Synthesis and Photovoltaic Properties of Two Benzo[1,2-b:3,4-b′]dithiophene-Based Conjugated Polymers

Jianhui Hou,* Hsiang-Yu Chen, Shaoqing Zhang, and Yang Yang*

Department of Materials Science and Engineering & California Nanosystems Institute, University of California Los Angeles, Los Angeles, California 90095

Received: June 28, 2009; Revised Manuscript Received: November 03, 2009

Side chains of conjugated polymers play an important role in their properties. To investigate the influence of side chains on photovoltaic properties, two conjugated polymers with benzo[1,2-b:3,4-b′]dithiophene (BDT) and 4,7-dithiophen-2,1,3-benzothiadiazole (DTBT) units, Z3 and Z4, were designed and synthesized. These two polymers have identical conjugated main chains and very similar side chains. In polymer Z3, hexyl groups are linked to the thiophene units directly, and in polymer Z4, hexyloxy groups are linked to the thiophene units. Since the hexyloxy group exhibits a smaller steric hindrance and a stronger electron donating effect than the hexyl group, properties of Z3 and Z4 are very different. The hole mobility of the Z3:PCBM blend film is 1.84 × 10−7 cm2/(V s), which is 2 orders lower than that of the Z4:PCBM blend, and photovoltaic results demonstrate that the fill factor (FF) of the Z3-based device is 0.37, while that of the Z4-based polymer solar cell (PSC) device reached 0.61. These results reveal that steric hindrance of the side chain is an important issue for a new material design, in order to obtain higher FF. Additionally, thermal stability, absorption spectra, electrochemical, PL quenching of the polymer:PCBM blend, and photovoltaic properties of the two polymers were investigated in detail. For Z3-based devices, a power conversion efficiency (PCE) of ∼2% was observed with an open circuit voltage (Voc) of 0.84 V, a short circuit current (Jsc) of 6.3 mA/cm2, which indicates this kind of conjugated polymer should be a promising material in the application of polymer solar cells.

Introduction

Since the discovery of photoinduced charge transfer in composites of conjugated polymers and C60,1 polymer solar cells (PSCs) have attracted considerable attention because of their potential for use in low-cost, lightweight, solution-processable, and flexible large area panels.2-5 As the electron donor material in the active layer of PSC devices, properties of conjugated polymers, such as absorption spectra, molecular energy levels, carrier mobility, etc., have great influence on the photovoltaic performance of devices. For example, as reported, the highest Jsc of the PSC devices based on poly(3-hexylthiophene) (P3HT) was 10.7 mA/cm2, due to the absorption range limitation of the active layer materials.6 To get a better response range of PSC device and hence higher Jsc, smaller bandgap conjugated polymers were applied to PSCs.7 In these works, poly[4,4-bis(2-ethylhexyl)cyclopenta[2,1-b;3,4-b′]dithiophene-alt-2,1,3-benzothiadiazole] (PCPDTBT) is one of the most successful small bandgap polymers for application of PSC. The absorption range of the PSC devices based on PCPDTBT was extended from 650 nm to around 850 nm. As a result, the Jsc of the PSC device reached 16.2 mA/cm2 after optimizing the morphology. The highest occupied molecular orbital (HOMO) level of conjugated polymers is another important issue of their photovoltaic properties.8 For instance, although the bandgap of poly[(2,7-silafluorene)-alt-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)](PSiFDBT) is similar to that of P3HT, this material exhibits a much lower HOMO level than P3HT. As a result, the Voc of the PSiFDBT-based PSC devices reached 0.9 V, which is much higher than that of P3HT-based devices. With such high Voc, an efficiency of 5.4% has been achieved by using PSiFDBT as the active layer material.10

Recently, several models were proposed to estimate photovoltaic properties of conjugated polymers,8,11,12 and these works provided valuable guidelines for conjugated polymer molecular structure design. As proposed, both molecular energy level and bandgap are of the most importance for obtaining highly efficient PSCs. There are many works focusing on optimizing bandgap and molecular energy level by changing the molecular structure of conjugated polymers. For example, Luping et al. reported a systematic work about the design of thieno[3,4-b′]thiophene-based conjugated polymers for solar cells, and in that work, several conjugated polymers with ideal bandgap and energy level were designed and synthesized, and also a PCE of 6.1% has been achieved.9 Although the results from PSC devices indicate that these polymers are promising photovoltaic materials, performances of these materials are much lower than the theoretical value as expected from their bandgap and energy level values. The deviation reveals that photovoltaic properties of conjugated polymers are not solely determined by the

SCHEME 1: Molecular Structures of Polymers Z3 and Z4
bandgap and energy level of the materials. Besides the bandgap and molecular energy level, some other properties, such as mobility and solubility, are also important to photovoltaic polymers. As known, these properties of conjugated polymers are more susceptible to molecular structures, such as regioregularity, orientation, or steric hindrance between repeated units. So, side chains of conjugated polymers play an important role in their photovoltaic properties. However, the influence of side chains of conjugated polymers on their photovoltaic properties is less reported. There is a great need for investigation and understanding of the side chain effects. Recently, we reported a family of benzo[1,2-b;3,4-b]dithiophene (BDT)-based conjugated polymers with promising photovoltaic properties, and in order to modify bandgap and molecular energy levels, BDT was copolymerized with different conjugated units. In this work, two polymers with BDT units, Z3 and Z4 in Scheme 1, were designed and synthesized in order to investigate the influence of side chains on their photovoltaic properties.

Synthesis of the Polymers. Synthesis routes of the two polymers were shown in Scheme 2. 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexoxy)benzo[1,2-b;3,4-b]dithiophene, compound 3, was synthesized by a similar method reported in our previous work, and purified by recrystallization with ethyl alcohol as solvent. Both polymers were prepared by Stille coupling reaction with good yield. The number average molecular weight ($M_n$) of Z3 and Z4 is 23.2K and 19.2K, with a PDI of 1.3 and 1.2, respectively.

Thermal Stability. These two polymers exhibited very similar thermal stability, as shown in the thermogravimetric analysis (TGA) plots of Z3 and Z4 in Figure 1. The onset decomposition temperatures of the polymers are around 280 °C in air, mainly due to the leaving of alkoxy groups. The thermal stability of these two polymers is adequate for their applications in PSCs and other optoelectronic devices.

Absorption Spectra of the Polymers. Absorption spectra of polymer Z3 and Z4 are shown in Figure 2, and some data from this figure were summarized in Table 1 for comparison. On the basis of the onset point of the absorption spectrum, the optical bandgap of Z4 was estimated to be about 1.55 eV, which is 0.27 eV lower than that of Z3. The lower bandgap of Z4 than Z3 should be attributed to the strong electron-donating effect of the alkoxy groups on Z4. As shown in Figure 2, both polymers exhibit two absorption peaks in the UV-vis region. In comparison with the absorption spectra in chloroform, absorption spectra of the polymer thin films shift to a longer wavelength region. Polymer Z3 exhibits a red shift of ∼51 nm while that of Z4 is only ∼8 nm. It is known that the absorption spectra of conjugated polymers closely relate to their effective conjugated length, which is susceptible to the steric hindrance caused by side chains. For example, the absorption spectrum of the regiorandom poly(3-hexylthiophene) film exhibits a peak at around 500 nm, but the absorption peak of the poly(3-cyclohexylthiophene) film is at 410 nm due to the strong steric hindrance caused by the cyclohexyl groups. As shown in Scheme 1, hexyl side chains of Z3 are linked to thiophene units directly; for Z4, they are linked to thiophene units through oxygen atoms. For both Z3 and Z4, there is no substituent on the 3 and 7 positions of the BDT units and the 4 position of the thiophene units, so the steric hindrance effects between BDT...
units and thiophene units of the two polymers are very similar. As a result, the steric hindrance between the thiophene and the
2,1,3-benzothiadiazole (BT) should play a more important role here. As reported, in polythiophenes, the alkyl group exhibits
bigger steric hindrance to the adjacent units than the alkoxy
group,\textsuperscript{15} and therefore, in comparison with
$Z_3$, more planar
structure will be formed in $Z_4$, in both solution state and solid
state. As shown in Figure 2, the $Z_3$ film has a larger red-shift
in absorption compared to its solution than that of $Z_4$. This
means that the steric hindrance in $Z_3$ caused by its side chain
is bigger than that of $Z_4$. Consequently, a more plane structure
of the main chain and hence a more effective interchain
$\pi-\pi^*$
stacking could be formed in the polymer $Z_4$. So, it can be
expected that $Z_4$ has a higher mobility than $Z_3$.

**Electrochemical Properties.** Electrochemical cyclic volta-
mmetry (CV) is often performed for determining the HOMO
level of conjugated polymers.\textsuperscript{16} Figure 3 shows the CV curves
of $Z_3$ and $Z_4$ films on the Pt electrode in 0.1 mol/L, $\text{Bu}_4\text{NPF}_6$,
$\text{CH}_3\text{CN}$ solution. It can be seen that there are reversible
p-doping/dedoping (oxidation/reduction) processes for both
polymers. The onset of the p-doping process of $Z_3$ is 0.43 V,
corresponding to a HOMO level of $-5.23$ eV, which is 0.4 eV
lower than that of $Z_4$. The strong electron-donating effect of
the alkoxy groups of $Z_4$ should be the main reason for the higher
HOMO level of $Z_4$, which indicates that although alkoxy is a
very effective functional group to reduce bandgap, it is not a
good choice for lowering the bandgap of photovoltaic materials,
because a deeper HOMO level is crucial to obtain a high $V_{oc}$.

**Photovoltaic Properties.** Figure 4 shows the $I-V$ curves of
the PSCs with $Z_3$:PCBM and $Z_4$:PCBM as active layer
materials, and the results of the devices were collected in Table
2. From these results, we found that the photovoltaic perform-
ance of $Z_3$-based devices was very sensitive to the annealing
process. With thermal annealing under 160 °C for 5 min, $V_{oc}$,
$J_{sc}$, and FF of the $Z_3$-based device were improved signifi-
cantly. As a result, PCE of the device increased more than two times,
from 0.85% to 1.95%. However, thermal treatment has little
influence on $Z_4$-based devices. After annealing, PCE of $Z_4$-
based devices slightly increased from 1.08% to 1.28%.

Absorption spectra of $Z_3$:PCBM and $Z_4$:PCBM composite
films are shown in Figure 5a. The film preparation conditions
of absorption measurements were kept the same as those in
device fabrication for clear comparison. As shown in Figure
5a, the $Z_4$:PCBM blend film exhibits a broader absorption band
in comparison with the $Z_3$:PCBM blend film. From their EQE
curves in Figure 5b, it can be seen that the response range of
$Z_4$-based devices is also much broader than that of $Z_3$-based
devices; however, in the range from 350 to 600 nm, $Z_3$-based
devices exhibit better EQE than $Z_4$-based devices, so $J_{sc}$ of the
$Z_3$-based device is higher. Absorption spectra of the polymer:
PCBM blend films have no change after annealing, but EQE of
two kinds of devices increased obviously.

As shown in Table 2, although FF of the $Z_3$-based device
increased from 30.7% to 36.9% after annealing, this value is
much lower than that of the $Z_4$-based device, which reached
60% after annealing. The difference in FF values indicates that
the charge carrier transport property of the two kinds of devices
could be different, so the space charge limit current (SCLC)
method was used to determine the hole mobility of the polymer:
PCBM composite films. As listed in Table 2, the hole mobility
of $Z_4$:PCBM blend films is about 2 orders of magnitude higher

---

**TABLE 1:** Optical Properties and HOMO Level Values of $Z_3$ and $Z_4$

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{max}$ (nm)</th>
<th>$E_g$ (eV)</th>
<th>$E_{ox}$ (V)/HOMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>soln/film</td>
<td>soln/film</td>
<td></td>
</tr>
<tr>
<td>$Z_3$</td>
<td>387/404</td>
<td>480/531</td>
<td>1.85</td>
</tr>
<tr>
<td>$Z_4$</td>
<td>443/451</td>
<td>613/625</td>
<td>1.55</td>
</tr>
</tbody>
</table>

---

**Figure 2.** Absorption spectra of polymers $Z_3$ and $Z_4$ as films and in chloroform.

**Figure 3.** Cyclic voltammogram plots of $Z_3$ and $Z_4$.

**Figure 4.** $I-V$ plots of the polymer solar cells based on $Z_3$ and $Z_4$, with and without the annealing process.
than that of Z3:PCBM blend films, which should be the main reason for the better FF of Z4-based devices. As mentioned above, the interchain stacking of the adjacent main chains of Z4 should be better than that of Z3, which might be the main reason that Z4:PCBM blend films exhibit much higher hole mobility than Z3:PCBM composite films.

Photoluminescence of the Polymer:PCBM Blends. Photoluminescence (PL) quenching provides direct evidence for exciton dissociation, and thus efficient PL quenching is necessary to obtain efficient organic solar cells. However, this does not necessarily mean that the stronger the PL quenching, the better the performance of the solar cells. In the P3HT/PCBM photovoltaic system, by using the solvent annealing process, the PL quenching effect of PCBM was weakened, but photovoltaic performance of the device was improved distinctly.17 Since behaviors of Z3- and Z4-based solar cells are different under the annealing process, it is necessary to investigate the PL quenching effect of the two polymers. As shown in Figure 6, Z3:PCBM and Z4:PCBM blend films exhibited much different PL quenching effects after annealing. For the Z4:PCBM blend film, the luminescence spectra have no change after the annealing process. However, PL of the Z3:PCBM blend film was quenched by PCBM significantly before annealing and increased a lot after annealing. Although the comparison between these two kinds of blends provided qualitative results only, the phenomenon of PL enhanced by annealing indicates that aggregation of the polymer in the blend is likely increased during the annealing process, and as the surface between the polymer and PCBM phases is reduced, the PL of the polymer cannot be quenched thoroughly.17 However, there is no clear exo- or endothermal process observed in the differential scanning calorimetry (DSC) measurement.

Conclusion

Two BDT-based conjugated polymers, Z3 and Z4, were designed and synthesized through a feasible approach. The hole mobility ($\mu_h$) of Z4 is 2 orders higher than that of Z4, due to the better planar structure of Z4. Photovoltaic results indicate that the Z4-based devices exhibited much higher FF values than the Z3-based devices, and also the Z4-based devices exhibited a broader response range than the Z3-based devices. Although, both bandgap and hole mobility of Z4 are desirable as a photovoltaic material, its HOMO level is too high to obtain a good $V_{oc}$, due to the strong electron-donating effect of its alkoxy groups. On the basis of these results, what we can conclude about molecular structure design of photovoltaic conjugated polymers is as follows: first, the steric hindrance between two adjacent units is an important issue, and second, to reduce the bandgap and hole mobility of Z4, both bandgap and hole mobility of Z4 are desirable as a photovoltaic material, its HOMO level is too high to obtain a good $V_{oc}$, due to the strong electron-donating effect of its alkoxy groups. On the basis of these results, what we can conclude about molecular structure design of photovoltaic conjugated polymers is as follows: first, the steric hindrance between two adjacent units is an important issue, and second, to reduce the bandgap by adding electron-donating groups is not a favorable approach for photovoltaic conjugated polymers. After annealing, $V_{oc}$ of the Z3-based device increased distinctly, from 0.58 to 0.84 V, and its FF also improved to 37%, and as a result, the efficiency of the device increased more than two times. However, the Z4-based device has little change after annealing. PL spectra indicate that PL intensity of the Z3:PCBM blend film increased after annealing, but PL of the Z4:PCBM blend film had no change after the annealing process, which indicates that the aggregation of polymer in the blend of Z3:PCBM is likely increased during the annealing process.
Experimental Section

Characterization. 1H NMR spectra were measured on a Bruker DMX-400 spectrometer. Absorption spectra were taken with a Varian Cary 50 ultraviolet–visible spectrometer. The molecular weight of polymers was measured by the GPC method with chloroform as eluent, and polystyrene was used as a standard. The electrochemical cyclic voltammetry was conducted with a Pt disk coated with the polymer film, Pt wire, and Ag electrode as working electrode, counter electrode, and quasireference electrode, respectively, in a 0.1 mol/L of tetraethylammonium hexafluorophosphate (Bu4NPF6) acetonitrile solution. Since Ag wire was used as a semireference electrode, a trace amount of ferrocene (Fc) was used as a standard material to determine the molecular energy level of the polymers. The thickness of the active layer of the polymer solar cell device was measured with a Dektak profilometer, and the devices was done in a N2-filled glovebox under AM 1.5G illumination (100 mW cm−2), using a Xenon lamp solar simulator calibrated with a silicon diode (with KG5 visible filter) calibrated with the assistance from the National Renewable Energy Laboratory (NREL).

Fabrication of PSC Devices. PSC devices with the typical structure of ITO/PEDOT-PSS/polymer:PCBM(1:3, w/w)/Ca/Al were fabricated under similar conditions as follows: After spincoating a 30 nm layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) onto a precleaned indium–tin oxide (ITO)-coated glass substrate, the polymer/PCBM blend solution was spin-coated. The typical concentration of the polymer/PCBM(1:3, w/w) blend solution used in this study for the spincoating active layer was 10 mg/mL, and chlorobenzene was used as solvent. The thickness of the active layer was ∼70 nm. The devices were completed by evaporating Ca/Al metal electrodes with area of 10.5 mm2 defined by masks.

Synthesis. 4,8-Bis(2-ethylhexyloxy)benzo[1,2-b:3,4-b]dithiophene, 1. 4,8-Dihydrobenzo[1,2-b:5,4-b]dithiophene-4,8-dion (4.4 g, 20 mmol), zinc powder (2.86 g, 44 mmol), and 60 mL of water were put into a flask. The solution was flushed again for 20 min. The oil bath was cooled to room temperature and then extracted by diethyl ether. After solvent was removed under vacuum, the residue was recrystallized by ethyl alcohol very slowly. A yield of 6.35 g of compound 1 (4.08 mmol, yield 68%) was obtained as a colorless needle crystal. 1H NMR (CDCl3, 400 MHz) δ (ppm) 7.52 (s, 2H), 4.23 (d, 4H), 1.79 (m, 2H), 1.54–1.36 (m, 16H), 1.02 (t, 6H), 0.96 (t, 6H). Elemental Anal. Calcd for C26H32O2S2: C, 66.62; H, 6.88, N, 6.23. Found: C, 66.91; H, 8.57. Found: C, 69.71; H, 8.45.

2,6-Dibromo-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:3,4-b]dithiophene, 2. Compound 1 (4.47 g, 10 mmol) was dissolved into 100 mL of methylene chloride in a 250 mL flask. Bromine (3.2 g, 20 mmol) was dissolved into 60 mL of methylene chloride in a funnel and slowly dropped into the flask under an ice–water bath, and then the reactant was stirred for 4–6 h at ambient temperature. When the color of the bromine was diminished, all of the volatile substances were removed under vacuum. The residue was purified by silica gel chromatography with hexane as eluent. A yield of 5.44 g of 2,6-dibromo-4,8-diododecyl-5H-dithiophene (9.0 mmol, yield 90%), compound 2, was obtained as a colorless or pale yellow sticky oil.

1H NMR (CDCl3, 400 MHz) δ (ppm) 7.42 (s, 2H), 4.12 (d, 4H), 1.77 (m, 2H), 1.54–1.36 (m, 16H), 1.02 (t, 6H), 0.96 (t, 6H). Elemental Anal. Calcd for C26H36Br2O2S2: C, 51.66; H, 6.10. Found: C, 51.23; H, 6.10.

2,6-Bis(trimethylsilyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:3,4-b]dithiophene, 3. Compound 2 (3.61 g, 6 mmol) and 60 mL of THF were added into a flask under inert atmosphere. The solution was cooled to −78 °C by a liquid nitrogen–acetone bath, and 4.55 mL of n-butyllithium (13.2 mmol, 2.9 M in n-hexane) was added. After the solution was stirred at −78 °C for 30 min, a great deal of white solid precipitate appeared in the flask. Then, 15 mmol of trimethylchloride (14 mL, 1 M in n-hexane) was added in one portion, and the reactant turned clear rapidly. The cooling bath was removed, and the reactant was stirred at ambient temperature for 2 h. Then, it was poured into 200 mL of cool water and extracted by ether 3 times. The organic layer was washed by water two times, and then dried by anhydrous MgSO4. After the solvent was removed under vacuum, the residue was recrystallized by ethyl alcohol very carefully. A yield of 3.2 g of compound 3 (4.08 mmol, yield 68%) was obtained as a colorless needle crystal. 1H NMR (CDCl3, 400 MHz) δ (ppm) 7.52 (s, 2H), 4.23 (d, 4H), 1.79 (m, 2H), 1.54–1.36 (m, 16H), 1.06 (t, 6H), 0.96 (t, 6H), 0.40 (s, 18H). 13C NMR (CDCl3, 100 MHz) δ (ppm) 143.3, 140.4, 133.9, 139.2, 128.0, 75.7, 40.7, 30.6, 29.3, 23.9, 23.2, 14.2, 11.4, −8.3. Elemental Anal. Calcd for C32H54O2S2Sn2: C, 49.76; H, 7.05. Found: C, 49.56; H, 7.12.

4,7-Bis(3-hexylthiophen-2-yl)-2,1,3-benzothiadiazole, 4. 3-Hexylthiophene that was prepared by a reported method19 (10 mmol, 1.68 g) was put into a flask with 20 mL of THF under an inert atmosphere. The solution was cooled to −78 °C by a liquid nitrogen–acetone bath, and 3.8 mL of n-butyllithium (11 mmol, 2.9 M in n-hexane) was added. The reactant was warmed to ambient temperature gradually and stirred at ambient temperature for an hour, and then tributylstannyl chloride (4.5 g, 14 mmol) was added in one portion. The reactant was stirred for an additional 2 h, and then extracted by diethyl ether. After removing solvent under vacuum, the residue, 2-(tributylstannyl)thiophene, was used directly for the Stille coupling reaction. 2-(Tributylstannyl)thiophene, 3 mmol of 4,7-dibromo-2,1,3-benzothiadiazole (0.88 g) prepared by a reported method19 and 30 mL of toluene were put into a flask. The solution was flushed with argon for 10 min, then 50 mg of Pd(PPh3)4 was added. The solution was flushed again for 20 min. The oil bath was heated to 110 °C, and the reactant was stirred for 16 h at this temperature under argon atmosphere. Then, the reactant was cooled to room temperature and extracted by diethyl ether several times. After solvent was removed, the crude product was purified by silica gel chromatography with hexane/methylene chloride (4:1, v/v) as eluent. The target compound, 0.94 g of 4,7-bis(3-hexylthiophen-2-yl)2,1,3-benzothiadiazole (2.0 mmol, 66%), was obtained as a yellow-orange oil. 1H NMR (CDCl3, 400 MHz) δ (ppm) 7.73 (s, 2H), 7.36 (d, 2H), 6.98 (d, 2H), 2.62 (t, 4H), 1.59 (m, 4H), 1.22 (m, 12H), 0.83 (t, 6H). 13C NMR (CDCl3, 100 MHz) δ (ppm) 154.2, 138.3, 132.4, 129.6, 127.5, 126.1, 124.2, 34.3, 31.8, 29.7, 24.6, 22.2, 14.1. Elemental Anal. Calcd for C28H19N5O2S2: C, 69.62; H, 6.88, N, 6.23. Found: C, 65.62; H, 6.47; N, 5.88.

4,7-Bis(5-bromo-3-hexylthiophen-2-yl)-2,1,3-benzothiadiazole, 5. Compound 4 (0.94 g, 2 mmol) was dissolved into 30 mL of chloroform, and 0.712 g of NBS (4 mmol) was added in small portions. The reactant was stirred at ambient temperature overnight. Then, the reactant was extracted by chloroform several times. After solvent was removed under vacuum, the crude product was purified by silica gel chromatography with
Pd(PPh₃)₄ was added into the flask, which was then flashed by toluene, and flushed with argon for 10 min. Then, 22 mg of compound Z₃ was added into the flask. The reactant was stirred for 1 h under that temperature, and then the cooling bath was removed. The reactant was warmed to room temperature and stirred overnight. After adding 50 mL of methanol to the reactant, the crude product was precipitated and filtered. The red precipitate was collected and purified by recrystallization with ethanol as solvent, and 1.1 g of compound 6 (2.2 mmol) was obtained as red crystals (yield 73%). ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 8.32 (s, 2H), 7.36 (d, 2H), 6.54 (d, 2H), 4.29 (t, 4H), 1.86 (m, 4H), 1.54 (m, 4H), 1.36 (m, 12H), 0.89 (t, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 154.4, 139.3, 131.4, 132.0, 129.7, 124.3, 116.8, 120.2, 72.1, 160.7, 157.2, 132.0, 124.3, 116.8, 120.2, 72.1, 34.2, 30.1, 26.3, 22.9, 14.2. Elemental Anal. Calcd for C₅₂H₆₆N₂O₂S₅: C, 68.53; H, 6.91; N, 3.07. Found: C, 66.90; H, 6.91; N, 3.07.

Polimerization of Z₄ by the Stille Coupling Reaction. In a 150 mL flask, compound 3 (0.74 g, 1 mmol) and compound 5 (0.627 g, 1 mmol) were dissolved into 50 mL of toluene, and flushed with argon for 10 min. Then, 22 mg of Pd(PPh₃)₄ was added into the flask, which was then flashed by argon for another 20 min. The solution was heated to reflux and stirred for 24 h under inert atmosphere. Then, the reactant was cooled to room temperature, and the polymer was precipitated by addition of 50 mL of methanol and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was recovered as a solid sample from the chloroform fraction by rotary evaporation. The deep red solid was dried under vacuum for 1 day to obtain the final product Z₄ (490 mg, yield 46%).

Acknowledgment. This work was financially supported by Solamere Energy Inc., UC Discovery Grant (Grant No. GCP05-10208).

References and Notes

(11) Thompson, B. C.; Kim, Y. G.; Reynolds, J. R. Macromolecules 2005, 38, 5359.