

## SYNTHESIS AND CHARACTERIZATION OF COPOLYMERS BASED ON BENZOTHIADIZOLE-THIOPHENE-PHENYLENEVINYLENE\*

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**Abstract** Two novel copolymers based on benzothiadizole-thiophene-phenylenevinylene have been synthesized through palladium catalyzed triple-bond polycondensation method. The copolymers exhibit good solubility in common organic solvents such as  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  and THF. The structures and properties of the two copolymers are characterized by FT-IR,  $^1\text{H-NMR}$ , UV-Vis absorbance (Abs), gel permeation chromatography (GPC), thermal gravimetric analysis and cyclic voltammetry (CV). The copolymers of **P**<sub>1</sub> and **P**<sub>2</sub> show absorption spectra with maximum peak at 532 nm and 573 nm in solution, respectively. Compare to their monomers **M**<sub>1</sub> and **M**<sub>2</sub>, the absorption peaks of **P**<sub>1</sub> and **P**<sub>2</sub> were red-shifted by 34 nm and 54 nm respectively. Thermal gravimetric analysis demonstrated that the polymers were stable and little weight loss was observed below 300°C. Cyclic voltammetry experiments showed that the band gaps of the copolymers were 1.81 eV and 1.62 eV, respectively, suggesting their potential for applications as organic solar cell materials.

**Keywords:** Benzothiadizole; Triple-bond polycondensation; Synthesis; Organic solar cell materials.

### INTRODUCTION

Polymer solar cells (PSC) have attracted strong interest in recent years because of their unique advantages such as renewable, low weight, low cost and processability. However, polymer-based solar cells are, in general, of low efficiency compared to their inorganic counterparts due to their relatively low mobility of charge carriers, narrow absorption bands and large band gaps<sup>[1–4]</sup>.

The photoconversion process in PSC materials is connected with efficient light absorption and charge transfer between these conjugated polymers, so the matching to the solar spectrum determines their applications for solar cells<sup>[5]</sup>. Among these conjugated polymers, poly(*p*-phenylenevinylene)s and polythiophenes are two kinds of typical materials which have been extensively studied<sup>[6–9]</sup>, while the relatively narrow spectra response have limited the applications of these polymers. In order to harvest as much as possible photon flux and match well to the solar spectrum, one of the most promising strategies is the donor-acceptor route. The central concept forming the basis of the route is that the interaction between alternating electron-rich donors and electron-deficient acceptors will result in a compressed band gap<sup>[10–12]</sup>.

Benzothiadizole is a typical example of imines nitrogen containing unit which may act as electron-accepting counterpart<sup>[13–15]</sup>. The strategies of introducing benzothiadizole units into the conjugated copolymer for achieving desirable properties of good absorption and electron transporting ability have been proved to be effective and viable. It is reported that most of benzothiadizole-based copolymers were synthesized by single-bond or double-bond polycondensation<sup>[16–21]</sup>. However, these methods couldn't keep the target copolymers

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planarity by the greatest extent. So in this work, we have studied and synthesized novel benzothiadiazole-thiophene-phenylenevinylene-based copolymers through the palladium-catalyzed triple-bond cross-coupling polycondensation.

The long alky chains on the central core could enhance the solubility of the copolymers. The incorporation of triple bond into the copolymer backbones can be as one approach to enhance  $\pi$ -electron delocalization to match well to the solar spectrum. In addition, the donor-acceptor route could enhance energy transfer from the alternating electron-rich monomer ( $M_1$  or  $M_2$ ) to electron-deficient benzothiadiazole and obtain good thermal stability. Actually, the electron-rich ( $M_1$  or  $M_2$ ) counterparts have included smaller donor-acceptor units of the cyanovinylene (acceptor) and the thiophene-phenylenevinylene, pyrrol-phenylenevinylene (donor). The main chain donor-acceptor between  $M_1$  (or  $M_2$ ) and benzothiadiazole, the smaller donor-acceptor units of  $M_1$  or  $M_2$  could be a promising strategy to improve the power conversion efficiency and cause strong and broad absorption of the conjugated polymers.

In this paper, we report the research results of synthesis, characterization, optical and electrochemical properties of the two novel copolymers.

## EXPERIMENTAL

### Materials

Reagents and chemicals were purchased from Aldrich or Acros Chemical companies and were used without further purification. All the solvents were purified according to the standard methods prior to use. The general synthetic routes toward the monomers and polymers were outlined in Schemes 1 and 2. 4,7-Dibromo-2,1,3-benzothiadiazole<sup>[22]</sup> (**1**), 5-bromo-4-dodecylthiophene-2-carbaldehyde<sup>[23]</sup> (**2**), alkyl-pyrrole-2-carbaldehyde<sup>[24]</sup> (**5**) and 2,5-di-*n*-octylox-1,4-xylene-diethylphosphonate ester<sup>[25]</sup> were prepared according to the similar procedures reported.

### Instruments

<sup>1</sup>H-NMR spectra were recorded on a Bruker DRX 400. 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-GPC model 210 chromatograph at 25°C, using THF as the eluent and standard polystyrene as the reference. TGA analysis was performed on a Perkin-Elmer series 7 thermal analysis system under nitrogen at a heating rate of 20 K/min. UV-Vis spectra in solutions and thin films were taken on a Shimadzu UV 2100 UV-Vis recording spectrophotometer. The cyclic voltammograms were recorded on a computer-controlled EG&G potential/galvanostat model 283.

### Synthesis of Monomers

#### 4,7-Bis(3-hydroxy-3-methyl-1-butyryl)-2,1,3-benzothiadiazole (**A**)

To a 100 mL three-necked flask, 4,7-dibromo-2,1,3-benzothiadiazole (0.5 g, 1.7 mmol), Pd (PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (6.3 mg), CuI (10 mg), PPh<sub>3</sub> (30 mg) were added, the mixture was degassed with nitrogen three times. In addition, N(Et)<sub>3</sub> (15 mL) was degassed at room temperature for 1 h and injected into the mixture. Then 2-methyl-3-butyryl-2-ol (0.37 g, 4.5 mmol) was injected. The mixture was heated to 90°C standing for 5 h, cooled to room temperature, then poured into water, extracted three times with methylene chloride. All organic layers were combined, washed with water and dried over anhydrous sodium sulfate over night, the solvent was evaporated. The crude was purified *via* column chromatography using petroleum ether/ethyl acetate (1:1) as eluent and recrystallized from toluene to afford a green solid in 81% yield. Mp 180–181°C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.71 (s, 12H), 2.0–2.2 (broad, 2H), 7.62 (s, 2H).

#### (*E*)-3-(5-bromo-4-dodecylthiophen-2-yl)-2-(thiophen-2-yl)acrylonitrile (**3**)

A mixture of 5-bromo-4-dodecylthiophene-2-carbaldehyde (**2**) (0.30 g, 0.813 mmol), thiophene-2-acetonitrile (0.10 g, 0.813 mmol), K<sub>2</sub>CO<sub>3</sub> (0.12 g, 0.870 mmol) and methanol (10 mL) was heated to 50°C stirred for 5 h, then cooled to 0°C. The precipitate was filtered and washed exhaustively with water and methanol. The precipitate was collected and dissolved in CH<sub>2</sub>Cl<sub>2</sub> and purified *via* column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as

eluent to afford a yellow solid in 78% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.86–0.89 (m, 3H), 1.12–1.61 (m, 20H), 2.57 (m, 2H), 7.05 (m, 1H), 7.29 (m, 1H), 7.32 (m, 3H).

*(E)-3-(5-bromo-4-dodecylthiophen-2-yl)-2-(5-formylthiophen-2-yl)acrylonitrile (4)*

To a mixture of DMF (11.30 g, 155.20 mmol) and 30 mL of 1,2-dichloroethane at  $0^\circ\text{C}$  was added dropwise phosphorus oxychloride (20.18 g, 131.92 mmol). Then the mixture was heated to  $35^\circ\text{C}$  and 3.6 g (7.76 mmol) of **3** was added. After standing for 48 h at  $90^\circ\text{C}$ , the mixture was poured into 300 mL of water, then extracted with chloroform. The organic phase was washed with water for three times and dried over anhydrous sodium sulfate. The solvent was removed and the residue was purified by column chromatography using petroleum ether/ $\text{CH}_2\text{Cl}_2$  (1:1) as eluent to afford a yellow solid in 72% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.86–0.89 (m, 3H), 1.26–1.61 (m, 20H), 2.56–2.61 (m, 2H), 7.39 (d,  $J = 4.0$  Hz, 2H), 7.50 (d,  $J = 6.0$  Hz, 1H), 7.71 (d,  $J = 4.0$  Hz, 1H), 9.88 (s, 1H).

*Monomer  $\mathbf{M}_1$*

To a mixture of **4** (0.20 g, 0.407 mmol), 2,5-di-*n*-octylox-1,4-xylene-diethylphosphonate ester (0.13 g, 0.204 mmol) and dry THF (10 mL) was added dropwise the mixture of NaH (0.020 g, 0.814 mmol) and THF (10 mL), then the mixture was heated to reflux 5 h, cooled to room temperature, poured into water and extracted three times with methylene chloride. All organic layers were combined, washed with water and dried over anhydrous sodium sulfate over night, the solvent was evaporated. The crude was purified *via* column chromatography using petroleum ether/ $\text{CH}_2\text{Cl}_2$  (2:1) as eluent ( $R_f = 0.34$ ), the product was further purified by recrystallizing from butan-1-ol to afford deep red solid in 56% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.86–0.89 (m, 12H), 1.25–1.90 (m, 64H), 2.57 (t,  $J = 4.8$  Hz, 4H), 4.06 (s, 4H), 6.97 (s, 2H), 7.01 (s, 2H), 7.22–7.25 (m, 10H).

*(E)-2-(5-bromothiophen-2-yl)-3-(1-(2-ethylhexyl)-1H-pyrrol-2-yl)acrylonitrile (6)*

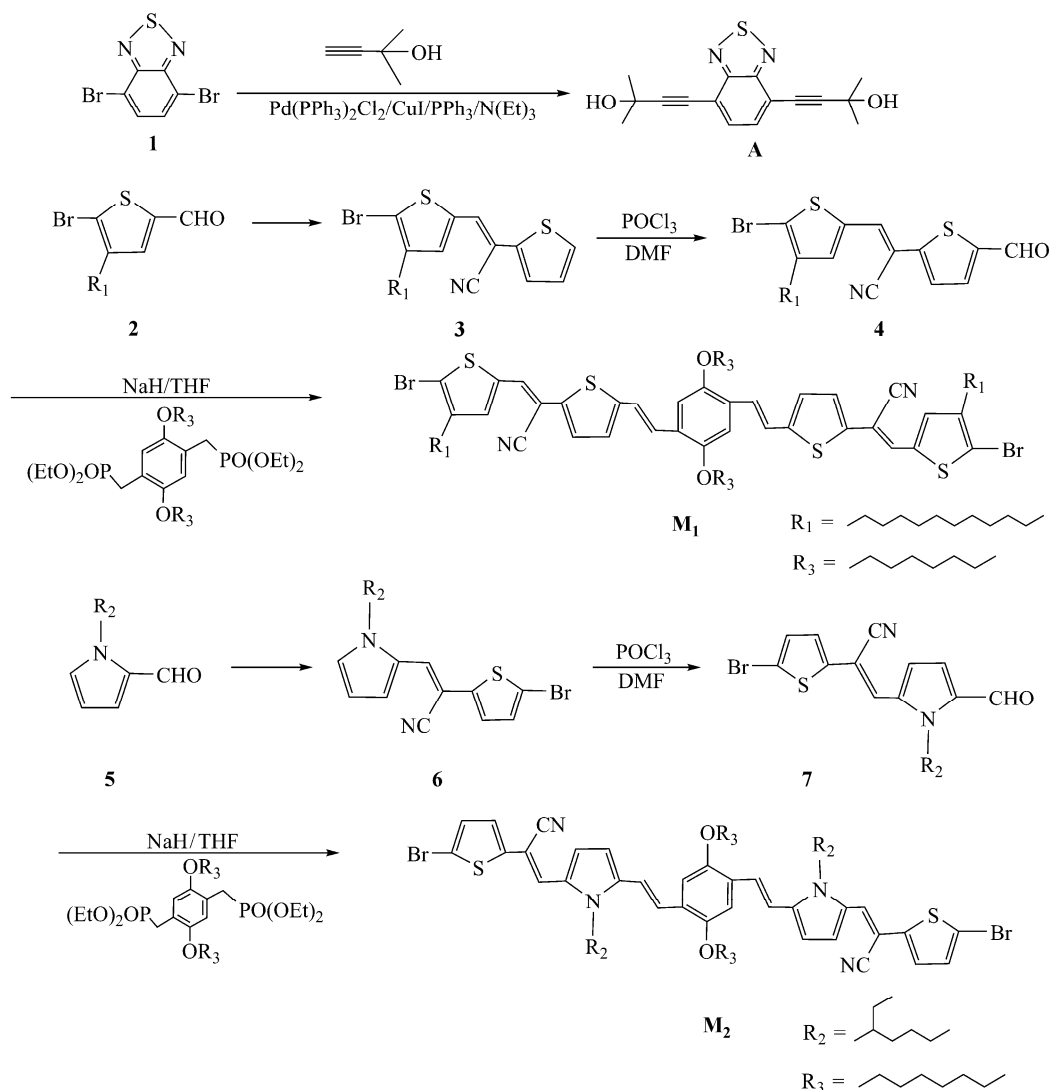
A mixture of **5** (0.50 g, 2.5 mmol), 5-bromo-thiophene-2-acetonitrile (0.51 g, 2.5 mmol),  $\text{K}_2\text{CO}_3$  (0.41 g, 3.0 mmol) and methanol (10 mL) was stirred at room temperature for 24 h, then poured into water, extracted three times with methylene chloride. All organic layers were combined, washed with water and dried over anhydrous sodium sulfate over night, the solvent was evaporated. The crude was purified *via* column chromatography using petroleum ether/ $\text{CH}_2\text{Cl}_2$  (1:1) as eluent to afford yellow oil in 67% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.87–0.93 (m, 6H), 1.20–1.64 (m, 9H), 3.78–3.86 (m, 2H), 6.29 (d,  $J = 2.0$ , 1H), 6.99 (s, 1H), 7.01 (m, 2H), 7.05 (m, 1H), 7.41 (d,  $J = 2.0$ , 1H).

*(E)-2-(5-bromothiophen-2-yl)-3-(1-(2-ethylhexyl)-5-formyl-1H-pyrrol-2-yl)acrylonitrile (7)*

To a flask containing DMF (3.0 mL, 38.4 mmol) was added dropwise  $\text{POCl}_3$  (3.5 mL, 38.4 mmol) over 0.5 h at  $0^\circ\text{C}$  under argon atmosphere, and the obtained red solution was stirred at room temperature for 1 h. A solution of **6** (3.0 g, 7.7 mmol) in 1,2-dichloroethane (12 mL) was added dropwise to the mixture, then the mixture was allowed to heat to  $90^\circ\text{C}$  and kept at this temperature for 1 h. The reaction products were poured into water, stirred at room temperature for 1 h, neutralized carefully with powder of sodium bicarbonate and extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated in vacuo. The crude was purified *via* column chromatography using petroleum ether/ $\text{CH}_2\text{Cl}_2$  (1:1) as eluent to afford a yellow solid in 81% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.85–0.92 (m, 6H), 1.18–1.66 (m, 9H), 4.41 (m, 2H), 7.02 (d,  $J = 1.6$  Hz, 1H), 7.07 (d,  $J = 9.2$  Hz, 2H), 7.14 (d,  $J = 2.4$  Hz, 1H), 7.39 (d,  $J = 2.8$  Hz, 1H), 9.62 (s, 1H).

*Monomer  $\mathbf{M}_2$*

The synthesis of  $\mathbf{M}_2$  is similar to that of  $\mathbf{M}_1$ . The corresponding mixture was stirred at room temperature for 24 h instead of heating, an eluent of petroleum ether/ $\text{CH}_2\text{Cl}_2$  (1:2) ( $R_f = 0.53$ ) was used for column chromatography and the product was further purified by recrystallizing from ethyl acetate/ $\text{CHCl}_3$  (1:1) to afford deep red solid in 52% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.86–0.97 (m, 18H), 1.30–1.89 (m, 60H), 3.95 (m, 4H), 4.05 (m, 4H), 6.71–6.72 (m, 3H), 6.99–7.02 (m, 8H), 7.05–7.08 (m, 3H), 7.52–7.54 (m, 2H).



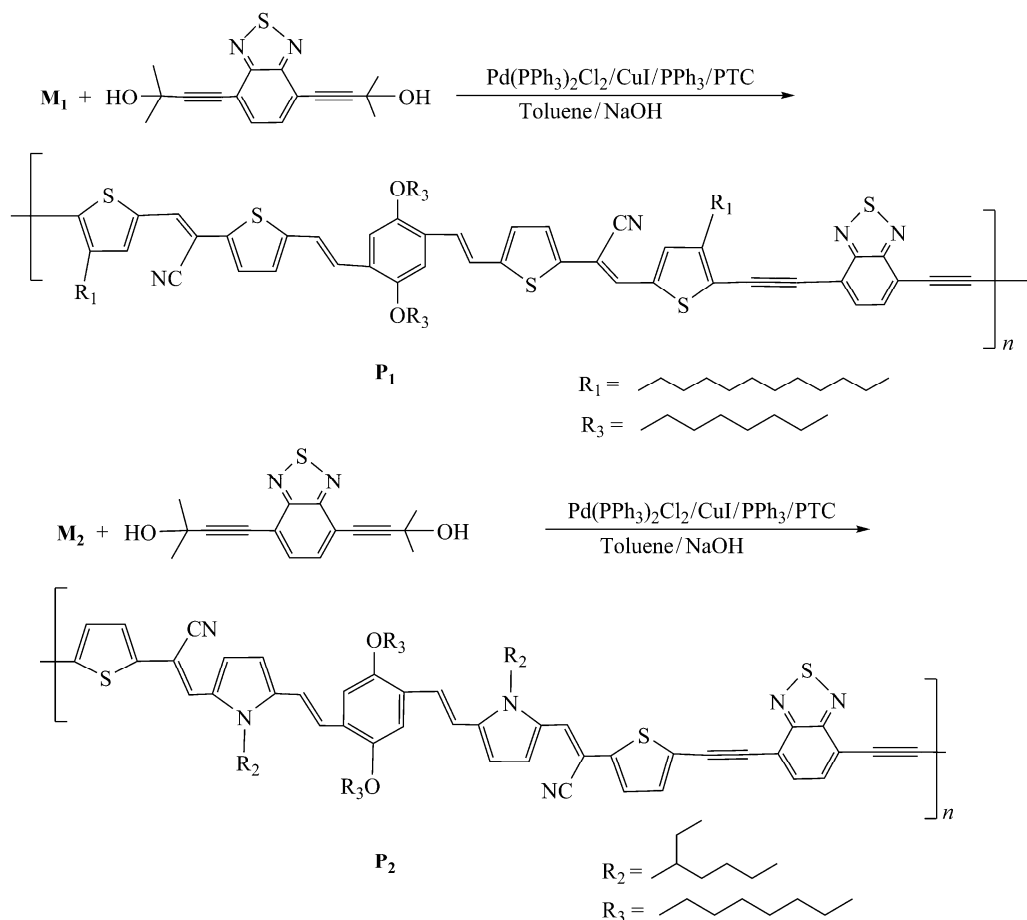
Scheme 1 Synthesis of the intermediates

### Synthesis of Polymers

General procedure: Monomer **M<sub>1</sub>** or **M<sub>2</sub>** (1.0 mmol), **A** (1.0 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.0876 mmol), CuI (0.333 mmol), PPh<sub>3</sub> (0.48 mmol) and benzyl-triethylammonium chloride (PTC) (0.0628 mmol) were added to a 50 mL three-necked flask and the mixture was degassed with nitrogen three times. In addition, toluene (10 mL) and 5.5 mol/L NaOH (3.0 mL) were degassed at room temperature for 1 h and injected into the mixture, respectively. The reaction was then stirred at 90°C for 48 h and the reactant was poured into 200 mL methanol, after stirring for 30 min, the precipitate was collected and washed repeatedly with water. The residue was dissolved in CHCl<sub>3</sub>, filtered, poured into methanol again, the precipitate then Soxhlet extracted with methanol for 48 h. The copolymer was collected by filtration and dried under vacuum.

**P<sub>1</sub>**: purple solid. IR (KBr pellet, cm<sup>-1</sup>): 3427, 2962, 2921, 2851, 2182, 1645, 1492, 1445, 1416, 1261, 1097, 1022, 868, 801. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 0.88 (m, 12H), 1.26–1.88 (m, 64H), 2.57 (t, *J* = 7.6 Hz, 4H), 4.05 (s, 4H), 6.91 (s, 4H), 7.00–7.24 (m, 10H), 7.35–7.69 (m, 2H).

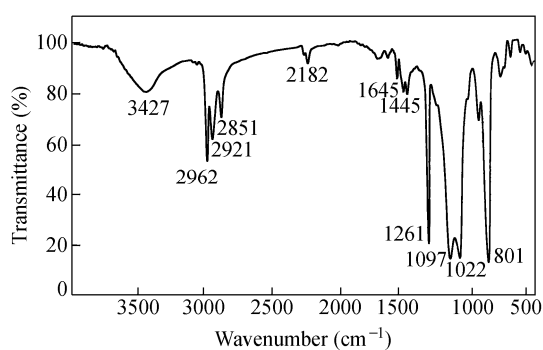
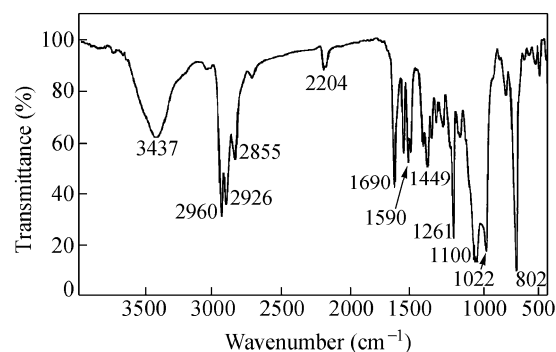
**P<sub>2</sub>**: purple solid. IR (KBr pellet, cm<sup>-1</sup>): 3437, 2960, 2855, 2204, 1690, 1590, 1481, 1449, 1260, 1100, 870, 802. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 0.85–0.93 (m, 18H), 1.10–2.03 (m, 42H), 4.04 (m, 4H), 4.19 (m, 4H), 7.32 (d, *J* = 8.4 Hz, 4H), 7.45 (d, *J* = 8.4 Hz, 4H), 7.59 (d, *J* = 7.6 Hz, 4H), 8.03 (d, *J* = 7.6 Hz, 2H), 8.27 (s, 2H), 8.56 (s, 2H).



Scheme 2 Synthesis of the copolymers

## RESULTS AND DISCUSSION

The chemical structure of the polymers was characterized by FT-IR and  $^1H$ -NMR. Figures 1 and 2 give the FT-IR spectra of the polymers. The absorption peaks at  $3427\text{ cm}^{-1}$  and  $3437\text{ cm}^{-1}$  correspond to the  $\equiv CH$  vibrations of **P**<sub>1</sub> and **P**<sub>2</sub>, respectively. That means the chain end of the copolymers is  $\equiv CH$  of benzothiadizole unit rather than bromo-aromatic of **M**<sub>1</sub> or **M**<sub>2</sub>. The absorption peaks at 2182 and  $2204\text{ cm}^{-1}$  may be attributed to the  $-\text{CN}$  and  $\text{RC}\equiv\text{CR}$  stretching mode of the polymers **P**<sub>1</sub> and **P**<sub>2</sub>. Bands appearing at 1645 and  $1690\text{ cm}^{-1}$  may

Fig. 1 FT-IR spectrum of the polymer **P**<sub>1</sub>Fig. 2 FT-IR spectrum of the polymer **P**<sub>2</sub>

be assigned to  $-\text{CH}=\text{CH}-$  vibrations of **P**<sub>1</sub> and **P**<sub>2</sub>. In addition, the strong absorption peak at 1097, 1022  $\text{cm}^{-1}$  (for **P**<sub>1</sub>) and 1100, 1022  $\text{cm}^{-1}$  (for **P**<sub>2</sub>) may be attributed to stretching vibration of  $\text{C}-\text{O}-\text{C}$ .

Figures 3 and 4 show the  $^1\text{H}$ -NMR spectrum of the polymers. The signals at  $\delta = 6.0\text{--}8.5$  are for the phenyl and vinyl protons. The peaks at  $\delta = 4.05$  and 4.04 correspond to the hydrogen atoms of  $-\text{OCH}_2$  linked to the phenyl ring of **P**<sub>1</sub> and **P**<sub>2</sub>, respectively. The peak at  $\delta = 4.18$  may be assigned to the hydrogen atoms of  $-\text{NCH}_2$  of **P**<sub>2</sub>. The signal at  $\delta = 2.56$  may be attributed to the hydrogen atoms of the dodecyl substitute. Every peak in the  $^1\text{H}$ -NMR spectra could be assigned to the corresponding hydrogen atoms of the polymers.

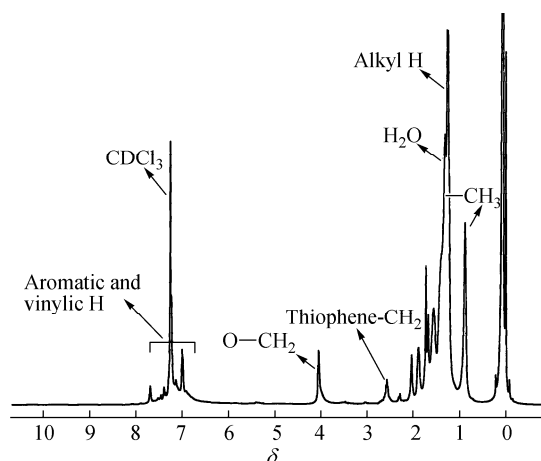


Fig. 3  $^1\text{H}$ -NMR spectra of the polymer **P**<sub>1</sub>

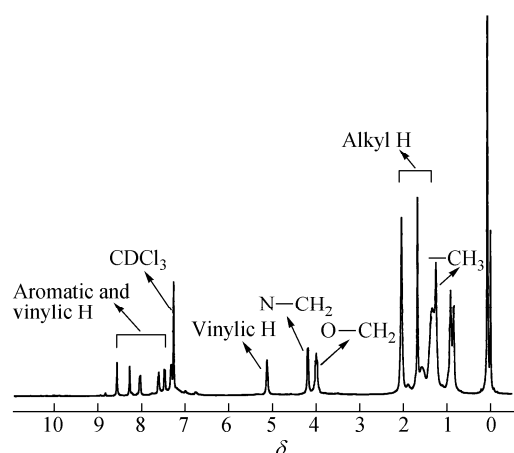


Fig. 4  $^1\text{H}$ -NMR spectra of the polymer **P**<sub>2</sub>

### Physical Properties

The copolymers exhibited good solubility in common organic solvents such as  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  and THF. Molecular weights of the polymers were determined by GPC using THF as an eluent, polystyrene as a standard, and the thermal stability of the polymers were measured by TGA (shown in Fig. 5). The results were summarized in Table 1.

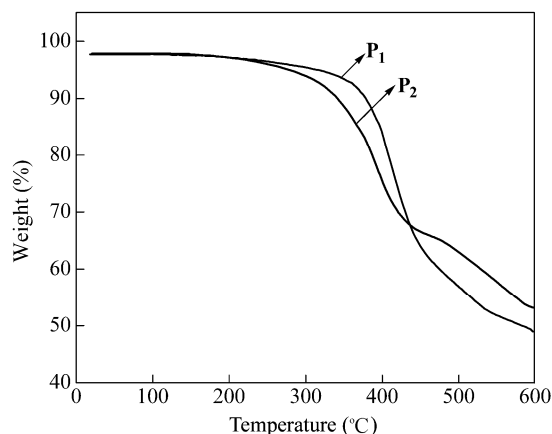


Fig. 5 Thermal gravimetric analysis curves of the polymers

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

| Polymer               | Yield (%) | $M_w^a$ | $M_n^a$ | PDI ( $M_w/M_n$ ) <sup>a</sup> | $T_d^b$ (°C) |
|-----------------------|-----------|---------|---------|--------------------------------|--------------|
| <b>P</b> <sub>1</sub> | 75        | 7800    | 3800    | 2.0                            | 383          |
| <b>P</b> <sub>2</sub> | 72        | 20200   | 8300    | 2.4                            | 356          |

<sup>a</sup> Molecular weights and polydispersity were measured by GPC, using THF as an eluent, polystyrene as a standard;

<sup>b</sup> Thermal gravimetric analysis (TGA) curve of the polymers (heating rate of 20 K/min under nitrogen)

As depicted in Table 1, the weight-average molecular weights ( $M_w$ ) of **P**<sub>1</sub>, **P**<sub>2</sub> were 7800 with polydispersity index ( $M_w/M_n$ ) of 2.0 and 20200 with polydispersity index ( $M_w/M_n$ ) of 2.4, respectively. The sterical hindrance induced by the alkyl side chains on the thiophene units made the monomer **M**<sub>1</sub> less reactive and caused the lower molecular weights of the copolymer **P**<sub>1</sub>.

Figure 5 shows that the onset temperatures of the weight loss of **P**<sub>1</sub> and **P**<sub>2</sub> were 383°C and 356°C, respectively, indicating that the target polymers had good thermal stability, and little weight loss was observed below 300°C.

### Optical and Electrochemical Properties

The UV-Vis absorption spectra of the monomers **M**<sub>1</sub>, **M**<sub>2</sub> and the polymers **P**<sub>1</sub>, **P**<sub>2</sub> are shown in Fig. 6. It could be seen from the figure that the absorption peaks of **P**<sub>1</sub>, **P**<sub>2</sub> in solution were at 532 nm and 573 nm, respectively, which could be attributed to the  $\pi \rightarrow \pi^*$  transition of the conjugated polymer chains. Compare to **M**<sub>1</sub> and **M**<sub>2</sub>, the absorption peak of **P**<sub>1</sub> and **P**<sub>2</sub> were red-shifted by 34 nm and 54 nm respectively. The spectral response of the polymers were extended up to 670 nm and 720 nm, which were broader than **M**<sub>1</sub> (586 nm) and **M**<sub>2</sub> (608 nm). These results could be attributed to the introduction of electron-accepting counterpart benzothiadizole and the forming of donor-acceptor segments. The absorption peak of **P**<sub>2</sub> was red-shifted by 41 nm comparing to **P**<sub>1</sub>, which may be attributed to the interaction between stronger electron-rich pyrrole unit and electron-deficient cyanovinylene unit. On the other hand, the sterical hindrance induced by the alkyl side chains on the thiophene units also resulted in the low molecular weight of **P**<sub>1</sub> and its blue-shifted absorption peak comparing to that of **P**<sub>2</sub>.

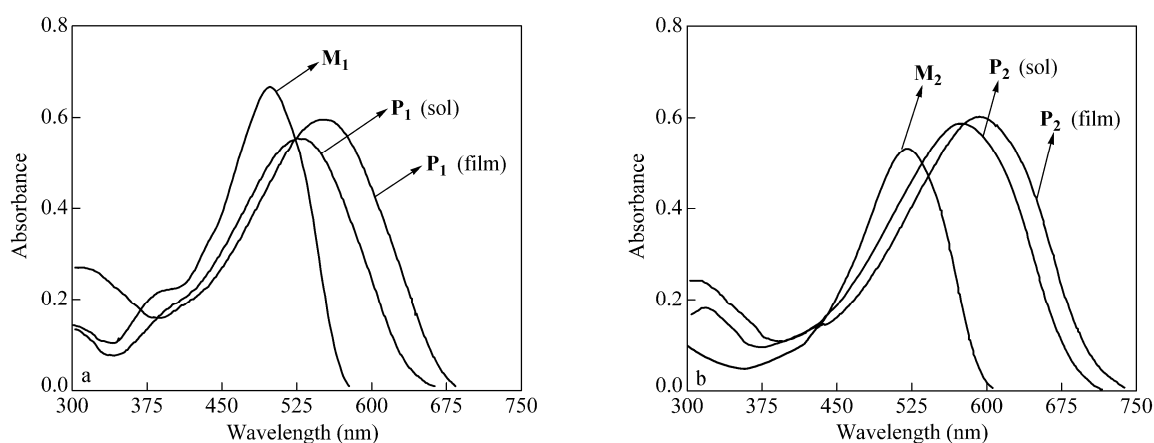


Fig. 6 UV-Vis absorption spectra for the monomers **M**<sub>1</sub>, **M**<sub>2</sub> and polymers **P**<sub>1</sub>, **P**<sub>2</sub>

The absorption peak maxima of **P**<sub>1</sub>, **P**<sub>2</sub> films were at 546, 585 nm, and the edges of the absorption bands were at 687 and 746 nm, respectively, which were red-shifted in comparison with those of polymer solutions. This was attributed to more aggregated configuration formed in solid state. In addition, the optical band-gaps ( $E_g$ ) estimated from the band edge of the UV-Vis absorption spectra of the polymer films were 1.82 eV and 1.66 eV for **P**<sub>1</sub> and **P**<sub>2</sub>, respectively according to the empirical relationships<sup>[21]</sup>:  $E_g = 1240/\lambda_{\text{edge}}$ .

The electrochemical properties of the polymers were measured by cyclic voltammetry (CV) at room temperature. 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 mol/L solution of tetra-*n*-butyl-ammonium perchlorate (*n*-Bu<sub>4</sub>NClO<sub>4</sub>) in anhydrous acetonitrile. Figure 7 shows the cyclic voltammetry of **P**<sub>1</sub>, **P**<sub>2</sub> and Table 2 summarizes the electrochemical properties of **P**<sub>1</sub>, **P**<sub>2</sub>. In the anodic scan, the onsets of oxidation of **P**<sub>1</sub>, **P**<sub>2</sub> occurred at 0.86, 0.75 V, respectively. The corresponding onsets of reduction appeared at -0.95, -0.87 V, respectively. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the copolymers could be obtained according to the following empirical

relationships<sup>[26]</sup>:

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

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

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

From these equations, the HOMO and the LUMO of **P**<sub>1</sub>, **P**<sub>2</sub> were estimated to be −5.25, −3.44 eV and −5.15, −3.53 eV, respectively. The band gaps of the polymers were estimated to be 1.81 and 1.62 eV. These results were in good agreement with the optical band-gaps ( $E_g$ ) estimated from the band edge of the UV-Vis absorption spectra of the polymer films. The relatively low band gaps were probably due to the energy transfer from the alternating electron-rich **M**<sub>1</sub> or **M**<sub>2</sub> to electron-deficient benzothiadiazole.

**Table 2.** Optical and electrochemical properties of the polymer **P**<sub>1</sub>, **P**<sub>2</sub>

| Polymer               | $\lambda_{\text{max, sol}}^a$ (nm) | $\lambda_{\text{max, film}}$ (nm) | $E_{\text{onset, ox}}^b$ (V) | $E_{\text{onset, red}}^b$ (V) | HOMO (eV) | LUMO (eV) | $E_g$ (eV) |
|-----------------------|------------------------------------|-----------------------------------|------------------------------|-------------------------------|-----------|-----------|------------|
| <b>P</b> <sub>1</sub> | 532                                | 546                               | 0.86                         | −0.95                         | −5.25     | −3.44     | 1.81       |
| <b>P</b> <sub>2</sub> | 573                                | 585                               | 0.75                         | −0.87                         | −5.15     | −3.53     | 1.62       |

<sup>a</sup> *ca.* 10<sup>−5</sup> mol/L in CHCl<sub>3</sub>, wavelength of maximum;

<sup>b</sup> Oxidation and reduction onset potential measured by cyclic voltammogram (versus SCE)

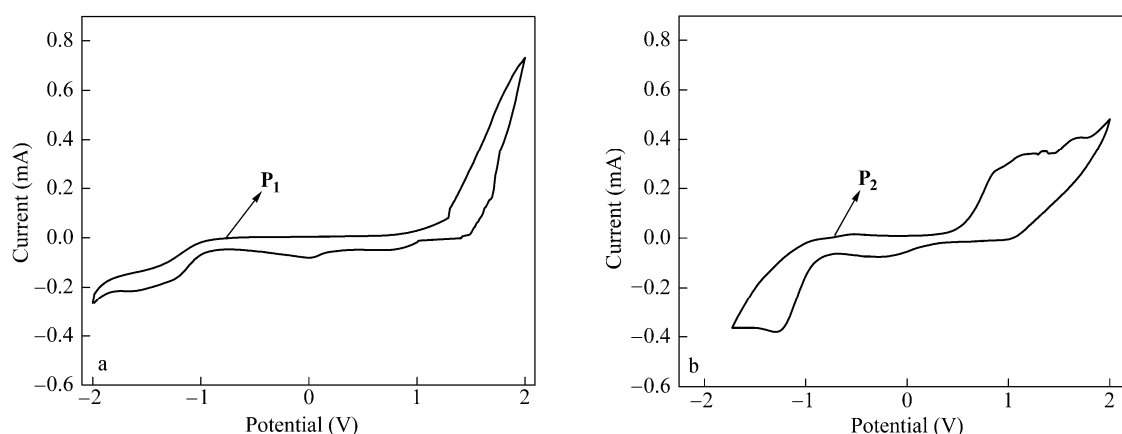


**Fig. 7** Cyclic voltammogram of the polymer **P**<sub>1</sub>, **P**<sub>2</sub> (in 0.1 mol/L *n*-Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN)

## CONCLUSIONS

Two novel copolymers based on benzothiadiazole-thiophene-phenylenevinylene have been synthesized through palladium catalyzed triple-bond polycondensation method. The copolymers exhibit good solubility in common organic solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and THF. The introduction of benzothiadiazole units into the conjugated copolymers has achieved desirable properties of broad optical absorption, the polymers show UV-Vis absorption spectra with maximum peak at 532 nm and 573 nm in solution and the spectral response are extended up to 670 nm and 720 nm, respectively. Thermal gravimetric analysis demonstrated that the polymers are stable and little weight loss is observed below 300°C, the onset temperatures of the weight loss of **P**<sub>1</sub> and **P**<sub>2</sub> are 383°C and 356°C. Cyclic voltammetry experiments show that the band gaps of the copolymers are 1.81 eV and 1.62 eV. These features make the copolymers attractive candidates for solar cell applications.

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