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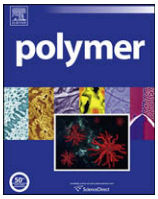

Synthesis of a soluble conjugated copolymer based on dialkyl-substituted dithienothiophene and its application in photovoltaic cells

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ABSTRACT

A soluble conjugated alternating 3,5-didecanyldithieno[3,2-*b*:2′,3′-*d*]thiophene–thiophene copolymer was synthesized by palladium(0)-catalyzed Stille coupling reaction. The thermal, absorption, emission, electrochemical, and photovoltaic properties of the polymer were examined. A weight-average molecular weight around 6.2×10^4 and a polydispersity index of 1.8 was estimated for the polymer using gel permeation chromatography. The polymer exhibits good thermal stability with decomposition temperature of 340 °C and glass-transition temperature of 136 °C. The polymer shows strong absorption peaked at 505 nm in diluted solution and 518 nm in thin film with an optical band gap 2.0 eV. The polymer exhibits intense emission located at 550 nm in solution and 603 nm in film. The HOMO and LUMO energies of the polymer were estimated to be −5.4 and −3.4 eV, respectively, by cyclic voltammetry. Polymer solar cells were fabricated based on the blend of the polymer and methanofullerene [6,6]-phenyl C61-butyric acid methyl ester (PCBM). The power conversion efficiency of 0.7% was achieved under AM 1.5, 100 mW/cm^2 using polymer:PCBM (1:4, w/w) as active layer.

1. Introduction

Since the discovery of conducting polyacetylene in 1970s, conjugated polymers have attracted considerable attention due to their potential for use in low-cost, light-weight, and flexible large-area electronic devices, such as organic light-emitting diodes (OLEDs) [1], organic field-effect transistors (OFETs) [2,3] and photovoltaic cells (OPVs) [4,5]. Soluble polymers that could be suitably modified at the molecular level are compatible with solution processing techniques such as spin coating, stamping, or inkjet printing, thereby eliminating expensive lithography and vacuum deposition necessary for silicon-based inorganic materials [6]. The introduction of fused aromatic rings into polymer chain could improve charge mobility, lower band gap and extend absorption. However, strong π-interactions and rigidity of the fused aromatic systems usually lead to poor solubility of the polymers. In order to improve the solubility and assembly property of the polymers, alky chains with different length are attached to various fused rings such as thienothiophene [7], tetrathienoacene [8], dithienopyrrole [9], dithienosilole [10,11] and cyclopentadithiophene [12,13].

Dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT), a sulfur rich (three S atoms) and electron rich building block, has been introduced into the conducting polymers [14]. Electrochemical polymerization of DTT [15,16] produced polydithienothiophene (polyDTT) with low energy gaps (1.1–1.7 eV) [17]. Moreover, polyDTT exhibited electrochromic property [18]. However, polyDTT is completely insoluble in common solvents, preventing the possibility of solution processing [19]. To improve the solubility of polyDTT, alkyl-substituted co-units were introduced into the polymer backbone. For example, a few groups incorporated alkyl-substituted bithiophene units into the polymer backbone and used the copolymers to fabricate OPVs [20] and OFETs [21]. Copolymers of DTT with fluorene [22] or *p*-bis(cyanovinyl)phenylene [23] emit intense fluorescence. Recently, we reported synthesis of perylene diimide–DTT [24,25] and porphyrin–DTT [26] copolymers and their applications in OPVs and OFETs. However, due to synthetic challenge [27], there has been only one report on polymers based on alkyl-substituted DTT, in which we described synthesis of dialkyl-substituted DTT homopolymers and application in OPVs [28]. In this paper, we present synthesis and characterization of a new 3,5-didecanyldithieno[3,2-*b*:2′,3′-*d*]thiophene–thiophene copolymer. This

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polymer exhibits strong absorption and relatively high oxidation potential. In addition, this polymer was used in OPV device configurations to demonstrate its potential utility; an improved power conversion efficiency was obtained compared to our previous homopolymer [28].

2. Experimental section

2.1. Materials

Toluene was distilled from sodium-benzophenone under nitrogen prior to use. All other reagents such as $Pd(PPh_3)_4$ (Strem) were used as commercially purchased without further purification. 3,5-Didecanyldithieno[3,2-*b*:2′,3′-*d*]thiophene was prepared from thiophene as described in literature [27]. 2,6-Dibromo-3,5-didecanyldithieno[3,2-*b*:2′,3′-*d*]thiophene was synthesized according to our published procedure [28]. 2,5-Bis-tributylstannanyl-thiophene was prepared according to literature procedure [29].

2.2. Characterization

The ^1H spectra were measured on a Bruker AVANCE 400 MHz spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. Elemental analyses were carried out using a FLASH EA1112 elemental analyzer. Solution (chloroform) and thin film (on quartz substrate) UV–vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. Emission spectra in chloroform and thin film (on quartz substrate) were collected on a Hitachi F-4500 spectrofluorophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) in acetonitrile using a computer-controlled Zahner IM6e electrochemical workstation, a glassy-carbon working electrode coated with polymer films, a platinum-wire auxiliary electrode, and an Ag wire anodized with AgCl as a pseudo-reference electrode. Potentials were referenced to the ferrocenium/ferrocene ($FeCp_2^{+/0}$) couple by using ferrocene as an internal standard. Thermogravimetric analysis (TGA) measurements were performed on Shimadzu thermogravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of 20 °C/min. Thermal induced phase transition behaviors were measured by differential scanning calorimetry (DSC) using a Perkin–Elmer differential scanning calorimeter (DSC7) under a nitrogen atmosphere at a heating rate of 20 °C/min. The gel permeation chromatography (GPC) measurements were performed on a Waters 515 chromatograph connected to a Waters 2414 refractive index detector, using toluene as eluent and polystyrene standards as calibrants. Three Waters Styragel columns (HT2, 3, 4) connected in series were used.

2.3. Fabrication and characterization of OPV

The OPV structure used in this study was ITO/PEDOT:PSS/polymer:PCBM/Al. ITO/PEDOT:PSS is the hole-collecting electrode and Al is the electron-collecting electrode. The polymer and PCBM were dissolved in *o*-dichlorobenzene at a same concentration of 20 mg/mL. The ITO-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone, detergent, and isopropyl alcohol sequentially, followed by spin coating of a 40 nm layer of PEDOT:PSS (Baytron pH 500 from H. C. Starck). After drying PEDOT:PSS at 120 °C for 20 min, a 50 nm layer of polymer:PCBM (from 1:1 to 1:4, w/w) was spin coated from *o*-dichlorobenzene solution onto the top of PEDOT:PSS (due to limited solubility of the polymer, a film with a higher thickness showed poor film quality). The film thickness was verified by a surface profilometer (Tencor, Alpha-500). A 100 nm thick aluminum as cathode was thermally evaporated in vacuum at a pressure below 3×10^{-4} Pa through a shadow mask. The active area of the device was 15 mm^2. The power conversion efficiency was measured under the illumination of AM 1.5 G from a solar simulator (Oriel model 91192) (100 mW/cm^2). The current density–voltage (*J*–*V*) characteristics were recorded with a Keithley 236 source unit. The spectral response was measured with a commercial photomodulation spectroscopic setup model (Merlin, Oriel). A calibrated Si photodiode was used as a standard in determination of photosensitivity. To investigate the effect of thermal annealing on device performance, the devices were annealed at 110 °C for 10 min.

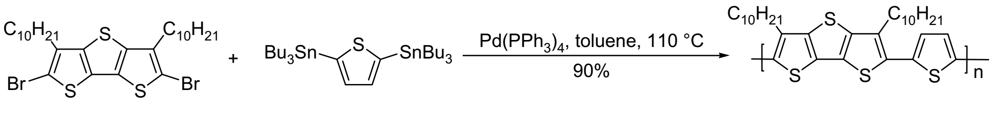
2.4. Synthesis of poly{[3,5-didecanyldithieno[3,2-b:2′,3′-d]thiophene-2,6-diyl]-alt-(thiophene-2,5-diyl)}

To a three-neck round bottom flask was added 2,5-bis-tributylstannanyl-thiophene (286 mg, 0.43 mmol) and 2,6-dibromo-3,5-didecanyldithieno[3,2-*b*:2′,3′-*d*]thiophene (273 mg, 0.43 mmol). The mixture was deoxygenated with nitrogen for 30 min, after which dry toluene (10 mL) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) were added under nitrogen stream. The mixture was heated to 110 °C and stirred for 3 days. After cooling down to room temperature, a solution of KF (5 g) in water (10 mL) was added and stirred at room temperature for 2 h to remove the tin impurity. The mixture was extracted with $CHCl_3$ (2×150 mL), washed with water (2×300 mL), and dried over anhydrous $MgSO_4$. The solution was concentrated to 3 mL, then dropped into 100 mL of methanol. The precipitate was filtered, and washed with methanol. The solid was redissolved in 10 mL of CH_2Cl_2, then dropped into 100 mL of acetone. The precipitate was filtered, and Soxhlet extracted with methanol for 2 days to afford a reddish black solid (217 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (br, 2H), 2.98 (br, 4H), 1.73–0.87 (m, 38H). Anal. Calcd for $(C_{32}H_{44}S_4)_n$: C, 69.01; H, 7.96. Found: C, 65.52; H, 8.06%. M_w, 6.2×10^4; M_w/M_n, 1.8. UV ($CHCl_3$), λ_{max} (ε_{max}): 505 (1.63×10^5) nm ($mol^{-1}\,L\,cm^{-1}$).

3. Results and discussion

3.1. Synthesis and characterization of the polymer

The synthesis of the polymer is outlined in Scheme 1. The polymer was obtained in high yield by Stille coupling condensation polymerization between thiophene ditin and dialkyl-substituted DTT dibromide. The polymer is soluble in chloroform, THF and *o*-dichlorobenzene, and can readily be processed from solution. The weight-average molecular weight and polydispersity index of the



Scheme 1. Synthetic route to the polymer.

polymer were estimated 6.2×10^4 and 1.8 respectively, using GPC against polystyrene standards.

The polymer exhibits good thermal stability with decomposition temperature of 338 °C (5% weight loss) under nitrogen (Fig. 1). According to the DSC measurement (Fig. 1), the polymer shows an obvious glass-transition at 136 °C, indicating that this polymer is amorphous.

3.2. Photophysical properties

Absorption and photoluminescence (PL) spectra of the polymer in chloroform and in thin film are shown in Fig. 2. The polymer exhibits absorption maxima at 505 nm in solution and at 518 nm in film. It is worthy noting that the absorption coefficient of the polymer in solution is 1.63×10^5 mol^{-1} L cm^{-1} at 505 nm, larger than that for most of photovoltaic materials [4,5]. The absorption in solid state red shifts 13 nm compared to that in solution, probably related to the strong intermolecular interaction caused by coplanar and rigid structure of the main chain. The optical band gap is estimated to be 2.0 eV from the onset absorption edge in thin film, similar to that of regioregular poly(3-hexylthiophene) (P3HT), a well established polymer donor. Fluorescence spectra of the polymer show emission peaked at 550 nm in solution and 603 nm in film.

3.3. Electrochemistry

The polymer was also studied using cyclic voltammetry; cyclic voltammogram is illustrated in Fig. 3. The polymer shows only one irreversible oxidation peak, indicating the charged species to be unstable in solution. The onset oxidation potential is 0.58 V versus $FeCp_2^{+/0}$. The HOMO level of the polymer is estimated at −5.4 eV from the onset oxidation potential, assuming the absolute energy level of $FeCp_2^{+/0}$ to be 4.8 eV below vacuum. The HOMO level of −5.4 eV is lower than that of P3HT (ca. −4.8 eV) [29]. The LUMO level of the polymer is estimated to be −3.4 eV from the HOMO energy and the optical band gap.

3.4. Photovoltaic cells

Solution-processable fullerene derivative – methanofullerene [6]-phenyl C61-butyric acid methyl ester (PCBM) is a typical electron acceptor in the fabrication of bulk heterojunction photovoltaic cells. To study the potential of the alkyl-substituted dithienothiophene–thiophene copolymer for photovoltaic applications, we employed this polymer as an electron donor and PCBM as an electron acceptor, and fabricated bulk heterojunction OPVs with a structure of ITO/PEDOT:PSS/polymer:PCBM/Al. Both estimated HOMO and LUMO levels of the donor are more than 0.6 eV higher than that of the acceptor PCBM, indicating that the energy level positions of the donor and acceptor are suitable for efficient charge transfer and separation at the interface between the donor and acceptor [30,31].

Fig. 4 shows UV–vis absorption spectra of thin films of neat polymer and polymer:PCBM blends with weight ratios of 1:1, 1:2, and 1:4. The polymer donor shows strong absorption from 400 to 600 nm, while PCBM exhibits weak absorption in visible region. Therefore, upon increasing polymer:PCBM weight ratio from 1:1 to 1:4, the absorption intensity of the blend decreases.

PL quenching in donor/acceptor composites is a symptom of efficient photoinduced charge transfer between the donor and acceptor [32]. Fig. 5 shows PL of blends of the polymer and PCBM in ratios of 1:1, 1:2, and 1:4 (w/w) as well as that of neat polymer. The polymer exhibits a strong emission peaked at 603 nm. PL of the blends with different weight ratios was completely quenched. Considering the matching of the HOMO and LUMO energy levels of the donor and acceptor, the PL quenching indicates that photoinduced charge transfer occurred between the polymer and PCBM [33].

The incident photon to converted current efficiency (IPCE) measurements of the OPV devices (Fig. 6) show good charge photogeneration properties, originated from photoinduced charge transfer process between the polymer and PCBM. The devices exhibit a maximum IPCE of 26% at 455 nm. The IPCE spectral response nearly follows the absorption spectrum.

Fig. 7 shows current density–voltage curves of the devices with the structure of ITO/PEDOT:PSS/polymer:PCBM (1:4, w/w)/Al under illumination of simulated AM 1.5 at 100 mW/cm^2. Table 1 summarizes the open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF), and the power conversion efficiency (PCE) of the device with different weight ratios of polymer:PCBM before and after thermal annealing at 110 °C [34]. Upon increasing the weight ratio of polymer:PCBM from 1:1 to 1:2, then to 1:4, the device efficiency increases from 0.12% to 0.29%, then to 0.37%, although the absorption of the blend decreases. This phenomenon is quite common in bulk heterojunction OPVs, e.g, poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV):PCBM [35], where the polymeric component has low hole mobility and the photogenerated charges are mainly transported by the PCBM phase [20]. Indeed, the DTT polymer exhibits quite low hole mobility (3.5×10^{-6} cm^2/V/s), as measured by OFET. The annealing of polymer:PCBM (1:4, w/w) induces significant improvement of J_{sc}, FF and PCE, similar to the well studied system, P3HT:PCBM. The thermal treatment is important for the ordering and demixing of the blend film, which plays a critical role in charge photo-generation and transportation in polymeric solar cells. The V_{oc} of 0.7 V is a little larger than that of P3HT/PCBM (ca. 0.6 V) [29], probably due to the lower HOMO of the polymer. The V_{oc} strongly depends on the

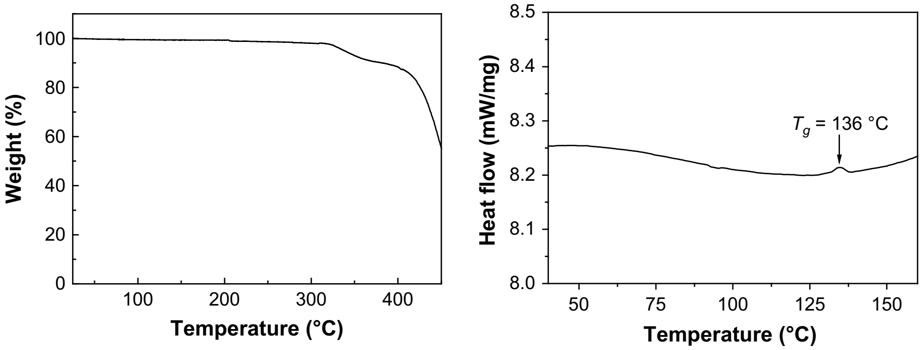


Fig. 1. TGA (left) and DSC (right) curves of the polymer.

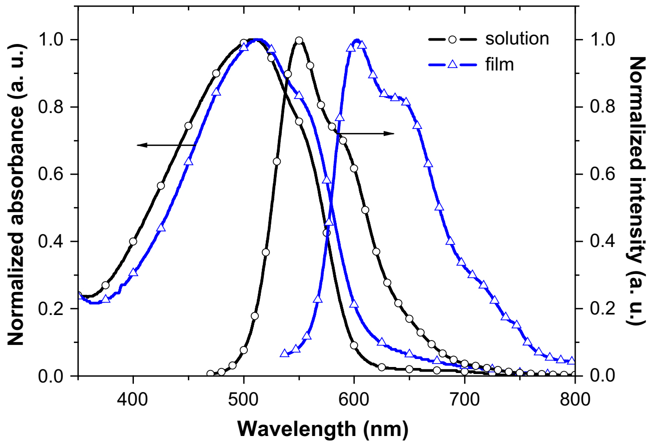


Fig. 2. Absorption and fluorescence spectra of the polymer in chloroform and thin film.

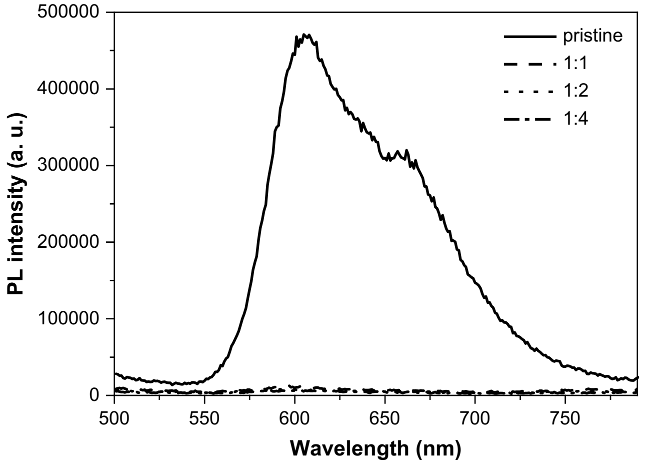


Fig. 5. PL spectra of the polymer film and polymer:PCBM blends with different weight ratios.

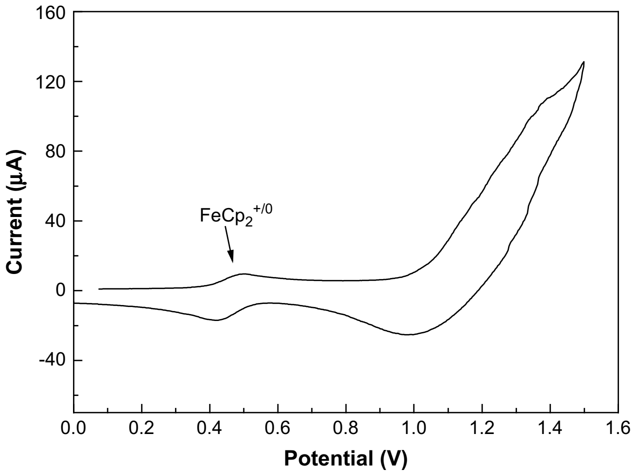


Fig. 3. Cyclic voltammogram for the polymer in CH_3CN/0.1 M $[^nBu_4N]^+[PF_6]^-$ at 100 mV/s. The horizontal scale refers to an anodized Ag wire pseudo-reference electrode.

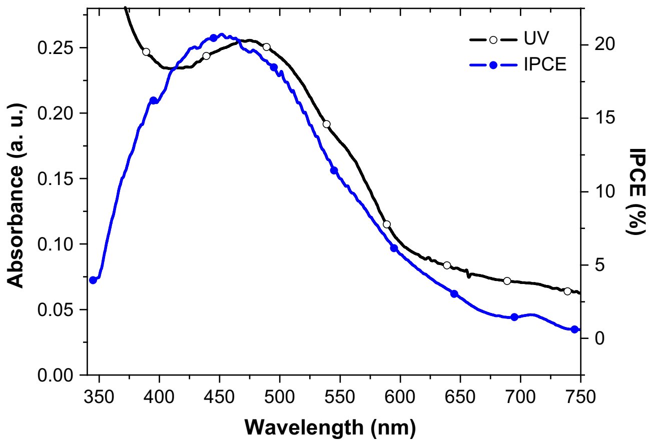


Fig. 6. Absorption spectrum of a film of polymer:PCBM (1:4, w/w) blend and IPCE as a function of wavelength.

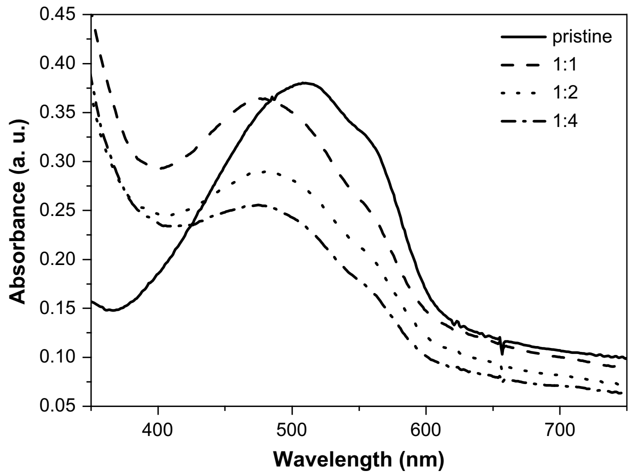


Fig. 4. Absorption spectra of the polymer film and polymer:PCBM blends with different weight ratios.

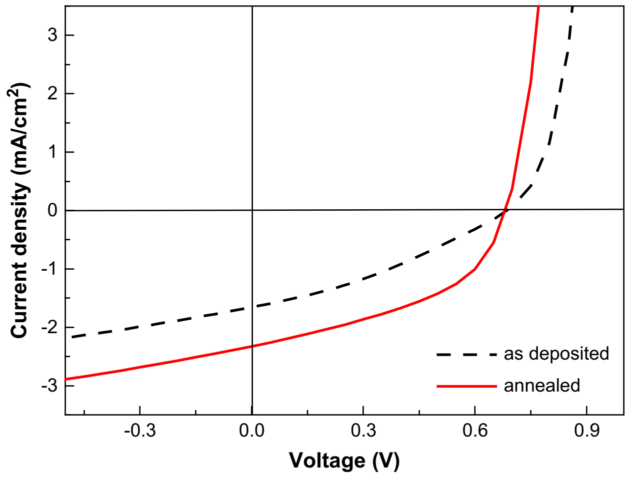


Fig. 7. Current density–voltage characteristics of a device with the structure ITO/PEDOT:PSS/polymer:PCBM (1:4, w/w)/Al under the illumination of an AM 1.5 solar simulator, 100 mW/cm^2.

Table 1
Photovoltaic performance of the OPV devices.

Polymer:PCBM (w/w)	Annealing[a]	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
1:1	No	0.67	0.60	0.29	0.12
1:2	No	1.43	0.65	0.31	0.29
1:4	No	1.65	0.70	0.32	0.37
1:4	Yes	2.33	0.70	0.44	0.71

[a] Annealing the device at 110 °C for 10 min.

difference between the HOMO of the donor and the LUMO of the acceptor [36]. Different from the J_{sc} and FF, the V_{oc} is much less dependent on the donor/acceptor weight ratio and the thermal treatment because it seems to be related to the nature of the components and less to the film morphology. After annealing, the OPV device exhibited the best performance; V_{oc}, J_{sc}, FF and PCE reached 0.7 V, 2.33 mA/cm^2, 0.44 and 0.71%, respectively. The PCE of 0.71% is higher than that (0.45%) of the OPV fabricated from the blend of poly(3,5-didecanyldithieno[3,2-b:2′,3′-d]thiophene-2,6-diyl-vinylene) and PCBM [28]. However, the J_{sc} and PCE are still not high, probably because of poor hole transport property of the polymer.

4. Conclusion

We have synthesized a conjugated copolymer of didecanyl-substituted dithienothiophene alternating with thiophene using Stille coupling reaction. The polymer has high molecular weight and good thermal stability. The polymer exhibits strong absorption in the visible with a relatively narrow band gap. Polymer solar cells were fabricated based on the blend of the polymer and PCBM. V_{oc} of 0.7 V, J_{sc} of 2.33 mA/cm^2, FF of 0.44, and PCE of 0.7% were achieved under AM 1.5, 100 mW/cm^2 using polymer:PCBM (1:4, w/w) as active layer after annealing at 110 °C. The relatively large V_{oc} is related to the relatively low HOMO of the polymer, while the low J_{sc} and PCE is mainly due to the low hole mobility of the polymer. While the results here are not competitive with other state-of-the-art OPV devices, they nonetheless demonstrate that solution-processed solar cells can be fabricated using dialkyl-substituted dithienothiophene polymers as donors.

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[34] In general, we fabricated 3 devices for every device structure. For example, the PCE values of the 3 devices with the structure ITO/PEDOT:PSS/polymer:PCBM (1:4, w/w)/Al before annealing were 0.367%, 0.334%, 0.370%, respectively, with an average PCE of 0.357% and a standard deviation of <5%. Table 1 lists the best result.
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