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Regioregular Copolymers of 3-Alkoxythiophene 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-alkoxythiophene monomers: poly(3-octylthiophene-2,5-diyl-*co*-3-decyloxythiophene-2,5-diyl) (**POT-*co*-DOT**) 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**). 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 C$_{61}$-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/cm^2) 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,[1,2] photovoltaic cells (PVs),[3−5] 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 C$_{61}$-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 (**P3AT**s) 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 cells[17−19] is largely due to the relatively low open-circuit voltages (V_{oc}). 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,

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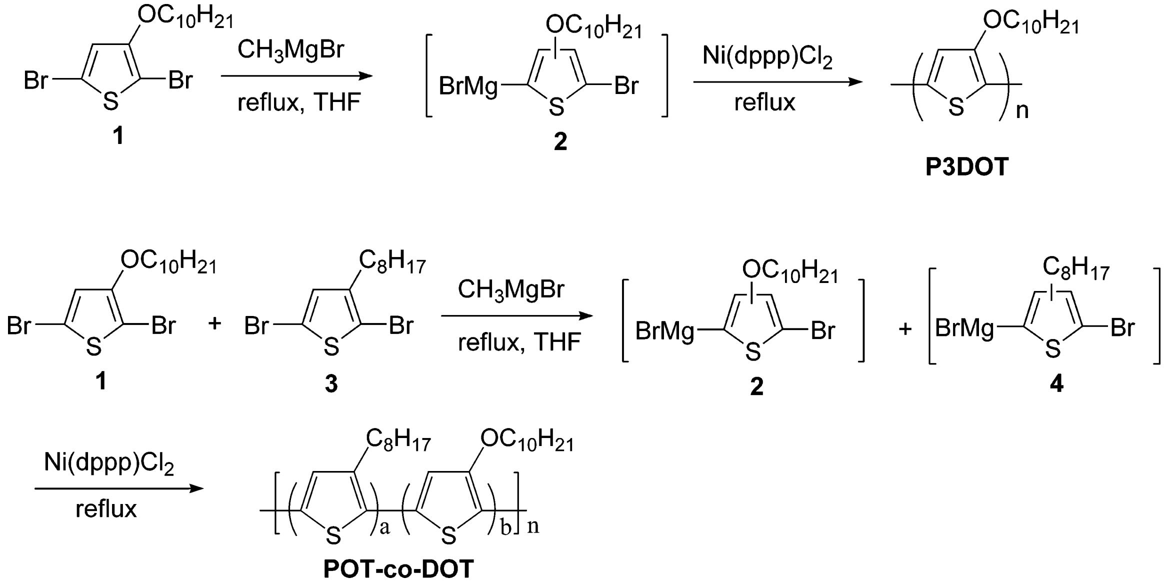
Scheme 1. GRIM Synthesis of Regioregular Poly(3-decyloxythiophene-2,5-diyl) (P3DOT) and Random Regioregular Poly(3-octylthiophene-2,5-diyl-*co*-3-decyloxythiophene-2,5-diyl) (POT-*co*-DOT)



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.[22,23] Compared to **P3AT**s, the incorporation of an alkoxy group to the 3-position of the thiophene ring yields poly(3-alkoxythiophenes) (**P3AOT**s) with optical absorption maxima at longer wavelength. This may be attributed to both the electron-donating effect of the alkoxy group and the more coplanar conformation of the **P3AOT**s.[24,25] Therefore, polymers and copolymers based on 3-alkoxythiophene may also have smaller band gaps than those based on **P3AT**s.[26,27] 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**),[28] 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)-2,1,3-benzothiadiazole]-5′,5″-diyl} (**PF-*co*-DTB**). The incorporation of 3-alkoxythiophene units onto the conjugated backbones enhances the electron-donating property 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.

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

	M_n[a]	M_w/M_n[a]	comonomer feed molar ratio[b]	comonomer molar ratio in copolymers[b,c]
P3DOT	1.07×10^4	1.48	–	
POT-*co*-DOT	1.45×10^4	1.75	1:1	2.5:1
PF-*co*-DTB	6.80×10^4	1.69	1:1	1:1

[a] Calculated from GPC (eluent: THF; polystyrene standards). [b] Comonomer ratios are 3-decyloxythiophene to 3-octylthiophene in **POT-*co*-DOT**, and **DOF** to **DTB** in **PF-*co*-DTB**; [c] Calculated from ^{1}H NMR spectra based on the relative abundances of the $-OCH_2-$ and $-CH_2-$ groups adjoining the thiophene rings.

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)s (**POT-*co*-DOT**) was synthesized via condensation polymerization using the Grignard metathesis (GRIM) method initially reported by McCullough et al.[28,29] (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.

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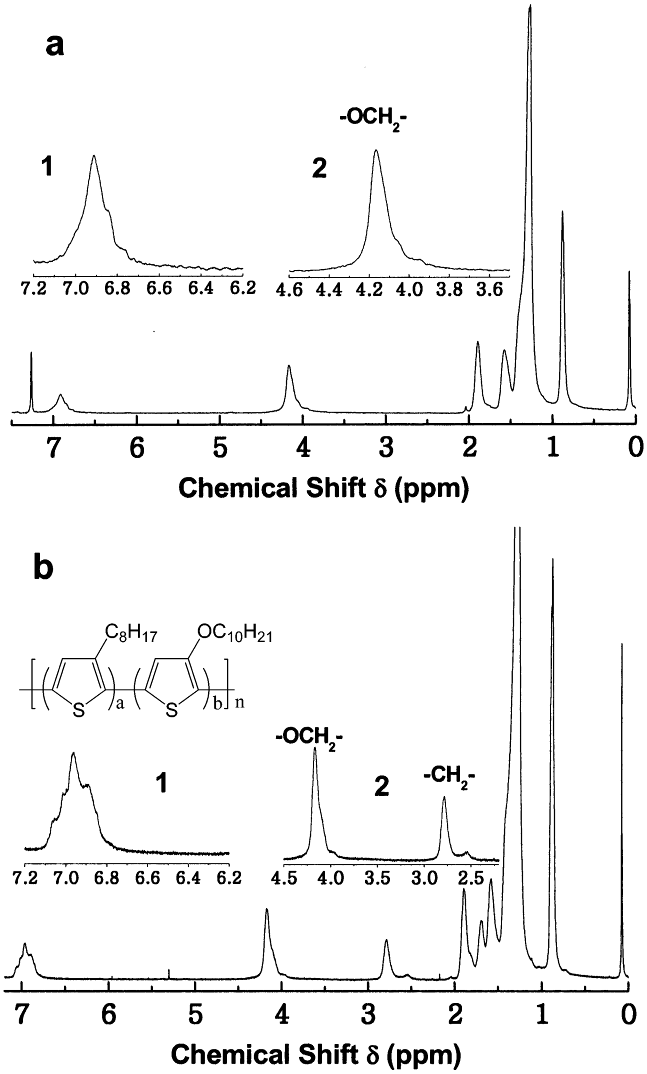

Figure 1. ^{1}H NMR spectra of (a) **P3DOT**: 1. aromatic region; 2. $-OCH_2-$ region; (b) **POT-*co*-DOT**: (1) aromatic region; (2) $-OCH_2-$ and $-CH_2-$ adjoining thiophene rings.

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 (M_n) and weight-average (M_w) molecular weights of **POT-*co*-DOT** are 1.45×10^4, and 2.55×10^4 respectively. The polydispersity index (M_w/M_n) is 1.75 (Table 1). These molecular weight values are slightly higher than those of **P3DOT**, whose M_n and M_w are 1.07×10^4 and 1.59×10^4, respectively, with polydispersity of 1.48. The ^{1}H 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 $-OCH_2-$ group. This is consistent with the extensive analysis on regioregular **P3AOT**s and **P3AT**s by McCullough et al.,[26,28,29] and it confirms a highly regioregular H−T linkage in **P3DOT**. The ^{1}H 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).[26,27] These ^{1}H NMR results are evidences of highly 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-thiophen-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-decyloxy-thiophen-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 $Pd(PPh_3)_4$ catalyst, K_2CO_3, 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 ^{1}H NMR spectroscopy. The $-OCH_2-$ protons from the **DTB** 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 **DTB** 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 $M_n = 6.8 \times 10^4$, $M_w = 1.15 \times 10^5$ (using polystyrene standards) and a polydispersity of 1.75 (Table 1). It is noted that the M_n of analogous poly[2,7-(9′(2′-ethylhexyl)-9-hexylfluorene)-*alt*-5,5′-(4′,7′-di(thien-2-yl)-2′,1′,3′-benzothiadiazole] (**COPF-1**) without any substituents on the thiophene units, reported by Svensson et al.,[30] 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 $\pi-\pi^*$ absorption band at $\lambda_{max} = 538$, approximately 30 nm blue-shifted compared to that of

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Scheme 2. Synthesis of 4,7-Bis-(3-decyloxy-thiophen-2-yl)-2,1,3-benzothiadiazole (DTB) and Its Alternating Copolymer with 9,9-Dioctylfluorene (PF-*co*-DTB)

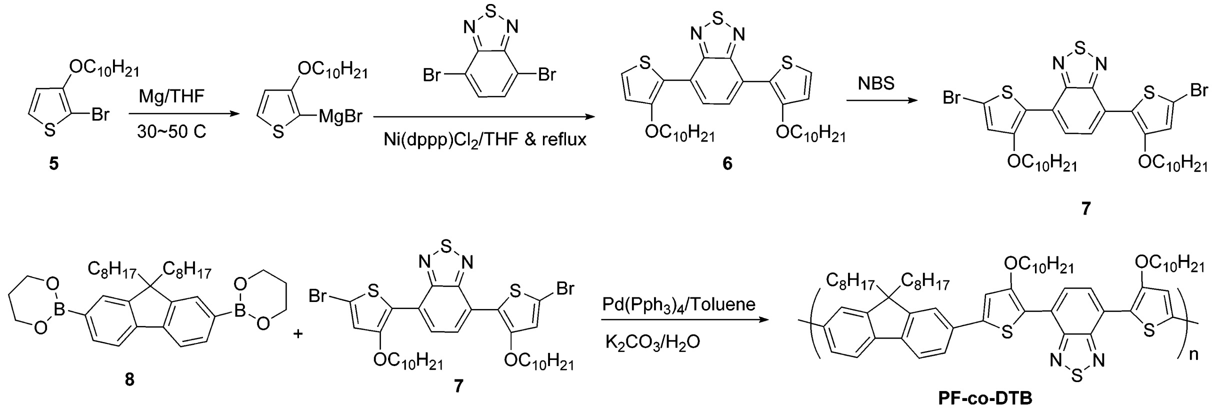

Table 2. UV–Vis Absorption and Electrochemical Properties of Various Polymers in Solution and in Solid State

	$\lambda_{\max}$ (nm) in $CHCl_3$	$\lambda_{\max}$ (nm) film	band gap (eV)	E_{ox} (V)[e]	HOMO (eV)	LUMO (eV)
P3DOT	565	624	1.60	0.075	−4.47	−2.87
POT-*co*-DOT	538	621	1.64	0.146	−4.55	−2.91
PF-*co*-DTB	412, 560	416, 581	1.78	0.740	−5.14	−3.36
P3HT[a]	425	514	1.92	0.348	−4.75	−2.83
P3OOT[B]	458	472	1.91	0.069	−4.47	−2.56
COPF-1[c]	380, 540	384, 545	2.02	1.07	−5.47	−3.46
COPF-2[d]	370, 520	370, 525	2.06	1.20	−5.60	−3.54

[a] Purchased from Sigma-Aldrich. [b] Prepared by $FeCl_3$ at 0 °C.[24] [c] From ref 30. [d] From ref 31. [e] E_{ox} is the onset potential of oxidation of polymer. The values for **COPF-1**[30] and **COPF-2**[31] were obtained by the same calculation method.

P3DOT, possibly due to the presence of 3-alkyl side groups in the copolymer which are less effective in lowering the band gap of the polymer than the electron-donating alkoxy side chains. Compared to the 98% regioregular poly(3-hexylthiophene) (**P3HT**) purchased from Aldrich, the $\pi-\pi^*$ absorption of copolymer **POT-*co*-DOT** is red-shifted by about 140 nm. In solution, **PF-*co*-DTB** has two distinct absorption peaks: one near 416 nm and another in 560 nm. The former peak is assigned to $\pi-\pi^*$ transition associated with the fluorene units. This peak is red-shifted by about ~30 nm compared to those of other fluorene copolymers.[30,31] The red-shift may be due to the strong electron-donating alkoxy side chains on thiophene rings that change the ionization potential of fluorene through the push–pull effect. The absorption peak at 560 nm may be assigned to the $\pi-\pi^*$ transition of the sum of the delocalized structure resulted from the alternating donor–acceptor structure in the copolymer (Figure 2c). We also evaluated the solvatochromic properties of the polymers. It is apparent that the absorption peak at 538 nm for **POT-*co*-DOT** in chloroform gradually shifts to 598 nm with the concentration of methanol (poor solvent) being increased to the methanol/chloroform = 3/2 (volume ratio). The peak also broadens (Figure 3b). This solvatochromism indicates that **POT-*co*-DOT** chains may have higher coplanarity and stronger intermolecular interaction in solid state than in solution. This phenomenon is also observed in **P3DOT** (Figure 3a) and **PF-*co*-DTB** (with much smaller red-shift as shown in Figure 3c).

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-octyloxythiphene) (**P3OOT)** prepared by oxidative polymerization using $FeCl_3$[24] 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 **P3AT**s. 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 $\lambda_{\max} = 581$ 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-

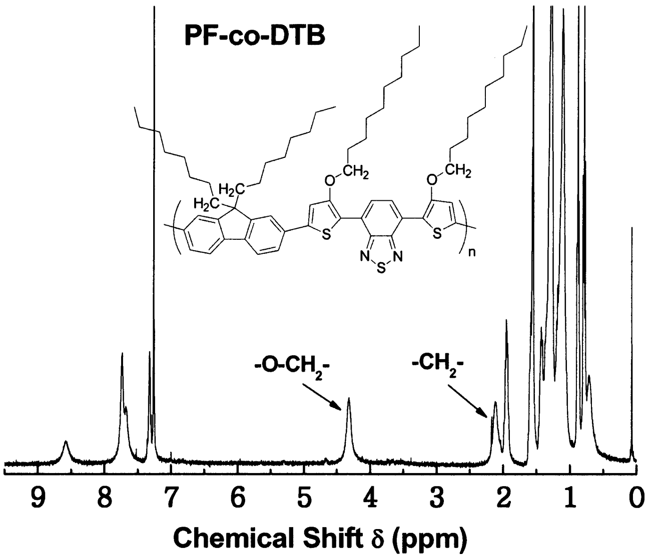

Figure 2. ^1H NMR spectra and chemical structure of **PF-*co*-DTB**.

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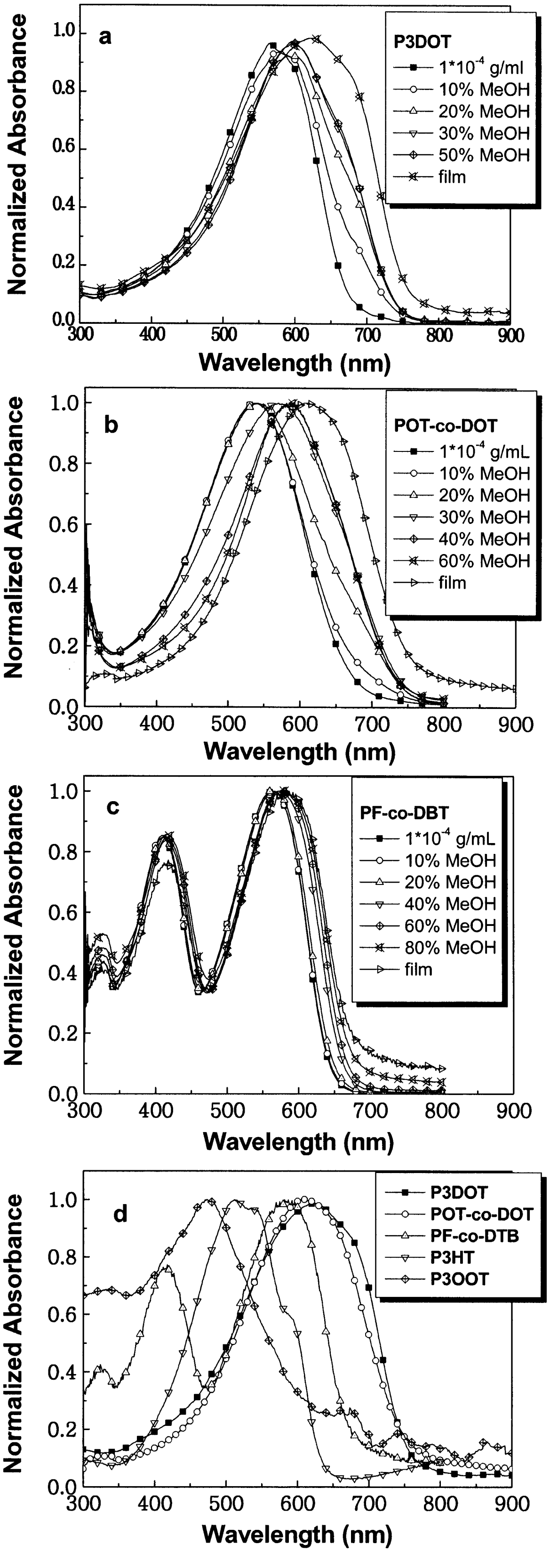

Figure 3. UV−vis absorption spectra of (a) **P3DOT**, (b) **POT-*co*-DOT**, and (c) **PF-*co*-DTB** in solution (1×10^{-4} g/mL chloroform as solvent), in solid state (thin film spin-coated from chlorobenzene solution), and in chloroform solution containing various volume concentrations of methanol. (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 $FeCl_3$[24]).

lecular electronic interactions in the solid state; nonetheless, the increase in coplanarity and/or the enhancement of intermolecular electronic interactions is less significant than in **P3DOT** and **POT-*co*-DOT**. The onset of the optical absorption in the thin film is at about 700 nm (E_g = 1.77 eV). This value is ∼0.14 eV lower than that of **P3HT**, a popular material used in polymer solar cells.

It is worthwhile to compare the band gap of **PF-*co*-DTB** with those of **COPF-1**[30] and poly[2,7-(9,9-dioctylfluorene)-*alt*-2′,2′-(4′,7′-di(3-hexylthien-2-yl)-2′,1′,3′-benzothiadiazole)] (**COPF-2**) (reported by Cao et al.[31]). The band gap of **PF-*co*-DTB** is ∼0.2 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 $Bu_4N{\cdot}BF_4$ solution in acetonitrile. The scan rate was 100 mV/s. The results are summarized in Table 2. The oxidation potentials, E_{ox}, were derived from the onset in the cyclic voltammograms. The E_{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_{ox} is 0.146 vs SCE, higher than the E_{ox} of 0.075 V for **P3DOT**, due to the presence of the 3-octylthiophene units. Compared to the E_{ox} values of the regiorandom **P3OOT** and regioregular **P3HT** shown in Table 2, the E_{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[32]

$$E_{\mathrm{HOMO}} = -e(E_{\mathrm{ox}} + 4.4\ \mathrm{V})$$

where E_{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 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

$$E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_g$$

From this equation, the LUMO values of **P3DOT** and **PO-*co*-DOT** were calculated to be −2.87 and −2.91 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.[33] The difference may

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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/cm^2)

	polymer/PCBM (w/w ratio)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
P3DOT	1:1	0.14	0.02	26.5	0.0007
POT-*co*-DOT	1:1	0.60	0.22	41.2	0.054
PF-*co*-DTB	2:1	0.74	0.83	25.5	0.16
PF-*co*-DTB	1:1	2.92	0.78	32.8	0.74
PF-*co*-DTB	1:2	4.00	0.76	44.6	1.27
PF-*co*-DTB	1:4	4.31	0.76	48.6	1.60

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 an ITO/glass substrate covered by poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (**PEDOT-PSS**). Thin layers of LiF (1 nm) and aluminum (80 nm) were thermally deposited under vacuum.[17] 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/cm^2) 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/cm^2), the cell based on **P3DOT**/**PCBM** as the active layer has a short circuit current density (J_{sc}) of 0.14 mA/cm^2, 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/cm^2, 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**).[34,35] 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.[12−17] Such an enhancement has not been attained in either the **P3DOT** or **POT-*co*-DOT** systems.

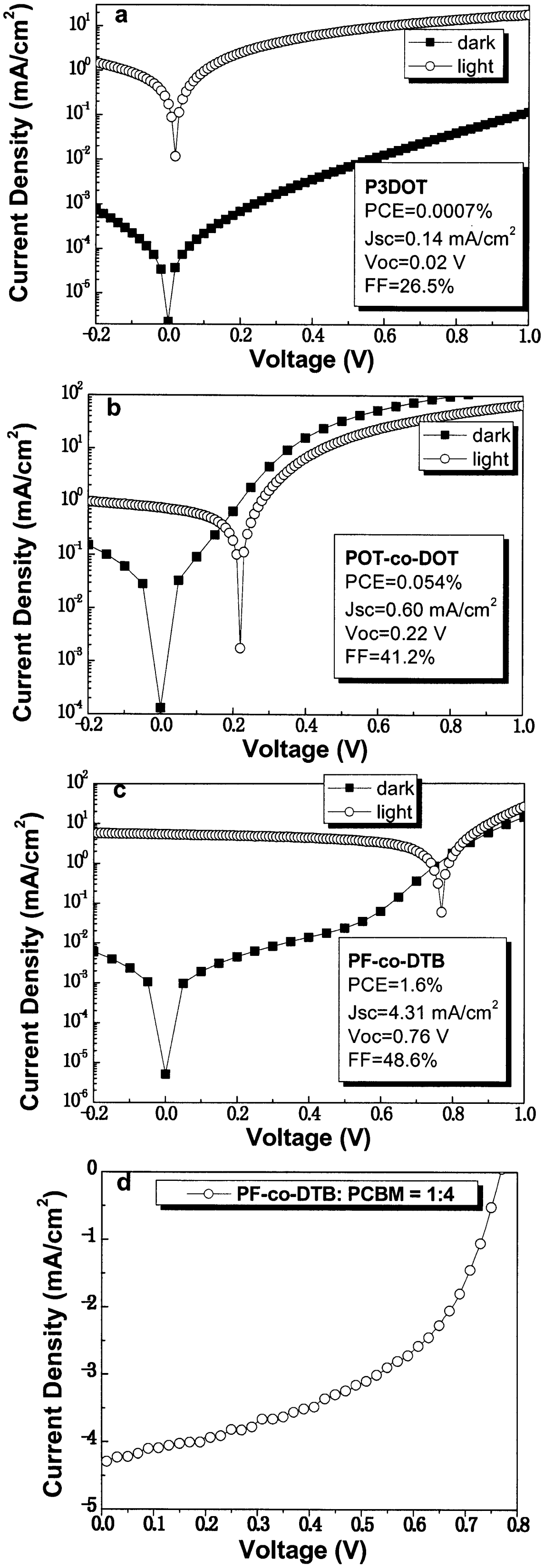

Figure 4. Current−voltage characteristics of polymer/**PCBM** bulk heterojunction solar cells in the dark and under white light illumination (AM 1.5 conditions). (a) **P3DOT**/**PCBM** = 1:1; (b) **POT-*co*-DOT**/**PCBM** = 1:1; (c) **PF-*co*-DTB**/**PCBM** = 1:4; (d) From (c), **PF-*co*-DTB**/**PCBM** = 1:4, with photocurrent plotted in linear scale between 0 V and V_{oc}.

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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 0.76V, 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.

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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.

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