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## Electronic and Structural Properties of Polymers Based in Phenylene vinylene and Thiophene Units. Control of Gap by the Gradual Increases of Thiophene Moieties.

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### Abstract

Several poly(thiophene) derivatives containing *p*-phenylenevinylene (PV) as electron-donor were synthesized using FeCl<sub>3</sub>. PV units are regularly spaced in two, four and eight thiophenyl units across the main chain. PV units and gradual increase of thiophene units effect on polymers properties, as compared to those of poly(3-hexylthiophene), (P3HT), is reported. Polymers, labeled as poly(FV1Th), poly(FVBiTh) and poly(FVTeTh) were characterized by FT-IR and UV-Vis spectrometry, elemental analysis, thermal stability (TGA), differential scanning calorimetry (DSC) and cyclic voltammetry (CV). Conjugation increases with increasing thiophene rings in the main chain and the conjugation is higher in polymers, they exhibited different optical absorption, effective conjugation, similar intrinsic viscosity, and high thermal stability with weight loss less than 10% at decomposition temperature higher than 300 °C (except poly(FVTeTh). DSC showed melting points over 200 °C and formation of crystalline zones was found in all the cases. Thiophene rings increase in the main chain evidences a more ordered crystalline molecular structure. Moreover, the polymers presented redox processes at a potential lower than that of P3HT. Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO) and optical band gap ( $E_g$ ) were measured and the obtained values compared with those of P3HT. The effect caused by PV units and the increase of thiophenyl units in the chains on HOMO, LUMO, band gap, fusion, crystallinity and TGA is reported. Monomers  $E_g$  is greater than P3HT  $E_g$ . The results proved that, with respect to P3HT, polymers HOMO and LUMO are lower and in some cases by a slight change in  $E_g$ . PV effect as electron donor causes a decrease in HOMO and LUMO, envisaging them as potential polymers to be studied in organic photocells.

### 1.0 Introduction

Poly(*p*-phenylenevinylene) (PPV), is a conducting polymer that has been processed into a highly ordered crystalline thin film. PPV is a diamagnetic material and has a very low intrinsic electrical conductivity, of the order of  $10^{-13}$  S cm<sup>-1</sup>. The electrical conductivity increases by doping with ferric chloride<sup>1,2</sup>. However, the stability of these doped materials is relatively poor<sup>3</sup>. In general, unaligned, unsubstituted PPV presents only moderate conductivity with doping ranging from  $<10^{-3}$  S cm<sup>-1</sup> (H<sub>2</sub>SO<sub>4</sub>-doped) to 200 S cm<sup>-1</sup> (I<sub>2</sub>

doped)<sup>4</sup>. Alkoxy-substituted PPVs are generally easier to oxidize than the parent PPV and hence display much higher conductivity<sup>4</sup>.

Due to its stability, processability and electrical and optical properties, PPV has been considered for a wide variety of applications. Although solid-state lasing has yet to be demonstrated in an organic LED, poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV) has been proven to be a promising laser dye due to its high fluorescence efficiency in solution<sup>5,6</sup>, besides, MEH-PPV doped with graphene oxide has been studied by its efficient charge transfer and photostability to be studied in organic solar cells<sup>7</sup>. Polymers derived from PPV studied in solar cells, with an external quantum efficiency higher than 30% and large energy conversion efficiency, have been reported<sup>8-11</sup>. PPV has also received considerable attention in applications such as light emitting diodes; moreover, PPV was used as the emissive layer in the first LED polymer<sup>12, 13</sup>, field effect transistors<sup>14</sup>. Usually PPV derivatives with alkoxy groups are soluble in organic solvents, show high thermal stability and are synthesized using Gilch's approach wherein R,R-dihalo-*p*-xylenes are treated with potassium *tert*-butoxide in organic solvents and then they are thermally treated to yield the conjugated PPV<sup>15-17</sup>. MEH-PPV and PPV has been employed as an electron-donor material in organic solar cells<sup>11,18,19</sup>. Although PPV-based devices suffer from poor absorption and photodegradation, PPV and PPV derivatives (especially MEH-PPV and MDMO-PPV) find frequent application in research cells<sup>11,20,21</sup>, diode and transistor<sup>22</sup>.

Polymers containing phenylenevinylene (PV) bound to 3,4-ethylenedioxythiophene has been studied because of their semiconducting properties<sup>23</sup>; besides, photovoltaic properties of thiophene and diketopyrrolopyrrole containing PV have been studied<sup>24</sup>. The efficiency of those polymers was 0.72% and the authors attribute the low efficiency to a high HOMO value; in addition, various polymers containing PV and dithienylene groups have been reported with very high band gap, greater than 8.4 eV. However, using theoretical calculations, the HOMO of thiophene-containing PPV tends to strongly decrease<sup>25</sup>. Xue et al.<sup>26</sup> have reported polymers, containing alternating thienylene and PV units, with band gap close to 2.0 eV. Besides, Huo et al.<sup>27</sup>, placing thiophene in the polymeric chain, decreased the gap 0.35 eV relative to PPV by increasing the HOMO and reducing the LUMO. Considering the above background, it was assumed the possibility of modifying HOMO-LUMO and band gap by incorporating a larger number of thiophene units to PV so that the new polymers may meet the requirements to be studied in organic photocells.

The aim of this paper is the synthesis of several polymers containing PV units bond to various thiophene units. Thus, in the polymer PV units were combined with 2, 4 and 8 thiophene units. It is thus expected that the new materials display the properties of both counterparts. Synthesized polymers were characterized by spectrometry, elemental analysis, cyclic voltammetry, TGA, DSC, and viscosimetry.

Physical properties such as HOMO, LUMO and optical band gap were assessed and compared with those of P3HT. Polymers physical properties are discussed with regard to their potential applications in organic photocells.

## 2.0 Experimental

### 2.1 Measurements

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a JASCO FT-IR 4200 spectrometer. Nuclear Magnetic Resonance (NMR) spectra were recorded using tetramethylsilane as internal reference on a 400 MHz Bruker spectrometer. Elemental analyses were conducted on an EA-1108 Fisons Elemental Analyzer. UV-Vis spectra were run on a Perkin-Elmer Lambda 35UV/VIS spectrometer. The spectra of 100 mg L<sup>-1</sup> polymers and monomers solution were run in chloroform (CHCl<sub>3</sub>). TGA measurements were performed using a thermo micro balance Netzsch TG 209 F1 Iris. Samples (about 2-4 mg) were placed inside Al<sub>2</sub>O<sub>3</sub> pans and heated under flowing nitrogen (20 mL min<sup>-1</sup>) from 30 to 1000 °C at 10 °C min<sup>-1</sup>, obtaining the corresponding thermal decomposition profiles. Calorimetric behavior was studied by DSC using a Netzsch DSC 204 F1 Phoenix differential scanning calorimeter. Samples (about 2-5 mg) were placed inside aluminum pans and heated under flowing nitrogen (250 mL/min), from 20 to 350 °C, at 10 (°C min<sup>-1</sup>) heating rate. To minimize differences in the thermal history of the samples, the corresponding thermograms were obtained considering decomposition temperatures detected in TGA, according to the following temperature program: heating from 50 °C up to 250, 180 and 100 °C for poly(FVBiTh), poly(FV1Th) and poly(FVTeTh) respectively (dynamic stage), isothermal stage at the final temperature °C (static), cooling until -50 °C (dynamic, quenching step) and heating until 350 °C (dynamic). Electro-polymerization was accomplished using a standard three-electrode cell. The working electrode was a 0.2 cm<sup>2</sup> platinum disc while a Pt wire was the counter electrode. Ag/AgCl was used as reference electrode. Unless otherwise stated, all potentials quoted in the current work are referred to this reference electrode. Monomers were electropolymerized from a 0.1 mg mL<sup>-1</sup> monomer solution in anhydrous CH<sub>3</sub>CN using 0.1 M tetrabutylammonium hexafluoro phosphate (TBAPF<sub>6</sub>) as supporting electrolyte. Cyclic voltammograms were recorded at 50 mV s<sup>-1</sup> scan rate. Intrinsic viscosity measurements were conducted on a Desreux-Bischoff dilution viscosimeter at 20 °C, using CHCl<sub>3</sub> as solvent.

### 2.2 Reagents

Thiophene-2-carboxaldehyde, triphenylphosphine,  $\alpha,\alpha'$ -Dibromo-p-xylene, [2,2'-bithiophene]-5-carboxaldehyde, potassium tert-butoxide, 3,3''-dihexyl-2,2':5',2'':5'',2'''-quaterthiophene, POCl<sub>3</sub>, TBAPF<sub>6</sub> and CH<sub>3</sub>CN were purchased from Sigma-Aldrich. FeCl<sub>3</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, N,N-Dimethylformamide

(DMF), ethanol, methanol and ether were Merck. Prior to use  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , DMF, ethanol and toluene were dried;  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  were dried utilizing a  $4\text{\AA}$  molecular sieves and  $\text{MgSO}_4$  mixture for 24 h, and then distilled. DMF was dried with a  $\text{CaCl}_2$  and  $4\text{\AA}$  molecular sieves mixture followed by vacuum-distillation. Ethanol was dried according to Vogel's<sup>26</sup>. Toluene was dried with Na followed by distillation.

### 2.3 Synthesis

(1,4-phenylenebis(methylene))bis(triphenylphosphonium) bromide (phosphonium sal) synthesis

To a 100 mL round bottom flask, equipped with a reflux condenser and a  $\text{CaCl}_2$  tube, 5.90 (22.5 mmole) of triphenylphosphine, 2.04 g (7.73 mmoles) of  $\alpha,\alpha'$ -Dibromo-p-xylene and 40 mL dried DMF was added; the mixture was heated at 110-116 °C for 18.5 h, then, the hot mixture was vacuum-filtered and the white product washed with plenty of ether and finally oven-dried at 45 °C. Yield 5.37 g (88 %). mp > 280°C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 7.60 m(30 H phenyl aromatic), 6.91 s (4H, aromatic), 5.40 s(2H aliphatic), 5.34 s(2H aliphatic).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ): 23.84 ppm. FT-IR (KBr):  $\nu\text{CH}$  at 3046  $\text{cm}^{-1}$  and 3005  $\text{cm}^{-1}$  (aromatic),  $\nu\text{CH}$  at 2876  $\text{cm}^{-1}$  and 2776  $\text{cm}^{-1}$  (aliphatic groups),  $\nu\text{C}=\text{C}$  at 1618  $\text{cm}^{-1}$ , 1584  $\text{cm}^{-1}$  (aromatic rings),  $\gamma\text{CH}$  (para-disubstitution pattern) at 837  $\text{cm}^{-1}$ .

3,3''-dihexyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5-carboxaldehyde synthesis

To a 25 mL round bottom flask, equipped with condenser and a  $\text{CaCl}_2$  tube, 0.95 g (1.9 mmole) of 3,3''-dihexyl-2,2':5',2'':5'',2'''-quaterthiophene, 10 mL of dried  $\text{CH}_2\text{Cl}_2$  was placed and then, under stirring and at room temperature (RT) 0.45 mL of a mixture of DMF/ $\text{POCl}_3$  (1+1, v/v) was added (The DMF/ $\text{POCl}_3$  mixture was prepared as follows: to a test tube immersed in an ice-salt bath, 2 mL dried DMF and 2 mL  $\text{POCl}_3$  was added. The mixture was removed from the ice-salt bath and left aside at RT until the mixture be liquefied. The reaction mixture was stirred at RT during 16 h (monitored by TLC, using  $\text{CHCl}_3$  and eluted with n-hexano- $\text{CHCl}_3$  (2+1). Subsequently, 3 mL of a 1.0 M NaOH aqueous solution was added and the mixture stirred for 10 min. Two extractions, 7 mL each, using  $\text{CH}_2\text{Cl}_2$  were then performed, dried with  $\text{MgSO}_4$ , and the  $\text{CH}_2\text{Cl}_2$  removed in a rotary evaporator. The sample was purified using a 44 cm long chromatographic column with 13 cm silica gel height (6 g of sample and 110 g silica gel were weighed). The sample was seeded with  $\text{CHCl}_3$  and eluted with n-hexane to remove the starting reagent. Next, a n-hexane- $\text{CHCl}_3$  (4+1, v/v) mixture was employed to elute the monoaldehyde, followed by n-hexano- $\text{CHCl}_3$  (2+1 v/v) and finally  $\text{CHCl}_3$ . 0.07 g of monoaldehyde was obtained (Yield 30%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 9.83 s(1H, -CHO), 7.59 s (1H aromatic), 7.26-7.15 m(4H, aromatic), 7.03 d(1H aromatic), 6.94 d (1H aromatic), 2.81 dd(4H, Th- $\text{CH}_2$ -), 1.66 dd(4H, - $\text{CH}_2$ -), 1.33 m(broad, 12H, - $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -), 0.88

m(broad, 6H, -CH<sub>3</sub>). FT-IR (KBr, cm<sup>-1</sup>): νCH at 2949, 2927 and 2853 (aliphatic groups), νC=O at 1650 (carbonyl group), νC=C at 1433, (aromatic rings). Elemental analysis found C 64.0, H = 7.2, S 25.1%, found mol:mol ratio C/S = 6.81 = 29/4.2; C/H = 0.83 = 29/35.

## 2.4 Monomers synthesis

1,4-bis(2-(thiophen-2-yl)vinyl)benzene, labeled as FV1Th

A 250 mL round bottom flask, equipped with a reflux condenser and a CaCl<sub>2</sub> tube, was charged with 3.6 g (4.57 mmol) of (1,4-phenylenebis(methylene))bis(triphenylphosphonium) bromide, 70 mL of dried CHCl<sub>3</sub> and, under stirring at RT, 1.02 g (9.09 mmol) of thiophene-2-carboxaldehyde dissolved in 10 ml of dry CHCl<sub>3</sub>. To this mixture a lithium ethoxide solution, prepared by dissolving 0.32 g of Li in 25 mL of dried ethanol, is slowly added. The mixture was stirred at RT for 4.5 h (monitored by TLC, using CHCl<sub>3</sub> and eluted twice, the first with a mix n-hexane/CHCl<sub>3</sub> (2:1, v/v) and then with CHCl<sub>3</sub>). The solvent was evaporated from the mixture to half its volume (remaining *ca.* 50 mL). After cooling down to RT, 8 mL of water containing 4 drops of 37 % HCl was added; the mixture was then filtered and the product washed with a little of CHCl<sub>3</sub> until a yellow color is attained. Finally the product was oven dried at 45 °C. 0.21 g was obtained. From the filtrate more product can be obtained by removing water using a separating funnel; the organic phase is then washed with 20 mL of 10% NaHCO<sub>3</sub> aqueous solution, dried with Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed in a rotary evaporator. To the orange solid, 10 mL of an aqueous solution containing 8 drops 37% HCl was added; the mixture was next vacuum filtered and the solid product washed with water, added CHCl<sub>3</sub>, filtered and the yellow solid washed with a little of CHCl<sub>3</sub>. Yield 0.10 g (23 %), mp 154-155 °C. The compound should be a solid whose impurities are removed by washing with aqueous acid and filtering to remove triphenyl phosphine oxide; other impurities are eliminated by washing with CHCl<sub>3</sub> and although somewhat of the product solubilizes it is quite pure. Triphenyl phosphine oxide was not detected by TLC. If the melting point of the product is greater than 159 °C, is an indicative of the presence of triphenyl phosphine oxide that is removed by the addition of aqueous acid solution and filtration. FT-IR (KBr): νCH at 3020 cm<sup>-1</sup>, νC=C at 1625 cm<sup>-1</sup> and 1518 cm<sup>-1</sup>; νC=C at 957 cm<sup>-1</sup> (vinylene group), γCH (p-disubstitution pattern benzene ring) at 828 cm<sup>-1</sup>; γCH (thiophene ring) at 694cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO, δ): 7.56 s(4H, phenylene group), 7.52 and 7.44 (d, 16 cps, 2H vinylene), 6.98 and 6.89 (d, 16 cps, 2H vinylene), 7.45 d(2H Th), 7.23 d (2H Th), 7.07 dd(2H, Th). Elemental analysis found C 75.1, H = 5.5, S 20.0%, found mol:mol ratio C/S = 1.80 = 18/1.8; C/H = 1.31 = 18/14.



(1,4-bis(2-([2,2'-bithiophen]-5-yl)vinyl)benzene), labeled as FVBiTh

A 100 mL round bottom flask, equipped with a reflux condenser and a CaCl<sub>2</sub> tube, was charged with 1.2 g of (1,4-phenylenebis(methylene))bis(triphenylphosphonium) and 50 ml dry CHCl<sub>3</sub>; the mixture was warmed and next cooled at RT; subsequently, 1.08 g of [2,2'-bithiophene]-5-carboxaldehyde dissolved in 8 mL of dry CHCl<sub>3</sub> and, slowly, 1.72 g of potassium tert-butoxide dissolved in 28 ml super-dry ethanol were added. The mixture was then stirred for 160 min (the reaction was monitored by TLC, using CHCl<sub>3</sub> and eluted with a mix n-hexane-CHCl<sub>3</sub> (1:1, v/v). The solvent was next evaporated at 65 °C down to 25 mL and the residue was chilled to RT; finally, 4 mL of HCl solution (3 drops 37% HCl in 4 mL of water) was added. The precipitate was separated by vacuum filtration and the white-orange solid was extracted with plenty of CHCl<sub>3</sub>. To the extracts 50 mL of methanol was added and the mixture left aside for one day. Subsequently, the solid was separated by vacuum filtration, washed with methanol and oven dried at 50 °C. Yield 0.27 g (39 %). mp 257 °C (decomposes). Elemental analysis found C 68.5, H 4.5 and S 29.0 %; found mol:mol ratio C/S = 6.31 = 26/4.1; C/H = 1.28 = 26/20. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, δ): 7.60 d(2H), 7.53(d, 1H), 7.43 (dd, 4H phenylene group), 7.34 (d, 1H), 7.26 (d, 1H), 7.15 (m, 3H), 7.09 (t, 2H), 7.04 (d, 1H), 6.96 (d, 1H, vinylene), 6.74 (d, 1 H vinylene), 6.58 (d, 1H vinylene). FT-IR (KBr): ν<sub>CH</sub> at 3065 cm<sup>-1</sup>, ν<sub>C=C</sub> at 1633 cm<sup>-1</sup> and 1618 cm<sup>-1</sup>; ν<sub>C=C</sub> at 943 cm<sup>-1</sup> (vinylene group), γ<sub>CH</sub> (p-disubstitution pattern benzene ring) at 808cm<sup>-1</sup>; γ<sub>CH</sub> (thiophene ring) at 689cm<sup>-1</sup>.

(1,4-bis(2-(3,3''-dihexyl-[2,2':5',2'':5'',2'''-quaterthiophen]-5-yl)vinyl)benzene), labeled as FVTeTh

To a 20 mL round bottom flask, equipped with a reflux condenser and a CaCl<sub>2</sub> tube, was added 61 mg (0.077 mmole) of [1,4-phenylenebis(methylene)]bis(triphenylphosphonium) bromide, 3 mL dried CHCl<sub>3</sub> and, under stirring at RT 0.14 g (0.27 mmole), 3,3''-Dihexyl-2,2':5',2'':5'',2'''-quaterthiophene-5-carboxaldehyde dissolved in 4 mL of dried CHCl<sub>3</sub>, was slowly added. The reaction was monitored by TLC (using CHCl<sub>3</sub> and eluted with CHCl<sub>3</sub>). The reaction mixture was stirred for 230 min and then poured into a 25 mL beaker and heated at 60 °C under stirring to reduce to half its original volume. The mixture was cooled at RT, and then 0.6 mL of HCl solution obtained by adding 1 drop of 37% HCl to 2 mL of water, was added. Subsequently, 30 mL of methanol was added to the resulting mixture that was let standing for some time previous to vacuum filtration. The product was washed with methanol and oven-dried at 50° C. The compound was purified by re-crystallization dissolving the sample in 4 mL of warm CHCl<sub>3</sub>, cooled at RT and 4 mL methanol added. The mixture was let standing, vacuum-filtered and oven-dried at 50 ° C. 30 mg of a bright red product (Yield 34 %) was obtained. mp 128° C°. <sup>1</sup>H-NMR (CDCl<sub>3</sub>),

$\delta$ ): 7.43 s(4H aromatic), 7.18-6.80 m(18H aromatic), 2.75 dd(8H aliphatic, Th-CH<sub>2</sub>-), 1.66 s (broad, 8H aliphatic -CH<sub>2</sub>-), 1.33 s (broad, 24H aliphatic -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 0.90 s (broad, 12H aliphatic, -CH<sub>3</sub>). Elemental analysis found C 68.70, H 6.86, S 22.26%, found mol:mol ratio C/S = 8.23 = 66/8.02; C/H = 0.00084 = 66/78. FT-IR (KBr):  $\nu$ CH at 3055 cm<sup>-1</sup> and 3020 cm<sup>-1</sup> (aromatic ring),  $\nu$ CH at 2955 cm<sup>-1</sup>, 2925 cm<sup>-1</sup> and 2854 cm<sup>-1</sup>,  $\nu$ C=C at 1615 cm<sup>-1</sup> and 1458 cm<sup>-1</sup>,  $\nu$ C=C at 946 cm<sup>-1</sup> (vinylene group),  $\gamma$ CH (p-disubstitution pattern benzene ring) at 837 cm<sup>-1</sup>;  $\gamma$ CH (thiophene ring) at 694cm<sup>-1</sup>.

## 2.5 Polymers synthesis

Poly(FV1Th) synthesis:

A 250 mL round-bottom flask equipped with a reflux condenser and a CaCl<sub>2</sub> tube, was charge with 44 g of monomer 1,4-bis(2-(thiophen-2-yl)vinyl)benzene and 100 mL dried CHCl<sub>3</sub>. The mixture was warmed to 40-50 °C, filtered and then, the filtrate placed into a 250 mL round bottom flask. 27 mL of a solution prepared by dissolving 1.02 g anhydrous FeCl<sub>3</sub> in 30 mL of dried CHCl<sub>3</sub> was then slowly added under stirring at RT. The mixture was then stirred at RT for 27 h, and the progress of the reaction monitored by TLC, seeded with CHCl<sub>3</sub> and eluted with a n-hexane-CHCl<sub>3</sub> mixture. The mixture was filtered, and the polymer was washed with plenty CHCl<sub>3</sub> and then methanol until colorless; next, the polymer was washed successively with hot water and methanol and finally oven-dried at 45°C. Yield 0.22 g (50 %). Elemental analysis found C 60.3, H 3.4, S 18.1 %, found mol:mol ratio C/S = 8.89 = 18/2; C/H = 1.49 = 18/12.1. FT-IR (KBr):  $\nu$ CH at 3005 cm<sup>-1</sup> (aromatic ring),  $\nu$ C=C at 1573 cm<sup>-1</sup> and 1538 cm<sup>-1</sup>,  $\nu$ C=C at 943 cm<sup>-1</sup> (vinylene group),  $\gamma$ CH (p-disubstitution pattern benzene ring) at 803 cm<sup>-1</sup>;  $\gamma$ CH (thiophene ring) at 699 cm<sup>-1</sup>.

Poly(FVBiTh) synthesis:

To a 50 mL round-bottom flask provided with reflux condenser and CaCl<sub>2</sub> tube, 0.27 g (0.61 mmole) of FVbiTh and 18 ml dried toluene were added. The mixture was flushed with nitrogen for 10 min, heated and then the supernatant of a hot mixture containing 0.30 g anhydrous FeCl<sub>3</sub> dissolved in 7 ml of dried toluene, added. The mixture was heated at 66 °C and kept under stirring for 2 h (monitored by TLC, using CHCl<sub>3</sub> and eluted with n-hexane-CHCl<sub>3</sub>); after this time the mixture was poured into 30 mL of methanol, the reaction mixture let stand, vacuum-filtered and the collected polymer washed with methanol. The polymer was oven-dried at 55 °C. Yield 0.13 g (50%). Elemental analysis found C 50.4, H 2,7 S 20.3 %, found mol:mol ratio C/S = 6.63 = 26/3.92; C/H = 1.57= 26/17. FT-IR (KBr):  $\nu$ CH at 3016 cm<sup>-1</sup> (aromatic ring),  $\nu$ C=C at 1514 cm<sup>-1</sup>,  $\nu$ C=C at 943 cm<sup>-1</sup> (vinylene group),  $\gamma$ CH (p-disubstitution pattern benzene ring) at 808 cm<sup>-1</sup>;  $\gamma$ CH (thiophene ring) at 689 cm<sup>-1</sup>.



Poly(FVTeTh) synthesis:

A 100 mL round bottom flask, equipped with a reflux condenser and CaCl<sub>2</sub> tube, was charged with 0.22 g (0.195 mmoles) FVTeTh and 17 mL of dry CHCl<sub>3</sub>. Subsequently, under stirring, 0.13 g (0.78 mmoles) of anhydrous FeCl<sub>3</sub> in 6 mL of dry CHCl<sub>3</sub> was added and the mixture stirred for 3 h at RT (monitoring by TLC, using CHCl<sub>3</sub> and eluted with CHCl<sub>3</sub>-n-hexane 1:1 (v/v)). The mixture was vacuum-filtered and the obtained polymer washed with CHCl<sub>3</sub> and methanol. The black product was oven-dried at 45 °C during 2 h. Yield, 0.05 g (22%). Elemental analysis found C = 69.8, H = 6.5, S = 23.1 %, found mol:mol ratio C/S = 66/8.2; C/H = 66/73. FT-IR (KBr): ν<sub>CH</sub> at 2921 cm<sup>-1</sup> and 2867 cm<sup>-1</sup> (aliphatic groups), ν<sub>C=C</sub> at 1618 cm<sup>-1</sup>, 1529 cm<sup>-1</sup> (aromatic rings), ν<sub>CH</sub> at 943 cm<sup>-1</sup> (vinylene group), γ<sub>CH</sub> (p-disubstitution pattern benzene ring) at 828 cm<sup>-1</sup>; γ<sub>CH</sub> (thiophene ring) at 673 cm<sup>-1</sup>.

### 3.0 Results and Discussion

**3.1** (1,4-phenylenebis(methylene))bis(triphenylphosphonium) bromide (sal of phosphonium) was synthesized according to Zheng et al. modified method<sup>16</sup> (Fig. 1). This salt is sensitive to moist-air, leading to low yield of the monomers.

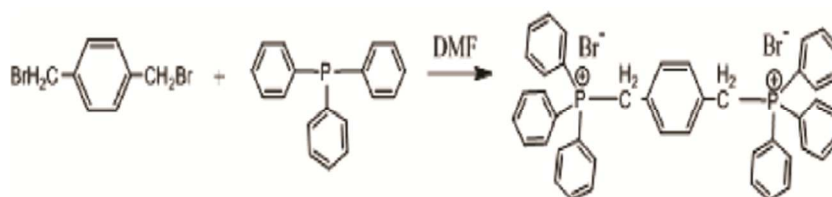


Fig. 1: Scheme of phosphonium salt synthesis

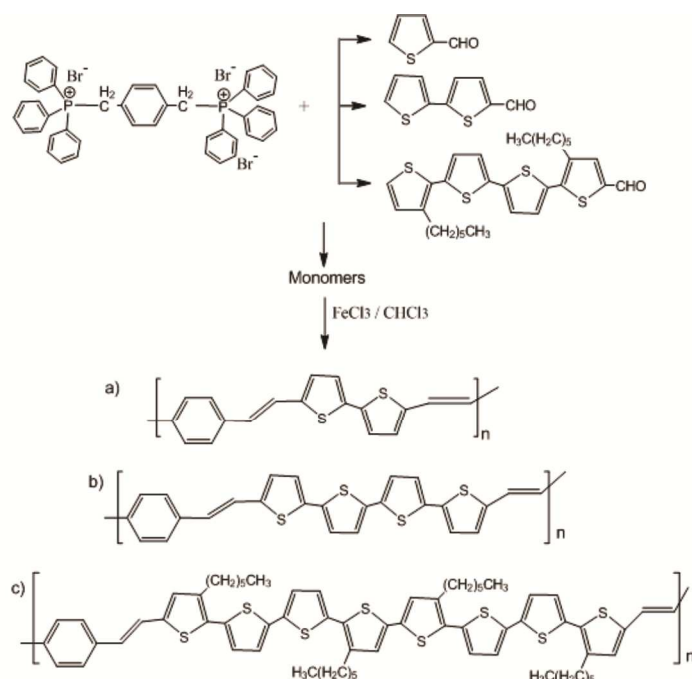


Fig. 2: Synthesis routes and polymer structure of a) poly(FV1Th); b) poly(FVBiTh); c) poly(FVTeTh).

FV1Th, FVBiTh and FVTeTh monomers were synthesized by condensation between the phosphonium salt with two moles of thiophene-2-carboxaldehyde, 2,2'-bithiophene-5-carboxaldehyde and 3,3''-dihexyl-[2,2':5',2'':5'':2''-quaterthiophene]-5-carboxaldehyde respectively, using potassium tert-butoxide or lithium ethoxide in dried CHCl<sub>3</sub> as base.

The polymers were synthesized using FeCl<sub>3</sub> as oxidant in dry chloroform. Synthesis routes for obtaining monomers and polymers, along with their structures, are illustrated in Fig. 2.

Monomers yield is low (23-39%) due to formation of several products originated from secondary or side reactions; these products were monitored by TLC. Moreover, long reaction times produce compounds with R<sub>f</sub> similar to those of monomers, making their purification difficult. Optima experimental conditions are described in experimental.

Reaction of the phosphonium salt with potassium tertbutoxide gives di(phosphonium ylide) and the negatively charged carbon can act as a nucleophile and to attack the carbonyl of the aldehyde, leading to a zwitterion-type, Betaine, species, which quickly form the cyclic form called oxaphosphetane that splits to give rise to the monomer and triphenyl phosphine oxide<sup>29</sup>. As example, scheme of FV1Th synthesis is shown in Fig. 3. Potassium tertbutoxide proved to be a more effective base than lithium ethoxyde, because a smaller number of unwanted compounds are produced, which facilitates the separation of the monomers from the reaction mixture.

Monomers and polymers characterization by spectroscopy and elemental analysis agree well with the proposed structure. Polymers elemental analysis and theoretical empirical formula are included in polymer synthesis section. Found C/H and C/S ratios are in agreement with the empirical formulas and polymeric structures. In polymers, the most important FT-IR observed bands are those associated to vinylene groups stretching localized at  $943\text{ cm}^{-1}$ .

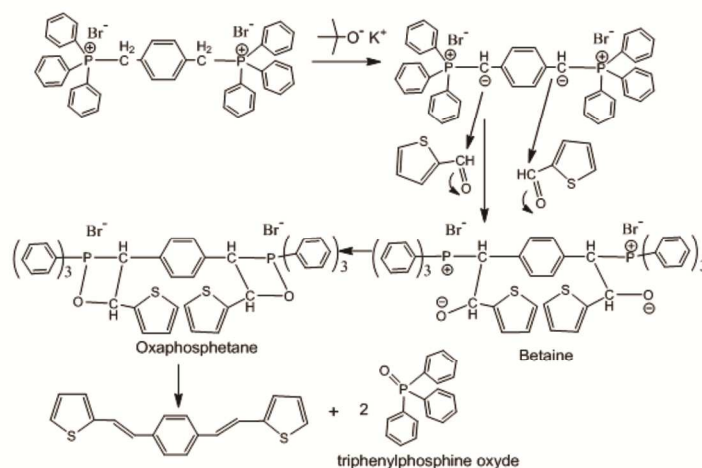


Fig. 3: FV1Th monomer synthetic route

### 3.2 Absorption and Intrinsic viscosity

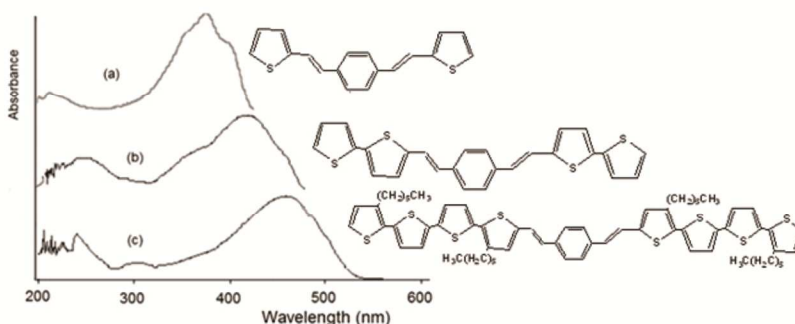


Fig. 4. UV-vis spectra in  $\text{CHCl}_3$  of a) FV1Th, b) FVBiTh and c) FVTeTh

The monomers exhibit different optical absorptions. Figure 4 shows the results. The maximum absorption appears at 340, 420 and 455 nm, for FV1Th, FVBiTh and FVTeTh respectively. If the number of thiophene rings is increased along the chain, greater electron delocalization occurs since the absorption maximum shifts to longer wavelength. Figure 5d shows the absorption spectrum of P3HT, synthesized under the same conditions used for the other polymers. P3HT has an absorption maximum at higher wavelength, 460 nm, accordingly the monomer (FVTeTh) possesses a higher electron delocalization than

P3HT. The increase of the electron delocalization effect is due to the electron-donor effect of the PV group that is found regularly alternating with 8 thiophene units in the polymeric backbone. As for FV1Th and FVBiTh, an opposite effect is observed since the absorption maximum is less than that of P3HT as the result of a decrease in the number of thiophene units that decreases the effective conjugation of the system.

Figure 5 shows polymers absorption. The absorption spectra correspond either to polymers of low molecular size or to oligomers. The intrinsic viscosity was 0.08, 0.07, 0.10 dLg<sup>-1</sup> for poly(FV1Th), poly(FVBiTh) and poly(FVTeTh), respectively. The higher conjugation of poly(FVTeTh) is consistent with the increased viscosity and, structurally, with the largest number of thiophenyl units in the skeleton. Absorption maxima are observed at 387 and 430 nm for poly(FV1Th) and poly(FVBiTh) respectively, while poly(FVTeTh) spectrum showed a set of absorption maxima at 260, 337 and 460 nm. This behavior is similar to that of monomers, *i.e.* increase of thiophene units on the polymeric backbone produces a bathochromic shift and, consequently, poly(FVTeTh) presents the greatest conjugation. Accordingly, polymers display greater conjugation than monomers. Besides, poly(FVTeTh) possesses higher conjugation than P3HT.

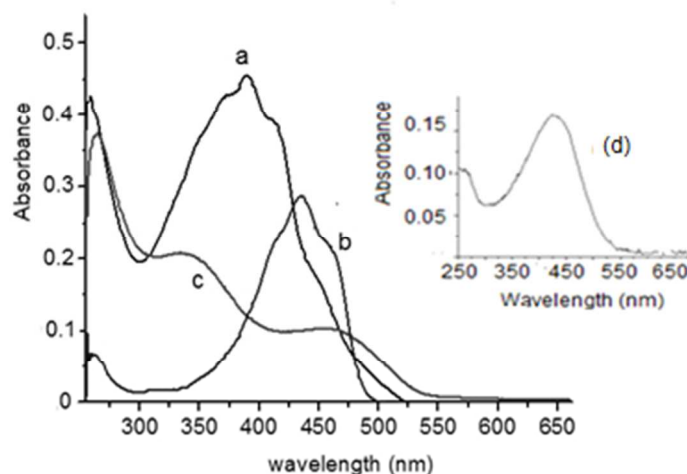


Fig. 5. UV-Vis spectra of a) poly(FV1Th), b) poly(FVBiTh), c) poly(FVTeTh) and d) P3HT

It can be observed that the difference in maximum absorption between monomers and polymers is 47 nm, 10 nm and 5 nm for poly(FV1Th), poly(FVBiTh) and poly(FVTeTh) respectively, the latter being similar to the monomer. Furthermore, polymers absorption onset is less than 540 nm, indicating that a conjugation barrier exists, probably ascribed to the non-coplanar system between PV and thiophene groups, *i.e.* the PV trans geometry along the chain prevents coplanarity in the conjugated system owing to the repulsion

between hydrogen of the vinylene group and the hydrogens from thiophene and phenylene rings, leading to lower coplanarity.

The polymers absorption corresponds to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions<sup>30,31</sup>. Poly(FVTeTh) shows several absorptions; those transitions of lower energy (maximum at 337 nm) correspond to species with different chain lengths in the polymer. Roncali et al. and Ribeiro et al.<sup>32,33</sup> have reported similar results with poly(thiophene) derivatives of different chain lengths obtained from terthiophene.

### 3.3 HOMO, LUMO and Band Gap

An approximation of the Tauc equation<sup>34,35</sup> was employed for optical band gap ( $E_g$ ) measurements.

$$A = B (h\nu - E_g)^{1/2} / h\nu$$

Thereby the relationship  $1241/\lambda_{\text{onset}} = E_g$  was used. Calculations for monomers showed the following sequence: 2.92, 2.59 and 2.30 eV for FV1Th, FVBiTh and FVTeTh, respectively. This decrease is due to conjugation enhancement. An increase from 2 to 4 units of thiophene units in the monomers provokes a 0.62 eV decrease in  $E_g$ , while for polymers the difference is just 0.05 eV. Table 1 shows results for poly(FV1Th) and poly(FVTeTh) that have  $E_g$  similar to P3HT.  $E_g$  values for poly(FVTeTh) and P3HT indicate that just eight units of conjugated thiophenyl in a polymer chain alternated with one electron-donor group (PV), is enough to obtain a polymer with  $E_g$  similar to P3HT. In general, PV units in the main chain precludes that  $E_g$  becomes less than 2.3 eV. This behavior can be found in several poly(p-phenylene vinylene) derivatives which present  $E_g$  lower than 2.3 eV<sup>36-38</sup>.

Table 1: Polymers physical properties

Polymers	HOMO (eV)	LUMO(eV)	Eg (eV)
Poly(FV1Th)	-5.76 <sup>b</sup>	-3.40	2.36
Poly(FVBiTh)	-6.39 <sup>b</sup>	-3.85	2.54
Poly(FVTeTh)	-6.12 <sup>b</sup>	-3.82	2.31
P3HT	-5.45 <sup>a</sup>	-3.29 <sup>a</sup>	2.30

<sup>a</sup> from reference 39; <sup>b</sup> HOMO values were calculated from LUMO and  $E_g$

The three polymers exhibit reduction waves (Fig. 6) and only in the case of poly(FV1Th) a clear oxidation wave was observed, hence HOMO values had to be worked out from the difference between the optical  $E_g$  obtained by UV-Vis spectroscopy and LUMO electrochemically obtained using cyclic voltammetry in

CH<sub>3</sub>CN. LUMO values were calculated from the onset peak of the corresponding redox wave ( $E_{\text{red}}$  vs. Ag/AgCl)<sup>40</sup>, according to the following equation.

$$E(\text{LUMO}) = -(E_{\text{red}} + 4.4) \text{ eV}$$

Polymers HOMO and LUMO energy values are exhibited in Table 1. HOMO and LUMO values for all synthesized polymers are less than HOMO and LUMO of P3HT. These results demonstrated that (PV) electron-donor effect on the chains attached to thiophenyl units enables a HOMO and LUMO decrease as compared to P3HT.

HOMO energy levels comparison revealed that (except poly(FV1Th) they increase in the following order: poly(FVBiTh) < poly(FVTeTh) < P3HT. This order is related to the increasing number of thiophenyl units evenly spaced with PV along the polymeric chain *i.e.* the progressive increase from 4 thiophene across the main chain spaced by PV units, increases the HOMO with regard to that of P3HT. LUMO also increases as thiophenyl units in the chains (exception poly(FV1Th) does. Thus, P3HT have the largest value while poly(FVBiTh) exhibits the lowest one. Furthermore, poly(FVBiTh) and poly(FVTeTh) display similar LUMO values. In general, the presence of PV in the backbone produces a LUMO decrease with respect to P3HT.

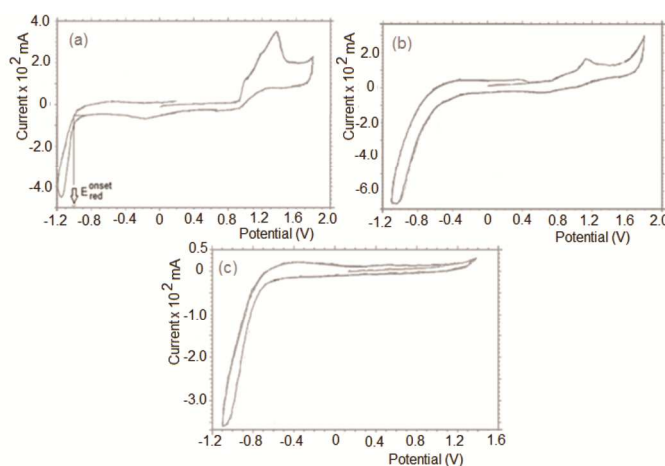


Fig. 6. Voltammograms in CH<sub>3</sub>CN of (a) poly(FV1Th), (b) poly(FVBiTh), and (c) poly(FVTeTh).

Polymers can be studied in organic solar cell. The device in its simplest form consists of an electron donor and electron acceptor material. The donor and acceptor should have their HOMO and LUMO well adapted, *i. e.*, it is necessary that in the photovoltaic device the LUMO of the donor be higher than the LUMO of the acceptor, while the HOMO of the donor must be significantly lower than the LUMO of the acceptor<sup>41</sup>. As a reference material, the well-known fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) small molecule, with HOMO -6.2 and LUMO -3.7 eV, is being used as electron



acceptor material<sup>42</sup>. Poly(FV1Th) and P3HT possess LUMO higher than PCBM's LUMO and all polymers exhibit HOMO lower than PCBM LUMO; consequently all polymers are good candidates to be studied in photovoltaic devices.

### 3.4 Crystallinity and Thermal stability

Figure 7 shows the thermal decomposition profiles obtained by TGA for poly(FVBiTh), poly(FV1Th) and poly(FVTeTh). The residual weight obtained is between 10.5 and 54.3 % at 1000 °C, which is indicative of a very high thermal stability, specially in the case of poly(FV1Th). The TGA profiles were also used as prior evidence when setting the temperature ranges for the DSC since the obtaining of information from the corresponding thermograms requires sample thermal stability.

Table 2 collects the values of the initial decomposition temperature ( $T_i$ ), the maximum decomposition temperature ( $T_{max}$ ), the temperature at which the weight reduction reaches 50 weight % ( $T_{50}$ ), and the residual weight %, which are used to represent the extent of the thermal decomposition in a polymer sample.  $T_i$ ,  $T_{max}$  and  $T_{50}$  values confirm the good thermal stability level suggested by the residual weights and by the shape of the profiles. Only the initial decomposition temperature for poly(FVTeTh) could be considered a relatively low value. However, it corresponds to a preliminary decomposition stage. Maximum decomposition happens at 446.2 °C.

Figure 8 shows the thermograms obtained for poly(FVBiTh), poly(FV1Th) and poly(FVTeTh). Endothermic signals are observed for all the studied polymers. From the corresponding thermograms shown in Figure 8, melting temperatures ( $T_m$ ) values are obtained over 200 °C (Table 2). The formation of crystalline zones is revealed in all the cases. However, poly(FVTeTh) shows a great fusion signal with a heat of fusion of 99.7 J/g, which reflects a more ordered and crystalline molecular structure. This behaviour corresponds to the polymer with the higher number of aromatic rings around the central group, which can originate a high molecular packing degree. Poly(FVBiTh) shows a second endothermic signal, which can be a consequence of a second crystallite group present in this polymer. Glass transition signals are not observed. This process represents a change in the mobility of the chain segments of a macromolecule in the amorphous phase, which should be prevented by the presence of bulky groups forming the polymer backbone.

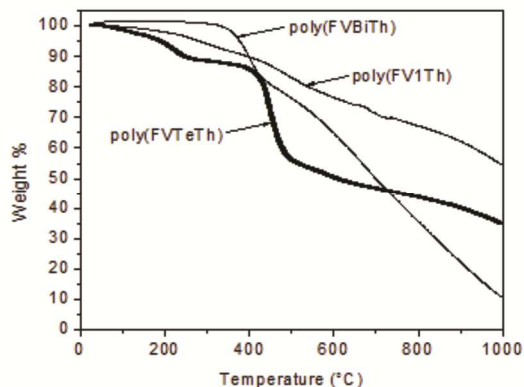


Fig. 7. Thermal decomposition profiles obtained by TGA

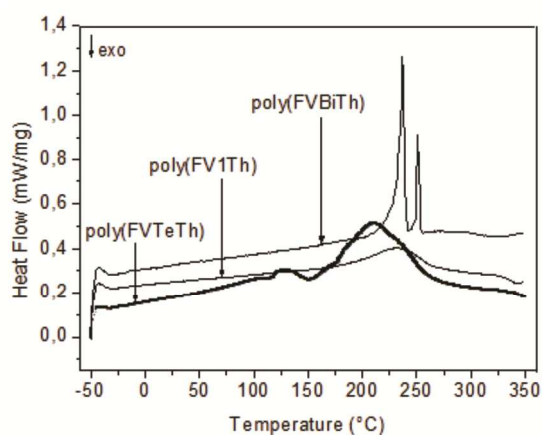


Fig. 8. Thermograms obtained by DSC of poly(FV1Th), poly(FVBiTh), and poly(FVTeTh).

Table 2. Physical Properties of Polymers obtained by TGA

Polymer	$T_i$ (°C)	$T_{max}$ (°C)	$T_{50}$ (°C)	Residual weight %	$T_m$ (°C)	$\Delta H_{fus}$ (J/g)
poly(FVBiTh)	338	401.2	700	10.5	237.4	31.8
					250.6	7.2
poly(FV1Th)	225	486.7	--	54.3	232.1	26.8
poly(FVTeTh)	186	446.2	607	34.6	211.2	99.7

#### 4.0 Acknowledgment

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## 5.0 Conclusions

Various polymers containing p-phenylene vinylene and 2, 4 and 8 thiophenyl units in the main chain were synthesized and characterized. The obtained polymers were of similar viscosity and the characterization by FT-IR and elemental analysis agrees well with the thought structures. P-phenylene vinylene units in the chains affect polymers properties as compared to P3HT. The polymers exhibited high thermal stability and they showed no glass transition temperature. When phenylene vinylene is incorporated to thiophene units, the HOMO and LUMO may decrease, modifying the band gap, with respect to P3HT HOMO and LUMO. P3HT band gap can be modified according to the phenylene vinylene sequence across the chain. Poly(FV1Th) possesses LUMO higher than the LUMO energy level of PCBM and all polymers exhibit HOMO lower than HOMO of PCBM; therefore all polymers are good candidates to be studied in photovoltaic devices. Those results will be reported later.

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