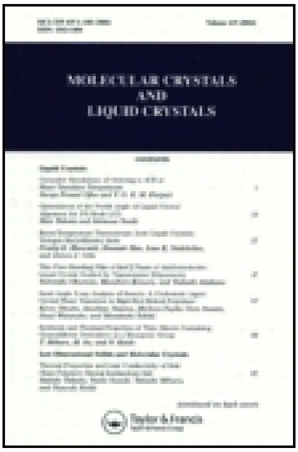

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π-Conjugated Main Chain Polymers Containing Bis(bithiophenyl dithienothiophene)-based Repeating Group and their Application to Polymer Solar Cells

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π-Conjugated Main Chain Polymers Containing Bis(bithiophenyl dithienothiophene)-based Repeating Group and their Application to Polymer Solar Cells

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New dithienothiophene (DTT)-containing conjugated polymers, such as poly(2,6-bis(2-thiophenyl-3-dodecylthiophene-2-yl)dithieno[3,2-b;2′,3′-d]thiophene, ***1*** *and poly(2,6-bis(2-thiophenyl-4-dodecylthiophene-2-yl)dithieno[3,2-b;2′,3′-d]thiophene,* ***2*** *have been successfully synthesized* via *Stille coupling reactions using dodecyl-substituted thiophene-based monomer, bistributyltin dithienothiophene, and bistributyltin bithiophene. The main difference between two polymers is the substitution position of dodecyl side chains in a repeating group. The semiconducting properties of the two polymers have been evaluated in organic photovoltaics (OPVs). Two conjugated polymers are also well mixed with methanofullerene [6,6]-phenyl C61-butyric acid methyl ester (PCBM) for fabricating bulk heterojunction PV devices. As a result, the polymer solar cell devices made of polymers* ***1*** *and* ***2*** *had the best preliminary results with an open-circuit voltage of 0.43–0.44 V, a short-circuit current density of 5.95–5.96 mA/cm^2, and a fill factor of 0.34, offering an overall power conversion efficiency (PCE) of 0.9%.*

Keywords Absorption; conjugated polymers; dithienothiophene; mobility; organic photovoltaics; semiconductor

Introduction

Organic semiconducting π-conjugated polymers are very intriguing and have been significantly developed over the past several years [1,2]. With regard to the application of organic semiconductors in electronic and optoelectronic devices, the polymer solar cell (PSC) in particular is an important device for developing future energy resources [3–5].

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Bulk heterojunction (BHJ) PSCs have been shown to be the most promising devices for OPV cells until now. Electron acceptor molecules were embedded into the p-type host polymers, and nanophase separation was driven by a thermal annealing process to build efficient charge transport channels. Although a number of studies have been conducted on PSCs made of regioregular poly(3-alkylthiophene), and poly[p-phenylene vinylene] (PPV) derivatives are commonly used in BHJ devices along with [6,6]-phenyl C (61 or 71) butyric acid methyl ester (PCBM), BHJ PSCs still demonstrate the highest power conversion efficiency (PCE), that is, approximately 3.0–6.1% [6–9]. In this study, we demonstrate the application of the new conjugated polymers to PSCs. The device properties were characterized and explained by possible mechanisms.

Experimental Section

The synthetic procedure of two conjugated polymers will be reported elsewhere. PCBM was purchased from Nano-C. The redox properties of two molecules were examined by using cyclic voltammetry (Model: EA161 eDAQ). Thin films were coated on a platinum plate using chloroform as a solvent. The electrolyte solution employed was 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in a freshly dried acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was at 50 mV/s.

In order to study absorption behavior, the film of two conjugated polymers and two conjugated polymers: PCBM (1:1 wt/wt) were prepared in chloroform. Thin films were fabricated on quartz substrates using the solution (2 wt%) of each molecule in monochlorobenzene. Absorption spectra of film samples were obtained using a UV-VIS spectrometer (HP 8453, photodiode array type) in the wavelength range of 190–1100 nm.

PSC Fabrication. The hole collecting electrode was 300–400 nm thick indium tin oxide (ITO) coated glass with resistance of 19.5 Ω/cm. ITO glass was cleaned by boiling in chloroform, isopropyl alcohol and acetone for 30 min in each solvent, sonification for 15 min in 50:50 isopropyl alcohol and acetone solution, and finally rinsed with de-ionized water. This cleaned ITO coated glass was treated with O_2 plasma for the purpose of removing any trace of organic materials leftover from solution cleaning and flattening ITO with a microwave-generated plasma reactor (Plasmatic Systems Inc., PLASMATIC-PREENII, 24 GHz) for 15 min. 30 nm thick PEDOT:PSS layer (Baytron P, 1 S cm^{-1}) was coated by spin coating stock solution at 2500 rpm for 30 s. PEDOT:PSS coating was heat treated in the glove box at 200°C for 5 min. 2.5 wt.% of polymer and PCBM was dissolved in anhydrous monochlorobenzene. The thickness of a resulting active layer was 80 nm and pre-annealed at 150°C for 10 min. 0.8 nm thick LiF which served as a buffer layer, was vacuum deposited on top of active layer and 150 nm thick aluminum was evaporated, and prepared device was post annealed at 120°C for 10 min. Thickness of the photoactive film was measured with surface profiler (TENCOR®, P-10 α-step). Current–voltage characteristics were measured with Keithley 2400 source-measure unit. 300 W Xe lamp was used as a light source to produce intensity of 100mW/cm^2. To mimic sunlight, AM 1.5 filter (Oriel) was used neutral density filter was used to reduce intensity as necessary. Intensity of incoming light power was measured with calibrated broadband optical power meter (Spectra Physics model 404).

Results and Discussion

We display here the structures of new p-type DTT-based semiconducting conjugated polymers. Figure 1 illustrates the structures of polymer **1** and polymer **2** including PCBM as an electron acceptor. As solubilizing groups and crystallization promoting moieties, two dodecyl groups were substituted in one repeating group with the positions of two dodecyl groups. Stille coupling of the proper monomers produces the conjugated-polymers, **1** and **2** respectively in high yields of 71–76%. The number-average molecular weights (M_n) of **1** and **2** were determined gel permeation chromatography (GPC) using a polystyrene standard and found to be 16,100 ($M_w/M_n = 1.84$) and 14,700 ($M_w/M_n = 1.93$), respectively.

They were found to have good self-film forming properties and were readily soluble in various organic solvents such as chloroform, xylene, MC, monochlorobenzene, and THF. In particular, more than 5 mg of polymers **1** and **2** can be dissolved in 1 mL monochlorobenzene at room temperature.

The absorption spectra of the thin films were illustrated in Figure 2. In the thermally annealed film of polymer **1**, the absorption spectrum was shown to be structureless and significantly red-shifted compared to the solution spectrum, which is attributed to the formation of an ordered structure in a localized domain with an intermolecular. π-stacking. The spectrum of polymer **1**, which indicates that the spin-coated films already contained nano-sized crystallites and chain arrangement was fully developed. When mixing PCBM with polymers and annealing the sample, we observed no spectral shift to a longer wavelength. This is attributed to the low bandgap properties of the polymers and the charge transfer band is ambiguous to be defined due to spectral overlap. Therefore, it is expected that they are easily associated with each other in order to improve nano-phase separation in the blended mixture.

Cyclic voltammograms (CV) of a film sample were recorded and the redox potentials relative to an internal ferrocene reference (Fc/Fc$^+$) were obtained. These

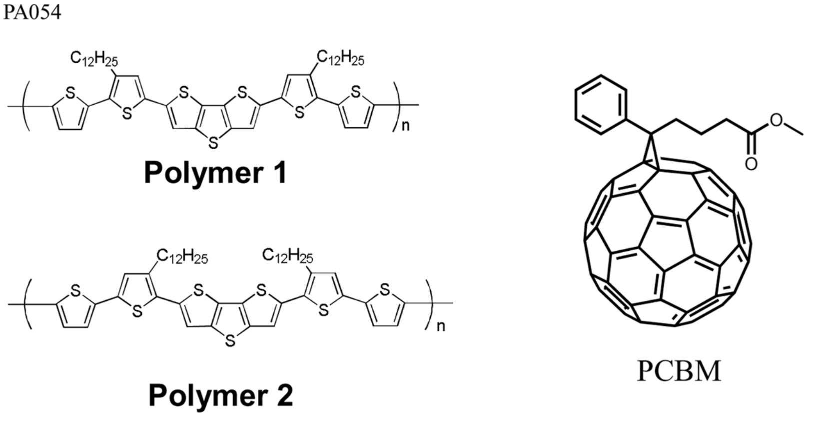

Figure 1. Structures of two conjugated polymers and PCBM used for bulk heterojunction PSCs.

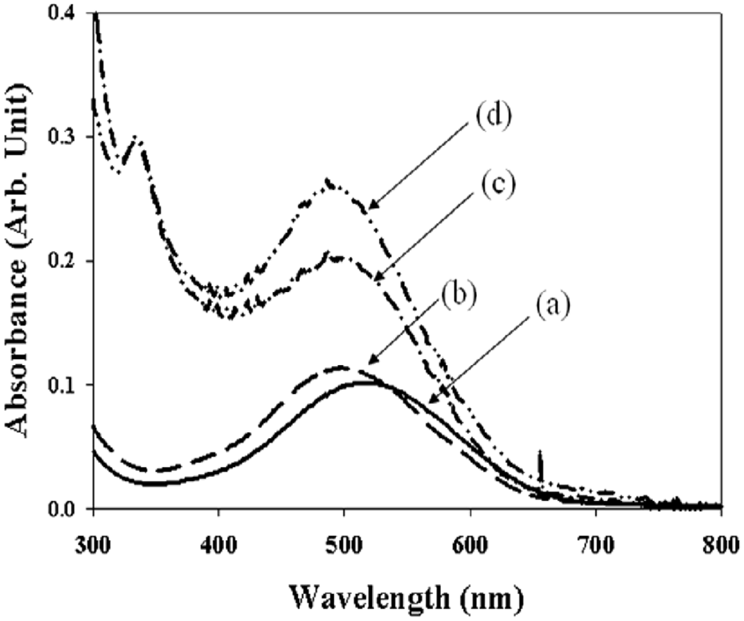

Figure 2. Absorption spectra of two conjugated polymers and its PCBM blend sample. *(a) annealed film of polymer **1**, (b) annealed film of Polymer **2**, (c) annealed film of Polymer **1**/PCBM (1:1 w/w), (d) annealed film of Polymer **2**/PCBM (1:1 w/w).

CV scans in the range −2.0 V to +2.0 V (vs Ag/Ag$^+$) showed quasi-reversible oxidation peaks. Unfortunately, the reduction behaviors were irreversible; we were therefore unable to estimate their HOMO and LUMO energies accurately. In order to determine the LUMO levels, we combined the oxidation potential in the CV with the optical energy bandgap (E_g^{opt}) resulting from the absorption edge in the absorption spectrum. Voltammograms of polymers **1** and **2** in the film state show that their lowest oxidative waves are at +0.77, and +0.81 V, respectively. Polymers **1** and **2** have HOMO levels of −5.17, and −5.21 eV, respectively.

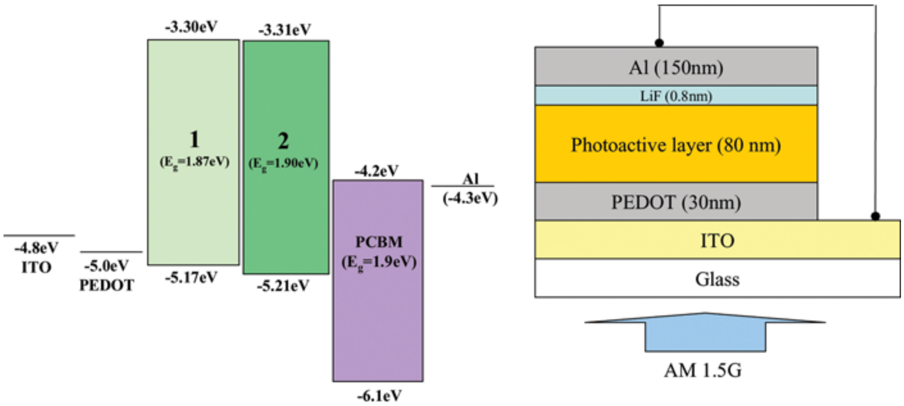

Figure 3. Molecular energy level alignment of two conjugated polymers and PSC device configuration.

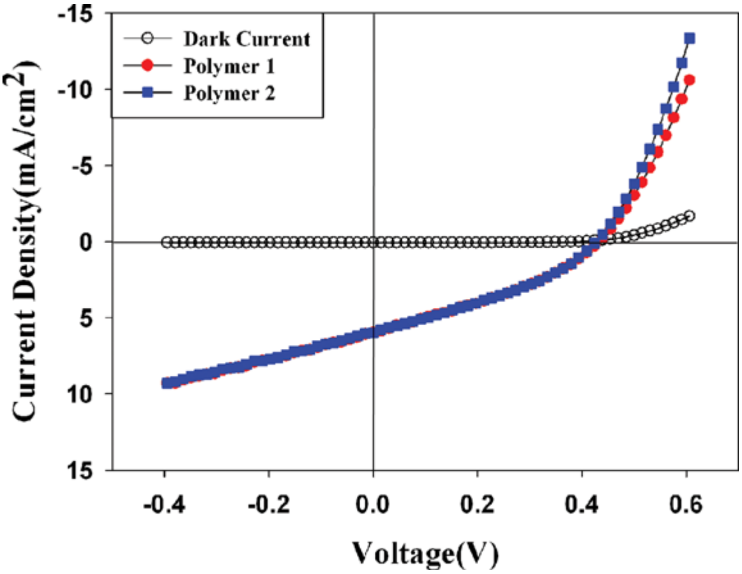

Figure 4. Current density versus voltage characteristics of Al/PEDOT/ Polymer:PCBM/LiF/ Al with the concentration of PCBM under AM 1.5 G illumination. *closed symbol (photocurrent density), open symbol (dark current density).

We demonstrated PSC devices fabricated with two conjugated polymers. In Figure 3, the molecular energy levels and device configuration are well illustrated. First, we fabricated the PSC devices using two polymers with PCBM (polymer : PCBM = 1:1 wt/wt). The device performances were characterized under identical conditions. The open circuit voltage of the polymer-based cell was 0.43–0.44 V lower than that of poly(3-heyxlthiophene)-based cell since the HOMO level of polymer was 5.17–5.21 eV. The energy difference between the HOMO of the donor and the LUMO of the acceptor was found to most closely correlate with the V_{oc} value. Theoretically, if the HOMO levels are identical, different devices having the same components should display the same V_{oc} value. However, the samples showed a slightly lower V_{oc} value, which might be attributed to different surface morphological properties. The binary blend samples with polymer and PCBM involve a short-circuit current density of 5.95–5.96 mA cm^{-2}. The fill factor, a measure of the squareness of the *J*(*V* characteristics, is equal to 0.34. (see Figure 4 and Table 1)

The power conversion efficiencies of two PSC devices were all around 0.9%. Although the substitution position of long alkyl chain is different in two conjugated polymers, almost identical power conversion efficiency was observed, implying that the nanophase separation behavior and internal morphology of two BHJ devices were not affected by the structural difference.

Table 1. Summary of PSC device performance

Polymer: PCBM = (1:1)	I_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
Polymer 1: PCBM	5.96	0.43	34	0.9%
Polymer 2: PCBM	5.95	0.44	34	0.9%

Conclusions

Soluble π-conjugated polymers based on DTT-fused ring structure in the repeating unit were synthesized by palladium(0)-catalyzed Stille coupling reaction successfully. Two polymers can also be exploited in bulk heterojunction polymer solar cells in combination with PCBM. Although the V_{oc} values are lower than that of P3HT/PCBM PSC, the PSC devices had power conversion efficiencies up to 0.9% under simulated AM1.5. In particular, the generation of high photocurrents is attributable to the photoinduced charge separation of the compound and the favorable internal morphology by fused ring-based polymer network for better carrier transport.

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