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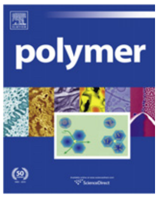

Conjugated polymers based on benzodithiophene and arylene imides: Extended absorptions and tunable electrochemical properties

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ABSTRACT

Three novel conjugated polymers have been designed and synthesized via the alternative copolymerization of the electron-donating monomer benzodithiophene (BDT) and three different electron-accepting monomers: perylene diimide (PDI), naphthalene diimide (NDI), and phthalimide (PhI). All obtained copolymers show good solubility in common organic solvents as well as broader absorptions in visible region and narrower optical band gaps compared to homopolymers from BDT units. It is found that the absorptions of the copolymers are red-shifted with increasing the electron-withdrawing ability of the co-monomer. In particular, the absorption edge of P(BDT-NDI) film extends to 760 nm, whereas that of P(BDT-PhI) film is only at 577 nm. Cyclic voltammograms of the three polymers disclose that P(BDT-PDI) and P(BDT-NDI) are typical n-type materials because PDI and NDI are strong electron-accepting groups, while P(BDT-PhI) is a stable p-type material where the weak electron-withdrawing monomer (PhI) is introduced. The results suggest that the absorption range and the electrochemical properties of the conjugated polymers can be tuned by appropriate molecule-tailoring, which will help exploring ideal conducting polymers for potential applications in polymer optoelectronics, especially in polymer solar cells.

1. Introduction

Conjugated polymers have recently attracted considerable attention because they can be applied to large-area, flexible optoelectronic devices, such as polymer light-emitting diodes [1–5], polymer solar cells (PSCs) [6–11], and organic thin-film transistors [12,13], etc., by low-cost solution-processing. Among these potential applications, PSCs are especially attractive as promising renewable energy sources. For conjugated polymers used in PSCs, a low band gap is of crucial importance for sunlight harvest since the maximum photon flux of the solar irradiation locates at ca. 680 nm [14]. The copolymers alternating electron-rich and electron-deficient monomers (D-*alt*-A polymers) are suggested as materials with a narrow band gap and a broad absorption, and more than 5% power conversion efficiency (PCE) has been achieved when some representative polymers are blended with fullerene derivatives to form bulk heterojunction PSCs [15–17]. However, most of the reported low band gap conjugated polymers are p-type materials, while n-type materials in PSCs, fullerene derivatives in particular, show little contributions to the sunlight absorption due to their high band gaps. Furthermore, the open circuit voltage (V_{OC}) of a PSC is proportional to the difference between the HOMO of the p-type material and the LUMO of the n-type material, thus it is difficult to increase V_{OC} once the n-type material is fixed [18].

The arylene imides units are attractive candidates as electron-accepting co-monomers of low band gap D-*alt*-A polymers by virtue of their extremely facile synthesis and readily varied substitution at the nitrogen, allowing manipulation of polymer solubility, packing and morphology. Moreover, when inserting into polymer backbones, the strongly electron-withdrawing imide groups would largely alter band energy levels, even change the semiconductive behavior from p-type to n-type [19–23]. Nevertheless, only a few published examples of conjugated polymers contain imide-functionalized π-systems such as thiophene imides [24], bithiophene imide [25], isothianaphthene imide [26], phthalimide [27,28] and arylene imide [19,23]. Herein we designed and successfully synthesized three

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new polymers, P(BDT-PDI), P(BDT-NDI) and P(BDT-PhI), with arylene imide units electronically conjugated along the backbone by alternative copolymerization of the electron-donating monomer benzodithiophene (BDT) and three different electron-accepting monomers of perylene diimide (PDI), naphthalene diimide (NDI), and phthalimide (PhI), respectively. The benzodithiophene (BDT) unit was utilized because of its planarity, stability and solubility [29]. In addition, its homopolymer (PBDT) was reported as a good semiconductor material [30–32]. All obtained polymers show broad visible absorption bands and narrow optical band gaps. Cyclic voltammograms display that P(BDT-PDI) and P(BDT-NDI) are typical n-type materials while P(BDT-PhI) is a stable p-type material.

2. Experimental

2.1. Instrument

^{1}H NMR spectra were recorded on a Bruker DMX-300 nuclear resonance spectroscope. Absorption spectra were obtained on a Shimadzu UV-2450 UV–vis spectrophotometer. Mass spectra were gotten on a VG 70-SE MS spectroscope under the electron impact (EI) mode. Elemental analyses were carried out on a LECO 932 CHNS elemental analyzer. The molecular weight of polymers was determined on Waters 1525/2414 gel permeation chromatography (GPC), and polystyrene was used as a standard. Thermogravimetric analysis (TGA) was performed on a WCT-2 thermal balance under a N_2 atmosphere at a heating rate of 10 °C min^{-1}. Electrochemical cyclic voltammetry was conducted on a CHI 600A electrochemical workstation with Pt disk, Pt plate, and SCE as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) CH_2Cl_2 solution.

2.2. Materials

Benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione (1) [14] and 1,7-dibromoperylene-3,4,9,10-tetracarboxydianhydride (4) [33] were synthesized according to the procedures reported in the literature. All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co. and used as received. All the solvents were freshly distilled prior to use.

2.3. Synthesis of the monomers

The synthesis routes of the monomers are shown in Scheme 1. The detailed synthetic processes are as follows.

2.3.1. 4,8-Bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]dithiophene (2)

Benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione (1) (2.2 g, 10 mmol) and zinc dust (1.43 g, 22 mmol) were put into a 100 mL flask. NaOH solution (40 mL, 20%) was added, and the mixture was heated to reflux for 1 h. Then, 2-ethylhexyl bromide (5.8 g, 30 mmol) and a catalytic amount of tetrabutylammonium bromide (TBAB) were added into the flask. After being refluxed for 8 h, the reactant was poured into 150 mL of cold water, and extracted by CH_2Cl_2 (2 × 100 mL). The organic extraction was dried with anhydrous Na_2SO_4 and evaporated *in vacuo*. Column chromatography on silica gel using a mixture of CH_2Cl_2 and hexane (1:1) as the eluent yielded compound 2 (3.66 g, yield 82%) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.46$–7.51 (d, 2H), 7.35–7.40 (d, 2H), 4.14–4.23 (br, 4H), 1.76–1.87 (m, 2H), 1.32–1.53 (m, 16H), 0.89–1.07 (m, 12H). MS (EI): Calcd, 446.2; found $(M+1)^+$, 446.9.

2.3.2. 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]dithiophene (3)

Compound 2 (0.45 g, 1.0 mmol) was dissolved in 15 mL of anhydrous THF under N_2 protection. The solution was cooled down to −78 °C by a liquid nitrogen–acetone bath, and *t*-butyllithium solution (1.9 mL, 2.5 mmol, 1.3 M in hexane) was added dropwise. The reaction mixture was stirred at this temperature for 1 h and allowed to warm to RT over 3 h, at which point it was stirred for an additional hour. Then the mixture was cooled to −78 °C, and trimethyltin chloride solution (3.0 mL, 3.0 mmol, 1 M in THF) was added dropwise. The mixture was allowed to warm to RT and stirred overnight. The reaction was quenched with 50 mL of cold water and extracted with hexane three times. The organic extraction was washed by water twice and then dried by anhydrous Na_2SO_4. After removing the solvent under vacuum, the residue was dissolved in hexane and quickly passed through a column pretreated with triethylamine. After removing the solvent under vacuum, recrystallization of the residue from methanol yielded compound 3 (0.67 g, yield 86%) as colorless needle crystals. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.52$ (s, 2H), 4.17–4.22 (d, 4H), 1.74–1.88 (m, 2H), 1.28–1.49 (m, 16H), 0.85–1.07 (m, 12H), 0.44 (s, 18H).

2.3.3. N,N′-bis(2-ethylhexyl)-1,7-dibromo-3,4,9,10-perylene diimide (5)

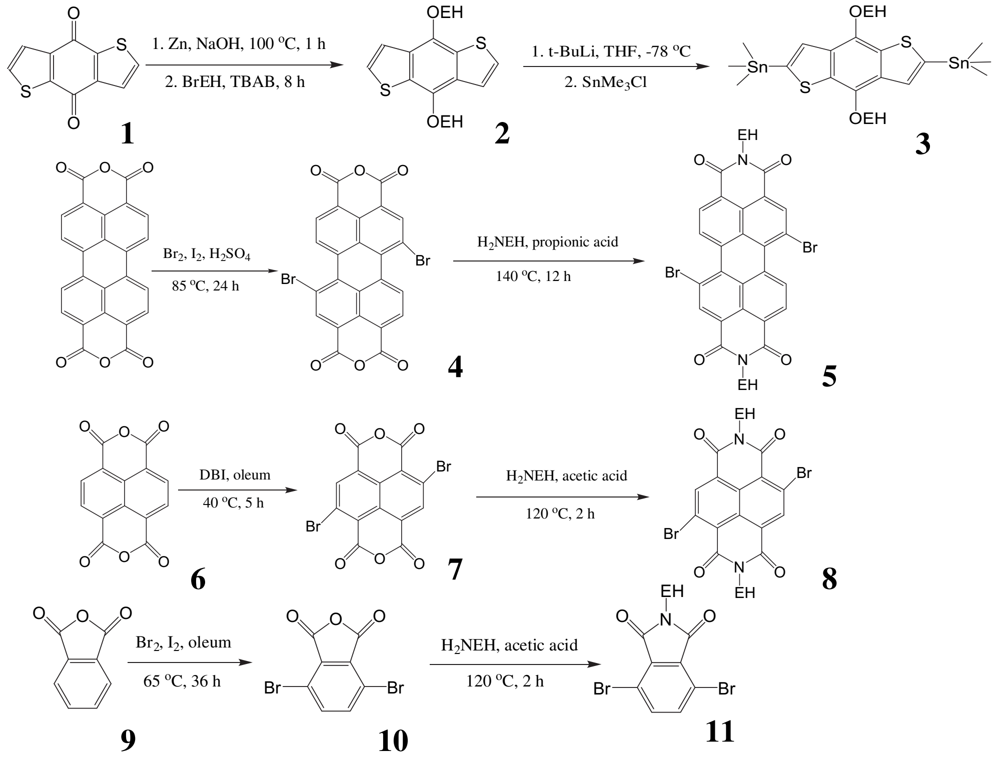
A mixture of 1,7-dibromoperylene-3,4,9,10-tetracarboxydianhydride (4) (1.65 g, 3.0 mmol) and 2-ethylhexylamine (H_2NEH, 1.55 g, 12 mmol) in propionic acid (40 mL) was heated to reflux at 140 °C for 12 h under a N_2 atmosphere. The resulting mixture was cooled and poured into water (200 mL), filtrated, and washed with water until the filtrate reached neutrality. The crude solid was dried at 70 °C under vacuum. After being purified by column chromatography on silica gel using a mixture of CH_2Cl_2/petroleum ether (1:1) as eluent, product 5 (2.08 g, yield 90%) was obtained as a deep red powder. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.47$–9.52 (d, 2H), 8.93 (s, 2H), 8.69–8.73 (d, 2H), 4.11–4.20 (m, 4H), 1.90–2.00 (m, 2H), 1.27–1.46 (m, 16H), 0.85–0.99 (m, 12H). $C_{40}H_{40}Br_2N_2O_4$: Calcd, C 62.19, H 5.22, N 3.63; found, C 62.34, H 5.31, N 3.35.

2.3.4. 2,6-Dibromonaphthalene-1,4,5,8-tetracarboxydianhydride (7)

A solution of dibromoisocyanuric acid (DBI) (1.47 g, 5.1 mmol) in oleum (30 mL, 20% SO_3) was added at RT to a solution of 1,4,5,8-naphthalenetetracarboxylic dianhydride (6) (1.43 g, 5.0 mmol) in oleum (30 mL, 20% SO_3) over a course of 1 h. The resulting mixture was stirred at 40 °C for 5 h and then cautiously poured into crushed ice (200 g). The mixture was diluted with water (200 mL) and then stirred at RT for 1 h. The precipitate was collected on a Buchner funnel, washed with water and methanol, and dried under vacuum, leading to a bright yellow solid (1.89 g, yield 83%). The crude product 7 was used for the next step without further purification.

2.3.5. N,N′-bis(2-ethylhexyl)-2,6-dibromo-1,4,5,8-naphthalene diimide (8)

A mixture of compound 7 (2.13 g, 5.0 mmol), 2-ethylhexylamine (1.94 g, 15 mmol), and acetic acid (50 mL) was stirred at 120 °C for 2 h under N_2 protection. Upon cooling to RT, the mixture was poured into 200 mL cold water, filtrated, and washed with water and methanol. After drying under vacuum, the resulting reddish solid was purified by column chromatography on silica gel using a mixture of CH_2Cl_2/petroleum ether (1:1) as eluent. And the resulting orange powder was further purified by recrystallization from hexane to obtain product 8 (1.10 g, yield 34%) as slight yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.00$ (s, 2H), 4.12–4.18 (q, 4H), 1.88–2.00 (m, 2H), 1.23–1.43 (m, 16H), 0.83–0.98 (m, 12H).



Scheme 1. Synthesis routes of the monomers. EH stands for 2-ethylhexyl, and H_2NEH is the abbreviation of 2-ethylhexylamine.

$C_{30}H_{36}Br_2N_2O_4$: Calcd, C 55.57, H 5.60, N 4.32; found, C 55.81, H 5.39, N 4.17.

2.3.6. *3,6-Dibromophthalic anhydride (10)*

A mixture of phthalic anhydride (9) (4.0 g, 27 mmol), oleum (30 mL, 20% SO_3), bromine (3.1 mL, 9.6 g, 60 mmol), and iodine (0.1 g, 0.4 mmol) was stirred at 65 °C for 36 h. The resulting mixture was cooled and cautiously poured into crushed ice (200 g), then extracted by $CHCl_3$ (100 mL × 3). The organic extraction was concentrated by rotary evaporation to produce a brown solid. The crude product was recrystallized twice from acetic acid to give compound 10 (1.4 g, yield 17%) as colorless crystals. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.85$ (s, 2H).

2.3.7. *N-(2-ethylhexyl)-3,6-dibromophthalimide (11)*

A mixture of compound 10 (1.53 g, 5.0 mmol), 2-ethylhexylamine (0.97 g, 7.5 mmol), and acetic acid (30 mL) was stirred at 120 °C for 2 h under N_2 protection. After most of the acetic acid was evaporated under reduced pressure, the crude product was purified by column chromatography on silica gel using a mixture of CH_2Cl_2/petroleum ether (1:4) as eluent. After recrystallization from hexane, compound 11 (1.94 g, yield 93%) was obtained as colorless crystals. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.65$ (s, 2H), 3.55–3.61 (d, 2H), 1.76–1.89 (m, 1H), 1.20–1.41 (m, 8H), 0.80–0.97 (m, 6H). $C_{16}H_{19}Br_2NO_2$: Calcd, C 46.07, H 4.59, N 3.36; found, C 46.19, H 4.30, N 3.47.

2.4. *General synthetic procedures of polymers*

The synthetic route to the polymers is shown in Scheme 2. The three polymers were prepared by the same procedure through the coupling reaction between compound 3 and arylene imide (compound 5, 8, or 11). A mixture of anhydrous toluene (20 mL), compound 3 (0.77 g, 1.0 mmol) and compound 5, 8 or 11 (1.0 mmol) was put into a 50 mL three-necked flask. The solution was flushed with N_2 for 10 min, and then 30 mg of Pd $(PPh_3)_4$ was added into the flask. The solution was further flushed with N_2 for 20 min, and then heated to 110 °C for 48 h under N_2. The raw product was collected by precipitating in methanol (100 mL). The precipitate was dissolved in $CHCl_3$ and quickly passed through a silica column to remove the metal catalyst. Then, the polymer was subjected to Soxhlet extractions with methanol, acetone, hexane, and $CHCl_3$ in succession. The polymer was obtained as a solid from the $CHCl_3$ fraction by rotary evaporation. The solid was dried under vacuum for 1 day to get the final product.

2.4.1. *P(BDT-PDI)*

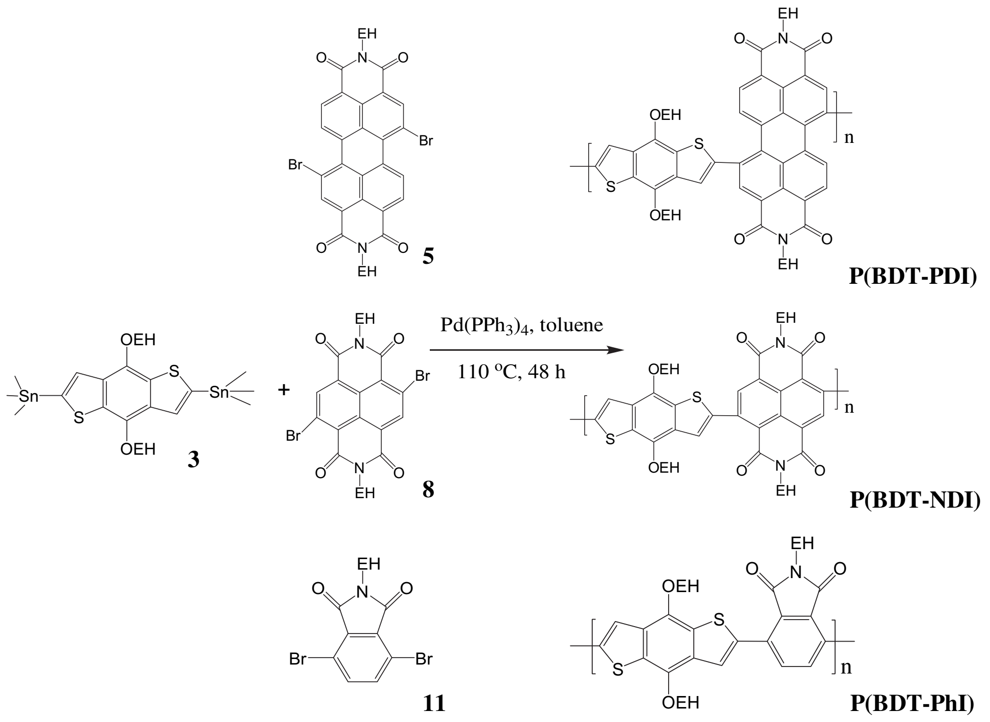
Purple solid powder, yield 63.7%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.87$–8.95 (br, 2H), 8.30–8.47 (br, 4H), 7.83–7.90 (br, 2H), 4.07–4.42 (br, 8H), 1.77–2.05 (br, 4H), 1.10–1.51 (br, 32H), 0.72–1.04 (br, 24H). GPC: $M_w = 5.6$ K, $M_n = 4.8$ K, PDI = 1.2. TGA: $T_d = 387$ °C.

2.4.2. *P(BDT-NDI)*

Black solid powder, yield 75.3%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.89$–9.01 (br, 2H), 7.58–7.71 (br, 2H), 3.87–4.39 (br, 8H), 1.76–2.06 (br, 4H), 1.15–1.52 (br, 32H), 0.73–1.12 (br, 24H). GPC: $M_w = 6.4$ K, $M_n = 4.5$ K, PDI = 1.4. TGA: $T_d = 382$ °C.

2.4.3. *P(BDT-PhI)*

Orange solid powder, yield 41.5%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.16$–8.52 (br, 2H), 7.39–7.64 (br, 2H), 3.55–4.45 (br, 6H), 1.97–2.36 (br, 3H), 1.09–1.69 (br, 24H), 0.71–0.95 (br, 18H). GPC: $M_w = 40.2$ K, $M_n = 20.7$ K, PDI = 1.9. TGA: $T_d = 368$ °C.



Scheme 2. Synthetic route to three polymers. EH stands for 2-ethylhexyl.

3. Results and discussion

3.1. Synthesis and characterization of the polymers

The general synthetic strategies for the monomers and polymers are outlined in Schemes 1 and 2. Compound 3 was obtained by introducing flexible alkyl side chains and trimethylstannyl groups into compound 1. Dibromation of perylene dianhydride 4 was achieved in concentrated sulfuric acid directly with bromine and a catalytic amount of iodine, while phthalic anhydride 9 was brominated in oleum in the same way. On the other hand, the bromination of naphthalene dianhydride 6 was achieved using dibromoisocyanuric acid (DBI) in oleum, which is known as one of the most powerful brominating agents. The reactions of compounds 4, 7, 10 with 2-ethylhexylamine in organic acid gave arylene imide compounds 5, 8, and 11 with moderate yield, respectively. Copolymers of P(BDT-PDI), P(BDT-NDI) and P(BDT-PhI) were synthesized through a Stille coupling reaction of compound 3 and compounds 5, 8, and 11, respectively. Toluene was used as the solvent while Pd(PPh$_3$)$_4$ was used as a catalyst. The obtained copolymers were completely soluble in common organic solvents, such as THF, CHCl$_3$, chlorobenzene and toluene.

^{1}H NMR spectra of three polymers exhibit the chemical shift of arylene-H at 8.1–9.0 ppm and thienyl-H at 7.4–7.9 ppm. Both imine-H of the polymers are located at 4.4 ppm. The molecular weights of the polymers were determined by GPC with polystyrene as standard. The weight-average molecular weights (M_w) are 5.6, 6.4 and 40.2 K with a polydispersity index (PDI) of 1.2, 1.4 and 1.9 for P(BDT-PDI), P(BDT-NDI) and P(BDT-PhI), respectively. As revealed by the TGA analyses (Fig. 1), the onset decomposition temperature (T_d) of P(BDT-PDI), P(BDT-NDI) and P(BDT-PhI) is about 387, 382 and 368 °C under N$_2$ protection, respectively, mainly due to the leaving of alkoxyl groups. The thermal stability of these three polymers is apparently good enough for their applications in PSCs and other optoelectronic devices.

3.2. Optical properties

Fig. 2 shows the normalized absorption spectra of the three polymers solutions in CHCl$_3$ and the corresponding spin-coated films on quartz substrates. The absorption spectrum of P(BDT-PDI) in solution displays an absorption band ranging from 350 to 693 nm with the centered absorption peak at 519 nm. The broad visible absorption should be attributed to the conjugated polymer main chains copolymerized by the PDI units with BDT groups. For a comparison, P(BDT-NDI) shows a broader absorption band extending to 750 nm with the absorption peak at 629 nm. This extension could be attributed to the large electron affinity of the NDI unit, comparable to that of far more π-extended PDI system [34]. It is worth noting that NDI-Br$_2$ can be easily isolated as pure

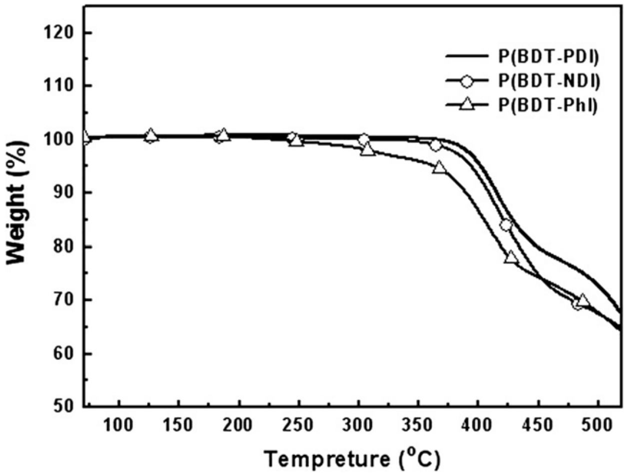


Fig. 1. TGA curves of the polymers.

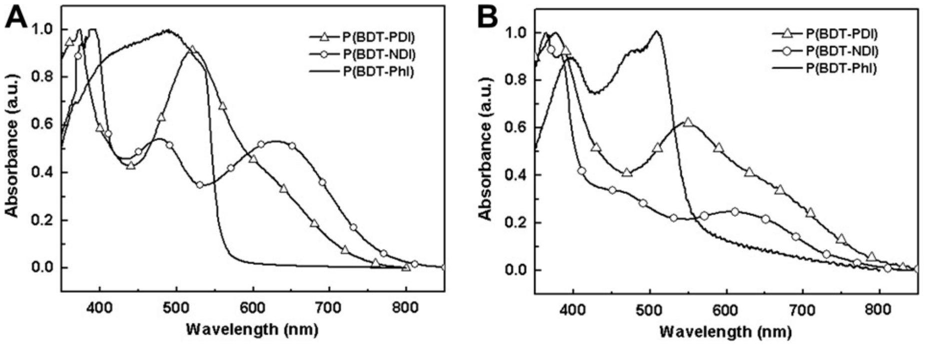


Fig. 2. UV–vis absorption spectra of three polymers in $CHCl_3$ solutions (A) and thin films (B).

2,6-diastereoisomers, enabling the synthesis of a regioregular polymeric backbone [35], while the isolation of PDI-Br_2 regioisomers is difficult. Therefore, compared to PDI-based polymers, P(BDT-NDI) should own stronger D–A interactions with a more delocalized π-conjugating system along the polymer main chain, leading to, a lower band gap. In comparison with P(BDT-PDI) and P(BDT-NDI), P(BDT-PhI) in solution shows a blue-shift with an absorption peak at 470 nm, which is due to the relatively weak electron affinity of the PhI unit with only one imide group.

There are some noticeable differences in the absorption spectra between the polymer solutions and thin films (Fig. 2 and Table 1). The main absorption peaks of polymer films appear at 549 nm for P(BDT-PDI) and 508 nm for P(BDT-PhI), 30 and 38 nm red-shifted compared to those of polymer solutions, respectively. This is because of the higher conjugation along polymer backbones and the stronger interchain interaction in the condensed solid films. On the contrary, the absorption peak of P(BDT-NDI) film appears at 604 nm, which is blue-shifted by 25 nm compared to that of the solution. Nevertheless, its absorption edge shows the same red-shift as P(BDT-PDI) and P(BDT-PhI). The absorption band-edge of the polymer films extend to 713, 760 and 577 nm, which are red-shifted by 20, 10, and 8 nm compared to those in solutions, respectively. Thus, the optical band gaps (E_g^{opt}) are calculated as 1.74, 1.63 and 2.15 eV for P(BDT-PDI), P(BDT-NDI) and P(BDT-PhI), respectively. All of three polymers show broader visible absorption bands and narrower optical band gaps than those of the homopolymer PBDT in film, which exhibits the absorption peak at 450 nm with the optical band gap of about 2.2 eV [30]. The broader absorption bands and the lower optical band gaps of the polymers are favorable for their application in polymer solar cells.

3.3. Electrochemical properties

The electrochemical redox behaviors of the polymers were investigated by cyclic voltammetry (CV). Fig. 3 shows the cyclic voltammograms of P(BDT-PDI), P(BDT-NDI) and P(BDT-PhI) in CH_2Cl_2. The electrochemical data are calculated in Table 1. For P(BDT-PDI) and P(BDT-NDI), there are quasi-reversible reduction and oxidation peaks at the negative potential range, while no obvious redox waves at the positive potential range are detected, indicating that these two polymers are typical n-type materials, mainly because of the strong electron-accepting ability of PDI and NDI groups. Oppositely, P(BDT-PhI) shows quasi-reversible reduction and oxidation waves only at the positive potential range, suggesting that it is an intrinsic p-type semiconductor because the weak electron-withdrawing monomer (PhI) is introduced.

In the negative potential region, the $E_{1/2}$ values for the first redox waves are −0.55 V vs SCE for P(BDT-PDI), and −0.75 V for P(BDT-NDI), respectively. In the positive potential region, the $E_{1/2}$ value for the first redox wave is 0.77 V vs SCE for P(BDT-PhI). From $E_{1/2}$ of the polymers, the HOMO and LUMO energy levels of the polymers can thus be calculated [36].

The LUMO energy levels were estimated to be −4.18 eV for P(BDT-PDI) and −3.99 eV for P(BDT-NDI), which are close to that of the commonly used [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) and other n-type conjugated polymers reported to date. From the LUMO energy level and the optical band gap (E_g^{opt}), the HOMO energy levels of P(BDT-PDI) and P(BDT-NDI) were deduced to be −5.92 and −5.62 eV, respectively. The results indicate that these two polymers could be used as electron acceptors in all polymer solar cells and other polymer optoelectronic devices.

The HOMO energy level of P(BDT-PhI) was estimated to be −5.51 eV, 0.4 eV lower-lying than that of poly(3-hexylthiophene) (P3HT), indicating a higher stability against oxidation and thus

Table 1
Optical and electrochemical properties of the polymers

Polymers	λ_{max}^{soln} (nm)	λ_{max}^{film} (nm)	$\Delta\lambda_{max}^{film-soln}$ (nm)	E_g^{opt},[a] (eV)	$E_{1/2}$ (V vs SCE)	LUMO (eV)	HOMO (eV)
P(BDT-PDI)	519	549	30	1.74	−0.55	−4.18	−5.92[c]
P(BDT-NDI)	629	604	−25	1.63	−0.75	−3.99	−5.62[c]
P(BDT-PhI)	470	508	38	2.15	0.77	−3.36[b]	−5.51

[a] Calculated from the absorption edge of the polymer films, $E_g = 1240/\lambda_{edge}$.
[b] Calculated from LUMO = HOMO + E_g^{opt}.
[c] Calculated from HOMO = LUMO − E_g^{opt}.

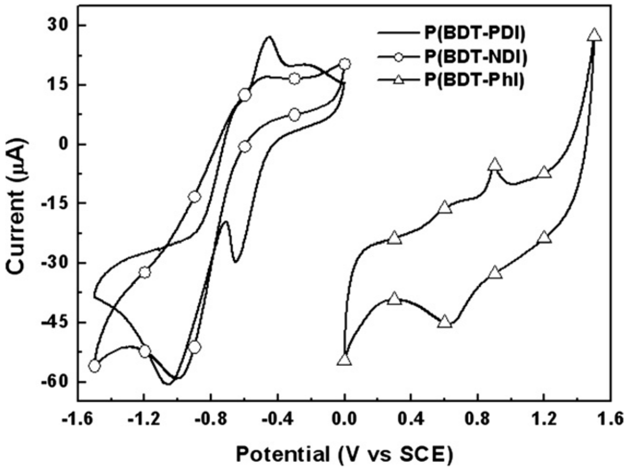


Fig. 3. Cyclic voltammograms of three polymers in CH_2Cl_2 solution. The scan rate is 50 mV s^{-1}.

a larger V_{OC} for polymer solar cell application. The LUMO level of P(BDT-PhI) was deduced to be −3.36 eV. The results suggest that the molecular energy level of conjugated polymers could be adjusted by appropriate molecule-tailoring.

4. Conclusion

Three low band gap conjugated polymers based on benzodithiophene and arylene imide units, P(BDT-PDI), P(BDT-NDI) and P(BDT-PhI), have been successfully synthesized by Stille coupling reaction. All obtained polymers are completely soluble in common organic solvents, thus applicable to solution-processing. All of the three copolymers show broader visible absorption bands and narrower optical band gaps than those of the homopolymer of BDT unit. The LUMO energy levels of P(BDT-PDI) and P(BDT-NDI) are −4.18 and −3.99 eV, respectively, suggesting that these two polymers are typical n-type polymers which could be used as electron acceptors in all polymer solar cells. The HOMO energy level of P(BDT-PhI) is −5.51 eV, indicating a stable p-type semiconductor and thus an advantage for polymer solar cell applications and other polymer optoelectronic devices.

Acknowledgments

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