

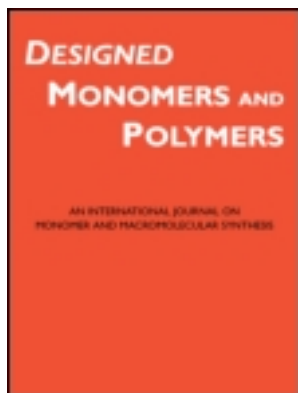
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### Synthesis and Characterization of Novel Polythiophenes Containing Azobenzene Units and Well-Defined Oligo(Ethylene Glycol) Spacers: Thermal and Optical Properties, and Preparation of Langmuir Films

Jorge Dircio <sup>a</sup>, Adriana Gelover-Santiago <sup>b</sup>, Carolina Caicedo <sup>c</sup>, Maria del Pilar Carreón-Castro <sup>d</sup>, Yazmín Valdez-Hernández <sup>e</sup> & Ernesto Rivera <sup>f</sup>

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# Synthesis and Characterization of Novel Polythiophenes Containing Azobenzene Units and Well-Defined Oligo(Ethylene Glycol) Spacers: Thermal and Optical Properties, and Preparation of Langmuir Films

Jorge Dircio<sup>a</sup>, Adriana Gelover-Santiago<sup>a</sup>, Carolina Caicedo<sup>a</sup>, Maria del Pilar Carreón-Castro<sup>b</sup>, Yazmín Valdez-Hernández<sup>b</sup> and Ernesto Rivera<sup>a,\*</sup>

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## Abstract

A new series of 3-alkyl-ester-substituted polythiophenes, bearing amino-nitro substituted azobenzenes and flexible tetra(ethylene glycol) spacers, have been synthesized and characterized. First an amphiphilic monomer (E)-2-(4-((4-nitrophenyl)diazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-yl 2-(tiophen-3-yl) acetate (AT) was prepared and homo-polymerized to give the corresponding polymer poly[(E)-2-(4-((4-nitrophenyl)diazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-yl 2-(tiophen-3-yl) acetate] (HP). This monomer was also co-polymerized in the presence of 3-butylthiophene, 3-hexylthiophene and 3-dodecylthiophene to give the corresponding co-polymers CP4, CP6 and CP12. These polymers exhibited molecular weights ranging between 16 500 and 46 990 g/mol. HP showed lower thermal stability than the corresponding co-polymers CP4, CP6 and CP12. The use of 3-alkylthiophene plasticant co-monomers conferred higher thermal stability to the obtained co-polymers. Polymers bearing higher azobenzene content showed to be more susceptible to degradation. All polymers exhibited a maximum absorption band at  $\lambda_{\max} = 456\text{--}475$  nm, due to the amino-nitro-substituted azobenzene units. Finally, Langmuir films were prepared with HP and CP4, whose formation was monitored by plotting their surface pressure vs. molecular area ( $\pi/A$ ) isotherms and by Brewster angle microscopy (BAM).

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## Keywords

Polythiophene, azobenzene, poly(ethylene glycol), optical properties, Langmuir films

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## 1. Introduction

In the last 30 years,  $\pi$ -conjugated polymers have been regarded as promising materials for the development of electronic devices such as light emitting diodes (LEDs) [1–6], photovoltaic and solar cells [7], chromic devices [8], chemical sensors [9] and non-linear optical systems [10, 11]. The opto-electronic properties vary remarkably, depending on the degree of conjugation between the consecutive repeat units. Particularly poly(3-alkylthiophenes) have been considered as promising materials, due to their good solubility, processability, thermal stability, electroactivity and other opto-electronic properties. Compared to other  $\pi$ -conjugated polymers, polythiophenes are relatively easy to functionalize. Some substituted polythiophenes, such as poly(3-alkylthiophene)s and poly(3-alkoxy-4-methylthiophene)s, show interesting properties: thermochromism [12, 13], solvatochromism [14] and ionochromism [15–17], which have not been observed in non-substituted polythiophenes.

On the other hand, azobenzene has been regarded as a versatile chromophore for the preparation of polymers with opto-photonics applications. Moreover, azopolymers have been widely used in the development of chemical sensors, materials with NLO properties [18–22]. The combination of a polythiophene backbone with photoactive azobenzene groups has led to the development of a new class of polymers with unique optical and electronic properties [23–28]. These polymers can be used in the elaboration of photochromic materials, reversible optical storage and THG nonlinear optical devices [10].

Zhao and co-workers [29] reported the synthesis and characterization of polythiophenes containing azobenzene units and alkyl side-chains with different lengths. These polymers showed thermochromic and photoresponsive properties in solution, as well as in thin films. It was found that the presence of lateral chains jointly with azobenzene groups give rise to thermochromic and photochromic effects in the polythiophene structure, resulting from the *trans*–*cis* photoisomerization of azobenzene. Similarly, Zhao *et al.* studied the structural dependence of the thermochromic behaviour of poly(3-hexylthiophene) and its co-polymers bearing azobenzene units [30].

Zhao and Hu [31] reported the synthesis of some polythiophenes, bearing disubstituted azobenzene units and spacers with different lengths. These polymers exhibited a large range of mesophase temperatures and good photoactivity. On the other hand, Dell-Casa *et al.* [32] reported the synthesis and characterization of azobenzene functionalized monomers with different spacer lengths, which were co-polymerized in the presence of 3-alkylthiophenes containing aliphatic chains as plasticizers. These materials showed NLO of second harmonic generation ( $\chi^2$ ) in the solid state.

In this work, we report the synthesis and characterization of a new series of polythiophenes, bearing amino–nitro-substituted azobenzene units linked to the polymer backbone *via* a flexible tetra(ethylene glycol) spacer, which make them amphiphilic. A new amphiphilic monomer (E)-2-(4-((4-nitrophenyl)diazenyl)phenyl)-

5-8-11-trioxa-2-azatridecan-13-yl 2-(tiophen-3-yl) acetate (AT) was prepared from 3-bromo-4-methylthiophene. This monomer was homo-polymerized to give the corresponding homo-polymer, poly[(E)-2-(4-((4-nitrophenyl)diazenyl)phenyl)-5-8-11-trioxa-2-azatridecan-13-yl 2-(tiophen-3-yl) acetate] (HP), and was also co-polymerized in the presence of 3-butylthiophene, 3-hexylthiophene and 3-dodecylthiophene to give the corresponding co-polymers CP4, CP6 and CP12.

These polymers were characterized by FT-IR,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopies; their thermal properties were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Moreover, the optical properties of these polymers were studied by UV-Vis spectroscopy in solution and in cast film. Finally, Langmuir films were prepared with HP and CP4, whose formation was monitored by plotting their surface pressure vs. molecular area ( $\pi/A$ ) isotherms and by Brewster angle microscopy (BAM).

## 2. Experimental

### 2.1. Apparatus

FT-IR spectra of monomers and polymers were recorded on a Nicolet 510 P spectrometer in KBr pellets for solids and in film for liquid compounds.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of the compounds were recorded in  $\text{CDCl}_3$  solution, using a Bruker Avance 400 spectrometer, operating at 400 and 100 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively. Thermal properties of the compounds such as thermal stability ( $T_{10}$ ), were determined by thermogravimetric analysis (TGA) on a Hi-Res TGA 2950 instrument from 0 to  $600^\circ\text{C}$ . Glass transition temperature ( $T_g$ ) and meeting point ( $T_m$ ) were determined by differential scanning calorimetry (DSC) on a DSC 2910 instrument, using a heating rate of  $20^\circ\text{C}/\text{min}$ . Absorption spectra of polymers in solution were recorded on a UNICAM UV-300 spectrophotometer using 1 cm quartz cells.

Molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a HPLC-GPC Waters 1525 Binary HPLC Pump, with two Waters columns HSP-GEL HRMB-M, one with  $M_w = 1000\text{--}4 \times 10^6$  and the other with  $M_w = 500\text{--}7 \times 10^5$ . Measurements were carried out using  $\text{CHCl}_3$  (HPLC grade) as eluent, against Waters polystyrene standards ( $M_w = 370\text{--}1.27 \times 10^6$ ).

### 2.2. Chemicals

All reagents and solvents used in synthesis of monomers and polymers were purchased from Aldrich and used as received. Prior to use, N-methylaniline was purified by distillation at reduced pressure; chloroform was dried using  $\text{CaCl}_2$  followed by simple distillation. UV-Vis spectroscopy analyses were carried out using  $\text{CHCl}_3$  (spectrophotometric grade) from Aldrich as solvent.

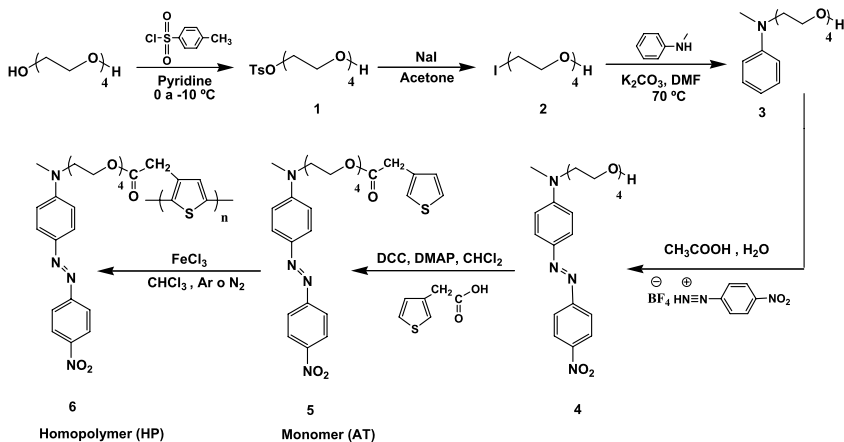
### 2.3. Synthesis of the Azo-Monomer (*E*)-2-(4-((4-Nitrophenyl)Diazenyl)Phenyl)-5-8-11-Trioxa-2-Azatriodecan-13-Yl 2-(Tiophen-3-Yl) Acetate (AT)

The synthesis of RED-PEG-4 dye [33] and monomer (*E*)-2-(4-((4-nitrophenyl)diazenyl)phenyl)-5-8-11-trioxa-2-azatriodecan-13-yl 2-(tiophen-3-yl) acetate (AT1) is described in Fig. 1 (*vide infra*). The preparation of monomer AT1 was carried out according to a synthetic method similar to that reported by Zhao *et al.* [31].

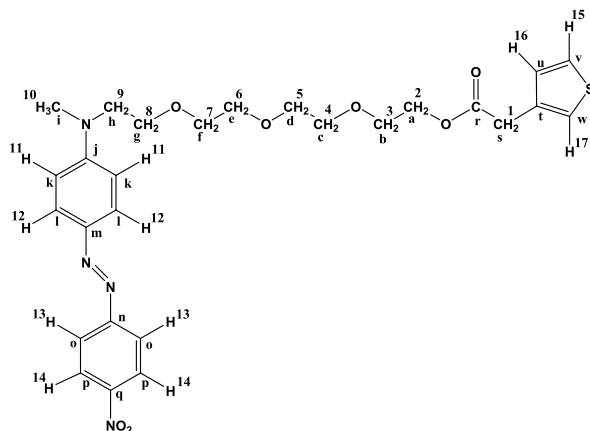
To a mixture of RED-PEG-4 (0.60 g, 1.39 mmol), 3-thiophenacetic acid (0.198 g, 1.397 mmol), 4-(dimethylamino) pyridine (DMAP) (0.017 g, 0.139 mmol), a solution of 1,3-dicyclohexylcarbodiimide (DCC) (0.783 g, 3.80 mmol) in 22 ml chloroform was added. The reaction mixture was stirred vigorously for 48 h at room temperature under inert atmosphere. Then, it was filtered with a Buchner funnel in order to eliminate the dicyclohexylurea formed during the reaction, and the remaining solvent was eliminated under vacuum. The crude product was purified by precipitation in hexane in order to eliminate unreacted DCC. Furthermore, it was purified by flash column chromatography, using a chloroform/hexane (1:1) mixture as eluent, increasing the polarity until 100% chloroform. AT was obtained as a dark purple solid (0.65 g, 1.168 mmol). Yield = 84%.

FT-IR (KBr,  $\text{cm}^{-1}$ )  $\nu$  = 3100 (s, C–H $\alpha$ ), 3070 (s, C–H $\beta$ ), 2866 (s, –OCH<sub>2</sub>), 2820 (s, –N–CH<sub>3</sub>), 1732 (s, C=O) 1598, 1585 (s, C=C aromatic ring), 1445 (s, N=N), 1513, 1352 (s, –NO<sub>2</sub>), 1251 (s, C–N), 1129, 1097 (s, –OCH<sub>2</sub>), 855, 754 (out-of-plane, C–H aromatic), 727 (out-of-plane, C–H aromatic).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, see Scheme 1)  $\delta$  = 8.28 (d,  $J$  = 9.2 Hz, 2H, H<sup>14</sup>), 7.89 (d,  $J$  = 6.8 Hz, 2H, H<sup>13</sup>), 7.81 (d,  $J$  = 6.8 Hz, 2H, H<sup>12</sup>), 7.26 (m, 1H, H<sup>15</sup>), 7.15 (m, 1H, H<sup>17</sup>), 7.03 (m, 1H, H<sup>16</sup>), 6.76 (d,  $J$  = 9.6 Hz, 2H, H<sup>11</sup>), 4.25 (t,  $J$  = 4.8, 2H, H<sup>2</sup>), 3.73–3.60 (m, 16H=2H<sup>9</sup>, 2H<sup>8</sup>, 2H<sup>7</sup>, 2H<sup>6</sup>, 2H<sup>5</sup>, 2H<sup>4</sup>, 2H<sup>3</sup>, 2H<sup>1</sup>, all OCH<sub>2</sub>), 3.12 (s, 3H, H<sup>10</sup>, CH<sub>3</sub>–N) ppm.



**Figure 1.** Synthesis of the azo-monomer AT and the homo-polymer HP.



**Scheme 1.** Assignment of the signals for monomer AT.

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz, see Scheme 1).  $\delta = 171.19$  (1C,  $\text{C}^r$ ), 156.91 (1C,  $\text{C}^n$ ), 152.69 (1C,  $\text{C}^j$ ), 147.45 (1C,  $\text{C}^q$ ), 143.91 (1C,  $\text{C}^m$ ), 133.61 (1C,  $\text{C}^t$ ), 131.67 (1C,  $\text{C}^u$ ), 128.64 (1C,  $\text{C}^v$ ), 126.24 (2C,  $\text{C}^l$ ), 124.80 (2C,  $\text{C}^p$ ), 123.49 (1C,  $\text{C}^w$ ), 122.73 (2C,  $\text{C}^o$ ), 111.64 (2C,  $\text{C}^k$ ), 70.95, 70.82, 70.77, 70.70 (4C= $\text{C}^f$ ,  $\text{C}^e$ ,  $\text{C}^d$ ,  $\text{C}^c$  all of  $\text{OCH}_2$ ), 69.16 (1C,  $\text{C}^b$ ), 68.68 (1C,  $\text{C}^g$ ), 64.10 (1C,  $\text{C}^a$ ,  $\text{CH}_2\text{OOC}$ ), 52.33 (1C,  $\text{C}^h$ ,  $\text{CH}_2\text{-N}$ ), 39.50 (1C,  $\text{C}^i$ ,  $\text{CH}_3\text{-N}$ ), 35.86 (1C,  $\text{C}^s$ ) ppm.

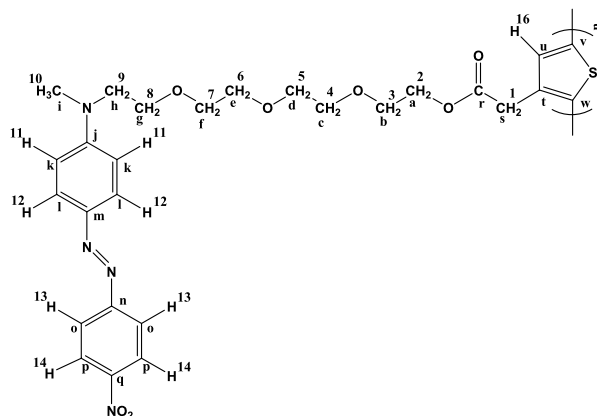
#### 2.4. Synthesis of the Homo-Polymer HP

The synthesis of the homo-polymer and the corresponding co-polymers was carried out by chemical oxidation of the corresponding monomers, using  $\text{FeCl}_3$ , according to the method previously reported in the literature [34, 35].

To a mixture of  $\text{FeCl}_3$  (0.44 g, 2.69 mmol) in 2 ml chloroform (previously distilled and dried with  $\text{CaCl}_2$ ) under inert atmosphere, a solution of monomer AT (0.30 g, 0.54 mmol) in 2 ml chloroform was added dropwise. The reaction mixture was stirred for 42 h at room temperature. After this time, it was poured into 200 ml MeOH in order to precipitate the polymer, which was collected in a Büchner funnel and washed with MeOH. Then, the obtained black solid polymer was reduced, washing it several times with a  $\text{NH}_4\text{OH}$  (1 M) solution. Finally, the crude product was purified with Soxhlet extraction, using a methanol/hexane (80:20) mixture. A brown–red polymer (0.241 g) was obtained. Relative yield: 80.5%.

FT-IR (KBr,  $\text{cm}^{-1}$ ): 3050 (s, C–H $\beta$  of thiophene), 2895 (wide band s,  $-\text{OCH}_2$ ), 2820 (s,  $-\text{N}-\text{CH}_3$ ), 1734 (s, C=O), 1598, 1586 (s, C=C aromatic ring), 1445 (s, N=N), 1513, 1335 (s,  $-\text{NO}_2$ ), 1249 (s, C–N), 1134, 1102 (s,  $-\text{OCH}_2$ ), 755 (out-of-plane, C–H aromatic), 856 (out-of-plane, C–H aromatic).

$^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 Mz) (see Scheme 2):  $\delta = 8.22$  (2H,  $\text{H}^{14}$ ), 7.82 (4H,  $\text{H}^{12}$ ,  $\text{H}^{13}$ ), 6.70 (2H,  $\text{H}^{11}$ ), 7.18 (1H,  $\text{H}^{16}$ ), 4.24 (2H,  $\text{H}^2$ ), 3.82–3.27 (16H= $2\text{H}^9$ ,  $2\text{H}^8$ ,  $2\text{H}^7$ ,  $2\text{H}^6$ ,  $2\text{H}^5$ ,  $2\text{H}^4$ ,  $2\text{H}^3$ ,  $2\text{H}^1$ , all of  $\text{OCH}_2$ ), 3.06 (3H,  $\text{H}^{10}$ ,  $\text{CH}_3\text{-N}$ ) ppm.



**Scheme 2.** Assignment of the signals for homopolymer HP.

### 2.5. Synthesis of the Co-Polymers CP4, CP6 and CP12.

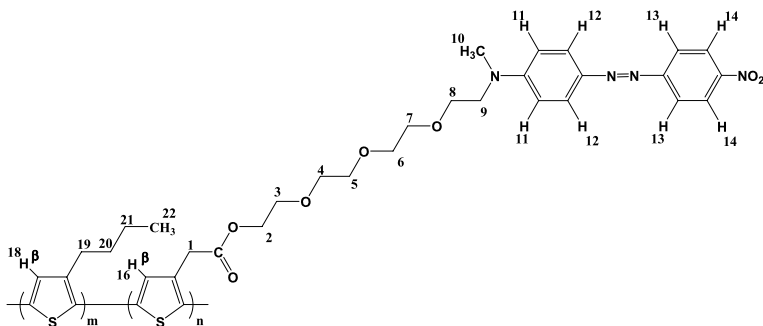
To a solution of  $\text{FeCl}_3$  (0.14 g, 0.90 mmol) in 2 ml chloroform (previously distilled and dried with  $\text{CaCl}_2$ ) under inert atmosphere, a solution containing AT (0.10 g, 0.18 mmol) in 2 ml chloroform, and another containing the correspondent 3-alkylthiophene ( $n = 4, 6$  and  $12$ ) (0.18 mmol) in 2 ml chloroform were added drop-wise. The reaction mixture was vigorously stirred for 42 h at room temperature. After this time, it was poured into 250 ml MeOH in order to precipitate the co-polymer. The obtained product was a black solid, which was collected in a Büchner funnel and washed with MeOH. Furthermore, the co-polymer was reduced, washing it several times with a  $\text{NH}_4\text{OH}$  (1 M) solution. Finally, the solid was purified by Soxhlet extraction, using methanol/hexane (80:20). After this treatment the co-polymer was obtained as a dark red solid.

#### 2.5.1. Co-Polymer CP4

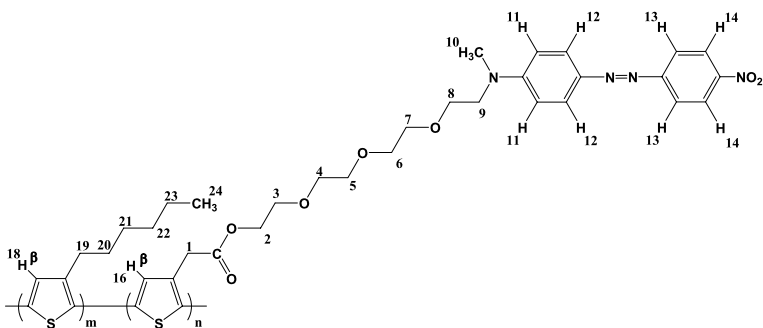
Yield: 40% (related to the co-monomers amount) FT-IR (KBr,  $\text{cm}^{-1}$ ): 3050 (s, C–H $\beta$  of thiophene), 2958, 2931, 2922 (s, –CH<sub>3</sub>–CH<sub>2</sub>, CH), 2869, 2820 (s, NCH<sub>2</sub>, OCH<sub>2</sub>), 1738 (s, C=O), 1599, 1585 (s, C=C aromatic ring), 1445 (s, N=N), 1514, 1333, (s, NO<sub>2</sub>), 1371 (b, –CH<sub>3</sub> alkyl chain), 1257 (s, C–N), 1131, 1101 (s, –OCH<sub>2</sub>), 755 (out-of-plane, C–H aromatic), 856 (out-of-plane, C–H aromatic).

<sup>1</sup>H-NMR ( $\text{CDCl}_3$ , 400 MHz) (see Scheme 3):  $\delta = 8.26$  (2H, H<sup>14</sup>), 7.85 (4H, H<sup>13</sup>, H<sup>12</sup>), 7.05 (1H,  $\beta$ -H of thiophene, coupling TT–HH), 7.03 (1H,  $\beta$ -H of thiophene, coupling HT–HH), 7.00 (1H,  $\beta$ -H of thiophene, coupling TT–HT), 6.68 (1H,  $\beta$ -H of thiophene, coupling HT–HT), 6.72 (2H, H<sup>11</sup>), 4.26 (2H, H<sup>2</sup>), 3.82–3.47 (16H; 2H<sup>9</sup>, 2H<sup>8</sup>, 2H<sup>7</sup>, 2H<sup>6</sup>, 2H<sup>5</sup>, 2H<sup>4</sup>, 2H<sup>3</sup>, 2H<sup>1</sup> all of OCH<sub>2</sub>), 3.09 (3H, H<sup>10</sup>, CH<sub>3</sub>–N), 2.81 (2H, H<sup>19</sup>, coupling HT), 2.56 (2H, H<sup>19</sup>, coupling HH), 1.70–0.94 (6H, H<sup>20</sup>, H<sup>21</sup>, H<sup>22</sup>) ppm.





**Scheme 3.** Assignment of the signals for co-polymer CP4.



**Scheme 4.** Assignment of the signals for co-polymer CP6.

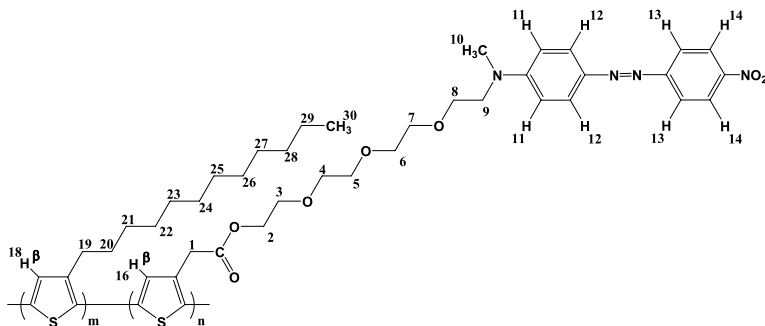
### 2.5.2. Co-Polymer CP6

Yield: 43% (related to the co-monomers amount). FT-IR (KBr,  $\text{cm}^{-1}$ ): 2936 (s,  $-\text{CH}_3$  alkyl chain), 2925, 2915 (C–H), 2870 (s,  $\text{OCH}_2$ ), 2820 (s,  $-\text{N}-\text{CH}_3$ ), 1736 (s, C=O), 1599, 1586 (s, C=C aromatic ring), 1450 (s, N=N), 1515, 1334, (s,  $-\text{NO}_2$ ), 1372 (s,  $-\text{CH}_3$  alkyl chain), 1257 (s, C–N), 1134, 1101 (s,  $-\text{OCH}_2$ ), 755 (s, C–H aromatic), 857 (s, C–H aromatic out-of-plane).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz) (see Scheme 4):  $\delta = 8.27$  (2H,  $\text{H}^{14}$ ), 7.85 (4H,  $\text{H}^{13}$ ,  $\text{H}^{12}$ ), 7.05 (1H,  $\beta$ -H of thiophene, coupling TT–HH), 7.02 (1H,  $\beta$ -H of thiophene, coupling HT–HH), 7.00 (1H,  $\beta$ -H of thiophene, coupling TT–HT), 6.98 (1H,  $\beta$ -H of thiophene, coupling HT–HT), 6.74 (2H,  $\text{H}^{11}$ ), 4.25 (2H,  $\text{H}^2$ ), 3.82–3.37 (16H=2 $\text{H}^9$ , 2 $\text{H}^8$ , 2 $\text{H}^7$ , 2 $\text{H}^6$ , 2 $\text{H}^5$ , 2 $\text{H}^4$ , 2 $\text{H}^3$ , 2 $\text{H}^1$  all of  $\text{OCH}_2$ ), 3.10 (3H,  $\text{H}^{10}$ ,  $\text{CH}_3$ –N), 2.80 (2H,  $\text{H}^{19}$ , coupling HT), 2.56 (2H,  $\text{H}^{19}$ , coupling HH), 1.70–0.91 (11H,  $\text{H}^{20}$ ,  $\text{H}^{21}$ ,  $\text{H}^{22}$ ,  $\text{H}^{23}$ ,  $\text{H}^{24}$ ).

### 2.5.3. Co-Polymer CP12

Yield 62% (related to the co-monomers amount). FT-IR (KBr,  $\text{cm}^{-1}$ ): 2950, 2917 (s,  $-\text{CH}_3\text{CH}_2$  alkyl chain), 2849 (s,  $\text{OCH}_2$ ), 2820 (s,  $-\text{N}-\text{CH}_3$ ), 1738 (s, C=O), 1598, 1585 (s, C=C aromatic ring), 1452 (s, N=N), 1514, 1334 (s,  $-\text{NO}_2$ ), 1372 (s,  $-\text{CH}_3$ ), 1253 (s, C–N), 1134, 1102 (s,  $-\text{OCH}_2$ ), 857, 755 (out-of-plane, C–H aromatic).



**Scheme 5.** Assignment of the signals for co-polymer CP12.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz) (see Scheme 5):  $\delta = 8.27$  (2H,  $\text{H}^{14}$ ), 7.85 (4H,  $\text{H}^{13}$ ,  $\text{H}^{12}$ ), 7.48 (1H,  $\beta\text{-H}$  of thiophene, coupling TT–HH), 7.02 (1H,  $\beta\text{-H}$  of thiophene, coupling HT–HH), 7.00 (1H,  $\beta\text{-H}$  of thiophene, coupling TT–HT), 6.97 (1H,  $\beta\text{-H}$  of thiophene, coupling HT–HT), 6.74 (2H,  $\text{H}^{11}$ ), 4.25 (2H,  $\text{H}^2$ ), 3.82–3.39 (16H=2 $\text{H}^9$ , 2 $\text{H}^8$ , 2 $\text{H}^7$ , 2 $\text{H}^6$ , 2 $\text{H}^5$ , 2 $\text{H}^4$ , 2 $\text{H}^3$ , 2 $\text{H}^1$  all of  $\text{OCH}_2$ ), 3.09 (3H,  $\text{H}^{10}$ ,  $\text{CH}_3\text{-N}$ ), 2.80 (2H,  $\text{H}^{19}$ ,  $\alpha\text{-CH}_2$ , coupling HT), 2.56 (2H,  $\text{H}^{19}$ , coupling HH), 1.70–0.85 (23H,  $\text{H}^{20}$ ,  $\text{H}^{21}$ ,  $\text{H}^{22}$ ,  $\text{H}^{23}$ ,  $\text{H}^{24}$ ,  $\text{H}^{25}$ ,  $\text{H}^{26}$ ,  $\text{H}^{27}$ ,  $\text{H}^{28}$ ,  $\text{H}^{29}$ ,  $\text{H}^{30}$ ) ppm.

## 2.6. Preparation of Langmuir Films

Langmuir films were prepared with HP and CP4, using a KSV 5000 system 3 Instrument. Data were collected using a Teflon trough with symmetrical compression and the temperature was controlled to  $\pm 0.1^\circ\text{C}$ ; all the isotherms presented here were recorded at  $22^\circ\text{C}$ . Ultrapure water used in these experiments as subphase was purified by a Milli-DIPAK/Milli-Q185 Ultra Purification system from Millipore, and the surface pressure was measured by a platinum Wilhelmy plate. Polymer solutions with a concentration about 1 mg/ml were prepared with pure chloroform. Normally 100  $\mu\text{l}$  of these solutions were spread on the water surface using a microsyringe and the formed films were left to equilibrate for 15 min prior to measurements. The monolayers were compressed using a typical barrier speed of 5 mm/min.

## 2.7. Brewster Angle Microscopy

Brewster angle microscopy is a useful technique for the observation of monolayers at the air–water interface. When a linearly polarized light beam, parallel to the plane of incidence, falls on an air–water interface at an angle of  $53.15^\circ$  (Brewster angle)  $\text{arc tan}(n_{\text{water}}/n_{\text{air}})$ , almost no light is reflected. However, if some kind of thin film is floating on the water, light will be reflected because the Brewster conditions are not fulfilled any more. Therefore, in the pictures the water surface appears dark, whereas the film looks white. In Brewster microscopy, the intensity of the reflected light is proportional to the thickness ( $d$ ) and refractive index ( $n$ ) of the film. Thus, it is possible to visualize the film and perform measurements of its thickness.

Brewster angle microscopy (BAM) pictures have been recorded on a miniBAM plus instrument (Nanofilm Technology).

### 3. Results and Discussion

#### 3.1. Synthesis of the Monomer and Polymers

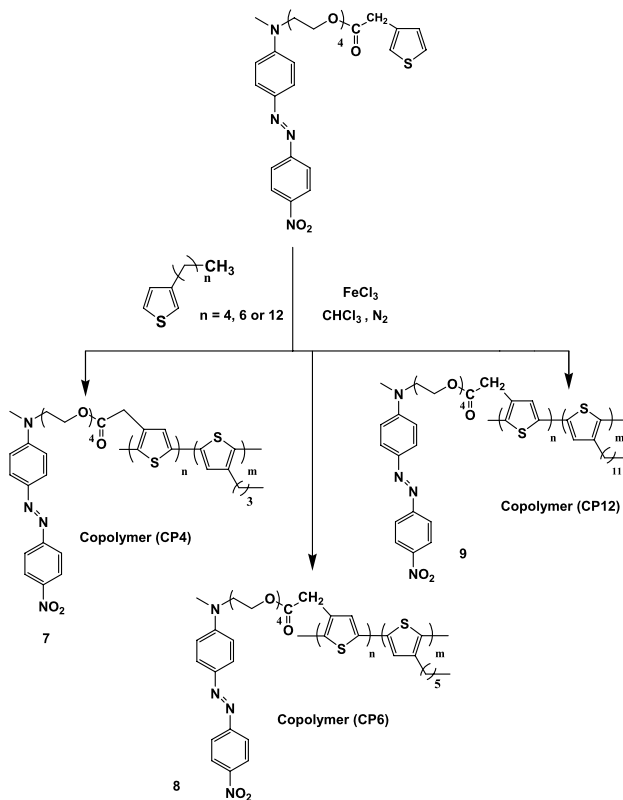
The synthesis of the monomer AT is illustrated in Fig. 1. First tetra(ethylene glycol) was treated in the presence of *p*-toluensulfonylchloride and pyridine in order to obtain the tosylate **1**. This compound was reacted with NaI in acetone to give the corresponding alkyl iodide **2**, which is highly unstable and was used in the next step without further purification. Afterwards, N-methylaniline was alkylated in the presence of compound **2**, using  $K_2CO_3$  as base and DMF as solvent, to yield the corresponding amino alcohol **3**. This intermediate was coupled in the presence of 4-nitrobenzediazonium tetrafluoroborate to give the desired azo-dye RED-PEG-4 (**4**). At last, **4** was esterified with 3-thiophenacetic acid, in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP), using chloroform as solvent under inert atmosphere to produce the desired monomer AT (**5**); this compound was obtained as a red solid.

Monomer AT was polymerized to obtain the corresponding homo-polymer HP (**6**) and further co-polymerized with 3-butyl thiophene, 3-hexyl thiophene and 3-dodecyl thiophene to give the corresponding co-polymers CP4 (**7**), CP6 (**8**) and CP12 (**9**), respectively. The synthesis of HP and the co-polymers (Fig. 2) was carried out using  $FeCl_3$  as oxidising agent and anhydrous chloroform as solvent under inert atmosphere.

#### 3.2. Characterization of Monomer AT

The  $^1H$ -NMR spectrum of monomer AT (Fig. 3) show a series of signals at 8.28, 7.89, 6.80 and 6.76 ppm, due to the aromatic protons of the azobenzene unit ( $H^{14}$ ,  $H^{12}$ ,  $H^{13}$  and  $H^{11}$ ), as well as three signals at 7.26, 7.15 and 7.03 ppm, corresponding to the protons of the thiophene ring,  $H^{15}(\alpha)$ ,  $H^{17}(\alpha')$  and  $H^{16}(\beta)$ . In addition, a series of signals appear at 4.25 ppm and 3.73–3.60, due to the protons of the methylenes present in the tetra(ethylene glycol) spacer. Finally, a singlet at 3.12 ppm, attributed to the protons of the  $CH_3-N$  group, was also observed.

In the  $^{13}C$ -NMR spectrum of monomer AT (Fig. 3), we can observe a peak at 171.19 ppm, due to the carbon of the carbonyl group, followed by eight signals at 156.91, 152.69, 147.45, 143.91, 126.24, 124.80, 122.73 and 111.64 ppm, corresponding to the aromatic carbons of the azobenzene unit. As well, four more signals at 133.61, 131.67, 128.64 and 123.49 ppm, due to the thiophene ring carbons can be also observed. Concerning the carbons of the tetra(ethylene glycol) chain, these appear between 70.95–52.33 ppm, followed by a signal at 39.50 ppm, related to the methyl group ( $NCH_3$ ). Finally, a signal at 35.86 ppm, due to the methylene group situated between the thiophene ring and the carbonyl group, was also seen.



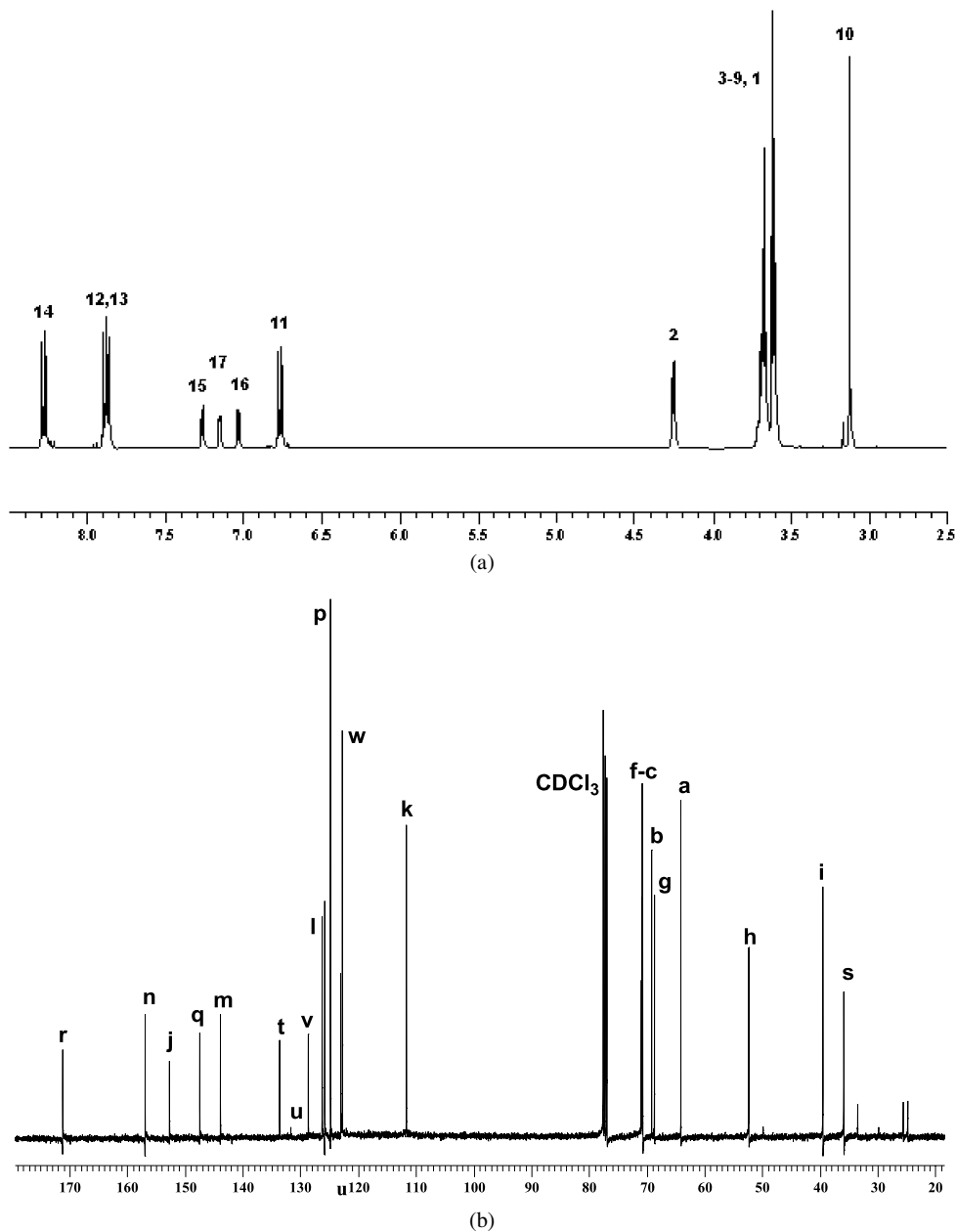
**Figure 2.** Synthesis of the co-polymers CP4, CP6 and CP12.

### 3.3. Synthesis and Characterization of the Polymers

The synthesis of the homo-polymer HP was carried out under inert atmosphere, using  $\text{FeCl}_3$  as catalyst and anhydrous chloroform as solvent, to give HP as a brown reddish powder with 80% yield. Solubility tests showed that HP is totally soluble in  $\text{CHCl}_3$ , and partially soluble in DMF, DMSO,  $\text{CH}_2\text{Cl}_2$  and THF. The structure of HP was confirmed by  $^1\text{H-NMR}$  spectroscopy in  $\text{CDCl}_3$  solution.

The  $^1\text{H-NMR}$  spectrum of HP (Fig. 4) shows a series of broad signals at 8.22, 7.82 and 6.70 ppm, due to the aromatic protons of the azobenzene unit  $\text{H}^{14}$ ,  $\text{H}^{12}$ ,  $\text{H}^{13}$  and  $\text{H}^{11}$ , followed by a discrete peak at 7.18 ppm, which corresponds to proton  $\text{H}^{16}(\beta)$  of the thiophene ring. On the other hand, a series of signals, corresponding to the protons present in the tetra(ethylene glycol) spacer appear at 4.25 ppm and between 3.82–3.27 ppm, followed by a singlet at 3.06 ppm, due the protons of the methyl group ( $\text{NCH}_3$ ).

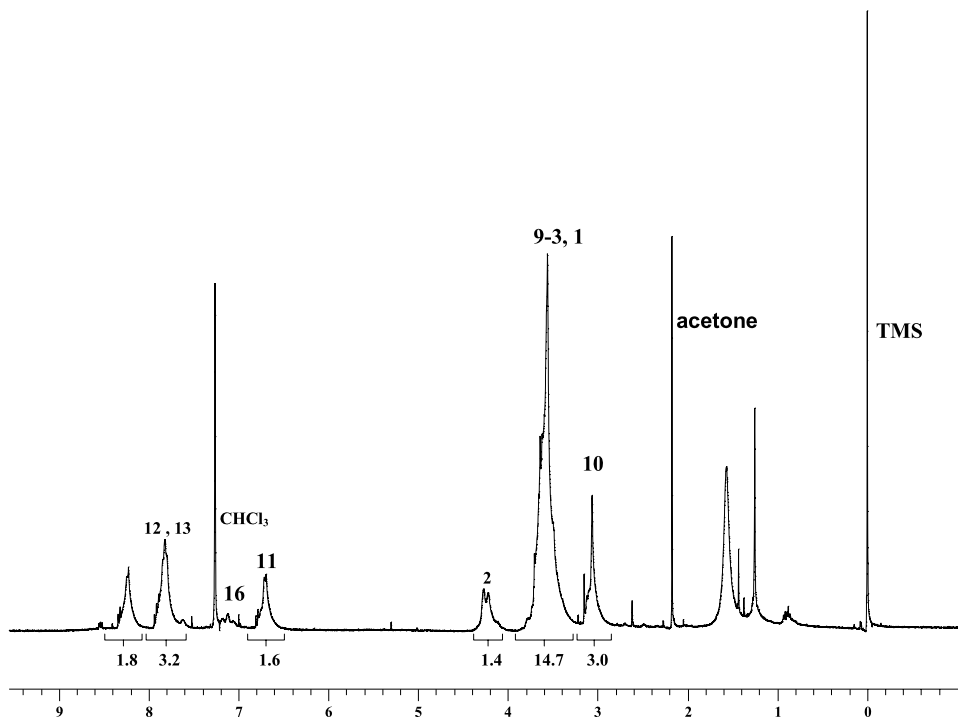
Similarly, co-polymer CP4 was prepared by oxidative polymerization, by reacting monomer AT with 3-butylthiophene in the presence of  $\text{FeCl}_3$  in  $\text{CHCl}_3$  under inert atmosphere. CP4 was obtained as a dark red solid with 40% yield with respect to the amount of co-monomers. CP4 showed to be more soluble than HP in common



**Figure 3.** (a)  $^1\text{H-NMR}$  spectrum and (b)  $^{13}\text{C-NMR}$  spectrum of the monomer AT.

organic solvents such as in DMF, DMSO,  $\text{CH}_2\text{Cl}_2$ , THF and  $\text{CHCl}_3$ . The structure of CP4 was confirmed by  $^1\text{H-NMR}$  spectroscopy in  $\text{CDCl}_3$  solution.

The  $^1\text{H-NMR}$  spectrum of CP4 (Fig. 5) shows a series of signals at 8.26, 7.85 and 6.72 ppm corresponding to the aromatic protons of the azobenzene,  $\text{H}^{14}$ ,  $\text{H}^{12}$ ,

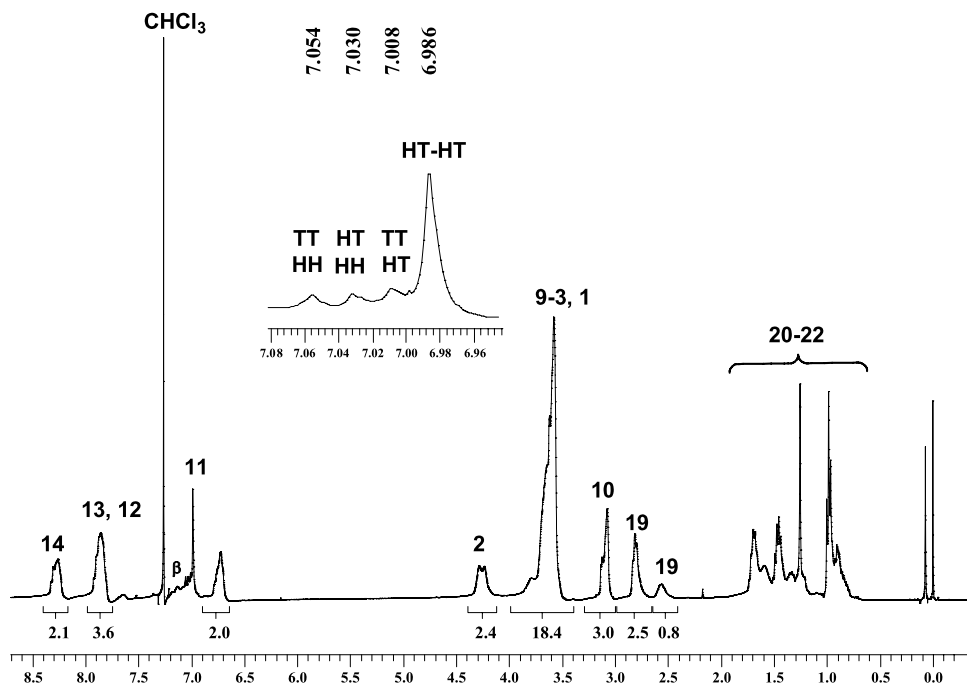


**Figure 4.**  $^1\text{H-NMR}$  spectrum of the homo-polymer HP in  $\text{CDCl}_3$  solution.

$\text{H}^{13}$  and  $\text{H}^{11}$ , followed by four signals at 7.05, 7.03, 7.00 and 6.98 ppm, due to protons  $\text{H}^{16}(\beta)$  and  $\text{H}^{18}(\beta)$  at position 4 of the thiophene ring. These signals can be attributed to the different possible couplings in the polythiophene backbone (HT–HT, TT–HT, HT–HH and TT–HH), respectively [36, 37]. On the other hand, the signals of the protons of the methylenes present in the tetra(ethylene glycol) chain were observed at 4.26 ppm and 3.82–3.47 ppm. Moreover, a singlet, attributable to the protons of the methyl group ( $\text{NCH}_3$ ) was perceived at 3.09 ppm, as well as two more signals at 2.81 (HT coupling) and 2.56 ppm (HH coupling), due to proton  $\text{H}^{19}$  of the aliphatic chain of 3-butylthiophene [38]. Based on their intensity ratio, it was determined that CP4 possesses a regioregularity of HT coupling about 75%, with respect to 3-butylthiophene content. Finally, between 1.70–0.94 ppm the signals of protons  $\text{H}^{20}$ ,  $\text{H}^{21}$  and  $\text{H}^{22}$ , present in the aliphatic chain of the 3-butylthiophene units, were also observed.

CP6 was prepared by reacting monomer AT with 3-hexylthiophene under the same reaction conditions mentioned above. This co-polymer was obtained with 53% yield, with respect to the amount of co-monomers, and showed to be more soluble than HP in common organic solvents. The  $^1\text{H-NMR}$  spectrum of CP6 in  $\text{CDCl}_3$  solution is shown in Fig. 6.

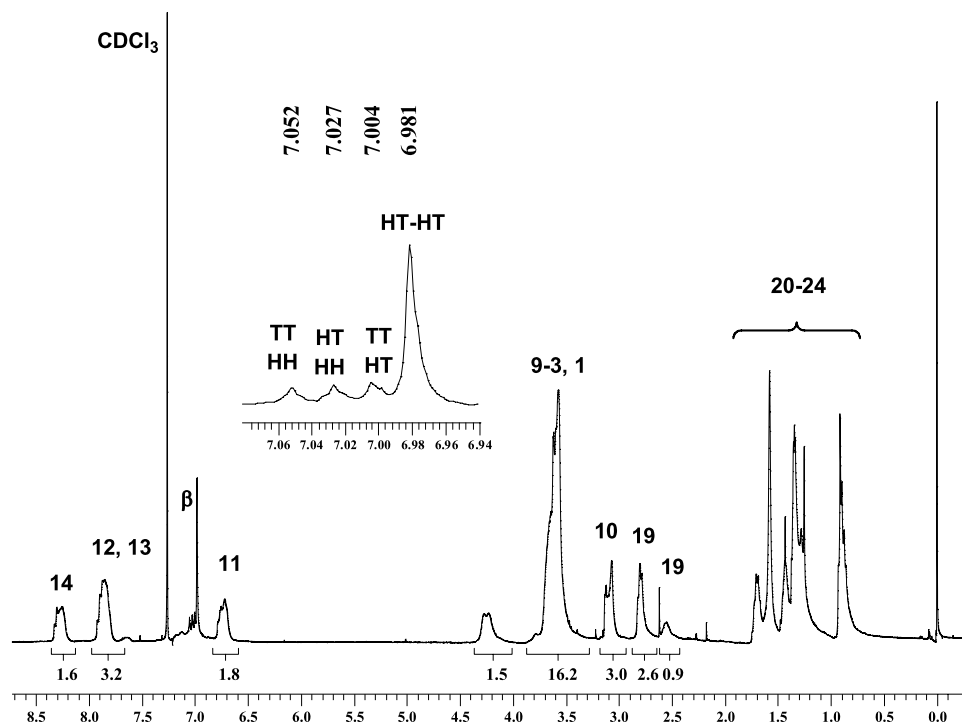
As we can notice, in the aromatic region there are three signals at 8.27, 7.85 and 6.74 ppm, due the protons of the azobenzene unit,  $\text{H}^{14}$ ,  $\text{H}^{12}$ ,  $\text{H}^{13}$  and  $\text{H}^{11}$ . In



**Figure 5.**  $^1\text{H}$ -NMR spectrum of co-polymer CP4 in  $\text{CDCl}_3$  solution.

addition, four more peaks, related to protons  $\text{H}^{16}(\beta)$  and  $\text{H}^{18}(\beta)$  were observed at 7.05, 7.02, 7.00 and 6.98 ppm, resulting from the different possible couplings HT–HT, TT–HT, HT–HH and TT–HH [36, 37], respectively. On the other hand, in the aliphatic region, two signals at 4.25 and between 3.82–3.37 ppm, due to the protons of the tetra(ethylene glycol), were also observed, as well as a singlet at 3.10 ppm, corresponding to the protons of the  $\text{NCH}_3$  group. Moreover, two more signals at 2.80 (HT coupling) and 2.56 ppm (HH coupling), due to protons  $\text{H}^{19}$  of the aliphatic chain of the 3-hexylthiophene were also seen [33]. Based on these signals, it was determined that CP6 exhibits 74% of HT coupling with respect to 3-hexylthiophene. Finally, the signals of the protons  $\text{H}^{20}$ ,  $\text{H}^{21}$ ,  $\text{H}^{22}$ ,  $\text{H}^{23}$  and  $\text{H}^{24}$  present in the aliphatic chain of the 3-hexylthiophene units appear between 1.70 and 0.91 ppm.

The synthesis of co-polymer CP12 was carried out under similar conditions as in the previous cases. This co-polymer was obtained as a dark red solid with 53% yield (related to the added co-monomers) and showed to be more soluble than HP in common organic solvents. The  $^1\text{H}$ -NMR spectrum of CP12 (Fig. 7) shows three signals in the aromatic zone at 8.27, 7.85 and 6.74 ppm, due to protons  $\text{H}^{14}$ ,  $\text{H}^{12}$ ,  $\text{H}^{13}$  and  $\text{H}^{11}$ , present in the azobenzene unit. Four more signals corresponding to protons  $\text{H}^{16}(\beta)$  and  $\text{H}^{18}(\beta)$  of the thiophene ring were observed at 7.05, 7.02, 7.00 and 6.97 ppm, which correspond to all possible HT–HT, TT–HT, HT–HH and TT–HH couplings, respectively [36, 37]. Moreover, the protons of the tetra(ethylene



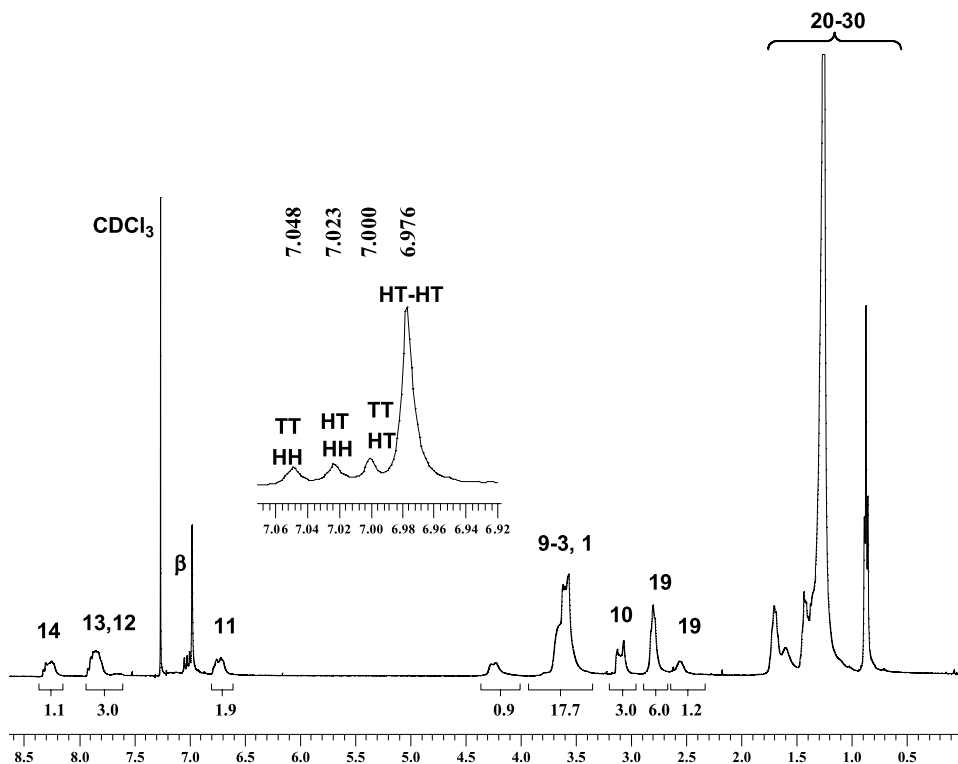
**Figure 6.**  $^1\text{H-NMR}$  spectrum of co-polymer CP6 in  $\text{CDCl}_3$  solution.

glycol) chain appear at 4.25 ppm and between 3.82–3.39 ppm, followed by a signal at 3.09 ppm, due to protons of the  $\text{NCH}_3$ . On the other hand, two more signals corresponding to proton  $\text{H}^{19}$  of the aliphatic chain of the 3-dodecylthiophene were observed at 2.80 (HT coupling) and 2.56 ppm (HH coupling) [38]. Taking into account the intensity ratio of these signals, it was determined that CP12 has 83% of HT coupling with respect to 3-dodecylthiophene. Finally, a broad signal between 1.70–0.85 ppm corresponding to protons  $\text{H}^{20}$ ,  $\text{H}^{21}$ ,  $\text{H}^{22}$ ,  $\text{H}^{23}$ ,  $\text{H}^{24}$ ,  $\text{H}^{25}$ ,  $\text{H}^{26}$ ,  $\text{H}^{27}$ ,  $\text{H}^{28}$ ,  $\text{H}^{29}$  and  $\text{H}^{30}$  present in the aliphatic chain of the dodecylthiophene units was also seen.

Molecular weights of the polymers were determined by gel-permeation chromatography (GPC), using two Waters columns,  $\text{CHCl}_3$  (HPLC grade) as eluent and polystyrene as standard reference; the obtained results are listed in Table 1.

As we can see, homo-polymer HP exhibited a molecular weight of  $M_w = 16\,500$  g/mol, whereas its co-polymers CP4, CP6 and CP12 showed higher molecular weights in the range between 26 700 and 46 990. It was observed that in the co-polymers the  $M_w$  values as well as the percentage of HT coupling increase within the aliphatic chain length of the co-monomer. This phenomenon occurs because during the polymerization co-monomers bearing short aliphatic chains generate less soluble co-polymers, which precipitate from the reaction mix-





**Figure 7.**  $^1\text{H-NMR}$  spectrum of co-polymer CP12 in  $\text{CDCl}_3$  solution.

**Table 1.**

Molecular weights of the polymers

Polymer	Yield (%) <sup>a</sup>	$M_w$ (g/mol)	$M_n$ (g/mol)	PDI ( $M_w/M_n$ )	Regioregularity (HT, %) <sup>b</sup>
HP	80.5	16 500	3200	5.2	—
CP4	40	33 400	4700	7.1	75
CP6	53.2	26 700	4200	6.4	74
CP12	61.6	46 900	5600	8.4	83

<sup>a</sup> Yield related to added monomer and co-monomers.

<sup>b</sup> Regularity related to amount of plastificant co-monomer added.

ture, thereby stopping the polymerization after having reached a certain size. Another interesting fact is that all the polymers possess high polydispersity values (between 5.2 and 8.4) because of the polymerization mechanism. Such pathway involves the formation of cation-radicals, which first form oligomers (dimers, trimers or tetramers), which couple with each other to give longer polymer chains.

### 3.4. Thermal Properties of the Polymers

The thermal properties of the obtained polymers were determined by thermogravimetric analysis (TGA) from 0 to 600°C and by differential scanning calorimetry (DSC) from 0 to 250°C, with a heating rate of 20°C/min. The obtained results are summarized in Table 2.

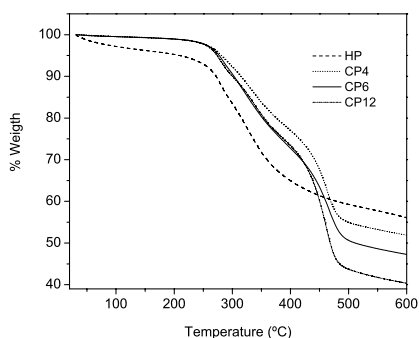
As we can see, all the polymers exhibited a good thermal stability with high  $T_5$  and  $T_{10}$  values. It is worth to point out that the homo-polymer HP showed lower thermal stability than co-polymers CP4, CP6 and CP12, due to the absence of 3-alkylthiophene units, which confer higher thermal stability to the polymer. The presence of plastificant thiophene moieties in the co-polymers tends to restrain the free rotation along the polymer backbone axis, compared to the homo-polymer. On the other hand, the azo-group N=N is very susceptible towards degradation at high temperatures; therefore, polymers bearing high azobenzene content start to degrade at lower temperatures.

Figure 8 shows the TGA curves of the different obtained polymers. As we can notice, these materials exhibited fast degradation in the range between 250 and 500°C. HP showed a good thermal stability with a  $T_5 = 208^\circ\text{C}$ , whereas the co-polymers showed higher  $T_5$  values, from 274 to 281°C. Moreover, it was found that the thermal stability of the co-polymers decreases as the alkyl chain length of the plastificant co-monomers augments.

**Table 2.**  
Thermal properties of the polymers

Polymer	$T_5$ (°C)	$T_{10}$ (°C)	$T_g$ (°C)	$T_s$ (°C)
HP	208	272	134	56
CP4	281	315	135	53
CP6	277	303	138	47
CP12	274	300	138	56

<sup>a</sup> Heating rate 10°C/min.



**Figure 8.** Thermogravimetric analysis of the polymers.

According to DSC, it was found that all polymers show a softening point ( $T_s$ ) between 47 and 56°C, resulting from the presence of the tetra(ethylene glycol) segments, which have a low melting point and allow the formation of discrete crystalline phases in the polymers. Finally,  $T_g$  values of polymers and co-polymers are very similar, with  $T_g$  values ranging between 134 and 138°C, since all polymers have a fairly rigid polythiophene backbone.

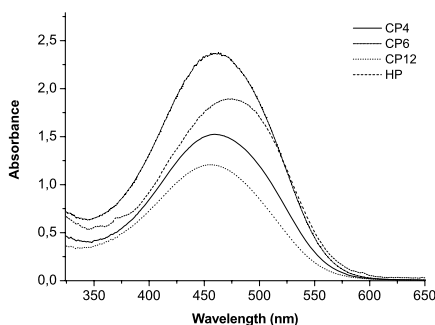
### 3.5. Optical Properties of the Polymers

The optical properties of polymers were studied by absorption spectroscopy in  $\text{CHCl}_3$  solution at room temperature. The results are summarized in Table 3 and the UV-Vis spectra are shown in Fig. 9.

All polymers exhibited maximum absorption bands around  $\lambda_{\text{max}} = 456\text{--}475$  nm. Since these polymers contain amino–nitro-substituted azobenzenes, which belong to the pseudostilbenes category, in their UV-Vis spectra the  $\pi\text{--}\pi^*$  and  $n\text{--}\pi^*$  bands are totally overlapped. Therefore, only one band can be observed in the visible region of the absorption spectrum [39]. In principle, a polythiophene should exhibit an absorption band around  $\lambda_{\text{max}} = 440$  nm, depending on its conjugation degree; however, azobenzene groups present in these polymers also absorb near this wavelength. Nevertheless, the UV-Vis spectrum of HP ( $\lambda_{\text{max}} = 475$  nm) exhibited a bathochromic shift with respect to CP4, CP6 and CP12 ( $\lambda_{\text{max}} = 456\text{--}461$  nm). These results indicate that HP has a higher degree of conjugation than its cor-

**Table 3.**  
Optical properties of the polymers (UV-Vis spectroscopy results)

Polymer	$\lambda_{\text{max}}$ (nm)	Cut-off (nm)
HP	475	700
CP4	461	640
CP6	463	640
CP12	456	640



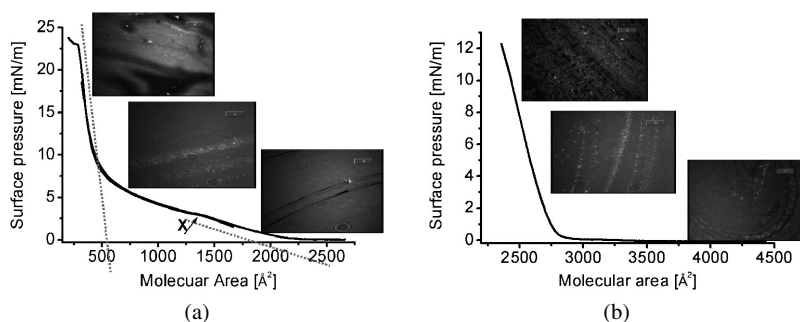
**Figure 9.** UV-Vis spectra of the polymers in  $\text{CDCl}_3$  solution.

responding co-polymers, which suggest that in HP the polythiophene backbone adopts a nearly planar conformation, where azobenzene chromophores are oriented perpendicularly to it. On the other hand, these co-polymers exhibited a red-shifted absorption band ( $\lambda_{\max} = 456\text{--}475\text{ nm}$ ), due to the high dipole moment of the azobenzene units, which confer them a high charge transfer character [40–42]. The absorption spectra of these polymers in the cast film (not shown) exhibited an additional blue shifted band at about  $\lambda = 420\text{ nm}$ , which indicate the formation of H-aggregates in these polymers, resulting from the coupling of neighbour azobenzene chromophores [40–42].

### 3.6. Preparation of Langmuir Films

Langmuir films were prepared with amphiphilic polymers HP and CP4. The formation of these films was monitored by plotting their surface pressure vs. molecular area ( $\pi/A$ ) isotherms and by Brewster angle microscopy (BAM). The  $\pi/A$  isotherm obtained with the HP is illustrated in Fig. 10a. The surface pressure rises from  $A \approx 2700\text{ \AA}^2$ , where two tangents to the isotherm have been drawn. The first one gives a molecular area of  $2250\text{ \AA}^2$  when extrapolated to  $\pi = 0$ , which is in agreement with our expectations if we suppose that point X indicates the collapse on the film. To our surprise, beyond point X BAM images showed no evidence of a collapse, instead the presence of a homogenous film was observed. However, a film collapse was seen when the surface pressure exceeded  $22\text{ mN/m}$ ; this value apparently corresponds to a molecular area of  $A_0 = 500\text{ \AA}^2$ . On the other hand, we have noticed that the isotherms are perfectly reversible as long as the surface pressure is maintained below  $18\text{ mN/m}$ . BAM experiments jointly with  $\pi/A$  isotherms showed that HP collapse occurs at  $\pi = 22\text{ mN/m}$ . It is well known that most of Langmuir films loose their reversibility, when they are compressed beyond the collapse pressure.

The  $\pi/A$  isotherm obtained for the fairly amphiphilic co-polymer CP4 is shown in Fig. 10b. The surface pressure rises from  $4500\text{ \AA}^2$ , giving a final molecular area



**Figure 10.** (a) Pressure–area isotherm for HP and Brewster angle microscopy images at  $A = 1700\text{ \AA}^2$  ( $\pi = 2.5 \pm 0.1\text{ mN/m}$ ),  $A = 700\text{ \AA}^2$  ( $\pi = 7.5 \pm 0.1\text{ mN/m}$ ) and  $500\text{ \AA}^2$  ( $\pi = 17.5 \pm 0.1\text{ mN/m}$ ). (b) Pressure–area isotherm for CP4 and Brewster angle microscopy images at  $A = 3750\text{ \AA}^2$  ( $\pi = 0 \pm 0.1\text{ mN/m}$ ),  $2750\text{ \AA}^2$  ( $\pi = 4 \pm 0.1\text{ mN/m}$ ) and  $2500\text{ \AA}^2$  ( $\pi = 10 \pm 0.1\text{ mN/m}$ ).

extrapolated to zero surface pressure at  $A_0 = 2750 \text{ \AA}^2$ . These films show excellent reversibility in successive compression–expansion cycles as long as the  $\pi$  is kept below the collapse pressure  $\pi_c = 12 \text{ mN/m}$ . BAM images along the compression process reveal the good quality of the films. As we can see, the Langmuir film of CP4 (Fig. 10b) is not continuous at large molecular areas and show defects (holes), through which water can be seen. The domains smoothly weld together when the molecular area goes below  $A \approx 4000 \text{ \AA}^2$ , and only defectless surfaces can be observed before the collapse. This clearly indicates the formation of an almost homogeneous monomolecular layer, when the molecular area reaches  $A = 2700 \text{ \AA}^2$  at  $\pi = 4 \text{ mN/m}$ . Here, a slope change takes place in the surface pressure curve, which shows a fairly good compressibility of the film. BAM images confirmed that the CP4 film collapses at a surface pressure of  $\pi_c = 12 \text{ mN/m}$ . Since HP is more amphiphilic than CP4, this polymer forms stable and homogeneous Langmuir films on the air–water interface, whereas CP4 forms fairly stable Langmuir films with some defects. We are currently working on the preparation of Langmuir–Blodgett films with these polymers for the future elaboration of NLO devices.

#### 4. Conclusions

A new series of polythiophenes containing amino–nitro-substituted azobenzene units and tetra(ethylene glycol) flexible spacers were synthesized and characterized. Monomer AT showed higher reactivity in the homo-polymerization than in co-polymerization reactions, which is evident when the polymerization yields are compared (HP 85.5%, CP4 40%, CP6 53% and CP12 62%). HP exhibited lower thermal stability than co-polymers CP4, CP6 and CP12, due to the presence of the 3-alkylthiophene units, which confer higher thermal stability to the co-polymers. Because of the amino-nitro substituted azobenzene units, absorption spectra of the polymers showed  $\lambda_{\text{max}}$  bands between 456 and 475 nm, which overlap with the polythiophene absorption band that should appear at *ca.*  $\lambda_{\text{max}} = 440 \text{ nm}$ . HP possesses a higher conjugation degree than the corresponding co-polymers CP4, CP6 and CP12. Finally, HP and CP4 are suitable amphiphilic derivatives for the preparation of stable Langmuir films and good prospects for the future elaboration of Langmuir–Blodgett films.

#### Acknowledgements

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