Design and Synthesis of Alternating Regioregular Oligothiophenes/Benzothiadiazole Copolymers for Organic Solar Cells

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ABSTRACT: Low-bandgap regioregular polythiophene derivatives, PTh₆BTD, PTh₈BTD, and PTh₈TBTBD, were synthesized through Stille coupling reaction. These are alternating copolymers of an electron-deficient benzothiadiazole unit and oligothiophene units including hexathiophene, octathiophene, and thieno[3,2-b]thiophene-bridged quarterthiophene, respectively. The polymers are soluble in halogenated solvents such as o-dichlorobenzene, affording good processability in solar cell fabrication. Meanwhile, the synthesized alternating copolymers show much broader absorption than P3HT, covering the spectral region from 350 to 800 nm. DSC analysis showed that all three polymers readily crystallized, indicating highly ordered intermolecular packing, which is beneficial for achieving higher charge carrier mobility. Bulk-heterojunction solar cells using 1:1 w/w PTh₆BTD:PC₆₁BM ([6,6]-phenyl C₆₁-butyric acid methyl ester) blends as the photovoltaic active layers were fabricated and characterized. Best power conversion efficiency of 1.7% was obtained from PTh₆BTD-based devices under a simulated AM 1.5 G solar irradiation of 100 mW/cm².

Introduction

Despite facing challenges in long-term stability,¹ organic solar cells based on conjugated polymers and soluble fullerene derivatives have attracted a great deal of attention due to their solution processability, mechanical flexibility, and the potential for low-cost large-area manufacturing.² Recently, power conversion efficiencies in the 5% range have been reported independently by several groups based on poly(3-hexylthiophene)/[6,6]-phenyl C₆₁ butyric acid methyl ester (P3HT:PC₆₁BM) bulk heterojunction (BHJ) solar cells.³⁻⁶ Although P3HT is one of the most promising materials ever tested in polymeric solar cells, the mismatch between its relatively large band gap (2.0 eV) and the energy distribution of the solar spectrum leads to insufficient light absorption and limits the further improvement in the power conversion efficiency. Hence, it is necessary to lower the bandgap to move the absorption toward longer wavelengths. In this regard, low-bandgap polymers based on internal electron donor–acceptor (D–A) interaction have been developed. For instance, in 2006, Inganaes et al. reported low-bandgap alternating fluorene copolymers containing electron-withdrawing thiophene, quinoxaline,²⁰ Muellbacher presented a copolymer of cyclopenta-dithiophene and 2,1,3-benzothiadiazole with a low bandgap of 1.73 eV,³ and more recently, Leclerc and co-workers developed a low-bandgap poly(2,7-carbazole) derivative demonstrating a power conversion efficiency of 3.6% when blended with PC₆₁BM as the photovoltaic (PV) active layer, and the efficiency was further improved to 6.1% after device optimization.⁹

On the other hand, due to strong interchain interaction in the solid state, some representative polythiophene systems like poly(3-hexylthiophene) (P3HT),³⁵ polyterthiophene (PTT),¹⁰ polyquarterthiophene (PQT),¹¹ and poly(2,5-bis(3-alkythiophen-2-yl)thieno[3,2-b]thiophene) (PBTT)²⁰ show high charge carrier mobility, which is a very attractive feature and critically important for high-performance solar cells. Our strategy to develop low-bandgap polymers with high charge carrier mobility is to introduce a frequently used electron-deficient 2,1,3-benzothiadiazole (BTD) unit into the polythiophene main chain to lower the bandgap and to increase the number of thiophene rings in the oligothiophene segments for better interchain packing and solubility. With these in mind, 2,1,3-benzothiadiazole-cored regioregular oligothiophene monomers were designed and synthesized. Our recent work demonstrated that these oligothiophene monomers can be used as novel building blocks to construct crystalline polymeric materials for solar cell applications via copolymerization with other π-conjugated compounds such as indolo[3,2-b]carbazole.¹³ In this work, these oligothiophenes were copolymerized with 5,5’-bis(stannyl)-2,2’-bithiophene or 2,5-bis(stannyl)thieno[3,2-f]thiophene via Stille reaction, resulting in three crystalline alternative copolymers, PTh₆BTD, PTh₈BTD, and PTh₈TBTBD, as shown in Scheme 1. The length of the oligothiophene unit varied from 6 to 8 thiophene rings and thieno[3,2-b]thiophene-bridged 4 thiophene rings. To our knowledge, there are a few examples in the literature on the low-bandgap copolymers consisting of oligothiophenes and electron acceptors (quinoxaline,⁴ oxadiazole,¹⁵ benzothia-diazole,¹⁶ or thiazolothiazole¹⁷). However, the maximum number of thiophene rings in the oligothiophene segments is no more than 4. Some of these polymers exhibited poor solubility in common organic solvents due to the lack of enough amount of alkyl side chains, and some polymers were synthesized via the oxidative polymerization method, in which the oxidant needs to be removed. In the previous work on the copolymers of oligothiophenes and benzothiadiazole, the best efficiency achieved was less than 1%.¹⁶
In this paper, we present the synthesis of PTh6BTD, PTh8BTD, and PTh4TTBTD, followed by a detailed discussion on their optical, thermal, electrochemical, and photovoltaic properties, and demonstrate that with rational design of the substitution pattern of the substituents, low-bandgap semiconducting polymers with both high crystallinity and good solubility can be obtained. The initial study of the bulk-heterojunction solar cells using 1:1 w/w PTh8BTD:PC61BM blend as the PV active layer showed a power conversion efficiency of 1.7% under a simulated AM 1.5 G solar irradiation at 100 mW/cm².

Results and Discussion

Synthesis. Two key monomers 4 and 6, dibrominated oligothiophenes incorporating benzothiadiazole in the center, were prepared in a divergent method from 4,7-dibromobenzothiadiazole via a repetitive Stille coupling and NBS bromination procedure (Scheme 2). We also attempted to synthesize quarterthiophene end-capped benzothiadiazole from compound 6 but failed due to the purification problem. It is worth pointing out that the bromination condition was different for each cycle in order to get high bromination yield at the desired position. For example, 4,7-dibromo-2,1,3-benzothiadiazole was synthesized using liquid Br2 as the brominating agent in 47% HBr solution with refluxing, while 4,7-bis(4-octyl-2-thienyl)-2,1,3-benzothiadiazole was readily brominated with N-bromosuccinimide (NBS) at room temperature.
in the presence of silica gel as a catalyst. In contrast, the bromination of 4,7-bis(3,4,4',5'-octyl-2,2',5'-terthiophen-5-yl)-1,2,3-benzothiadiazole should be performed under even milder condition, such as at $-10^\circ$C. Otherwise, bromination would also occur at other positions, leading to the formation of a mixture that is difficult to purify.

All three polymers PTh$_x$BTD, PTh$_x$BTD, and PTh$_x$TTBTD were successfully synthesized by Stille coupling between 5,5'-bis(trimethylstannyl)-2,2'-bithiophene or 2,5-bis(stannyl)thieno[3,2-b]thiophene and appropriate dibromo compounds in anhydrous toluene at $110^\circ$C for 36 h. Since the palladium catalyst is quite sensitive to oxygen and light, the polymerization reaction was run in the dark using a standard Schlenk technique. To increase the stability of the polymers, end-capping reactions were performed using

Figure 2. Absorption spectra of polymers PTh$_x$BTD, PTh$_x$BTD, and PTh$_x$TTBTD in 1,2-dichlorobenzene solution and in solid film state (50 nm thick). The annealing temperatures for PTh$_x$BTD, PTh$_x$BTD, and PTh$_x$TTBTD films are 120, 100, and 200 $^\circ$C, respectively.

Figure 3. Second scan DSC curves of PTh$_x$BTD and PTh$_x$BTD. PTh$_x$TTBTD at a heating/cooling rate of 10 $^\circ$C under nitrogen.

2,5-bis(stanny)thieno[3,2-b]thiophene and appropriate dibromo compounds in anhydrous toluene at $110^\circ$C for 36 h. Since the palladium catalyst is quite sensitive to oxygen and light, the polymerization reaction was run in the dark using a standard Schlenk technique. To increase the stability of the polymers, end-capping reactions were performed using
bromobenzene and 2-stannyliophene. The polymers were purified through Soxhlet extraction in refluxing acetone for 12 h and then in hexane for an additional 12 h to remove oligomers. PTh4TTBTD was further extracted with THF.

Finally, high-molecular-weight polymers were extracted with chlorobenzene, concentrated, and precipitated in methanol. Black fibers for three polymers (PTh8BTD, PTh6BTD, and PTh4TTBTD) were obtained in moderate yields of 49%, 63%, and 45%, respectively. PTh8BTD was soluble in refluxing toluene, and no polymer precipitated out of solution during polymerization. As a result, high-molecular-weight PTh8BTD with narrow polydispersity was obtained in relatively higher yield. As shown in Figure 1, GPC analysis (gel permeation chromatography) showed that the number-average molecular weight \( M_n \) of polymer PTh8BTD reached as high as 32 000 \((M_n/M_w = 1.25)\). On the contrary, polymers PTh8BTD and PTh4TTBTD precipitated out during polymerization due to their rigid backbone and hence lower solubility in refluxing toluene, leading to low molecular weights and reaction yields. The \( M_n \) of PTh8BTD only reached 8200 \((M_n/M_w = 1.39)\). The molecular weight of PTh4TTBTD cannot be measured on our GPC because of its extremely low solubility in the eluent (THF).

**Optical Property.** Figure 2 shows the UV–vis absorption spectra for polymers PTh8BTD, PTh6BTD, and PTh4TTBTD in solution and solid state, respectively. The dichlorobenzene solutions of all three polymers show broad absorption bands covering from 350 to 650 nm. The peak maxima located at ∼550 nm arise from the intramolecular charge-transfer (ICT) transition. These absorption maxima are accompanied by a strong absorption band at shorter wavelength (∼425 nm) corresponding to the \( \pi-\pi^* \) transition of the oligothiophene units. The absorption shoulder peak at ∼697 nm for PTh4TTBTD solution can be ascribed to the formation of polymer interchain aggregates because this absorption peak disappears upon heating. Figure 2 also shows the absorption spectra of polymer thin films spin-cast from dichlorobenzene solution using a slow solvent evaporation process. Compared with the solution absorption spectra, all three polymers showed pronounced peak broadening and red shifts of > 100 nm of absorption edges upon forming thin films. This phenomenon is attributed to the planarization of aryl rings and the presence of strong interchain interaction in the solid state. It seems that the increase in the polymer backbone rigidity from PTh8BTD to PTh6BTD and PTh4TTBTD resulted in more pronounced interchain interaction, leading to more broadening of the absorption peaks. It is interesting to point out that the thin films of the three polymers showed slightly blue-shifted and reduced absorption upon annealing. This behavior is in sharp contrast to P3HT, which shows increased and red-shifted absorption upon annealing.

The polymers synthesized here are quite similar to P3HT, except that an electron-deficient moiety was incorporated into the main-chain structure. However, their optical properties are quite different from that of P3HT, indicating the introduction of D–A structure in the polymer backbone has a strong impact on the interchain interaction.

**Thermal Properties.** The thermal properties of the polymers were investigated by differential scanning calorimetry (DSC). DSC analysis reveals that all three polymers are crystalline materials and have a strong tendency to crystallize, as evidenced by the appearance of the crystallization peaks in the DSC cooling scan and the absence of apparent glass transition in the heating scan. This property is beneficial for applications in organic solar cells since a highly ordered heterojunction nanostructure enhanced by the crystallization of the polymer in a PV active layer is desirable for charge separation and transport. As can be seen from Figure 3, the increase of the benzothiadiazole content in the polymer backbone from PTh8BTD to PTh6BTD and PTh4TTBTD leads to monotonic increase in both the polymer melting point and melting enthalpy. It is worth pointing out that when the thiophene moieties in polymer PTh8BTD was fused to become thieno[3,2-b]thiophene in polymer PTh6BTD, the melting point increased by 109 °C. This indicates that the thieno[3,2-b]thiophene moiety significantly increased the backbone rigidity and enhanced the interchain interaction. Perhaps, this is one of the reasons why thieno[3,2-b]thiophene semiconducting copolymers exhibited superior performance in organic transistors.

**Electrochemical Properties.** To investigate the electrochemical properties of the synthesized polymers and estimate their HOMO and LUMO energy levels, cyclic voltammetry (CV) measurement was carried out in a three-electrode cell under Ar using 0.1 M Bu4 NPF6 in anhydrous CH3CN as the supporting electrolyte. A Pt disk (1 mm diameter), a Pt wire (0.5 mm diameter), and a silver wire (2 mm diameter) served as the working electrode, counter electrode, and quasi-reference electrode, respectively. Polymers were coated onto the working electrode from dichlorobenzene solution. Prior to the CV measurement, the Ag quasi-reference electrode was first calibrated using a ferrocene/ferrocenium (Fc/Fc+) redox couple (0.35 V vs Ag/AgCl) as an external standard and was found to be −0.02 V vs SCE. Therefore, the LUMO and HOMO energy levels of the polymers can be estimated using the following empirical equations: \( E_{LUMO} = E_{p}^o + 4.38 \text{ eV} \) and \( E_{HOMO} = E_{p}^o + 4.38 \text{ eV} \), where \( E_{p}^o \) and \( E_{p}^c \) are the onset potentials for oxidation and reduction relative to the Ag quasi-reference electrode, respectively. The results are summarized in Table 1, and the cyclic voltammograms are shown in Figure 4. All three polymers underwent reversible cathodic reduction and anodic oxidation, and the CV curves remained almost unchanged after successive multiple potential scans, indicating high stability of the materials for both hole and electron injection. For comparison purposes, the CV curve of widely used r,r-P3HT was also included in Figure 4. As can be seen from Figure 4, all three polymers show additional redox pairs in the n-doping process owing to the presence of the electron-withdrawing benzothiadiazole units in the polymer backbone, leading to narrower energy gaps than P3HT. Meanwhile, the HOMO energy levels of both PTh8BTD and PTh6BTD remain low at ∼5.25 eV, which are important for achieving large open-circuit voltage \( V_{oc} \) and high air stability. Surprisingly, the HOMO energy level of PTh4TTBTD is relatively high.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \lambda_{\text{max}} ) [nm]</th>
<th>optical gap [eV]</th>
<th>( E_{\text{HOMO}} ) [eV]</th>
<th>( E_{\text{LUMO}} ) [eV]</th>
<th>energy gap [eV]</th>
<th>( T_m ) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTh8BTD</td>
<td>556</td>
<td>1.78</td>
<td>−1.10, −1.45</td>
<td>−5.26</td>
<td>−3.37</td>
<td>189</td>
</tr>
<tr>
<td>PTh6BTD</td>
<td>537</td>
<td>1.82</td>
<td>−1.11, −1.49, −1.70</td>
<td>−5.23</td>
<td>−3.30</td>
<td>193</td>
</tr>
<tr>
<td>PTh4TTBTD</td>
<td>554</td>
<td>1.75</td>
<td>−1.29, −1.66</td>
<td>−5.03</td>
<td>−3.13</td>
<td>190</td>
</tr>
</tbody>
</table>

\( ^{a} \text{Measured in 1,2-dichlorobenzene.} \)
\( ^{b} \text{Estimated from the absorption edge of DCB solutions.} \)
\( ^{c} \text{Estimated by CV measurements.} \)
\( ^{d} \text{Energy gap} = \text{HOMO} − \text{LUMO.} \)
\( ^{e} \text{Determined by differential scanning calorimeter from remelt after cooling with a heating rate of 10 °C/min under N}_2. \)

Determined from hot DCB solution.

Table 1. Physical Properties of Oligothiophenes—Benzothiadiazole Copolymers

- measured in 1,2-dichlorobenzene.
- estimated from the absorption edge of DCB solutions.
- estimated by CV measurements.
- energy gap = HOMO – LUMO.
- determined by differential scanning calorimeter from remelt after cooling with a heating rate of 10 °C/min under N2.
- Estimated from hot DCB solution.
(5.03 eV) probably due to the more coplanar backbone conformation induced by the rigid thieno[3,2-b]thiophene moieties.

**Photovoltaic Properties.** The PV response of the synthesized low-bandgap polymers PTh₆BTD, PTh₈BTD, and PTh₄TTBTD were investigated using bulk heterojunction PV cells with a device structure of ITO/PEDOT-PSS/PThₓBTD:PC₆₁BM (1:1 w/w)/LiF (1 nm)/Al (120 nm). The active layer was spin-cast from dichlorobenzene solution using a slow solvent evaporation process.5 Because of the very low solubility of PTh₄TTBTD in dichlorobenzene at room temperature, it was difficult to get a dense and uniform film, and the resulting device was somewhat short-circuited. Figure 5 shows the current–voltage characteristics of the fabricated PV cells in the dark and under simulated AM 1.5 G solar irradiation of 100 mW/cm². PTh₈BTD-based devices have a Vₒc of 0.68 V, higher than P3HT-based devices (~0.60 V). This can be explained by the higher oxidation potential of PTh₈BTD. PTh₈BTD has a HOMO energy level similar to PTh₆BTD; however, to our surprise the Vₒc of PTh₆BTD-based devices is only 0.51 V, which is 0.17 V lower than that of PTh₈BTD-based devices. The reason is not very clear at this moment. Our conjecture is that the relatively poor film quality of PTh₆BTD due to its low solubility caused more
energy loss during charge transport process. This is supported by the fact that the $V_{oc}$ of PTh$_n$BTD-based devices was improved to 0.61 V upon annealing. PTh$_8$BTD has a very good solubility in dichlorobenzene even at room temperature and can be readily cast into a dense film, leading to higher shunt resistance and a good fill factor. The device performance is summarized in Table 2. On the contrary to P3HT-based devices, thermal annealing of PTh$_n$BTD-based devices did not improve the device performance. Indeed, the device series resistance increased after annealing, leading to the degradation of overall device performance. UV-vis absorption study showed that the absorption of the active layers blue-shifted and decreased in intensity after annealing, as displayed in Figure 6. This result is consistent with the change in the absorption spectra of polymer neat films upon annealing. We also carried out external quantum efficiency (EQE) measurement on our devices. As can be seen from Figure 7, the EQE curves of the devices are similar to the absorption spectra of the respective active layers except some small blue shifts in the polymer PV response peaks. EQE spectra clearly proved that the absorption of low-bandgap polymers PTh$_6$BTD and PTh$_8$BTD in the near-IR region (above 700 nm) contributed to the overall photocurrent generated by the devices under illumination. EQE measurement also confirmed that the photocurrent decreased after annealing.

Conclusions

Polythiophene derivatives bearing electron-withdrawing benzo-thiadiazole moieties in the main chain were synthesized, and their optical, thermal, electrochemical, and photovoltaic properties were investigated in detail. The broad absorption and good
crystallinity demonstrate the potential of these polymers in solar cell applications. Bulk-heterojunction organic solar cells were fabricated with configuration of ITO/PEDOT-PSS/Thb/BTD: PCBM (1:1)/LiF/Al and examined under simulated AM 1.5 G solar irradiation. Preliminary results showed that Thb-BTD-based solar cells gave better performance with a PCE of 1.73%, a $V_{oc}$ of 0.68 V, a short-circuit current ($I_{sc}$) of 5.2 mA/cm$^2$, and a fill factor (FF) of 0.49 in the unoptimized devices because of its high solar absorption, good solubility, and excellent film-forming property. This suggests that we have to make a compromise between solubility and high crystallinity when designing new polymeric materials for organic solar cell applications. In future work, we will focus on device optimization to further improve the power conversion efficiency, such as changing PC$_{61}$BM loading work, we will focus on device optimization to further improve the property. This suggests that we have to make a compromise fill factor (FF) of 0.49 in the unoptimized devices because of its.

Experimental Section

Materials. All reagents and solvents were purchased from Aldrich and Fisher Chemicals. Anhydrous tetrahydrofuran was distilled over sodium/benzophenone under Ar prior to use.

Characterization. NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrometer using tetramethylsilane or trace chlorofrom in deuterium chlorofrom as internal references. Gel permeation chromatography (GPC, Viscotek TDA 302) was used for measuring the molecular weight and polydispersity index. UV–vis spectra were measured using a Varian Cary 50 Spectrometer. Differential scanning calorimetry (DSC) analysis was carried out on a TA Instruments DSC 2920 under nitrogen at a heating/cooling rate of 10 °C/min.

Photovoltaic Device Fabrication and Testing. Glass slides patterned with ITO (Colorado Concept Coatings LLC) were cleaned by sonicating sequentially in detergent, DI water, acetone, and isopropanol. The active area of each solar cell device was $5 \times 7$ mm$^2$. Immediately prior to device fabrication, the ITO substrate was treated in a UV-ozone oven for 15 min. Thereafter, the ITO-coated slides were spin-coated (5000 rpm for 60 s) with a filtered (0.45 μm NYL with GMF syringe filter) aqueous suspension of poly(ethylene dioxythiophene) doped with poly(styrenesulfonic acid), PEDOT:PSS (Baytron P, H. C. Starck), and then baked at 120 °C under N$_2$ for 2 h. The resulting thin PEDOT:PSS layer was about 50 nm thick. A dichlorobenzene solution of polymer and PCBM (10.0 mg/mL each) was stirred at 50 °C overnight and then spun-cast on top of PEDOT-PSS at 600 rpm for 60 s. The film was kept in a Petri dish overnight. The thickness of the resulting film was found to be about 130 and 110 nm for Thb-BTD/PCBM and Thb-BTD/PCBM blend, respectively. The device fabrication was completed by the vacuum deposition of LiF (1 nm) and Al cathode (120 nm). The solar cells with no protective encapsulation were prepared based on literature procedures. Fabricated with configuration of ITO/PEDOT-PSS/Th$_4$/C$_{176}$Pd(BP)$_3$/Al, the signal detected with Newport Merlin Xe lamp on a Newport 90015832 monochromator with New-quantum efficiency (EQE) studies were performed using a solar irradiation. Preliminary results showed that Th$_4$BTD:PCBM (10.0 mg/mL) with PC$_{61}$BM blend, respectively. The device fabrication was completed by the vacuum deposition of LiF (1 nm) and Al cathode.

General Procedure for the Preparation of Alternating Copolymers P(Th4BT). To a solution of appropriate dibromide (0.3 mmol) and 5,5’-bis(trimethylstannyl)-2,2’-bithiophene (0.3 mmol) in anhydrous toluene (6 mL), tetra(triphenylphosphine)-palladium(0) (7 mg, 0.006 mmol) was added in glovebox. The reaction mixture was stirred at ambient temperature for 5 min and then heated to reflux for 48 h. 2-(Trimethylstannyl)-bithiophene (10 mg) was added, and 8 h later 2-bromothiophene (15 mg) was added and allowed to react for further 8 h. After the solution was cooled to 75 °C, chlorobenzene (10 mL) was added. The polymer was precipitated in methanol and collected by filtration. A dark purple fiberlike solid obtained was first washed with hexanes on Soxhlet extraction apparatus to remove low-molecular-weight oligomers and then extracted with chlorobenzene. The chlorobenzene solution was concentrated under reduced pressure and precipitated in methanol. The purified polymer was collected and dried in vacuum oven at 80 °C.

Sol. Cells 71, 93–107. (b) Thompson, B. C.; Fr
c, H. 67, 5.26, 1997. PTh$_4$BTD: 157 mg, 49% yield. GPC: $M_n: 8200$, $M_w/M_n$ = 1.39 (relative to polystyrene standards). Anal. Calcd for C$_{69}$H$_{78}$N$_2$S$_7$: C 69.22, H 7.31, N 2.60. Found: C 69.05, H 6.67, N 2.84.

References and Notes


