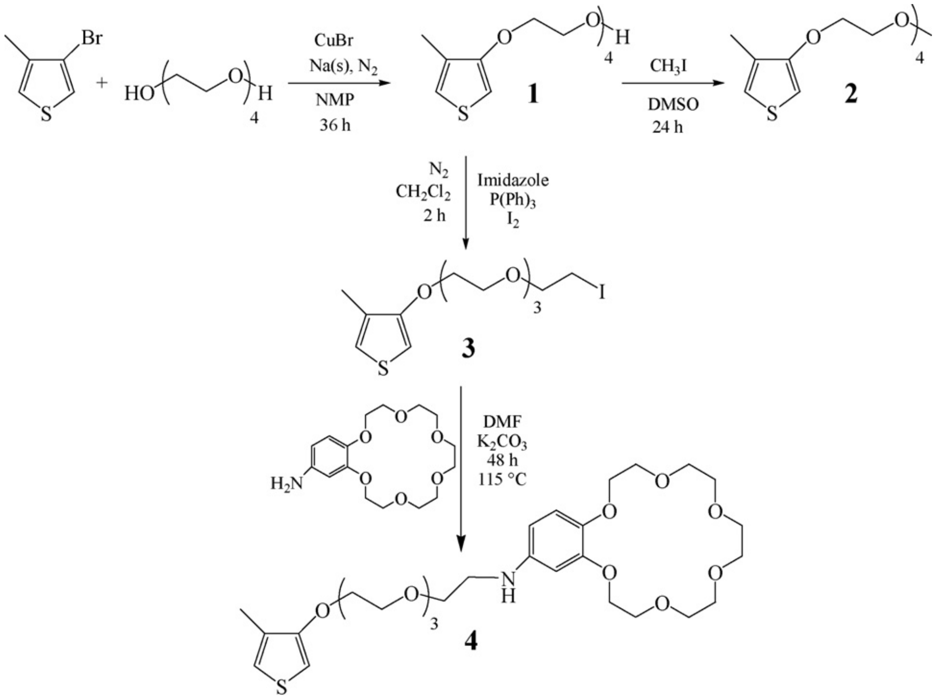


Fig. 1. Synthesis of the monomers: 3-methyltetra(oxyethylene)oxy-4-methyltiophene) (**2**), and 3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene (**4**).

The stability of the crown ether–metal ion complex depends on the number of the ether donor atoms. Of particular importance is the size and shape of the cavity with respect to the cation size. Even though some crown ethers tend to form stable complexes with ions having diameters comparable to those of their opened cavity, they can also form complexes with larger size ions [29]. There are three main methods to incorporate crown ethers into polymer matrices. The former is the direct polymerization of a crown ether containing monomer through a step-growth mechanism; the second is polymerization through a chain-growth mechanism and the latter is a post-functionalization, wherein a crown ether is covalently bound to a precursor polymer [29].

The main goal of this work is the synthesis and characterization of novel copolymers of crown ether containing thiophenes (**TM2**) with both 3-dodecylthiophene and 3-methyltetra(oxyethylene)-oxy-4-methyltiophene (**TM1**), as well as the study of the chromic properties of these copolymers. The synthetic route and molecular structures of the monomers and the obtained polymers: poly(3-methyltetra(oxyethylene)oxy-4-methyltiophene) (**PT1**), poly(3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene) (**PT2**), copolymer of 3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene and 3-methyltetra-(oxyethylene)oxy-4-methylthiophene (**CPT1**), and copolymer of 3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene and 3-dodecylthiophene (**CPT2**) are shown in Figs. 1 and 2, respectively (*vide infra*).

2. Experimental

2.1. Apparatus

^{1}H and ^{13}C NMR spectra of the intermediates, monomers and polymers were recorded using a Bruker Avance 400 spectrometer, operating at 400 and 100 MHz, respectively. Thermal properties of the polymers were studied 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 was carried out 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 solid state were recorded 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 model Waters 2414. Measurements were carried out using tetrahydrofurane (THF) as solvent against a polystyrene standard. For cyclic voltammetry of the polymers, an Autolab PGSTAT100 potentiostat was employed. All experiments were carried out in a three-electrode undivided cell, using 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 the auxiliary electrode.

2.2. Chemicals

3-Bromo-4-methylthiophene, 4′-aminobenzo-18-crown-6 ether, N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), methyl iodide and $FeCl_3$ used in the synthesis were purchased from Aldrich and used as received. Tetra(ethylene glycol) was dried in a vaccum oven prior to be employed. Chloroform used in the polymerizations was distilled over calcium hydride (CaH_2) in order to remove traces of water.

2.2.1. 3-Methyl-4-(tetraethoxy)thiophene (1)

3-Methyl-4-(tetraethoxy)thiophene (**1**) (see Fig. 1) was synthesized using a procedure similar to that reported in the literature [8]. 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. Afterwards, a mixture of 3-bromo-4-methylthiophene (2.01 g, 11.4 mmol), CuBr (1.96 g, 13.6 mmol) in 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. The organic phase was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. Finally, the product was purified by flash column chro-

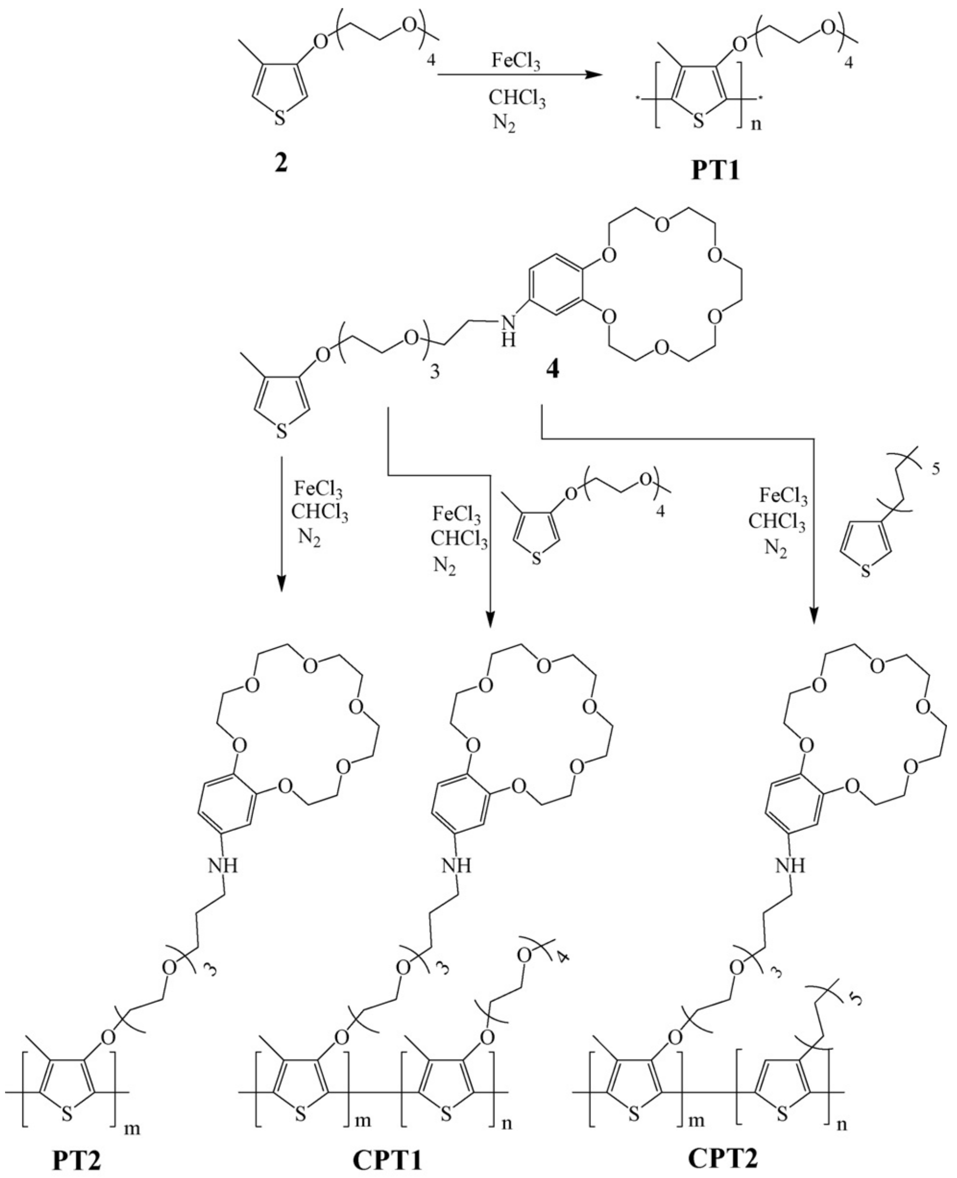
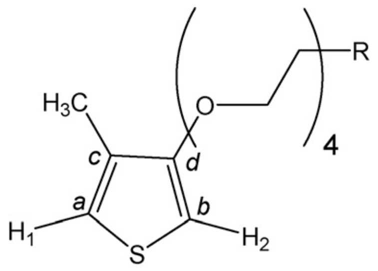


Fig. 2. Synthesis of the polymers and copolymers: (A) **PT1**, (B) **PT2**, (C) **CPT1** and (D) **CPT2**.



(a) **1** (R = OH)
(b) **2** (R = OCH$_3$)
(c) **3** (R = I)

Scheme 1.

matography on silica gel, 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) (see Scheme 1a): 6.81 (s, 1H, H^1), 6.16 (s, 1H, H^2), 4.11 (t, J_1 = 4.80, Hz J_2 = 4.56 Hz, 2H, tioph–O–CH$_2$), 3.85 (t, J_1 = 4.81 Hz, J_2 = 4.44 Hz, 2H, tioph–CH$_2$–$\underline{CH_2}$–O), 3.75–3.66 (m, 10H, all other OCH$_2$), 3.59 (t, J_1 = 4.51 Hz, J_2 = 4.08 Hz, 2H, $\underline{CH_2}$–OH), 2.73 (br s, OH), 2.09 (s, 3H, CH$_3$–tioph). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) (see Scheme 1a): 155.96 (1C, C^d), 129.29 (1C, C^c), 120.10 (1C, C^a), 96.74 (1C, C^b), 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).

*2.2.2. 3-Methyltetra(oxyethylene)oxy-4-methylthiophene (**2**)*

3-Methyltetra(oxyethylene)oxy-4-methylthiophene (**2**) (**TM1**) was obtained from **1** (see Fig. 1) following a similar method to that reported in the literature [6]. **1** (0.13 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 in order to form the corresponding alcoxide. Methyl iodide (0.573 g, 4.03 mmol) was added and the reaction mixture was stirred for 24 h. Afterwards, it was filtered and poured into water in order to remove the DMSO; the product was extracted with dichloromethane. The organic phase was dried with anhydrous $MgSO_4$ and concentrated at reduced pressure. The resulting product was purified by flash column chromatography on silica gel, using ethyl acetate as eluent. The pure product was obtained as a yellow oil (0.91 g, 0.3 mmol). Yield: 67%. ^1H NMR ($CDCl_3$, 400 MHz, ppm) (see Scheme 1b): 6.80 (s, 1H, H^1), 6.15 (s, 1H, H^2), 4.08 (t, J_1 = 5.04 Hz, J_2 = 4.78 Hz, 2H, tioph–O–CH_2), 3.84 (t, J_1 = 5.04 Hz, J_2 = 4.78 Hz, 2H, tioph–CH_2–$\underline{CH_2}$–O), 3.73–3.71 (m, 2H, OCH_2), 3.68–3.62 (m, 8H, all other OCH_2), 3.54–3.52 (m, 2H, $\underline{CH_2}$–OCH_3), 3.36 (s, 3H, O–CH_3), 2.08 (s, 3H, tioph–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) (see Scheme 1b): 155.99 (1C, C^d), 129.27 (1C, C^c), 120.03 (1C, C^a), 96.63 (1C, C^b), 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).

2.2.3. Poly(3-methyltetra(oxyethylene)oxy-4-methyltiophene

Poly(3-methyltetra(oxyethylene)oxy-4-methyltiophene (**PT1**) (see Fig. 2) was synthesized from (**2** or **TM1**) according to a similar procedure reported in the literature [6]. 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 and it was poured into methanol (200 mL) in order to precipitate the product. The resulting polythiophene **PT1** was isolated by filtration, washed with methanol and dried; then it was reduced in an ammonium hydroxide solution. The polymer was obtained as a black powder, which is very soluble in $CHCl_3$, THF and ethyl acetate. Yield: 85%. M_w = 196,800 g/mol, M_n = 183,200 g/mol, PD = 1.1 (from GPC, in THF against a polystyrene standard).

*2.2.4. 3-(((2-Iodoethyl)triethoxy)oxy)-4-methylthiophene (**3**)*

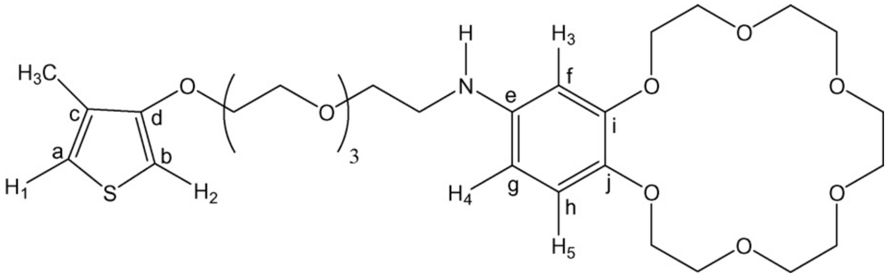
3-(((2-Iodoethyl)triethoxy)oxy)-4-methylthiophene (**3**) was obtained from **1** (see Fig. 1) using a procedure similar to that described by Lange and Gottardo [30]. First, CH_2Cl_2 (5 mL), triphenylphosphine (0.393 g, 1.5 mmol), imidazole (0.102 g, 1.5 mmol) and iodine (0.381 g, 1.5 mmol) were mixed in a bottom round flask under argon atmosphere. Then, a solution of **1** (0.290 g, 1 mmol) in anhydrous dichloromethane (1 mL) was added. The solution was reacted for 3 h and the crude product was washed with water, in order to remove salts formed during the reaction. The organic phase was dried with anhydrous $MgSO_4$ and concentrated at reduced pressure. Finally, this compound was purified by flash column chromatography on silica gel, using a mixture of 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%. ^1H NMR ($CDCl_3$, 400 MHz, ppm) (see Schema 1c): 6.81 (s, 1H, H^1), 6.17 (s, 1H, H^2), 4.11 (t, J_1 = 4.89 Hz, J_2 = 4.73 Hz, 2H, tioph–O–$\underline{CH_2}$), 3.86 (t, J_1 = 4.86 Hz, J_2 = 4.72 Hz, 2H, tioph–O–CH_2–$\underline{CH_2}$), 3.76–3.73 (m, 4H, OCH_2), 3.69–3.66 (m, 6H, all other OCH_2), 3.25 (t, J_1 = 6.92 Hz, J_2 = 6.73 Hz, 2H, CH_2–I), 2.10 (s, 3H, tioph–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) (see Scheme 1c): 156.0 (1C, C^d), 129.28 (1C, C^c), 120.07 (1C, C^a), 96.68 (1C, C^b), 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). HRMS ($C_{13}H_{21}O_4I$) M^+: m/z = 368.19 Calculated: 368.20.

*2.2.5. 3-(((2-Aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene (**4**)*

3-(((2-Aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene (**4**) (**TM2**) (see Fig. 1) was obtained from **3**. A solution of 4′-aminobenzo-18-crown-6 (0.20 g, 0.611 mmol) and K_2CO_3 (0.096 g, 0.695 mmol) dissolved in the minimum amount of DMF was prepared. Then, a solution of **3** (0.244 g, 0.611 mmol) in DMF (1 mL) was added. The resulting solution was stirred for 48 h under inert atmosphere at 115 °C. Afterwards the reaction mixture was filtered, poured into water and extracted with chloroform. The organic phase was dried with anhydrous $MgSO_4$ and concentrated at reduced pressure. The crude product was purified by flash column chromatography on silica gel, using a mixture ethyl acetate:methanol 10:1 as eluent. The pure product was obtained as a brown oil. Yield: 35%. ^1H NMR ($CDCl_3$, 400 MHz, ppm) (Scheme 2): 6.81 (s, 1H, H^1), 6.77 (d, J = 8.56 Hz, 1H, H^5), 6.30 (d, J = 2.45 Hz, 1H, H^4), 6.21 (s, 1H, H^3), 6.16 (s, 1H, H^2), 4.32–4.26 (s, 1H, NH–Ar), 4.20–4.08 (m, 6H, tioph–OCH_2 and Ar–OCH_2 in the crown), 3.85 (t, 2H, tioph–OCH_2–$\underline{CH_2}$), 3.75–3.74 (m, 4H, Ar–OCH_2–$\underline{CH_2}$ in the crown), 3.74–3.69 (m, 20H, all other OCH_2 present in the oligo(ethylene glycol) spacer and in the crown ether), 3.67 (t, J_1 = 5.62 Hz, J_2 = 5.14 Hz, 2H, $\underline{CH_2}$–CH_2–NH–Ar), 3.24 (t, J_1 = 5.14 Hz, J_2 = 4.89 Hz, 2H, $\underline{CH_2}$–NH–Ar), 2.09 (s, 3H, CH_3–tioph). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) (see Scheme 2): 156.01 (1C, C^d), 150.45 (1C, C^i), 143.37 (1C, C^j), 141.70 (1C, C^e), 129.28 (1C, C^c), 120.10 (1C, C^a), 117.36 (1C, C^g), 105.68 (1C, C^h), 101.77 (1C, C^f), 96.72 (1C, C^b), 71.03 (1C, $\underline{CH_2}$–CH_2–NH–Ar, 70.92 (2C, Ar–OCH_2–$\underline{CH_2}$ in the crown ether), 70.87 (1C, OCH_2 in the spacer), 70.83 (4C, all other OCH_2 of the crown ether), 70.76, 70.58, 70.40, 69.86, 69.84 (5C, all other OCH_2 in the spacer) 69.77 (2C, Ar–O–CH_2 in the crown ether), 44.79 (1C, CH_2–NHAr), 12.90 (1C, CH_3–tioph).

*2.2.6. Poly(3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene) (**PT2**)*

Poly(3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene) (**PT2**) (see Fig. 2). A solution of $FeCl_3$ (0.162 g, 1.00 mmol) in $CHCl_3$ (2 mL) was prepared. Another solution of (**4** or **TM2**) (0.149 g, 0.25 mmol) in $CHCl_3$ (2 mL) was added and the reaction mixture was stirred for 24 h at room temperature under inert atmosphere. The obtained polymer was filtered on a Buchner funnel, washed with methanol and dried; then it was reduced in an ammonium hydroxide solution. The obtained black polymer is insoluble in common organic solvents, so that it could not be characterized.



Scheme 2.

*2.2.7. Copolymer of 3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene and 3-methyltetra(oxyethylene)oxy-4-methylthiophene (**CPT1**)*

Copolymer of 3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)-oxy)-4-methylthio-phene and 3-methyltetra(oxyethylene)oxy-4-methylthiophene (**CPT1**) (see Fig. 2). Two solutions of **4** or **TM2** (0.050 g, 0.084 mmol) in $CHCl_3$ (2 mL) and **2** or **TM1** (0.725 g, 0.252 mmol) in $CHCl_3$ (2 mL) were mixed and added to $FeCl_3$ (0.218 g, 1.344 mmol) dissolved in $CHCl_3$ (2 mL). The reaction mixture was stirred for 24 h at room temperature, and the solution was poured into methanol (200 mL) in order to precipitate the product. The resulting polymer was filtered on a Buchner funnel, washed with methanol and dried. Then the polymer was reduced in an ammonium hydroxide solution. The pure polymer is a dark-red solid. Yield 47%.

*2.2.8. Copolymer of 3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene and 3-dodecylthiophene (**CPT2**)*

Copolymer of 3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)-oxy)-4-methylthiophene and 3-dodecylthiophene (**CPT2**) (see Fig. 2). A solution of **4** or **TM2** (31.5 mg, 0.053 mmol) in $CHCl_3$ (2 mL) and a solution of 3-dodecylthiophene (0.040 g, 0.158 mmol) in $CHCl_3$ (2 mL) were mixed and added to another solution of $FeCl_3$ (0.137 g, 0.842 mmol) in $CHCl_3$ (2 mL). The reaction mixture was stirred for 24 h at room temperature and it was poured into methanol (200 mL), in order to precipitate the product. The resulting polymer was filtered on a Buchner funnel, washed with methanol, dried and reduced in an ammonium hydroxide solution. The pure polymer is a dark-red solid. Yield 50%.

3. Results and discussion

3.1. Synthesis of the monomers

Monomers were prepared from 3-bromo-4-methyltiophene according to the synthetic sequence illustrated in Fig. 1. Tetra(ethylene glycol) was treated in the presence of metallic sodium to generate the corresponding alcoxide, which was reacted with 3-bromo-4-methyltiophene, using CuBr as catalyst and NMP as solvent, to give 3-methyl-4-(tetraethoxy)thiophene (**1**). This compound was treated with KOH in DMSO in order to deprotonate the hydroxyl group and it was further alkylated with methyl iodide to give 3-methyltetra(oxyethylene)oxy-4-methylthiophene **2** (**TM1**). On the other hand, the intermediate **1** was treated in the presence of iodine, triphenyl phosphine and imidazole in CH_2Cl_2 under inert atmosphere to lead 3-(((2-iodoethyl)triethoxy)oxy)-4-methylthiophene (**3**). This compound was further reacted in the presence of 4′-aminobenzo-18-crown-6, using K_2CO_3 as base and DMF as solvent, to give 3-(((2-aminobenzo-18-crown-6-ethyl)triethoxy)oxy)-4-methylthiophene **4** (**TM2**).

Table 1
Molecular weights and thermal properties of the polymers.

Polymer	M_w (g/mol)	M_n (g/mol)	PD	T_g (°C)	T_s (°C)	T_5 (°C)
PT1	196,800	183,200	1.10	−28.4	126.2	190
CP1	20,200	10,800	1.86	6.2	72	302
CP2	90,500	46,800	1.93	3.9	142	398

3.2. Synthesis and characterization of the polymers

Monomers were polymerized via an oxidative coupling, using $FeCl_3$ as oxidative agent and dry chloroform as solvent. The synthesis of the different polymers and copolymers is illustrated in Fig. 2.

The obtained polymers and copolymers were characterized by ^1H NMR spectroscopy and their molecular weights were determined by gel permeation chromatography in THF against a polystyrene standard. The molecular weights and thermal properties (*vide infra*) of the polymers are summarized in Table 1.

The ^1H NMR spectrum of poly(3-methyltetra(oxyethylene)oxy-4-methyltiophene) (**PT1**) with the assigment of the signals is shown in Fig. 3. As we can see, two signals appear at 2.30 and 2.00 ppm due to the protons of the methyl groups linked to the thiophene rings, followed by a signal at 3.36 ppm due to the terminal OCH_3 groups of the end-capped oligo(ethylene glycol) side chains. A series of signals between 3.54–4.02 ppm, due to all the $–OCH_2$ groups present in the side chains, can be also observed. The broad signal at 2.30 ppm indicates a highly regioregular head-to-tail pattern along the backbone, whereas the weak signal at 2.00 ppm indicates the presence of traces of head-to-head couplings (defaults) [5]. Comparing the intensity of both signals in this spectrum, we can realize that **PT1** has a head-to-tail regioregular content about 85%. Since **PT2** was totally insoluble in common organic solvents, this poly-

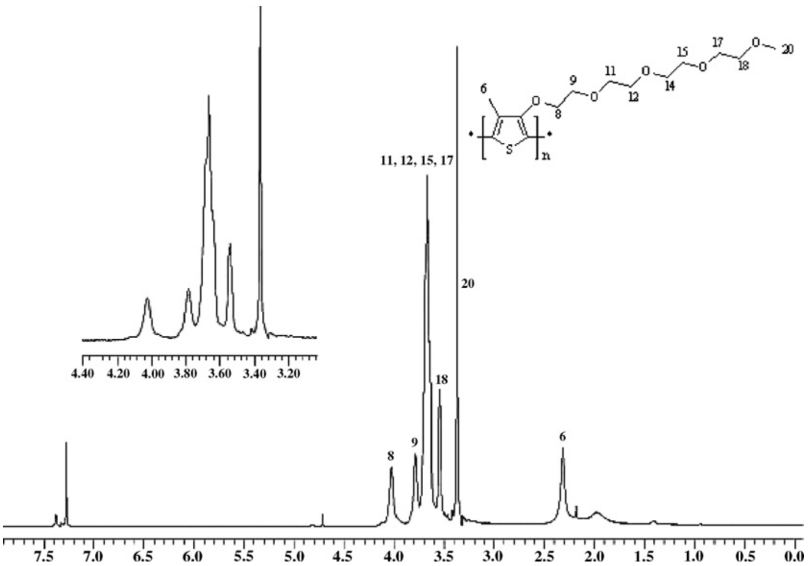


Fig. 3. ^1H NMR spectrum 400 MHz of the polymer **PT1** in $CDCl_3$.

mer could not be characterized. However, the FTIR spectrum of this polymer (not shown) confirmed that the polymerization took place.

The ^{1}H NMR spectrum of **CPT1** (Fig. 4A) shows a series of signals in the aromatic region between 5.6 and 7.0 ppm, due the aromatic protons present in the phenyl group of the 4′-aminobenzo-18-crown-6 unit (**a**). Besides, a signal centered at 3.15 ppm (**b**, **c**, **d**) assigned to the protons of the methylenes present in the oligo(ethylene glycol) spacer and the crown ether, as well as a signal at 2.8 ppm due to the terminal CH_3 groups of the spacer (**e**) can be also seen. On the other hand, a broad signal at 1.85 ppm (**f**, **g**), due to the protons of the methyl group in position 4 of the thiophene units in a head-to-tail coupling and a weak signal at 0.90 ppm (**f**, **g**) coming from head-to-head defaults are also observed. A comparison between both signals intensity revealed that **CPT1** has a high head-to-tail content about 80%.

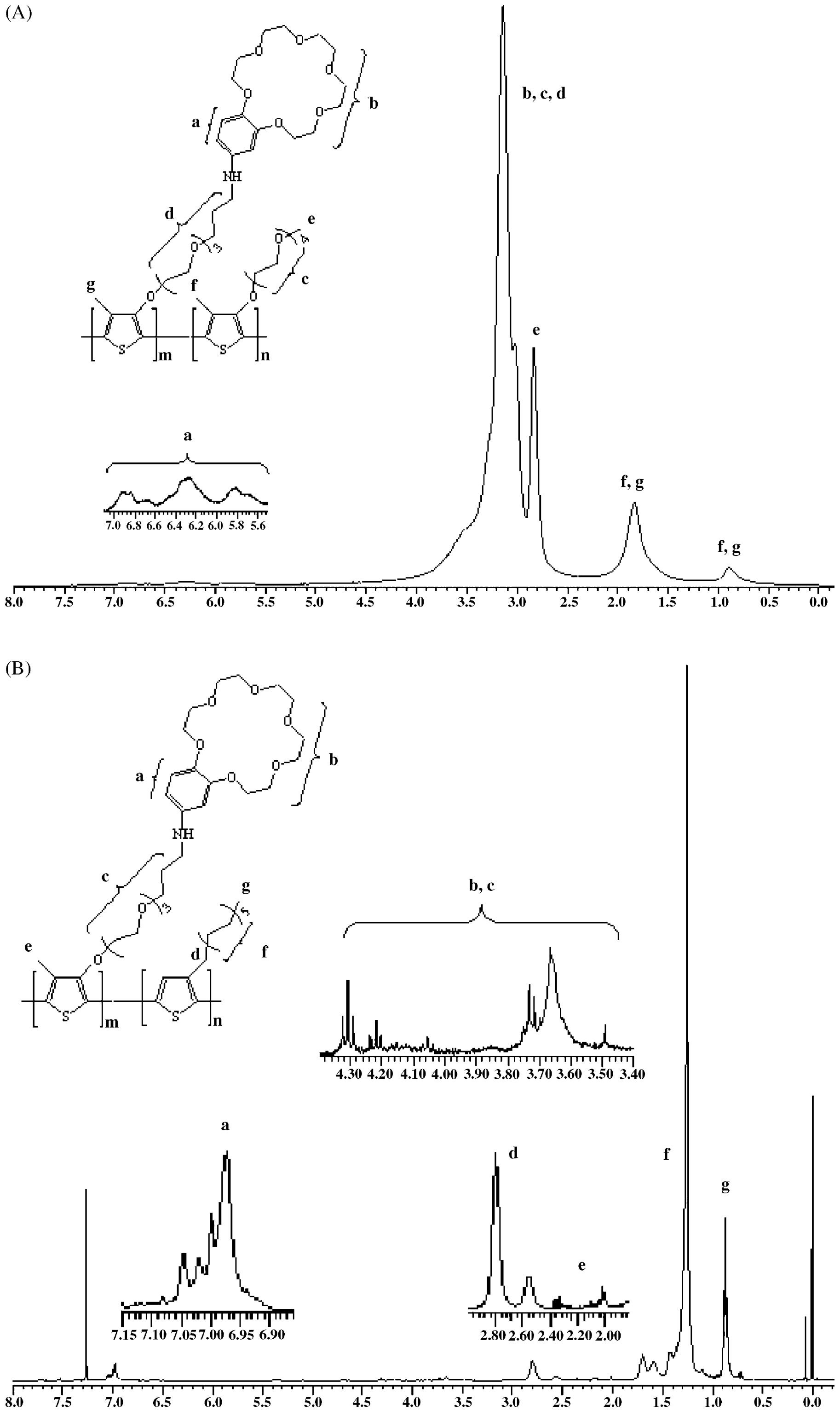


Fig. 4. ^{1}H NMR spectrum 400 MHz of the copolymers in $CDCl_3$: (A) **CPT1** and (B) **CPT2**.

The ^{1}H NMR spectrum of **CPT2** (Fig. 4B) show a series of signals in the region 7.06–6.9 (**a**), due to the aromatic protons of the 4′-aminobenzo-18-crown-6 ether. The absence of the characteristic signals of the aromatic thiophene protons at 6.17 and 6.81 ppm (**b**, **c**) in the ^{1}H NMR spectra of these copolymers indicates that the polymerization takes place, reaching high molecular weights. Besides, the signals between 4.3 and 3.5 ppm (**b**, **c**), are due to the protons of the CH_2 groups present in the crown ether and the oligo(ethylene glycol) spacer. In addition, two signals at 2.80 and 2.57 ppm (**d**, **e**) related to the protons of the α-CH_2 group of 3-dodecyl thiophene and the methyl group linked to the tiophene unit (**e**) can be also observed; the signal at 2.80 ppm (**d**) is assigned to a head-to-tail coupling. Finally, two intense signals appear at 1.27 (**f**) and 0.9 ppm (**g**), which correspond to the CH_2 groups and the terminal CH_3 group present in the dodecyl side chain, respectively.

3.3. Optical properties of the polymers

The thermochromic and solvatochromic behaviors of these polymers were investigated in solution and in the solid state. Fig. 5 shows the absorption spectra of **PT1** in solution and in casted film. This polymer exhibits a maximum absorption band at λ_{max} = 432 nm in chloroform solution (a good solvent) (Fig. 5A), which is attributed to a non-planar conformation of the polythiophene backbone, according to the literature [31,32]. Since any twisting of the polythiophene main chain leads to a decrease in the effective conjugation length [23], and taking into account that the resulting solution is yellow, we can affirm that **PT1** adopts a non-planar conformation in chloroform solution [32]. On the other hand, the spectrum of **PT1** in acetone solution (Fig. 5B) shows an absorption band at λ = 428 nm, due to non-conjugated polythiophene sequences, followed by a maximum absorption band centered at λ_{max} = 560 nm, which can be attributed to nearly planar conjugated sequences in the polymer [5,32]. These bands reveal the coexistence of two conformational structures in the polymer backbone [5,32]. Indeed, the acetone solution of **PT1** is light yellow, but after shaking it becomes violet.

When a poor solvent is used, the resulting solution is usually violet. The UV–vis spectrum of **PT1** in chloroform–methanol 10:90 (Fig. 5C) is very similar to that obtained in acetone solution. **PT1** exhibits an absorption band at λ = 425 nm, followed by a maximum absorption band centered at λ_{max} = 574 nm. The first band, related to a non-planar polythiophene sequences, is less intense compared to that observed in acetone solution (Fig. 5B). This means that a poor solvent favors the existence of a planar conformation of the polythiophene backbone [32]. On the other hand, Fig. 5D shows the absorption spectrum of **PT1** in the solid state. Herein, we can distinguish only a maximum absorption band, centered at λ_{max} = 574 nm, which reveals that the polythiophene backbone is highly conjugated and adopts a planar conformation. The color of the thin casted film obtained is dark violet, but it becomes yellow when it is heated over 100 °C. This thermochromic effect results from conformational changes in the polymer backbone, which passes from a nearly planar to a twisted geometry. Similarly, copolymers **CPT1** and **CPT2** exhibited also thermochromic behaviors.

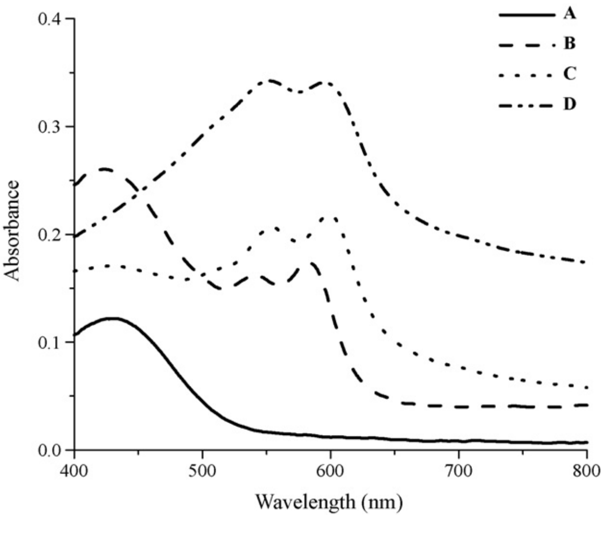


Fig. 5. UV–vis absorption spectra of polymer **PT1**: (A) in chloroform, (B) in acetone, (C) in chloroform–methanol (10:90), and (D) in solid state, at room temperature.

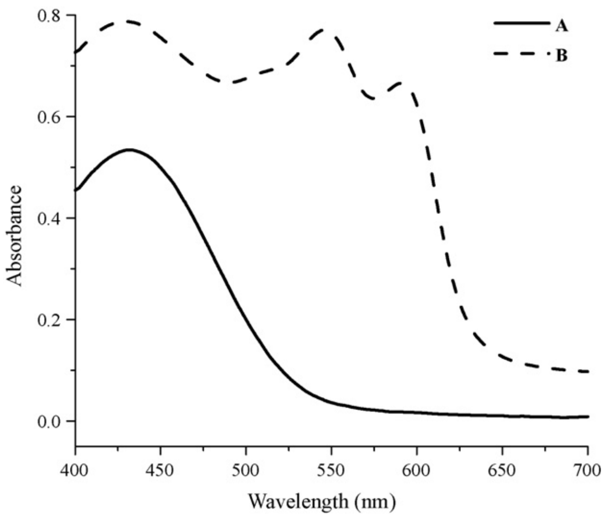


Fig. 6. UV–vis absorption spectra of copolymer **CPT1**: (A) in chloroform and (B) in chloroform–methanol (10:90), at room temperature.

Fig. 6 shows the absorption spectra of **CPT1** in chloroform (A) and in chloroform–methanol 10:90 (B), respectively. As we can see, in pure chloroform this copolymer exhibits a maximum absorption band at λ_{max} = 432 nm (Fig. 6A). By contrast, in chloroform–methanol 10:90 (Fig. 6B), the UV–vis spectrum of this copolymer shows the same band, followed by a maximum absoption band centered at λ_{max} = 574 nm. In chloroform solution, the absorption band is associated to a non-planar conformation of the polythiophene backbone [32], whereas in chloroform–methanol 10:90, the presence of the second band reveals the coexistence of twisted and planar sequences in the copolymer backbone. In chloroform, **CPTI** gives an orange solution, whereas in chloroform–methanol 10:90 the solution is violet.

A similar behavior was observed in the absorption spectra of **CPT2** (Fig. 7). When this copolymer is dissolved in chloroform, the resulting solution is orange and its UV–vis spectrum shows a maximum absorption band at λ_{max} = 441 nm (Fig. 7A). Since **CPT2** was poorly soluble in chloroform–methanol 10:90, its spectrum was recorded using a mixture THF–acetonitrile 50:50; the resulting solution is light violet and the absorption spectrum of **CPT2** in this medium is shown in Fig. 7B. As we can notice, there is a broader absorption band centered at λ = 444 nm, compared to that observed in chloroform solution. Besides, the presence three red-shifted shoulders at λ = 522, 561 and 612 nm, reveals the coexistence of twisted, quasi-planar and planar sequences along the copolymer backbone; an analogous behavior was reported for other polytiophenes bearing similar structures [32].

The absorption spectra of **CPT1** and **CPT2** in casted films are shown Fig. 8. The spectrum of **CPT1** (Fig. 8A), exhibits a very

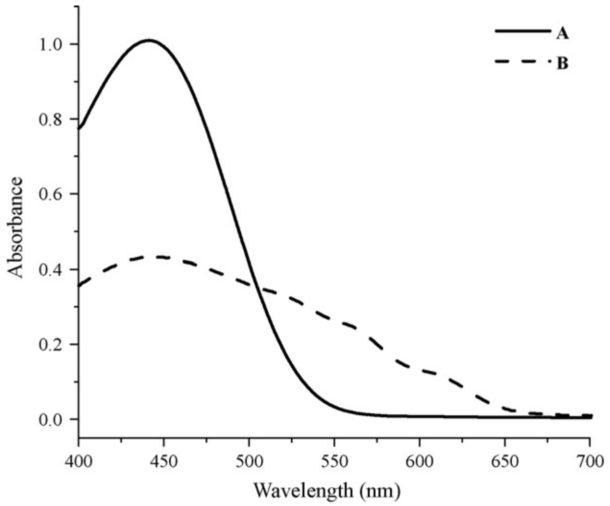


Fig. 7. UV–vis absorption spectra of copolymer **CPT2**: (A) in chloroform and (B) in THF:acetonitrile (50:50), at room temperature.

broad absorption band at about λ = 456 nm, followed by two additional bands situated at λ = 533 and λ_{max} = 575 nm. Since these overlapped bands have similar intensities and given the dark red color of the thin film, we can realize that **CPT1** displays also planar, semi-twisted and twisted conformations along its polythiophene backbone [32]. When the **CPTI** film is heated over 200 °C and further cooled, it shows a reversible color change from dark red to yellow. By contrast, the UV–vis spectrum of **CPT2** (Fig. 8B) shows also a broad absorption band centered at λ_{max} = 512 nm, with two discrete red-shifted shoulders at λ = 561 and 610 nm. In this case, a less planar conformation predominates, so that we can affirm that **CPT1** (λ_{max} = 575 nm), which has a λ_{max} value, 63 nm red-shifted compared to that of **CPT2**, is more conjugated in the solid state. When the dark red **CPT2** film is heated over 200 °C and further cooled, it shows a reversible color change from dark red to orange. We attempted to do some ionochromism studies with these polymers in the presence of Na^+ and K^+ solutions. Unfortunately, no significant ionochromic effects were observed, because the content of crown ethers in the copolymers seems to be relatively low. However, good solvatochromic effects were observed for these polymers, which behaved similarly to other polytiophenes previously reported in the literature [32].

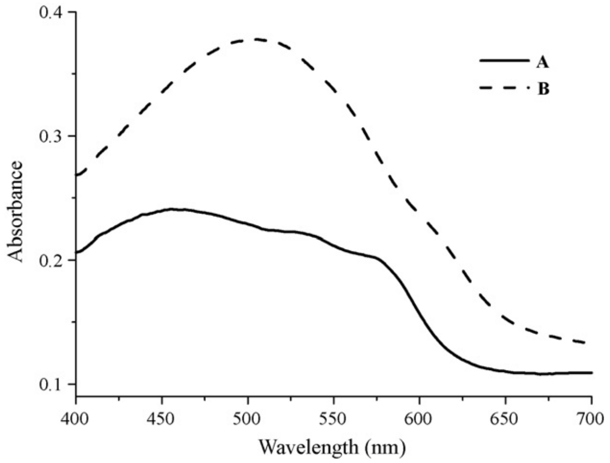


Fig. 8. UV–vis absorption spectra of copolymers: (A) **CPT1** and (B) **CPT2** in solid state at room temperature.

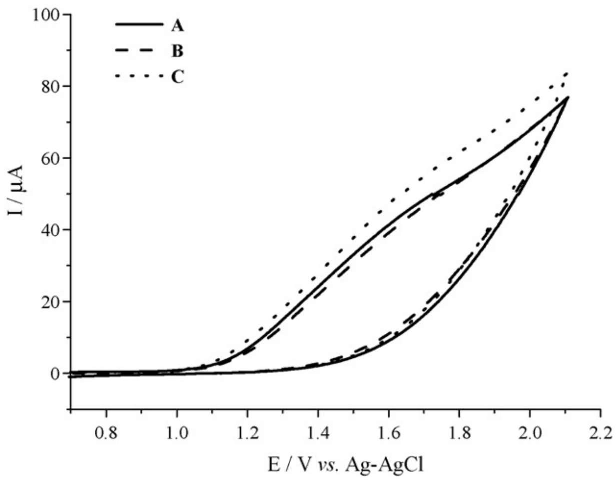


Fig. 9. Typical cyclic voltammograms of polymers: (A) **PT1**, (B) **CPT1** and (C) **CPT2** in 0.1 M $LiClO_4$/THF solution. Scan rate 50 mV/s.

3.4. *Thermal properties of the polymers*

Thermal properties of the polymers were determined by TGA from 0 to 500 °C and DSC from −100 to 200 °C. The glass transition temperature (T_g), 5% weight loss temperature (T_5) and softening point (T_s) of **PT1**, **CPT1** and **CPT2** were determined and are summarized in Table 1. According to these data, **CPT1** and **CPT2** exhibit higher glass transition temperatures (T_g = 6.8 and 3.9 °C, respectively) than **PT1** (T_g = −28.4 °C). This is due to an increase in the rigidity of the polymer because of the presence of 4′-aminobenzo-18-crown-6 units in **CPT1** and **CPT2**. **CPT1** shows a higher Tg value than **CPT2**, because of the lower content of 4′-aminobenzo-18-crown-6 units and the presence of oligo(ethylene glycol) side chains in this copolymer. On the other hand, **PT1**, **CPT1** and **CPT2** exhibit T_5 (5% weight loss temperature) values of 190, 302 and 398 °C, respectively. However, **PT1** shows drastic degradation from 300 °C, whereas **CPT1** and **CPT2** do it beyond 400 and 500 °C, respectively. **CPT2** is thermally more stable than **CPT1**, due to the presence of 3-dodecylthiophene units in its structure and its higher molecular weight.

3.5. *Electrochemical properties of the polymers*

The electrochemical behavior of polymers **PT1**, **CPT1** and **CPT2** has been investigated by cyclic voltammetry on a platinum disk electrode, using a THF solution containing $LiClO_4$ as supporting electrolyte at scan rate of 50 mV/s. All potentials were measured with respect to an Ag/AgCl reference electrode. Since THF is a good solvent for all these polymers, their backbone adopts a twisted conformation. Fig. 9 shows the voltammograms obtained for **PT1**, **CPT1** and **CPT2**, respectively. All of them exhibited a similar behavior, showing an irreversible potential cathodic shoulder at about 1.6 V, due to a partial oxidation of the polymer backbone to give the corresponding radical-cation. This oxidation process is limited because of the steric hindrance of the substituents and side chains present the polythiophene backbone.

4. Conclusion

PT1, **CPT1** and **CPT2** exhibited solvatochromic effects, when they were dissolved in poor and good solvents. In chloroform, these polymers adopt a twisted conformation, giving rise to a yellow solution for **PT1** and orange solutions for **CPT1** and **CPT2**. On the other hand, in poor solvents, such as chloroform–methanol 10:90 or THF–CH_3CN 50:50, a planar conformation of the polymer backbone is favored and the solution turns violet (different tonalites), depending on the polymer structure. These copolymers exhibit also an extended conjugation length in the solid state at room temperature and a less conjugated geometry upon heating. These conformational changes are reversible, so that when films are heated, the color change is reversible from violet to yellow for **PT1**, from dark red to yellow for **CPT1**, and from dark red to orange for **CPT2**, respectively. Because of the presence of oligo(ethylene glycol) side chains in their structure, **CPT1** has a higher T_g value than its homologue **CPT2**. Nevertheless, **CPT2** exhibits a higher thermal stability, due to its higher molecular weight.

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