

프탈이미드 유도체를 기본으로 하는 공액고분자의 합성과 특성, 그리고 태양전지의 적용

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Synthesis and Characterization of π -Conjugated Polymer Based on Phthalimide Derivative and its Application for Polymer Solar Cells

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초록: 프탈이미드 유도체와 티오펜 단량체들을 이용하여 새로운 고분자인 poly((5,5-(2-butyl-5,6-bisdecyloxy-4,7-dithiophen-2-yl-isoindole-1,3-dione))-*alt*-(2,5-thiophene))(T-TI24T)를 Stille법을 이용하여 합성하였다. T-TI24T의 수평균 분자량은 86500 g/mol로 매우 높으며 클로로포름, 1,2-디클로로벤젠, 톨루엔과 같은 용매에 매우 잘 용해된다. 또한 380 °C까지 매우 우수한 열적 안정성을 갖고 있다. T-TI24T는 꽤 낮은 호모에너지 준위(-5.33 eV)를 갖고 있다. 서로 다른 T-TI24T와 (6)-1-(3-(methoxycarbonyl)-{5}-1-phenyl[5,6]-fullerene(PCBM)의 무게비를 갖는 블렌드를 광활성층으로 하는 태양전지를 제작하여 특성을 살펴본 결과 고분자와 PCBM의 비율이 1:3일 때 가장 최적화된 결과를 보였으며, 이 때 광전변환 효율과 개방전압은 각각 0.199%와 0.99V였다. T-TI24T 기반 태양전지들은 비록 매우 작은 광전변환 효율을 갖지만 잘 알려진 P3HT:PC61BM으로 구성된 태양전지와 비교해 큰 매우 큰 개방전압을 갖는다(약 0.5 V).

Abstract: A new copolymer named T-TI24T (poly((5,5-(2-butyl-5,6-bisdecyloxy-4,7-dithiophen-2-yl-isoindole-1,3-dione))-*alt*-(2,5-thiophene))) based on phthalimide derivative and thiophene is synthesized by the Stille-coupling reaction. The polymer shows relatively high number average molecular weight of 86500 g/mol with good solubility in common organic solvents such as chloroform, 1,2-dichlorobenzene, and toluene and is thermally stable up to 380 °C. Besides, it possesses a relatively low highest occupied molecular orbital (HOMO) energy level of -5.33 eV, promising the high open circuit voltage (V_{oc}) for photovoltaic applications. Active layer solution of polymer T-TI24T-as a donor and (6)-1-(3-(methoxycarbonyl)-{5}-1-phenyl[5,6]-fullerene (PCBM)-as an acceptor in different weight ratios is applied to fabricate the polymer solar cell devices. The ratio of polymer/PCBM affects the solar cell efficiency and the best performance exhibits in the device with polymer/PCBM = 1:3 (w/w), which shows a power conversion efficiency (PCE) of 0.199% and a V_{oc} of 0.99 V, respectively. Even though the device shows the very low PCE, the V_{oc} is higher than that of well known bulk heterojunction type solar cell based on P3HT:PC61BM (c.a. 0.5 V).

Keywords: polymer solar cells, conjugated polymer, phthalimide, stille coupling reaction.

Introduction

Polymer solar cells (PSCs) have attracted much attention during the past years due to their outstanding advantages such as low fabrication cost of large area devices, light weight, possibility of using flexible substrates, and easy to tune with chemical properties of the polymer materials.¹⁻⁸ Recently, the

performance of PSC has increased rapidly, high power conversion efficiency (PCE) has reported.⁹⁻¹⁴ Among factors affecting solar cell efficiency, the conjugated polymer related to photon harvesting is the most important factor. Therefore, the exploiting and design of new conjugated polymers with ideal properties such as low band gap, broad absorption range, low highest occupied molecular orbital (HOMO) energy levels to enhance the open circuit voltage (V_{oc}) and suitable lowest unoccupied molecular orbital (LUMO) energy levels for efficient electron transfer to the fullerene moieties, are necessary.

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In attempt to further improvement of the light harvesting, an effective method is to design conjugated polymers with incorporation of electron-rich units (as a donor) and electron-deficient (as an acceptor), forming a donor-acceptor (D-A) structure. The interactions between electron-rich units and electron-deficient units result in a compressed band gap, which could be easily tuned by changing one of the units or both of them.¹⁵⁻¹⁷

Recently, phthalimide has become one of candidates for an electron accepting unit in the D-A type copolymer¹⁸⁻²¹ due to its attractive properties such as high electron affinity, high charge transport and good π - π stacking which are results of advantages in the phthalimide structure. First, two carbonyl bonds (C=O) in the phthalimide group are strong electron withdrawing group result in low-lying HOMO which leads to improve the V_{oc} value of the PSCs. Second, nitrogen atom in the phthalimide provides an open position for alkylation directed away from the adjacent polymer backbone. One of the challenges in organic semiconductor is to maintain a balance between solubility and close π - π stacking. Alkyl side chains can impart solubility to polymers, but their effect on backbone planarity and packing depends critically on their placement. However, imide groups provide such open positions for alkylation without sacrificing conjugation. The coplanarity and efficient π - π stacking can be maintained.²²⁻²⁴

We modify phthalimide compound by introducing two decyloxy groups on the 5- and 6-position of benzene ring which are very helpful for the construction of the conjugated polymers with better solubility and high molecular weight. The good solubility of conjugated polymers is crucial for its purification and the formation of high quality film for efficient PSC devices.¹⁵ Whereas, the molecular weight of polymers can significantly influence the performance of PSCs, usually the high molecular weight sample gives better photovoltaic performance than the low molecular weight sample.⁶ Besides, we also add a butyl group on nitrogen atom to form the new acceptor moiety. A newly synthesized compound, 2-butyl-5,6-bisdecyloxy-4,7-dithiophen-2-yl-isoindole-1,3-dione, is incorporated into thiophene rings through the Stille coupling reaction. A newly synthesized copolymer is investigated and explored in bulk heterojunction (BHJ) solar cells.

Experimental

Materials. Methylene chloride (MC) was distilled over CaH₂. All other chemicals were purchased from Sigma-Ald-

rich Co, Tokyo Chemical Industry (TCI) or Alfa Aesar (Alfa Johnson Matthey Company) and were used as received unless otherwise described.

Synthesis of 1,2-Bisdecyloxybenzene (1). Sodium hydroxide (8 g, 0.2 mol) was dissolved in methanol (200 mL) at 0 °C for 30 min and then catechol (10 g, 90.8 mmol) was added slowly. White solution turned to deep green and finally dark. At this time 1-bromodecane (42.5 mL, 0.2 mmol) was added into the mixture dropwise. Next, the mixture was refluxed in a dry nitrogen atmosphere with stirring. After 8 h, the reaction mixture was cooled down to room temperature and the solvent was evaporated under the reduced pressure. A portion of 250 mL of water and a portion of 200 mL of ethyl acetate (EA) were added. The organic layer was separated, dried over anhydrous magnesium sulfate (MgSO₄) and concentrated. The combined organic layer was triturated from methanol (26.5 g, 74.7%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 6.87 (s, 4H), 3.99~3.95 (t, J = 7.0 Hz, 4H), 1.83~1.76 (m, 4H), 1.48~1.41 (m, 4H), 1.33~1.26 (m, 24H), 0.88~0.85 (t, J = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 150.29, 122.34, 115.46, 65.81, 32.89, 30.24, 30.51, 30.44, 30.19, 29.65, 26.09, 23.67, 15.05.

Synthesis of 1,2-Diiodo-4,5-bisdecyloxybenzene (2). 1,2-Bisdecyloxybenzene (15.63 g, 40 mmol), iodine (I₂, 9.14 g, 36 mmol), iodic acid (4.22 g, 24 mmol), and sulfuric acid (30% aqueous solution, 12 mL) in carbon tetrachloride (CCl₄, 4 mL) and acetic acid (150 mL) were heated at 75 °C overnight under stirring. The resulting mixture was cooled, diluted with water (50 mL) and extracted with EA. The organic phase was washed with an aqueous solution of sodium bisulfite (10%, 100 mL) and water (100 mL), dried over anhydrous MgSO₄. The organic layer was evaporated at reduced pressure. The crude product was purified by column chromatography with a 100% hexane. The yield of the white solid product yield was 20.6 g (80.2%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.22 (s, 2H), 3.91~3.88 (t, J = 6.6 Hz, 4H), 1.80~1.73 (m, 4H), 1.45~1.38 (m, 4H), 1.28~1.25 (m, 24H), 0.88~0.84 (t, J = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 150.83, 124.83, 97.02, 70.54, 32.97, 30.65, 30.62, 30.4, 30.1, 30.02, 26.98, 23.74, 15.18.

Synthesis of 1,2-Dicyano-4,5-bisdecyloxybenzene (3). A suspension of 1,2-diiodo-4,5-bisdecyloxybenzene (19.27 g, 30 mmol) and copper (I) cyanide (12.1 g, 135 mmol) in dimethylformamide (80 mL) was refluxed overnight under the nitrogen atmosphere. The cooled reaction mixture was then poured into a solution of hydrated ferric chloride (58.38 g,

216 mmol) in 90 mL of 2 M hydrochloric acid and stirred vigorously for 1 h at 60–70 °C. After being filtered, the mixture was extracted four times with a portion of 200 mL of MC. The organic layer was washed successively with two portions of 6 M hydrochloric acid, water, saturated sodium bicarbonate solution and water. The organic phase was dried over anhydrous MgSO_4 . After removal of the solvent, the crude product was purified by column chromatography and recrystallized from hexane. The yield of the white solid product yield was 5.96 g (45.1%). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.24 (s, 2H), 4.09–4.03 (t, $J = 6.5$ Hz, 4H), 1.88–1.8 (m, 4H), 1.49–1.42 (m, 4H), 1.36–1.25 (m, 24H), 0.88–0.84 (t, $J = 6.5$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 169.12, 154.80, 126.51, 107.32, 70.45, 32.75, 30.43, 30.4, 30.18, 30.16, 29.7, 26.75, 23.53, 14.96.

Synthesis of 4,5-Bisdecyloxyphthalic acid (4). A mixture of 4,5-dicyano-1,2-bisdecyloxybenzene (5.95 g, 13.5 mmol), 10% NaOH (50 mL) and ethanol (15 mL) was stirred at 80 °C for 2 h. After being cooled, the resulting mixture was acidified with concentrated hydrochloric acid. The white solid was collected by filtration, washed with distilled water and dried at 60 °C. The yield of the white solid product was 5.56 g (86.0%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, ppm): δ 7.53 (2, 2H), 7.37 (s, 2H), 4.02–3.99 (t, $J = 6.2$ Hz, 4H), 1.74–1.67 (m, 4H), 1.46–1.39 (m, 4H), 1.33–1.25 (m, 24H), 0.86–0.83 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 170.31, 154.75, 127.04, 108.06, 70.86, 33.07, 30.68, 30.56, 30.27, 30.19, 29.73, 26.74, 23.92, 15.08.

Synthesis of 2-Butyl-5,6-bisdecyloxyisoindole-1,3-dione (5). 4,5-Bisdecyloxyphthalic acid (5.27 g, 11 mmol) was dissolved in acetic acid (40 mL) and then *n*-butylamine (5.45 mL, 55 mmol) was added. The mixture was heated at reflux for overnight under the nitrogen atmosphere. After the reaction mixture was cooled to room temperature, water and EA were added. The aqueous phase was extracted with EA and then the combined organic layer was dried over MgSO_4 . The solvent was removed under the reduced pressure and the residue was purified by column chromatography with a hexane:ether (10:1 v/v). The yield of the white solid product yield was 4.82 g (85.0%). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.23 (s, 2H), 4.08–4.05 (t, $J = 6.6$ Hz, 4H), 3.62–3.59 (t, $J = 6.6$ Hz, 2H), 1.87–1.8 (m, 4H), 1.64–1.59 (m, 2H), 1.49–1.42 (m, 4H), 1.36–1.23 (m, 26H), 0.93–0.9 (t, $J = 7.4$ Hz, 4H), 0.88–0.84 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 169.87, 154.59, 126.20, 107.53, 70.57, 38.72, 32.91, 31.83, 30.72, 30.59, 30.55, 30.34, 29.91, 26.92, 23.69, 21.08, 15.11, 14.68.

Synthesis of 4,7-Dibromo-2-butyl-5,6-bisdecyloxyisoindole-1,3-dione (6). 2-Butyl-5,6-bisdecyloxyisoindole-1,3-dione (4.64 g, 9 mmol) was dissolved in a mixture of H_2SO_4 (14 mL) and trifluoroacetic acid (TFA, 46 mL). The solution was kept in the dark. A portion of *N*-bromosuccinimide (NBS, 4.81 g, 27 mmol) was added in four portions and the reaction mixture was stirred at room temperature for overnight. The brown-red solution was poured into water and extracted with MC. The organic phases were combined and dried over anhydrous MgSO_4 . The solvent was removed under the reduced pressure and the crude product was purified by column chromatography using MC:hexane as a eluent (3:2 v/v) to afford 4.55 g of the product as white powder (yield = 75.1%). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 4.08–4.05 (t, $J = 6.6$ Hz, 4H), 3.66–3.63 (t, $J = 7.4$ Hz, 2H), 1.85–1.78 (m, 4H), 1.66–1.59 (m, 2H), 1.51–1.44 (m, 4H), 1.38–1.25 (m, 26H), 0.94–0.9 (t, $J = 7.4$ Hz, 4H), 0.88–0.84 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 165.95, 156.69, 127.93, 115.76, 75.89, 39.35, 32.92, 31.44, 31.14, 30.74, 30.59, 30.40, 30.34, 26.95, 23.70, 21.07, 15.12, 14.61.

Synthesis of 2-Butyl-5,6-bisdecyloxy-4,7-di-thiophen-2-yl-isoindole-1,3-dione (7). A mixture of 4,7-dibromo-2-butyl-5,6-bisdecyloxyisoindole-1,3-dione (4.04 g, 6 mmol), 2-tributylstannylthiophene (5.6 g, 15 mmol), [1,1-bis(diphenylphosphino) ferrocene] dichloropalladium (II), complex with MC ($\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$, 0.245 g, 0.3 mmol) was dissolved in dry toluene (30 mL) and then the reaction mixture was heated under reflux for 16 h under the nitrogen atmosphere. After the reaction mixture was cooled to room temperature, water and EA were added. The aqueous phase was extracted with EA and the combined organic layer was dried over MgSO_4 . The solvent was removed under the reduced pressure and the residue was purified by column chromatography with hexane:MC (10:1 v/v) afforded a yellow oil (3.06 g, 75.0%). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.51–7.49 (dd, $J_1 = 1.1$ Hz, $J_2 = 5.2$ Hz, 2H), 7.29–7.28 (dd, $J_1 = 1.1$ Hz, $J_2 = 3.3$ Hz, 2H), 7.15–7.13 (t, $J = 3.7$ Hz, 2H), 3.87–3.84 (t, $J = 6.6$ Hz, 4H), 3.53–3.50 (t, $J = 7.7$ Hz, 2H), 1.58–1.53 (m, 6H), 1.3–1.22 (m, 36H), 0.94–0.86 (m, 9H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 167.59, 156.66, 132.20, 131.17, 129.51, 128.48, 127.48, 126.79, 75.48, 38.90, 32.94, 31.52, 31.04, 30.96, 30.61, 30.58, 30.37, 26.78, 23.72, 21.20, 15.15, 14.65.

Synthesis of 4,7-Bis-(5-bromo-thiophen-2-yl)-2-butyl-5,6-bisdecyloxyisoindole-1,3-dione (8). 2-Butyl-5,6-bisdecyloxy-4,7-di-thiophen-2-yl-isoindole-1,3-dione (2.72 g, 4 mmol) was dissolved in DMF (40 mL). The reaction mixture was then

placed in an ice bath, and a portion of NBS (1.78 g, 10 mmol) was added. The reaction mixture was then stirred in the dark for 24 h, with the temperature being gradually raised to room temperature. The reaction mixture was then extracted with EA and excess of water (to remove NBS and DMF). The EA layer was dried over MgSO_4 and the solvent was removed under the reduced pressure, and the residue was chromatographically purified on silica gel column eluting with a MC:hexane (1:10 v/v) to afford yellow oil (3.02 g, 90.1%). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.12~7.11 (d, $J = 3.7$ Hz, 2H), 7.09~7.08 (d, $J = 3.7$ Hz, 2H), 3.91~3.88 (t, $J = 6.2$ Hz, 4H), 3.56~3.52 (t, $J = 7.3$ Hz, 2H), 1.63~1.52 (m, 6H), 1.34~1.25 (m, 36H), 0.9~0.85 (m, 9H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 167.37, 156.37, 133.48, 131.91, 130.36, 128.68, 126.61, 115.78, 75.65, 39.01, 32.93, 31.50, 31.04, 30.95, 30.61, 30.59, 30.37, 26.84, 23.71, 21.19, 15.14, 14.64.

Synthesis of Poly((5,5-(2-butyl-5,6-bisdecyloxy-4,7-dithiophen-2-yl-isoindole-1,3-dione))-*alt*-(2,5-thiophene)) (T-TI24T). 4,7-Bis-(5-bromo-thiophen-2-yl)-2-butyl-5,6-bisdecyloxyisoindole-1,3-dione (0.167 g, 0.20 mmol), 2,5-bis(trimethylstannyl)thiophene (0.132 mg, 0.20 mmol), tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3 , 9.2 mg, 10 μmol) and tri-(*o*-tolyl)phosphine (24.4 mg, 8 μmol) was mixed in dry degassed toluene (6 mL). The reaction mixture was heated to reflux for 48 h under nitrogen. After cooling to room temperature, a portion of ammonia water was added to the mixture and the reaction mixture was stirred at room temperature overnight. The reaction mixture was then extracted with chloroform. The chloroform layer was dried over MgSO_4 and concentrated using a rotary evaporator. The concentrated reaction mixture was poured into methanol and the polymer was allowed to precipitate. The polymer was filtered and purified by Soxhlet extraction using methanol, hexane, respectively, and then dried in the vacuum to get product. Yield: 114 mg (75%), reddish orange solid. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.32~7.31 (d, $J = 3.7$ Hz, 2H), 7.23~7.22 (br, 2H), 7.16~7.13 (br, 2H), 3.99~3.92 (br, 4H), 3.64~3.52 (br, 2H), 1.70~1.63 (m, 4H), 1.62~1.54 (br, 2H), 1.34~1.26 (m, 6H), 1.25~1.19 (br, 24H), 0.91~0.87 (t, $J = 7.3$ Hz, 3H), 0.86~0.83 (t, $J = 6.6$ Hz, 6H). Anal. Calcd. for $\text{C}_{44}\text{H}_{57}\text{NO}_4\text{S}_4$: C, 69.52; H, 7.56; N, 1.84; O, 8.42; S, 12.66. Found: C, 70.46; H, 7.22; O, 8.27; S, 12.71.

Fabrication of Devices. Bulk heterojunction solar cells using polymer T-TI24T as a donor material and PCBM as an acceptor material were fabricated with a structure of ITO/PEDOT:PSS/active layer/Al. The ITO-glass substrates were pre-cleaned with deionized water, acetone, methanol, 2-pro-

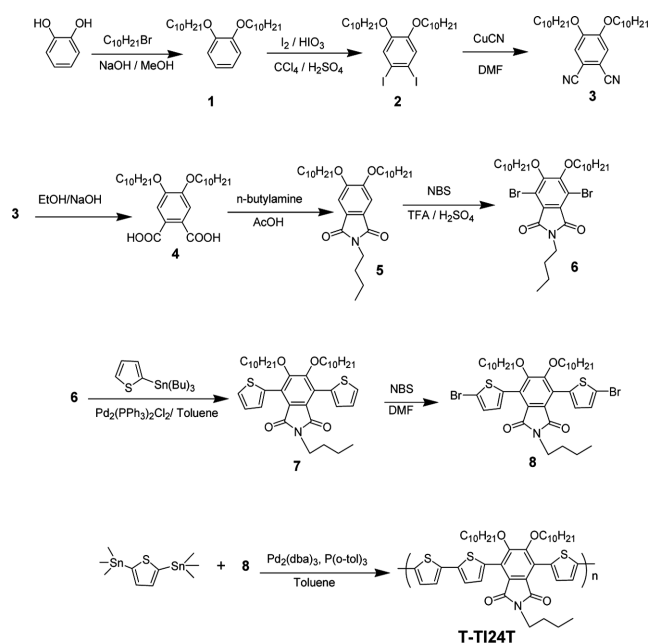
panol in ultrasonic bath. Then the substrates were dried on a hot-plate at 150 °C for 10 min and treated by UV/ O_3 for 120 sec. A layer (~40 nm) of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios P) (diluted with 2-propanol, PEDOT:2-propanol = 1:2 by volume) was spin-coated on ITO substrate (sheet resistance = 15 Ω/sq). After being baked at 150 °C for 10 min under the air, the active layer was spin-cast from the blend solution of polymer/PCBM at 600 rpm for 120 s. The blend of polymer (concentration of polymer was kept at 15 mg/mL) and PCBM with different weight ratios were dissolved in *o*-dichlorobenzene (DCB). The blended solution was stirred for overnight at 60 °C in the glove box. Prior to spin coating, the active solution was filtered through 0.45 μm membrane filter. Then, the aluminum cathode was deposited with a thickness of 110 nm through a shadow mask with a device area of 0.13 cm^2 at 2×10^{-6} Torr.

Measurements. Synthesized compounds were characterized by ^1H NMR and ^{13}C NMR spectrum, which were obtained with a JEOL JNM ECP-400 spectrometer. The elemental analysis was carried out an Elementar Vario macro/micro elemental analyzer. Gel permeation chromatography (GPC) measurements were conducted by GPC system equipped with a Varian 212-LC pump, a Rheodyne 6-port sample injection valve, a Waters Temperature Control Module, a Waters 410 differential RI detector, and two Waters Styragel HR4E columns. The monodispersed polystyrene was used as standards and toluene used as an eluent. The thermogravimetric analysis (TGA) was carried out under the nitrogen atmosphere at a heating rate of 10 °C/min with a Perkin-Elmer TGA 7 thermal analyzer. The UV-vis spectrum was recorded using a JASCO V-530 UV-vis spectrophotometer. The cyclic voltammetry (CV) was performed by an Ivium B14406 with a three electrode cell in a solution of Bu_4NPF_6 (0.1 M) in mixture of freshly distilled MC and DCB (1:1 v/v) at a scan rate of 100 mV/s. A Pt wire was used as the counter and the working electrode and a Ag/Ag^+ electrode was used as the reference electrode. The J-V measurements under 1.0 sun (100 mW/cm^2) condition from a 150 W Xe lamp with an AM 1.5G filter were performed using a KEITHLEY Model 2400 source-measure unit. A calibrated Si reference cell with a KG5 filter certified by National Institute of Advanced Industrial Science and Technology was used to confirm 1.0 sun condition.

Results and Discussion

Synthesis and Characterization. General synthetic strat-

egy for monomers and polymer is outlined in Scheme 1. 1,2-Bis(decyloxy)benzene (1) were prepared by alkylation of catechol with 1-bromodecane in methanol and sodium hydroxide at 80 °C. 1,2-Diiodo-4,5-bis(decyloxy)-benzene (2), 1,2-dicyano-4,5-bis(decyloxy)-benzene (3), 4,5-bis(decyloxy)-phthalic acid (4), 2-butyl-5,6-bis(decyloxy)-isoindole-1,3-dione (5) and 4,7-dibromo-2-butyl-5,6-bis(decyloxy)-isoindole-1,3-dione (6), were synthesized according to modified literature procedures.²⁵⁻²⁹ Combination of 6 with 2-tributylstannylthiophene affords 2-butyl-5,6-bis(decyloxy)-4,7-di-thiophen-2-yl-isoindole-1,3-dione (7). Finally, bromination of 7 gives monomer 4,7-bis-(5-bromo-thiophen-2-yl)-2-butyl-5,6-bis(decyloxy)-isoindole-1,3-dione (8). Compound 8 copolymerized with 2,5-bis(trimethylstannyl)thiophene through the Stille coupling reaction to afford the poly((5,5-(2-butyl-5,6-bis(decyloxy)-4,7-di-thiophen-2-yl-isoindole-1,3-dione))-*alt*-(2,5-thiophene)) (T-TI24T).³⁰ The polymer of T-TI24T was good soluble in common organic solvents such as chloroform, toluene, chlorobenzene and dichlorobenzene. The molecular weight of the polymer was determined by the gel permeation chromatography (GPC). The number average molecular weight (M_n) of the T-TI24T is 86500 g/mol with a polydispersity index (PDI) of 1.36. The thermal property of the polymer was investigated by the thermogravimetric analysis (TGA), and its thermogram is depicted in Figure 1. The polymer is thermally stable up to 380 °C, which is 5% weight-loss temperatures (T_d) of T-TI24T.



Scheme 1. Synthesis route of monomer and polymer.

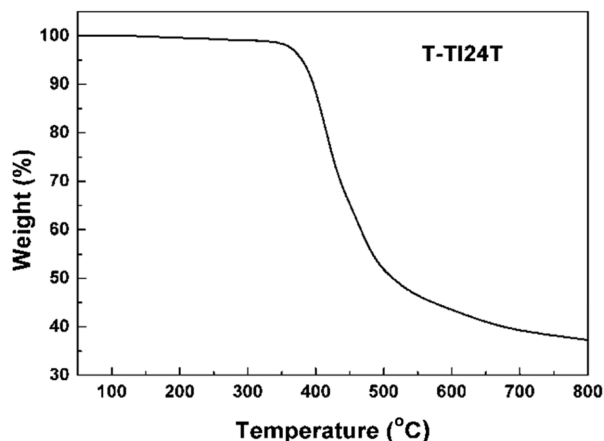


Figure 1. TGA curve of polymer T-TI24T with a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

Optical and Electrochemical Properties. The UV-vis absorption spectra of T-TI24T in dilute chloroform solution and in solid state are depicted in Figure 2. The T-TI24T solution shows an absorption band in the wavelength range 340–500 nm and the maximum absorption peak at 433 nm. Whereas, the T-TI24T film displays an absorption band in the wavelength range 340–560 nm and the maximum absorption peak at 456 nm. In the film state, the polymer exhibits red-shifted and broader absorption than that of the solution. It's possibly due to higher conjugation along polymer backbones and stronger intermolecular interaction in condensed solid state. The UV-vis absorption range of T-TI24T was not wide in comparison with other DA-type copolymers such as the polymers based on typical electron-withdrawing moiety 2,1,3-benzothiadiazole with various electron-donating moieties fluorene derivative (PF-TBT),³¹ carbazole derivative (PCD-TBT)³² or

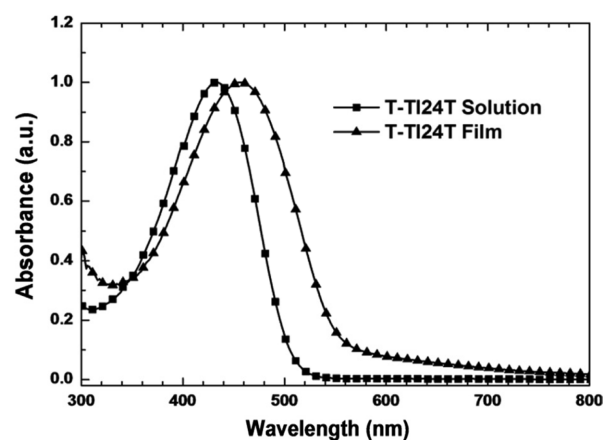


Figure 2. UV-vis absorption spectra of T-TI24T in dilute CH₂Cl solution and film.

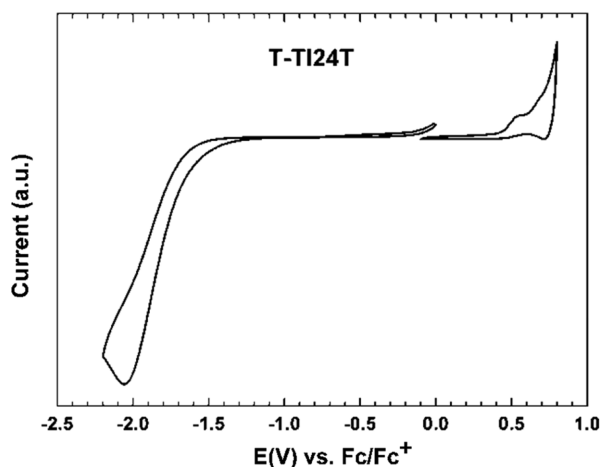


Figure 3. Cyclic voltammogram of T-TI24T in an MC:DCB (1:1 v/v) of $0.1 \text{ molL}^{-1} \text{ Bu}_4\text{NPF}_6$.

cyclopentadithiophene (PCPD-TBT).³³ Generally, the band gap energy of DA-type polymer which comprises of an electron-rich “donor” moiety and an electron-deficient “acceptor” moiety is effectively decreased by orbital overlap through the internal charge transfer between an electron-donating material and an electron-withdrawing material. Therefore, in the DA-type polymer back-bone, the stronger electron-withdrawing property of electron-deficient material leads to the narrower the band gap.^{24,34} The optical band gap of T-TI24T estimated from the absorption edge in the UV-vis spectrum of the thin solid film is 2.24 eV.

Cyclic voltammetry was usually applied to estimate the HOMO and LUMO energy levels of conjugated polymers. The onset oxidation and reduction potentials obtained from the cyclic voltammogram are strongly related to the HOMO and LUMO energy levels, respectively. The HOMO and LUMO levels figured out from the oxidation and reduction onset potential of cyclic voltammogram (Figure 3) were -5.33 and -3.18 eV, respectively. It should be noted that the HOMO energy level of T-TI24T was relatively low in comparison with other photovoltaic polymers based on thiophene derivatives such as polymers based on thiophene combined with various electron-deficient moieties 2,1,3-benzothiadiazole,³⁰ 2,1,3-benzoxadiazole,¹⁶ 2,1,3-benzotriazole³⁵ or polymers based on thiophene derivatives and diketopyrrolopyrrole.³⁶ Since the V_{oc} value of BHJ solar cell is directly related to the energy difference between the HOMO level of the photoactive polymer and the LUMO level of fullerene derivatives, high V_{oc} are expected in the device.

Photovoltaic Properties. BHJ solar cells using T-TI24T as

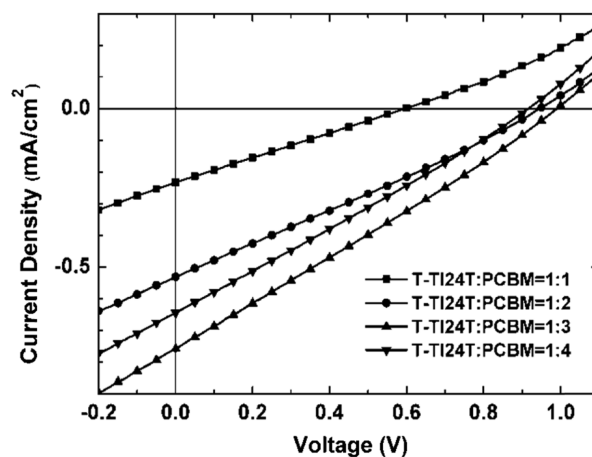


Figure 4. J-V curves of conventional type PSCs based on T-TI24T under the illumination of AM 1.5G and intensity of 100 mW/cm^2 .

Table 1. Summary of Photovoltaic Properties

| T-TI24T:PCBM weight ratio | J_{sc} (mA/cm^2) | V_{oc} (V) | FF (%) | PCE (%) |
|---------------------------|-------------------------------|--------------|--------|---------|
| 1:1 | 0.23 | 0.60 | 25.0 | 0.035 |
| 1:2 | 0.53 | 0.94 | 26.9 | 0.134 |
| 1:3 | 0.76 | 0.99 | 26.5 | 0.199 |
| 1:4 | 0.64 | 0.92 | 26.4 | 0.157 |

a photoactive material and PCBM as an acceptor material were fabricated with a structure of ITO/PEDOT:PSS/active layer/Al. Devices were fabricated from the different weight ratios of T-TI24T/PCBM and the concentration of polymer solution was kept at 15 mg/mL. A comparison of the devices with a different weight ratio of polymer/PCBM was depicted in Figure 4 and Table 1. When the ratio of T-TI24T/PCBM increased from 1:1 to 1:3, the J_{sc} , V_{oc} , FF and PCE of devices increased. Whereas the ratio reached to 1:4, the performance of device decreased. The ratio between the polymer and the fullerene in bulk heterojunction devices is of great importance in terms of photovoltaic response.³⁷⁻⁴⁰ The optimum ratio depends on the type of polymer and the morphology is affected by ratio between the polymer and PCBM.^{41,42} The best PCE of 0.199% was exhibited in the device with T-TI24T/PCBM = 1:3 (w/w). This device exhibits a relatively high value of V_{oc} of 0.99 V, which is contributed from a relatively low-lying HOMO energy level of polymer. The relatively low V_{oc} obtained from blending ratio 1:1 compared to others ratios possibly due to the morphology not being fully organized for efficient inter-penetrating networks in the thin film.⁴³ The similar results have been reported for polymers based on carbazole and dithie-

nylbenzothiadiazole (PBTC, PCDTBT).⁴⁴ All the devices showed low J_{sc} (0.23-0.76 mA/cm²) which could be related to a narrow absorption band of T-TI24T. The PCE of devices was governed by the J_{sc} value and FF which are primarily determined by the photon absorption property and charge carrier mobility.²³

Conclusions

A newly synthesized D-A type copolymer, T-TI24T, was synthesized with a high molecular weight and showed good thermal stability. The polymer had a maximum UV-vis absorption peak at 456 nm. The HOMO and LUMO energy levels of the polymer were -5.33 and -3.15 eV, respectively. The ratio of polymer/PCBM affected solar cell performance. The best PCE of devices based on T-TI24T/PCBM exhibited in device with active layer ratio 1:3 (w/w) was 0.199% with a V_{oc} of 0.99 V, a J_{sc} of 0.76 mA/cm² and a FF of 26.5%, under the illumination of AM 1.5G, 100 mW/cm².

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