



# Synthesis and characterization of pendant phenyl ester-substituted thiophene based copolymers



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## ABSTRACT

In an attempt to synthesize low band gap copolymers, three new monomers 3-ethyl-2-(2,5-dibromothiophene)-3-ylacetate (**ETA**), 3-phenylethyl-2-(2,5-dibromothiophene)-3-ylacetate (**PTA**), and 3,3-diphenylpropyl-2-(2,5-dibromothiophene)-3-ylacetate (**DPTA**) were synthesized. **ETA**, **PTA**, and **DPTA** were copolymerized with 2,5-bis(trimethylstannyl)thiophene to yield poly[3-ethyl 2-(thiophene-3-yl)acetate-2,2'-thiophene] (**PETAT**), poly[3-phenylethyl 2-(thiophene-3-yl)acetate-2,2'-thiophene] (**PPTAT**) and poly[3,3-diphenylpropyl 2-(thiophene-3-yl)acetate-2,2'-thiophene] (**PDPTAT**) respectively. Additionally, these mildly electron-donating monomers as well as 2,5-bis(trimethylstannyl)thiophene were incorporated with the electron withdrawing monomer, 4,7, dibromobenzo[c]-1,2,5-thiadiazole (**BT**), to develop three push-pull polymeric systems; poly[3-ethyl 2-(thiophene-3-yl)acetate-2,2'-thiophene-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl] (**PETATBT**), poly[3-phenylethyl 2-(thiophene-3-yl)acetate-2,2'-thiophene-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl] (**PPTATBT**), and poly[3,3-diphenylpropyl 2-(thiophene-3-yl)acetate-2,2'-thiophene-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl] (**PDPTATBT**). Copolymers **PETAT**, **PPTAT**, and **PDPTAT** exhibit band gaps from 1.94–1.92 eV respectively, where as **PETATBT**, **PPTATBT**, and **PDPTATBT** show a reduction in the band gaps to 1.66–1.48 eV. The impact of the phenyl moiety was investigated using atomic force microscopy; increased order within films of **PPTAT** and **PPTATBT** can be attributed to the increased  $\pi$ - $\pi$  stacking in the solid state from the pendant phenyl moiety.

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## 1. Introduction

Currently,  $\pi$ -conjugated polymers have a large number of applications such as organic light-emitting diodes (OLEDs), semiconductors and organic field effect transistors (OFETs) [1]. Applications in polymer solar cells (PSCs) have been of increasing interest in the field of solar energy due to the strong light harvesting capabilities, low production costs and the variable solubility of the polymers [2]. Bulk heterojunction (BHJ) PSCs containing poly-3-hexylthiophene (P3HT) as the electron-donor material and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) as the organic electron-acceptor are the most extensively studied and mechanistically well understood [3]. The device performance is heavily dependent on the morphology and supramolecular structure of the P3HT and related poly(3-alkyl)thiophenes (P3ATs) and have therefore been intensely studied [4]. X-Ray diffraction studies have shown that lamellar structures with regions filled by alkyl side-

chains separated by parallel stacks of polymer main-chains is the common crystalline polymorph [4][4d]. These properties allow for the device performance to be optimized however, P3HT only absorbs photons up to 650 nm when optimized and therefore these subsequent devices only exhibit power conversion efficiencies up to 4–5% [5].

Recently, a class of “push-pull” copolymers, which consists of alternating electron withdrawing and electron donating blocks, have been developed [6]. These components increase the double bond character between the units, thereby stabilizing the quinoidal resonance form of the polymer, which in turn decreases the band gap of the copolymer [7]. This class of copolymers is very attractive because of the ability to tune the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values of the material. The HOMO levels are dictated by the electron-donating monomer and the LUMO by the electron-withdrawing monomer [8]. One such polymer, poly[(4,4-bis(2-ethylhexyl)-cyclopenta-[2,1-*b*;3,4-*b'*]dithiophene)-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl] (PCPDTBT) has HOMO levels similar to P3HT, however the lower lying LUMO explains its ability to harvest light from a larger

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portion of the solar spectrum [6][6d]. BHJ devices made in a similar fashion to those with P3HT do not display a high efficiency due to poorly ordered morphology [6d,9]. Improved efficiency has been documented when high boiling additives are used while solution processing the materials because they affect the degree of phase separation between the donor/acceptor materials as well as the polymorph size, perfection and population of PCPDTBT crystallites [5,10].

Structural modifications to low band-gap polymers have also recently been investigated. These structures include the introduction of carbazole derivatives [11] and silicon atoms substituted at the 9-position of the fluorene [12]. Similarly to PCPDTBT, these structures also absorb a wide range of the solar spectrum but suffer from low device efficiencies due to poorly ordered structures. In order to improve the ordered solid state packing of these polymers, the addition of  $\pi$ -conjugated side chains have been of increasing interest [13]. However, the addition of these modifications negatively affects the solubility of these materials and has proven to be rather synthetically challenging. Recently, Yamamoto synthesized a library of thieno[3,4-*b*]thiophene-cobenzo[1,2-*b*:4,5-*b'*]dithiophene based copolymers with pendant phenyl ester substituents [14]. The use of the ester functionality provides a synthetic handle that is easily modified allowing facile incorporation of aromatic functionality. However, some of these polymeric structures still displayed poor solubility in common organic solvents. Herein we describe the synthesis of thiophene-based monomers with ethyl, phenyl, and diphenyl ester pendant groups. Two series of copolymerizations were then performed. The first between the ester containing monomers and 2,5-bis(trimethylstannyl)thiophene, while the second incorporated 4,7-dibromobenzo[*c*]-1,2,5-thiadiazole (**BT**), as an additional comonomer. The facile incorporation of these ester moieties has allowed for tuning of the band gap energy ( $E_g$ ) as well as improved film morphologies with increasing  $\pi$ - $\pi$  stacking of the pendent phenyl rings while maintaining favorable solubilities.

## 2. Experimental

### 2.1. Materials and instrumentation

3-Thiopheneacetic acid, 2-phenylethanol, 3,3-diphenyl-1-propanol, *N*-bromosuccinimide, 4,7-dibromobenzo[*c*]-1,2,5-thiadiazole, 2,5-bis(trimethylstannyl)thiophene, sulfuric ( $H_2SO_4$ ), 95% ethanol and acetic acid ( $CH_3COOH$ ) were used as received from Sigma Aldrich. Tetrakis(triphenylphosphine)palladium(0) was used as received from Strem Chemicals. All solvents were obtained from an Innovative Technology Solvent Purification System and were degassed before use. Absorption spectra were obtained using an HP 8453 Diode Array. Emission spectra were obtained on a Jasco FP8500. The molecular weight of the polymers was determined on a Polymer Labs GPC-50 Plus in BHT stabilized THF using polystyrene standards. AFM was performed on a Nanoscience Instruments NanoSurf using tapping mode with 160 MHz resonance frequency tip. Cyclic Voltammetry was performed on a single cell CH Instruments Electrochemical Analyzer. Nuclear magnetic resonance ( $^1H$  NMR and  $^{13}C$  NMR) spectra were obtained using a Bruker Advance DPX-400 or 300 NMR spectrometer; chemical shifts are reported in ppm downfield from tetramethylsilane ( $\delta$  scale).

### 2.2. Preparation of 3-ethyl-2-thiophene-3-ylacetate (1)

Degassed 95% ethanol was added to a dry 25 mL flask under inert atmosphere. 3-Thiopheneacetic acid (0.853 g, 6.0 mmol) was added followed by 98% sulfuric acid (0.060 g, 0.6 mmol) via syringe

in succession. The reaction mixture was refluxed at 120 °C for 20 h under  $N_2$ . The resulting yellow reaction mixture was washed two times with  $H_2O$  (~10 mL). The organic layer was subsequently dried with  $Na_2SO_4$  and excess solvent was removed under vacuum to yield yellow oil (0.713 g, 48% yield). NMR  $^1H$  ( $CDCl_3$ ) (Th=thiophene): 1.29 (t, 3H,  $J_{H-H}$  = 7.1 Hz, Th- $CH_2COOCH_2CH_3$ ), 3.67 (s, 2H, Th- $CH_2COOCH_2CH_3$ ), 4.19 (q, 2H,  $J_{H-H}$  = 7.1 Hz Th- $CH_2COOCH_2CH_3$ ) 7.07 (d of d, 1H,  $J_{Ha-Hb}$  = 4.95 Hz,  $J_{Hb-Hc}$  = 1.44 Hz, 4-position, Th- $CH_2COOCH_2CH_3$ ), 7.17–7.19 (m, 1H, 5-position, Th- $CH_2COOCH_2CH_3$ ), 7.31 (d of d, 1H,  $J_{Ha-Hb}$  = 4.95 Hz,  $J_{Ha-Hc}$  = 2.95 Hz, 2-position, Th- $CH_2COOCH_2CH_3$ ), NMR  $^{13}C$  ( $CDCl_3$ ): 14.3, 36.0, 61.0, 122.8, 125.8, 128.6, 133.8, 171.3.

### 2.3. Preparation of 3-phenylethyl-2-thiophene-3-ylacetate (2)

Anhydrous toluene (~20 mL) and 98% sulfuric acid (0.180 g, 1.8 mmol) were added to a dry 50 mL flask under inert atmosphere. 3-Thiopheneacetic acid (2.484 g, 18.0 mmol) and 2-phenylethanol (2.15 mL, 18.0 mmol) and were added via syringe in succession. The reaction mixture was refluxed at 120 °C for 20 h under  $N_2$ . The black/yellow reaction mixture was washed two times with  $H_2O$  (~10 mL). The organic layer was subsequently dried with  $Na_2SO_4$  and solvent was removed under vacuum to yield brown/yellow oil (3.815 g, 88% yield). NMR  $^1H$  ( $CD_2Cl_2$ ) (Th=thiophene): 2.93 (t, 2H,  $J_{H-H}$  = 7 Hz, Th- $CH_2COOCH_2CH_2-Ph$ ), 3.63 (s, 2H, Th- $CH_2COOCH_2CH_2-Ph$ ), 4.30 (t, 2H,  $J_{H-H}$  = 6.9 Hz Th- $CH_2COOCH_2CH_2-Ph$ ) 6.99 (d of d, 1H,  $J_{Ha-Hb}$  = 4.95 Hz,  $J_{Hb-Hc}$  = 1.36 Hz, 4-position Th- $CH_2COOCH_2CH_2-Ph$ ), 7.13–7.15 (m, 1H, 5-position, Th- $CH_2COOCH_2CH_2-Ph$ ), 7.21–7.35 (overlapping m, 6H, Th- $CH_2COOCH_2CH_2-Ph$ ); NMR  $^{13}C$  ( $CDCl_3$ ): 35.0, 35.9, 65.3, 122.9, 125.7, 126.6, 128.5, 128.9 133.5, 137.7, 171.0. The  $^{13}C$  NMR should display twelve unique carbons for **2**, however only eleven are observed. A spectrum calculated with MestraNova software indicates resonances at 128.75 and 128.87 for the ortho and meta carbons of the phenyl ring. The resonance observed at 128.9 is attributed to these two carbons.

### 2.4. Preparation of 3,3-diphenylpropyl-2-thiophene-3-ylacetate (3)

Anhydrous toluene (~12 mL) and 98% sulfuric acid (0.120 g, 1.2 mmol) were added to a dry 50 mL flask under inert atmosphere. 3-Thiopheneacetic acid (1.706 g, 12.0 mmol) and 3,3-diphenyl-1-propanol (2.55 mL, 12.0 mmol) was added via syringe in succession. The reaction mixture was refluxed at 120 °C for 20 h under  $N_2$ . The yellow/orange reaction mixture was washed two times with  $H_2O$  (~10 mL). The organic layer was subsequently dried with  $Na_2SO_4$  and excess solvent was removed under vacuum to yield yellow oil (3.582 g, 88% yield). NMR  $^1H$  ( $CDCl_3$ ) (Th=thiophene): 2.40 (q, 2H,  $J_{H-H}$  = 7.2 Hz Th- $CH_2COOCH_2CH_2CH-Ph_2$ ) 3.64 (s, 2H, Th- $CH_2COOCH_2CH_2CH-Ph_2$ ), 4.01 (t, 2H,  $J_{H-H}$  = 7.8 Hz Th- $CH_2COOCH_2CH_2CH-Ph_2$ ), 4.08 (t, 2H,  $J_{H-H}$  = 6.7 Hz, Th- $CH_2COOCH_2CH_2CH-Ph_2$ ), 7.07 (d of d, 1H,  $J_{Ha-Hb}$  = 4.95 Hz,  $J_{Hb-Hc}$  = 1.28 Hz, 4-position Th- $CH_2COOCH_2CH_2CH-Ph_2$ ), 7.18–7.22 (m, 9H, Th- $CH_2COOCH_2CH_2CH-Ph_2$ ), 7.26–7.34 (overlapping m, 3H, Th- $CH_2COOCH_2CH_2CH-Ph_2$ ); NMR  $^{13}C$  ( $CDCl_3$ ): 34.2, 35.9, 47.5, 63.3, 122.9, 125.8, 126.4, 127.8, 128.5 128.6, 133.7, 143.9, 170.9.

### 2.5. Preparation of 3-ethyl-2-(2,5-dibromothiophene)-3-ylacetate (ETA)

Compound **1** (0.712 g, 4.2 mmol) was added to a 100 mL round-bottom flask followed by 50 mL of a 1:1 mixture by volume of chloroform and acetic acid. *N*-Bromosuccinimide (1.81 g, 10.8 mmol) was added to the reaction mixture and the reaction was

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