J Mater Sci (2012) 47:323–331
DOI 10.1007/s10853-011-5801-4

Novel thieno[3,4-c]pyrrole-4,6-dione-based conjugated copolymers with donor–acceptor structures

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Received: 24 May 2011 / Accepted: 16 July 2011 / Published online: 27 July 2011

Abstract A series of novel copolymers with alkylthiophene/alkoxythiophene and the thieno[3,4-c]pyrrole-4,6-dione moieties were synthesized by Sonogashira cross-coupling reactions. The structures and properties of these copolymers were characterized using FT–IR, ^{1}H NMR, UV–Vis, thermal gravimetric analysis, different scanning calorimetry, and cyclic voltammetry (CV). All of the copolymers possess adequate thermal stability, and exhibit good solubility in common organic solvents such as THF, chloroform, and toluene. The electrochemical and photophysical properties were investigated, and the results show that the spectral response of these copolymers are extended up to 700, 750, and 640 nm for $\mathbf{P_1}$, $\mathbf{P_2}$, and $\mathbf{P_3}$, respectively. CV studies reveal that the band gaps of these copolymers range from 1.51 to 1.97 eV, implying that the resulted polymers may be promising candidates for solar cells.

Introduction

Polymer solar cells (PSCs), a promising alternative to silicon-based solar cells, have the potential for sustainable energy exploitation in the future. The low cost, lightweight, and large-area processability of PSCs make them highly attractive for future photovoltaic applications [1–6]. As a result, the development of polymer solar cells has increased rapidly, and power conversion efficiencies (PCEs) of 6–7% have been reported in recent years [7, 8]. By exploiting better polymer materials and optimizing the device designs, further improvement may be achieved.

In order to obtain high-performance photovoltaic polymer materials, it is necessary to design and synthesize conjugated polymers with ideal properties, such as low band gap, broad absorption range, and appropriate molecular energy levels. One efficient strategy to make this kind of polymers is through incorporation of electron-rich units (as donor) and electron-deficient (as acceptor), forming a donor–acceptor (D–A) structure [9–11]. The interaction between electron-rich units and electron-deficient units results in a compressed bandgap, which could be easily tuned by changing one of the units or both of them [12, 13].

The thieno[3,4-c]pyrrole-4,6-dione (TPD) moiety shows a symmetric, rigidly fused, coplanar structure and strong electron-withdrawing property, which make it a potential system for increasing intermolecular interactions, reducing bandgaps when incorporated into polymer backbones. Recent researches on D–A polymers have shown that TPD unit is very effective as an acceptor, and it can copolymerize with different donor segments, such as benzodithiophene and bi(dodecyl)thiophene units. When applied to PSCs, PCEs in the range of 2.9–5.5% have been reported, suggesting its great potential in synthesizing novel solar materials [14–17].

Herein, we designed and synthesized a novel series of donor–acceptor copolymers based on alternating electron-deficient TPD and electron-rich 3-alkylthiophene, 3-alkoxythiophene, and 3,4-dialkoxythiophene units through palladium catalyzed sonogashira cross-coupling condensation polymerization. Thiophene derivatives have strong electron-donating ability, which may lead to the low band gap polymers when it is copolymerized with TPD. The incorporation of triple-bond into the polymer backbones can be as one approach to enhance π-electron

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delocalization to match well to the solar spectrum. Finally, the simple introduction of alkyl side chains on the thiophene and TPD units could improve the solubility and processability of the resulting materials. The electrochemical and photophysical properties were investigated, and the results show that the copolymers have broad optical absorption, low band gaps and adequate thermal stability. To the best of our knowledge, these polymers are first TPD-based poly(aryleneethynylene)s.

Experimental

Materials

Unless otherwise indicated, all starting materials were obtained from Aldrich and were used without purification. All the solvents were properly purified before use. 3,4-dibromothiophene (**1**) [18], thiophene-3,4-dicarbonitrile (**2**) [14], thiophene-3,4-dicarboxylic acid (**3**) [14], thiophene-3,4-dicarboxylic anhydride (**4**) [14], 3-decyloxythiophene (**7**) [19], 3,4-dimethoxythiophene (**11**) [20], and 3-dodecyl-2,5-diethynylthiophene (**16**) [21]were prepared following the published procedures.

Measurements

The FT–IR spectra were obtained on a Perkin-Elmer 2000 infrared spectrometer as KBr pellets. ^{1}H NMR spectra were recorded on Bruker DRX 400 spectrometer with tetramethylsilane as an internal reference. UV–Vis spectra in solutions and thin films were taken on a Shimadzu UV2100 UV–Vis recording spectrophotometer. Thermo gravimetric analysis (TGA) was performed on Perkin-Elmer series 7 thermal analysis system under nitrogen. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSCII under N_2. Number-average (M_n) and weight-average (M_w) molecular weights and polydispersity indices (M_w/M_n) of the polymers were measured on a PL-gel permeation chromatography (GPC) model 210 chromatograph at 25 °C, using THF as the eluent and standard polystyrene as the reference. The cyclic voltammograms were recorded on a computer-controlled EG&G potential/galvanostat model 283 at room temperature.

Synthesis of monomers

*5-Dodecylthieno[3,4-c]pyrrole-4,6-dione (**5**)*

A solution of thiophene-3,4-dicarboxylic anhydride (1.23 g, 7.98 mmol) and *n*-dodecylamine (1.08 g, 8.38 mmol) in 120 mL of anhydrous toluene was refluxed for 24 h under nitrogen. The product was collected by filtration of the cold reaction mixture. Another portion of product was achieved by evaporating the solvent, and then recrystallization from toluene afforded purified white crystals. After dried in vacuo for 4 h, it was added in 30 mL of thionyl chloride and refluxed for 3 h. The reaction mixture was concentrated and thoroughly dried to pale yellow solid. The residue was purified by column chromatography (silica gel, hexane/dichloromethane, 1:1) to afford the product as white solid (1.58 g, 5.99 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (t, $J = 13.6$ Hz, 3H), 1.28 (m, 10H), 1.61 (m, 2H), 3.60 (t, $J = 14.4$ Hz, 2H), 7.80 (s, 2H).

*1,3-Dibromo-5-octylthieno[3,4-c]pyrrole-4,6-dione (**6**)*

5-Octylthieno[3,4-c]pyrrole-4,6-dione (0.40 g, 1.51 mmol) was dissolved in 2.3 mL of concentrated sulfuric acid and 7.7 mL of trifluoroacetic acid. NBS (0.83 g, 4.67 mmol) was added in one portion and the reaction mixture was stirred at room temperature over night. The brown solution was then diluted with 100 mL of cold water and extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4. The solvent was removed and the crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane, 1:1) to give white solid (0.51 g, 1.21 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (t, $J = 13.6$ Hz, 3H), 1.29 (m, 10H), 1.60 (m, 2H), 3.59 (t, $J = 14.4$ Hz, 2H).

*2,5-Dibromo-3-decyloxythiophene (**8**)*

N-bromosuccinimide (1.48 g, 8.34 mmol) was added to a solution of 3-decyloxythiophene (1.0 g, 4.17 mmol) in CCl_4 (15 mL) as one portion. The mixture was reacted under argon and protected from light for 24 h at room temperature. Afterward, the mixture was filtered to remove insoluble residue before CCl_4 was removed under reduced pressure. The residue was purified by column chromatography (silica gel, hexane) to afford the product as colorless liquid (1.33 g, 2.66 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.88$ (t, 3H), 1.27-1.45 (m, 14H), 1.75 (m, 2H), 4.00 (t, 2H), 6.77 (s, 1H).

*3-Decyloxy-2,5-bis (3-methyl-3-hydroxybut-1-ynyl)thiophene (**9**)*

2,5-Dibromo-3-decyloxythiophene (1.42 g, 1 mmol) and 3-methyl-3-hydroxy-1-butyne (0.90 mL, 2.6 mmol) were dissolved in 30 mL triethylamine. After a gentle stream of nitrogen was bubbled into the mixture for 1 h, $Pd(PPh_3)_2Cl_2$ (0.007 g, 0.01 mmol), PPh_3 (0.010 g, 0.038 mmol) and CuI (0.007 g, 0.037 mmol) were added. The mixture was refluxed overnight and then cooled to room temperature. After filtration, the solvent was vacuum eliminated and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 4:1) to afford the product as light yellow solid (1.04 g, 2.57 mmol, 72%): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 13.6$ Hz, 3H), 1.27-1.43 (m, 14H), 1.59 (d, $J = 2.0$ Hz, 12H), 1.73 (m, 2H), 1.99 (s, 1H), 2.02 (s, 1H), 4.07 (t, $J = 13.2$ Hz, 2H), 6.77 (s, 1H).

*3-Decyloxy-2,5-diethynylthiophene (**10**)*

A mixture of 3-decyloxy-2,5-bis (3-methyl-3-hydroxybut-1-ynyl)thiophene (**9**) (0.28 g, 0.69 mmol) and KOH (0.12 g, 2.14 mmol) in 10 mL of toluene was heated to 90 °C under nitrogen with a vigorous stirring for 10 min. The reaction mixture was cooled and then the solvent was removed and the crude product was purified by column chromatography (silica gel, petroleum ether) to give a light yellow liquid (0.14 g, 0.49 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 13.6$ Hz, 3H), 1.27–1.42 (m, 14H), 1.75 (m, 2H), 3.34 (s, 1H), 3.44 (s, 1H), 4.10 (t, $J = 13.2$ Hz, 2H), 6.87 (s, 1H).

*3,4-Di(2-ethylhexyloxy)thiophene (**12**)*

3,4-Dimethoxythiophene (5.5 g, 38.19 mmol), 2-ethylhexanol (19.86 g, 152.78 mmol), and *p*-toluenesulfonic acid (0.66 g, 3.82 mmol) were added into 44 mL dry toluene. The flask was equipped with a constant pressure funnel with $CaCl_2$ to absorb methanol which generated from the reaction. The solution was refluxed for 8 h and then cooled to room temperature. The solvent was removed and the crude product was purified by column chromatography (silica gel, petroleum ether) to give a colorless oil (11.69 g, 34.37 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.93$ (m, 12H), 1.31–1.50 (m, 16H), 1.75 (m, 2H), 3.84 (d, $J = 6.0$ Hz, 4H), 6.16 (s, 2H).

*2,5-Dibromo-3,4-di(2-ethylhexyloxy)thiophene (**13**)*

3,4-Di(2-ethylhexyloxy)thiophene (2.0 g, 5.88 mmol) was dissolved in 130 mL dry DMF. *N*-bromosuccinimide (2.09 g, 11.76 mmol) with 20 mL DMF was added dropwise through the addition funnel and the reaction was stirred overnight at room temperature under argon. Water (150 mL) was added to the reaction and the aqueous phase was extracted with dichloromethane four times, washed with brine eight times. The organic layer was dried over anhydrous Na_2SO_4. After solvent evaporation, the resulting oil was purified by column chromatography (silica gel, petroleum ether) to give a colorless oil (2.40 g, 4.82 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.93$ (m, 12H), 1.29–1.65 (m, 18H), 3.94 (m, 4H).

*3,4-Di(2-ethylhexyloxy)-2,5-bis (3-methyl-3-hydroxybut-1-ynyl)thiophene (**14**)*

2,5-Dibromo-3,4-di(2-ethylhexyloxy)thiophene (2.0 g, 4.02 mmol) and 3-methyl-3-hydroxy-1-butyne (1.16 mL, 12.04 mmol) were dissolved in 35 mL triethylamine. After a gentle stream of nitrogen was bubbled into the mixture for 1 h, $Pd(PPh_3)_2Cl_2$ (0.007 g, 0.01 mmol), PPh_3 (0.010 g, 0.038 mmol), and CuI (0.007 g, 0.037 mmol) were added. The sample was refluxed overnight and then cooled to room temperature. After filtration, the solvent was vacuum eliminated and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 4:1) to afford the product as light yellow oil (1.05 g, 2.09 mmol, 52%): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.92$ (m, 12H), 1.38–1.65 (m, 30H), 1.95 (s, 2H), 4.16 (m, 4H).

*3,4-Di(2-ethylhexyloxy)-2,5-diethynylthiophene (**15**)*

A mixture of 3,4-di(2-ethylhexyloxy)-2,5-bis (3-methyl-3-hydroxybut-1-ynyl)thiophene (**14**) (0.20 g, 0.40 mmol) and KOH (0.067 g, 1.20 mmol) in 10 mL of toluene was heated to 100 °C under N_2 with a vigorous stirring for 2 h. The reaction mixture was cooled and then the solvent was removed and the crude product was purified by column chromatography on silica gel (petroleum ether) to give a light yellow liquid (0.11 g, 0.28 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.90$ (m, 12H), 1.25–1.51 (m, 16H), 1.63 (m, 2H), 3.39 (s, 2H), 4.20 (m, 4H).

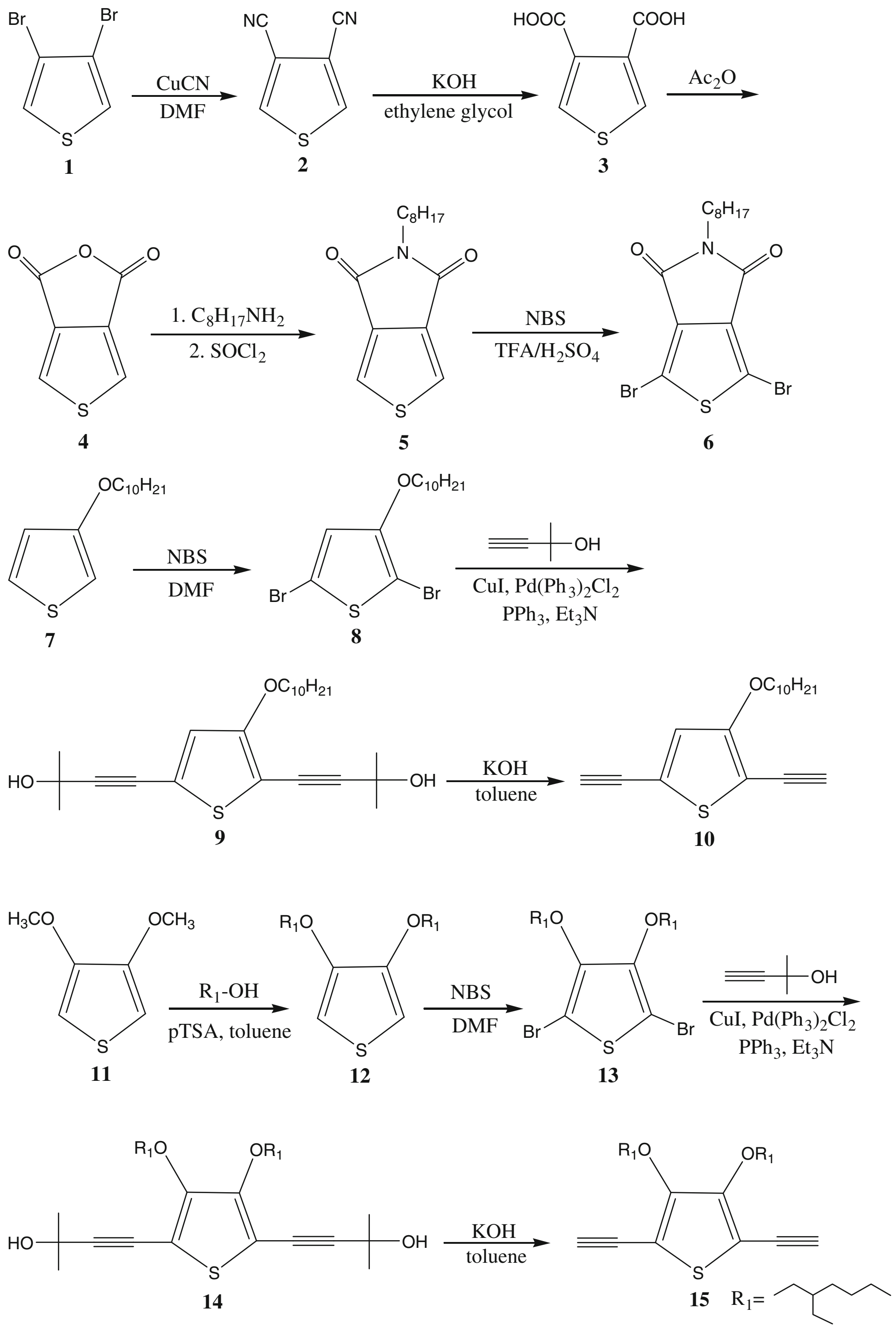
Synthesis of polymers

General procedure

To a mixture of the dibromo monomer (**6**) (0.07 mmol), diethynyl monomer (**10**, **15** or **16**) (0.07 mmol), $Pd(PPh_3)_2Cl_2$ (4 mg, 0.0057 mmol), CuI (4 mg, 0.021 mmol), and anhydrous K_2CO_3 (24 mg, 0.175 mmol) was added anhydrous THF (6 mL) under argon. The mixture was stirred at reflux for 48 h. After being cooled to room temperature, the resulting solution was poured into a mixture of 300 mL methanol and deionized water (10:1). A solid was obtained by filtration and then it was washed with methanol and water repeatedly. Soxhlet extraction was performed for 24 h with acetone.

P_1

Red powder, yield: 75%. IR (KBr pellet, cm^{-1}): 3440, 2959, 2922, 2852, 2187, 1760, 1708, 1576, 1507, 1394, 1341, 1261, 1096, 1024, 802, 746. ^{1}H NMR (400 MHz,



Scheme 1 Synthesis of the intermediate

$CDCl_3$): $\delta = 0.87$–1.59 (m,38 H), 2.70–2.72 (m, 2H), 3.54 (d, 2H), 7.45–7.63 (d, 1H).

P_2

Red powder, yield: 70%. IR (KBr pellet, cm^{-1}): 3447, 2923, 2853, 2184, 1759, 1709, 1577, 1518, 1394, 1260, 1087, 1023, 801, 746, 722, 614, 534. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.81$–1.61 (m, 38H), 3.54 (br, 2H), 4.16 (m, 2H), 7.45–7.65 (d, 1H).

P_3

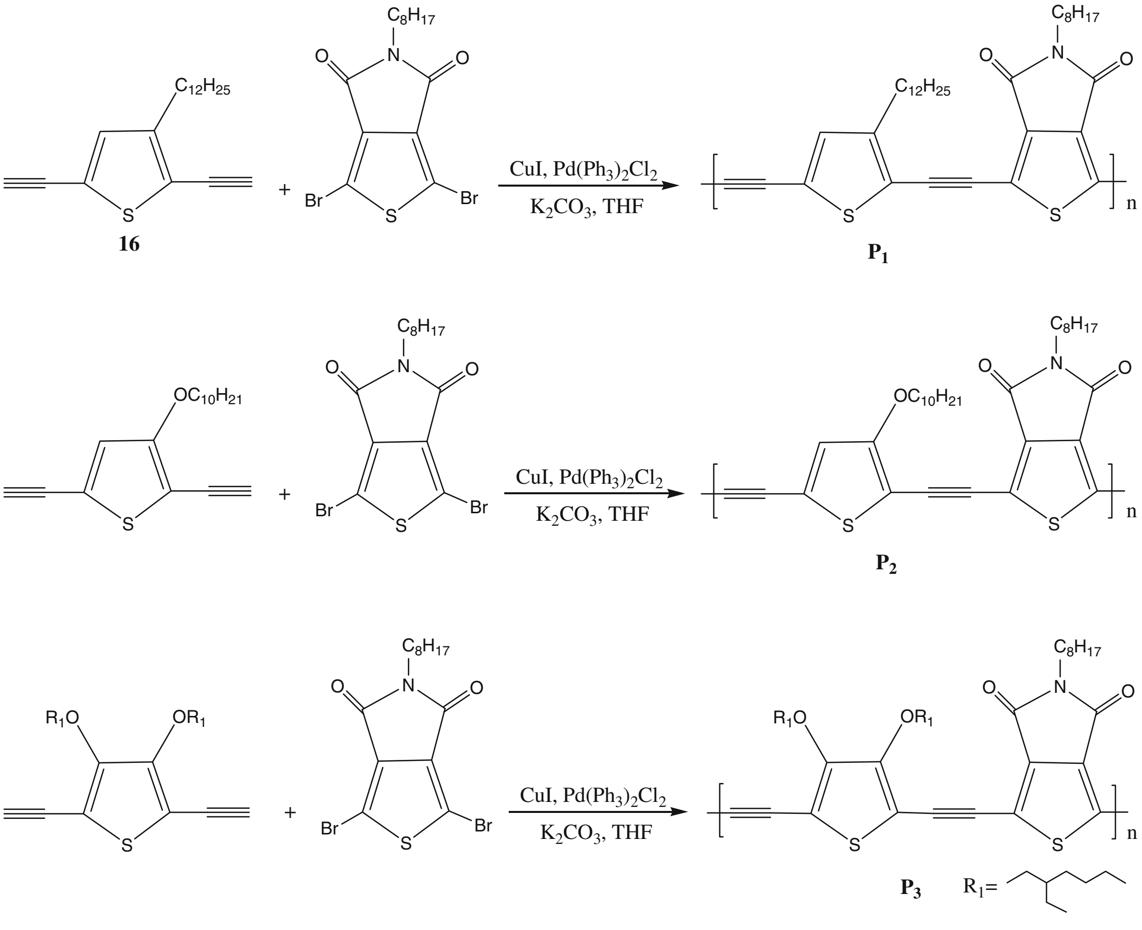
Red powder, yield: 82%. IR (KBr pellet, cm^{-1}): 3419, 2962, 2927, 2857, 2183, 1760, 1711, 1460, 1395, 1364, 1261, 1096, 1023, 867, 802, 700, 617. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.86$–1.74 (m, 45 H), 3.61 (br, 2H), 4.24 (m, 4H).

Results and discussion

Synthesis and characterization

The synthetic route used to prepare the monomers is shown in Scheme 1. The intermediates **4**, **7**, **11**, and **16** were prepared following the already published procedures. 2,5-dibromo-3-decyloxythiophene (**8**) was synthesized in 80% yield by bromination reaction of 3-decyloxythiophene (**7**) with NBS. After palladium catalyzed Sonogashira coupling with 3-methyl-3-hydroxy-1-butyne and subsequent deprotection with KOH, 3-decyloxy-2,5-diethynylthiophene (**10**) was obtained in moderate yield. Another new monomer 3,4-di(2-ethylhexyloxy)-2,5-diethynylthiophene (**15**) was synthesized following the similar method.

Copolymerizations leading to the final polymers $\mathbf{P_1}$, $\mathbf{P_2}$, and $\mathbf{P_3}$ are outlined in Scheme 2. The polymers were synthesized via Sonogashira cross-coupling reaction [22, 23] in yields of over 70% with alkylthiophene diacetylenes (**16**)/alkoxythiophene diacetylenes (**10/15**) and



Scheme 2 Synthesis of the copolymers

dibromo-substituted TPD (**6**) as the starting materials. All of these polymers are readily soluble in common solvents, such as chloroform, THF, and toluene, this may be assigned to alkoxyl and alkyl attached on the thiophene rings and the TPD units, respectively. Their molecular weights were determined by GPC using polystyrene as standard, the results indicated that they have weight-average molecular weights (M_w) of 17400–27900 with polydispersity indices (M_w/M_n) of 1.9–2.6, respectively. The molecular weight of $\mathbf{P_3}$ is apparently lower than $\mathbf{P_1}$ and $\mathbf{P_2}$, which could be attributed to the higher steric hindrance occurring during polymerization. In addition, the polymers were found to be air stable in both chloroform and solid state.

The chemical structure of the polymers was characterized by FT–IR, and ^{1}H NMR. Figure 1 gives the FT–IR spectra of the polymers. The spectrum of the polymers exhibited characteristic bands of carbonyl group of maleimide structure at 1760 and 1708 cm^{-1} for $\mathbf{P_1}$, 1759 and 1709 cm^{-1} for $\mathbf{P_2}$, 1760 and 1710 cm^{-1} for $\mathbf{P_3}$, respectively. The absorption peak at 2187, 2184, and 2183 cm^{-1} can be attributed to the C≡C stretching mode of the polymers $\mathbf{P_1}$, $\mathbf{P_2}$, and $\mathbf{P_3}$.

^{1}H NMR spectra of polymers are shown in Fig. 2. The signals of the alkyl chain dominated in the region of $\delta = 0.81$–1.74 ppm. The peaks at $\delta = 2.70$ ppm could be assigned to the hydrogen atoms of –CH$_2$ of thiophene of $\mathbf{P_1}$. The peaks at about $\delta = 3.6$ ppm correspond to the hydrogen atoms of –NCH$_2$ of TPD units, and the signals of the –OCH$_2$ of alkoxy group of thiophene appeared at $\delta = 4.16$ ppm and $\delta = 4.24$ ppm for $\mathbf{P_2}$ and $\mathbf{P_3}$, respectively. The signals of thiophene were between $\delta = 7.45$ and $\delta = 7.65$ ppm. Every peak in the ^{1}H NMR spectra could be assigned to the corresponding hydrogen atoms of the polymers.

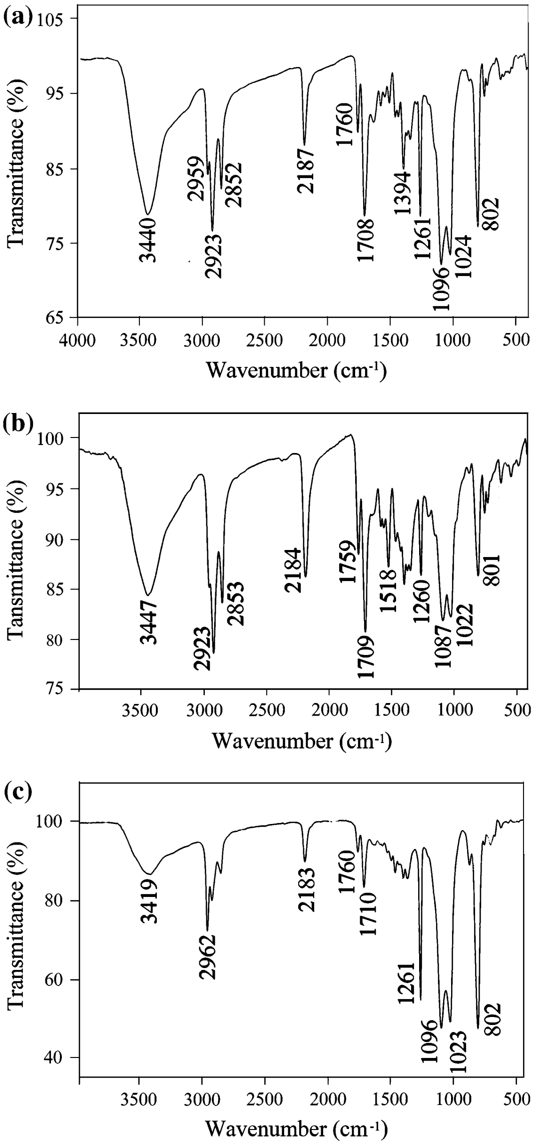


Fig. 1 FT–IR spectra of **a** the polymer $\mathbf{P_1}$, **b** the polymer $\mathbf{P_2}$, and **c** the polymer $\mathbf{P_3}$

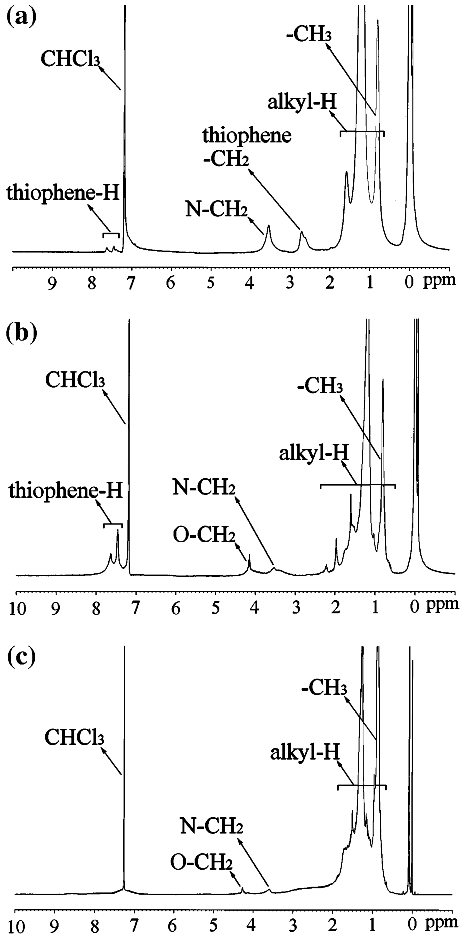


Fig. 2 ^{1}H-NMR spectra of **a** the polymer $\mathbf{P_1}$, **b** the polymer $\mathbf{P_2}$, and **c** the polymer $\mathbf{P_3}$

Thermal properties

The thermal properties of the polymers measured by TGA and DSC are summarized in Table 1. The sample holders were carefully weighed and the sample introduced. TGA was then carried out using heating rate at 10 °C min^{-1} under nitrogen. As shown in Fig. 3, these polymers possessed adequate thermal stability. The onset points of the weight loss with 5% weight loss temperature (T_d) are 260, 298, and 274 °C for $\mathbf{P_1}$, $\mathbf{P_2}$, and $\mathbf{P_3}$, respectively, and no weight loss was observed at lower temperatures. The increasing trend of Td ($\mathbf{P_2} > \mathbf{P_3} > \mathbf{P_1}$) may be related to the polydispersity indices of the polymers ($\mathbf{P_2} < \mathbf{P_3} < \mathbf{P_1}$). The DSC curves of polymers are shown in Fig. 4. The glass transition temperature of $\mathbf{P_1}$ and $\mathbf{P_3}$ are 132 and 122 °C, respectively, whereas $\mathbf{P_2}$ has no obvious T_g before the weight loss. The thermal stability of the polymers is adequate for the fabrication processes of the photovoltaic devices.

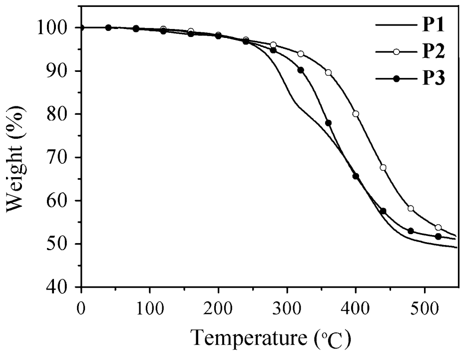


Fig. 3 TGA thermograms of the polymers

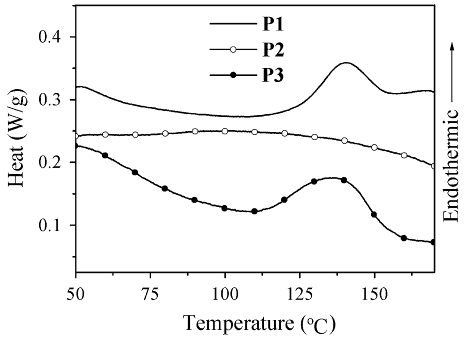


Fig. 4 DSC thermograms of the polymers

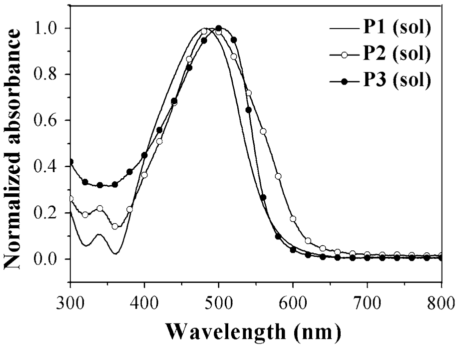


Fig. 5 UV–Vis absorption spectra of the polymers solutions in $CHCl_3$

Optical properties

The UV–Vis absorption characteristics of the copolymers were measured both in chloroform solutions (Fig. 5) and as thin films on quartz (Fig. 6). The relevant spectroscopic data of the polymers are summarized in Table 1. It can be seen from Fig. 5, $\mathbf{P_3}$ exhibits the most red-shifted absorption maximum ($\lambda_{\max}$) in solution at 501 nm, followed by $\mathbf{P_2}$ at 490 nm, and $\mathbf{P_1}$ at 481 nm, which could be assigned to internal charge transfer between the TPD acceptor and the thiophene derivatives donor. $\mathbf{P_2}$ and $\mathbf{P_3}$ have 9 and 20 nm red-shifted, respectively compared to that of $\mathbf{P_1}$. Such red-shift in absorption can be explained by the fact that alkoxythiophene units are stronger donors than the alkylthiophene units.

Thin films of the polymers were obtained by spin-coating on quartz substrates from their toluene solution. As shown in Fig. 6, the thin film absorption spectra of two copolymers have more broad absorption range than solution absorption spectra. The UV–Vis spectra of $\mathbf{P_1}$, $\mathbf{P_2}$, and $\mathbf{P_3}$ show absorption peak maxima at 491, 495, and 512 nm, respectively, and there are 5–11 nm red-shifts compared with their absorbance in solutions. These red-shifts indicate better coplanarity of the polymers and enhanced intermolecular electronic interactions in the solid state [24]. Additionally, a vibronic shoulder of $\mathbf{P_2}$ at 560 nm shows an ordered arrangement of the polymer in the solid

Table 1 Yield, molecular weight, and thermal properties of the polymers

Polymer	Yield (%)	M_w	M_n	PDI (M_w/M_n)	T_d (°C)	T_g (°C)
$\mathbf{P_1}$	75	27900	10700	2.61	260	132
$\mathbf{P_2}$	70	28500	19700	1.45	298	\
$\mathbf{P_3}$	82	17400	9100	1.91	274	122

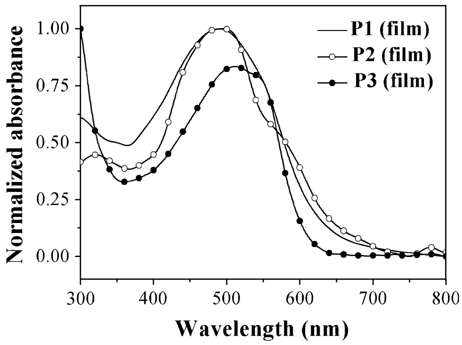


Fig. 6 UV–Vis absorption spectra of the polymers films on quartz plate

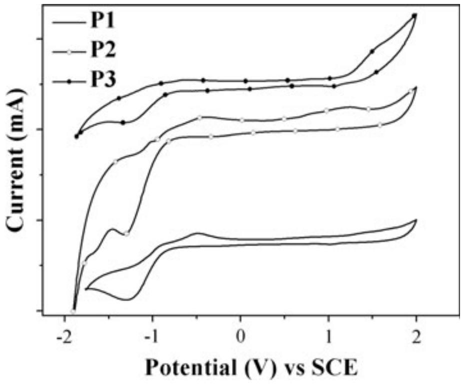


Fig. 7 Cyclic voltammogram of the polymer

film, with strong π–π stacking between the polymer backbones, a feature that also appears in regioregular poly(3-hexylthiophene) [17].

The optical band gaps (E_g^{opt}) of $\mathbf{P_1}$, $\mathbf{P_2}$, and $\mathbf{P_3}$, derived from the absorption edge of the thin film spectra, are 1.77, 1.65, and 1.94 eV. The band gap of $\mathbf{P_3}$ is lager than that of other two polymers, which may be may be caused by the different structure with extended lengths of π-conjugation.

Electrochemical properties

Cyclic voltammetry (CV) was employed to investigate the electrochemical properties of the polymers. The polymer films were obtained by dip-casted onto a Pt working electrode, the positively and negatively scans were performed at a scan rate of 100 mV/s in 0.1 M solution of tetra-*n*-butylammonium perchlorate (n-Bu_4NClO_4) in anhydrous acetonitrile, and SCE serves as the reference electrode. Figure 7 shows the CV of polymers and Table 2 summarizes the electrochemical properties of $\mathbf{P_1}$–$\mathbf{P_3}$. The onset oxidation potentials ($E_{onset,ox}$) of $\mathbf{P_1}$–$\mathbf{P_3}$ occur at 1.16, 0.69, and 1.19 V, respectively. The corresponding onset reduction potentials ($E_{onset,red}$) appear at −0.72, −0.82, and −0.78 V, respectively. From the onset potentials of the oxidation and reduction process, the electrochemical band gaps (E_g^{el}) are estimated to be 1.88, 1.51, and 1.97 eV for polymers $\mathbf{P_1}$, $\mathbf{P_2}$, and $\mathbf{P_3}$, which are largely consistent with their optical band gaps. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the materials could be calculated from the onset oxidation potentials and the onset reduction potentials of the polymers, according to the following equations [25].

$$I_p(\mathrm{HOMO}) = -(E_{onset,ox} + 4.39)\ \mathrm{eV}$$

$$E_a(\mathrm{LUMO}) = -(E_{onset,red} + 4.39)\ \mathrm{eV}$$

$$E_g = E_{onset,ox} - E_{onset,red}$$

Therefore, the LUMO and HOMO energy levels of the polymers are −3.67, −3.57, and −3.61 eV and −5.55, −5.08, and −5.58 eV for $\mathbf{P_1}$, $\mathbf{P_2}$, and $\mathbf{P_3}$. The position of LUMO levels of the polymers are close to each other, indicating that the LUMO energy levels are mainly determined by the electron acceptors. The higher HOMO level of the polymer $\mathbf{P_2}$ indicates the stronger intramolecular charge transfer effects [26].

Conclusions

Novel donor–acceptor conjugated copolymers consisting of alternating electron-rich alkyl-thiophene/alkoxythiophene and electron-deficient TPD units have been synthesized through Sonogashira cross-coupling reactions. These copolymers exhibit good solubility in common organic solvents and were found to be both air stable and thermally stable, which may improve the operating lifetime of the solar cells. The electrochemical and photophysical properties were investigated, and the results show that the

Table 2 Optical and electrochemical properties of the polymers $\mathbf{P_1}$ and $\mathbf{P_2}$

	$\lambda_{max,sol}$ (nm)	$\lambda_{max,film}$ (nm)	E_g^{opt} (eV)[a]	$E_{onset,ox}$ (V)	$E_{onset,red}$ (V)	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)
$\mathbf{P_1}$	481	491	1.77	1.16	−0.72	−5.55	−3.67	1.88
$\mathbf{P_2}$	490	495	1.65	0.69	−0.82	−5.08	−3.57	1.51
$\mathbf{P_3}$	501	512	1.94	1.19	−0.78	−5.58	−3.61	1.97

[a] E_g^{opt} were calculated from the absorption band edge of the copolymer films, $E_g^{opt} = 1240/\lambda_{edge}$

polymers may be suitable solar cells materials due to their broad optical absorption, low band gaps, and good stability. Further studies on the application as the photovoltaic materials are in progress.

Acknowledgements This study was supported by the key foundation of education ministry of China (20070610053) and Sichuan Province Foundation for Youths (2008JY0050). The authors also acknowledge the Analytical & Testing Center of Sichuan University for the NMR measurements.

References

1. Cheng YJ, Yang SH, Hsu CS (2009) Chem Rev 109:5868
2. Goris L, Haenen K, Nesladek M (2005) J Mater Sci 40:1413. doi:10.1007/s10853-005-0576-0
3. Boudreault PLT, Najari A, Leclerc M (2011) Chem Mater 23:456
4. Qiao F, Liu A, Zhou Y (2009) J Mater Sci 44:1283. doi:10.1007/s10853-009-3280-7
5. Zhu Y, Babel A, Jenekhe SA (2005) Macromolecules 38:7983
6. Zhang R, Li B, Lovu MC, Jeffriese-EL M, Sauve G, Cooper J, Jia S, Tristram-Nagle S, Smilgies DM, Lambeth DN, McCullough RD, Kowalewski T (2006) J Am Chem Soc 128:3480
7. Liu MS, Niu YH, Luo J, Chen B, Kim TD, Bardecker J, Jen AKY (2006) Polym Rev 46:7
8. Zhang X, Chen Z, Yang C, Li Z, Zhang K, Yao H, Qin J, Chen J, Cao Y (2006) Chem Phys Lett 422:386
9. Zhang GB, Fu YY, Zhang Q (2010) Polymer 51:2313
10. Roncali J (1997) Chem Rev 97:173
11. Cai TQ, Zhou Y, Wang EG (2010) Sol Energy Mater Sol Cells 94:1275
12. Chen CH, Hsieh CH, Dubosc M, Cheng YJ, Hsu CS (2010) Macromolecules 43:697
13. Yuan MC, Chiu MY, Chiang CM, Wei KH (2010) Macromolecules 43:6270
14. Nielsen CB, Bjornholm T (2004) Org Lett 6:3381
15. Zhang Y, Hau SK, Yip HL, Ying Sun, Acton O, Jen AKY (2010) Chem Mater 22:2696
16. Zou YP, Najari A, Berrouard P, Beaupre S, Aich BR, Tao Y, Leclerc M (2010) J Am Chem Soc 132:5330
17. Yuan MC, Chiu MY, Liu SP, Chen CM, Wei KH (2010) Macromolecules 43:6936
18. Wang Z, Tao F, Xi LY, Meng KG, Zhang W, Li Y, Jiang Q (2011) J Mater Sci 46:4005. doi:10.1007/s10853-011-5328-8
19. Shi CJ, Yao Y, Yang Y, Pei QB (2006) J Am Chem Soc 128:8980
20. Shallcross RC, D'Ambruoso GD, Korth BD, Hall HK Jr, Zheng ZP, Pyun J, Armstrong NR (2007) J Am Chem Soc 129:11310
21. Ashraf RS, Klemm E (2005) J Polym Sci A 43:6445
22. Dieck HA, Heck RF (1975) J Organomet Chem 93:259
23. Sonogashira K, Tohda Y, Hagihara N (1975) Tetrahedron Lett 16:4467
24. Chen H, Cai XR, Xu ZG, Zhang T, Song BF, Li Y, Jiang Q, Xie MG (2008) Polym Bull 60:581
25. Bredas JL, Silbey R, Boudreaux DS (1983) J Am Chem Soc 105:6555
26. Tsai JH, Chueh CC, Lai MH (2009) Macromolecules 42:1897