Macromolecules **2006,** *39,* 4657−4662

Articles

Branched Poly(thienylene vinylene)s with Absorption Spectra Covering the Whole Visible Region

Jianhui Hou,[†,‡] Zhan'ao Tan,[†,‡] Youjun He,[†] Chunhe Yang,[†] and Yongfang Li*,[†]

Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, and Graduate School of Chinese Academy of Sciences, Beijing 100039, China

Received March 23, 2006; Revised Manuscript Received May 2, 2006

ABSTRACT: Three branched poly(thienylene vinylene)s, i.e., poly(thienylene vinylene) derivatives with bi-(thienylene vinylene) side chains (biTV−PTVs), biTV−PTV1−3, were synthesized for obtaining the conjugated polymers with broad and strong visible absorption spectra. The polymers were characterized by thermogravimetric analysis (TGA), absorption spectroscopy, cyclic voltammetry, in situ spectroelectrochemical and photovoltaic measurements, and compared with poly(3-hexyl-thienylene vinylene) (P3HTV). The absorption peaks of the conjugated side chains and main chains of the biTV−PTVs both red-shifted in comparison with those of the monomer and P3HTV, indicating that the conjugation degree of both the side chains and the main chains is extended in the biTV−PTVs. In particular, the biTV−PTV3 film shows a strong and broad absorption band covering the whole visible region from 380 to 780 nm. Cyclic voltammograms of the polymers revealed that the LUMO of the biTV−PTVs decreased and their HOMO increased a little so that the E_g values of the biTV−PTVs were reduced in comparison with P3HTV. In situ absorption spectra of biTV−PTV3 at different potentials indicate that the oxidation of the polymer is accompanied by the p-doping of the conjugated main chains and the polymer can be used as an electrochromic material. Photovoltaic properties of biTV−PTV3 were investigated with the polymer solar cell (PSC) based on the blend of the polymer and PCBM (1:1, w/w) under the illumination of AM 1.5, 100 mW/cm^2. The power conversion efficiency of the PSC reached 0.32%, which is 52% increased in comparison with that of the device based on P3HTV under the same experimental conditions.

1. Introduction

Conjugated polymers have drawn much attention since the discovery of conducting polyacethylene in 1977[1] due to the basic research interests on their curious structure−property relationship and their promising applications in many fields.[2] The important properties of the conjugated polymers include conductivity of their doped state for the applications as conducting polymers,[1,3] absorption spectra for applications in polymer solar cells[4] and electrochromic displays,[5] electrochemical properties for applications as electrode materials[6] and for estimating the HOMO and LUMO energy levels of the conjugated polymers,[7] and photoluminescent properties for applications in polymer light-emitting devices.[8] Therefore, design and synthesis of new conjugated polymers possessing special properties should be of crucial importance for the development of the studies on the conjugated polymers.

In recent years, side chain conjugated polymers attracted attention for the modulation of the electronic structures of the conjugated polymers. Bunz et al. synthesized the side-chain conjugated poly(*p*-phenyleneethynylene)s with phenylene-vinylene side chains for the band gap engineering of the conjugated polymers.[9] Recently, the authors designed and synthesized a series of side-chain conjugated polythiophenes (PTs) aimed at broad absorption conjugated polymers for the application in polymer solar cells (PSCs).[10,11] The side chain conjugated PTs show two absorption peaks in their UV−vis absorption spectra, a UV peak corresponding to the absorption of the conjugated side chains and a visible peak attributed to the $\pi-\pi^*$ transition of the PT main chains.[10,11a] By using bi-(thienylene vinylene) as the conjugated side chains, the UV peak was red-shifted to visible region. The conjugated polymers of the biTV−PTs show broad and strong absorption from 380 to 650 nm and high power conversion efficiency of the PSCs based on the biTV−PTs was obtained.[11b]

In this paper, we synthesized the bi(thienylene vinylene) substituted poly(thienylene vinylene)s (biTV−PTVs), for further extending the absorption of the conjugated polymers to a longer wavelength region, in considering that PTVs possess narrower band gap and broader absorption band than PTs.[12] The biTV−PTVs could also be called as branched poly(thienylene vinylene)s because the composition of the conjugated side chains is the same with the main chains. Scheme 1 shows the molecular structures of the biTV−PTVs together with that of P3HTV for comparison. The biTV−PTVs show very broad absorption band covering the whole visible region from 380 to 780 nm. The in

---

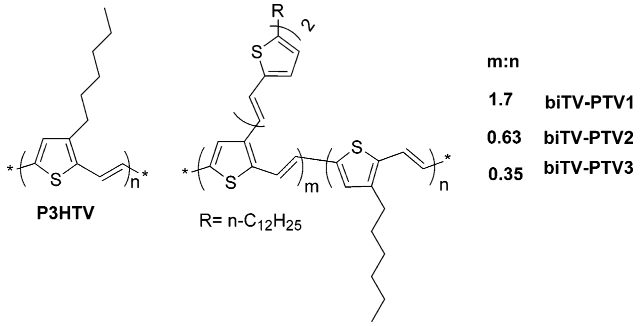
* Corresponding author: E-mail: liyf@iccas.ac.cn. Fax: 86-10-62559373.

[†] Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences.

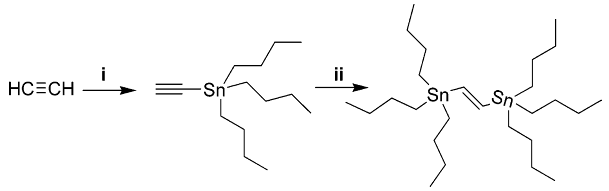
[‡] Graduate School of Chinese Academy of Sciences, Beijing 100039, China

10.1021/ma060662u CCC: $33.50

Scheme 1. Molecular Structures of the Poly(thienylene vinylene) Derivatives

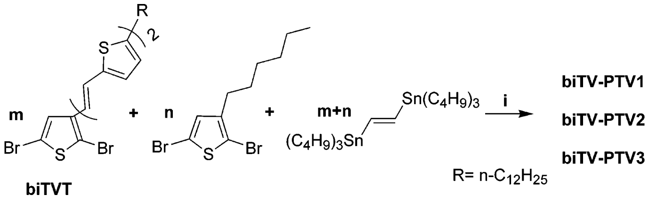


Scheme 2. Synthesis Route of (*E*)-1,2-bis(tributylstannyl)Ethane[a]



[a] Key: (i) *n*-butyllithium, THF, −78 °C, 1 h, then tributylchlorostannane, −10 °C to ambient temperature; (ii) tributyltin hydride, 2,2′-azobis(2-methylpropionitrile), 100 °C.

Scheme 3. Synthesis Routes of the Polymers of BiTV−PTV1−3[a]



[a] Key: (i) Pd(PPh$_3$)$_4$, toluene, reflux, argon, 12 h.

situ spectroelectrochemical and photovoltaic properties of the biTV−PTVs were also investigated.

2. Results and Discussion

2.1. Synthesis of Monomers and Polymers. The polymers of biTV−PTVs were synthesized by Stille coupling of 2,5-dibromo-3-bi(thienylene vinylene)thiophene monomers with (*E*)-1,2-bis(tributylstannyl)ethane.[13] The synthesis routes of (*E*)-1,2-bis(tributylstannyl)ethane and the polymers are shown in Schemes 2 and 3, respectively. The vinyl bonds on the 3-position of monomer biTVT in Scheme 3 were formed by Horner−Emmons reaction. The ^{1}H NMR spectrum of biTVT shows very neat peaks for the protons of the *trans*-vinyl bond, indicating that the vinyl bonds are all in trans structure.[11b]

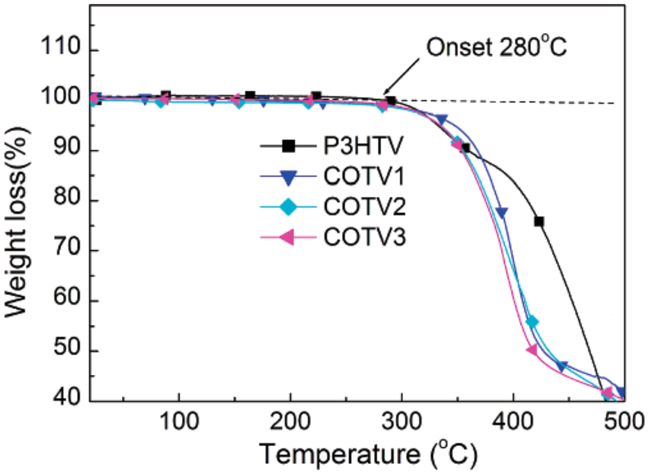


Figure 2. TGA plots of the polymers with a heating rate of 10 °C/min under inert atmosphere.

The values of m:n of the biTV−PTV1−3 were estimated roughly by ^{1}H NMR. As shown in Figure 1, the hydrogen on position a shows a peak at δ2.69 ppm, and the hydrogen on position b shows a peak at δ2.74 ppm. Hence, the values of *m*:*n* could be calculated from the ratio of the integral areas of the two peaks. The *m*:*n* values obtained are not accurate due to the overlap of the two peaks. Since the three polymers have similar structure, we only put the ^{1}H NMR spectrum of biTV−PTV2 in Figure 1.

2.2. Thermal Analysis. Thermal stability of the three polymers was investigated with thermogravimetric analysis (TGA), as shown in Figure 2. The three biTV−PTVs show similar onset decomposition temperatures as P3HTV at about 280 °C, which indicates that the conjugated side chains had little effect on the thermal stability of the PTVs. The onset decomposition temperature of the biTV−PTVs is a little lower than that (ca. 300 °C) of the bi(thienylene vinylene) substituted polythiophenes (biTV−PTs),[11b] but the thermal stability is enough for most applications. Differential scan calorimetric (DSC) analysis of the biTV−PTVs showed no detectable T_g or

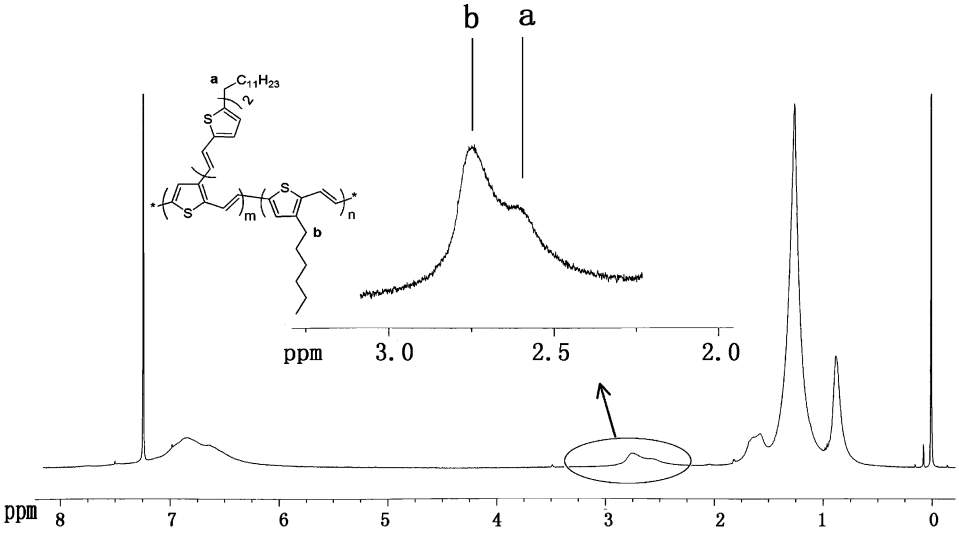


Figure 1. ^{1}H NMR spectrum of aromatic region of the polymer biTV−PTV2.

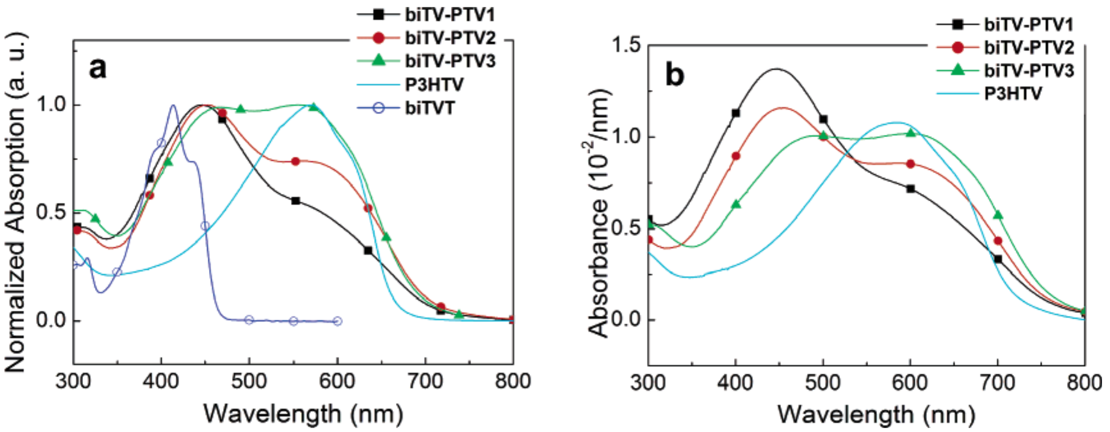


Figure 3. Absorption spectra of (a) biTVT, biTV−PTV1−3, and P3HTV solutions in chloroform and (b) biTV−PTV1−3 and P3HTV films.

Table 1. Absorption Spectral Properties of the PTVs Films

polymers	λ_{max}(nm)/absorbance[a] (10^{-2}/nm)		full width at half-maximum[b] (nm)	integral area for 1 nm thickness film[c]
P3HTV		585/1.08	210	2.31
BiTV−PTV1	448/1.37		230	3.03
BiTV−PTV2	453/1.16	600/0.86	263	3.01
BiTV−PTV3	488/1.01	605/1.02	328	3.10

[a] The absorbance values were obtained by dividing the maximum absorbance by the thickness of the films. [b] The absorption in the UV region is not included. [c] The integration was performed from 380 to 780 nm.

T_m in the range from 30 to 250 °C.

2.3. Absorption Spectra. Figure 3 shows the absorption spectra of the biTV−PTVs, and the absorption spectra of biTVT and P3HTV were also put in the figure for comparison. Similar to the side chain conjugated polythiophenes (PTs),[10,11] the absorption spectra of the biTV−PTVs also show two absorption peaks. One at the shorter wavelength region is attributed to the conjugated side chains, another at the longer wavelength region is attributed to the conjugated main chains.[10,11] From the solution absorption spectra in Figure 3a, it can be seen that the absorption peaks of the bi(thienylenevinylene) side chains in biTV−PTV1−3 red-shifted to about 440 nm in comparison with that of the monomer biTVT. While for the thienylenevinylene substituted PTs, the short wavelength absorption peak position is entirely the same as that of its monomer.[11] Probably, the same thienylenevinylene composition of the side-chain and main-chain in the biTV−PTVs benefited the mutual interaction and extended the conjugation degree of the side chains. For the main chain absorption peaks of the biTV−PTVs, the solution absorption peaks are almost the same with that of P3HTV, while the absorption peaks of the biTV−PTVs films are obviously red-shifted in comparison with that of P3HTV film although the absorption of P3HTV film is also slightly red-shifted than its solution, and the absorption edge of biTV−PTV3 is red-shifted to 780 nm.

Most importantly, biTV−PTV3 film shows a very broad plateau absorption peak with strong absorbance, covering the whole visible region from 380 to 780 nm. In comparison with that of biTV−PTs,[11b] the absorption spectra of the biTV−PTVs broadened by more than 100 nm in the long wavelength region, which benefited from their PTV main chains. Table 1 listed the peak absorbance and full width at half-maximum (fwhm) of the absorption spectra of the polymers. For the polymer of biTV−PTV3, the fwhm is much broader than P3HTV, with the absorbance at the peak position of 605 nm close to that of P3HTV at the peak wavelength of 585 nm. To investigate the light harvest ability of the polymer films for the application in polymer solar cells, we calculated the integral areas of the absorbance of a 1 nm thick film of the polymers in the visible region, and the results were also listed in Table 1. The integral area of biTV−PTV3 is 34% more than that of P3HTV, which indicates that biTV−PTV3 possesses a better light harvest ability than P3HTV.

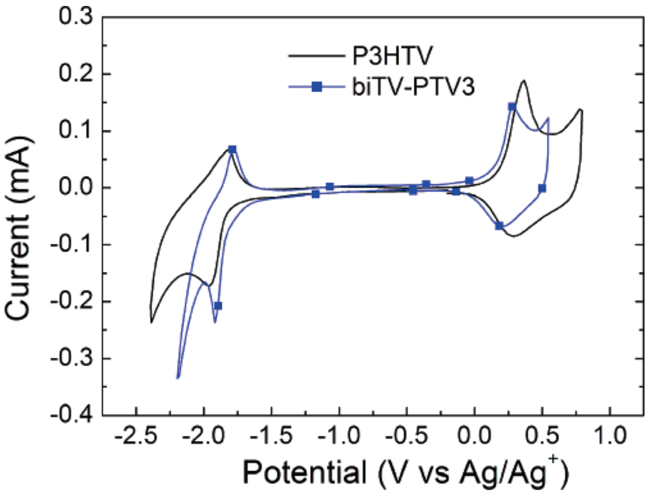


Figure 4. Cyclic voltammograms of the PTVs films on platinum electrode in 0.1 mol/L Bu_4NPF_6, CH_3CN solution.

It should be mentioned here that no photoluminescent (PL) emission was observed in the measurement of the PL spectrum of the biTV−PTVs, which agrees with the nonluminescent characteristic of the poly(thienylene vinylene)s due to the fact that its lowest energy excited state ($2A_g$) to the ground state ($1A_g$) is forbidden.[14]

2.4. Electrochemical Properties. The electrochemical properties of various conjugated polymers have attracted great attention[6,7,15] since the discovery of conducting polymers, because it is one of the most important properties of the conjugated polymers and many applications of the conjugated polymers are depending on the electrochemical properties. Here we studied the electrochemical properties of the biTV−PTVs by cyclic voltammetry and in situ spectroelectrochemical measurements.

Figure 4 shows the cyclic voltammograms (CVs) of the biTV−PTV3 and P3HTV. Since the three polymers of biTV−PTV1−3 showed similar CV curves, we only put the CV of biTV−PTV3 in Figure 3. It can be seen that the biTV−PTVs exhibit reversible p-doping/dedoping (oxidation/rereduction) processes at positive potential range and n-doping/dedoping (reduction/reoxidation) processes at negative potential range.

Table 2. Electrochemical Onset Potentials and Electronic Energy Levels of the Polymer Films

polymers	φ_{ox} (V vs Ag/Ag$^+$)/ E_{HOMO} (eV)	φ_{red} (V vs Ag/Ag$^+$)/ E_{LUMO} (eV)	$E_{g,EC}$ (eV)	$E_{g,opt}$ (eV)[a]
P3HTV	0.09/−4.80	−1.72/−2.99	1.81	1.62
BiTV−PTV1	0.06/−4.77	−1.63/−3.08	1.69	1.61
BiTV−PTV2	0.06/−4.77	−1.62/−3.09	1.68	1.60
BiTV−PTV3	0.06/−4.77	−1.63/−3.08	1.69	1.57

[a] The optical band gap was obtained from empirical formula, $E_g = 1240/\lambda_{edge}$, in which the λ_{edge} is the onset value of the absorption spectrum in the longer wavelength direction.

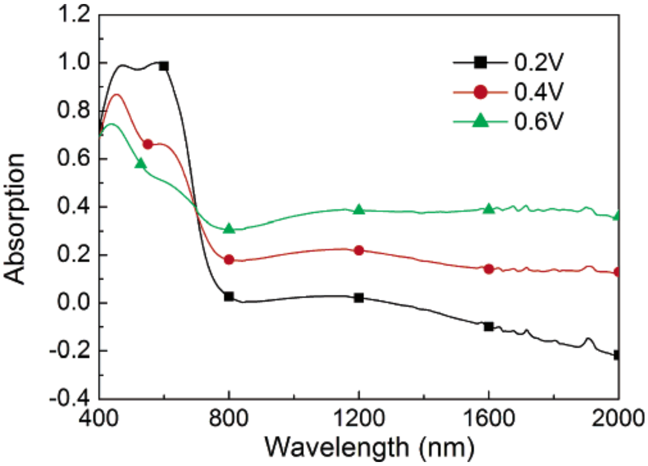


Figure 5. In situ absorption spectra of biTV−PTV3 at different potentials in 0.1 mol/L Bu_4NPF_6, CH_3CN solution.

From the onset oxidation potentials (φ_{ox}) and the onset reduction potentials (φ_{red}) of the polymers, HOMO and LUMO energy levels as well as the energy gap (E_g^{ec}) of the polymers were calculated according to the equations:[16]

$$\mathrm{HOMO} = -e(\varphi_{ox} + 4.71)\ (\mathrm{eV});$$

$$\mathrm{LUMO} = -e(\varphi_{red} + 4.71)\ (\mathrm{eV});$$

$$E_g^{ec} = e(\varphi_{ox} - \varphi_{red})\ (\mathrm{eV})$$

where the units of φ_{ox} and φ_{red} are V vs Ag/Ag$^+$. The values obtained are listed in Table 2. In comparison with P3HTV, φ_{red} of biTV−PTV3 shifted positively by 0.09 V, while φ_{ox} of biTV−PTV3 shifted negatively by ca. 0.03 V, and the electrochemical energy gap of biTV−PTV3 is narrower than that of P3HTV by 0.12 eV. Obviously, the conjugated side chain lowered the LUMO and raised the HOMO of the PTVs. The results of the electrochemical measurements agree with the absorption spectra mentioned above. It is interesting to compare the effect of the bi(thienylene vinylene) (biTV) side chains on the onset oxidation potentials of the biTV−PTVs with that of the biTV−PTs, it is a little negatively shifted for the biTV−PTVs as mentioned above, but it is positively shifted by ca. 0.2 V for the biTV−PTs.[11b] Probably, the branched structure in biTV−PTVs (the same composition of the conjugated side chains and the main chains in the polymers) plays an important role for the negative shift of the biTV−PTVs.

To investigate the electrochemical oxidation mechanism of the biTV−PTVs, in situ absorption spectra of biTV−PTV3 were measured at the potentials of 0.2, 0.4, and 0.6 V vs Ag/Ag$^+$, as shown in Figure 5. It can be seen that with the increase of the potential from 0.2 to 0.6 V, the absorption peak at 605 nm decreases and the absorption in the near-infrared region increases. The appearance of the near-infrared absorption peak and the decrease of the main chain absorption are the characteristics of the doped structure of the conducting polymers such as polypyrrole,[15b] polyaniline,[15a] and poly(3-alkylthoiphene).[17] Therefore, the result in Figure 5 indicates that the main chain of biTV−PTV3 was oxidized and doped in the potential range corresponding to the oxidation peak in Figure 4. In addition, a color change of the polymer film from black to yellow was observed after the oxidation, which indicates that the polymer could be used as an electrochromic material.

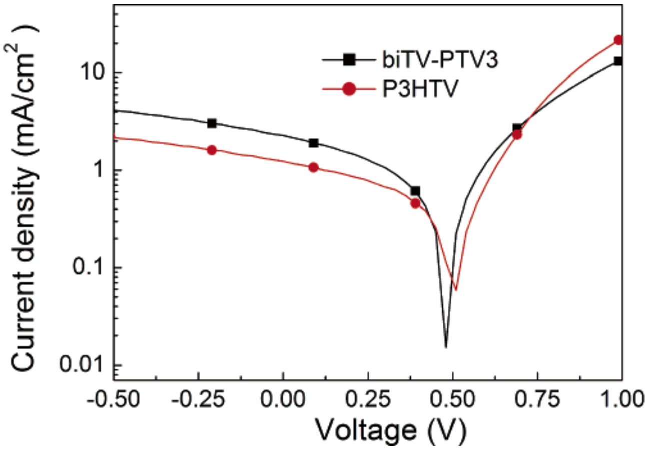


Figure 6. *I*−*V* curves of the polymer solar cells based on biTV−PTV3 and P3HTV under the illumination of AM 1.5, 100 mW/cm^2.

Table 3. Photovoltaic Properties of the Polymer Solar Cells Based on the Blend of Polymer/PCBM (1:1, w/w) under the Illumination of AM 1.5, 100 mW/cm^2

polymers	V_{oc} (V)	I_{sc} (mA/cm^2)	FF	PCE (%)
BiTV−PTV3	0.48	2.27	0.30	0.32
P3HTV[a]	0.51	1.24	0.31	0.21
P3HTV[b]	0.51	1.30	0.32	0.26

[a] The device in this work with the weight ratio of P3HTV: PCBM = 1:1. [b] The device in our previous work,[22] where the weight ratio of P3HTV to PCBM was 1:2.

2.5. Photovoltaic Properties of biTV—PTV3. Polymer solar cells (PSCs) have attracted much interest in recent years,[4,11,18−21] because of their advantages of low cost, light weight, and easy fabrication. For the conjugated polymers used in the PSCs, strong and broad absorptions in visible region as well as high charge carrier mobility are most important for fabricating highly efficient PSCs. As mentioned above, the branched poly(thienylene vinylene) biTV−PTV3 possesses a strong and broad absorption band in visible region; hence, we used it as electron donor material to fabricate bulk heterojunction PSC[4] with the structure of ITO/PEDOT-PSS(30 nm)/biTV−PTV3:PCBM(1:1, w/w, 70 nm)/Mg(10 nm)/Al(150 nm) where PCBM (1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-C_{61}) was used as the electron acceptor. To make clear comparisons with P3HTV, the device based on P3HTV was also fabricated with the same device structure. Figure 6 shows the *I*−*V* curves of the PSCs based on biTV−PTV3 and P3HTV under the illumination of AM 1.5, 100 mW/cm^2, and Table 3 lists the photovoltaic properties obtained from the *I*−*V* curves.

It can be seen from Table 3 that the open circuit voltage (V_{oc}) of the PSC based on biTV−PTV3 was 0.03 V lower than that of the PSC based on P3HTV, which agrees with the 0.03 eV higher of the HOMO level of biTV−PTV3 (see Table 2), since the V_{oc} of PSCs is related to the difference of the LUMO of the acceptor and the HOMO of the donor.[23] The power conversion efficiency (PCE) of the device based on biTV−PTV3 was 0.32% under the illumination of AM 1.5, 100 mW/cm^2, increased by 52% in comparison with that of the device based

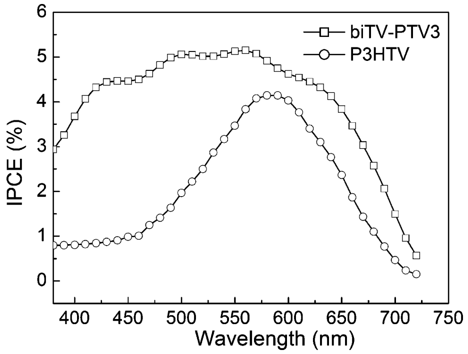


Figure 7. IPCE of the polymer solar cells based on biTV−PTV3 and P3HTV.

on P3HTV under the same experimental conditions. As listed in Table 3, the short circuit current (I_{sc}) of the device based on biTV−PTV3 was 2.27 mA/cm^2, while that of the device based on P3HTV was only 1.24 mA/cm^2, which should be the main reason for the increase of the PCE. Although, the weight ratio of donor to acceptor of 1:1 was not the optimal ratio for P3HTV, the PCE (0.21%) of the device based on P3HTV by this ratio was close to the best results of the PTVs based devices reported by Smith et al. with a value of 0.24%[24] and by us with a value of 0.26%.[22] However, the PCE value of the device based on biTV−PTV3 is much lower than that based on the bi(thienylene vinylene) substituted polythiophenes,[11b] which is probably related to the nonluminescent property of the poly(thienylene vinylene)s.[14]

The input photon to converted current efficiency (IPCE) curves of the devices based on biTV−PTV3 and P3HTV are shown in Figure 7. The IPCE of the device based on P3HTV exhibited a similar to that from the PSC device based on poly(3-dodecylthienylene vinylene).[24] The device based on biTV−PTV3 exhibited a rather broader IPCE curve than that of P3HTV. biTV−PTV3 showed high IPCE values (external quantum efficiency) of 4.5−5.1% in a wide wavelength range from 420 to 660 nm, which is coincident with the broad absorption band of biTV−PTV3 mentioned above. Obviously, the higher I_{sc} value of the device based on biTV−PTV3 was benefited from the broader absorption band of the branched PTV, and it also provided a solid proof that the conjugated side chain enhanced the light harvest ability of the PTVs.

3. Conclusion

Three bi(thienylene vinylene)-substituted poly(thienylene vinylene)s (biTV−PTVs), were synthesized by the Stille coupling reaction. The absorption peaks of the conjugated side chains of the branched biTV−PTVs red-shifted in comparison with that of the monomer biTVT, indicating that the conjugation degree of the side chains is extended in the biTV−PTVs. Most interestingly, the biTV−PTV3 film shows a strong and broad absorption band covering the whole visible region from 380 to 780 nm. Cyclic voltammograms of the polymers indicate that the HOMO and LUMO energy levels of the biTV−PTVs were raised and decreased respectively so that the E_g values of the biTV−PTVs were reduced in comparison with that of P3HTV. In situ absorption spectra of biTV−PTV3 at different potentials reveal that the oxidation of the polymer is accompanied by the p-doping of the conjugated main chains, and the electrochromic phenomen was observed with the color of the biTV−PTV3 film changed from black to yellow after the oxidation by applying higher potentials. Photovoltaic property of biTV−PTV3 was investigated and compared with that of P3HTV, with the polymer solar cells (PSCs) based on the blend of the polymers and PCBM (1:1, w/w) under the illumination of AM 1.5, 100 mW/cm^2. The power conversion efficiency (PCE) of the PSC based on biTV−PTV3 reached 0.32%, which is 52% increased in comparison with that of the device based on P3HTV under the same experimental conditions. Although the PCE of the device based on PTVs is rather lower than the devices based on polythiophenes,[11b,18,19] the results in this paper indicate that the photovoltaic properties of PTVs can be improved by the modulation of their molecular structures.

4. Experimental Section

Materials. The monomer 2,5-dibromo-3-((1*E*)-2-(5-((*E*)-2-(5-dodecylthiophene-2-yl)vinyl)thiophene-2-yl)vinyl)thiophene (biTVT) for the synthesis of the biTV−PTVs, was synthesized by the method reported previously.[11b] 2,5-Dibromo-3-hexylthiophene was synthesized as reported in the literature.[25] The other materials were common commercial level and used as received.

Characterization. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker DMX-300 spectrometer. Absorption spectra were taken on a Hitachi U-3010 UV−vis spectrophotometer. Photoluminescence spectra were measured using a Hitachi F-4500 spectrophotometer. Molecular weight of the polymers was measured by GPC method, and polystyrene was used as a standard. TGA measurement was performed on a Perkin-Elmer TGA-7. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt disk, Pt plate, and Ag/Ag$^+$ electrode as working electrode, counter electrode, and reference electrode respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) acetonitrile solution.

Fabrication and Characterization of Polymer Solar Cells. Polymer solar cells were fabricated with ITO glass as an anode, Mg/Al as a cathode and the blend film of the polymer/PCBM between them as a photosensitive layer. The ITO glass was precleaned and modified by a thin layer of PEDOT:PSS (Bayer) which was spin-cast from a PEDOT:PSS aqueous solution on the ITO substrate, and the thickness of the PEDOT:PSS layer is about 30 nm. The photosensitive layer was prepared by spin-coating a blend solution of the polymer and PCBM with a weight ratio of 1:1 in o-dichlorobenzene at 1000 rpm on the ITO/PEDOT:PSS electrode. Then the metal cathode, which is made up of Mg and Al, was deposited on the polymer layer by vacuum evaporation under 3 × 10^{-4} Pa. The thickness of the photosensitive layer is ca. 70 nm, measured on an Ambios Tech. XP-2 profilometer. The effective area of one cell is ca. 4 mm^2.

The current−voltage ($I-V$) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. A xenon lamp with AM1.5 filter was used as the white light source, and the optical power at the sample was around 100 mW/

Table 4. Components of Monomers in Stille Coupling Reaction & the Elemental Analysis Results and Molecular Weight of the Polymers

	amounts of monomers (mmol)		anal. (%) (calcd/found)[c]			mol wt		
polymers	monomer 1[a]	monomer 2[b]	C	H	S	m:n[d]	M_n	PDI
P3HTV	0	1.0	75.00/74.82	8.33/8.23	16.67/16.45		21K	2.30
BiTV−PTV1	0.5	0.5	- - -/71.82	- - -/7.46	- - -/18.45	1.7	16K	2.41
BiTV−PTV2	0.33	0.66	- - -/72.84	- - -/7.62	- - -/17.86	0.63	26K	1.33
BiTV−PTV3	0.25	0.75	- - -/72.96	- - -/7.82	- - -/17.35	0.35	12K	3.01

[a] biTVT. [b] 2,5-Dibromo-3-hexylthiophene. [c] For biTV−PTV1−3, there was no theoretical elemental content. [d] This value was estimated by the ^{1}H NMR.

cm^2. The input photon to converted current efficiency (IPCE) was measured using a Keithley 195 System DMM coupled with a WDG3 monochromator and a 500 W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

Synthesis of Tributylethynylstannane. In a 500 mL well-dried three-neck flask, 120 mL freshly distilled THF was charged under the protection of N_2, and the flask was cooled by a dry ice/acetone bath. Then, dry acetylene was bubbled in until a saturated solution was obtained. *n*-Butyllithium (35 mL, 0.10 mol, 2.88 mol/L in hexane) was added dropwise. After being stirred for 1 h at -78 °C, the temperature of the reactant was allowed to rise slowly. ***Caution!*** A great deal of flammable gas evolved! It is necessary to carry out this reaction in a well-ventilated hood! When the temperature of the cooling bath was raised to -10 °C, tributylchlorostannane (33 g, 0.1 mol) was added into the flask in one portion. The cooling bath was removed and the solution was stirred overnight. After removing the solvent, the residue was distilled under vacuum. A colorless oil of tributylethynylstannane was obtained after the distillation at 110 °C (131 Pa).

GC$-$MS: $m/z = 315$. ^{1}H NMR (δ/ppm, $CDCl_3$): 2.18 (s, 1H), 1.49$-$1.60 (m, 6 H), 1.25$-$1.36 (m, 6 H), 0.91$-$1.02 (m, 6 H), 0.88 (t, 9 H).

(*E*)-1,2-Bis(tributylstannyl)ethane. This compound was synthesized with the procedure reported by Stille et al.[13] Tributylethynylstannane (15.8 g, 50 mmol) and tributyltin hydride (15.3 g, 52.5 mmol) were put into a flask, and 0.15 g 2,2′-azobis(2-methylpropionitrile) was added. Under the protection of nitrogen, the mixture was heated to 100 °C for 6 h. Distillation (170 °C, 40 Pa) yields 27.5 g (90%) of (*E*)-1,2-bis(tributylstannyl) ethylene as a clear, colorless oil.

GC$-$MS: $m/z = 606$. Purity (by GC/Ms) > 97%. ^{1}H NMR (δ/ppm, $CDCl_3$): 6.82 (s, 2H), 1.49$-$1.65 (m, 12 H), 1.25$-$1.46 (m, 12 H), 0.80$-$1.0 (m, 30 H). Anal. Calcd for $C_{26}H_{56}Sn_2$: C, 51.52; H, 9.31; Found: C, 51.32; H, 9.78.

2,5-Dibromo-3-((1*E*)-2-(5-((*E*)-2-(5-dodecylthiophen-2-yl)-vinyl)thiophen-2-yl)vinyl)thiophene (biTVT). biTVT was synthesized by the method reported in ref 11b. GC$-$MS: $m/z = 624$. ^{13}C NMR (δ/ppm, $CDCl_3$): 145.98, 142.70, 140.34, 139.86, 138.81, 128.02, 127.10, 126.56, 124,75, 124.33, 122.60, 119.98, 119.25, 111.91, 109.78, 31.93, 31.50, 30.43, 29.67, 29.65, 29.57, 29.37, 29.18, 29.10, 22.70, 14.15. ^{1}H NMR (δ/ppm, $CDCl_3$): 7.14 (s, 1H), 7.00$-$6.64 (m, 8H), 2.79 (t, 2H), 1.67 (p, 2H), 1.33$-$1.10 (m, 18H), 0.89 (t, 3H). Anal. Calcd for $C_{28}H_{34}Br_2S_3$: C, 53.67; H, 5.47; Br, 25.51; S, 15.35. Found: C, 53.58; H, 5.62; Br, 25.34; S, 15.22.

Synthesis of the Polymers Using the Stille Coupling Reaction. biTV$-$PTV1$-$3 and P3HTV were prepared by a similar procedure of coupling 2,5-dibromo-3-substituted-thiophene monomers with (*E*)-1,2-bis(tributylstannyl)ethane. The monomers used were 2,5-dibromo-3-hexylthiophene for P3HTV, in the first case, and biTVT and 2,5-dibromo-3-hexylthiophene for biTV$-$PTV1$-$3, and the detailed contents of the monomers for the synthesis of each polymer are listed in Table 4. First, 1.0 mmol of the monomer or the monomer mixtures was put into a three-neck flask. Then, 15 mL of degassed toluene and 1.0 mmol of (*E*)-1,2-bis(tributylstannyl)-ethane were added under the protection of argon. The solution was flushed with argon for 10 min, and then 50 mg of $Pd(PPh_3)_4$ was added. After another flushing with argon for 20 min, the reactant was heated to reflux for 12 h. Then the reactant was cooled to room temperature, and the polymer was precipitated by adding 50 mL methanol, and filtered through a Soxhlet thimble, then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was recovered as solid from the chloroform fraction by rotary evaporation. The solid was dried under vacuum for 1 day. In the preparation of the 4 polymers, the yield of the polymerization reactions were about 35$-$60%. The elemental analysis results and the molecular weight of the polymers are also listed in Table 4.

Acknowledgment. This work was supported by NSFC (No. 50373050, 20373078, 20474069, 20421101, 20574078, and 60440420149) and The Ministry of Science and Technology of China (973 Project, No. 2002CB613404).

References and Notes

(1) (a) Shirakawa, H.; Louis, E. L.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578. (b) Chiang, C. K.; Fincher, C. R., Jr.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. L.; Gau, S. C.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098.

(2) Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds. *Handbook of Conducting Polymers*, 2nd ed.: Marcel Dekker: New York, 1998; Chapters 32$-$38.

(3) (a) Ouyang, J. Y.; Li, Y. F. *Polymer* **1997**, *38*, 1971. (b) Ouyang, J. Y.; Li, Y. F. *Polymer* **1997**, *38*, 3997.(c) Li, Y. F.; Ouyang, J. Y. *Synth. Met.* **2000**, *113*, 23. (d) He, C.; Li, Y. F. *Synth. Met.* **2003**, *139*, 417.

(4) (a) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789. (b) Brabec, C. J. *Solar Energy Mater. Solar Cells* **2004**, *83*, 273.

(5) (a) Kumar, A.; Welsh, D. M.; Morvant, M. C.; Piroux, F.; Abboud, K. A.; Reynolds, J. R. *Chem. Mater.* **1998**, *10*, 896. (b) Sonmez, G.; Shen, C. K. F.; Rubin, Y.; Wudl, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 1498.

(6) (a) Mu, S. L.; Ye, J. H.; Wang, Y. H. J. *Power Sources* **1993**, *45*, 153. (b) Wang, P.; Li, Y. F. *J. Electroanal. Chem.*, **1996**, *408*, 77. (c) Shi, Y. J.; Yang, Y. F.; Kan, J. Q.; Mu, S. L.; Li, Y. F. *Biosensors Bioelectron.* **1997**, *12*, 655.

(7) Li, Y. F.; Cao, Y.; Gao, J.; Wang, D. L.; Yu, G.; Heeger, A. J. *Synth. Met.* **1999**, *99*, 243.

(8) (a) Tang, R. P.; Tan, Z. A.; Li, Y. F.; Xi, F. *Chem. Mater.* **2006**, *18*, 1053$-$1061. (b) Hou, J. H.; Fan, B. H.; Huo, L. J.; He, C.; Yang, C. H.; Li, Y. F. *J. Polym. Sci., A: Polym. Chem.* **2006**, *44*, 1279$-$1290.

(9) Wilson, J. N.; Windscheif, P. M.; Evans, U.; Myrick, M. L.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, 8681.

(10) (a) Hou, J. H.; Yang, C. H.; Li, Y. F. *Synth. Met.* **2005**, *153*, 93. (b) Hou, J. H.; Huo, L. J.; He, C.; Yang, C. H.; Li, Y. F. *Macromolecules*, **2006**, *39*, 594.

(11) (a) Hou, J. H.; Yang, C. H.; He, C.; Li, Y. F. *Chem. Commun.* **2006**, 871$-$873. (b) Hou, J. H.; Tan, Z. A.; Yan, Y.; He, Y. J.; Yang, C. H.; Li, Y. F. *J. Am. Chem. Soc.* **2006**, *128*, 4911.

(12) (a) Eckhardt, H.; Shacklette, L. W.; Jen, K. Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, *91*, 1303. (b) Loewe, R. S.; McCullough, R. D. *Chem. Mater.* **2000**, *12*, 3214.

(13) Renaldo, A. F.; Labadie, J. W.; Stille, J. K. *Org. Synth.* **1993**, *Collect. Vol. 8*, 268.

(14) Brassett, A. J.; Colaneri, N. F.; Bradley, D. D. C.; Lawrence, R. A.; Friend, R. H.; Murata, H.; Tokito, S.; Tsutsui, T.; Saito, S. *Phys. Rev. B* **1990**, *41*, 10586.

(15) (a) Li, Y. F.; Yan, B. Z.; Yang, J.; Cao, Y.; Qian, R. Y. *Synth. Met.* **1988**, *25*, 79. (b) Li, Y. F.; Qian, R. Y. *J. Electroanal. Chem.* **1993**, *362*, 267.

(16) Sun, Q. J.; Wang, H. Q.; Yang, C. H.; Li, Y. F. *J. Mater. Chem.* **2003**, *13*, 800.

(17) Louarn, G.; Trznadel, M.; Buisson, J. P.; Laska, J.; Pron, A.; Lapkowski, M.; Lefrant, S. *J. Phys. Chem.* **1996**, *100*, 12532.

(18) (a) Ma, W. L.; Yang, C. Y.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617. (b) Reyes-Reyes, M.; Kim, K.; Carroll, D. L. *Appl. Phys. Lett.* **2005**, *87*, 083506.

(19) (a) Li, G.; Shrotriya, V.; Yao, Y.; Yang, Y. *J. Appl. Phys.* **2005**, *98*, 043704. (b) Li, G.; Shrotriya, V.; Huang, J. S.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864.

(20) Wang, F.; Luo, J.; Yang, K. X.; Chen, J. W.; Huang, F.; Cao, Y. *Macromolecules* **2005**, *38*, 2253.

(21) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; Mcculloch, I.; Ha, C. S.; Ree, M. *Nat. Mater.* **2006**, *5*, 197.

(22) Hou, J. H.; Yang, C. H.; Qiao, J.; Li, Y. F. *Synth. Met.* **2005**, *150*, 297.

(23) (a) Mihailetchi, V. D.; Blorn, P. W. M.; Hummelen, J. C.; Rispens, M. T. *J. Appl. Phys.* **2003**, *94*, 6849. (b) Dyakonov, V. *Appl. Phys. A: Mater. Sci. Process.* **2004**, *79*, 21.

(24) Smith, A. P.; Smith, R. R.; Taylor, B. E.; Durstock, M. F. *Chem. Mater.* **2004**, *16*, 4687.

(25) Loewe, R. S.; Ewbank, P. C.; Liu, J. S.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324.

MA060662U