Regioregular Copolymers of 3-Alkoxithiophene and Their Photovoltaic Application

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Abstract: Low band gap conjugated polymers with proper energy levels for charge transfer are required to achieve high-efficiency polymer solar cells. We report the synthesis and characterization of two new regioregular copolymers that are based on 3-alkoxithiophene monomers: poly(3-octylthiophene-2,5-diyl) (POT-co-DOT) and poly(9,9-diptyoxyfluorene-2,7-diyl-alt-[3,7-bis(3-decyloxythiophen-2-yl)-1,3-benzothiadiazole]-5,5′-diyl) (PF-co-DTB). Compared to the alkyl substituents, the alkoxy side chains on the thiophene units can effectively lower the band gap of copolymers and enhance the charge transfer to electron acceptors such as (6,6)-phenyl C61-butyric acid methyl ester (PCBM). The chemical structure and regioregularity of the copolymers were confirmed by NMR. Both copolymers are readily soluble in organic solvents and form high-quality thin films. Electrochemical and photophysical studies reveal band gaps of 1.64 eV for POT-co-DOT and 1.78 eV for PF-co-DTB. Bulk heterojunction photovoltaic devices were fabricated using blends of these copolymers with PCBM as the active layer, ITO-glass as the anode, and aluminum as the cathode. Power conversion efficiency of 1.6% was obtained under simulated solar light AM 1.5 G (100 mW/cm2) from a solar cell with an active layer containing 20 wt % PF-co-DTB and 80 wt % PCBM. Regioregular poly(3-decyloxythiophene-2,5-diyl) (P3DOT) was also studied for comparison purposes.

1. Introduction

Conjugated polymers have been developed into useful materials for a variety of applications, including light-emitting diodes,1–3 photovoltaic cells (PVs),4–5 and thin-film transistors (TFTs).6–8 In the past few years, photovoltaic devices based on conjugated polymers have been extensively studied.3–5 The most widely used configuration of polymer solar cells is the so-called “bulk heterojunction” devices in which the active layer consists of a blend of an electron-donating material, e.g., a p-type conjugated polymer, and an electron-accepting material (n-type) such as (6,6)-phenyl C61-butyric acid methyl ester (PCBM). Photoinduced charge transfer from conjugated polymers to PCBM with quantum yields up to 100% has been obtained.9–11 Regioregular poly(3-alkylthiophene)s (P3ATs) have been found to be among the most promising conjugated polymers. They can be used as photosensitizers and hole transporters in bulk heterojunction polymer solar cells.12–17 Power conversion efficiencies (PCE) exceeding 3% under AM1.5 G illumination and between 4 and 5% under white light illumination from a solar simulator have recently been reported.12–17 Further improvement on the PCE entails new conjugated polymers with higher carrier mobility and broader absorption of the solar spectrum, especially in the red and infrared range. Moreover, the relatively low PCE of the polymer cells17–19 is largely due to the relatively low open-circuit voltages (Voc). The maximum open-circuit voltage is limited by the difference between the electronegativity, i.e., the lowest unoccupied molecular orbital (LUMO) of PCBM and the polymer’s ionization potential, i.e., the highest occupied molecular orbital (HOMO).20,21 Therefore,

HOMO level is also an important parameter to consider when designing new, electron-donating polymers of low band gap.

Polythiophenes with substituents other than alkyl groups have also been investigated, among which those with electron-donating alkoxy groups have displayed promising electronic and optical properties. Compared to donating alkoxy groups have displayed promising electronic and also been investigated, among which those with electron-donating effect of the alkoxy group and the more coplanar conformation of the POTs. Therefore, polymers and copolymers based on 3-alkoxythiophene may also have smaller band gaps than those based on POTs. Consequently, they can more efficiently absorb the red and near-infrared portion of the solar emission spectrum.

In our effort to synthesize new conjugated polymers for photovoltaic application, we began with regioregular poly(3-decyloxythiophene-2,5-diyl) (P3DOT), but we found that thin films of P3DOT did not have sufficiently high uniformity and environmental stability. Therefore, we turned to copolymers. In this paper, we describe the synthesis, characterization, and optical and electrochemical properties of a regioregular copolymer, poly(3-octylthiophene-2,5-diyl-co-3-decyloxythiophene-2,5-diyl) (POT-co-DOT), and an alternating regioregular copolymer, poly{[9,9-dioctylfluorene]-2,7-diyl-alt-[4,7-bis(3-decyloxythien-2-yl)-1,3-benzo-thiadiazole]-5′,5″-diyl} (PF-co-DTB). The incorporation of 3-alkoxythiophene units onto the conjugated backbones enhances the electron-donating properties of the polymer and lowers its band gap. The fabrication and performance of photovoltaic cells with bulk heterojunction architecture based on blends of these copolymers with PCBM are also described.

2. Results and Discussion

2.1. Polymer Synthesis and Characterization. The random copolymer, poly(3-octylthiophene-2,5-diyl-co-3-decyloxythiophene-2,5-diyl) (POT-co-DOT) was synthesized via condensation polymerization using the Grignard metathesis (GRIM) method initially reported by McCullough et al. (Scheme 1). Equimolar amounts of 2,5-dibromo-3-decyloxythiophene (1) and 2,5-dibromo-3-octylthiophene (3) were employed. The results of polymerization are summarized in Table 1. The obtained copolymer POT-co-DOT has a dark blue color similar to the regioregular P3DOT prepared also by the GRIM method. It is readily soluble, at high concentrations and room temperature, in common organic solvents such as chlorobenzene, tetrahydrofuran (THF) and chloroform. In comparison, P3DOT exhibits limited solubility in chlorobenzene and dichlorobenzene. At ambient temperature, the solubility of P3DOT is limited to less than 0.5%. We were able to prepare solutions of higher concentrations at elevated temperatures; however, thin films spin-coated from such solutions contained numerous particles and pinholes.


Table 1. Molecular Weight and Composition of Polymers Synthesized for This Study

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M&lt;sub&gt;θ&lt;/sub&gt;</th>
<th>M&lt;sub&gt;θ&lt;/sub&gt;</th>
<th>Comonomer feed molar ratio</th>
<th>Comonomer molar ratio in copolymer &lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3DOT</td>
<td>1.07 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.48</td>
<td>1:1</td>
<td>2.5:1</td>
</tr>
<tr>
<td>POT-co-DOT</td>
<td>1.45 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.75</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>PF-co-DTB</td>
<td>6.80 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.69</td>
<td>1:1</td>
<td>1:1</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from GPC (eluent: THF; polystyrene standards). <sup>b</sup> Comonomer ratios are 3-decyloxythiophene to 3-octylthiophene in POT-co-DOT, and DOF to DTB in PF-co-DTB.
thiophene protons of regioregular H–T linkages of the thiophene units in POT-co-DOT.

On the basis of the relative areas of the peaks at 4.16 and 2.79 ppm, the molar ratio of 3-decyloxythiophene to 3-octylthiophene units in POT-co-DOT was estimated to be 2.5:1. This ratio is much higher than the comonomer feed ratio, 1:1, for copolymerization. This discrepancy indicates that during the GRIM copolymerization, the intermediate Grignard compound (2) in Scheme 2, which contains the alkoxy side chain, is more reactive and adds onto the propagating polymer chain more readily than the intermediate Grignard compound (4) containing an alkyl side chain. The resulting copolymer is mainly made up of 3-alkoxythiophene units.

Scheme 2 illustrates the synthetic routes to 4,7-bis-(3-decyloxy-thiophene-2-yl)-2,1,3-benzothiadiazole (DTB) (6) and poly{[9,9-dioctylfluorene]-2,7-diyl-alt-[4,7-bis(3-decyloxythien-2-yl)-2,1,3-benzothiadiazole]-5,5'-diyl} (PF-co-DTB). DTB was synthesized via Kumada coupling method from 5 and 4,7-dibromo-2,1,3-benzothiadiazole. 4,7-Bis-(5-bromo-3-decyloxythien-2-yl)-2,1,3-benzothiadiazole (monomer 7) was synthesized from 6 and NBS in THF. PF-co-DTB was synthesized via Suzuki cross-coupling polymerization using equimolar amounts of 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) (DOF) and 7 in the presence of a Pd(PPh₃)₄ catalyst, K₂CO₃, and Aliquat336. At the end of the polymerization, bromobenzene and phenylboronic acid were added successively to convert the boronic acid and bromine located at the ends of the polymer chain to the more inert phenyl groups. The resulting PF-co-DTB is a dark red solid and has better solubility in organic solvents such as toluene, chloroform, THF, etc., than do P3DOT and POT-co-DOT.

The chemical structure of PF-co-DTB was confirmed by ¹H NMR spectroscopy. The –OCH₂– protons from the DBT units appear at chemical shift 4.16 ppm, whereas the α-methylene protons of the DOF units are at 2.07 ppm. The molar ratio of fluorene to DBT in the copolymer, which can be calculated from the integrated areas of the peaks at 4.16 and 2.07 ppm, is 1:1. This value is the same as the comonomer feed ratio in copolymerization. It is also consistent with an alternative copolymer structure. The GPC shows relatively high molecular weights, with Mₘ = 6.8 × 10⁴, Mₕ = 1.15 × 10⁵ (using poly(styrene) standards) and a polydispersity of 1.75 (Table 1). It is noted that the Mₘ of analogous poly[2,7-(9′(9′′-ethylhexyl)-9-hexyfluorene)-alt-5,5′-4,4′-di(thien-2-yl)]-2′,1′,3′-benzothiadiazole] (COPF-1) without any substituents on the thiophene units, reported by Svensson et al., is about 4800. This low molecular weight was attributed to the poor solubility of COPF-1. Compared to COPF-1, PF-co-DTB has substantially higher molecular weights and better solubility.

2.2. UV–Visible Absorption. Optical absorption spectra of the polymers were measured in dilute chloroform solution (1 × 10⁻⁴ g/mL) as well as in solid thin films. The spectra are depicted in a, b, and c of Figure 3. The spectroscopic data of the polymers are summarized in Table 2. In dilute chloroform solution, POT-co-DOT has a π→π* absorption band at λmax = 538, approximately 30 nm blue-shifted compared to that of

Figure 1. ¹H NMR spectra of (a) P3DOT: 1. aromatic region; 2. –OCH₂– region; (b) POT-co-DOT: 1 aromatic region; 2 –OCH₂– and –CH₂– adjoining thiophene rings.

Gel permeation chromatography (GPC) showed that POT-co-DOT has a single and narrow molecular weight distribution. This is consistent with POT-co-DOT being a copolymer rather than a blend of two homopolymers. Using THF as the eluent and polystyrene as the standards, the GPC data demonstrate that the number-average (Mₙ) and weight-average (Mₕ) molecular weights of POT-co-DOT are 1.45 × 10⁴ and 2.55 × 10⁴ respectively. The polydispersity index (Mₕ/Mₙ) is 1.75 (Table 1). These molecular weight values are slightly higher than those of P3DOT, whose Mₙ and Mₕ are 1.07 × 10⁴ and 1.59 × 10⁴, respectively, with polydispersity of 1.48. The ¹H NMR spectrum of P3DOT displayed in Figure 1a reveals one aromatic-H peak at chemical shift 6.91 ppm, and one singlet peak at 4.16 ppm for the –OCH₂– group. This is consistent with the extensive analysis on regioregular P3AOTs and P3ATs by McCullough et al., and it confirms a highly regioregular H–T linkage in P3DOT. The ¹H NMR of POT-co-DOT shown in Figure 1b has one sharp singlet peak at 4.16 ppm, similar to that of the regioregular P3DOT homopolymer shown in Figure 1a, and another singlet peak at 2.79 ppm corresponding to the α-methylene protons of regioregular H–T linked poly(3-octylthiophene). These ¹H NMR results are evidences of highly regioregular H–T linkages of the thiophene units in POT-co-DOT.
**Scheme 2.** Synthesis of 4,7-Bis-(3-decyloxy-thiophen-2-yl)-2,1,3-benzothiadiazole (DTB) and Its Alternating Copolymer with 9,9-Dioctyfluorene (PF-co-DTB)

**Table 2.** UV–Vis Absorption and Electrochemical Properties of Various Polymers in Solution and in Solid State

<table>
<thead>
<tr>
<th></th>
<th>λ(_{\text{max}}) (nm)</th>
<th>band gap (eV)</th>
<th>E(_{\text{a}}) (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3DOT</td>
<td>565, 624</td>
<td>1.60</td>
<td>0.075</td>
<td>-4.47</td>
<td>-2.87</td>
</tr>
<tr>
<td>POT-co-DOT</td>
<td>538, 621</td>
<td>1.64</td>
<td>0.146</td>
<td>-4.55</td>
<td>-2.91</td>
</tr>
<tr>
<td>PF-co-DTB</td>
<td>412, 560, 416, 581</td>
<td>1.78</td>
<td>0.740</td>
<td>-5.14</td>
<td>-3.36</td>
</tr>
<tr>
<td>P3HT(^a)</td>
<td>425, 514</td>
<td>1.92</td>
<td>0.348</td>
<td>-4.75</td>
<td>-2.83</td>
</tr>
<tr>
<td>P3OOT(^b)</td>
<td>458, 472</td>
<td>1.91</td>
<td>0.069</td>
<td>-4.47</td>
<td>-2.56</td>
</tr>
<tr>
<td>COPF-1(^c)</td>
<td>380, 540, 384, 545</td>
<td>2.02</td>
<td>1.07</td>
<td>-5.47</td>
<td>-3.46</td>
</tr>
<tr>
<td>COPF-2(^d)</td>
<td>370, 520, 370, 525</td>
<td>2.06</td>
<td>1.20</td>
<td>-5.60</td>
<td>-3.54</td>
</tr>
</tbody>
</table>

\(^a\) Purchased from Sigma-Aldrich.  
\(^b\) Prepared by FeCl\(_3\) at 0 °C.  
\(^c\) From ref 31.  
\(^d\) From ref 30.  
\(E_\text{ox}\) is the onset potential of oxidation of polymer. The values for COPF-1\(^c\) and COPF-2\(^d\) were obtained by the same calculation method.

Thin films of the copolymers 50–80 nm thick were spin-coated from their solutions in chlorobenzene. For comparison convenience, the UV–vis absorption spectra of thin films of P3DOT, POT-co-DOT, PF-co-DTB, regiorandom poly(3-octylthiophene) (P3OOT) prepared by oxidative polymerization using FeCl\(_3\)\(^b\) and regioregular P3HT are all plotted in Figure 3d. The spectrum of regioregular POT-co-DOT thin film has an absorption maximum at ~621 nm (Figure 3d and Table 2). The band gap, determined from the onset of the absorption spectrum, is 1.64 eV. This value is similar to that of P3DOT but lower than those of the regiorandom P3OOT and regioregular P3HT. McCullough et al.\(^{26}\) and Rieke et al.\(^{27}\) reported similarly large red-shifts of the absorption spectra from regiorandom to regioregular P3ATs. They attributed the red-shift to high percentages of head-to-tail linkages in the regioregular polymers that lead to longer conjugated length and more orderly packing of the polymer chains. Because POT-co-DOT has a regioregular structure and electron-donating decyloxy side chain, the absorption is substantially red-shifted compared to those of P3OOT and P3HT.

The general feature of the UV–vis absorption spectrum of PF-co-DTB in solid state is similar to that in solution. The lower energy absorption peak at \(\lambda_{\text{max}} = 581\) nm is red-shifted only by 20 nm from solution to thin film. This red-shift indicates higher coplanarity of the polymer and/or enhanced intermo-

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Figure 3. UV–vis absorption spectra of (a) P3DOT, (b) POT-co-DOT, and (c) PF-co-DTB in solution (1 \times 10^{-4} \text{ g/mL}, chloroform as solvent), in solid state (thin film spin-coated from chlorobenzene solution), and in chloroform solution containing various volume concentrations of methanol. (d) UV–vis absorption spectra of solid films of P3DOT, POT-co-DOT, PF-co-DTB, P3HT (purchased from Aldrich), and P3OOT (prepared by oxidative polymerization using FeCl₃ \textsuperscript{2+}).

Peter and co-workers \textsuperscript{24} reported that the band gap of PF-co-DTB is \( \sim 0.2 \text{ eV} \) smaller than those of COPF-1 and COPF-2. The UV–vis absorption peak of PF-co-DTB is approximately 40 and 60 nm red-shifted compared to those of COPF-1 and COPF-2, respectively (Table 2). The electron-donating decyloxy groups in PF-co-DTB raise the HOMO level and consequently reduce the band gap of the copolymer. The smaller band gap should help improve the absorption efficiency in the solar spectrum.

2.3. Electrochemical Characterization. The electrochemical characteristics of polymer thin films coated on Pt electrode were studied by cyclic voltammetry in a 0.1 M Bu₄NBF₄ solution in acetonitrile. The scan rate was 100 mV/s. The results are summarized in Table 2. The oxidation potentials, \( E_{\text{ox}} \), were derived from the onset in the cyclic voltammograms. The \( E_{\text{ox}} \) values of COPF-1 and COPF-2 (Table 2) were cited from references 30 and 31 and were calculated by the same method. The cyclic voltammogram of POT-co-DOT reveals a broad and reversible oxidation (p-doping) wave. The \( E_{\text{ox}} \) is 0.146 vs SCE, higher than the \( E_{\text{ox}} \) of 0.075 V for P3DOT, due to the presence of the 3-octylthiophene units. Compared to the \( E_{\text{ox}} \) values of the regiorandom P3OOT and regioregular P3HT shown in Table 2, the \( E_{\text{ox}} \) of PO-co-DOT is at lower potentials. This is not unexpected since longer conjugation and/or alkoxy side groups make PO-co-DOT more oxidizable.

The highest occupied molecular orbital (HOMO) is calculated according to \textsuperscript{32}

\[
E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.4 \text{ V})
\]

where \( E_{\text{ox}} \) is the onset oxidation potential vs SCE. From this equation, the HOMO values of P3DOT and POT-co-DOT were calculated to be \(-4.47 \) and \(-4.55 \text{ eV} \), respectively.

Because no reversible n-doping process was observed on the cyclic voltammograms, the LUMO levels were estimated from the HOMO values and values of optical band gaps by

\[
E_{\text{LUMO}} = E_{\text{HOMO}} + E_g
\]

From this equation, the LUMO values of P3DOT and PO-co-DOT were calculated to be \(-2.87 \) and \(-2.91 \text{ eV} \), respectively.

The cyclic voltammogram of the copolymer PF-co-DTB exhibits two reversible \( p \)-doping processes. No reversible \( n \)-doping process was observed. The first \( p \)-doping process with an onset potential of 0.740 V may be assigned to the oxidation associated with the DTB units. The second oxidation process at 0.940 V may be associated with the oxidation of the fluorene segments. This potential is lower than the typical oxidation onset of polyfluorene homopolymer at 1.4 V. \textsuperscript{33} The difference may


have resulted from the possible charge transfer between neighboring fluorene and DTB units. Using the equations above, the HOMO and LUMO values of PF-co-DTB were calculated to be $-5.14$ and $-3.36$ eV, respectively.

2.4. Polymer Solar Cells. The polymer solar cells had a layered structure of glass/ITO/PEDOT-PSS/polymer:PCBM blend/LiF/Al. The active layer is a polymer:PCBM blend at various polymer/PCBM weight ratios. It was spin-coated from a solution containing the polymer and PCBM in chlorobenzene onto a ITO/glass substrate covered by poly(3,4-ethylene-oxithiophene)/poly(styrenesulfonate) (PEDOT-PSS). Thin layers of LiF (1 nm) and aluminum (80 nm) were thermally deposited under vacuum. Representative characteristics of the solar cells are listed in Table 3. All data were obtained under white light illumination (air mass 1.5 G, 100 mW/cm²) from a solar simulator which had been calibrated by silicon diode with Hamamatsu KG-5 filter. The spectral mismatch of our measuring system has been taken into the calculations.

The current-voltage characteristics of the solar cells based on the three blends P3DOT:PCBM, POT-co-DOT:PCBM, and PF-co-DTB:PCBM are shown in Figure 4a–c. Under white light illumination (100 mW/cm²), the cell based on P3DOT/PCBM as the active layer has a short circuit current density ($J_{sc}$) of 0.14 mA/cm², an open circuit voltage ($V_{oc}$) of 0.020 V, and a fill factor (FF) of 26.5%. The low rectification ratio (~1) may be resulted from one of these two factors: that the polymer blend layer was not uniform due to poor film-forming ability of P3DOT or that P3DOT was oxidized upon exposure to air ($E_{ox} = 0.075$ vs SCE), thus reducing shunt resistance. These negative factors with P3DOT are alleviated in POT-co-DOT:PCBM which are better film-forming and have higher oxidation potential. Under the same white light illumination, $J_{sc}$ is 0.60 mA/cm², $V_{oc}$ is 0.22 V, and FF is 41.2%. The power conversion efficiency (PCE) is increased to 0.054%, a substantial improvement compared to that of the P3DOT-based cell (PCE = 0.0007%) but is still far from being satisfactory. The rectification ratio of the POT-co-DOT cell is still low, due to high dark current or low shunt resistance. The $V_{oc}$ of this device is also low. Generally, $V_{oc}$ is a measure of the difference between the oxidation potential of the donor (POT-co-DOT and P3DOT) and the reduction potential of the acceptor (PCBM). Thus, raising HOMO, as in POT-co-DOT, closer to the LUMO of PCBM diminishes the value of $V_{oc}$. Annealing has been effective in enhancing the performance of the P3HT/PCBM bulk heterojunction solar cells. Such an enhancement has not been attained in either the P3DOT or POT-co-DOT systems.

### Table 3. Characteristics of Bulk Heterojunction Polymer Solar Cells: Short-Circuit Current Density ($J_{sc}$), Open-Circuit Voltage ($V_{oc}$), Fill Factor (FF), Power Conversion Efficiency (PCE) at Various Polymer/PCBM Weight Ratios (AM 1.5 G irradiation at 100 mW/cm²)

<table>
<thead>
<tr>
<th>polymer/PCBM (w/w ratio)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3DOT 1:1</td>
<td>0.14</td>
<td>0.02</td>
<td>26.5</td>
<td>0.0007</td>
</tr>
<tr>
<td>POT-co-DOT 1:1</td>
<td>0.60</td>
<td>0.22</td>
<td>41.2</td>
<td>0.054</td>
</tr>
<tr>
<td>PF-co-DTB 2:1</td>
<td>0.74</td>
<td>0.83</td>
<td>25.5</td>
<td>0.16</td>
</tr>
<tr>
<td>PF-co-DTB 1:1</td>
<td>2.92</td>
<td>0.78</td>
<td>32.8</td>
<td>0.74</td>
</tr>
<tr>
<td>PF-co-DTB 1:2</td>
<td>4.00</td>
<td>0.76</td>
<td>44.6</td>
<td>1.27</td>
</tr>
<tr>
<td>PF-co-DTB 1:4</td>
<td>4.31</td>
<td>0.76</td>
<td>48.6</td>
<td>1.60</td>
</tr>
</tbody>
</table>


![Figure 4](image-url)

**Figure 4.** Current-voltage characteristics of polymer:PCBM bulk heterojunction solar cells in the dark and under white light illumination (AM 1.5 conditions). (a) P3DOT:PCBM = 1:1; (b) POT-co-DOT:PCBM = 1:1; (c) PF-co-DTB:PCBM = 1:4; (d) From (c), PF-co-DTB:PCBM = 1:4, with photocurrent plotted in linear scale between 0 V and $V_{oc}$.
Preliminary study showed that annealing at 110 and 130 °C had little effect on the PCEs of P3DOT- and POT-co-DOT-based solar cells.

The solar cell made from copolymer PF-co-DTB exhibits higher PCE. PF-co-DTB has not only much better solubility and processability than P3DOT and POT-co-DOT but also has the lowest HOMO value (−5.14 eV). The low HOMO value accounts for a high value of $V_{oc}$ up to 0.76 V. The weight ratio of PF-co-DTB to PCBM has a significant influence on the performance of the cell, similar to the performance of bulk heterojunction solar cells based on poly-[2-methoxy-5-(3′,7′-dimethyloctyloxy)-p-phenylenevinylene]- (MDMO-PPV):PCBM.\(^{36,37}\) The composition dependence of the polymer solar cells reflects the combined results of the exciton generation efficiency (absorption efficiency), the efficiency of e−−h+ separation at the polymer/PCBM interfaces, and the percentage of electrons and holes reaching the charge-collecting electrodes. Lower content of PCBM leads to inefficient dissociation of exciton and a decrease in photocurrent. With increasing PCBM content, both the $J_{sc}$ and FF are increased (Table 3). It is noted that in the PF-co-DTB/PCBM blends, light is mainly absorbed by PF-co-DTB. Therefore, the very high content of PCBM lowers the absorption efficiency. The best performance we have obtained thus far is from the blend with the weight ratio of PF-co-DTB to PCBM being 1:4. Under white light illumination (AM 1.5 G, 100 mW/cm\(^2\)), the obtained $J_{sc}$ is 4.31 mA/cm\(^2\), $V_{oc}$ is 0.76 V, FF is 48.6%, and PCE is 1.6% (Figure 4c,d). These results may be compared with those of the high-performance polymer solar cell based on COPF-1 reported by Svensson et al.\(^{30}\) The spectrum of PF-co-DTB is red-shifted by about 30 nm. The chart of incident photon to charge carrier efficiency (IPCE) as a function of wavelength (see Supporting Information) follows the copolymer’s UV−vis absorption spectrum. Therefore, red-shift of the absorption spectrum indeed helps increase the total photovoltaic current because the solar photon flux is higher in this energy range. On the other hand, as the polymer’s HOMO is increased to −5.14 eV from the −5.47 eV for COPF-1, the $V_{oc}$ is decreased. Overall, the PCE is on the same level. Annealing at 110 °C increased the $V_{oc}$ from 0.76 to 0.79 V (see Supporting Information). However, the $J_{sc}$ was decreased. The overall PCE was not enhanced. On the other hand, annealing at 130 °C had detrimental effect on the PCE. The $V_{oc}$ and $J_{sc}$ decreased to 0.6 V and 2.3 mA/cm\(^2\), respectively. Since annealing has complicated effects on both the $p$- and $n$-channel materials, as well as the bulk heterojunction, extensive study on annealing is underway. We are also experimenting with other $n$-type materials having LUMO values higher than those of PCBM to further improve the $V_{oc}$ and the PCE values. The results will be reported in a future publication.

3. Conclusion

We have synthesized a series of new conjugated polymers using alkoxythiophene as the building block. The copolymer POT-co-DOT has high head-to-tail regioregularity similar to the homopolymer P3DOT. The alternating copolymer PF-co-DTB is also regioregular as the comonomers have symmetric structures. Optical and electrochemical characterizations reveal that all these copolymers have low band gaps and high regioregularity, making them promising materials for the photosensitizers, electron donors, and hole transporters in polymer solar cells. The bulk heterojunction solar cells fabricated using blends of these polymers with PCBM have exhibited varied performances, depending on the polymers’ film-forming ability, environmental stability, and HOMO level. The best solar cell performance obtained has a layered structure of ITO/PEDOT-PSS/PF-co-DTB:PCBM(1:4)/LiF/Al. Under white light illumination (AM 1.5 G, 100 mW/cm\(^2\)), the obtained $J_{sc}$ is 4.3 mA/cm\(^2\), $V_{oc}$ is 0.76 V, FF is 48.6%, and PCE is 1.6%. All these results were calibrated by the spectral mismatch of our measuring system. Study to further improve the solar cell architecture and PCE is underway.

Acknowledgment. We thank Han Zhang and Dr. Wei Wu of our laboratory for critically reviewing the manuscript.

Note Added after ASAP Publication. The axis scales were missing from Figures 1−4 and from the figures in the Supporting Information and the structure of POT-co-DOT was incorrect in Scheme 1, Figure 1b, and the table of contents graphic in the version published ASAP on June 14, 2006. The corrected graphics are present in the version published ASAP on June 20, 2006.

Supporting Information Available: All experimental details for the syntheses of monomers (1−7) and polymers (P3DOT, POT-co-DOT, and PF-co-DTB); cyclic voltammograms of polymers; details for device fabrication; IPCE plot of PF-co-DTB; current−voltage characteristics for the solar cells as a result of annealing. This material is available free of charge via the Internet at http://pubs.acs.org.
