

“Synthesis and characterization of novel luminescent polythiophenes containing pyrene units and oligo(ethylene glycol) spacers: Thermal and optical properties”



Eric G. Morales-Espinoza^a, Edgar Aguilar-Ortíz^a, Aldo Vázquez-Arce^a,
Efraín Rodríguez-Alba^a, Humberto Vázquez-Torres^b, Ernesto Rivera^{a,*}

^a Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ciudad Universitaria, C.P. 04510 D.F. Mexico

^b Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco No. 186, Col. Vicentina, C.P. 09340 D.F, Mexico

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ABSTRACT

A novel pyrene containing thiophene monomer 3-methyl-4-(4-(pyren-1-yl)butoxy) thiophene was synthesized and fully characterized by FTIR and ¹H and ¹³C NMR spectroscopies. This monomer was polymerized and copolymerized in the presence of 3-methyl-4-(tetraethoxy) thiophene, 3-hexylthiophene, 3-decylthiophene, and 3-dodecylthiophene using FeCl₃ as oxidizing agent, to give the corresponding homopolymer **HP3** and copolymers (**CP1**, **CP2**, **CP3**, **CP4**, **CP5** and **CP6**). These polymers exhibited good thermal stability with *T*₁₀ values between 312 and 414 °C, and *T*_g values varying from −38 to 24 °C. **CP5** exhibited two absorption bands at 246 and 416 nm whereas **CP6** absorbed only at 242 nm. The emission spectra of both polymers showed a monomer emission at 376–396 followed by an intense excimer emission at 570 nm, which reveals the presence of intramolecular non parallel pyrene–pyrene interactions.

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1. Introduction

Polythiophene (**PT**) is one of the most promising π -conjugated polymers due to its high stability, ease of structural modification and controllable optical and electrochemical behaviour. At the beginning, its applications were limited because of its insolubility in many organic solvents, due to its extended π -conjugated structure. Furthermore, alkyl chains have been introduced into the thiophene unit in order to get monomers able to give soluble polymers. The resulting poly(3-alkylthiophene)s showed to be processable conducting polymers, whose electronic properties can be modified, allowing their full characterization by spectroscopic 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. The incorporation of alkoxy groups into polythiophenes increases significantly their conductivity without diminishing their solubility in organic media [2,3].

For many polythiophenes, interesting properties such as thermochromism [4–6], ionochromism [5–7], photochromism [8], piezochromism [9] and biochromism [10] have been reported in the literature. Colour changes are due to transitions from planar to twisted conformation of the polymer backbone and viceversa, thereby modifying the effective conjugation length, which produces a shift of the absorption bands in their UV–vis spectra [11]. In polymers bearing alkoxy groups at 3-position of the thiophene rings, the lone pairs of the oxygen atom enter into conjugation with the polymer backbone, inducing a planar conformation [12]. This causes an augment in the effective degree of conjugation, which improves significantly the electronic mobility and conductivity in these polymers.

The chromic properties of substituted polythiophenes make them excellent prospects for light emitting diodes [13], gas sensors [14–16], biomedical applications [17], metal ions sensors [18,19] and biosensors [20–23]. Besides, due to their potential medical and industrial applications in the elaboration of electrochemical ion sensors, porphyrin functionalized conducting polymers based on polythiophene have been also prepared, in order to get a controlled electrochemical response to metal ions [24–26].

On the other hand, pyrene is a very powerful fluorescent probe which has been widely used for polymer labeling because it easily

* Corresponding author. Tel.: +52 55 5622 4733; fax: +52 55 5616 1201.
E-mail address: riverage@unam.mx (E. Rivera).

forms excimers. In addition, pyrene has a longer singlet lifetime than other chromophores, which facilitates the excimer formation. The main photophysical properties of pyrene excimers have been studied in detail by Winnik [27]. An excimer emission band appears if an excited-state molecule associates with a ground-state molecule after which the photon is delocalized over the conjugate to show a net change in the fluorescence spectral profile. The resulting photophysical properties give us useful information about the conjugated geometry, internal stacking and long distance interactions.

In our research group, we have synthesized a huge variety of π -conjugated polymers and oligomers bearing pyrene units in their structure. We studied the effect of the internal stacking in the optical and photophysical properties [28–32]. Very recently, we studied the incorporation of pyrene into dendritic molecules bearing porphyrin and fullerene moieties in order to study the fluorescence energy transfer phenomenon (FRET) as a function of the distance between the donor (pyrene) and the acceptor group (porphyrin or fullerene) [33–35].

In this work, we report the synthesis and characterization of novel series of thiophene monomers (Fig. 1) and polythiophenes bearing pyrene units and flexible alkyl spacers (Fig. 2). Monomers and polymers were fully characterized by FTIR, ^1H and ^{13}C NMR spectroscopies, and their thermal properties were analyzed by TGA and DSC. The optical properties of the soluble part of the polymers were studied by absorption and fluorescence spectroscopy. Because of their chromic properties, pyrene's ability to form excimers and oxygen sensitivity these polymers can be used as sensors and can be incorporated in luminescent devices as promising orange light emitters.

2. Experimental

2.1. Apparatus

FTIR spectra of monomers and polymers were recorded on a Nicolet 510 P spectrometer in KBr pressed pellets for solid samples and in film for liquid compounds. ^1H NMR and ^{13}C NMR spectra of all the compounds were carried out in CDCl_3 solution, using a Bruker Avance 400 spectrometer, operating at 400 MHz for ^1H and at 100 MHz for ^{13}C , respectively.

Thermogravimetric analysis (TGA) was conducted with samples of 5 mg on a Hi-Res TGA 2950 Instrument (from 20 to 600 °C) and differential scanning calorimetry (DSC) was carried out in a differential scanning calorimeter (MDSC) TA Instruments 2920 on samples of 5–7 mg (from –50 to 250 °C), in both cases with a

heating rate of 10 °C/min. Absorption spectra of the polymers in CHCl_3 solution (spectrometric grade, concentration 3×10^{-5} M) were scanned on a Varian Cary 1 Bio UV/vis spectrophotometer model 8452 A. Molecular weights of the polymers, were determined by gel permeation chromatography (GPC), using a Waters 2695 Instrument connected to a differential refractive index detector model Waters 2414. Measurements were performed using tetrahydrofuran (THF) as solvent against a polystyrene standard.

Steady state fluorescence spectra were recorded on a Photon Technology International LS-100 steady-state system with a pulsed xenon flash lamp as the light source. The slit widths on the excitation and emission monochromators equaled 2 and 1 nm, respectively. All spectra were obtained in CHCl_3 solution (spectrometric grade, concentration 1.2×10^{-6} M, 1.7×10^{-8} M, 1.9×10^{-8} M, for monomer **4**, **CP5** and **CP6**, respectively) with the usual right-angle configuration, exciting at $\lambda = 345$ nm.

2.2. Chemicals

3-Bromo-4-methylthiophene, 3-hexylthiophene, *N*-methyl-2-pyrrolidone (NMP, reagent grade), dimethyl sulfoxide (DMSO, reagent grade), methyl iodide, 1-pyrenebutanol, and FeCl_3 employed in the synthesis were purchased from Aldrich and used as received. Prior to use, tetra(ethylene glycol) was dried under vacuum. Chloroform, used in the polymerizations was distilled over calcium hydride (CaH_2) in order to remove traces of water.

2.3. Synthesis of monomers and polymers

3-Methyl-4-(tetraethoxy) thiophene (**1**) (Fig. 1) was synthesized using a procedure previously reported by us [24]. Tetra(ethylene glycol) (5.5 g, 28.3 mmol) and Na (0.64 g, 27.8 mmol) were reacted for 5 h under nitrogen atmosphere to give the corresponding alkoxide. Afterwards, a mixture of 3-bromo-4-methylthiophene (2.0 g, 11.3 mmol), CuI (2.3 g, 12.1 mmol) in NMP (10 mL) was added and the reaction mixture was heated at 110 °C for 48 h. Then, it was cooled to room temperature, filtered, and the filtrates were extracted with diethyl ether (3×15 mL), dried with MgSO_4 , and concentrated under reduced pressure. Finally, the product was purified by column chromatography in silica gel, using ethyl acetate as eluent to give a light yellow oil (1.51 g, 5.20 mmol). Compound **1** was obtained as main product. Yield: 46%.

^1H NMR (CDCl_3 , 300 MHz, ppm) (Fig. 3): 6.79–6.81 (m, 1H, H^5), 6.15 (d, 1H, $J = 3.0$ Hz, H^2), 4.08–4.11 (m, 2H, Thioph–O– CH_2), 3.82–3.86 (m, 2H, Thioph–O– CH_2CH_2), 3.64–3.74 (m, 10H, all the other OCH_2), 3.57–3.60 (m, 2H, CH_2 –OH), 2.68 (br s, OH), 2.08 (s, 3H,

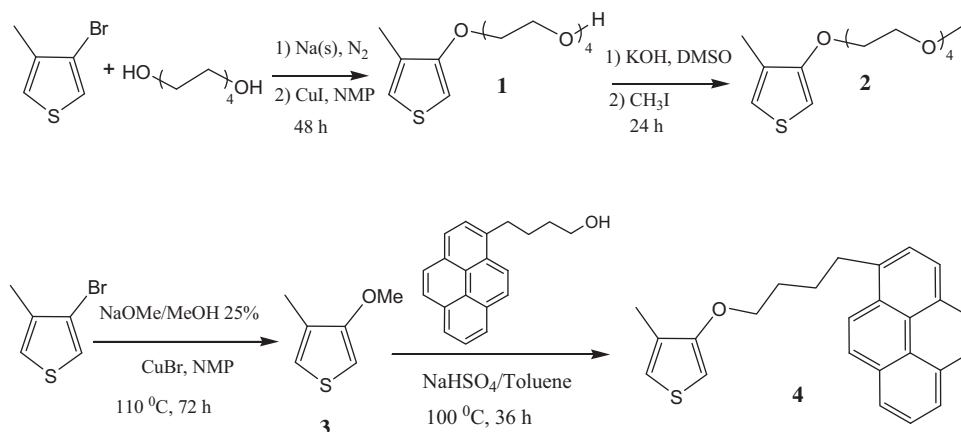


Fig. 1. Synthesis of the thiophene monomers.

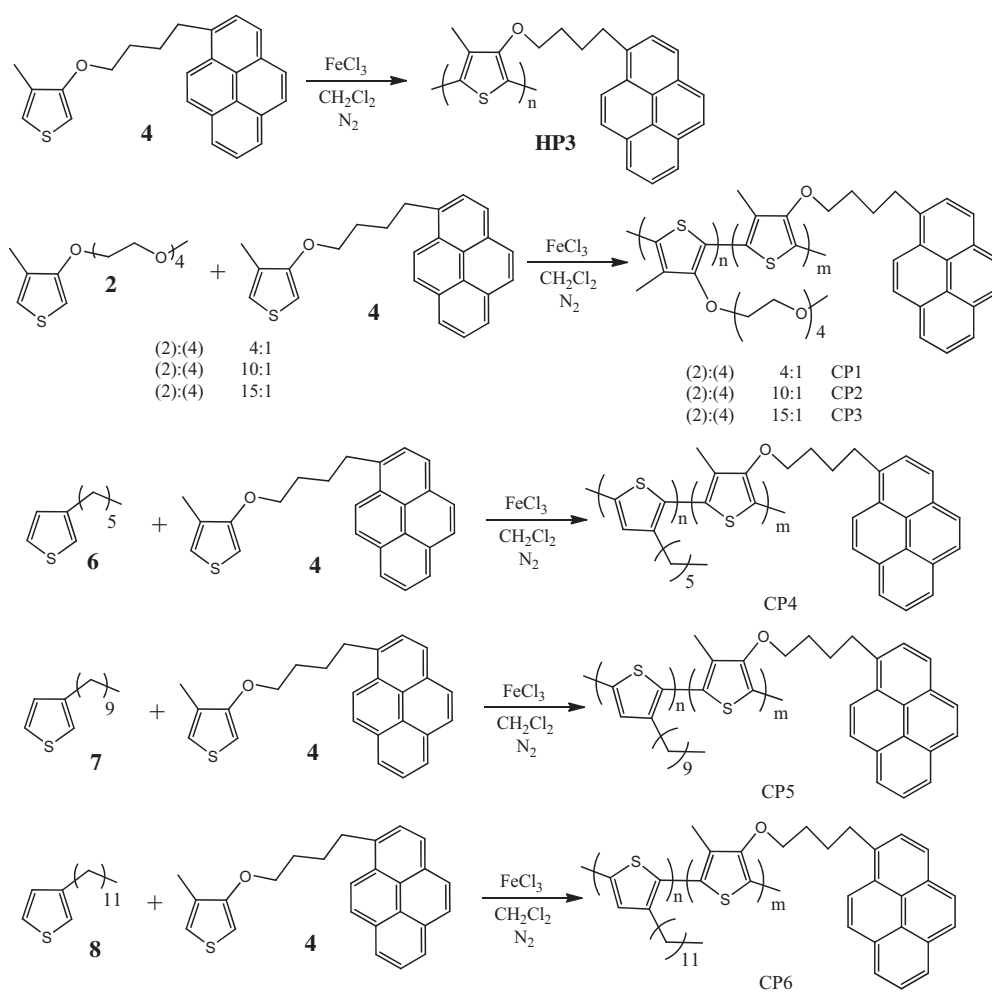


Fig. 2. Synthesis of the obtained polythiophenes.

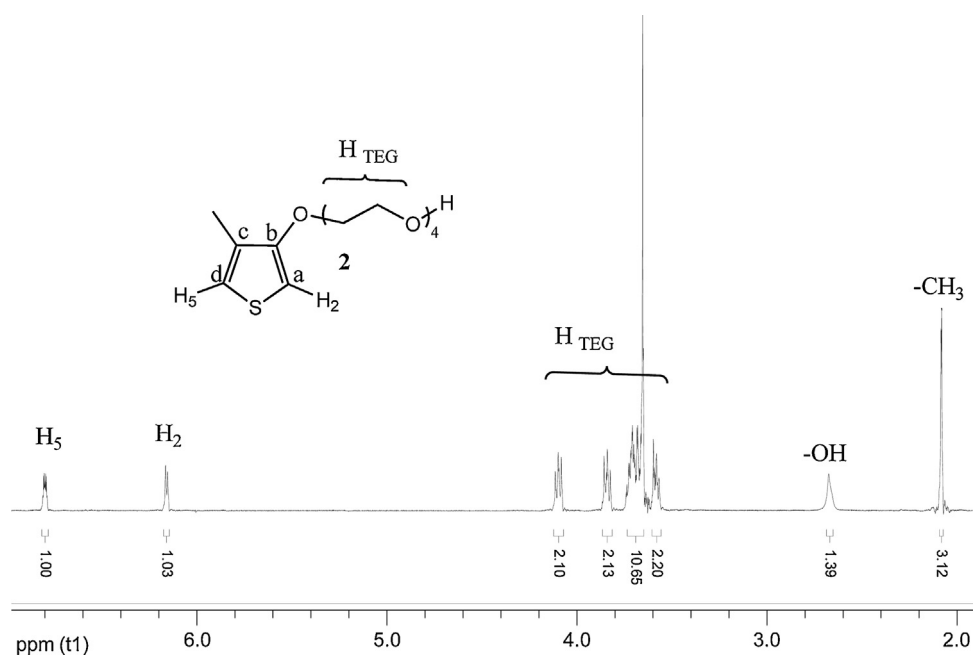


Fig. 3. ^1H NMR spectrum of monomer **(2)** in CDCl_3 solution.

CH₃–Thioph). ¹³C NMR (CDCl₃, 100 MHz, ppm): 155.96 (1C, C^b), 129.29 (1C, C^c), 120.10 (1C, C^d), 96.74 (1C, C^a), 72.71, 70.99, 70.79, 70.74, 70.44, 69.85, 69.75, 61.85 (8C, all OCH₂), 12.89 (1C, CH₃–Thioph).

3-Methyltetra(oxyethylene) oxy-4-methylthiophene (**2**) was obtained from **1**, according to the procedure previously reported by us [13]. **1** (0.5 g, 1.7 mmol) was added to a solution of KOH (0.453 g, 8.1 mmol) dissolved in DMSO (10 mL); the mixture was reacted for 1 h at room temperature to form the corresponding alkoxide. Then, methyl iodide (1.9 g, 13.4 mmol) was added and the reaction mixture was stirred for 24 h. Afterwards, it was filtered and poured into water to remove the DMSO and the product was extracted with dichloromethane. The organic phase was dried with MgSO₄ and concentrated at reduced pressure. The resulting product was purified by flash column chromatography in silica gel, using ethyl acetate as eluent. The pure product resulted to be yellow oil (0.28 g, 0.9 mmol). Yield: 54%.

¹H NMR (CDCl₃, 400 MHz, ppm) (Fig. 4): 6.80–6.81 (m, 1H, H⁵), 6.15 (d, 1H, *J*=3.2 Hz, H²), 4.08–4.11 (m, 2H, Thioph–O–CH₂), 3.84–3.86 (m, 2H, Thioph–O–CH₂–CH₂), 3.72–3.74 (m, 2H, OCH₂), 3.62–3.71 (m, 8H, all the other OCH₂), 3.52–3.55 (m, 2H, CH₂–O–CH₃), 3.37 (s, 3H, O–CH₃), 2.09 (s, 3H, ThiophCH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm): 156.01 (1C, C^b), 129.25 (1C, C^c), 119.98 (1C, C^d), 96.62 (1C, C^a), 72.03, 70.98, 70.76, 70.61, 69.68, 69.73 (all CH₂–O), 59.10 (1C, OCH₃), 12.80 (CH₃).

3-Methoxy-4-methylthiophene (**3**) was synthesized using a procedure similar to that reported in reference [14]. 3-bromo-4-methylthiophene (2 g, 11.29 mmol) and CuI (1.29 g, 6.78 mmol) were added to a mixture of 7.5 mL of sodium methoxide (28% in methanol) and NMP (6 mL); then the mixture refluxed for 3 days under N₂ atmosphere. After cooling, the solid was filtrated, and the filtrates were extracted three times with diethyl ether. The organic phase was dried with magnesium sulfate and evaporated at reduced pressure. The crude product was purified by column chromatography in silica gel, using hexane as eluent to give **3** as a light yellow oil (1.15 g). Yield: 80%.

¹H NMR (CDCl₃, 400 MHz, ppm) (Fig. 5): 6.88–6.91 (m, 1H, H⁵), 6.23 (d, 1H, H², *J*=3.0 Hz), 3.89 (s, 3H, OCH₃), 2.17 (s, 3H, CH₃). ¹³C

NMR (CDCl₃, 100 MHz, ppm): 157.17 (1C, C^b), 129.16 (1C, C^c), 120.17 (1C, C^d), 95.77 (1C, C^a), 57.36 (1C, OCH₃), 12.74 (1C, CH₃).

3-Methyl-4-(4-(pyren-1-yl) butoxy) thiophene (**4**) was synthesized using a procedure similar to that reported in the literature [15]. 3-Methoxy-4-methylthiophene (0.071 g, 0.554 mmol) was added to a mixture of 1-pyrenebutanol (0.177 g, 0.645 mmol) and NaHSO₄ (0.01 g, 0.083 mmol) in toluene (30 mL) under argon atmosphere and the mixture was heated at 100 °C until all the produced methanol was removed by distillation. The reaction mixture was cooled to room temperature, washed several times with water, and extracted with diethyl ether. The organic phase was combined and dried with MgSO₄, filtered and evaporated to dryness. The crude product was purified by column chromatography in silica gel using hexane as eluent. The desired product was obtained as a yellow solid (0.143 g). Yield: 70%.

¹H NMR (CDCl₃, 400 MHz, ppm) (Fig. 6): 7.89–8.30 (m, 9H, Py), 6.84–6.89 (m, 1H, H⁵), 6.14 (d, 1H, H², *J*=3.19 Hz), 4.00–4.03 (m, 2H, OCH₂), 3.41–3.45 (m, 2H, Py–CH₂), 2.12 (s, 3H, CH₃), 2.03–2.09 (m, 2H, CH₂), 1.94–2.01 (m, 2H, CH₂). ¹³C NMR (CDCl₃, 75 MHz, ppm): 156.31 (C^b, Thioph), 128.96 (C^c, Thioph), 119.89 (C^d, Thioph), 96.14 (C^a, Thioph), 136.70, 131.55, 131.02, 129.95, 129.34, 128.76, 127.62, 127.33, 126.71, 125.91, 125.22, 125.15, 124.97, 124.91, 124.80, 123.47 (C_{Py}), 69.79 (OCH₂), 33.25 (Py–CH₂), 29.29 (CH₂), 28.36 (CH₂), 12.84 (CH₃–Thioph).

2.3.1. Synthesis of homopolymer (HP3)

Poly(3-methyl-4-(4-(pyren-1-yl) butoxy) thiophene) (**HP3**) (Fig. 2) was obtained according to the procedure reported in [13]. A solution of FeCl₃ (0.14 g, 0.864 mmol) in CHCl₃ (5 mL) was prepared; then, **4** (0.08 g, 0.216 mmol) dissolved in CHCl₃ (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 **HP3** was isolated by filtration, washed with methanol, dried, and reduced, washing it several times with an ammonium hydroxide solution (1 M). The polymer was obtained as a yellow solid. Yield: 90%.

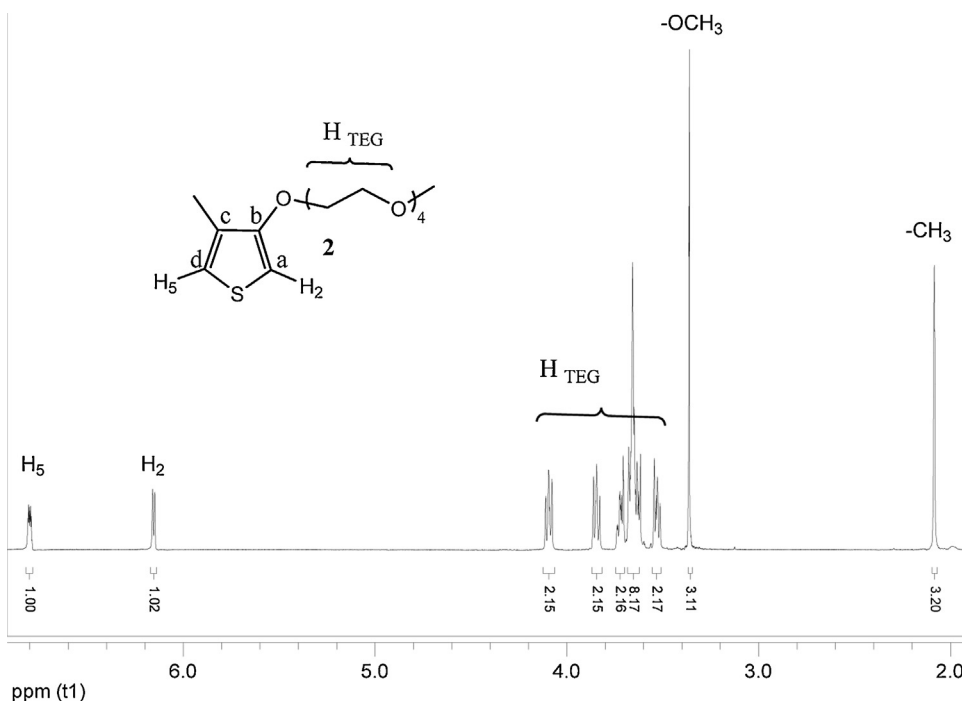


Fig. 4. ¹H NMR spectrum of **2** in CDCl₃ solution.

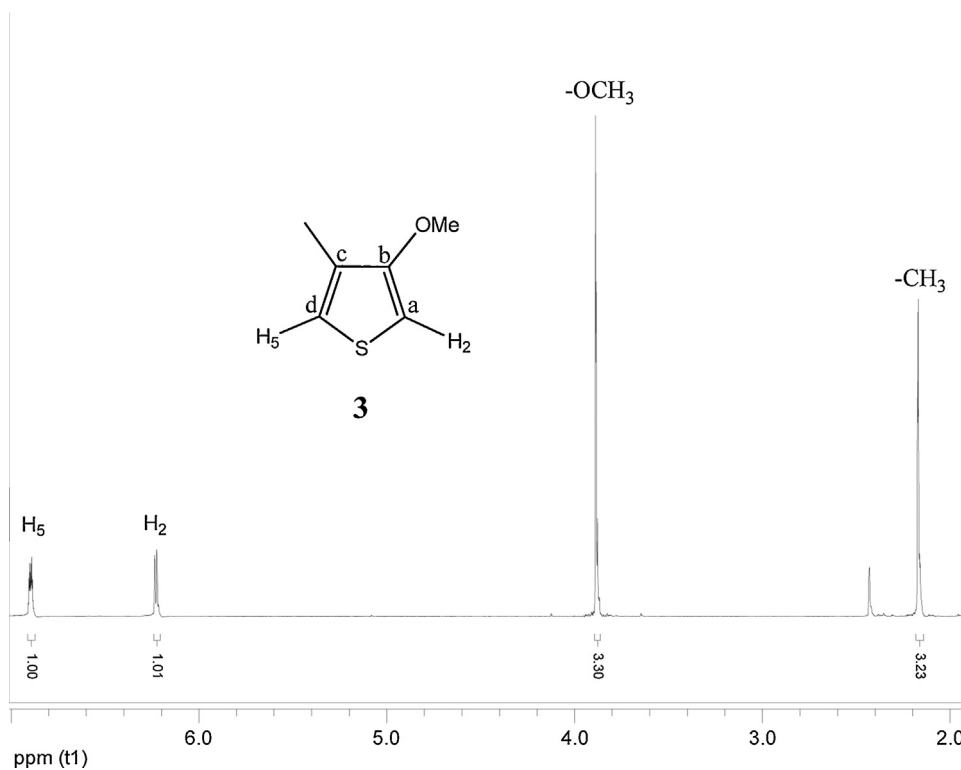


Fig. 5. ¹H NMR spectrum of **3** in CDCl₃ solution

2.3.2. Synthesis of copolymer (CP1)

A solution of FeCl₃ (0.17 g, 1.08 mmol) in CHCl₃ (3 mL) was prepared. Another mixture of **4** (0.02 g, 0.054 mmol) dissolved in CHCl₃ (1 mL) and **2** (0.065 g, 0.213 mmol) in CHCl₃ (1 mL) were added dropwise to the FeCl₃ solution. The reaction mixture was reacted for 24 h at room temperature; then the resulting solution

was poured into methanol (200 mL) in order to precipitate the polymer. The crude product was separated by filtration, washed with methanol, dried and reduced, washing it several times with an ammonium hydroxide solution (1 M). A black copolymer was obtained. Yield: 78%.

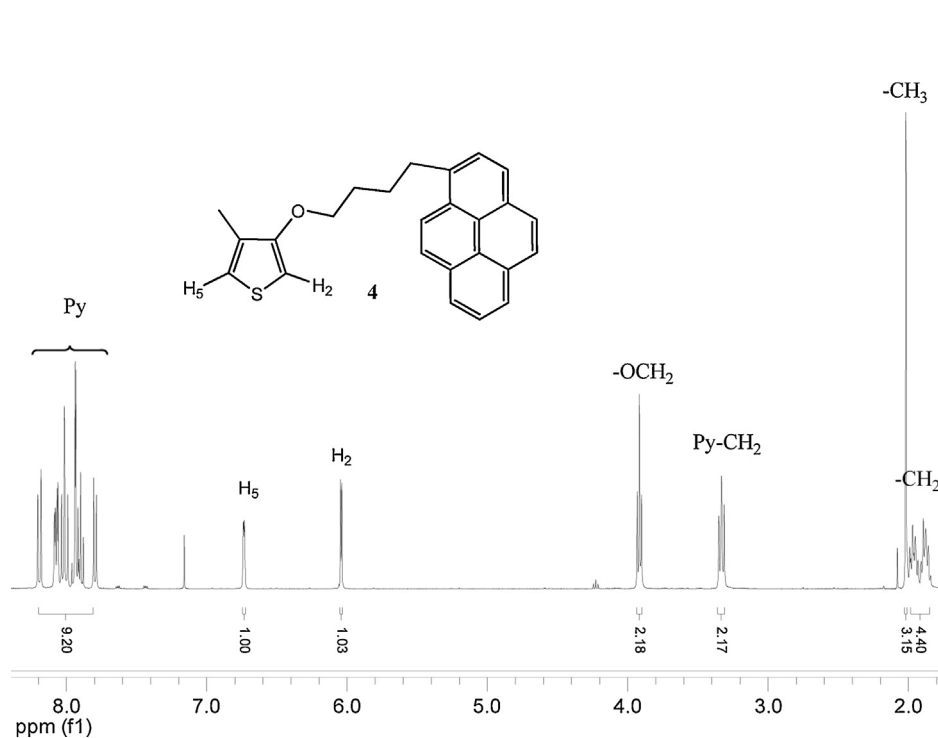


Fig. 6. ¹H NMR spectrum of monomer (**4**) in CDCl₃ solution.

2.3.3. Synthesis of copolymer (CP2)

A solution of FeCl₃ (0.19 g, 1.18 mmol) in CHCl₃ (3 mL) was prepared. Other solutions of **4** (0.01 g, 0.027 mmol) dissolved in CHCl₃ (1 mL) and **2** (0.082 g, 0.269 mmol) dissolved in CHCl₃ (1 mL) were added dropwise to the FeCl₃ solution. The reaction mixture was stirred for 24 h at room temperature. Then it was poured into methanol (200 mL) in order to precipitate the product. The obtained polymer was separated by filtration, washed with methanol, dried, and reduced, washing it several times with an ammonium hydroxide solution (1 M). A black copolymer was obtained. Yield: 80%.

2.3.4. Synthesis of copolymer (CP3)

A solution of FeCl₃ (0.225 g, 1.387 mmol) in CHCl₃ (3 mL) was prepared. Two solutions of **4** (0.0081 g, 0.0218 mmol) dissolved in CHCl₃ (1 mL) and **2** (0.1 g, 0.328 mmol) dissolved in CHCl₃ (1 mL) were added dropwise to the FeCl₃ solution. The reaction mixture was stirred for 24 h at room temperature. Then the solution was poured into methanol (200 mL) in order to precipitate the product. The polymer was separated by filtration, washed with methanol, dried, and reduced, washing it several times with an ammonium hydroxide solution (1 M). A black copolymer was obtained. Yield: 80%.

2.3.5. Synthesis of copolymer (CP4)

A solution of FeCl₃ (0.192 g, 1.18 mmol) in CHCl₃ (3 mL) was prepared. Two solutions of **4** (0.01 g, 0.027 mmol) dissolved in CHCl₃ (1 mL) and 3-hexylthiophene (0.045 g, 0.27 mmol) dissolved in CHCl₃ (1 mL) were added dropwise to the FeCl₃ solution. The reaction mixture was stirred for 24 h at room temperature. Afterwards, the resulting solution was poured into methanol (200 mL) in order to precipitate the polymer. The product was isolated by filtration, washed with methanol, dried, and reduced, washing it several times with an ammonium hydroxide solution (1 M). A black copolymer was obtained. Yield: 70%.

2.3.6. Synthesis of copolymer (CP5)

A solution of FeCl₃ (0.56 g, 2.35 mmol) in CHCl₃ (3 mL) was prepared. Other solutions of **4** (0.02 g, 0.054 mmol) dissolved in CHCl₃ (1 mL) and 3-decylthiophene (0.121 g, 0.54 mmol) dissolved in CHCl₃ (1 mL) were added dropwise to the FeCl₃ solution. The reaction mixture was reacted for 24 h at room temperature. Then, the resulting solution was poured into methanol (200 mL) in order to precipitate the polymer. The crude product was separated by filtration, washed with methanol, dried, and reduced, washing it with an ammonium hydroxide solution (1 M). A black copolymer was obtained. Yield: 41%.

2.3.7. Synthesis of copolymer (CP6)

A solution of FeCl₃ (0.578 g, 3.5 mmol) in CHCl₃ (3 mL) was prepared. Two solutions: **4** (0.03 g, 0.081 mmol) dissolved in CHCl₃ (1 mL) and 3-dodecylthiophene (0.204 g, 0.81 mmol) dissolved in CHCl₃ (1 mL), were added dropwise to the FeCl₃ solution. The reaction mixture was stirred for 24 h at room temperature. After that, the solution was poured into methanol (200 mL) in order to precipitate the polymer. The product was separated by filtration, washed with methanol, dried, and reduced with an ammonium hydroxide solution (1 M). A black copolymer was obtained. Yield: 61%.

3. Results and discussion

In this work, we report the synthesis and characterization of a new series of polythiophenes: one homopolymer (**HP3**) and six copolymers (**CP1**, **CP2**, **CP3**, **CP4**, **CP5** and **CP6**). The synthesis of the monomers and polymers are illustrated in Figs. 1 and 2, respectively. The new monomers were synthesized from 3-

bromo-4-methyl-thiophene. This compound was reacted with the tetra(ethylene glycol) alkoxide (prepared *in situ* with sodium), using CuI as catalyst and NMP as solvent under inert atmosphere to give the corresponding 3-alkoxythiophene (**1**). This intermediate was reacted with CH₃I, using KOH as base and DMSO as solvent to afford the desired monomer (**2**). On the other hand, 3-bromo-4-methyl-thiophene was reacted with sodium methoxide using CuI as catalyst and NMP as solvent under inert atmosphere to give the corresponding 3-methoxy-4-methylthiophene (**3**). This intermediate was further reacted with 1-pyrenbutanol and NaHSO₄ using toluene as solvent to yield the desired monomer (**4**).

Compound **4** was polymerized by using FeCl₃ as oxidizing agent and CHCl₃ as solvent to give the corresponding homopolymer **HP3**. On the other hand, co-monomer **2** was also co-polymerized in the presence of **4**, using ratios 2:4 (4:1, 10:1 and 15:1) in order to obtain the corresponding copolymers **CP1**, **CP2**, and **CP3**, respectively. Monomer **4** was also co-polymerized in the presence of 3-hexylthiophene, 3-decylthiophene and 3-dodecylthiophene (ratio 1:10) to give the corresponding copolymers **CP4**, **CP5**, and **CP6**, respectively. Since most of these polymers were fairly or poorly soluble in common organic solvents, they were analyzed by ¹H NMR spectroscopy in gel. For that, the polymers were swollen in minimum amount of chloroform in order to get good quality gels.

3.1. Characterization of monomers and polymers

The structure of monomer (**4**) was confirmed by FTIR and NMR spectroscopies, whereas the characterization of monomer (**2**) has been previously reported by us [13]. Since not all the polymers resulted to be soluble in organic media, the molecular weights of the soluble ones, **CP5** and **CP6**, were estimated by GPC, giving Mw values of 20,000 g/mol (**CP5**) and 22,000 g/mol (**CP6**), and polydispersities of 1.5 (**CP5**) and 1.8 (**CP6**).

3.1.1. FTIR and NMR spectroscopy

In the FTIR spectra of the polymers, the existence of the alkoxy chains was confirmed by the presence of C–H stretching band at 2865 and 2960 cm⁻¹ due to –CH₂– and –CH₃ groups. Ring vibrational modes are also seen at 1570, 1447 and 1348 cm⁻¹. The band at 1080 cm⁻¹ can be assigned to C(ring)–O–C stretching.

The ¹H NMR spectra of monomer (**4**) in CDCl₃ solution is shown in (Fig. 6). As we can see, there is a multiplet at 7.89–8.30 ppm due to the protons of the pyrene unit, followed by a multiplet at 6.84–6.89 assigned to proton H⁵ of thiophene ring and a doublet at 6.14 ppm, which is attributed to proton H² with J = 3.19 Hz. In addition, a multiplet at 4.00–4.03 ppm arising from the protons of OCH₂, as well as a multiplet at 3.41–3.45 ppm corresponding to protons of Py-CH₂ can be also observed. The signal related to protons of the methyl group appears at 2.12 ppm, followed by two multiplets at 2.03–2.09 and 1.94–2.01 ppm due to the protons of the CH₂–CH₂ groups.

In the ¹³C NMR spectrum of **4** there are four signals due to the thiophene ring at 156.31, 128.96, 119.89 and 96.14 ppm, corresponding to carbons C^b, C^c, C^d, and C^a, respectively. Moreover, the signals arising from the carbons of pyrene unit (sixteen carbons) appeared in the range between 136.70–123.47 ppm. The signal of OCH₂ appears at 69.79 ppm, as well as a peak at 33.25 ppm corresponding to Py-CH₂, which is followed by two more signals at 29.29 and 28.36 attributed to the methylene groups CH₂–CH₂ of the aliphatic chain. Finally, we can observe a signal at 12.84 ppm due to the CH₃ group.

In the ¹H NMR spectrum in gel [38] of copolymer **CP1** (swollen in chloroform), we can perceive a low intensity multiplet at 7.65–8.98 ppm corresponding to the pyrene unit present in the

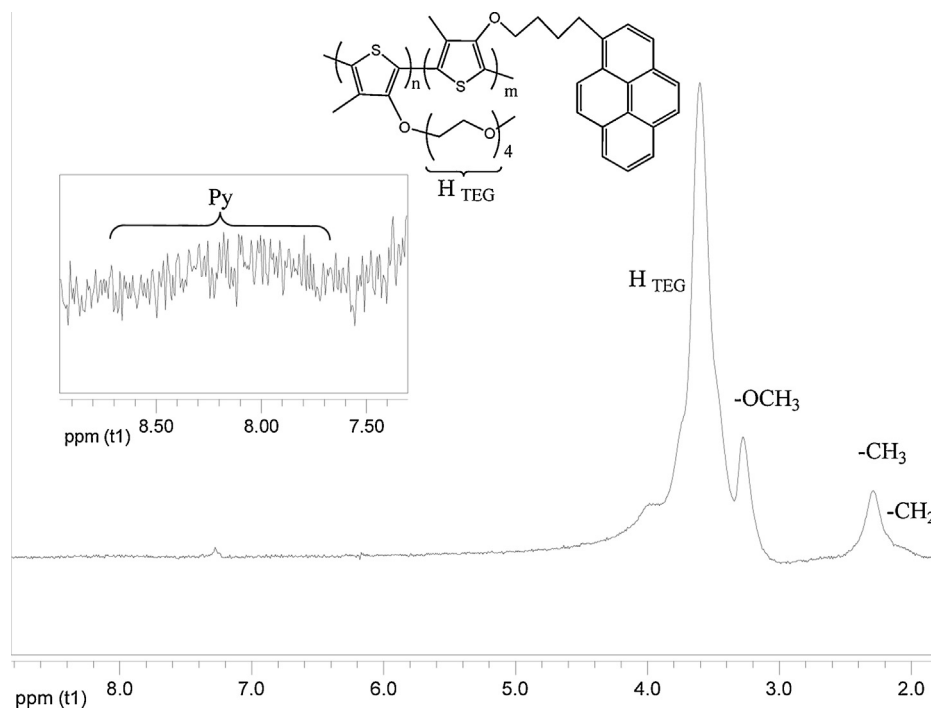


Fig. 7. ^1H NMR spectrum in gel of **CP2** swollen in CDCl_3 .

monomer, which is an indication that the copolymerization effectively occurred. The signal at 3.60 ppm and the discrete peak at 3.98 ppm are observed for the α -methylene protons of the alkoxy group, and similar observations were obtained for copolymer **CP2** (Fig. 7).

3.1.2. Thermal properties of the polymers

TGA thermograms of the polymers are shown in Fig. 8. Homopolymer **HP3** shows a good thermal stability with the T_{10} (10 wt% loss temperature) value of 340 °C, which can be due to a fragmentation of the oligo(ethylene glycol) chain, remaining 36 wt

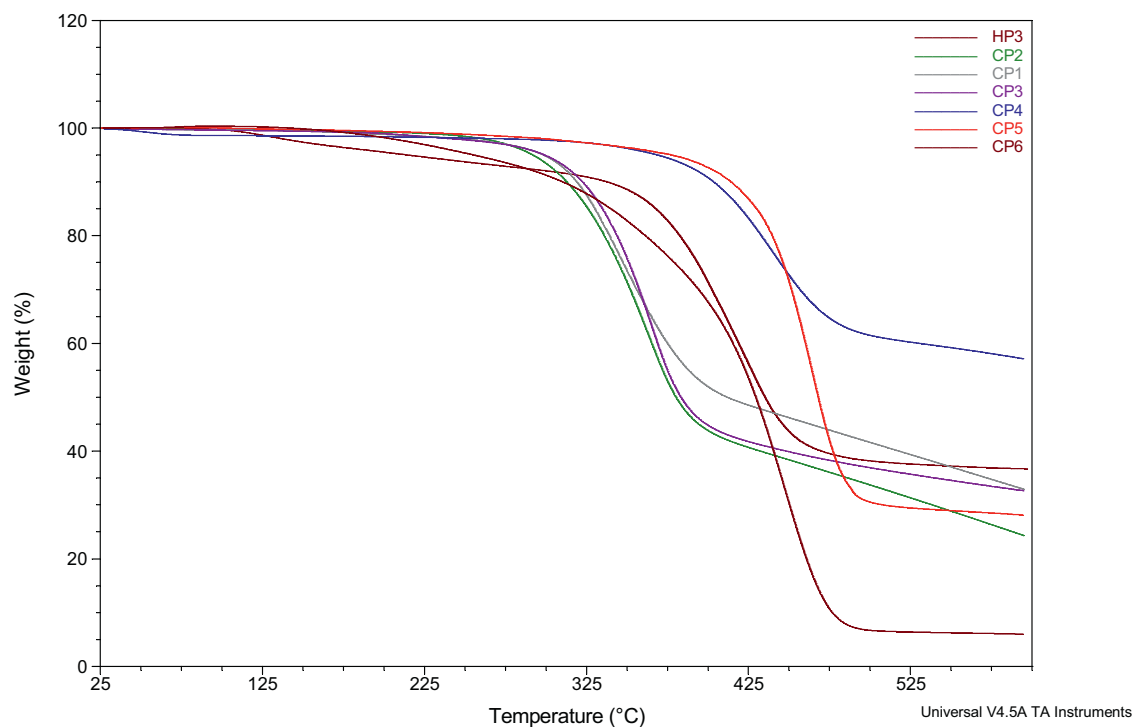


Fig. 8. TGA curves of the polymers **HP3**, **CP1**, **CP2**, **CP3**, **CP4**, **CP5** and **CP6**.

Table 1
Thermal properties of the polymer samples.

Polymer	T_g (°C)	T_{10} (°C)	Drastic degradation (°C)	Wt% remaining
HP3	23	340	364–455	37
CP1	24	318	311–403	33
CP2	–	312	302–391	25
CP3	22	323	310–400	32
CP4	23	403	387–488	57
CP5	–38	414	417–495	28
CP6	–34	312	330–476	5

% at 600 °C. Glass transition temperature (T_g) was measured with a differential scanning calorimeter (MDSC) TA Instruments 2920 on samples of 5–7 mg from –50 to 250 °C with a heating rate of 5 °C/min under N_2 flux of 50 cc/min, a period of 40 s and an amplitude of 0.5 °C. T_g was assigned at the medium point of transition on the reversing heat flow thermograms. The thermal properties, including the T_g values of all the polymer samples, are summarized in Table 1.

TGA thermograms the obtained polymers are shown in (Fig. 8). The decomposition profile of the polymers CP4 and CP5 resembles that reported for polythiophene [36] with a higher remaining mass for the former (57 wt%) than for the latter (28 wt%) after heated up to 600 °C, due to the relative high content of thiophene rings in the backbone chain for CP4 (Table 1). CP4 and CP5 showed a drastic degradation above 450 °C with T_{10} values between 403 and 414 °C, whereas the other copolymers showed to be thermally less stable with T_{10} values between 312–323 °C, exhibiting degradation beyond 300 °C.

In contrast, the decomposition profile of polymers HP3, CP1, CP2, and CP3 resembles to that of polyethylene and poly(ethylene glycol), [37] which seems to be in agreement with the structures drawn in Fig. 2. It is worth noting that CP6 exhibits a very low remaining mass (5 wt%) and a smooth decomposition profile, which is typical for polyethylene segments, due to the highest alkyl character of this polymer, compared to the others (Table 1).

Regarding the T_g measurement of the polymers, it is important to mention that such a transition was clearly showed in the reversing heat flow signal of the second run. The T_g values for all the polymers were very similar among them (from 22 to 24 °C), except those for CP2, CP5, and CP6. Indeed, CP2 did not show any T_g in the temperature range applied for DSC tests, and appeared to be a crosslinked network, whereas CP5 and CP6 showed a T_g of –38 and –34 °C, respectively. These last results are due to the influence of the large alkyl chains attached to thiophene rings of these polymers: C_9 and C_{11} , for CP5 and CP6, respectively.

3.1.3. Optical properties of the polymers

Since some of the polymers were poorly soluble, we decided to study the optical properties of those that showed a good solubility in organic media. The optical properties of the monomer (4) and soluble copolymers, CP5 and CP6, were studied by absorption and

Table 2
Optical properties of the monomer 4 and the copolymers.

Compound	Absorption λ (nm)	Cut off (nm)	Emission λ (nm)	Cut off λ (nm)
4	345 ^a	360	376–396 ^c	480
CP5	246 ^a , 416 ^b	538	350–450 ^c 570 ^d	–
CP6	242 ^a	470	350–450 ^c 570 ^d	–

^a absorption band of the pyrene.

^b absorption band of the polythiophene backbone.

^c monomer emission.

^d excimer emission.

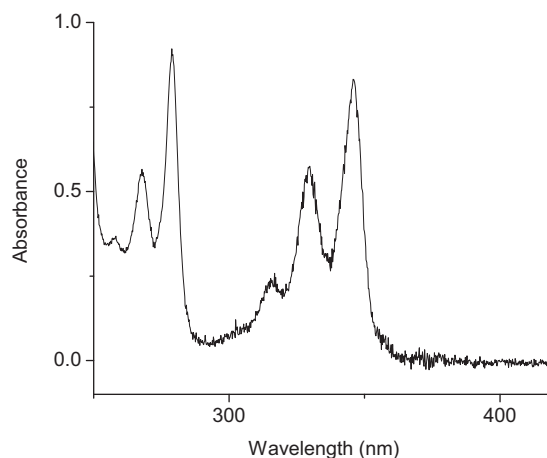


Fig. 9. Absorption spectrum of the monomer (4) in $CHCl_3$ solution.

steady state fluorescence spectroscopy. The results are summarized in Table 2.

The absorption spectrum of the monomer (4) in $CHCl_3$ solution (Fig. 9) exhibited a well-structured absorption band at $\lambda = 344$ nm, due to the $S_0\tilde{O}S_2$ transition of the pyrene units. Since the $S_0\tilde{O}S_1$ transition band of this chromophore has a very low intensity and appears at 370 nm, for practical purposes monomer (4) was excited at $\lambda = 344$ nm in order to obtain the emission spectra [27]. This compound has a molar extinction coefficient of $\epsilon = 40,926 M^{-1} cm^{-1}$ at $\lambda = 344$ nm, very close to that reported for pyrene in THF solution ($\epsilon = 45,000$).

On the other hand, the absorption spectra of copolymers CP5 and CP6 (Fig. 10) are very different. For instance CP5 exhibited two absorption bands at 246 and 416 nm, due to the thiophene units and the conjugated sequences, respectively. However, CP6 only showed one absorption band at 242 nm followed by a tail that indicates a lower degree of conjugation for this copolymer. This can be attributed to the presence of longer aliphatic chains in CP6, which causes a twist of polythiophene backbone skewing it from planarity. Since the pyrene content is very low with respect to that of thiophene, the $S_0\tilde{O}S_2$ band ($\lambda = 345$ nm) is partially hidden by the absorption band of the polythiophene backbone in these copolymers.

The fluorescence spectrum of the monomer (4) is shown in Fig. 11 and exhibits a broad emission band in the range between 360 and 465 nm, which is due to the $S_1 \rightarrow S_0$ transition of pyrene

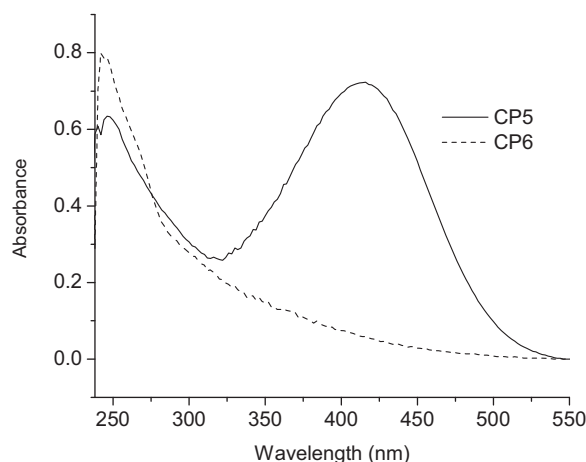


Fig. 10. Absorption spectra of copolymers CP5 and CP6 in $CHCl_3$.

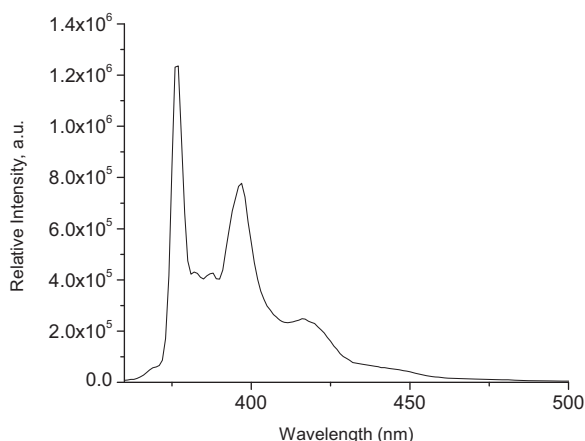


Fig. 11. Emission spectrum of the monomer (4) in CHCl_3 solution.

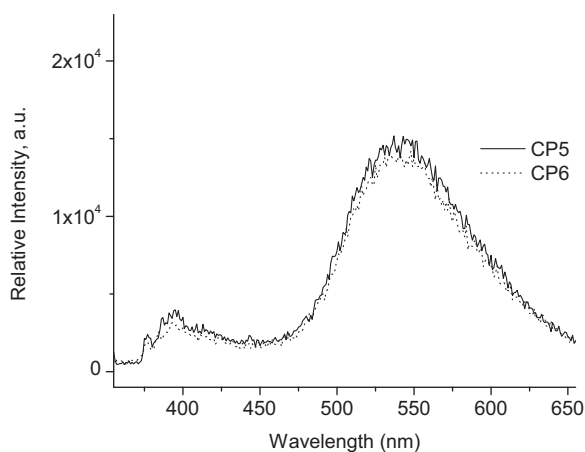


Fig. 12. Emission spectra of copolymers CP5 and CP6 in CHCl_3 solution.

in the non-associated state, named “monomer emission” this emission is very similar to that of the pyrene molecule according to the literature [27]. For this monomer, practically no excimer emission was observed.

In contrast, when the emission spectra of copolymers CP5 and CP6 (Fig. 12) were recorded, we observed a broad “monomer emission” band at 350–450 nm followed by a very intense excimer emission at 570 nm, which reveals the presence of intramolecular pyrene–pyrene interactions in these copolymers. Although the pyrene content in these copolymers is not very high, the long aliphatic spacers present in the polymer allowed pyrene units to encounter giving rise to the formation of excimers. Since the excimer band is very red-shifted, we can affirm that in these polymers the pyrene units interact in a non parallel way. A similar behavior was observed in other conjugated polymers containing pyrene such as *cis*-poly(1-ethylenepyrene) (*cis*-PEP) [31,32].

4. Conclusions

A new series of polythiophenes bearing pyrene units and well defined oligo(ethylene glycol) spacers were synthesized and characterized. The obtained polymers exhibited a good thermal stability with T_{10} values between 312 and 414 °C and T_g values varying from –38 to 24 °C. Only copolymers CP5 and CP6 showed a good solubility in organic media. The absorption spectra of CP5 exhibited absorption two bands at 246 and 416 nm, whereas CP6

showed one absorption band at 242 nm revealing that the former possesses a higher degree of conjugation. The emission spectra of both polymers exhibited a monomer emission at 376–396 nm followed by an intense excimer emission at 570 nm, which reveals the presence of intramolecular pyrene–pyrene interactions in these polymers despite the low pyrene content. This can be due to a twist of the polymer backbone jointly with the effect of the long alkyl spacers.

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