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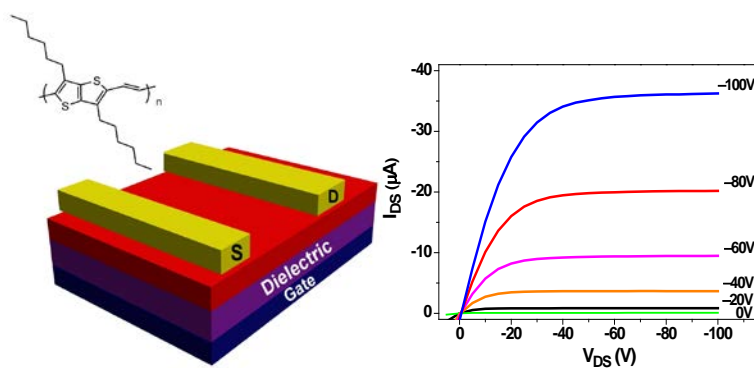
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## Poly(thieno [3, 2-b] thiophene vinylene)s: Synthesis, Field-Effect Transistors and Photovoltaic Properties

*Youjun He, Weiping Wu, Guangjing Zhao, Yunqi Liu\* and Yongfang Li\**

Poly (thieno [3, 2-b] thiophene vinylene) derivatives were synthesized by Pd-Catalyzed Stille-coupling method. The polymers show high field-effect transistors performance with hole mobility of  $0.032 \text{ cm}^2/\text{Vs}$  and on/off ratio of  $10^5$ .



**Title Running Head:** Poly (thieno [3, 2-b] thiophene vinylene) s.

# Poly (thieno [3, 2-b] thiophene vinylene) s: Synthesis, Field-Effect Transistors and Photovoltaic Properties

*Youjun He<sup>1,2</sup>, Weiping Wu<sup>1,2</sup>, Guangjin Zhao<sup>1,2</sup>, Yunqi Liu<sup>\*1</sup> and Yongfang Li<sup>\*1</sup>*

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**Abstract:** Two poly (thieno [3, 2-b] thiophene vinylene) derivatives (**P2** and **P3**) were prepared by Pd-catalyzed Stille-coupling method. Compared with poly (3-hexylthienylene vinylene) (**P1**), strong photoluminescence was observed for **P2** and **P3** solutions, while the maximum absorption of **P2** and **P3** are blue-shifted. The solution-processed organic field-effect transistors (OFETs) were fabricated with bottom gate/top contact geometry. The highest FET hole mobility of **P3** after thermal annealing at 180 °C for 30 min reached 0.032 cm<sup>2</sup>/Vs with the on/off ratio of 10<sup>5</sup>, which is a high value for the conjugated polymers. Polymer solar cells base on the polymers were fabricated, the power conversion efficiency of the devices based on **P1**, **P2** and **P3** was 0.19%, 0.17% and 0.28%, respectively, under the illumination of AM1.5, 100 mW/cm<sup>2</sup>. The efficiency of the device based on **P3** is ca. 50% higher than that of the devices based on **P1** and **P2**, which could be benefited from the higher hole mobility of **P3**.

**Keywords:** Poly (thieno [3, 2-b] thiophene vinylene) s, organic field-effect transistors, photovoltaic properties

## Introduction

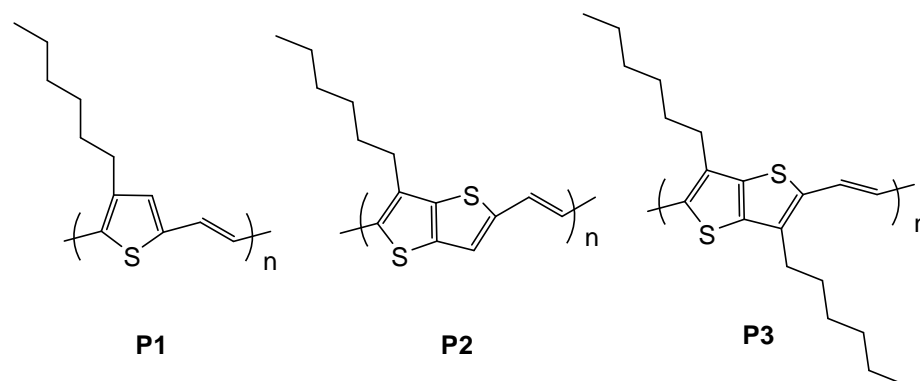
In the past decades, conjugated organic and polymer materials are the focus of great research activity, mainly due to their interesting electronic and optoelectronic properties. They are being investigated for a variety of applications, including field-effect transistors (FETs),<sup>1-2</sup> organic light-emitting diodes (OLEDs), polymer solar cells (PSCs), etc.<sup>3-5</sup> Conjugated poly (thienylenevinylene)s (PTVs) is one important class of conjugated polymers. These polymers display high nonlinear optical responses<sup>6</sup> and electroluminescence properties.<sup>7</sup> Although PTVs exhibit smaller bandgap (below 1.8 eV)<sup>6, 8-9</sup> than the polyaromatic polythiophene (PT) and the PT derivatives,<sup>10</sup> the power conversion efficiency (PCE) of the PSCs based on PTVs are still very low.<sup>11-13</sup> Moreover, PTVs show relatively high-charge carrier mobility ( $10^{-4}$  -  $10^{-2}$  cm<sup>2</sup>/Vs measured in field-effect transistor geometry)<sup>14-18</sup> which is one of the prerequisites for high efficient solar cells and field-effect transistors.

Fused thiophenes has higher hole-mobility, because of good  $\pi$ -stacking in those kinds of materials, so many polymers containing fused thiophene rings<sup>19-21</sup> were synthesized and used in FETs. Fused thiophene oligomers display generally low solubility at room temperature, and indeed polymers of thieno [3, 2-*b*] thiophenes have been reported to be insufficiently soluble to preclude full characterization and utilization in devices.<sup>22-24</sup> As far as we know, there were little reports of p-polythiophenes with fused thiophene units used in PSCs,<sup>25, 26</sup> and was only one report of poly(thieno[3,2-*b*]thiophen-2,5-diyliethynylene).<sup>27</sup> We have not seen any report of polythieno [3, 2-*b*] thiophene vinylene being synthesized and used in organic electronic devices.

For increasing the absorption of the polymers to the sunlight and hole-mobility, we designed and synthesized a novel class of polythieno [3, 2-*b*] thiophene vinylenes, as shown in Scheme 1. For getting polythieno [3, 2-*b*] thiophene vinylenes with good solubility and high regioregularity, we used direct methods by the Stille cross-coupling between 2, 5-dibromo-thieno [3, 2-*b*] thiophene monomers and (*E*)-1, 2-bis (tributylstannyl) ethane. Because of the higher degree of unsaturation in the fused rings, relatively long hexyl chains were used to increase the solubility of the thieno [3, 2-*b*] thiophene-based

polymers. FETs and PSCs based on those polymers were fabricated, the relationship between structure and properties of the polymers and the devices were also investigated.

**Scheme 1.** Molecular structure of the polymers.



## Experimental Section

**Materials.** 3-bromo-thiophene, Pd (PPh<sub>3</sub>)<sub>4</sub>, bromine, tributyltin chloride, NBS, *n*-Butyllithium (2.88 mol/L in hexane, heptanoyl chloride), ethyl mercaptoacetate, K<sub>2</sub>CO<sub>3</sub>, DMF, 18-Crown-ether, LiOH, tetrabutylammonium iodide, copper powder, quinoline, Bromobenzene and Benzene boronic acid were obtained from Acros organics. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled prior to use. The monomer 2, 5-dibromo-3-hexylthiophene for the synthesis of **P1** was synthesized as reported in the literature.<sup>28</sup> (*E*)-1, 2-bis (tributylstannyl) ethane was synthesized as reported in the literature.<sup>29</sup> The other materials were common commercial level and used as received.

## Measurement and Characterization.

General Methods: All new compounds were characterized by <sup>1</sup>H-NMR. Nuclear magnetic resonance (NMR) spectra were taken on a Bruker DMX-400 spectrometer. Chemical shift of <sup>1</sup>H-NMR were reported in ppm relative to the singlet at 7.26 ppm. Splitting patterns were designated as s (singlet), t (triplet), d (doublet), m (multiplet), and br (broaden). Absorption spectra were taken on a Hitachi U-3010 UV-vis spectrophotometer. Photoluminescence spectra were measured using a Hitachi F-4500 spectrophotometer. Absorption and Photoluminescence spectra measurements of the polymer solutions were carried out in chloroform (analytical reagent) at 25 °C. Absorption and photoluminescence (PL) spectra measurements of the polymer films were carried out on the quartz plates with the polymer films

spin-coated from the polymer solutions in chloroform (analytical reagent) at 25 °C. Molecular weight of the polymers was measured by GPC method, and polystyrene was used as a standard. TGA measurement was performed on a Perkin-Elmer TGA-7. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt disk, Pt plate, and Ag/Ag<sup>+</sup> electrode as working electrode, counter electrode, and reference electrode respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) acetonitrile solution. Polymer thin films were formed by drop-casting 1.0 mm<sup>3</sup> of polymer solutions in THF (analytical reagent, 1 mg /mL) onto the working electrode, and then dried in the air.

#### **Fabrication of Field-effect transistor Devices.**

Thin-film organic field-effect transistors (OFETs) were fabricated on highly doped silicon substrates with thermally grown silicon oxide (SiO<sub>2</sub>) insulating layer of 500 nm thickness, where the substrate served as a common gate electrode. Prior to organic semiconductor deposition, the substrates were treated with silylating agent octyltrichlorosilane (OTS). Thin semiconductor films were then deposited by spin-coating the polymer solutions in dichlorobenzene (1 wt %) on the substrates. Film thickness was about 30 nm, as measured by an XP-2 surface profilometer (Ambios Technology). The samples were then dried and annealed at 120-180 °C under nitrogen for 30 min. Transistor source-drain gold electrodes were vacuum-deposited on the polymer layer. The electrical characterization of the transistor devices was performed using a Keithley 4200 Semiconductor Parameter Analyzer.

#### **Fabrication of Photovoltaic Devices.**

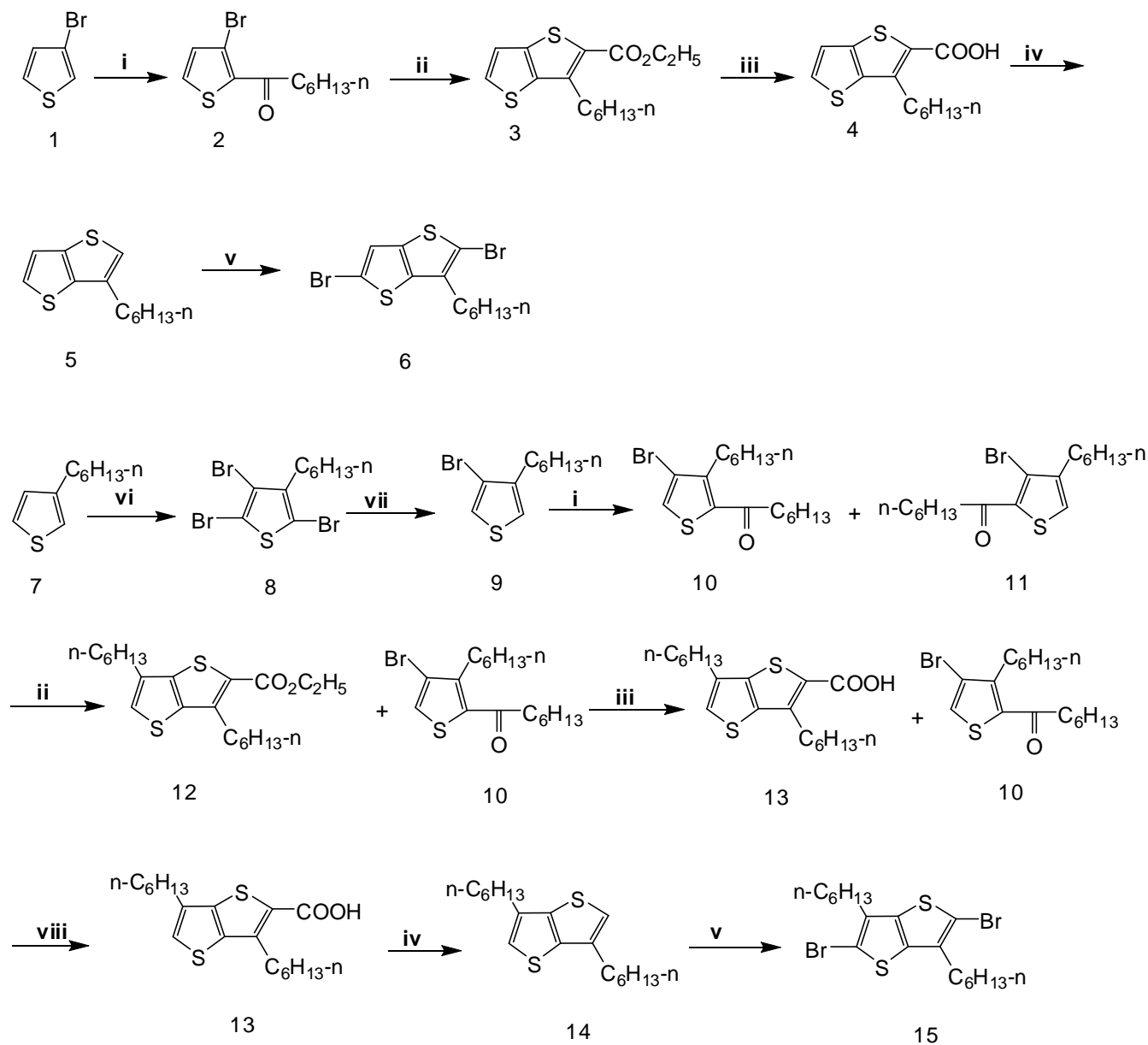
Polymer solar cells were fabricated with ITO glass as a positive electrode, Ca/Al as a negative electrode and the blend film of the polymer/PCBM between them as a photosensitive layer. The ITO glass was precleaned and modified by a thin layer of PEDOT: PSS (Bayer) which was spin-cast from a PEDOT: PSS aqueous solution on the ITO substrate, and the thickness of the PEDOT: PSS layer is about 60 nm. The photosensitive layer was prepared by spin-coating a blend solution of the polymer and PCBM with a weight ratio of 1:1 in o-dichlorobenzene at 1000 rpm on the ITO/PEDOT: PSS electrode. Then the Ca/Al cathode, was deposited on the polymer layer by vacuum evaporation under  $3 \times 10^{-4}$  Pa.

The thickness of the photosensitive layer is ca.80 nm, measured on an Ambios Tech. XP-2 profilometer. The effective area of one cell is ca. 4 mm<sup>2</sup>. The current-voltage (*I-V*) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. A xenon lamp with AM1.5 filter was used as the white light source, and the optical power at the sample was around 100 mW/cm<sup>2</sup>. The input photon to converted current efficiency (IPCE) was measured using a Keithley 195 System DMM coupled with a WDG3 monochromatic and a 500 W xenon lamp. The light intensity at each wavelength was calibrated with a standard single crystal Si photovoltaic cell.

### **Preparation of the monomers.**

The monomers were prepared by the methods as shown in Scheme 2.

**Scheme 2.** The synthetic routes of the monomers



(i) AlCl<sub>3</sub>, C<sub>6</sub>H<sub>13</sub>COCl, C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>, room temperature, 2 h; (ii) HSCOC<sub>2</sub>H<sub>5</sub>, K<sub>2</sub>CO<sub>3</sub>, 18-Crown-ether, 60 °C, 24 h; (iii) THF/CH<sub>3</sub>OH, LiOH, tetrabutylammonium iodide, reflux, 24 h; (iv) Cu, quinoline, 260 °C, 4 h; (v) NBS, DMF, room temperature, 24 h; (vi) Br<sub>2</sub>, HOAc, 4 h, then 60-70 °C, 24 h; (vii) Butyl lithium, THF, -78 °C, 1 h, then H<sub>2</sub>O; (viii) separate by column chromatography.

### 1-(3-bromothiophenyl) heptanone, 2.

To a mixture of 3-bromothiophene (16.30 g, 0.10 mol), AlCl<sub>3</sub> (26.80 g, 0.20 mol) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL), heptanoyl chloride (14.90 g, 0.10 mol) was added dropwise at room temperature. The final mixture was stirred for 2 h. The reaction mixture was poured into cold HCl (6 mol/L, 200 mL).



Organics were extracted with hexane (3 × 100 mL). The combined organic extracts were washed with brine (2 × 100 mL) and water (100 mL). After drying over anhydrous MgSO<sub>4</sub>, the target was purified by silica column chromatography eluted with hexane to yield **2** (25.10 g, 90.9%). GC/MS: M/z = 275-277. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 7.53 (d, 1H), 7.12 (d, 1H), 3.01 (t, 2H), 1.71 (m, 2H), 1.38 (m, 6H), 0.92 (t, 3H).

*3-Hexylthieno [3, 2-b] thiophene-2-ethyl-carboxylate, 3.*

Compound **2** (35.40 g, 0.13 mol) and K<sub>2</sub>CO<sub>3</sub> (27.60 g, 0.20 mol) were mixed with DMF (100 mL). To this mixture, ethyl mercaptoacetate (14.00 mL, 0.13 mol) was added dropwise at 60 °C. A catalytic amount of 18-Crown-ether was added. The mixture was stirred overnight and poured into water (500 mL). The organic material was extracted with ethyl acetate (3 × 80 mL). The combined organic was washed with brine (2 × 100 mL) and water (100 mL). The organic layer was then dried over anhydrous MgSO<sub>4</sub>. After evaporating solvent, the crude compound **3** was obtained and purified by silica column chromatography, eluting with 5% ethyl acetate giving yellow oil (32.10 g, 77.4%). EI: m/z = 319. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 7.56 (d, 1H), 7.24(d, 1H), 4.34(q, 2H), 3.15(t, 2H), 1.71(m, 2H), 1.32(m, 6H), 0.88(m, 6H).

*3-Hexylthieno [3, 2-b] thiophene-2-carboxylic acid, 4.*

Compound **3** (32.10 g, 0.10 mol) was mixed with LiOH (50 mL, 10% water solution), THF (100 mL), MeOH (30 mL) and a catalytic amount of tetrabutylammonium iodide in a 500 mL flask. This mixture was refluxed overnight. After cooling to room temperature, the liquid was acidified with concentrated HCl. A yellow solid was collected by filtration and washed several times with water. The solid was heated with hexane (100 mL) and cooled to room temperature. After filtration, the solid was collected and dried under vacuum to give light yellow powder (26.26 g, 98.00%). EI: m/z = 268. mp 111-112 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 7.66 (d, 1H), 7.31 (d, 1H), 3.20 (t, 2H), 1.79 (m, 2H), 1.33 (m, 6H), 0.91 (t, 3H).

*3-Hexylthieno [3, 2-b] thiophene, 5.*

A solution of compound **4** (14.60 g, 0.05 mol), copper powder (2.00 g, 0.030 mol) and quinoline (80 mL) was heated at 260 °C in a Woods-metal bath. After refluxing four hours, the mixture was cooled to room temperature and hexane (200 mL) was added to the quinoline mixture. This mixture was washed repeatedly with 1 mol/L HCl. The organic layer was dried over anhydrous MgSO<sub>4</sub> and solvent was removed. The compound **5** (8.20 g, 73.2%) was obtained by chromatography on silica gel eluted with hexane. GC/MS: m/z = 224. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 7.36 (m, 1H), 7.25 (m, 1H), 7.01 (m, 1H), 2.73 (t, 2H), 1.69 (m, 2H), 1.34 (m, 6H), 0.89 (t, 3H).

*2, 5-Dibromo-3-hexylthieno [3, 2-b] thiophene, 6.*

Compound **5** (6.72 g, 0.030 mol) was dissolved in 100 mL DMF, NBS (10.68 g, 0.060 mol) was added to the mixture for several portions. After addition was complete, the reaction mixture was stirred for overnight, and then was added to 300 mL water. The organic phase was separated, and water phase was extracted with chloroform (3 × 100 mL). The combined organics were washed with brine (3 × 100 mL) and water (3 × 100 mL). The organics were dried over anhydrous MgSO<sub>4</sub>. The solvent was removed in vacuo. The residue was purified with silica column chromatography eluted with light petroleum to yield **6** (8.71 g, 76.0%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 7.15 (s, 1H), 2.68 (t, 2H), 1.65 (m, 2H), 1.33 (m, 6H), 0.90 (t, 3H). m/z = 382.

*2, 4, 5-Tribromo-3-hexylthiophene, 8.*

3-hexylthiophene **7** (100.00 g, 0.60 mol) was mixed with 200 mL acetic acid. To this mixture, bromine (92.60 mL, 1.80 mol) was added dropwise. After finishing the addition of bromine, the mixture was then stirred at room temperature for 4 h and heated to 60-70 °C overnight. The final mixture was poured into 800 mL ice water and neutralized with NaOH solution (6 mol/L). The organic was extracted with ethyl acetate (3 × 100 mL). The combined organic was washed with brine (2 × 100 mL), water (100 mL) and dried over anhydrous MgSO<sub>4</sub>. After evaporating solvent, 234.00 g (96.5%) of crude product **8** was obtained. This product was found good enough for the next reaction. GC/MS: 404 (M-1). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 2.64 (t, 2H), 1.51 (m, 2H), 1.32 (m, 6H), 0.89 (t, 3H).

*3-Bromo-4-hexylthiophene, 9.*

Compound **8** (70.00 g, 0.17 mol) was mixed with dry THF (400mL). To this mixture n-butyllithium (138 mL, 2.5M in hexane, 0.35 mol) was added dropwise at  $-78\text{ }^{\circ}\text{C}$  under argon. After finishing the addition, the mixture was stirred another 10 minutes and water was added to quench the reaction. The THF was evaporated and organic was extracted with ethyl acetate ( $2 \times 100\text{ mL}$ ). The combined organic layer was washed by brine ( $2 \times 100\text{ mL}$ ), water (70 mL) and dried over anhydrous  $\text{MgSO}_4$ . After evaporating solvent, the crude product was purified by vacuum distillation at  $136^{\circ}\text{C}/0.20\text{ millibar}$  giving the product of **9** (35.30 g, 84.1%). GC/MS: 246(M-1).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm) 7.22(s, 1H), 6.96(s, 1H), 2.57(t, 2H), 1.61(m, 2H), 1.32(m, 6H), 0.88(t, 3H).

*1-(3-Bromo-4-hexyl-2-thienyl) heptanone, 11.*

To a mixture of compound **9** (24.70 g, 0.10 mol) and  $\text{AlCl}_3$  (26.80 g, 0.20 mol) in dry  $\text{CH}_2\text{Cl}_2$  (100 mL), heptanoyl chloride (14.90 g, 0.10 mol) was added dropwise at room temperature. This mixture was stirred for two hours and GC/MS shown 3:1 mixtures of target compound **11** and heptanone **10** were formed. This mixture was poured into HCl (6 mol/L) and washed with water ( $3 \times 50\text{ mL}$ ). The organic mixture then was dried over anhydrous  $\text{MgSO}_4$ . After evaporating solvent, 34.70 g of **10** and **11** mixtures of crude products was obtained as confirmed by GC/MS and used for the next reaction without separation.

*3, 6-Dihexyl-thieno [3, 2-b] thiophene-2-carboxylic acid, 13.*

A mixtures of compounds **10** and **11** (66.50 g, 0.19 mol) was mixed with  $\text{K}_2\text{CO}_3$  (53.60 g, 0.39 mol) and a catalytic amount of 18-Crown-6 in 200 mL DMF. To this mixture, ethyl mercaptoacetate (20.30 mL, 0.19 mol) was added dropwise at  $60\text{-}70\text{ }^{\circ}\text{C}$ . The mixture was stirred at this temperature overnight and poured into water (800 mL). The organic was extracted with ethyl acetate ( $3 \times 100\text{ mL}$ ), washed with brine ( $2 \times 100\text{ mL}$ ) and water (100 mL). The organic layer was collected and solvent was evaporated. The residue included 3, 6-dihexyl-thieno [3, 2-b] thiophene-2-carboxylic acetate **12** and compound **10** as confirmed by GC/MS. This mixture was then dissolved in THF (300 mL). To this THF solution LiOH (84 mL, 10% w/w solution in water), MeOH (50 mL) and a catalytic amount of tetrabutylammonium iodide were added. The mixture was refluxed for 3 hours and the solvent then was

evaporated. The residue was then acidified with concentrated HCl (50 mL). The organic was extracted with ethyl acetate (3 × 100 mL) after dilution by water. The combined organic layer was washed with brine (2 × 100 mL), water (100 mL) and dried over anhydrous MgSO<sub>4</sub>. After evaporating solvent, compound **13** was obtained by silica gel column chromatography (5% ethyl acetate in hexane and then 20% ethyl acetate in hexane to elute). Yield 30.00 g (44.9%) (Calculated from mixture). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 7.24 (s, 1H), 3.18 (t, 2H), 2.73 (t, 2H), 1.75 (m, 4H), 1.34 (m, 14H), 0.89 (m, 6H). m/z 352.

*3, 6-Dihexyl-thieno [3, 2-b] thiophene, 14.*

A solution of compound **13** (30.00 g, 0.09 mol), copper powder (3.76 g) and quinoline (80 mL) was heated at 260 °C in a Woods-metal bath. After refluxing 4 h, the mixture was cooled to room temperature and hexane (200 mL) was added to the quinoline mixture. This mixture was washed repeatedly with 1 mol/L HCl. The organic layer was dried over anhydrous MgSO<sub>4</sub> and solvent was removed. Compound **14** was obtained after silica gel chromatography. Light petroleum eluted **14** (18.00 g, 68.8%). mp 58-59 °C, <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 6.97 (s, 2H), 2.70 (t, 4H), 1.73 (m, 4H), 1.37 (m, 12H), 0.88 (t, 6H). m/z 308.

*2, 5-Dibromo-3, 6-dihexyl-thieno [3, 2-b] thiophene, 15.*

Compound **14** (18.00 g, 0.06 mol) was dissolved in 200 mL chloroform, NBS (21.00 g, 0.12 mol) was added to the mixture for several portions. After addition was complete, the reaction mixture was stirred for overnight, and then was added to 300 mL water. The organic was separated, and water phase was extracted with chloroform (3 × 100 mL). The combined organics were washed with brine (3 × 100 mL) and water (3 × 100 mL). The organics were dried over anhydrous MgSO<sub>4</sub>. The solvent was removed in vacuo. The residue was purified with silica column chromatography eluted with light petroleum to yield **15** (21.60 g, 79.9%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 2.67 (t, 4H), 1.65 (m, 4H), 1.32 (m, 12H), 0.88 (t, 6H). M/z = 466.

**Preparation of the polymers.**

The synthesis of all the polymers was carried out using palladium-catalyzed Stille-coupling between monomer 2,5-dibromo-3-hexylthiophene, **6**, **15** and (*E*)-1, 2-bis (tributylstannyl) ethane, as shown in Scheme 3. All starting materials, reagents and solvents were carefully purified, and all procedures were performed under an air-free environment. Under the protection of Argon atmosphere, monomer 2, 5-dibromo-3-hexylthiophene or **6** or **15** (1 mmol) was dissolved in 10 mL dried toluene, (*E*)-1, 2-bis (tributylstannyl) ethane (1 mmol) was added to the mixture. The solution was flushed with argon for 10 min, and then 10 mg of Pd (PPh<sub>3</sub>)<sub>4</sub> were added. After another flushing with argon for 20 min, the reactant was heated to reflux for 12 h. The terminal bromobenzene and benzene boronic acid were added as end-cappers, with the bromobenzene added first and the benzene boronic acid added 12 h later. After stirring for another 12 h, the reaction solution was cooled to room temperature, the reaction mixture was added dropwise to 200 mL methanol, and then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. Polymer was recovered from the chloroform fraction by rotary evaporation as solid. The polymer was purified with bio-beads S-1 column chromatography eluted with THF, the solvent was removed in vacuo. The solid was dried under vacuum for 1 day. The yields of the polymerization reactions were about 30-50%.

**P1:**

GPC:  $M_w = 28$  K,  $M_n = 9.1$  K,  $M_w/M_n = 3.08$ . <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 7.13-6.67 (br, 3H), 2.59 (m, 2H), 1.58 (m, 2H), 1.34 (m, 6H), 0.87 (t, 3H). Elemental analysis for (C<sub>12</sub>H<sub>16</sub>S)<sub>n</sub> Calculated: C, 75.00; H, 8.33; S, 16.67. Found: C, 74.36; H, 8.21; S, 14.98.

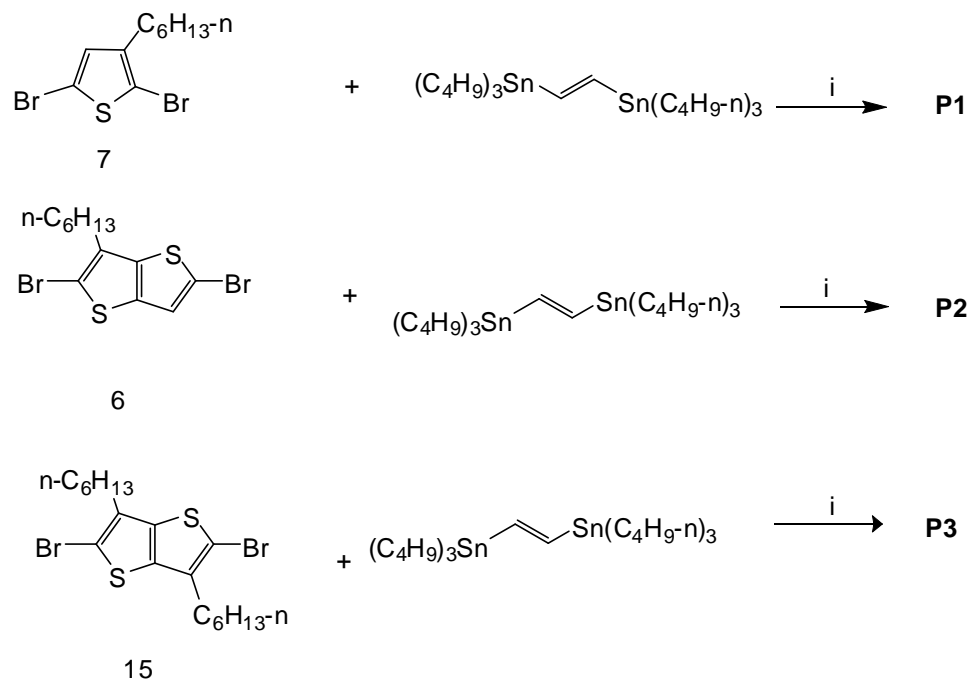
**P2:**

GPC:  $M_w = 36$  K,  $M_n = 29$ K,  $M_w/M_n = 1.23$ . <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 7.15-6.80 (br, 3H), 2.71 (m, 2H), 1.68 (m, 2H), 1.32 (t, 6H), 0.90 (t, 3H). Elemental analysis for (C<sub>14</sub>H<sub>16</sub>S<sub>2</sub>)<sub>n</sub> Calculated: C, 67.74; H, 6.45; S, 25.80. Found: C, 67.56; H, 6.38; S, 25.93.

**P3:**

GPC:  $M_w = 32$  K,  $M_n = 28$  K,  $M_w/M_n = 1.13$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm) 7.15-6.99 (br, 2H), 2.79 (m, 4H), 1.74 (m, 4H), 1.38 (m, 12H), 0.93 (t, 6H). Elemental analysis for  $(\text{C}_{20}\text{H}_{28}\text{S}_2)_n$  Calculated: C, 72.29; H, 8.43; S, 19.28. Found: C, 72.18; H, 8.72; S, 18.96.

**Scheme 3.** Synthetic routes of the polymers.



(i) Pd ( $\text{PPh}_3$ )<sub>4</sub>, toluene, Argon, reflux, 12 h.

## Results and Discussion

### Synthesis of monomers and polymers

The synthetic routes of monomers and corresponding polymers are outlined in Scheme 2 and Scheme 3, respectively. **P1**, **P2** and **P3** were prepared by Stille-coupling reaction<sup>28</sup> and confirmed by  $^1\text{H-NMR}$  spectroscopy and elemental analysis. In the  $^1\text{H-NMR}$  spectra (see Figure 1), the  $\alpha$ -hydrogen linking to the thieno[3,2-b]thiophene of compound **15** peaks at 2.67 ppm, the other hydrogen positions are analyzed as shown in Figure 1. Figure 2 shows the  $^1\text{H-NMR}$  spectrum of **P3**, where the double-bond

hydrogen 7 and 8 correspond to the peaks in the range from 6.99 to 7.15 ppm. The  $\alpha$ -hydrogen linking to the thieno [3, 2-b] thiophene of **P3** positions at 2.79 ppm.

The polymers are soluble in common organic solvents, such as chloroform, toluene, and THF at room temperature. The elemental analysis, weight-average molecular weight ( $M_w$ ) and polydispersity index (PDI) are shown in Table 1.

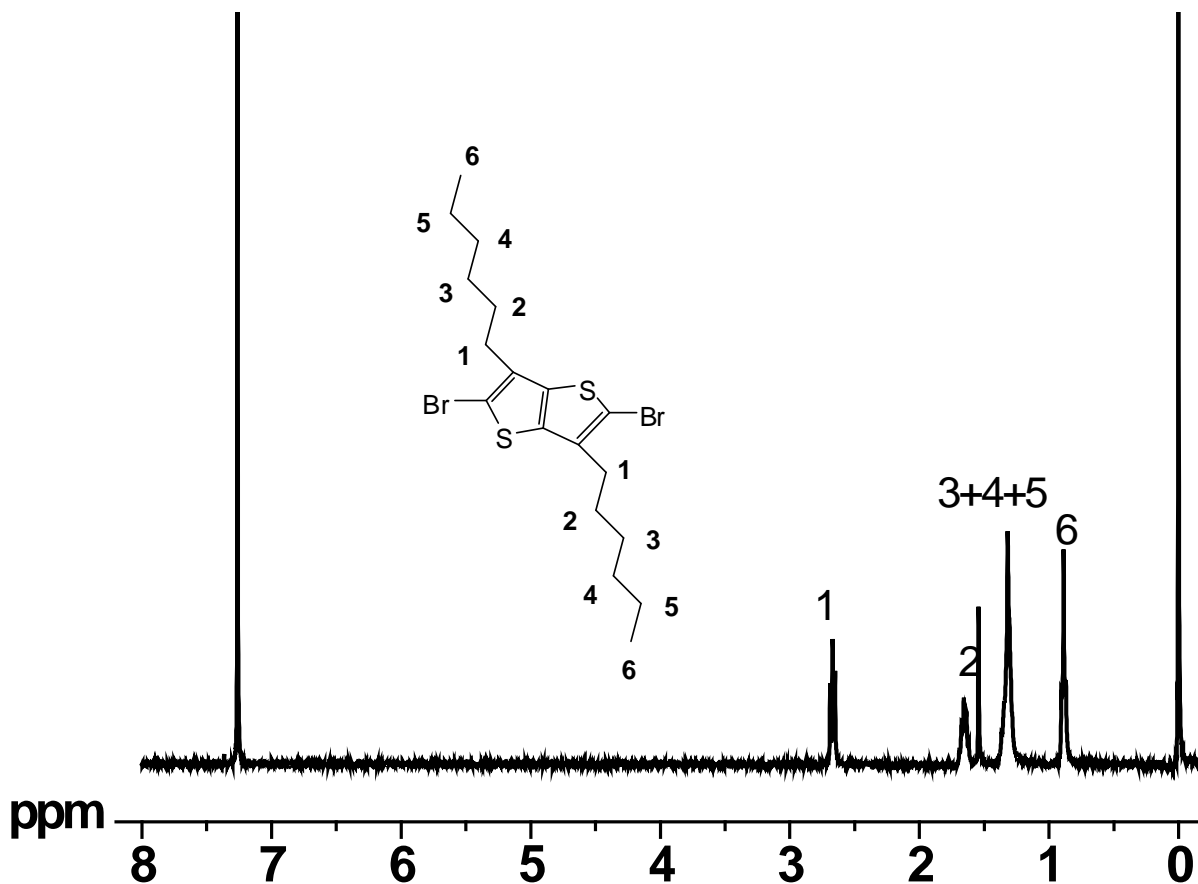


Figure 1. <sup>1</sup>H-NMR spectrum of Compound 15.

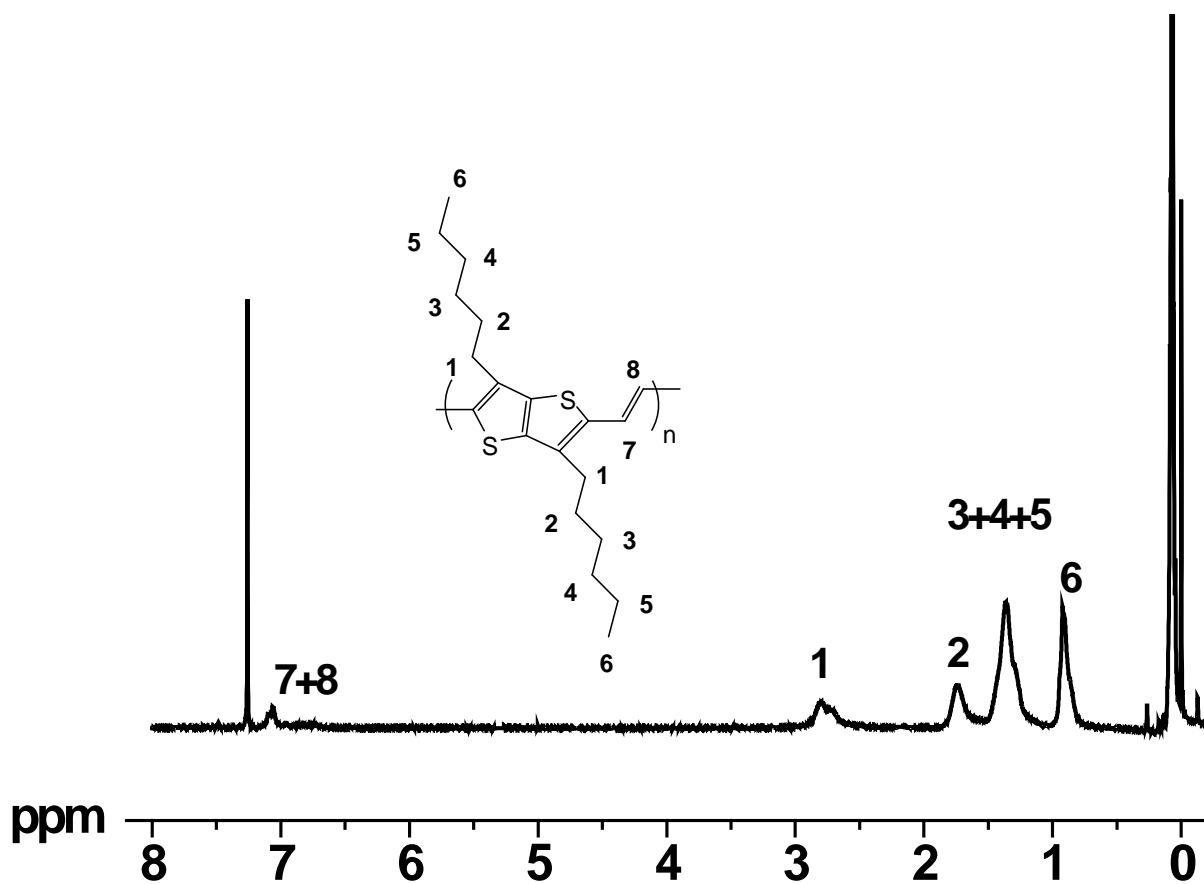


Figure 2.  $^1\text{H-NMR}$  spectrum of polymer **P3**.

Table 1. The elemental analysis, weight-average molecular weight and TGA properties of the polymers

Polymers	Elemental analysis (%) calculated/found			Molecular weight by GPC		
	C	H	S	$M_w^a$	PDI	$T_{5d}$ ( $^{\circ}\text{C}$ ) <sup>b</sup>
<b>P1</b>	75.00/74.36	8.33/8.21	16.66/14.98	28K	3.08	350
<b>P2</b>	67.74/ 67.56	6.45/6.38	25.81/25.93	36K	1.23	321
<b>P3</b>	72.29/72.18	8.43/8.72	19.28/18.96	32K	1.13	314

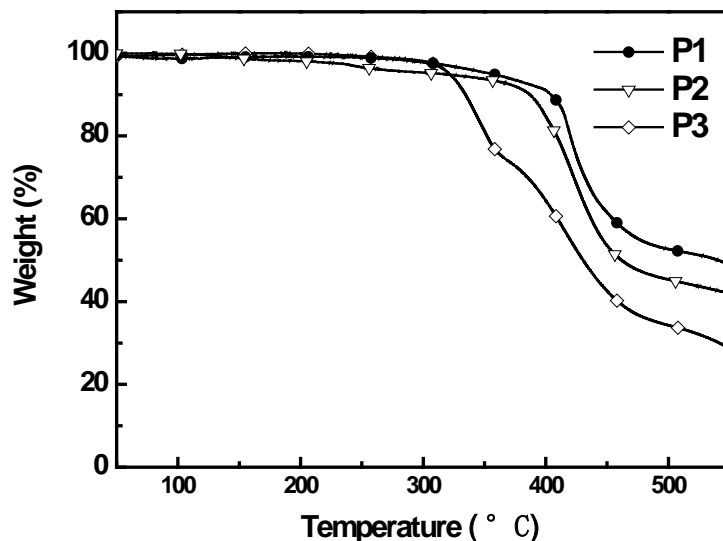
a Weight-average molecular weight determined by GPC using polystyrene as the standard in THF solution.

b Decomposition temperature determined by TGA in  $\text{N}_2$  gas at 5% weight loss.



## Thermal Analysis.

Thermal stability of the polymers was investigated with thermo gravimetric analysis (TGA), as shown in Figure 3. The **P1**, **P2** and **P3** show onset decomposition temperatures with 5% weight loss at 350 °C, 321 °C and 314 °C, respectively, which was also listed in Table 1. The thermal stability is enough for most applications.



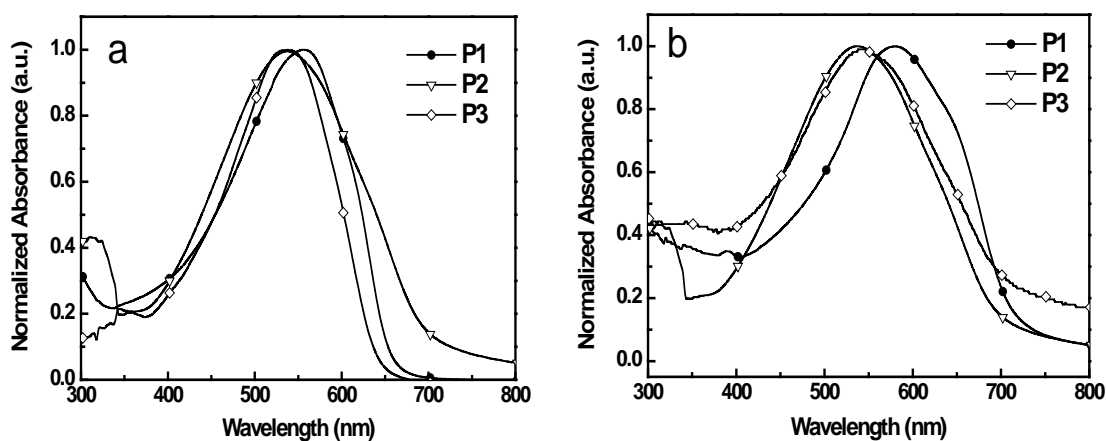
**Figure 3.** TGA plots of the polymers with a heating rating of 10 °C/min under inert atmosphere.

## Optical properties of the polymers.

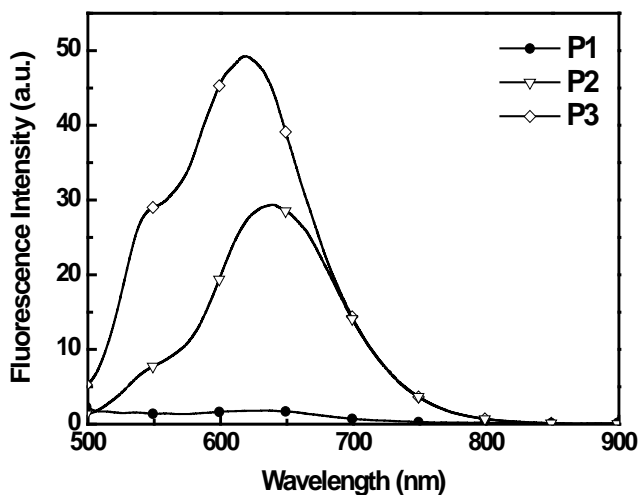
Figure 4 shows the absorption spectra of the polymer solutions in chloroform and films. The absorption peaks of **P2** and **P3** solutions centered at 537 nm and 538 nm, respectively, which are about 18 nm blue-shifted in comparison with that of **P1**, as shown in Figure 4(a). This blue shift of the absorption spectra of **P2** and **P3** could result from the rigid structure of the fused thiophene rings in the polymers. Probably, the steric repulsion between  $\beta$ -alkyl chains prevents the coplanarity of ring units and causes a decrease in the effective conjugation length of the polymer chain in **P3**. As reported in the literature,<sup>30</sup> the absorption peak of poly (3, 6-dinonylthieno[3, 2-*b*]thiophene) was blue-shifted a lot compared to that of poly(3-nonylthieno[3, 2-*b*]thiophene), because of steric repulsion between  $\beta$ -alkyl chains. In our work, the absorption peak of **P2** is very close to that of **P3**, which is probably due to the vinylene units in the main chains of **P2** and **P3**. The vinylene units in the main chains increase the

distance between two neighbor thieno [3, 2-b] thiophene rings, and thus decrease steric repulsion between  $\beta$ -alkyl chains.

Figure 4b shows the absorption of the polymer films on quartz plates. The absorption peaks of **P1**, **P2** and **P3** films are located at 580 nm, 538 nm and 542 nm, respectively. The absorption peaks of **P1** and **P3** films are red-shifted relative to that of their solutions by 24 and 4 nm respectively, which result from the interchain interactions in the polymer films. For **P2**, the absorption peak in solid state is very close to that of its solution, which suggests that the chain conformation is nearly identical under both conditions to **P2**. The absorption peak and edge wavelength of the polymers were outlined in Table 2.



**Figure 4.** Normalized absorption spectra of the polymers (a) in chloroform solutions; (b) films spin-coated on quartz plates.



**Figure 5.** Fluorescence spectra of the polymers in chloroform solutions (concentration  $10^{-5}$  M).

Interestingly, **P2** and **P3** show strong photoluminescence in the wavelength range between 500~750 nm peaked at ca. 650 nm, as shown in Figure 5. It is well known that poly (thienylenevinylene) is nonluminescent polymer. The strong PL spectra of **P2** and **P3** indicate that the fused thiophene units in the polymers influence the optical properties of the polymers greatly.

**Table 2.** Absorption spectral properties of **P1**, **P2** and **P3**.

Polymers	$\lambda_{\max}(\text{nm})/\text{in solutions}$	$\lambda_{\max}(\text{nm})/\text{in films}$	$\lambda_{\text{edge}}(\text{nm})/\text{in films}$
<b>P1</b>	556	580	712
<b>P2</b>	537	538	685
<b>P3</b>	538	542	700

### Electrochemical Properties.

The electrochemical property is one of the most important properties of the conjugated polymers and many applications of the conjugated polymers depend on the electrochemical properties. We studied the electrochemical properties of the polymers by cyclic voltammetry (CVs).

Figure 6 shows the cyclic voltammograms of the polymer films on Pt electrode. It can be seen that they exhibit *p*-doping/dedoping (oxidation/re-reduction) processes at positive potential range and *n*-doping/dedoping (reduction/re-oxidation) processes at negative potential range. From the onset oxidation potentials ( $\varphi_{\text{ox}}$ ) and the onset reduction potentials ( $\varphi_{\text{red}}$ ) of the polymers, HOMO and LUMO energy levels as well as the energy gap ( $E_{\text{g}}^{\text{ec}}$ ) of the polymers were calculated according to the following equations:<sup>31</sup>

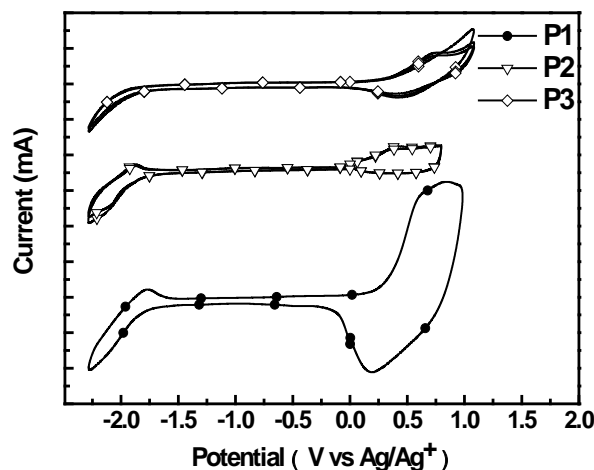
$$E_{\text{HOMO}} = -e (\varphi_{\text{ox}} + 4.71) \text{ (eV)};$$

$$E_{\text{LUMO}} = -e (\varphi_{\text{red}} + 4.71) \text{ (eV)};$$

$$E_{\text{g}}^{\text{ec}} = e (\varphi_{\text{ox}} - \varphi_{\text{red}}) \text{ (eV)}$$

Where the units of  $\varphi_{\text{ox}}$  and  $\varphi_{\text{red}}$  are V vs Ag/Ag<sup>+</sup>. The values obtained are listed in Table 3.  $\varphi_{\text{red}}$  of **P2** shifted negatively by 0.02 V compared to **P1**,  $\varphi_{\text{ox}}$  of **P2** shifted negatively by 0.09 V compared to **P1**,

and the electrochemical energy gap of **P2** is narrower than that of **P1** by 0.07 eV. The  $\phi_{\text{ox}}$  of **P3** is shifted positively by 0.12 V compared to **P1**, but the value of  $\phi_{\text{red}}$  is shifted negatively by 0.01 V compared to **P1**. The electrochemical energy gap of **P3** is larger than that of **P1** by 0.13 eV.



**Figure 6.** Cyclic voltammograms of the polymer films on Pt electrode in 0.1 mol/L  $\text{Bu}_4\text{NPF}_6$ ,  $\text{CH}_3\text{CN}$  solution at a scan rate of 100 mV/s.

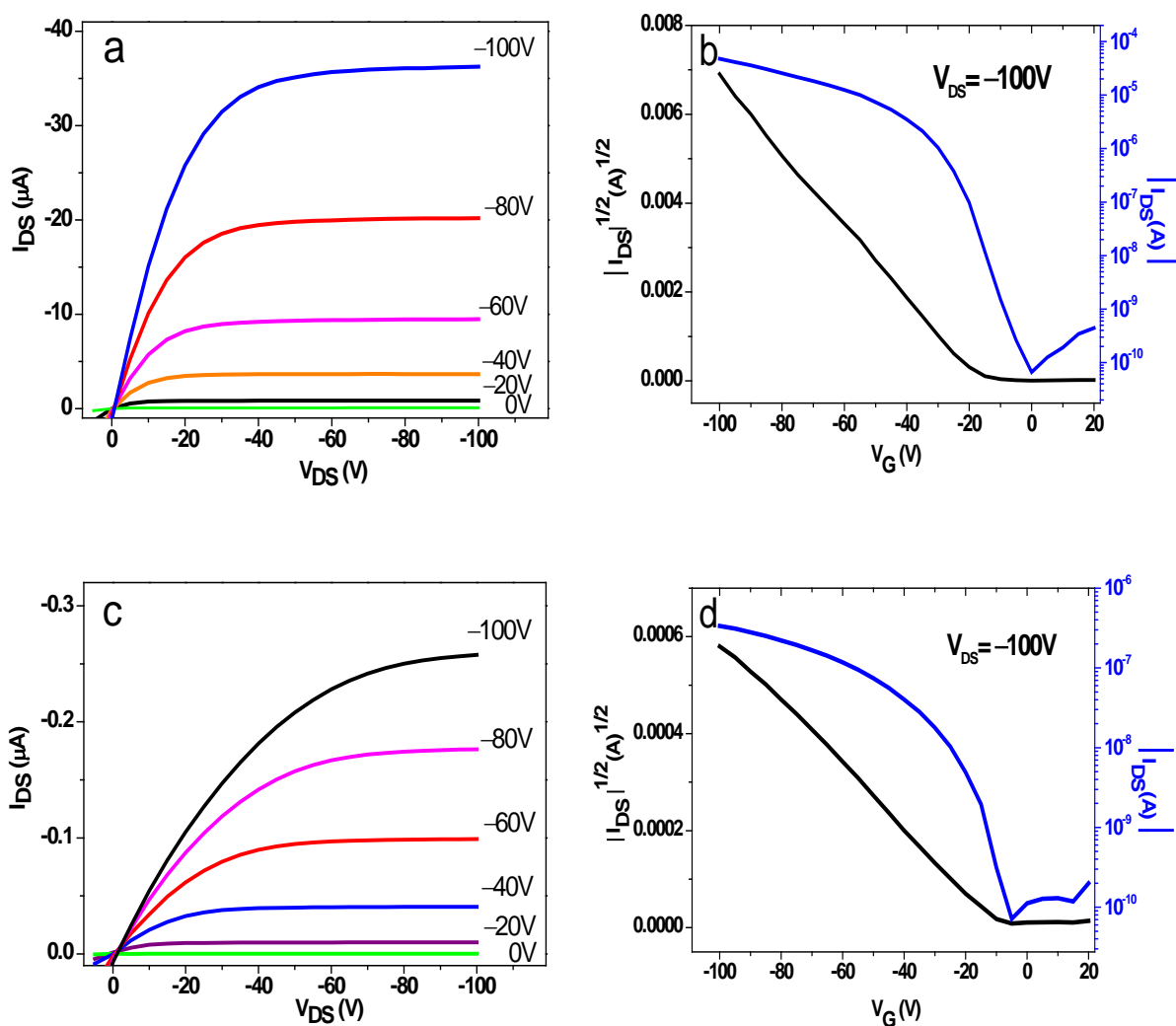
**Table 3.** Electrochemical onset potentials and electronic energy levels of the polymer films.

Polymers	$\phi_{\text{ox}}(\text{V vs Ag/Ag}^+)/E_{\text{HOMO}}(\text{eV})$	$\phi_{\text{red}}(\text{V vs Ag/Ag}^+)/E_{\text{LUMO}}(\text{eV})$	$E_{\text{g}}^{\text{ec}}(\text{eV})$	$E_{\text{g}}^{\text{opt}}(\text{eV})^{\text{a}}$
<b>P1</b>	0.21/-4.92	-1.73/-2.98	1.94	1.74
<b>P2</b>	0.12/-4.83	-1.75/-2.96	1.87	1.81
<b>P3</b>	0.33/-5.04	-1.74/-2.97	2.07	1.77

<sup>a</sup> the optical band gap was obtained from empirical formula,  $E_{\text{g}} = 1240/\lambda_{\text{edge}}$ , in which the  $\lambda_{\text{edge}}$  is the onset value of the absorption spectrum in the longer wavelength direction.

### Field-effect transistor properties of the polymers.

Figure 7 shows the typical output and transfer curves of a representative OFET device, and the device performances of the three polymers are summarized in Table 4. The output behaviors followed closely the metal oxide-semiconductor FET gradual channel model with very good saturation and no observable contact resistance (Figure 7a and 7c).



**Figure 7.** (a) Output and (b) transfer characteristics of OFETs using **P3** as active layer, (c) output and (d) transfer characteristics of OFETs using **P1** as active layer.  $I_{DS}$  was obtained at  $V_{DS} = -100$  V for transfer characteristics.

The transfer characteristics of **P3** show near-zero turn-on voltage and a small threshold voltage (Figure 7b), indicating its high air stability due to low HOMO ( $-5.04$  eV). Without annealing, the OFET with **P3** as active layer showed a mobility of  $4.64 \times 10^{-4}$   $\text{cm}^2/\text{Vs}$  in the saturation regime, together with an on/off ratio of  $10^3$  when measured in ambient conditions. Annealing the devices at  $150$  °C and  $180$  °C for  $0.5$  h led to improved charge carrier mobilities up to  $7.54 \times 10^{-3}$   $\text{cm}^2/\text{Vs}$  and  $0.019$   $\text{cm}^2/\text{Vs}$  respectively. The highest mobility of **P3** reached  $0.032$   $\text{cm}^2/\text{Vs}$  with the on/off ratio of  $10^5$ . The on/off ratio increased to  $10^4$ - $10^5$  (the highest on/off ratio is  $7.2 \times 10^5$ ) because of the increased drain current

and low current at zero gate voltage (below  $10^{-9}$  A). With low HOMO ( $-4.92$  eV), **P1** also showed very high air stability despite its relative low mobility (on the order of  $10^{-4}$   $\text{cm}^2/\text{Vs}$ ), in sharp contrast to that of most polymer semiconductors such as P3HT and its analogues. However, the devices fabricated with **P2** under similar conditions displayed poorer performance, with mobility of  $1.50 \times 10^{-4}$   $\text{cm}^2/\text{Vs}$  and low on/off ratio of  $10^2$ - $10^3$  without annealing, and even lower performance (with mobility of  $1.48 \times 10^{-5}$   $\text{cm}^2/\text{Vs}$  and on/off ratio of  $10^2$ - $10^3$ ) after annealing at high temperature. This is probably due to the low solubility of the polymer **P2**, the higher HOMO level ( $-4.83$  eV) and the roughness of its thin films (the surface of **P2** films appeared many small particles after annealing).

**Table 4.** FET properties of devices with films spun coated on OTS-modified  $\text{SiO}_2/\text{Si}$  substrates.

Polymers	HOMO	LUMO	Untreated		120 °C		180 °C	
			$\mu$ ( $\text{cm}^2/\text{Vs}$ )	$I_{\text{on}}/I_{\text{off}}$	$\mu$ ( $\text{cm}^2/\text{Vs}$ )	$I_{\text{on}}/I_{\text{off}}$	$\mu$ ( $\text{cm}^2/\text{Vs}$ )	$I_{\text{on}}/I_{\text{off}}$
<b>P1</b>	-2.98	-4.92	$2.02 \times 10^{-4}$	$10^3$	$3.12 \times 10^{-4}$	$10^3$	$3.76 \times 10^{-4}$	$10^3$ - $10^4$
<b>P2</b>	-2.96	-4.83	$1.50 \times 10^{-4}$	$10^2$	$2.17 \times 10^{-4}$	$10^2$ - $10^3$	$1.48 \times 10^{-5}$	$10^2$ - $10^3$
<b>P3</b>	-2.97	-5.04	$4.64 \times 10^{-4}$	$10^3$ - $10^4$	$7.54 \times 10^{-3}$	$10^4$ - $10^5$	0.019	$10^4$ - $10^5$

### Photovoltaic properties of the polymers.

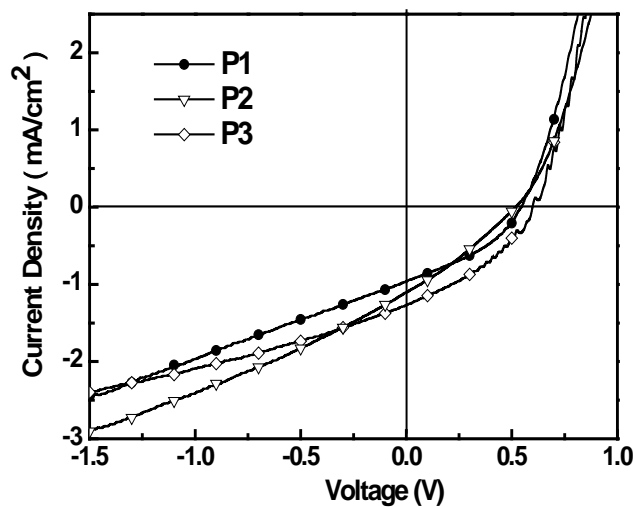
The motivation of design and synthesis of the three polymers is to look for novel thiophene vinylene polymers used in PSCs. We fabricate the PSCs with the structure of ITO/PEDOT-PSS/Polymer: PCBM (1:1, w/w)/Ca/Al, where the polymer (**P1**, **P2** and **P3**) was used as electron donor and PCBM was used as electron acceptor.

Figure 8 shows the  $I$ - $V$  curves of the PSCs under the illumination of AM 1.5,  $100 \text{ mW}/\text{cm}^2$ , and Table 4 lists the photovoltaic properties obtained from the  $I$ - $V$  curves for the best devices. In comparison with the device based on **P1**, the open circuit voltage ( $V_{\text{oc}}$ ) of the device based on **P2** decreased by ca 0.02 V. The lower  $V_{\text{oc}}$  is expected from the higher HOMO energy level of **P2** than that of **P1**. The  $V_{\text{oc}}$  of the device based on **P3** increased by ca 0.06 V compared with **P1**, which is benefited

from the lower HOMO energy level of **P3** than that of **P1**. For the best devices, the PCE of the devices based on **P3** reached 0.28%. The PCE of the device based on **P3** is ca. 50% increased than those of the devices based on **P1** and **P2**, which could be ascribed to the higher hole mobility of **P3**.

**Table 5.** Photovoltaic properties of the polymer solar cells.

Polymers	$V_{oc}(v)$	$I_{sc}(mA/cm^2)$	FF	HOMO(eV)	LUMO(eV)	PCE
<b>P1</b>	0.54	0.96	0.37	-4.92	-2.98	0.19%
<b>P2</b>	0.52	1.11	0.29	-4.83	-2.96	0.17%
<b>P3</b>	0.60	1.27	0.37	-5.04	-2.97	0.28%



**Figure 8.** I-V curves of the PSCs based on the polymers under the illumination of AM 1.5, 100  $mW/cm^2$

## Conclusions

Two poly (thieno [3, 2-b] thiophene vinylene) derivatives (**P2** and **P3**) were prepared by the Pd-catalyzed Stille-coupling method. Compared with poly (3-hexylthienylene vinylene) (**P1**), the absorption peaks of **P2** and **P3** are blue-shifted a little, while the PL intensity of **P2** and **P3** solutions enhanced greatly. The solution-processed polymer OFETs were fabricated with bottom gate/top contact geometry and characterized. The OFET using **P3** as active layers showed a hole mobility of  $4.64 \times 10^{-4}$  cm<sup>2</sup>/Vs in the saturation regime, together with an on/off ratio of  $10^3$  when measured in ambient conditions. Annealing the devices at 150 °C and 180 °C for 0.5 h led to improved hole mobilities of up to  $7.54 \times 10^{-3}$  cm<sup>2</sup>/Vs and 0.019 cm<sup>2</sup>/Vs respectively. The highest hole mobility of **P3** reached 0.032 cm<sup>2</sup>/Vs with the on/off ratio of  $10^5$ . However, the OFET devices based on **P2** under similar conditions displayed poorer performance, with hole mobility of  $1.50 \times 10^{-4}$  cm<sup>2</sup>/Vs and on/off ratio of  $10^2$ - $10^3$  without annealing, and even lower hole mobility of  $1.48 \times 10^{-5}$  cm<sup>2</sup>/Vs after thermal annealing at 180 °C for 0.5 h. This phenomenon could result from the lower solubility of **P2** and the roughness of its thin film after thermal annealing. PSCs based on the three polymers were fabricated, the PCE of the devices based on **P1**, **P2** and **P3** was 0.19%, 0.17% and 0.28%, respectively. The PCE of the device based on **P3** is ca. 50% increased than those of the devices based on **P1** and **P2**, which could be ascribed to the higher hole mobility of **P3**.

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## Figure captions:

**Figure 1.**  $^1\text{H-NMR}$  spectra of Compound **15**.

**Figure 2.**  $^1\text{H-NMR}$  spectra of polymer **P3**.

**Figure 3.** TGA plot of the polymers with a heating rating of  $10\text{ }^\circ\text{C/min}$  under inert atmosphere.

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**Figure 7.** (a) Output and (b) transfer characteristics of OFETs using **P3** as active layer, (c) output and (d) transfer characteristics of OFETs using **P1** as active layer.  $I_{\text{DS}}$  was obtained at  $V_{\text{DS}} = -100\text{ V}$  for transfer characteristics.

**Figure 8.**  $I-V$  curves of the PSCs based on the polymers under the illumination of AM 1.5,  $100\text{ mW/cm}^{-2}$ .