

# Synthesis and Characterizations of Poly(4-alkylthiazole vinylene)

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Received 9 July 2010; accepted 17 June 2011

DOI 10.1002/app.35106

Published online 10 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Two poly(thiazole vinylene) derivatives, poly(4-hexylthiazole vinylene) (P4HTzV) and poly(4-nonylthiazole vinylene) (P4NTzV), were synthesized by Pd-catalyzed Stille coupling method. The polymers are soluble in common organic solvents such as *o*-dichlorobenzene and chloroform, and possess good thermal stability. P4HTzV and P4NTzV films exhibit broad absorption bands at 400–720 nm with an optical bandgap of 1.77 eV and 1.74 eV, respectively. The HOMO (the highest occupied molecular orbital) energy levels of P4HTzV and P4NTzV are –5.11 and –5.12 eV, respectively,

measured by cyclic voltammetry. Preliminary results of the polymer solar cells based on P4HTzV : PC<sub>61</sub>BM ([6,6]-phenyl-C-61-butyric acid methyl ester) (1 : 1, w/w) show a power conversion efficiency of 0.21% with an open-circuit voltage of 0.55 V and a short circuit current density of 1.11 mA cm<sup>-2</sup>, under the illumination of AM1.5G, 100 mW cm<sup>-2</sup>. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 847–854, 2012

**Key words:** conjugated polymers; poly(thiazole vinylene); bandgap; polymer solar cells; synthesis

## INTRODUCTION

Polymer solar cells (PSCs) have attracted great attention in recent years, owing to their advantages of easy fabrication, light weight, low cost, and flexibility.<sup>1–5</sup> PSCs are usually composed of a thin blend layer of conjugated polymer (as donor) and [6,6]-phenyl-C-61-butyric acid methyl ester (PC<sub>61</sub>BM) (as acceptor) sandwiched between an ITO (tin-doped indium oxide) positive electrode and a low work function metal negative electrode. To achieve high power conversion efficiency (PCE) of the PSCs, broad absorption in visible range, higher charge carrier mobility, and suitable electronic energy levels of the conjugated polymers have been pursued by the researchers. Recently, some new donor conjugated polymers, such as poly[(4,4'-bis(2-ethylhexyl)cyclopenta[2,1-b:3,4-b']dithiophene)-5,5-(4,7-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCPDTBT),<sup>6,7</sup> poly[2,7-(9,9-dioctylfluorene)-*alt*-5,5-(4,7-di-2-thienyl-2',1',3'-benzothiadiazole)] (PFDTBT),<sup>8–10</sup> poly[(2,7-dioctylsilafluorene)-*alt*-5,5-(4,7-di-2-thienyl-2',1',

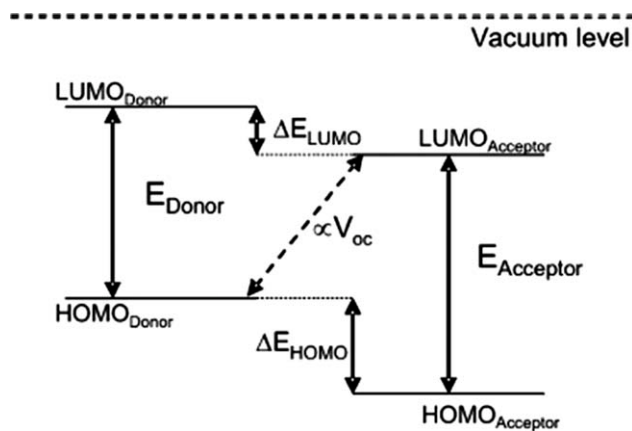
3'-benzothiadiazole)] (PSiFDTBT),<sup>11</sup> and poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl] (PSBTBT),<sup>12</sup> have been designed and synthesized. Especially, copolymers containing benzo[1,2-b:4,5-b']dithiophene (BDT) as the donor unit have exhibited outstanding photovoltaic properties for the applications in PSCs.<sup>1,13–15</sup> For instance, the PSCs based on poly(BDT-thieno[3,4-b]thiophene) derivatives can achieve high PCE higher than 7%.<sup>1</sup> In addition, conjugated polymer acceptor materials were also attracted interests for the applications in PSCs,<sup>16–18</sup> because the visible absorption of conjugated polymer acceptors is usually stronger than that of PCBM and the electronic energy of the conjugated polymer can be modified by structural modification.

As for the electronic energy levels of the conjugated polymer photovoltaic materials, both the LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) energy levels of the acceptor materials should be lower than those of the donor materials. And the difference between the LUMO of the acceptor and HOMO of the donor determines the open circuit voltage of the PSCs (as shown in Fig. 1).<sup>19</sup> Therefore, appropriately tuning the electronic energy levels is very important for the conjugated polymer photovoltaic materials.

Thiazole is more electronegative than other five-ring heterocyclic such as thiophene or pyrrole due to

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Contract grant sponsor: NSFC; contract grant numbers: 20874106, 50633050, 20721061, 50973092.



**Figure 1** The energy levels in polymer solar cells.

its C=N bond. The intermolecular interactions of thiazole could be enhanced by forming good  $\pi$ - $\pi$  stacking.<sup>20</sup> Besides, the 4-position of thiazole unit is available for facile chemical engineering to modulate the solubility and electronic energy levels, etc., by introducing different functional substituents. In the last few years, thiazole or thiazolothiazole based on small molecules or oligomers are intensively studied as n-type materials for field effect transistors (FET) and exhibit good performances,<sup>20–25</sup> but the solubility of the molecules is out of their concern. Therefore, solution processable thiazole-based polymers may be more desirable not only in FET but also in the PSCs.<sup>26–29</sup>

In previous work in our group, some poly(thiophene vinylene) derivatives were synthesized for the photovoltaic application.<sup>30,31</sup> To decrease the HOMO level of polymers further, here we synthesized the poly(thiazole vinylene) derivatives with the substituent of alkyl group on 4-position of thiazole unit, poly(4-hexylthiazole vinylene) (P4HTzV) and poly(4-nonylthiazole vinylene) (P4NTzV). They have the simple structure and good solubility due to introducing the alkyl group to 4-position of thiazole unit effectively. The absorption spectrum, electrochemical properties, and photovoltaic properties of the polymers were characterized.

## MATERIALS AND METHODS

### Materials and measurements

Isopentyl nitrite, *n*-butyllithium, (*E*)-1,2-bis(tributylstannyl)ethylene, Pd(PPh<sub>3</sub>)<sub>4</sub>, 2-octanone, and 2-dodecanone were purchased from Aldrich or Alfa-Aesar Chemical Co. and used as received. Thiourea and CuBr<sub>2</sub> were purchased from Beijing Chemical Factory and used without further purification. Tetrahydrofuran was dried over Na/benzophenone ketyl and freshly distilled prior to use.

<sup>1</sup>H-NMR spectra were measured on a Bruker DMX-400 spectrometer. Absorption spectra were

taken on a Hitachi U-3010 UV-vis spectrophotometer. Photoluminescence (PL) spectra were measured using a Hitachi F-4500 spectrophotometer. The gel permeation chromatography (GPC) measurements were performed on a Waters 515 chromatograph connected to a Waters 2414 refractive index detector, using THF as eluent and polystyrene standards as calibrants. TGA measurement was performed on a Perkin-Elmer TGA-7. Cyclic voltammetry (CV) was performed on a Zahner IM6e Electrochemical Workstation with a three-electrode system in a solution of 0.1M Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile at a scan rate of 100 mV s<sup>-1</sup>. The polymer films were coated on a Pt plate electrode (1.0 cm<sup>2</sup>) by dipping the electrode into the corresponding solutions and then drying. A Pt wire was used as the counter electrode, and Ag/Ag<sup>+</sup> was used as the reference electrode.

### Synthesis

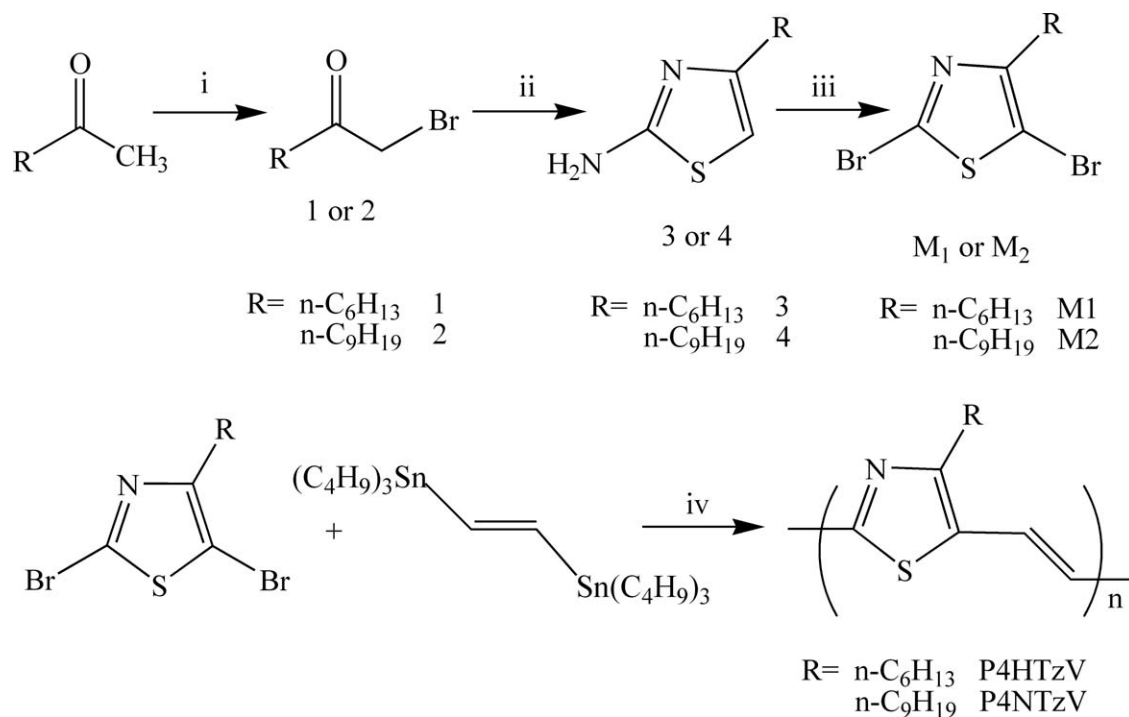
The synthetic routes of the monomer and polymers are shown in Scheme 1. The detailed synthetic processes are as follows.

#### 1-Bromo-2-octanone (1)<sup>26</sup>

2-Octanone (40 mL, 0.251 mol), urea (25.0 g, 0.417 mol), and glacial acetic acid (125 mL) were put in a 250-mL, two-necked, round-bottom flask with an ice bath for cooling. A solution of bromine (14.0 mL, 0.275 mol) in glacial acetic acid (40 mL) was added dropwise to the flask, and the solution was stirred overnight at room temperature. Water (250 mL) was then added to the solution, and the solution was extracted with dichloromethane. The combined extracts were washed with 10% sodium carbonate and brine and then dried over anhydrous magnesium sulfate. The pure product was obtained after vacuum distillation (b.p. 80°C at 0.45 mmHg) (28.591 g, 55% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm,  $\delta$ ): 3.88 (s, 2H), 2.62 (t, 2H), 1.58 (m, 2H), 1.35–1.15 (m, 6H), 0.86 (t, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm,  $\delta$ ): 202.1, 39.7, 34.3, 31.4, 28.6, 23.7, 22.4, 13.9. MS: *m/z* = 206.

#### 1-Bromo-2-undecanone (2)<sup>27</sup>

Bromine (10.4 g, 65.1 mmol) was added dropwise to a stirred solution of 2-undecanone (11.1 g, 64.9 mmol) in methanol (100 mL) at -10°C. The mixture was stirred at 0°C for 1 h and then at room temperature another 1 h. Water (20 mL) and then concentrated sulfuric acid (98% wt, 35 mL) was added to the mixture in an ice bath. After the mixture was stirred overnight at room temperature, white crystals precipitated from the reaction mixture. The precipitate was filtered, washed with water, and then dried under vacuum to produce 1-bromo-undecan-2-one (15.2 g, 94% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm,  $\delta$ ): 3.87



**Scheme 1** Synthetic routes of monomers and polymers. (i)  $\text{Br}_2$ , r. t., overnight; (ii) Thiourea, reflux, 2 h; (iii) NBS,  $\text{CH}_3\text{CN}$ ,  $\text{CuBr}_2$ , by dropwise addition of isopentyl nitrite; (iv)  $\text{Pd}(\text{PPh}_3)_4$ , toluene.

(s, 2H), 2.63 (t, 2H), 1.61–1.58 (m, 2H), 1.32–1.25 (m, 12H), 0.86 ppm (t, 3H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , ppm,  $\delta$ ): 202.29, 39.84, 34.30, 31.82, 29.36, 29.30, 29.22, 29.01, 23.84, 22.64, 14.08. MS:  $m/z = 249$ .

#### 2-Amino-4-hexylthiazole (3)<sup>32</sup>

Thiourea (7.6 g, 0.1 mol) is suspended in 200 mL of water in a 500-mL flask equipped with a reflux condenser, dropping funnel. The stirrer is started, and 1-bromo-2-octanone (20.6 g, 0.1 mol) is added in 30 min. As the reaction proceeds the thiourea dissolves and the temperature rises. The yellow solution is refluxed for 2 h and cooled, while the mixture is stirred continuously but not too fast to produce a troublesome emulsion, sodium hydroxide (20 g) was added with cooling. The upper, oily layer is separated in a separatory funnel and the aqueous layer is extracted three times with ether. The combined extracts were washed three times with saturated brine (200 mL) and then dried over anhydrous magnesium sulfate. The pure product of **3** was obtained after vacuum distillation (b.p. 118°C at 0.45 mmHg) (13.8 g, 75% yield).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , ppm,  $\delta$ ): 6.06(s, 1H), 5.10(s, 2H), 2.52(t, 2H), 1.36–1.29(m, 8H), 0.87(t, 3H). MS:  $m/z = 184$ .

#### 2-Amino-4-nonylthiazole<sup>6</sup>

The preparation process of **4** was the same as that for **3** except that compound **2** was used instead of

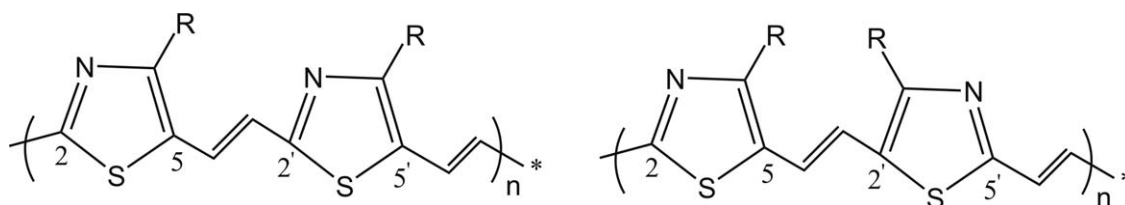
compound **1** (13.56 g, 60% yield).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , ppm,  $\delta$ ): 6.08(s, 1H), 5.02(s, 2H), 2.52(t, 2H), 1.35–1.29(m, 14), 0.87(t, 3H). MS:  $m/z = 226$ .

#### 2, 5-Dibromo-4-hexylthiazole (M1)<sup>33</sup>

A mixture of 2-amino-4-hexylthiazole (9.2 g, 50 mmol) and (*N*-bromosuccinimide) (NBS, 10.68 g, 60 mmol) in  $\text{CH}_3\text{CN}$  (200 mL) was stirred overnight at room temperature. The reaction mixture was cooled to 0°C and  $\text{CuBr}_2$  (18.8 g, 75 mmol) was added followed by dropwise addition of isopentyl nitrite (8.8 g, 75 mmol). The mixture was stirred for 2 h. The solvent was removed by evaporation under reduced pressure and the residue was extracted with EtOAc/hexane (1 : 2) and dried over anhydrous magnesium sulfate. After the solvent was removed, the product was purified by column chromatography (silica gel, hexanes as eluent) resulting in the desired product of **M1** as a yellow liquid. (6.54 g, 40% yield).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , ppm,  $\delta$ ): 2.69(t, 2H), 1.68–1.26(m, 8H), 0.89(t, 3H). MS:  $m/z = 327$ .

#### 2, 5-Dibromo-4-nonylthiazole (M2)<sup>21</sup>

The preparation process of **M2** was the same as that for **M1** except that compound **4** (11.3 g, 50 mmol) was used instead of compound **3** (13.56 g, 60% yield).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , ppm,  $\delta$ ): 2.69(t, 2H), 1.68–1.26(m, 14H), 0.88(t, 3H). MS:  $m/z = 369$ .



**Figure 2** Two arrangements 5-2' and 5-5' between two thiazole rings of P4HTzV.

### Synthesis of the polymers

The mixture of **M1** or **M2** (1 mmol) and (*E*)-1, 2-bis(tributylstannyl) ethane (1 mmol) were put into a two-necked flask. Then, 15 mL of degassed toluene was added under the protection of argon. The solution was flushed with argon for 15 min, and then 15 mg of Pd(PPh<sub>3</sub>)<sub>4</sub> were added. After another flushing with argon for 20 min, the reactant was heated to reflux for 24 h. The reagents were cooled to room temperature, and the polymer was precipitated by addition of 50 mL methanol, and filtered. The crude polymer was washed on Soxhlet apparatus with methanol, hexanes, and chloroform. The polymer was recovered as a solid sample from the chloroform fraction by rotary evaporation. The solid was dried under vacuum for 1 day to give the final product.

**P4HTzV**: GPC:  $M_w = 11.6\text{k}$ ;  $M_n = 4.5\text{K}$ ;  $M_w/M_n = 2.58$ . <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm,  $\delta$ ): 7.47(br, 1H), 6.85(br, 1H), 2.82(t, 2H), 1.74-1.34(m, 8H), 0.91(t, 3H). Elemental analysis for (C<sub>11</sub>H<sub>15</sub>NS)<sub>n</sub>. Calculated: C, 67.64%; H, 8.77%; N, 7.17%; S, 16.42%. Found: C, 67.42%; H, 8.50%; N, 7.15%; S, 16.58%.

**P4NTzV**: GPC:  $M_w = 22.23\text{k}$ ;  $M_n = 8.49\text{K}$ ;  $M_w/M_n = 2.62$ . <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm,  $\delta$ ): 7.46(br, 1H), 6.82(br, 1H), 2.85(t, 2H), 1.75-1.35(m, 14H), 0.91(t, 3H). Elemental analysis for (C<sub>14</sub>H<sub>21</sub>NS)<sub>n</sub>. Calculated: C, 70.83%; H, 9.77%; N, 5.90%; S, 13.51%. Found: C, 70.70%; H, 9.72%; N, 5.56%; S, 13.30%.

### Fabrication and characterization of polymer solar cells

PSCs were fabricated with ITO glass as a positive electrode, Al as a negative electrode, and the blend film of the polymer/PC<sub>61</sub>BM between them as a photosensitive layer. Prior to use, the substrates were cleaned with detergent and deionized water. Then, they were ultrasonicated in deionized water, acetone, and isopropanol. ITO substrates were spin-coated (2000 rpm, 60 s) with a thin film (50 nm) of PEDOT : PSS, (Baytron P, H. C. Starck) and dried at 120°C for 10 min. The photosensitive layer was prepared by spin-coating a blend solution of polymers and PC<sub>61</sub>BM (1 : 1, 20 mg mL<sup>-1</sup> in *o*-dichlorobenzene) on the ITO/PEDOT : PSS electrode. Then the Al cathode was deposited on the polymer layer by vacuum

evaporation under  $5 \times 10^{-5}$  Pa. The thickness of the photosensitive layer is about 70 nm, measured on an Ambios Tech. XP-2 profilometer. Current versus potential curves (*I*-*V* characteristics) were measured with a Keithley 236 Digital Source Meter. Illumination of the cells was done through the ITO side using light from 150 W Oriel Instruments Solar Simulator and xenon lamp with AM1.5G filter to provide an intensity of 100 mW cm<sup>-2</sup>.

## RESULTS AND DISCUSSION

### Synthesis and characterization

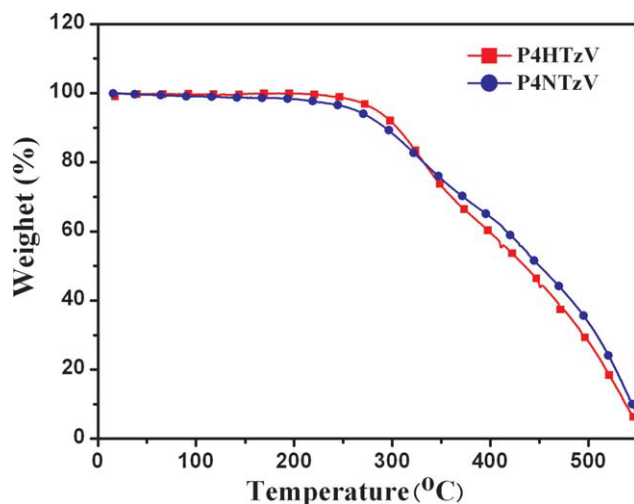
The synthesis of the monomers and polymers is outlined in Scheme 1. The polymers were easily synthesized by Stille-coupling reaction and identified by <sup>1</sup>H-NMR spectroscopy. In the downfield region of <sup>1</sup>H-NMR spectrum of P4HTzV, there is two broad peak, corresponding to the protons of vinyl group, indicating two possible main arrangement between thiazole rings<sup>21</sup> (5-2' and 5-5', as shown in Fig. 2). The optimization of the synthetic route to get region-regular P4HTzV derivatives is still underway. The molecular weight determined by GPC against polystyrene standard is  $M_n = 5.1 \times 10^3$  and  $8.4 \times 10^3$  for P4HTzV and P4NTzV, respectively, with polydispersity 2.5 and 2.6 for P4HTzV and P4NTzV, respectively. All the polymers are random polymers and readily soluble in common organic solvents such as toluene, chloroform, and THF.

### Thermal analysis

Thermal stability of the two polymers was investigated with thermogravimetric analysis (TGA) in N<sub>2</sub> inert atmosphere, as shown in Figure 3. The decomposition temperatures based on 5% weight loss of P4HTzV, P4NTzV are at 260°C and 244°C, respectively. The thermal stability of the two polymers is good enough for the optoelectronic applications.

### Optical properties of the polymers

UV-vis absorption spectra could provide a good deal of information on the electronic structure of the conjugated polymers. Figure 4 displays the UV-vis absorption spectra of the polymer solutions in

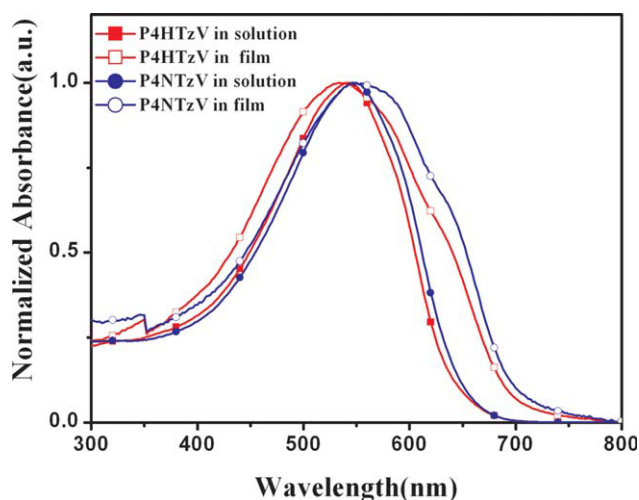


**Figure 3** TGA plots of P4HTzV and P4NTzV with a heating rating of 10 °C/min under inert atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chloroform and polymer films on quartz plates. The absorption peak of polymer solutions is at 540 nm and 545 nm for P4HTzV and P4NTzV, respectively. In comparison with the absorption spectrum of P4HTzV, the small red-shift of the absorption peak for P4NTzV should be attributed to the influence of the longer alkyl in P4NTzV. For the polymer films, the absorbance maximum is at 540 nm and 554 nm for P4HTzV and P4NTzV, respectively. Compared with those of corresponding solutions, the absorption edges of the polymer films red-shifted by ~ 50 nm. This indicates that the  $\pi$ - $\pi$  intermolecular stacking is increased in film.<sup>22</sup> The optical optical bandgaps ( $E_g^{\text{opt}}$ ) of the polymers can be calculated according to  $E_g^{\text{opt}} = 1240/\lambda_{\text{edge}}$ . The  $E_g^{\text{opt}}$  values of P4HTzV and P4NTzV are 1.77 eV and 1.74 eV, respectively. The absorption properties and bandgaps of the polymers were outlined in Table I.

### Electrochemical properties

The electrochemical property is one of the most important properties of the conjugated polymers and many applications of the conjugated polymers depend on the electrochemical properties. We studied the electrochemical properties of the polymers



**Figure 4** Absorbance spectra of polymers in chloroform solutions and solid films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

by cyclic voltammetry. Figure 5 shows the cyclic voltammograms (CVs) of the P4HTzV and P4NTzV films on Pt disc electrode. Two polymers show similar irreversible p-doping/dedoping (oxidation/reduction), and reversible n-doping/dedoping (reduction/reoxidation) processes. The onset oxidation potential ( $\phi_{\text{ox}}$ ) is 0.60 V versus Ag/Ag<sup>+</sup> for P4HTzV and 0.59 V for P4NTzV, and the onset reduction potential ( $\phi_{\text{red}}$ ) is -1.13 V for P4HTzV and -1.12 V for P4NTzV. The HOMO and LUMO energy levels of the polymers were calculated from the onset oxidation potentials ( $\phi_{\text{ox}}$ ) and the onset reduction potentials ( $\phi_{\text{red}}$ ) and by assuming the energy level of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) to be -4.8 eV below the vacuum level.<sup>34</sup> The formal potential of Fc/Fc<sup>+</sup> was measured as 0.09 V versus Ag/Ag<sup>+</sup>. From  $\phi_{\text{ox}}$  and  $\phi_{\text{red}}$  of the polymers, HOMO and LUMO energy levels as well as the energy gap ( $E_g^{\text{EC}}$ ) of the polymers were calculated according to the following equations.<sup>35,36</sup>

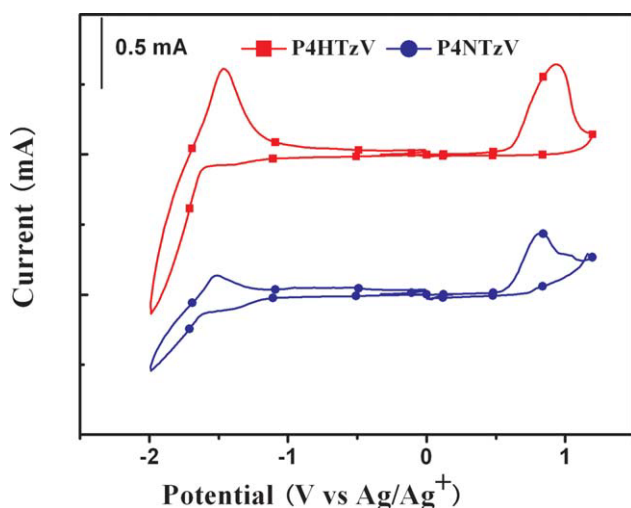
$$E_{\text{HOMO}} = (e(\phi_{\text{ox}} + 4.71))(\text{eV});$$

$$E_{\text{LUMO}} = (e(\phi_{\text{red}} + 4.71))(\text{eV});$$

$$E_g^{\text{EC}} = e(\phi_{\text{ox}} - \phi_{\text{red}})(\text{eV}).$$

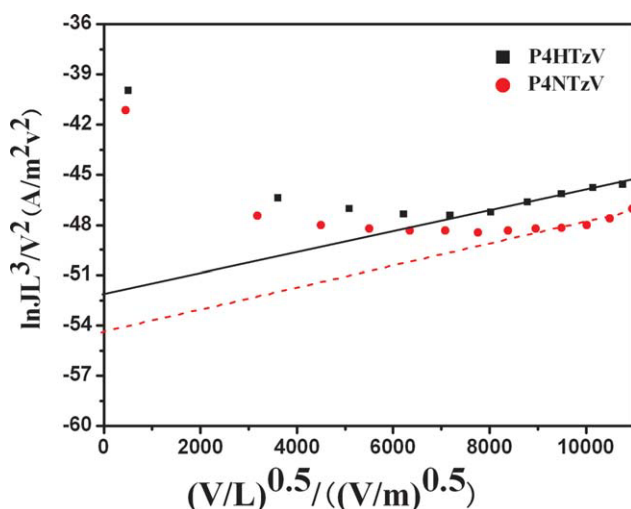
**TABLE I**  
Optical and Electrochemical Properties of the Polymers

Polymers	UV-vis absorption spectra				Cyclic voltammetry		
	Solution		Film		p-doping	n-doping	$E_g^{\text{EC}}$ (eV)
	$\lambda_{\text{max}}$ (nm)	$\lambda_{\text{max}}$ (nm)	$\lambda_{\text{onset}}$ (nm)	$E_g^{\text{opt}}$ (eV)	$\phi_{\text{ox}}$ /HOMO (V)/(eV)	$\phi_{\text{red}}$ /LUMO (V)/(eV)	
P4HTzV	540	540	702	1.77	0.56/-5.27	-1.60/-3.11	2.16
P4NTzV	545	554	712	1.74	0.57/-5.28	-1.59/-3.12	2.16



**Figure 5** Cyclic voltammograms of P4HTzV and P4NTzV film on a platinum electrode measured in 0.1 mol/L Bu4NPF6 acetonitrile solutions at a scan rate of 100 mV s<sup>-1</sup>. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

where the units of  $\phi_{\text{ox}}$  and  $\phi_{\text{red}}$  are V versus Ag/Ag<sup>+</sup>. The values obtained are also listed in Table I. They have the similar HOMO and LUMO at about -5.3 eV and -3.1 eV, which indicates that length of the alkyl chains have little effect on the HOMO and LUMO levels of the polymers. The introduction of thiazole unit in the main chain of the polymers effectively decreases the HOMO level of the polymers, compared with poly(3-hexyl thienylenevinylene) (-5.05 eV),<sup>37</sup> which could be probably beneficial to a higher  $V_{\text{oc}}$  of the PSCs with the polymers as donor materials.



**Figure 6**  $\ln(JL^3/V^2)$  versus  $(V/L)^{0.5}$  plots of the polymers for the measurement of hole mobility by the SCLC method. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Hole mobility

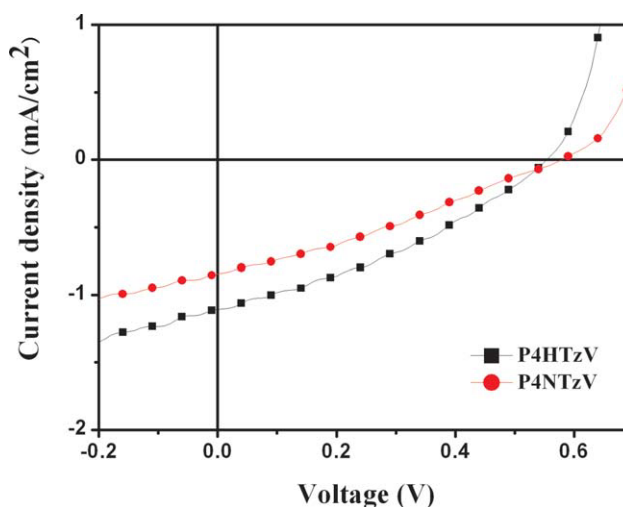
Hole mobility is a very important parameter for the conjugated polymer donor photovoltaic materials. Here we measured the hole mobility of the copolymers P4HTzV and P4NTzV by space-charge limited current (SCLC) method by using a device structure of ITO/PEDOT : PSS/polymer/Au. For the hole-only devices, SCLC is described by

$$J \cong (9/8)\epsilon\epsilon_0\mu_0V^2\exp(0.89\sqrt{V/E_0L})/L^3 \quad (1)^{38}$$

where  $\epsilon$  is the dielectric constant of the polymer, which is usually assumed to be 3,<sup>39</sup> which is a typical value for conjugated polymers.  $\epsilon_0$  is the permittivity of the vacuum,  $\mu_0$  is the zero-field mobility,  $E_0$  is the characteristic field,  $J$  is the current density,  $L$  is the thickness of the blended films layer,  $V = V_{\text{appl}} - V_{\text{bi}}$ ,  $V_{\text{appl}}$  is the applied potential, and  $V_{\text{bi}}$  is the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure,  $V_{\text{bi}} = 0.2$  V). The results are plotted as  $\ln(JL^3/V^2)$  versus  $(V/L)^{0.5}$  (as shown in Fig. 6). According to eq. (1) and Figure 6, the hole mobilities obtained are  $1.0 \times 10^{-6}$  cm<sup>2</sup>/V s and  $1.39 \times 10^{-7}$  cm<sup>2</sup>/V s for P4HTzV and P4NTzV, respectively.

### Photovoltaic properties

To investigate the potential applications of the polymers in PSCs, the PSCs were fabricated with a device structure of ITO/PEDOT : PSS/polymers : PC<sub>61</sub>BM (1 : 1, w/w)/Al. Figure 7 shows the  $I$ - $V$  curves of the devices under the illumination of AM



**Figure 7**  $I$ - $V$  curves of the polymer solar cells based on P4HTzV and P4NTzV under the illumination of AM1.5G, 100 mW cm<sup>-2</sup>. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE II**  
**Summary of the Photovoltaic Properties of**  
**P4HTzV-P4NTzV : PC<sub>61</sub>BM**

Active layer (w/w)	$V_{oc}$ (V)	$I_{sc}$ (mA cm <sup>-2</sup> )	FF	PCE (%)
P4HTzV : PC <sub>61</sub> BM (1 : 1)	0.55	1.11	0.34	0.21
P4NTzV : PC <sub>61</sub> BM (1 : 1)	0.58	0.84	0.30	0.15

1.5 G, 100 mW cm<sup>-2</sup> and the corresponding open-circuit voltage ( $V_{oc}$ ), short circuit current ( $I_{sc}$ ), fill factor (FF), and PCE of the devices are summarized in Table II. It can be seen that the  $V_{oc}$  and  $I_{sc}$  values are 0.55 V and 1.11 mA cm<sup>-2</sup> for P4HTzV, and 0.58 V and 0.84 mA cm<sup>-2</sup> for P4NTzV. The PCE of the PSCs based on P4HTzV and P4NTzV are 0.21% and 0.15%, respectively. The poorer photovoltaic performance of the polymers could be suffered from their lower hole mobility mentioned above. P4HTzV possessed a little better photovoltaic properties, which may be ascribed to a relatively higher hole mobility,<sup>40,41</sup> leading to relatively higher  $I_{sc}$  and fill factor FF. Given the low values of the FF and low molecular weight of the copolymers, it is believed that the photovoltaic performance of this kind of copolymer can be further improved from two aspects. One is from the material aspect, such as optimizing the polymerization method to increase the molecular weight.<sup>42</sup> The other is the device fabrication conditions, such as optimizing the interpenetrating network morphology through different polymer/PCBM ratios, processing additives, or annealing, etc. It is believed that higher  $I_{sc}$ , FF, and PCE values should be obtained.

## CONCLUSIONS

We have synthesized two new low-band gap poly (thiazole-vinylene) derivatives by Stille coupling polymerization. The polymers P4HTzV and P4NTzV exhibit a broad absorption band in the visible region, preferable HOMO/LUMO energy levels, and a good thermal stability. Preliminary studies on photovoltaic cells using blends of P4HTzV and PC<sub>61</sub>BM (1 : 1, w/w) as active layers afforded PSCs with an open circuit voltage of 0.55 V, and a PCE of 0.21%, under the illumination of AM1.5G, 100 mW cm<sup>-2</sup>.

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