



Synthesis and Photovoltaic Properties of a New Thiophene-Cyclopentadiene-Based Conjugated Polymer

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A new low-band gap polymer containing thiophene and cyclopentadiene, poly(5,2,2'-dioctyldithiophenylcyclopentadiene) (PDTCP), has been synthesized via the FeCl₃ oxidative polymerization. PDTCP showed a broad absorption band and a low energy band gap of 1.82 eV. The photoluminescence (PL) of PDTCP is completely quenched upon addition of PCBM indicative of efficient charge transfer. Bulk heterojunction organic photovoltaic cells (OPVs) fabricated from PDTCP as an electron donor showed an open-circuit voltage (V_{OC}) of 0.50 V, a short-circuit current (J_{SC}) of 1.24 mA/cm², and the power conversion efficiency of up to 0.20% under AM 1.5 (100 mW/cm²).

Keywords: Cyclopentadiene, Organic Photovoltaic Cell, Organic Solar cell.

1. INTRODUCTION

OPVs are promising sources of electrical power that have attracted considerable attention because of their efficiency, low cost, and potential renewable energy applications.^{1,2} During the last decade the field of polymer photovoltaics has seen a remarkable progress in both device performance and understanding of the governing physical processes. To date, most efforts have been devoted to developing bulk-heterojunction polymer solar cells composed of polymer donors and soluble fullerene, acceptors, because of the easy fabrication and low cost of such cells. The prototypical large band gap material system consisting of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methylester (PC₆₁BM) is nearing optimal device performance.³ However, because the large band gap material system consisted of poly(3-hexylthiophene) (P3HT) can harvest photons with wavelengths below ~650 nm, low-band gap conjugated polymers with proper energy levels are required for efficient charge transfer and high-efficiency polymer solar cells.⁴⁻⁷

In continuing search of low-band gap (<2.0 eV) materials, conjugated polymers based on thiophene and cyclopentadiene have also been studied. Following the theoretical study by Bäuerle et al. in which an energy band gap of poly(thiophenecyclopentadiene) was estimated as 1.7 eV,⁸ the real copolymers containing thiophene and cyclopentadiene have been reported by Berlin et al.⁹ In their work, the regular copolymers were

successfully synthesized by electrochemical oxidation, whereas the chemical polymerization was not considered because of low solubility of their non-substituted monomers. Here we first demonstrate the synthesis and characterization of the chemically polymerized regular copolymer of dithienylcyclopentadiene. In this work, we have synthesized new conjugated polymer based on thiophene and cyclopentadiene, poly(5,2,2'-dioctyldithiophenyl-cyclopentadiene) (PDTCP), via FeCl₃ oxidative polymerization. The alkyl groups were introduced into the 5 position of the cyclopentadiene to improve the solubility of the resulting polymer as well as to protect the undesired coupling between the acidic hydrogen atoms of non-substituted cyclopentadienes.⁹ The general properties of the polymer including its thermal, electrochemical, and optical properties, are investigated herein. Moreover, photovoltaic properties of new synthesized polymer were discussed on the basis of the optical and electrochemical analysis.

2. EXPERIMENTAL DETAILS

2.1. Characterization

¹H NMR (600 MHz) spectra were obtained using a Bruker spectrometer. The molecular weight of copolymers were measured by gel permeation chromatography (GPC) using a polystyrene as standard and THF as eluent. Elemental analyses were performed with a Thermo Fisher Flash EA 1112 elemental analyzer. Differential scanning calorimetry (DSC) was performed on a TA instrument Q100 at heating and cooling rates of 10 °C/min under a nitrogen

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atmosphere. Thermal gravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min through the use of the Perkin Elmer TGA7 thermogravimetric analyzer. UV-vis spectra were obtained using a Shimadzu UV-vis spectrometer and PL spectra were obtained using a PerkinElmer spectrofluorometer. The electrochemical properties of the polymers were characterized by cyclic voltammetry (CV). The films were prepared by dip-coating the polymer solution onto Pt wire and the measurements were calibrated using the ferrocene value of -4.8 eV as the standard. Film thicknesses were measured using a TENCOR surface profiler. Atomic force microscopy (AFM) images were obtained with a Digital Instruments D3100 microscope in the tapping-mode.

2.2. Materials

All reagents purchased commercially were used without further purification. 4-(Thien-2-yl)-4-oxobutyric acid methyl ester (**3**) was synthesized according to the literature procedure.¹⁰

2.3. Synthesis

1,4-Bis(thien-2-yl)-1,3-cyclopentadiene (**4**): Compound **3** (3.0 g, 15.2 mmol, 1.1 eq) was added dropwise to a stirred suspension of sodium ethoxide (2.47 g, 34.5 mmol, 2.5 eq) in benzene (50 ml). After 15 min stirring, 1-(thien-2-yl)ethanone (1.52 mL, 13.8 mmol) and tetrabutylammonium bromide (4.49 g, 15.2 mmol, 1.1 eq) were added to the red solution. The reaction mixture was stirred at 50 °C overnight. After cooling to room temperature, 0.4 M HCl (50 ml) was added and the resulting mixture was extracted with ether. The organic phase was dried with MgSO₄ and the solvent evaporated. Flash chromatography of the residue (silica gel, ethyl acetate/hexane 1:9) afforded the title compound as a yellow solid (0.77 g, Yield: 22%). ¹H NMR (CDCl₃, 600 MHz), δ (ppm): 3.78 (s, 2 H), 6.67 (s, 2 H), 6.98 (dd, 2 H), 7.06 (d, 2 H), 7.14 (d, 2 H).

5,5-Dioctyl-1,4-bis(thien-2-yl)-1,3-cyclopentadiene (DTCP): Octane bromide (1.99 mL, 11.5 mmol, 2.2 eq) was added to a mixture of **4** (1.20 g, 5.21 mmol) and K₂CO₃ (7.2 g, 52.1 mmol, 10 eq) in N,N-dimethylformamide (DMF, 70 ml). The reaction mixture was stirred at 80 °C overnight, then filtered and the solvent evaporated. The organic layer was washed with 1 M HCl and then dried by anhydrous MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: hexane) to give the final product (0.28 g, Yield: 12%). ¹H NMR (CDCl₃, 600 MHz), δ (ppm): 0.75 (t, 6 H), 1.08 (m, 24 H), 2.01 (m, 4 H), 6.70 (s, 2 H), 7.03 (dd, 2 H), 7.13 (d, 2 H), 7.19 (d, 2 H).

Poly(5,2,2'-dioctyldithiophenylcyclopentadiene) (PDTCP): The polymer PDTCP was synthesized by the chemical oxidation route using FeCl₃ as the oxidant.¹¹

A solution of DTCP in chlorobenzene was added dropwise to a stirred mixture of FeCl₃ in chlorobenzene under an argon atmosphere. The resulting mixture was refluxed for two days at 65 °C. After cooling down to room temperature, the mixture was poured into methanol. The precipitated polymer was collected by filtration and re-precipitated from methanol. The re-precipitated polymer was added to a mixture of methanol and 30% aqueous ammonia solution, and then was stirred for 3 days, in order to remove ionic impurity. The final product, a dark brown solid, was obtained after drying in vacuo at 60 °C. Anal. Calcd for (C₂₉H₄₀S₂)_n: C, 76.93; H, 8.90; S, 14.16. Found: C, 79.63; H, 9.77; S, 10.61.

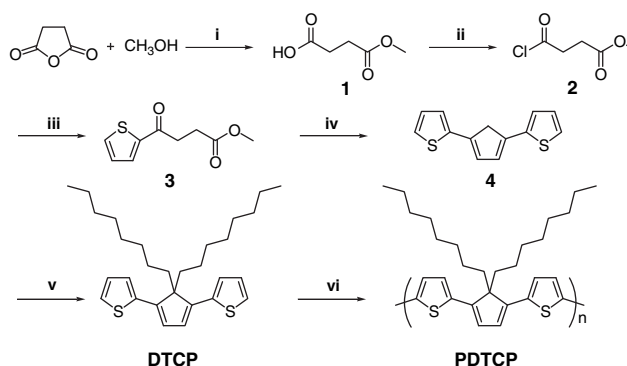
2.4. Device Fabrication

The OPVs were fabricated with the configuration ITO/PEDOT:PSS (40 nm)/PDTCP:PCBM/Al (100 nm). The ITO-coated glass substrates were cleaned by ultrasonic treatment in acetone and deionized water. The PEDOT:PSS layer was spin-coated on the substrate (3000 rpm, 30 s) and annealed at 120 °C for 20 min. The active layer consisting of polymer and PCBM was spin-coated from a chlorobenzene solution and subsequently annealed at 60 °C in vacuo. The devices were completed by evaporating Al metal electrode. The area of the device was 4 mm². The current–voltage (*J*–*V*) characteristics of the OPV cells were measured with a Keithley 2400 source-measure unit under white light illumination of AM 1.5, 100 mW/cm². All fabrication and characterizations were performed in an ambient environment.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization

A new low-band gap polymer containing thiophene and cyclopentadiene, poly(5,2,2'-dioctyldithiophenylcyclopentadiene) (PDTCP), has been synthesized via the FeCl₃



Scheme 1. Synthetic procedure of PDTCP: (i) 60 °C, 4 h; (ii) CH₂Cl₂, SOCl₂, reflux, 2 h; (iii) 1 M SnCl₄, CH₂Cl₂, thiophene, 0 °C, then rt, overnight; (iv) EtONa, benzene, rt, 15 min, then 2-acetylthiophene, Bu₄NBr, reflux, 10 h; (v) 1-bromooctane, K₂CO₃, DMF, 80 °C, overnight; (vi) FeCl₃, chlorobenzene, reflux, 2 days.

oxidative polymerization. Scheme 1 outlines the synthetic route to the polymer PDTCP. Firstly, 3-carbomethoxypropionyl chloride (**2**) was easily obtained from succinic anhydride in one-pot synthesis (yield: > 98%). The following Friedel-Crafts reaction of acid chloride (**2**) resulted in the formation of γ -keto ester, 4-(thien-2-yl)-4-oxobutyric acid methyl ester (**3**).¹⁰ Next, 1,4-bis(thien-2-yl)-1,3-cyclopentadiene (**4**) was obtained by a procedure adapted from the literature in the presence of Bu_4NBr .⁹ Then, octyl side groups were introduced into the 5 position of **4** to yield monomer (DTCP). Finally, the polymer was synthesized by the chemical oxidation route using FeCl_3 as the oxidant.¹¹ The weight-average molecular weight (M_w) of PDTCP, determined by GPC, was 9,800 ($M_w/M_n = 3.5$). The relatively low molecular weight of PDTCP might be due to the rigid polymer backbone and low solubility of polymer. Thermal characteristics of the polymer were studied by DSC and TGA measurements (Fig. 1). The 5% weight loss of PDTCP occurred at around 300 °C.

3.2. Photophysical Properties

Figure 2 shows UV-visible absorption and PL emission spectra of PDTCP in chloroform solution together with those of monomer (DTCP) for comparison. While the absorption and emission maxima of DTCP monomer solution occurred at 350 and 465 nm, respectively, the polymer PDTCP showed the absorption and emission maxima at 425 and 540 nm, respectively. Both the absorption and emission peaks of the polymer are clearly red-shifted with respect to those of DTCP, which confirms the extended conjugation length of the polymer. More importantly, the polymer solution showed a very broad absorption band, covering the visible region from 340 to 700 nm with a maximum at 425 nm, which is favorable for the light harvesting ability.¹² The optical band gap (E_g) of PDTCP, estimated from the absorption onset wavelength ($E_g = 1240/\lambda_{\text{onset}}$ eV), is 1.82 eV, which is close to the previous

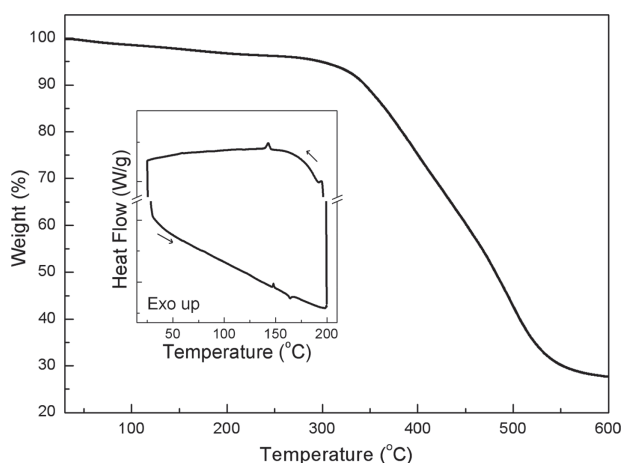


Fig. 1. DSC and TGA thermograms of PDTCP.

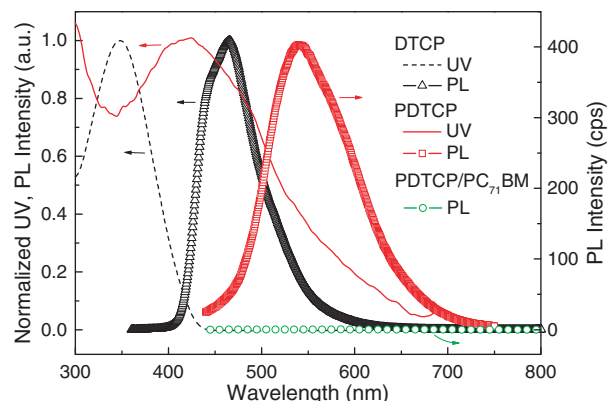


Fig. 2. UV-visible absorption and PL emission spectra of DTCP, PDTCP, and PDTCP/PC₇₁BM blend in solution.

theoretical study.⁹ This low-band gap indicates the possibility of the use of PDTCP in OPVs. Moreover, the PL of PDTCP is completely quenched upon addition of PC₇₁BM showing efficient charge transfer. The electrochemical property of PDTCP was also studied by cyclic voltammetry (CV) (Fig. 3). The films were prepared by dip-coating the polymer solution onto Pt wire and the measurements were calibrated using ferrocene value of -4.8 eV as the standard.¹³ In the anodic scan, the onset of oxidation of PDTCP occurs at 0.71 V (vs. SCE), which corresponds to the HOMO level of -5.10 eV according to the empirical relationship proposed by Leeuw et al. ($I_p(\text{HOMO}) = -(E_{\text{onset}} + 4.39)$ (eV), where E_{onset} is the onset potential of oxidation). The LUMO level of the polymer, calculated from the optical band gap and the HOMO level, is -3.28 eV.

3.3. Photovoltaic Properties

The OPVs were fabricated with the configuration of ITO/PEDOT:PSS/PDTCP:PCBM (65 nm)/Al. The polymer

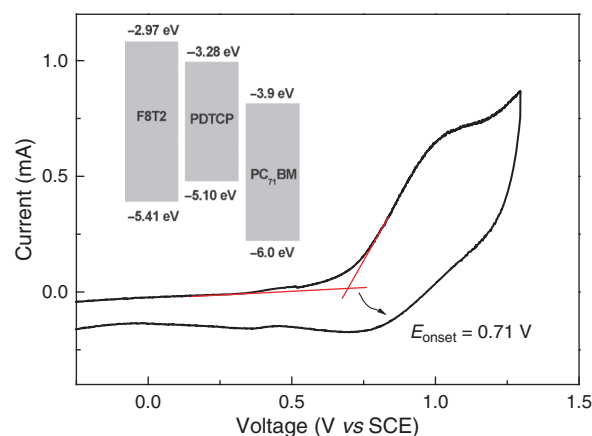


Fig. 3. Cyclic voltammogram of the polymer film. Inset: Energy level diagram.

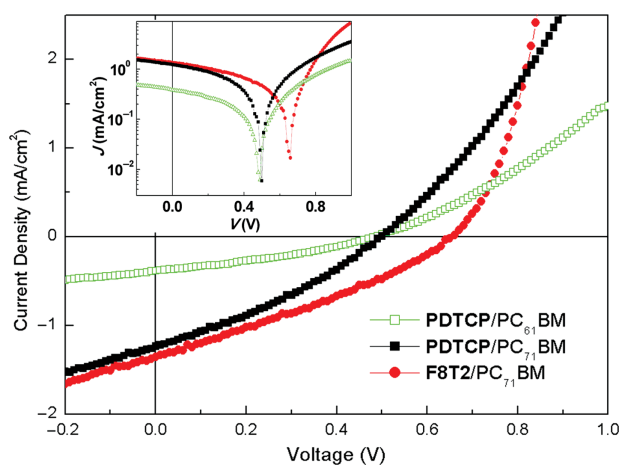


Fig. 4. J - V curve of polymer:PCBM blend films.

and PCBM blend films (1:3, 6 wt-%) were spin-coated to form bulk-heterojunction active layers. Figure 4 shows the J - V curves for polymer:PCBM devices and the photovoltaic properties of the films with various fabrication conditions are summarized in Table I. AFM morphology of PDTCP:PC₇₁BM blend film is shown in Figure 5. While PDTCP:PC₆₁BM showed low device performance of 0.07%, the efficiency of PDTCP:PC₇₁BM was increased up to 0.20% owing to the increased J_{SC} from 0.39 to 1.24 mA/cm². This acceptor effect in the PDTCP:PCBM blends can be explained by increased absorption in the visible region of PC₇₁BM than PC₆₁BM.¹⁴ For comparison, the OPV device with a well-known fluorene-thiophene-based copolymer, poly(9,9'-dioctyl-fluorene-*alt*-bithiophene) (F8T2),¹³ was also fabricated in the same way. The V_{OC} of PDTCP (\sim 0.50 V) was lower than that of F8T2 (0.66 V) due to the higher HOMO level of PDTCP (Inset of Fig. 3), however, it is worth noting that OPV performance of PDTCP (0.20%) is comparable to that of F8T2 (0.27%) showing similar J_{SC} and FF values. Because the lower band gap and broader UV absorption of PDTCP than F8T2 is preferable for OPVs, we can expect that the efficiency of PDTCP can be improved by further optimization. Further improvements in the photovoltaic characteristics could potentially be achieved by improving solubility of polymer with longer alkyl chain and/or incorporating other co-monomers such as benzothiadiazole.

Table I. Photovoltaic properties of OPV cells^a.

	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
PDTCP/PC ₆₁ BM	0.39	0.49	34.6	0.07
PDTCP/PC ₇₁ BM	1.24	0.50	32.2	0.20
F8T2/PC ₇₁ BM	1.31	0.66	30.7	0.27

Note: ^a J_{SC} : short circuit current, V_{OC} : open circuit voltage, FF: fill factor, PCE: power conversion efficiency.

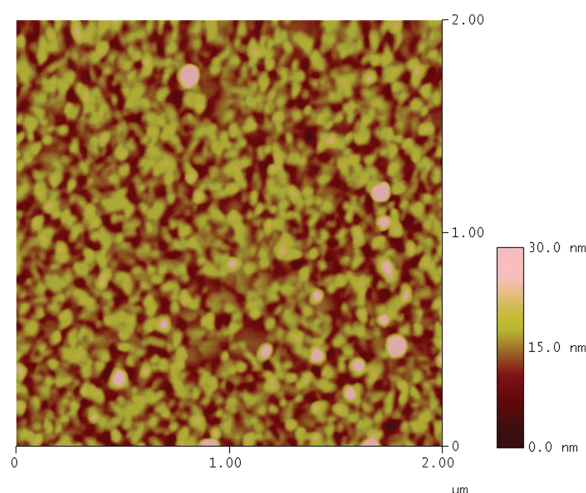


Fig. 5. AFM morphology of PDTCP:PC₇₁BM blend film (scan size: $2 \times 2 \mu\text{m}^2$, rms = 3.5 nm).

4. CONCLUSION

In summary, we have developed a new thiophene-cyclopentadiene-based copolymer, which exhibited a low energy band gap of 1.82 eV. Our preliminary device work showed the possibility of the use of PDTCP as a donor in OPVs. In this work, the best PCE value of 0.20% was achieved with PDTCP:PC₇₁BM blend, which is comparable to that of F8T2:PC₇₁BM blend.

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