



# The influence of electron-deficient comonomer on chain alignment and OTFT characteristics of polythiophenes

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## ARTICLE INFO

### Article history:

Received 17 June 2010

Received in revised form 24 August 2010

Accepted 26 August 2010

Available online 28 September 2010

### Keywords:

Conjugated polymers

Polythiophenes

Stille polymerization

Structure–property relations

Thiazole

Transistors

## ABSTRACT

The structure–property relations of polythiophene derivatives have been the subject of research for both materials and electronic device applications. We have designed and prepared two kinds of polythiophene derivatives with similar chemical structures but different electronic properties by Stille polymerization. One is composed of only electron-rich thiophenes (PQT2T), while the other is composed of both electron-rich thiophenes and electron-deficient thiazoles (PTZT2T). The number-average molecular weights of PQT2T and PTZT2T were 23,000 (PDI = 1.5) and 13,000 (PDI = 1.7), respectively. PTZT2T showed a large bathochromic shift of absorption maximum from solution to film by 57 nm. Further investigation by differential scanning calorimetry and X-ray diffraction revealed the formation of well-ordered interdigitated structure of PTZT2T in the solid state ( $d_1 = 20.7 \text{ \AA}$ ). From absorption onset, optical band-gap of PQT2T and PTZT2T was calculated to be 2.22 eV and 1.92 eV, respectively. A mobility of  $1.1 \times 10^{-3} \text{ cm}^2/\text{Vs}$ , an on/off ratio of  $4.7 \times 10^4$  have been obtained from organic thin-film transistors (OTFTs) using PTZT2T as a channel. By comparison with PQT2T, the mobility was 18 times and the on/off ratio was 52 times higher for PTZT2T, which shows the usefulness of electron-deficient thiazoles as comonomer units of polythiophene derivatives for OTFT applications.

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## 1. Introduction

In recent years, enormous research effort has been given to the development of organic semiconductors. The research interest in these materials is driven by the manifold applications such as organic light-emitting diodes (OLEDs) [1], organic thin-film transistors (OTFTs) [2], organic photovoltaic cells (OPVCs) [3], etc. These organic electronic devices are attractive owing to their low production cost by solution/printing processes, and their light, thin, and flexible characteristics which are essential to next-generation electronic devices. In particular, thiophene-based  $\pi$ -conjugated materials have been widely used as *p*-type semiconductors in OTFTs due to their high charge-carrier mobility and solution processability [4,5]. There have been many attempts to systematically control the optical and electronic properties of such polythiophenes by designing novel chemical structures. For example, unsubstituted bithiophene (PQT) [6] or fused thienothiophene (PBTTT) [7] has been introduced into the polythiophene main-chain, which resulted in an improvement of OTFT characteristics compared with regioregular poly(3-hexylthiophene) (P3HT).

To increase the electron density of the polymer main-chain, more electron-rich selenophene has also been introduced instead of thiophene (PDTSe2) [8], and well-ordered structure was obtained with those selenophene-containing polymers (PTmSe) [9]. Furthermore, the optical and electronic properties of polythiophenes could also be tuned by introducing alkylsulfanyl side-chains (SPQT) instead of alkyl side-chains without modification of main-chain structures [10].

Unlike the above-mentioned examples which are mostly composed of electron-rich units, introduction of relatively electron-deficient comonomers into the polythiophenes has also been reported. For example, copolymers of bithiophene and bithiazole were applied to OTFTs, and their packing structures were also investigated [11]. In addition, the introduction of electron-deficient thiazole units was reported to exhibit high charge-carrier mobility and good bias-stress stability as well as ordered intermolecular stacking [12]. High-lamellar ordering and high carrier mobility were also observed from polythiophenes containing fused thiazolothiazole units (PTzQT) [13]. This design concept, which utilizes electron-deficient thiazoles as the main-chain building units of the polymers, has not only been limited to OTFTs, but also applied to OPVCs [14–16].

As is shown from the above examples, various approaches are possible to the designing of high performance OTFT channel materials. However, there is something in common throughout

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the approaches, that is, molecular ordering of the polymers. The charge transport in conjugated polymers occurs by combination of intra-chain charge transport and inter-chain charge transport. In particular, the inter-chain charge transport is usually known to be slower than the intra-chain charge transport, so the overall charge-carrier mobility of the polymer is dominated by the inter-chain charge transport. Control of inter-chain interactions among the polymer chains is therefore an important issue in OTFT research.

In this paper, we report new  $\pi$ -conjugated polymers composed of thiophene and thiazole units, and investigated the effect of electron-deficient thiazole comonomer on the optical, physical and electrochemical properties of the thiophene-based polymers. Two kinds of polymers (PQT2T and PTZT2T) with similar chemical structures but different electronic properties have been designed and synthesized for the purpose of structure–property relations comparison. While the two polymers are structurally very similar, they showed quite different characteristics from ultraviolet–visible (UV–vis) spectroscopy, differential scanning calorimetry (DSC), and X-ray diffraction (XRD) analyses. The main difference between PQT2T and PTZT2T was revealed to ordering and alignment characteristics of the polymer chains. OTFT device characteristics of the two polymers were also examined, and the existence of thiazole units in the main-chain of the polymer resulted in an improvement in OTFT performances.

## 2. Experimental

### 2.1. Materials

2,2'-Bithiophene, *n*-butyllithium (*n*-BuLi) (2.5 M solution in hexane), trimethyltin chloride (1.0 M solution in tetrahydrofuran (THF)), *N*-bromosuccinimide (NBS) and tetraethylammonium iodide were purchased from Aldrich Co. Tris(dibenzylideneacetone)dipalladium(0) ( $\text{Pd}_2(\text{dba})_3$ ), tri-*o*-tolylphosphine ( $\text{P}(o\text{-tol})_3$ ), and dibromobis(triphenylphosphine)nickel(II) were purchased from Strem Co. Activated Zn was purchased from Rieke Metals Inc. Anhydrous-grade tetrahydrofuran and chlorobenzene were used throughout the experiments. All other chemicals were commercially available and used without further purification.

### 2.2. Instrumentation and characterization

The microwave reactions were carried out using a CEM Discover microwave reactor in sealed vessels. The nuclear magnetic resonance (NMR) spectra were recorded at room temperature using a Bruker 300 NMR spectrometer. Gel permeation chromatography (GPC) was conducted using Shodex<sup>®</sup> KF-800 series columns with chloroform as an eluent to obtain molecular weight and molecular weight distribution (relative to polystyrene standards). Absorption spectra were measured using a SHIMADZU UV-2550 UV–Visible Spectrophotometer. Thermogravimetric analysis (TGA) measurements of the polymers were performed under nitrogen atmosphere at a heating rate of 10 °C/min using TA Q500 instrument. Differential scanning calorimetry (DSC) was carried out using a NETZSCH DSC 204 F1 Phoenix<sup>®</sup> under nitrogen purging. Cyclic voltammetric measurements were performed on a BAS 100 voltammetric system with a three-electrode cell in a solution of 0.10 M tetrabutylammonium tetrafluoroborate in acetonitrile at a scanning rate of 50 mV/s. An Ag/Ag<sup>+</sup> electrode (0.01 M AgNO<sub>3</sub> in acetonitrile) was used as a reference electrode, and platinum wires were used as a counter electrode and a working electrode, respectively. X-ray diffraction measurements were performed at room temperature on a D/Max III-B. Current–voltage characteristics of the OTFT devices were measured using Agilent 4155C semiconductor parameter analyzer.

### 2.3. Synthesis of the monomers and polymers

#### 2.3.1. 5,5'-Bis(trimethylstannyl)-2,2'-bithiophene (**2**)

To a solution of 2,2'-bithiophene (5 g, 0.03 mol) in THF (240 mL), 2.5 M solution of *n*-BuLi in hexane (28.8 mL, 0.072 mol) was added dropwise at –78 °C. The solution was stirred at –78 °C for 30 min and at room temperature for another 2 h. The solution was cooled again to –78 °C, and 1.0 M solution of trimethyltinchloride in THF (72 mL, 0.072 mol) was added in one portion. After stirring 2 h at –78 °C, the mixture was poured into water and extracted with ethyl acetate. The organic layer was washed thrice with water and dried over magnesium sulfate. After removing the solvent, the residue was purified by crystallization in methanol to give the product (yield 80%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.24–7.23 (d, 1H), 7.06–7.05 (d, 1H), 0.36 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.98, 136.99, 135.82, 124.81, –8.23.

#### 2.3.2. 5,5'-Bis(trimethylstannyl)-2,2'-bithiazole (**3**)

The compound **3** was synthesized using the same method as for the compound **2** with 2,2'-bithiazole (1.7 g, 0.01 mol), 2.5 M solution of *n*-BuLi in hexane (9.6 mL, 0.024 mol), 1.0 M solution of trimethyltinchloride in THF (24 mL, 0.024 mol) (yield 80%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.80 (s, 1H), 0.44 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 166.14, 150.05, 132.05, –8.05.

#### 2.3.3. 5,5'-Bis(4-dodecylthiophene-2-yl)-2,2'-bithiophene (**4**)

A solution of 2-bromo-3-dodecylthiophene (2.96 g, 8.94 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (2 g, 4.06 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.074 g, 0.0812 mmol), tri-*o*-tolylphosphine (0.098 g, 0.324 mmol) were dissolved in chlorobenzene under nitrogen. The solution was stirred at 100 °C for 12 h under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with chloroform. The organic layer was washed thrice with water and dried over magnesium sulfate. The solvent was evaporated and the residue was purified by column chromatography on silica gel with 4:1 *n*-hexane/dichloromethane to give the product (yield 62%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.16–7.14 (d, 1H), 7.10–7.09 (d, 1H), 7.00–6.99 (d, 1H), 6.92–6.91 (d, 1H), 2.78–2.73 (d, 2H), 1.62–1.60 (t, 2H), 1.34–1.23 (m, 18H), 0.87–0.82 (t, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.50, 137.01, 134.03, 132.69, 131.66, 126.93, 123.96, 110.63, 31.92, 30.51, 29.67, 29.65, 29.55, 29.39, 29.36, 29.12, 22.69, 14.13.

#### 2.3.4. 5,5'-Bis(4-dodecylthiophene-2-yl)-2,2'-bithiazole (**5**)

The compound **5** was synthesized using the same method as for the compound **4** with 2-bromo-3-dodecylthiophene (2.7 g, 8.12 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiazole (2 g, 4.04 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.074 g, 0.0809 mmol), tri-*o*-tolylphosphine (0.098 g, 0.323 mmol) (yield 60%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.83 (s, 1H) 7.24–7.22 (d, 1H), 6.95–6.93 (d, 1H), 2.76–2.71 (t, 2H), 1.64–1.59 (t, 2H), 1.33–1.22 (m, 18H), 0.84–0.82 (t, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 160.23, 141.94, 141.34, 133.44, 130.24, 126.01, 125.34, 31.91, 30.58, 29.63, 29.57, 29.50, 29.46, 29.42, 29.34, 22.69, 14.12.

#### 2.3.5.

#### 5,5'-Bis(5-bromo-4-dodecylthiophene-2-yl)-2,2'-bithiophene (**6**)

Into a stirred solution of 5,5'-bis(4-dodecylthiophene-2-yl)-2,2'-bithiophene (0.4 g, 0.599 mmol) in chloroform–acetic acid (1:1), NBS (0.21 g, 1.229 mmol) was added portionwise, and the mixture was stirred at room temperature for an hour. It was then hydrolyzed with water followed by addition of dichloromethane. The organic layer was washed thrice with water and dried over

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