Synthesis, Characterization, and Application to Polymer Solar Cells of Polythiophene Derivatives with Ester- or Ketone-Substituted Phenyl Side Groups

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Received 25 October 2014; accepted 26 November 2014; published online 00 Month 2015
DOI: 10.1002/pola.27513

ABSTRACT: Four polythiophene derivatives including regiorandom polymers **P1**, **P2**, and **P3** and a regioregular polymer **P4**, containing a phenyl side chain with electron-withdrawing carbonyl groups such as an ester and a ketone at the 3-position of the thiophene ring, were synthesized by Stille coupling reaction. Bulk-heterojunction polymer solar cells (PSCs) based on these polymers as p-type semiconductors and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) were fabricated, and their photovoltaic performances were evaluated for the first time. The PSC devices based on the regioregular polymer **P4**:PCBM = 1:2 (w/w) exhibited a high-open-circuit voltage (V_{oc}) of 0.943 V because of the low-lying highest occupied molecular orbit energy level of **P4**. The short π–π stacking distance (0.355 nm) in the parallel direction to the substrate and "face-on" rich orientation were observed by the grazing incidence wide-angle X-ray scattering experiment, which might reflect higher J_{sc} and FF values of the **P4**:[6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) PSC device than others. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *00*, 000–000

KEYWORDS: conducting polymers; conjugated polymers; high-performance polymers; high V_{oc} value; low HOMO level; polymer solar cells; polythiophene; Stille coupling

INTRODUCTION In the recent years, several serious environmental problems from climate change to environmental pollution or the inadequacy of fossil fuels have been caused by the overuse of nonrenewable resources. Among all of the new technologies that have been developed to solve these problems, the solar cell has been considered as one of the most promising approaches because of its ability to directly convert energy of light from solar radiation into electricity by the photovoltaic effect without exhausting toxic gases into the atmosphere. Until now, with the high power conversion efficiency (PCE) of more than 25%, silicon-based solar cells are still the most efficient photovoltaic technologies.[1–3] However, silicon-based solar cells have some disadvantages, for example, the lack of flexibility and high cost production processes, thus it is difficult to develop this kind of technology in large areas, and their widespread commercialization is limited. Instead of silicon-based solar cells, in the past few years, polymer solar cells (PSCs), which have a lot of potential advantages such as light weight, flexibility, and fast/cheap roll-to-roll production, have attracted much attention in both academic and industrial research studies and have been rapidly developed as one of the most promising candidates for low-cost solar cells.[4–12] In general, the most widely used device structure of PSCs currently involves the concept of bulk heterojunctions (BHJs), where the electron donor, such as conjugated polymers, plays the role of a p-type organic semiconductor, and the electron acceptor, such as fullerene derivatives, plays the role of a n-type organic semiconductor. These two types of organic semiconductor are blended and

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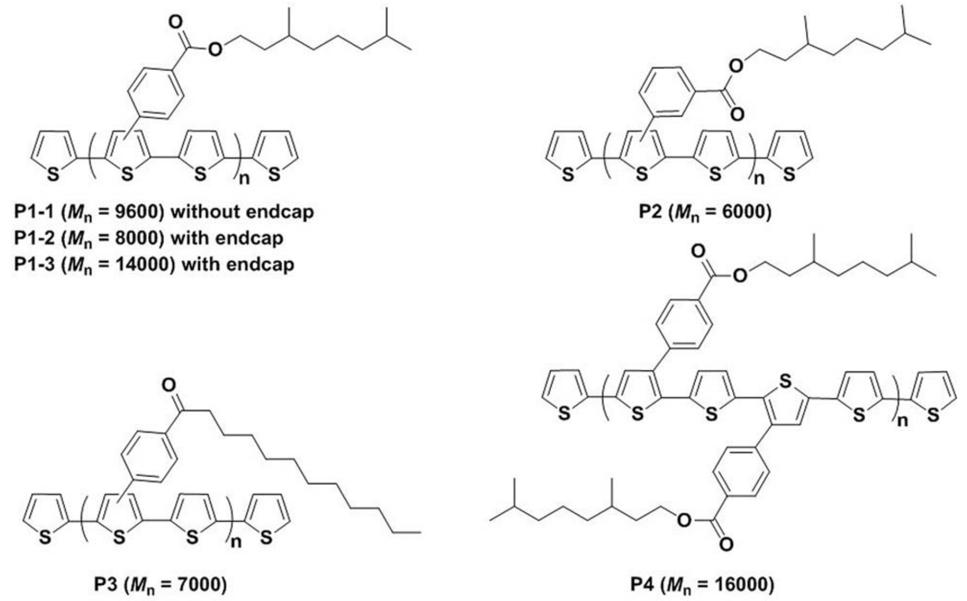


FIGURE 1 Molecular structures of the polythiophene derivatives.

sandwiched between transparent indium tin oxide (ITO) and metal electrodes.[6]

Among the large number of conjugated polymer systems, which have been synthesized and investigated as donor materials, regioregular poly(3-hexylthiophene) (P3HT) is known as one of the most studied conjugated polymers. Because P3HT has a semicrystalline structure, high hole mobility, and also a favorable mixing ratio with fullerene acceptors, the combination of P3HT:[6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as an active layer leads to solar cell efficiencies of up to 5%.[13–16] However, the open-circuit voltage (V_{oc}) of P3HT-based solar cells is still limited to about 0.6 V because of the relatively high-lying highest occupied molecular orbit (HOMO) level (−4.76 eV)[17,18] of P3HT. Therefore, improving the V_{oc} of polythiophene derivative-based solar cells by a molecular structure design should be an interesting approach to increase their PCE along with other physical approaches.

There are only a few reports about the synthesis of new polythiophene derivatives with lower HOMO energy levels than that of P3HT. Among these, the incorporation of aromatic heterocyclic rings into a polythiophene backbone by copolymerization is one of the successful strategies, leading to an enhanced oxidative stability when compared with P3HT.[19–26] For example, the polythiophene derivative P3HDTTT with fewer electron-donating groups, which was synthesized and reported by Yang and coworkers, showed a lower HOMO level and thus higher V_{oc} than P3HT in PSCs.[19] By attaching the alkoxycarbonyl substitution instead of the hexyl side chain of poly(3-hexylthienylene vinylene) (P3HTV), a new polymer, P3CTV, which has its HOMO energy level shifted downward by 0.21 eV when compared with P3HTV, was synthesized. The solar cell device based on this polymer attained a relatively high V_{oc} of 0.86 V.[27] Ueda and coworkers[28] have previously reported the synthesis of poly{3-[4′-(3″,7″-dimethyloctoxy)phenyl]thiophene} (P3PhT) by introducing an alkoxyphenyl group at the 3-position of each thiophene ring and successfully lowered the HOMO energy level from −4.93 eV for P3HT to −5.13 eV for P3PhT. A new polythiophene derivative PDCBT was recently designed and synthesized by Ma and coworkers.[29] By attaching electron-withdrawing carboxylate substituents to the side chain, it successfully decreased the HOMO level from −4.76 eV for P3HT to −5.26 eV for PDCBT. These results indicated that the introduction of appropriate substituents is also an effective way to lower the HOMO energy level of π-conjugated polymers.

In this study, to extend the molecular design of polythiophene derivatives with lower HOMO energy levels, four polythiophene derivatives including regiorandom polymers **P1**(**1-1**, **1–2**, and **1–3**), **P2**, and **P3** and a regioregular polymer **P4** (Fig. 1), containing a phenyl side chain with electron-withdrawing carbonyl groups such as an ester and ketone at the 3-position of the thiophene ring, were synthesized by Stille coupling reaction. The chemical structure, molecular weight, and thermal, optical, electrochemical, and photovoltaic properties of the polymers were fully characterized. All polymers showed a deeper HOMO energy level than that of P3HT, and the BHJ PSC based on the regioregular polymer **P4**:PCBM = 1:2 (w/w) exhibited the high V_{oc} value of 0.943 V. Based on the grazing incidence wide-angle X-ray scattering (GIWAXS) experiment, a very short π-stacking distance (0.355 nm) was observed for the **P4** film with a "face-on" rich orientation in which the π-plane tends to lie parallel to the substrate, possibly reflecting the relatively high J_{sc} and FF values of the **P4**:PCBM and **P4**:[6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) PSC devices.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was dried over sodium benzophenone and distilled under nitrogen before use. 2,5-Bis(trimethylstannyl)thiophene was prepared according to the literature.[24] All other reagents and solvents were used without further purification.

General Measurements

The molecular weights and dispersities (*Đ*) were measured by size exclusion chromatography (SEC) on a JASCO GULLIVER 1500 equipped with a pump, an absorbance detector (UV, $\lambda = 254$ nm), and three polystyrene gel columns based on a conventional calibration curve using polystyrene standards. $CHCl_3$ (40 °C) was used as a carrier solvent at a flow rate of 1.0 mL min^{-1}. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 spectrometer in $CDCl_3$ calibrated to tetramethylsilane as an internal standard ($\delta H = 0.00$). Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C min^{-1} for thermogravimetry (TG) and a TA Instruments Q-100 connected to a cooling system at a heating rate of 10 °C min^{-1} for differential scanning calorimetry (DSC). UV–vis absorption spectra were recorded using a Hitachi U-4100 spectrophotometer. For the thin film spectra, polymers were first dissolved in $CHCl_3$, followed by filtering through a 0.45-μm pore size PTFE membrane syringe filter and then drop-casted onto quartz substrate. Cyclic voltammetry (CV) was performed with the use of a three-electrode cell in which ITO was used as a working electrode, and the polymer film was coated on it in 0.5×0.7 cm^2. A platinum wire was used as an auxiliary electrode. All cell potentials were taken in a 0.1 mol L^{-1} acetonitrile solution of tetrabutylammonium perchlorate at a scan rate of 0.1 V s^{-1} with the use of a homemade Ag/AgCl, KCl saturated reference electrode.

Fabrication and Characterization of Organic Field-Effect Transistor Devices

We used solution-based fabrication to make field-effect transistor devices with **P1–P4**. The source and drain electrodes were formed on a 300-nm-thick layer of thermally grown SiO_2 on a Sb-doped n-type Si substrate [capacitance (C_i) = 11.5 nF cm^{-2}] by photolithography of Au (90 nm)/Cr (10 nm) layers. The standard channel length and width were 10 and 500 µm, respectively. The channels were spin coated with a 1.0 wt % $CHCl_3$ solution of **P1–P4**. The devices were fabricated under a dry N_2 atmosphere.

Fabrication and Characterization of PSC Devices

We fabricated solar cells to evaluate photovoltaic characteristics of **P1–P4**. The cell structure was conventional as follows: glass/ITO/MoO_3 (20 nm)/polymer:fullerene (100 nm)/phenyl-dipyrenylphosphine oxide ($POPy_2$; 4.5 nm)/Al. The ITO layer on glass substrate was 145 nm thick with a sheet resistance of 8 Ω^{-2}. The stripe pattern with 5 mm width of the ITO layer was etched by conventional photolithographic technique. Prior to the formation of the buffer layer, the patterned ITO glass was ultrasonically cleaned using surfactant, rinsed in water, and finalized with UV–ozone treatment. As an anode buffer layer, MoO_3 was vacuum deposited with a thickness of 20 nm on the ITO electrode. Polymer:fullerene BHJ layer was formed on MoO_3 layer by spin coating (300–600 rpm) of a blended solution, which contains **P1–P4** as a donor and PCBM or $PC_{71}BM$ as an acceptor with an optimized ratio in chlorobenzene. The coating process was performed in a nitrogen glove box. After drying the films, the substrate was transferred from glove box to a vacuum chamber without being exposed to air. The evaporation of $POPy_2$ was carried out at a pressure of about 2×10^{-4} Pa. After the deposition of $POPy_2$ layer (4.5 nm), the top electrode (Al) was successively deposited with a metal shadow mask, which defines 5-mm stripe pattern perpendicular to the ITO stripe. The photocurrent of the fabricated PSC devices was investigated with a sweeping voltage using a Keithley 2400 source measurement unit controlled by a computer under simulated solar light using an AM1.5G light source with 100 mW cm^{-2} intensity. Incident light intensity was calibrated to 1 Sun (100 mW cm^{-2}) with a standard Si photodiode (BS-520; Bunkoukeiki, Japan). The current density versus voltage (*J–V*) characteristics was measured for an area of 0.16 cm^2.

GIWAXS Measurement

The samples were prepared according to the following method: 4.0 mg of the polymers was dissolved in 0.4 mL of $CHCl_3$. These solutions were drop-cast on Si wafers with filtration (pore size = 0.40 µm) followed by air-drying for 30 min. Then, the samples were completely dried under vacuum at room temperature for 1 h. The thickness of films was almost 1 µm. GIWAXS measurements were conducted at beamline BL19B2 of SPring-8, Japan. The sample was irradiated at a fixed incident angle on the order of 0.12° through a Huber diffractometer with an X-ray energy of 12.398 keV (X-ray wavelength $\lambda = 0.10$ nm), and the GIWAXS patterns were recorded with a 2D image detector (Pilatus 300K) with the sample-to-detector distance of 174 mm.

Synthesis of (3,7-Dimethyloctyl)−4-bromobenzoate (1b)

To 4-bromobenzoic acid (6.00 g, 29.8 mmol), thionyl chloride (30 mL) was added, and then the reaction mixture was stirred at 90 °C for 6 h. After the reaction, thionyl chloride was removed under reduced pressure. Then, to the residue, CH_2Cl_2 (75 mL), triethylamine (4.2 mL, 30.0 mmol), and 3,7-dimethyloctan-1-ol (11.4 mL, 59.6 mmol) were added, and the solution was stirred at 0 °C overnight. After the reaction, the product was extracted with CH_2Cl_2, and the organic layer was washed with water. After drying the solution over anhydrous $MgSO_4$ followed by filtration, the filtrate was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (EtOAc; 9/1, v/v) as an eluent to give **1b** as a colorless oil (9.86 g, 97%).

^1H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 7.88 (d, $J = 8.7$ Hz, Ar*H*, 2H), 7.55 (d, $J = 8.6$ Hz, Ar*H*, 2H), 4.34 (t, $J = 7.7$ Hz, $-OCH_2CH_2-$, 2H), 1.81–1.11 (m, $-CH_2-$, 10H), 0.95 (d, $J = 6.4$ Hz, $-CH_3$, 3H), 0.86 (d, $J = 6.6$ Hz, $-CH_3$, 6H). ^{13}C

NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 165.8, 131.6, 131.0, 129.4, 127.8, 63.8, 39.1, 37.1, 35.5, 29.9, 27.9, 24.6, 22.7, 22.6, 19.6. Anal. Calcd for $C_{17}H_{25}BrO_2$: C, 59.77; H, 7.32. Found: C, 59.90; H, 7.18.

Synthesis of (3,7-Dimethyloctyl)-4-(3-thienyl)benzoate (1c)

A *N*,*N*-dimethylformamide (DMF) solution (50 mL) of **1b** (5.30 g, 15.5 mmol), 3-thiopheneboronic acid (2.30 g, 18.6 mmol), K_2CO_3 (6.40 g, 46.6 mmol), and $Pd(PPh_3)_4$ (0.80 g, 0.77 mmol) was degassed by three freeze–thaw–pump cycles and then stirred at 90 °C for 18 h under argon atmosphere. After the reaction, the product was extracted with $CHCl_3$, and the organic layer was washed with water. After drying the solution over anhydrous $MgSO_4$ followed by filtration, the filtrate was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/EtOAc (9/1, v/v) to give **1c** as an orange oil (5.05 g, 94%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 8.05 (d, *J* = 8.4 Hz, Ar*H*, 2H), 7.62 (d, *J* = 8.4 Hz, Ar*H*, 2H), 7.50 (t, *J* = 2.1 Hz, Ar*H*, 1H), 7.37 (m, Ar*H*, 2H), 4.35 (t, *J* = 7.5 Hz, $—OCH_2CH_2—$, 2H), 1.83–1.14 (m, 11H), 0.95 (d, *J* = 6.4 Hz, $—CH_3$, 3H), 0.86 (d, *J* = 6.6 Hz, $—CH_3$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 166.8, 141.6, 140.3, 130.6, 129.4, 127.0, 126.5, 122.2, 63.9, 39.6, 37.6, 36.0, 30.4, 28.3, 25.0, 23.1, 23.0, 20.0. Anal. Calcd for $C_{21}H_{28}SO_2$: C, 73.14; H, 8.12. Found: C, 72.66; H, 8.06.

Synthesis of (3,7-Dimethyloctyl)-4-(2-bromo-3-thienyl)benzoate (1d)

To a solution of **1c** (2.39 g, 6.93 mmol) in THF (25 mL), *N*-bromosuccinimide (NBS; 1.29 g, 7.28 mmol) was added at 0 °C under argon atmosphere. The reaction mixture was stirred at 0 °C for 4 h and then at room temperature for 18 h. After the reaction, the resultant pale yellow solution was diluted with Et_2O, and 1 M aqueous NaOH was added to quench the residual NBS. The organic layer was separated by extraction and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The crude product was then purified by silica gel column chromatography using hexane/EtOAc (19/1, v/v) to give **1d** as a colorless oil (2.69 g, 92%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 8.09 (d, *J* = 8.4 Hz, Ar*H*, 2H), 7.62 (d, *J* = 8.3 Hz, Ar*H*, 2H), 7.32 (d, *J* = 5.6 Hz, Ar*H*, 1H), 7.04 (d, *J* = 5.7 Hz, Ar*H*, 1H), 4.37 (t, *J* = 7.5 Hz, $—OCH_2CH_2—$, 2H), 1.86–1.12 (m, 11H), 0.96 (d, *J* = 6.4 Hz, $—CH_3$, 3H), 0.86 (d, *J* = 6.6 Hz, $—CH_3$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 166.3, 140.1, 139.3, 129.6, 129.5, 128.8, 128.5, 126.3, 109.6, 63.6, 39.1, 37.1, 35.5, 29.9, 27.9, 24.6, 22.7, 22.6, 19.6. Anal. Calcd for $C_{21}H_{27}BrSO_2$: C, 59.51; H, 6.37. Found: C, 59.49; H, 6.38.

Synthesis of (3,7-Dimethyloctyl)−4-(2,5-dibromo-3-thienyl)benzoate (1e)

To a solution of **1c** (0.92 g, 2.69 mmol) in $CHCl_3$ and acetic acid (15 mL, 1:1, v/v), NBS (1.05 g, 5.92 mmol) was added at 0 °C under argon atmosphere. The reaction mixture was stirred at 0 °C for 4 h and then at room temperature for 18 h. After the reaction, the resultant pale yellow solution was diluted with $CHCl_3$, and 1 M aqueous NaOH was added to quench the residual NBS. The organic layer was separated by extraction and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The crude product was then purified by silica gel column chromatography using hexane/EtOAc (19/1, v/v) to give **1e** as a colorless oil (1.21 g, 90%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 8.09 (d, *J* = 8.6 Hz, Ar*H*, 2H), 7.57 (d, *J* = 8.6 Hz, Ar*H*, 2H), 7.04 (s, Ar*H*, 1H), 4.37 (t, *J* = 7.5 Hz, $—OCH_2CH_2—$, 2H), 1.86–1.12 (m, 11H), 0.96 (d, *J* = 6.4 Hz, $—CH_3$, 3H), 0.86 (d, *J* = 6.6 Hz, $—CH_3$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 165.2, 140.0, 137.2, 130.3, 128.9, 128.7, 127.4, 110.7, 107.6, 62.7, 38.1, 36.1, 34.5, 28.9, 26.9, 23.6, 21.6, 21.5, 18.6. Anal. Calcd for $C_{21}H_{26}Br_2SO_2$: C, 50.21; H, 5.22. Found: C, 50.19; H, 5.21.

Synthesis of (3,7-Dimethyloctyl)−4-(2-bromo-5-iodo-3-thienyl)benzoate (1f)

To a solution of **1d** (1.44 g, 3.41 mmol) in $CHCl_3$ and acetic acid (30 mL, 1:1, v/v), *N*-iodosuccinimide (NIS; 0.84 g, 3.75 mmol) was added, and then the reaction mixture was stirred at room temperature overnight. After the reaction, saturated aqueous $Na_2S_2O_3$ solution was added to quench the excess amount of NIS, and the product was extracted with EtOAc and then washed with 1 M aqueous NaOH, water, and brine. After drying the solution over anhydrous $MgSO_4$ followed by filtration, the filtrate was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/EtOAc (19/1, v/v) to give **1f** as a dark red oil (1.60 g, 86%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 8.08 (d, *J* = 8.5 Hz, Ar*H*, 2H), 7.56 (d, *J* = 8.5 Hz, Ar*H*, 2H), 7.21 (s, Ar*H*, 1H), 4.37 (t, *J* = 7.6 Hz, $—OCH_2CH_2—$, 2H), 1.83–1.12 (m, 12H), 0.96 (d, *J* = 6.4 Hz, $—CH_3$, 3H), 0.86 (d, *J* = 6.6 Hz, $—CH_3$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 166.2, 142.2, 138.3, 138.0, 129.9, 129.7, 128.4, 112.4, 72.5, 63.7, 39.2, 37.1, 35.5, 29.9, 27.9, 24.6, 22.7, 22.6, 19.6. Anal. Calcd for $C_{21}H_{26}BrISO_2$: C, 45.87; H, 4.73. Found: C, 46.32; H, 4.75.

Synthesis of (3,7-Dimethyloctyl)−3-bromobenzoate (2b)

To 3-bromobenzoic acid (3.00 g, 14.9 mmol), thionyl chloride (15 mL) was added, and then the reaction mixture was stirred at 90 °C for 6 h. After the reaction, thionyl chloride was removed under reduced pressure. Then, to the residue, CH_2Cl_2 (37.5 mL), triethylamine (5.7 mL, 41.0 mmol), and 3,7-dimethyloctan-1-ol (2.10 mL, 11.0 mmol) were added, and the solution was stirred at 0 °C overnight. After the reaction, the product was extracted with CH_2Cl_2, and the organic layer was washed with water. After drying the solution over anhydrous $MgSO_4$ followed by filtration, the filtrate was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/EtOAc (9/1, v/v) as an eluent to give **2b** as a colorless oil (4.78 g, 94%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 8.15 (t, $J = 1.8$ Hz, ArH, 1H), 7.94 (d, $J = 7.8$ Hz, ArH, 1H), 7.64 (d, $J = 8.0$ Hz, ArH, 1H), 7.30 (t, $J = 7.9$ Hz, ArH, 1H), 4.35 (t, $J = 7.8$ Hz, $-\mathrm{OC}H_2\mathrm{CH}_2-$, 2H), 1.81–1.11 (m, 11H), 0.95 (d, $J = 6.4$ Hz, $-\mathrm{C}H_3$, 3H), 0.86 (d, $J = 6.6$ Hz, $-\mathrm{C}H_3$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 165.2, 135.7, 132.5, 132.4, 129.9, 128.1, 122.4, 64.0, 39.1, 37.1, 35.4, 29.9, 27.9, 24.6, 22.7, 22.6, 19.6. Anal. Calcd for $C_{17}H_{25}BrO_2$: C, 59.77; H, 7.32. Found: C, 59.70; H, 7.13.

Synthesis of (3,7-Dimethyloctyl)−3-(3-thienyl)benzoate (2c)

A DMF solution (30 mL) of **2b** (2.69 g, 7.88 mmol), 3-thiopheneboronic acid (1.21 g, 9.46 mmol), K_2CO_3 (3.26 g, 23.6 mmol), and $Pd(PPh_3)_4$ (0.45 g, 0.39 mmol) was degassed by three freeze–thaw–pump cycles and then stirred at 90 °C for 18 h under argon atmosphere. After the reaction, the product was extracted with $CHCl_3$, and the organic layer was washed with water. After drying the solution over anhydrous $MgSO_4$ followed by filtration, the filtrate was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/EtOAc (9/1, v/v) to give **2c** as an orange oil (2.30 g, 85%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 8.26 (t, $J = 1.6$ Hz, ArH, 1H), 7.95 (d, $J = 8.0$ Hz, ArH, 1H), 7.75 (d, $J = 7.8$ Hz, ArH, 1H), 7.53 (m, ArH, 1H), 7.47–7.37 (m, ArH, 3H), 4.37 (t, $J = 6.8$ Hz, $-\mathrm{OC}H_2\mathrm{CH}_2-$, 2H), 1.83–1.14 (m, 11H), 0.95 (d, $J = 6.4$ Hz, $-\mathrm{C}H_3$, 3H), 0.86 (d, $J = 6.6$ Hz, $-\mathrm{C}H_3$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 166.2, 140.9, 135.7, 130.7, 130.3, 128.5, 127.7, 127.1, 126.6, 125.8, 120.6, 63.4, 38.8, 36.8, 35.2, 29.7, 27.6, 24.3, 22.2, 19.3. Anal. Calcd for $C_{21}H_{28}SO_2$: C, 73.14; H, 8.12. Found: C, 72.84; H, 8.03.

Synthesis of (3,7-Dimethyloctyl)−3-(2-bromo-3-thienyl)benzoate (2d)

To a solution of **2c** (1.70 g, 4.95 mmol) in THF (20 mL), NBS (0.92 g, 5.20 mmol) was added at 0 °C under argon atmosphere. The reaction mixture was stirred at 0 °C for 4 h and then at room temperature for 18 h. After the reaction, the solution was diluted with Et_2O, and 1 M aqueous NaOH was added to quench the residual NBS. The organic layer was separated by extraction and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The crude product was then purified by silica gel column chromatography using hexane/EtOAc (19/1, v/v) to give **2d** as a colorless oil (1.49 g, 71%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 8.22 (t, $J = 1.7$ Hz, ArH, 1H), 8.02 (d, $J = 7.8$ Hz, ArH, 1H), 7.74 (d, $J = 7.7$ Hz, ArH, 1H), 7.53 (t, $J = 7.8$ Hz, ArH, 1H), 7.34 (d, $J = 5.6$ Hz, ArH, 1H), 7.05 (d, $J = 5.7$ Hz, ArH, 1H), 4.37 (t, $J = 6.8$ Hz, $-\mathrm{OC}H_2\mathrm{CH}_2-$, 2H), 1.86–1.12 (m, 11H), 0.96 (d, $J = 6.4$ Hz, $-\mathrm{C}H_3$, 3H), 0.86 (d, $J = 6.6$ Hz, $-\mathrm{C}H_3$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 166.4, 140.2, 135.2, 132.9, 130.8, 129.7, 128.9, 128.7, 128.5, 126.2, 109.3, 63.7, 39.2, 37.2, 35.6, 30.0, 28.0, 24.7, 22.7, 22.6, 19.6. Anal. Calcd for $C_{21}H_{27}BrSO_2$: C, 59.51; H, 6.37. Found: C, 59.45; H, 6.33.

Synthesis of (3,7-Dimethyloctyl)−3-(2-bromo-5-iodo-3-thienyl)benzoate (2e)

To a solution of **2d** (1.20 g, 2.84 mmol) in $CHCl_3$ and acetic acid (20 mL, 1:1, v/v), NIS (0.67 g, 2.98 mmol) was added, and then the reaction mixture was stirred at room temperature overnight. After the reaction, saturated aqueous $Na_2S_2O_3$ solution was added to quench the excess amount of NIS, and the product was extracted with EtOAc. After drying the solution over anhydrous $MgSO_4$ followed by filtration, the filtrate was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/EtOAc (19/1, v/v) to give **2e** as a dark red oil (1.47 g, 95%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 8.15 (t, $J = 1.6$ Hz, ArH, 1H), 8.02 (d, $J = 7.9$ Hz, ArH, 1H), 7.67 (d, $J = 7.7$ Hz, ArH, 1H), 7.50 (t, $J = 7.8$ Hz, ArH, 1H), 7.22 (s, ArH, 1H), 4.37 (t, $J = 6.8$ Hz, $-\mathrm{OC}H_2\mathrm{CH}_2-$, 2H), 1.83–1.12 (m, 12H), 0.96 (d, $J = 6.4$ Hz, $-\mathrm{C}H_3$, 3H), 0.86 (d, $J = 6.6$ Hz, $-\mathrm{C}H_3$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 166.2, 142.3, 138.4, 133.9, 132.8, 130.9, 129.6, 129.1, 128.5, 112.1, 72.4, 63.8, 39.2, 37.1, 35.6, 30.0, 28.0, 24.7, 22.7, 22.6, 19.6. Anal. Calcd for $C_{21}H_{26}BrISO_2$: C, 45.87; H, 4.73. Found: C, 45.85; H, 4.75.

Synthesis of 4-Bromododecanoylbenzene (3b)

To bromobenzene (7.17 g, 45.7 mmol) and aluminum chloride (3.65 g, 27.4 mmol), dodecanoyl chloride (5.00 g, 5.43 mL, 22.8 mmol) was slowly added, and the reaction mixture was then stirred at 50 °C for 1 h. After the reaction, the reaction mixture was poured into ice water, and the product was extracted with CH_2Cl_2 and washed with HCl solution (2 N) and brine. After drying the solution over anhydrous $MgSO_4$ followed by filtration, the filtrate was evaporated under reduced pressure. The crude product was purified by recrystallization from methanol:acetone (2:5, v/v) to afford **3b** as a colorless plate-like solid (7.17 g, 93%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 7.73 (d, $J = 8.5$ Hz, ArH, 2H), 7.52 (d, $J = 8.5$ Hz, ArH, 2H), 2.83 (t, $J = 7.4$ Hz, $-\mathrm{COC}H_2\mathrm{CH}_2-$, 2H), 1.63 (q, alkyl group, 2H), 1.31–1.08 (m, alkyl group, 16H), 0.89 (t, $J = 6.7$ Hz, $-\mathrm{C}H_3$, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 199.8, 136.2, 132.2, 130.0, 128.3, 39.0, 32.3, 30.0, 29.9, 29.7, 24.7, 23.1, 14.5.

Synthesis of 1-(4-(Thiophen-3-yl)phenyl)dodecanone (3c)

A DMF solution of **3b** (2.95 g, 8.72 mmol), 3-thiopheneboronic acid (1.33 g, 10.5 mmol), K_2CO_3 (3.61 g, 26.2 mmol), and $Pd(PPh_3)_4$ (0.50 g, 0.43 mmol) was degassed by three freeze–thaw–pump cycles and then stirred at 90 °C for 18 h under argon atmosphere. After the reaction, the product was extracted with $CHCl_3$, and the organic layer was washed with water. After drying the solution over anhydrous $MgSO_4$ followed by filtration, the filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography using $CHCl_3$ as an eluent and recrystallization from $CHCl_3$:methanol (5:1, v/v) to give **3c** as a white solid (2.72 g, 97%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 7.98 (d, $J = 8.2$ Hz, Ar*H*, 2H), 7.65 (d, $J = 8.2$ Hz, Ar*H*, 2H), 7.54 (t, $J = 2.1$ Hz, Ar*H*, 1H), 7.40 (m, Ar*H*, 2H), 2.94 (t, $J = 7.3$ Hz, $—COCH_2CH_2—$, 2H), 1.83–1.26 (m, 19H), 0.87 (t, $J = 6.7$ Hz, $—CH_3$, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 199.9, 141.3, 140.0, 135.8, 128.8, 126.7, 126.4, 126.2, 121.9, 38.7, 31.9, 29.6, 29.5, 29.5, 29.4, 29.3, 14.0. Anal. Calcd for $C_{22}H_{30}SO$: C, 77.14; H, 8.83. Found: C, 77.11; H, 8.97.

Synthesis of 1-(4-(2,5-Diiodothiophen-3-yl)phenyl)dodecanone (3d)

To a solution of **3c** (0.76 g, 2.23 mmol) in $CHCl_3$ and acetic acid (20 mL, 1:2, v/v), NIS (1.10 g, 4.91 mmol) was added, and then the reaction mixture was stirred at room temperature overnight. After the reaction, saturated aqueous $Na_2S_2O_3$ solution was added to quench the excess amount of NIS, and the product was extracted with $CHCl_3$. After drying the solution over anhydrous $MgSO_4$ followed by filtration, the filtrate was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/$CHCl_3$ (2/1, v/v) to give **3d** as a white solid (1.10 g, 90%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 7.99 (d, $J = 8.58$ Hz, Ar*H*, 2H), 7.53 (d, $J = 8.5$ Hz, Ar*H*, 2H), 7.10 (s, 1H), 2.99 (t, $J = 7.4$ Hz, $—COCH_2CH_2—$, 2H), 1.83–1.26 (m, 20H), 0.87 (d, $J = 6.7$ Hz, $—CH_3$, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 199.9, 147.7, 139.5, 138.3, 136.3, 128.8, 128.2, 38.7, 31.9, 29.7, 29.4, 29.3, 24.3, 22.6, 14.1. Anal. Calcd for $C_{22}H_{28}I_2SO$: C, 44.46; H, 4.75. Found: C, 44.40; H, 4.73.

Synthesis of Bis(3′,7′-dimethyloctyl) 4,4′-([2,2′,5′,2″-Terthiophene]-3,3″-diyl)dibenzoate (4a)

To a mixture of 25 mL dry toluene in a two-necked flask, 2,5-bis(trimethylstannyl)thiophene (0.33 g, 0.81 mmol), compound **1d** (0.72 mg, 1.70 mmol), $Pd_2(dba)_3$ (0.04 g, 0.05 mmol), and P(*o*-Tolyl)$_3$ (0.02 g, 0.09 mmol) were added. The mixture was degassed by three freeze–pump–thaw cycles and then heated to 90 °C for 18 h under argon atmosphere. After the reaction, the solution was cooled to room temperature, and the product was extracted with EtOAc and washed with water and brine. After drying the solution over $MgSO_4$ followed by filtration, the filtrate was evaporated under reduced pressure. The crude product was purified by silica column chromatography using hexane/$CHCl_3$ (1/1, v/v) and then hexane/EtOAc (19/1, v/v) as eluents to give **4a** (1.04 g, 80%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 7.93 (d, $J = 8.3$ Hz, Ar*H*, 2H), 7.32 (d, $J = 8.2$ Hz, Ar*H*, 2H), 7.21 (d, $J = 5.2$ Hz, Ar*H*, 1H), 6.97 (d, $J = 5.2$ Hz, Ar*H*, 1H), 6.69 (s, Ar*H*, 1H), 4.35 (t, $J = 6.7$ Hz, $—OCH_2CH_2—$, 2H), 1.81–1.11 (m, 11H), 0.95 (d, $J = 6.3$ Hz, $—CH_3$, 3H), 0.86 (d, $J = 6.6$ Hz, $—CH_3$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 166.8, 141.0, 138.5, 136.3, 132.3, 130.6, 130.0, 129.8, 129.5, 127.4, 125.1, 64.0, 38.6, 37.6, 36.9, 30.3, 28.3, 25.0, 23.1, 23.0, 20.0. Anal. Calcd for $C_{46}H_{56}S_3O_4$: C, 71.83; H, 7.34. Found: C, 71.32; H, 7.35.

Synthesis of Bis(3′,7′-dimethyloctyl) 4,4′-(5,5″-Dibromo-[2,2′,5′,2″-terthiophene]-3,3″-diyl)dibenzoate (4b)

To a solution of **4a** (0.29 g, 0.37 mmol) in DMF (8 mL), NBS (0.13 g, 0.75 mmol) was added at 0 °C under argon atmosphere, and the mixture was stirred at 0 °C for 4 h and then at room temperature for 18 h. After the reaction, the solution was diluted with Et_2O, and then 1 M aqueous NaOH was added to quench the residual NBS. The organic layer was then washed with brine and water. After drying the solution over $MgSO_4$ followed by filtration, the filtrate was evaporated under reduced pressure. The crude product was then purified by silica gel column chromatography using hexane/EtOAc (19/1, v/v) as an eluent to give **4b** as a red oil (0.35 g, 100%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 7.95 (d, $J = 8.4$ Hz, Ar*H*, 2H), 7.34 (d, $J = 8.4$ Hz, Ar*H*, 2H), 7.00 (s, Ar*H*, 1H), 6.72 (s, Ar*H*, 1H), 4.36 (t, $J = 6.8$ Hz, $—OCH_2CH_2—$, 2H), 1.86–1.12 (m, 11H), 0.96 (d, $J = 6.4$ Hz, $—CH_3$, 3H), 0.86 (d, $J = 6.6$ Hz, $—CH_3$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 166.6, 148.4, 138.7, 138.5, 136.5, 133.1, 130.2, 130.1, 129.4, 128.0, 127.6, 127.2, 69.8, 39.5, 37.5, 35.9, 30.3, 28.3, 25.0, 23.1, 20.0. Anal. Calcd for $C_{46}H_{54}Br_2S_3O_4$: C, 59.61; H, 5.87. Found: C, 59.64; H, 5.93.

General Procedure for Polymerization (P1-1, P1–2, P1–3, P2, P3, and P4)

$Pd_2(dba)_3$ (6 mol %) and P(*o*-tolyl)$_3$ (50 mol %) were added to a toluene solution of monomer (1.0 equiv) and 2,5-bis(trimethylstannyl)thiophene (1.0 equiv) in argon, which was deoxidized by bubbling with dry argon for 1 h. The solution was refluxed for 3 days. After the reaction, the solution was cooled down to room temperature and poured into methanol to precipitate the polymer. The polymer was purified by Soxhlet extraction using methanol, acetone, and $CHCl_3$. After evaporating $CHCl_3$, the polymer was further purified by flash silica gel column chromatography using $CHCl_3$ as an eluent, and the solution was concentrated and dried under reduced pressure to give a polymer as a dark red solid.

Synthesis of P1-1

The title polymer, **P1-1**, was synthesized according to the general procedure performed with 0.30 g (0.55 mmol) of **1f**, 0.22 g (0.55 mmol) of 2,5-bis(trimethylstannyl)thiophene, 0.03 g (0.020 mmol) of Pd $(PPh_3)_4$, and 30 mL of toluene. After purification, the polymer **P1-1** (0.16 g, 68%) was isolated as a dark red solid.

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 7.98–6.66 (m, Ar*H*, 8H), 4.29 (t, $J = 5.5$ Hz, $—OCH_2CH_2—$, 2H), 1.86–0.77 (m, alkyl group, 22H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 168.1, 128.8, 128.7, 128.1, 62.7, 38.1, 36.1, 34.5, 28.9, 26.6, 25.9, 23.6, 21.7, 21.6, 18.6.

Synthesis of P1–2

The title polymer, **P1–2**, was synthesized according to the general procedure performed with 0.36 g (0.73 mmol) of **1e**, 0.30 g (0.73 mmol) of 2,5-bis(trimethylstannyl)thiophene, 0.04 g (0.03 mmol) of $Pd(PPh_3)_4$, and 30 mL of toluene. After refluxing for 3 days, 2-tributylstannyl thiophene (0.02 mL) was added to the reaction, and after 2 h, 2-bromothiophene (0.01 mL) was added. The mixture was stirred overnight to complete the end-capping reaction. After purification, the polymer **P1–2** (0.22 g, 71%) was isolated as a dark red solid.

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 7.92–6.66 (m, Ar*H*, 7H), 4.29 (t, $J = 5.5$ Hz, $—OCH_2CH_2—$, 2H), 1.86–0.77 (m, alkyl group, 22H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 168.1, 166.7, 140.5, 139.4, 135.9, 131.3, 130.2, 129.5, 129.2, 66.6, 64.1, 39.6, 37.5, 36.0, 30.4, 30.1, 28.3, 25.0, 23.1, 23.0, 20.0.

Synthesis of P1–3

The title polymer, **P1–3**, was synthesized according to the general procedure performed with 0.16 g (0.33 mmol) of **1e**, 0.13 g (0.33 mmol) of 2,5-bis(trimethylstannyl)thiophene, 0.01 g (0.02 mmol) of $Pd_2(dba)_3$, 0.05 g (0.16 mmol) of P(*o*-Tolyl)$_3$, and 20 mL of toluene. After refluxing for 3 days, 2-tributylstannyl thiophene (0.02 mL) was added to the reaction, and after 2 h, 2-bromothiophene (0.01 mL) was added. The mixture was stirred overnight to complete the end-capping reaction. After purification, the polymer **P1–3** (120 mg, 70%) was isolated as a dark red solid.

Synthesis of P2

The title polymer, **P2**, was synthesized according to the general procedure performed with 0.30 g (0.54 mmol) of **2e**, 0.21 g (0.54 mmol) of 2,5-bis(trimethylstannyl)thiophene, 0.03 g (0.03 mmol) of $Pd_2(dba)_3$, 0.08 g (0.27 mmol) of P(*o*-Tolyl)$_3$, and 25 mL of toluene. After refluxing for 3 days, 2-tributylstannyl thiophene (0.02 mL) was added to the reaction, and after 2 h, 2-bromothiophene (0.01 mL) was added. The mixture was stirred overnight to complete the end-capping reaction. After purification, the polymer **P2** (0.21 g, 70%) was isolated as a dark red solid.

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 7.92–6.69 (m, Ar*H*, 7H), 4.27 (s, $—OCH_2CH_2—$, 2H), 1.86–0.77 (m, alkyl group, 22H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 165.2, 132.6, 129.7, 129.1, 127.9, 127.4, 125.8, 125.5, 62.7, 38.1, 36.1, 34.4, 28.9, 28.6, 28.2, 26.9, 23.5, 21.7, 21.6, 18.6, 13.1.

Synthesis of P3

The title polymer, **P3**, was synthesized according to the general procedure performed with 0.30 g (0.56 mmol) of **3d**, 0.22 g (0.56 mmol) of 2,5-bis(trimethylstannyl)thiophene, 0.03 g (0.03 mmol) of $Pd_2(dba)_3$, 0.08 g (0.28 mmol) of P(*o*-Tolyl)$_3$, and 25 mL of toluene. After refluxing for 3 days, 2-tributylstannyl thiophene (0.02 mL) was added to the reaction, and after 2 h, 2-bromothiophene (0.01 mL) was added. The mixture was stirred overnight to complete the end-capping reaction. After purification, the polymer **P3** (0.20 g, 68%) was isolated as a dark red solid.

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 7.85–6.69 (m, Ar*H*, 7H), 2.89 (s, $—COCH_2CH_2—$, 2H), 1.66 (s, alkyl group, 2H), 1.18 (s, alkyl group, 17H), 0.79 (s, $—CH_3$, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 200.8, 129.7, 128.6, 39.1, 32.3, 30.1, 29.9, 29.8, 29.7, 24.7, 23.1, 14.5.

Synthesis of P4

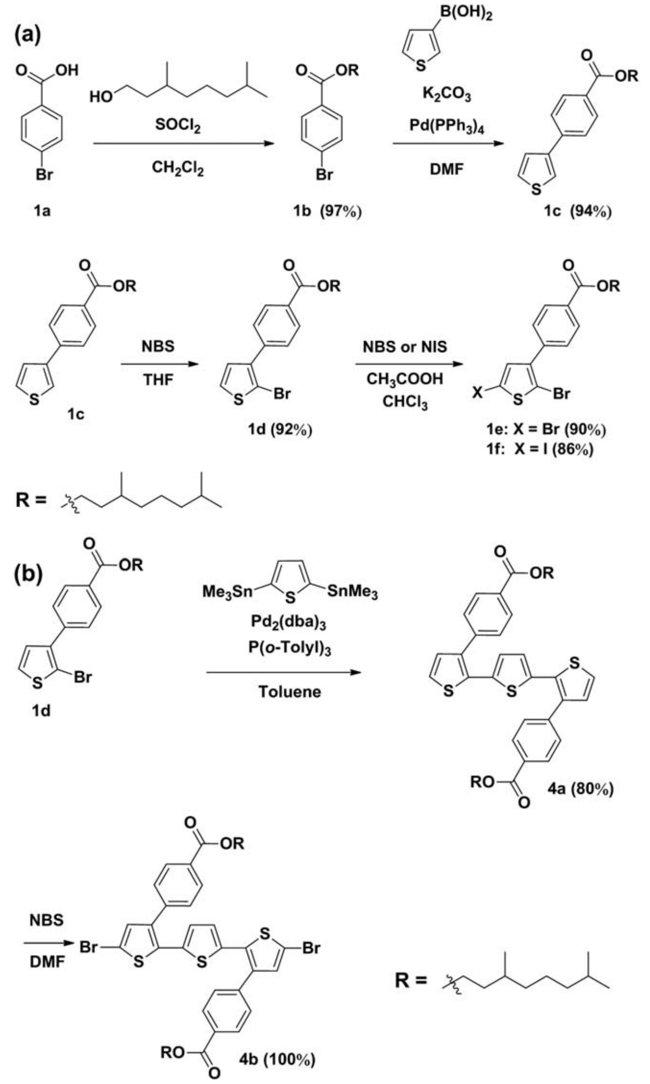
$Pd_2(dba)_3$ (0.0203 g, 0.020 mol%) and P(*o*-tolyl)$_3$ (0.0563 g, 0.18 mmol) were added to a toluene solution of **4b** (0.343 g, 0.37 mmol) and 2,5-bis(trimethylstannyl)thiophene (0.152 g, 0.37 mmol) in argon, which was deoxidized by bubbling with dry argon for 1 h. The solution was refluxed for 3 days. After refluxing for 3 days, 2-tributylstannyl thiophene (0.02 mL) was added to the reaction, and after 2 h, 2-bromothiophene (0.01 mL) was added. The mixture was stirred overnight to complete the end-capping reaction. After the end-capping reaction, the solution was cooled down to room temperature and poured into methanol to precipitate the polymer. The polymer was purified by Soxhlet extraction using methanol, acetone, and $CHCl_3$. After evaporating $CHCl_3$, the polymer was further purified by flash silica gel column chromatography using $CHCl_3$ as an eluent, and the solution was concentrated and dried under reduced pressure to give **P4** (0.243 g, 77%) as a dark red solid.

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, 25 °C): 8.00 (d, $J = 8.1$ Hz, Ar*H*, 2H), 7.41 (d, $J = 7.9$ Hz, Ar*H*, 2H), 7.07 (s, Ar*H*, 2H), 6.74 (s, Ar*H*, 1H), 4.36 (t, $J = 5.5$ Hz, $—OCH_2CH_2—$, 2H), 1.86–1.12 (m, 11H), 0.96 (d, $J = 6.2$ Hz, $—CH_3$, 3H), 0.86 (d, $J = 6.6$ Hz, $—CH_3$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm, 25 °C): 166.7, 140.5, 139.2, 135.9, 131.9, 131.2, 130.2, 129.5, 127.3, 125.3, 124.5, 64.1, 39.6, 37.5, 36.0, 31.3, 30.4, 28.3, 25.0, 23.0, 20.0.

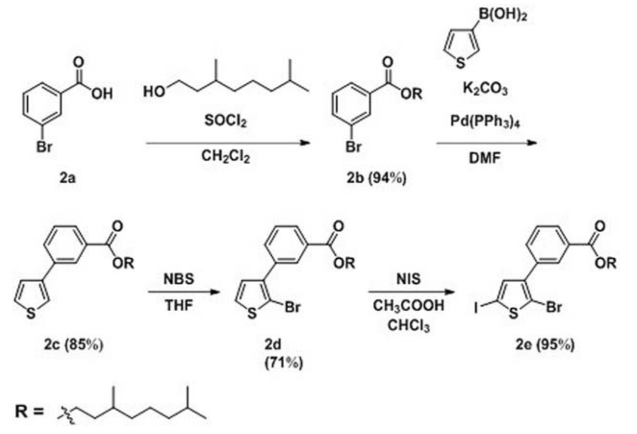
RESULTS AND DISCUSSION

Monomer Synthesis

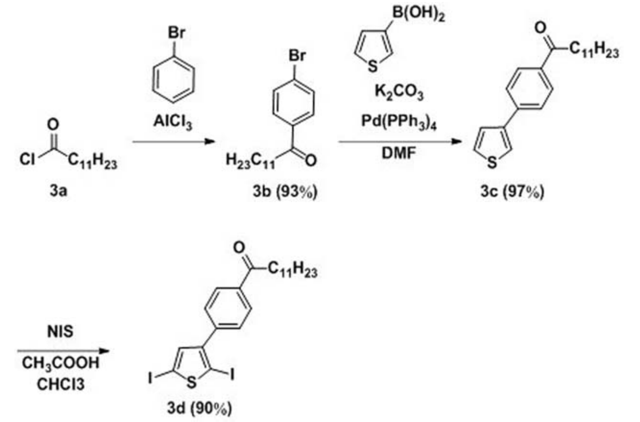
To prepare polythiophene derivatives with low HOMO levels while maintaining narrow energy band gaps, we selected monomers containing a phenyl group with an electron-withdrawing ester group (**1e**, **1f**, **2e**, and **4b**) and ketone group (**3d**). The thiophene unit has an electron density lower than that of P3HT because of the electron-withdrawing group in the side chain. We expect that the new polymers will have (1) a narrower energy band gap than that of P3HT because the presence of a phenyl group in the side chain will extend the conjugation length of the polymer, and (2) a deeper HOMO level than that of P3HT because of the effect of electron-withdrawing groups, such as ester and ketone groups, or in other words, the new polymers will exhibit a better oxidative stability than that of P3HT. Furthermore, 3,7-dimethyloctyl and undecanyl groups were introduced to increase the solubility of the polythiophene derivatives. These monomers were successfully prepared in good yield in four steps [Schemes 1(a) and 2], that is, esterification of bromobenzoic acid, Suzuki-Miyaura coupling



SCHEME 1 Synthetic route to (a) monomers having ester group at the *p*-position and (b) monomer **4b**.



SCHEME 2 Synthetic route to monomer having ester group at the m-position.



SCHEME 3 Synthetic route to monomer having ketone group at the p-position.

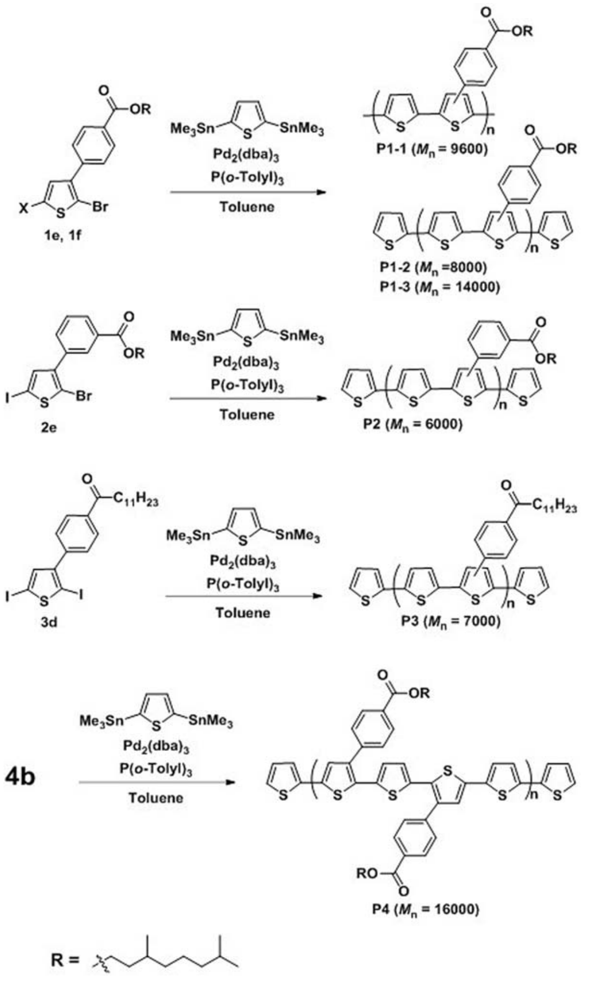
reaction, and bromination and iodination at the 2- and 5-positions of the 3-aromaticthiophene group, and in three steps (Scheme 3), that is, Friedel-Crafts reaction, Suzuki-Miyaura coupling reaction, and iodination at both the 2- and 5-positions of the 3-aromaticthiophene group. Monomer **4b** was synthesized by the Stille coupling reaction between **1d** and 2,5-bis(trimethylstannyl)thiophene [Scheme 1(b)]. The synthesized monomers were identified by ^{1}H and ^{13}C NMR analyses and elemental analysis (EA).

Polymer Synthesis

The polymers of **P1** (**P1-1**, **P1–2**, and **P1–3**), **P2**, **P3**, and **P4** were synthesized by Stille coupling reactions between the appropriate monomers and 2,5-bis(trimethylstannyl)thiophene (Scheme 4). At first, **P1-1** and **P1–2** were synthesized by using $Pd(PPh_3)_4$ as a typical catalyst. Changing the catalyst to $Pd_2(dba)_3/P(o\text{-}Tolyl)_3$ somewhat improved the molecular weight (**P1–3**). **P1–2**, **P1–3**, **P2**, **P3**, and **P4** were end-capped with thiophene rings. The polymers were purified by Soxhlet extraction using methanol, acetone, and chloroform. All of these polymers have a good solubility in the common organic solvents, such as chloroform, toluene, and THF. The molecular weights and dispersities (*Đ*s) of these polymers were determined by SEC analysis with chloroform as the eluent. The number–average molecular weight (M_n), the weight–average molecular weight (M_w), and the *Đ* values of these polymers were calculated and summarized in Table 1.

Thermal Properties

The thermal properties of these polymers were analyzed by thermogravimetric analysis (TGA) and DSC, and the results are shown in Figure 2. The decomposition temperature $T_{d,5\%}$ of all the polymers are higher than 348 °C, demonstrating the sufficiently high thermal stability for applications to PSCs. The DSC was used to investigate the possible crystallization of the prepared polymers. From the DSC measurements of the regiorandom copolymers **P1-1**, **P1–2**, **P2**, and **P3**, neither melting point nor glass transition temperature was observed (see Supporting Information Fig. S1 for enlarged DSC curves), suggesting that these copolymers tend to be amorphous.



SCHEME 4 Synthetic routes to polymers **P1–P4**.

In contrast, as shown in Figure 2 (bottom), there are exothermic peaks for the melting temperatures (T_m) of **P1–3** at 176 °C and **P4** at 224 °C. The T_c values at 139 °C (**P1–3**) and 143 °C (**P4**) were also clearly observed, indicating the crystallinity of **P1–3** and **P4**. These results were caused by the effect of the high molecular weight in both cases and the effect of the regioregular structure in the case of **P4**.

TABLE 1 Physical Properties of the Synthesized Polymers

Polymer	M_n (g mol^{-1})[a]	M_w (g mol^{-1})[a]	$Đ$[a]	$T_{d,5\%}$ (°C)
P1–1	9,120	14,000	1.54	348
P1–2	7,840	14,200	1.81	358
P1–3	13,800	33,300	2.42	360
P2	6,140	10,000	1.63	380
P3	6,590	9,880	1.50	377
P4	15,500	36,300	2.34	373

[a] M_n, M_w, and $Đ$ values of the polymers were determined by SEC in $CHCl_3$.

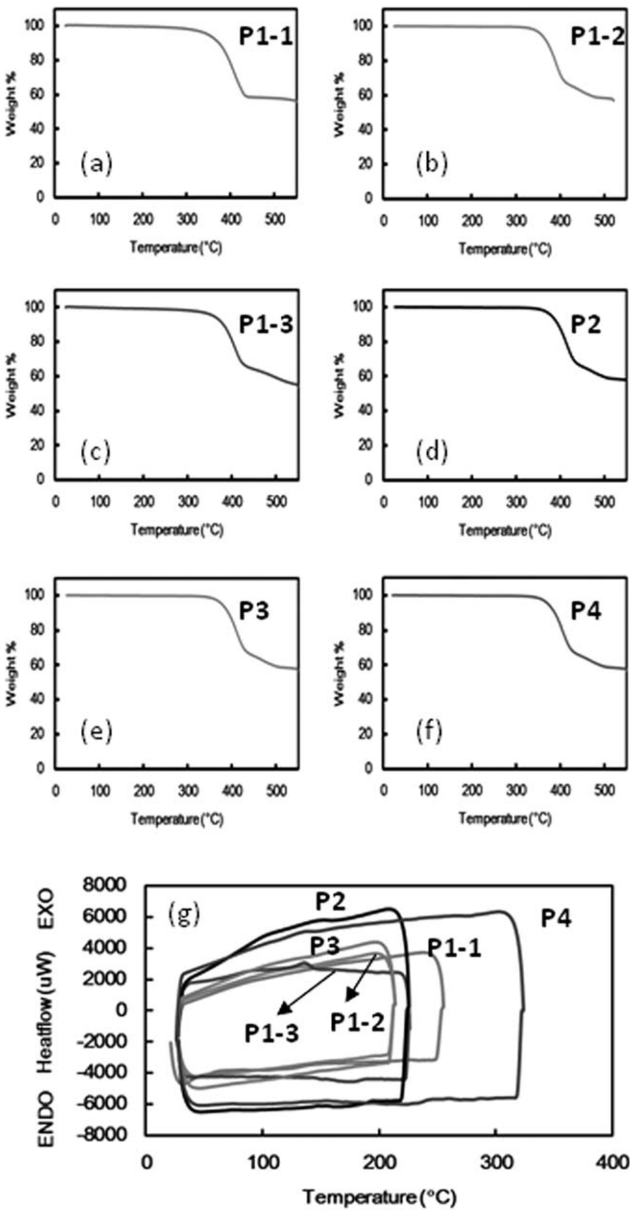


FIGURE 2 TGA curves of (a) **P1-1**, (b) **P1–2**, (c) **P1–3**, (d) **P2**, (e) **P3**, and (f) **P4**, and (g) DSC thermograms of **P1–P4** at the heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

Optical and Electronic Properties

The absorption spectra of the synthesized polymers measured in both dilute chloroform and in a thin film are shown in Figure 3. The related optical parameters are summarized in Table 2. The solution absorption spectra of the polymers showed a broad absorption band in the range of 300–700 nm with maximum absorption peaks at 471 nm (**P1-1**), 482 nm (**P1–2**), 494 nm (**P1–3**), 485 nm (**P2**), 468 nm (**P3**), and 486 nm (**P4**). The absorption spectra of the polymers in the thin film were red-shifted ~50 nm when compared with those in solution. This result indicates the formation of a π-stacked intermolecular packing through interchain delocalization or chain planarization. The optical band gaps (E_g^{opt}) of the regiorandom polymers obtained from the absorption

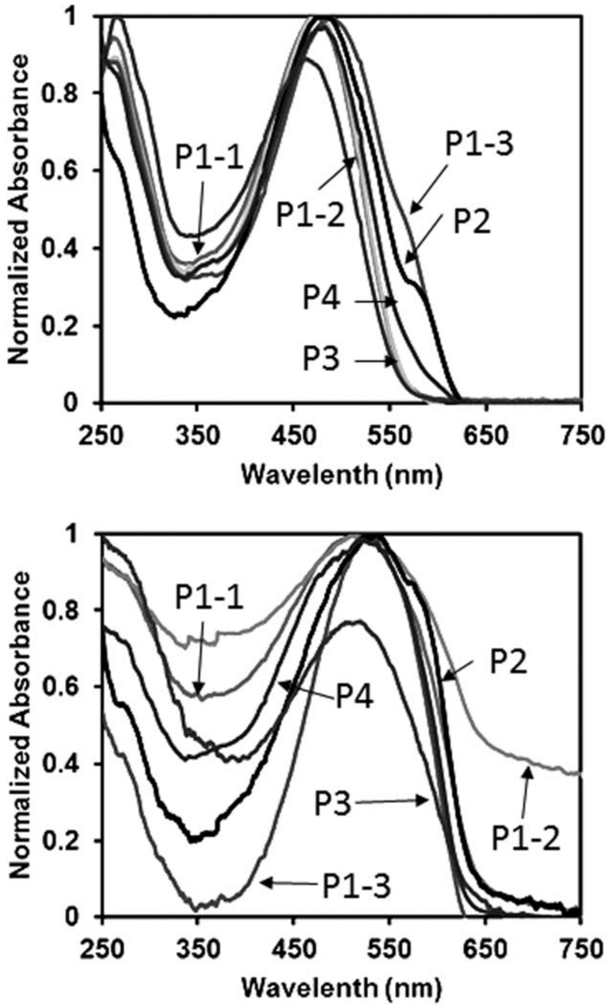


FIGURE 3 UV–vis spectra of **P1–P4** in chloroform solution (top) and in thin films (bottom).

onset of the polymer films ranged from 1.94 to 1.97 eV. In the case of **P1**, which has an ester group at the p-position of the phenyl side chain, the polymer without an end cap with the thiophene unit (**P1-1**) exhibited a smaller band gap than that of the polymer with an end cap (**P1–2** and **P1–3**), and the polymer with a lower molecular weight (**P1-1** and **P1–2**) exhibited a smaller band gap than that of the polymer with a higher molecular weight (**P1–3**). This result indicates that to obtain a lower HOMO energy level, the ideal polymer requires a high molecular weight and end-capping. The polymer which has the ester group at the m-position of phenyl side chain (**P2**) and ketone group at the p-position of the phenyl side chain (**P3**) showed the same band gap level as the **P1**s. This result implied that the ester group and ketone group showed a similar effect to the band gap of the synthesized polymers; however, the polymer with an ester group at the side chain tends to exhibit a lower HOMO level than that of the others. The ester group at the m-position of the phenyl side chain did not decrease the HOMO level because of the small electronic effect. In contrast to the regiorandom polymers, the regioregular polymer **P4** exhibited a smaller band gap (1.90 eV), probably due to chain planarization. According to the previous reports, P3HT has maximum absorption peak at 456 nm in $CHCl_3$ solution and 560 nm in the thin film.[30] The optical band gap of P3HT is 2.02 eV,[31] indicating that all synthesized polymers have slightly narrower band gap than P3HT. It may be caused by the extended π-conjugation length resulting from the introduction of aromatic side groups.

The CV curves recorded for the synthesized polymers referenced to an Ag/AgCl reference electrode are shown in Figure 4. The HOMO energy levels of the synthesized polymers were determined to be lower than −5.29 eV from the corresponding $E_{\mathrm{onset}}^{\mathrm{ox}}$ according to the following equation: $E_{\mathrm{HOMO}} = -e[E_{\mathrm{onset}}^{\mathrm{ox}} - E^{1/2}(\mathrm{ferrocene}) + 4.80]$ (eV).[32] Based on the relationship between the HOMO energy level and $E_{\mathrm{g}}^{\mathrm{opt}}$ estimated from the UV–vis absorption spectrum of the film sample ($E_{\mathrm{g}}^{\mathrm{opt}} = E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}}$), the LUMO energy levels of the polymers were calculated to be from −3.34 eV to −3.47 eV. All the polymers with an ester group or ketone group at the p-position of the phenyl side chain exhibited deep HOMO energy levels from −5.31 eV (**P3**) to −5.40 eV (**P1–3**). This is due to the high electron-withdrawing effect. In contrast, the polymer with the ester group at the m-position of the phenyl side chain (**P2**) showed an HOMO energy level up to −5.29 eV. This is due to the weak electron-withdrawing effect through the m-position. In the case of the regioregular polymer **P4**, the lower LUMO level (−3.47 eV) and slightly higher HOMO level (−5.37 eV) than those of the regiorandom polymers were observed because of the high planarity of the main chain. A comparison of the energy levels between the

TABLE 2 Optical and Electrochemical Properties of **P1–P4**

Polymer	$\lambda_{\mathrm{max}}^{\mathrm{sol}}$ (nm)[a]	$\lambda_{\mathrm{max}}^{\mathrm{film}}$ (nm)	$\lambda_{onset}^{\mathrm{sol}}$ (nm)[a]	$\lambda_{onset}^{\mathrm{film}}$ (nm)	HOMO (eV)	LUMO (eV)[b]	$E_{\mathrm{g}}^{\mathrm{opt}}$ (eV)[c]
P1–1	471	521	588	639	−5.34	−3.40	1.94
P1–2	482	530	598	633	−5.35	−3.39	1.96
P1–3	494	531	627	628	−5.40	−3.43	1.97
P2	485	538	625	637	−5.29	−3.34	1.95
P3	468	523	578	634	−5.31	−3.44	1.96
P4	486	530	625	652	−5.37	−3.47	1.90

[a] Measurements performed in chloroform.

[b] Calculated using the optical band gap energy.

[c] Estimated from the onset of the absorption in thin films.

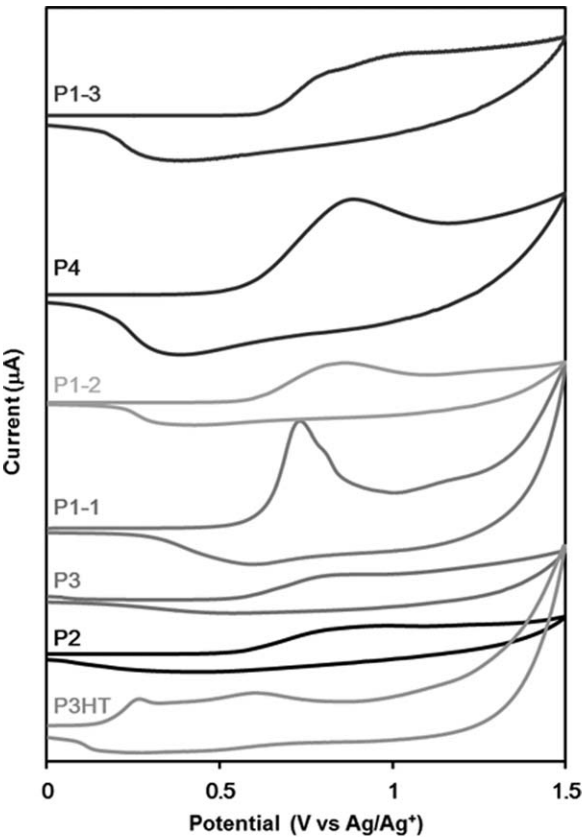


FIGURE 4 Cyclic voltammograms of polymer films on ITO glass performed at a scanning rate of 100 mV s^{-1} in CH_3CN/0.1 M Bu_4NClO_4.

polymers and PCBM revealed that the LUMO energy levels of these synthesized polymers are about 0.8 eV higher than that of PCBM, indicating that excitons can successfully dissociate at the interface between these polymers and PCBM.

Organic Photovoltaic Properties

PSC devices were fabricated using the synthesized polymers as electron donors and PCBM as an electron acceptor. The device structure was ITO/MoO_3 (10 nm)/polymer:PCBM/$POPy_2$ (4.5 nm)/Al. The photovoltaic performances of the polymer:PCBM devices are summarized in Table 3. The PCEs of the **P1-1**, **P1–2**, **P1–3**, and **P2** devices were found to be 0.16, 0.32, 0.75, and 0.21%, respectively. The V_{oc} values of the **P1-1**, **P1–2**, **P1–3**, and **P2** devices were found to be 0.644, 0.728, 0.926, and 0.648 V, respectively. The high V_{oc} value for the **P1–3** devices could be explained by the low HOMO energy level of **P1–3** (−5.40 eV) when compared with those of **P1-1** (−5.34 eV), **P1–2** (−5.35 eV), and **P2** (−5.29 eV). Among the organic photovoltaic devices based on the polythiophene derivatives, the V_{oc} value of the **P1–3**-based device could be one of the highest values. Because the synthesized polymers showed no crystallinities, the hole mobilities of these polymers are too low ($\sim 10^{-5}$ cm^2 V^{-1} s^{-1}). The FF values of the **P1-1**, **P1–2**, **P1–3**, and **P2** devices were relatively low, probably due to the low hole mobilities. In contrast, the **P4**/PCBM system exhibited a higher PCE than that of the regiorandom polymer **P1–3**/PCBM system.

The PCE of this system was found to be 1.95%. The V_{oc} value of the **P4** device was 0.943 V, slightly higher than the V_{oc} obtained from the **P1–3** device. The J_{sc} and FF values of the regioregular polymer **P4** device were much improved to 4.57 mA cm^{-2} and 0.453, respectively. When using $PC_{71}BM$, which has a stronger absorption in the long-wavelength region than PCBM as an electron acceptor, the **P4**/$PC_{71}BM$ system showed a V_{oc} value of 0.930 V, a FF value of 0.391, and an improved J_{sc} value of 5.43 mA cm^{-2} because of the stronger absorption of $PC_{71}BM$ in the long-wavelength region. As a result, the PCE value was slightly improved to 1.98%.

Morphological Properties

To investigate the crystalline structure of the new p-type semiconductors, the GIWAXS measurement was performed on the pristine polymer films. The GIWAXS image and 1D profiles of the **P4** film, which showed the best PCE, are representatively displayed in Figure 5. The **P4** film shows weak scattering peaks, and the higher order of scattering peaks was not observed, suggesting that the **P4** film has a low crystallinity. Focusing on the scattering corresponding to the lamella spacing ($q = 2$–4 nm^{-1}), it has a higher intensity in the q_{xy} direction rather than that in the $\sim q_z$ direction. The result proves that the lamellar direction of the **P4** film is parallel to the q_{xy} direction; in other words, **P4** film has the

TABLE 3 Polymer Solar Cell Performances of the Synthesized Polymers

Polymer	Acceptor	μ (cm^2 V^{-1} s^{-1})[a]	D:A	V_{oc} (V)[b]	J_{sc} (mA cm^{-2})[b]	FF[b]	PCE (%)
P1-1	PCBM	1.50×10^{-5}	1:0.9	0.644	0.92	0.271	0.16
P1–2	PCBM	3.03×10^{-6}	1:1	0.728	1.53	0.283	0.32
P1–3	PCBM	2.24×10^{-5}	1:1	0.926	2.52	0.321	0.75
P2	PCBM	1.02×10^{-4}	1:2	0.648	0.48	0.306	0.21
P4	PCBM	1.02×10^{-4}	1:2	0.943	4.57	0.453	1.95
P4	$PC_{71}BM$	1.02×10^{-4}	1:2	0.930	5.43	0.391	1.98

[a] Hole mobilities of the synthesized polymers were investigated by fabricating thin film transistor (TFT) with a bottom-contact geometry using Au and Cr as the source and drain electrode.

[b] Devices were fabricated with a layer structure of ITO/MoO_3 (10 nm)/polymer:PCBM/$POPy_2$ (4.5 nm)/Al.

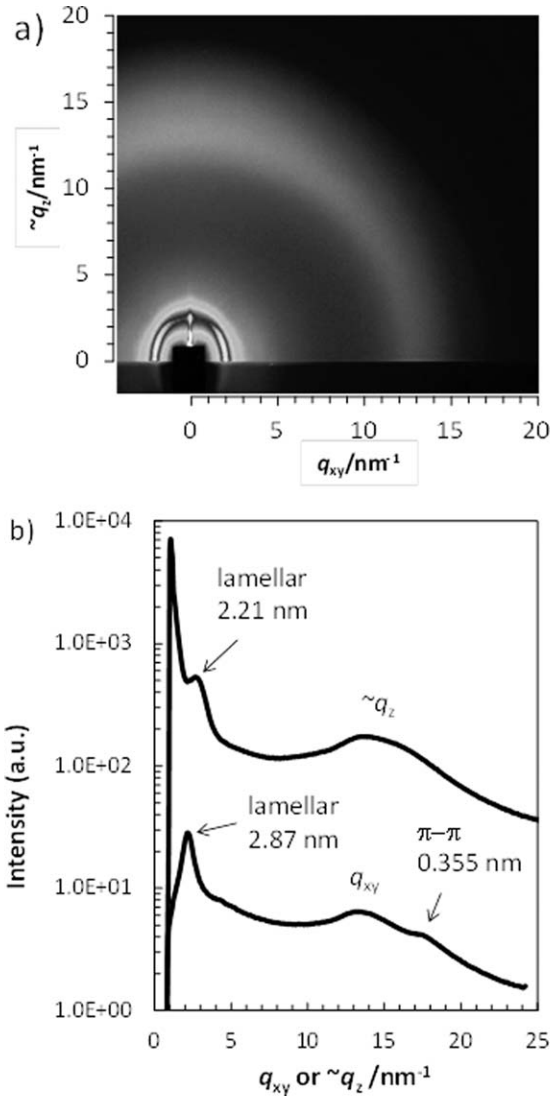


FIGURE 5 GIWAXS image (a) and 1D profiles (b) of the pristine **P4** film drop-casted on the Si wafer.

face-on rich orientation. In addition, the **P4** film has a small lamellar spacing in the $\sim q_z$ direction (2.21 nm) than that in the q_{xy} direction (2.87 nm), suggesting the interdigitation of the side chains in the $\sim q_z$ direction (edge-on orientation). Considering these results, the interdigitation might prevent the growth of the edge-on oriented crystalline structure so that the face-on rich structure is induced.

The π–π stacking distance, which strongly affects the carrier mobility, can be quantified from the scattering peaks in the range of $q = 15$–20 nm^{-1}.[33,34] The crystalline structure of **P4** has a significantly short π–π stacking distance (0.355 nm) in the q_{xy} direction, reflecting the extended π-conjugation length by aromatic side chains as well as the regioregular polymer structure. Although the (010) diffraction of the π–π stacking is not observed in the $\sim q_z$ direction ($q = 10$–20 nm^{-1}) by overlapping with a broad halo, the face-on rich structure should provide a high hole mobility in the q_z direction. Consequently, the PSC using **P4** showed higher J_{sc} and FF values than those of the other polymers.

CONCLUSIONS

In summary, we successfully synthesized four polythiophene derivatives including regiorandom polymers **P1**(**1-1**, **1–2**, and **1–3**), **P2**, and **P3** and the regioregular polymer **P4**, containing a phenyl side chain with an electron-withdrawing carbonyl group such as an ester and a ketone at the 3-position of the thiophene ring. All the polymers showed a good solubility in common organic solvents because of the presence of alkyl side chains. **P1-1**, **P1–2**, **P1–3**, **P2**, and **P3** exhibited UV–vis absorption peaks at 521, 530, 531, 538, and 523 nm, respectively. A photovoltaic device using the **P1–3**:PCBM (1:1) film as the active layer exhibited a V_{oc} value of 0.926 V, a J_{sc} value of 2.52 mA cm^{-2}, and a FF value of 0.321. However, only a low PCE (0.75%) was achieved due to no crystallinity of the synthesized polymers. We assumed that the regiorandom structure is the main reason for the no crystallinity of the synthesized polymers. The regioregular polymer **P4** showed a better absorption than the regiorandom polymer **P1–3** in the long-wavelength region and a similar HOMO energy level to **P1–3**. A photovoltaic device using the **P4**:PC$_{71}$BM (1:2) film as the active layer exhibited a high V_{oc} value of 0.943 V, a J_{sc} value of 4.57 mA cm^{-2}, a FF value of 0.453, and a PCE value up to 1.98%. The V_{oc} value of 0.943 V would be the highest among the polythiophene derivative-based PSCs.

ACKNOWLEDGMENTS

This work received financial support from the Mitsubishi Chemical Group Science and Technology Research Center, Inc. This work was partly supported by the Japan Science and Technology Agency (JST), PRESTO program (JY 220176). GIWAXS experiments were performed at the BL19B2 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal No. 2012B1728). The authors thank Itaru Osaka (RIKEN) for operating the GIWAXS experiments.

REFERENCES AND NOTES

1 J. H. Zhao, A. H. Wang, M. A. Green, F. Ferrazza, *Appl. Phys. Lett.* **1998**, *73*, 1991–1993.

2 A. Shah, P. Torres, R. Tscharner, N. Wyrsch, H. Keppner, *Science* **1999**, *285*, 692–698.

3 C. Duan, F. Huang, Y. Cao, *J. Mater. Chem.* **2012**, *22*, 10416–10434.

4 J. C. Bijleveld, A. P. Zoombelt, S. G. J. Mathijssen, M. M. Wienk, M. Turbiez, D. M. de Leeuw, R. A. J. Janssen, *J. Am. Chem. Soc.* **2009**, *131*, 16616–16617.

5 N. S. Lewis, *Science* **2007**, *315*, 798–801.

6 G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, *270*, 1789–1791.

7 S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, A. J. Heeger, *Nat. Photonics* **2009**, *3*, 297–302.

8 R. C. Coffin, J. Peet, J. Rogers, G. C. Bazan, *Nat. Chem.* **2009**, *1*, 657–661.

9 L. Huo, J. Hou, S. Zhang, H. Y. Chen, Y. Yang, *Angew. Chem. Int. Ed. Engl.* **2010**, *49*, 500–503.

10 S. R. Forrest, *Nature* **2004**, *428*, 911–918.

11 H. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dotz, M. Kastler, A. Facchetti, *Nature* **2009**, *457*, 679–686.

12 I. Kang, T. K. An, J.-A. Hong, H.-J. Yun, R. Kim, D. S. Chung, C. E. Park, Y.-H. Kim, S.-K. Kwon, *Adv. Mater.* **2013**, *25*, 524–528.

13 Y. J. Cheng, S. H. Yang, C. S. Hsu, *Chem. Rev.* **2009**, *109*, 5868–5923.

14 G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nat. Mater.* **2005**, *4*, 864–868.

15 X. N. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels, R. A. J. Janssen, *Nano Lett.* **2005**, *5*, 579–583.

16 B. Burkhart, P. P. Khlyabich, B. C. Thompson, *Macromolecules* **2012**, *45*, 3740–3748.

17 R. F. Service, *Science* **2011**, *332*, 293.

18 J. H. Hou, Z. A. Tan, Y. Yan, Y. J. He, C. H. Yang, Y. F. Li, *J. Am. Chem. Soc.* **2006**, *128*, 4911–4916.

19 J. Hou, T. L. Chen, S. Zhang, L. Hou, S. Sista, Y. Yang, *Macromolecules* **2009**, *42*, 9217–9219.

20 I. Osaka, R. Zhang, G. Sauve, D. M. Smilgies, T. Kowalewski, R. D. McCullough, *J. Am. Chem. Soc.* **2009**, *131*, 2521–2529.

21 M. C. Yuan, M. Y. Chiu, S. P. Liu, C. M. Chen, K. H. Wei, *Macromolecules* **2010**, *43*, 6936–6938.

22 X. Guo, F. S. Kim, S. A. Jenekhe, M. D. Watson, *J. Am. Chem. Soc.* **2009**, *131*, 7206–7207.

23 H. Xin, X. Guo, F. S. Kim, G. Ren, M. D. Watson, S. A. Jenekhe, *J. Mater. Chem.* **2009**, *19*, 5303–5310.

24 Y. Zhu, R. D. Champion, S. A. Jenekhe, *Macromolecules* **2006**, *39*, 8712–8719.

25 P. T. Wu, F. S. Kim, R. D. Champion, S. A. Jenekhe, *Macromolecules* **2008**, *41*, 7021–7028.

26 D. H. Kim, B. L. Lee, H. Moon, H. M. Kang, E. J. Jeong, J. I. Park, K. M. Han, S. Lee, W. B. Yoo, B. W. Koo, J. Y. Kim, W. H. Lee, K. Cho, H. A. Becerril, Z. Bao, *J. Am. Chem. Soc.* **2009**, *131*, 6124–6132.

27 L. Hou, T. L. Chen, Y. Zhou, J. Hou, H. Y. Chen, Y. Yang, Y. Li, *Macromolecules* **2009**, *42*, 4377–4380.

28 K. Oshimizu, A. Takahashi, Y. Rho, T. Higashihara, M. Ree, M. Ueda, *Macromolecules* **2011**, *44*, 719–727.

29 M. J. Zhang, X. Guo, W. Ma, H. Ade, J. H. Hou, *Adv. Mater.* **2014**, *26*, 5880–5885.

30 T. A. Chen, X. Wu, R. D. Rieke, *J. Am. Chem. Soc.* **1995**, *117*, 233–244.

31 Y. He, G. Zhao, B. Peng, Y. Li, *Adv. Funct. Mater.* **2010**, *20*, 3383–3389.

32 J. L. Bredas, R. Silbey, D. S. Boudreaux, R. R. Chance, *J. Am. Chem. Soc.* **1983**, *105*, 6555–6559.

33 R. Noriega, J. Rivnay, K. Vandewal, F. P. V. Koch, N. Stingelin, P. Smith, M. F. Toney, A. Salleo, *Nat. Mater.* **2013**, *12*, 1038–1044.

34 A. T. Yiu, P. M. Beaujuge, O. P. Lee, C. H. Woo, M. F. Toney, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2012**, *134*, 2180–2185.