Synthesis and Absorption Spectra of Poly(3-(phenylenevinyl)thiophene)s with Conjugated Side Chains

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ABSTRACT: Six soluble polythiophene derivatives with phenylene−vinylene conjugated side chains were synthesized by GRIM or Stille methods. The absorption spectra of the polymers show two peaks located in the UV and visible region, where the visible absorption peak is attributed to the $\pi-\pi^*$ transition of the conjugated main chains and the UV absorption peak results from the conjugated side chains. By doubling the conjugation length of the phenylene−vinylene side chains and reducing the concentration of the conjugated side chains, we synthesized PT4, which possesses a strong and broad absorption in the visible region from 380 to 650 nm and is promising for the application in polymer solar cells. For the polymers of PEHPVT and PMEHPVT where every thiophene unit is attached with a conjugated side chain, the absorption spectra of their films red-shifted by 30 and 50 nm, respectively, in comparison with their solution. After thermal annealing at 130 °C for 10 min, the absorption of the films red-shifted further, and the band gap of the polymers was reduced. XRD results reveal that the ordering structure of the two polymers was enhanced and their interlayer *d*-spacing expanded after the annealing. Cyclic voltammograms display that the p-doping/dedoping and n-doping/dedoping processes of all the six polymers are reversible. The HOMO and LUMO energy levels and energy gap of the polymers were calculated from the electrochemical measurements.

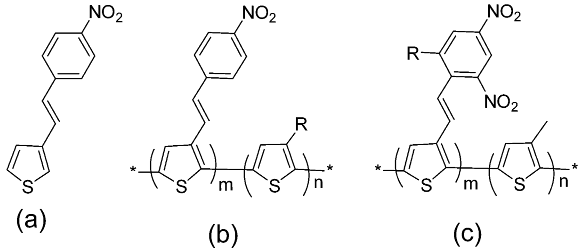
1. Introduction

Polythiophene (PT) and its derivatives have attracted considerable attention since the discovery of conducting polymers in 1977 due to their versatile applications in the fields of conducting polymers and conjugated polymer optoelectronic devices.[1] For the applications such as the optoelectronic materials, PTs are broadly used in polymer light-emitting diodes (PLEDs),[2] polymer field effect transistors (PFETs),[3] and polymer photovoltaic cells (PPVCs).[4] Especially for PFETs and PPVCs, PTs are the most promising conjugated polymers because of its relatively higher charge carrier mobility in comparison with other conjugated polymers. For example, regioregular poly(3-alkylthiophene)s have exhibited very interesting properties in the optoelectronic devices,[5] and efficient PPVCs have been fabricated with poly(3-alkylthiophene).[6,7] To further improve the related properties and explore the full potential applications of these materials, chemical modifications of PTs have been performed actively in recent years.[8]

Most of the modifications on PTs focused on side-chain functionalization or end-group functionalization of the conjugated polymers. To modify the electronic properties of polythiophene, such as redox cycling,[9] band gap,[10] and photovoltaic behavior,[11] aromatic substituents have been introduced into polythiophenes. For example, poly(3-arylthiophenes) have improved the doping capacity and cyclability of polythiophene,[12] and poly(isothianaphthene) by fusing benzene to thiophene leads to the prototypical small-band-gap polymer.[13]

Recently, Greenwald and co-workers introduced a nitro-substituted styryl group into the 3-position of polythiophene (polymer **b** in Scheme 1) to improve the photoconductivity of polythiophene.[14] In 1994, Smith et al. reported that electrochemical homopolymerization of styryl-substituted thiophenes (polymer **a** in Scheme 1) produced a nonconductive material; presumably the polymerization was carried out through side-chain connection.[15] Electrically conducting polymers (polymer **c** in Scheme 1) were obtained by copolymerization of styryl derivatives with 3-methylthiophene.[16] Although the polymers in Scheme 1, which are attached with the conjugated styryl side chains, have been reported in the literature, they were synthesized by oxidation polymerization and have irregular and random structures. Moreover, the effect of the conjugated side chains on the absorption spectra of the polymers has not been studied. To look for new photovoltaic conjugated polymer materials, we synthesized a series of PT derivatives, poly[3-(phenylenevinyl)thiophene] (P3PVT), with the conjugated phenylene−vinylene side chains by GRIM[17] and Stille[18] methods in this paper. The molecular structures of the PTs are shown in Scheme 2. With this synthesis route, we obtained the PT derivatives with high purity and good solubility. The absorption spectra and electrochemical properties of the PTs were systematically characterized and described.

Scheme 1. Molecular Structure of Some Styryl-Substituted Polythiophenes



2. Results and Discussion

2.1. Synthesis of P3PVTs. Synthetic routes of the poly[3-(phenylenevinyl)thiophene] (P3PVT)s are shown in Schemes 3−5.

Monomers of the P3PVTs were synthesized by the Horner−Emmons reaction. Figure 1 shows the ^{1}H NMR spectrum of

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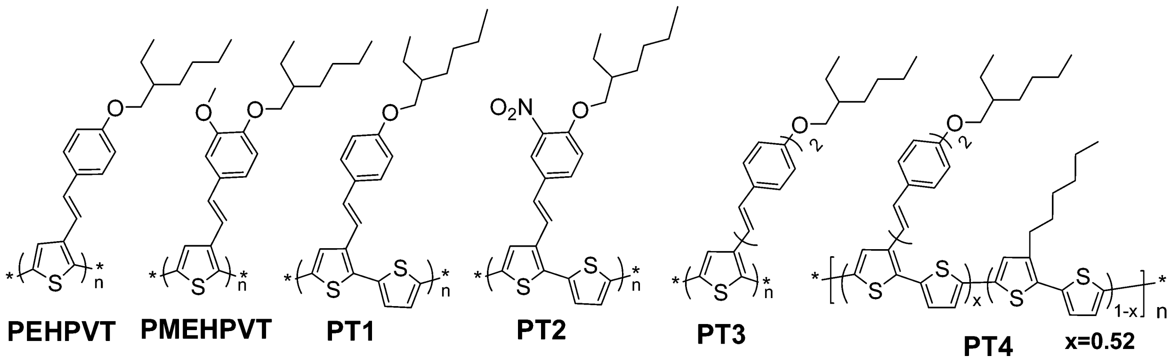
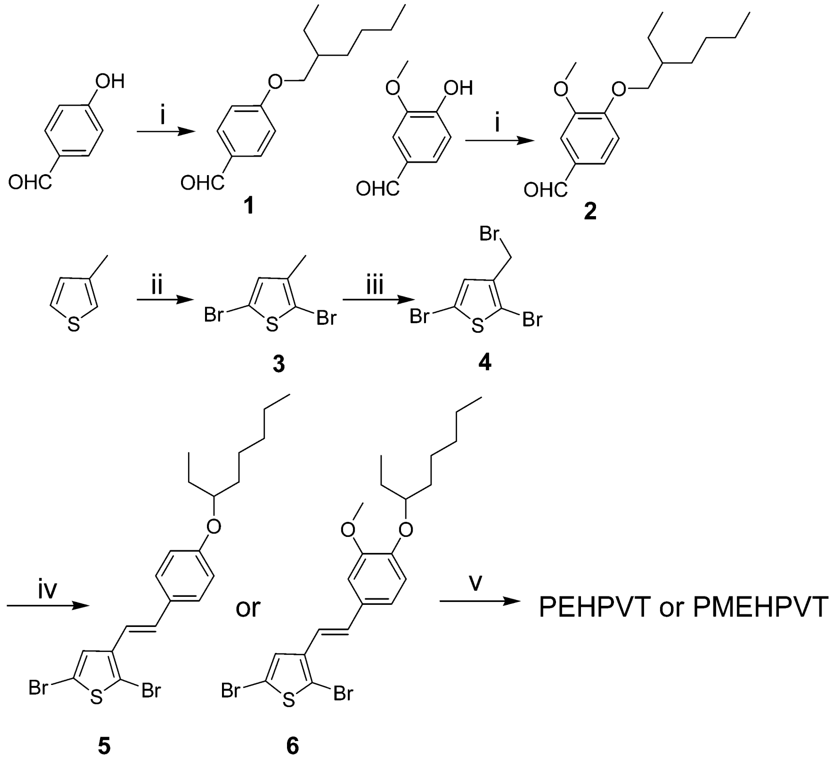
Scheme 2. Molecular Structures of the Phenylene−Vinylene-Substituted Polythiophenes

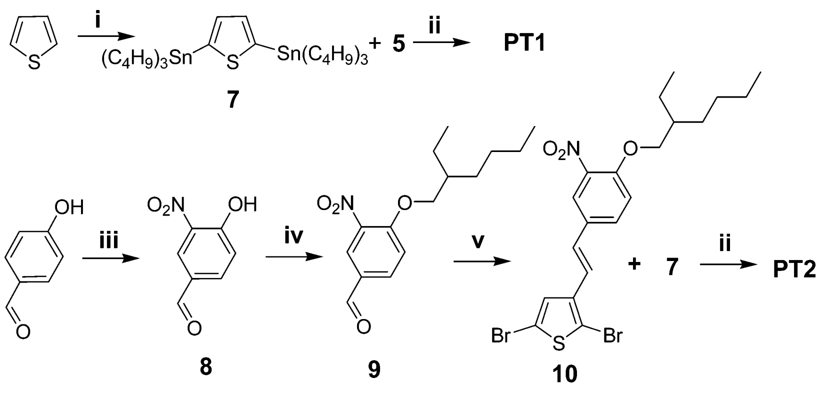


Scheme 3. Synthesis of PEHPVT and PMEHPVT[a]



[a] (i) $BrCH_2CH(C_2H_5)(CH_2)_3CH_3$, K_2CO_3, DMF, reflux, 4 h; (ii) NBS, CH_3Cl/HOAc, 2 h; (iii) NBS, BPO, CCl_4, reflux, 3 h; (iv) $P(OC_2H_5)_3$, 160 °C, 2 h; then 1 or 2, $NaOCH_3$, DMF, 20 °C, 30 min; (v) CH_3MgBr, THF, reflux, 1 h, then $Ni(dppp)Cl_2$, reflux, 1 h.

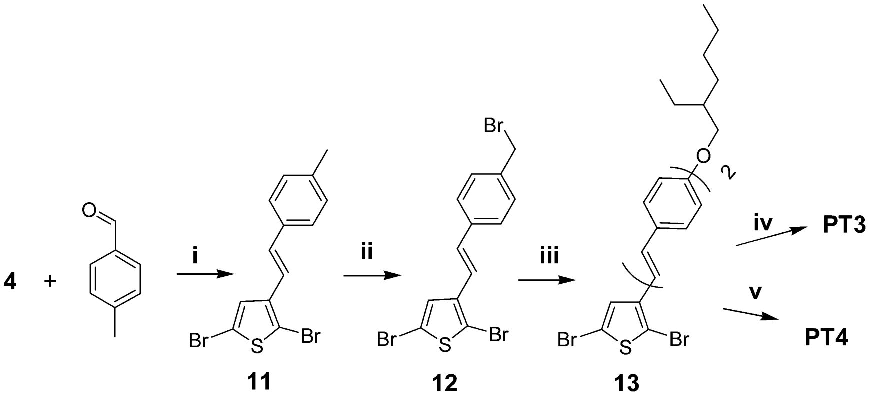
Scheme 4. Synthesis of PT1 and PT2[a]



[a] (i) *n*-butyllithium, THF, reflux, 1 h; then $(C_4H_9)_3SnCl$, rt, overnight; (ii) $Pd(PPh_3)_4$, toluene, Ar, reflux, 12 h; (iii) HNO_3(fuming), HOAc, 0 °C; (iv) $BrCH_2CH(C_2H_5)(CH_2)_3CH_3$, K_2CO_3, DMF, reflux, 4 h; (v) compound **4**, $P(OC_2H_5)_3$, 160 °C, 2 h; then compound **9**, $NaOCH_3$, DMF, 20 °C, 30 min.

the monomer of 2,5-dibromo-3-[4-(2-ethylhexyloxy)phenylene−vinyl]thiophene (compound **5** in Scheme 3). The two protons in the vinyl unit at 6.8−7.1 ppm exhibit four very neat peaks, and no obvious *cis*-isomer was detected. The ^{1}H NMR result indicates that the main product of the reaction was the *trans*-isomer, and from compounds **6**, **11**, and **13**, the same results were obtained. However, in the ^{1}H NMR spectrum of compound **10**, as shown in Figure 1b, the amount of *cis*-isomer increased,

Scheme 5. Synthesis Rout of PT3 and PT4[a]



[a] (i) Compound **4**, $P(OC_2H_5)_3$, 160 °C, 2 h; then 4-methylbenzaldehyde, $NaOCH_3$, DMF, 20 °C, 30 min; (ii) NBS, BPO, CCl_4, reflux, 3 h; (iii) $P(OC_2H_5)_3$, 160 °C, 2 h; then compound **1**, $NaOCH_3$, DMF, 20 °C, 30 min; (iv) CH_3MgBr, THF, reflux, 1 h, then $Ni(dppp)Cl_2$, reflux, 1 h; (v) compound **7** $Pd(PPh_3)_4$, toluene, Ar, reflux, 12 h.

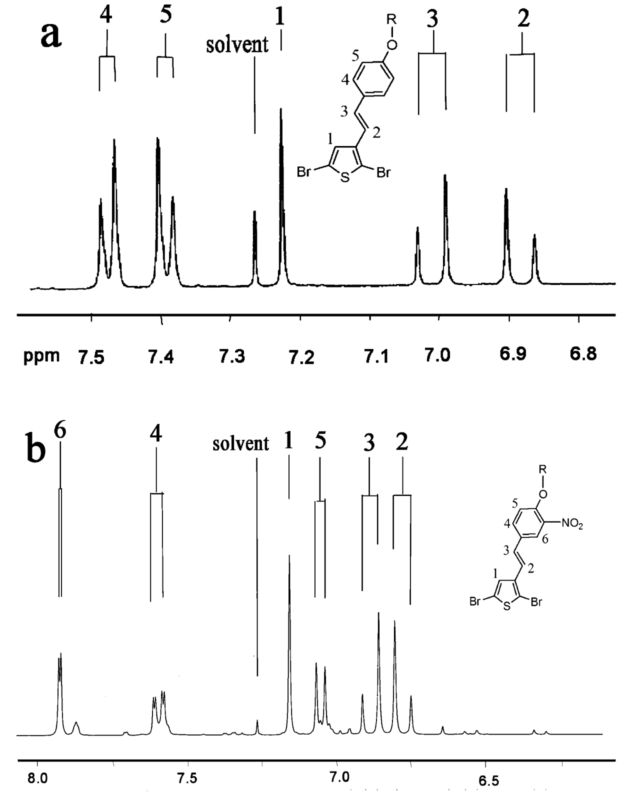


Figure 1. ^{1}H NMR spectra in aromatic region of (a) 2,5-dibromo-3-[4-(2-ethylhexyloxy)phenylenevinyl]thiophene and (b) 2,5-dibromo-3-[4-(2-ethylhexyloxy)-3-nitrophenylenevinyl]thiophene.

which exhibits four weak peaks at 6.60−6.30 ppm, and the ratio of the *trans*-isomer to *cis*-isomer is about 95:5. These results indicate that we could get holo *trans*-monomers from the Horner−Emmons reaction, except for compound **10**.

Polythiophenes can be prepared by the chemical or electrochemical oxidation polymerization directly or by Pd- or Ni-catalyzed coupling reaction of organometallic reagents with organic halides,[19] including the Grignard metathesis method[17] and the Stille method.[18] The GRIM (Grignard metathesis) method and Stille method have been used to produce regioregular, head-to-tail (HT) poly(3-alkylthiophene),[17,18] so we chose the two methods to synthesize the P3PVTs. By the GRIM method, PEHPVT and PMEHPVT were synthesized with high molecular weight (M_n > 22K). But the M_n of PT3 synthesized by this method was only 4.3K. We thought that steric hindrance of the big side chains of PT3 should be the main reason for the low polymerization degree. The polymers of PT2, PT3, and PT4, with high molecular weight (M_n = 62K for PT2) and low polymerization dispersity (PDs = 1.6 for PT2), were synthesized by the Stille coupling reaction between 2,5-bis(tributylstannyl)-thiophene and 2,5-dibromo-3-substituted thiophenes.

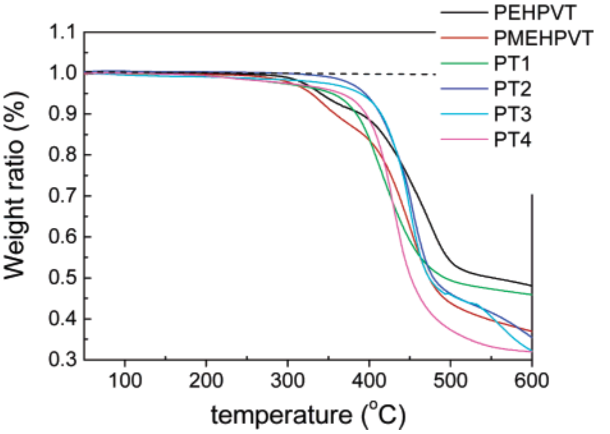


Figure 2. TGA plots of the polymers with a heating rate of 10 °C/min.

The regularity of poly(3-alkylthiophene)s and poly(3-arylthiophene)s can be determined by^{1}H NMR.[20] But for PEHPVT and PMEHPVT, the chemical shift of the proton on the 4-position of thiophene is overlapped with the proton on vinyl units, so regularity of them could not be analyzed with ^{1}H NMR.

2.2. Thermal Stability. Figure 2 shows the thermogravimetric analysis (TGA) plots of the P3PVTs. The TGA results reveal that the onset decomposition temperatures of the polymers are around 300 °C in nitrogen, which indicates that the polymers are as stable as ploy(3-alkylthiophene).[21] Obviously, the stability of the polymers is adequate for the fabrication processes of PPVCs and other optoelectronic devices.

2.3. UV−vis Absorption and PL Spectra of the Polymer Solutions. The UV−vis absorption spectra could provide a good deal of information on the electronic structures of the conjugated polymers. Figure 3a shows the UV−vis normalized absorption spectra of the polymer solutions. These polymers show two maximum absorption peaks: the one in visible region is attributed to the $\pi-\pi^*$ transition of the conjugated polymer main chains; another in the UV region is attributed to the conjugated side chains. It is well-known that an electron donor substitution on the conjugated polymer chains could reduce the band gap efficiently.[22] For example, the band gap of poly(3-alkyloxythiophene) is narrower than that of poly(3-alkylthiophene).[23]

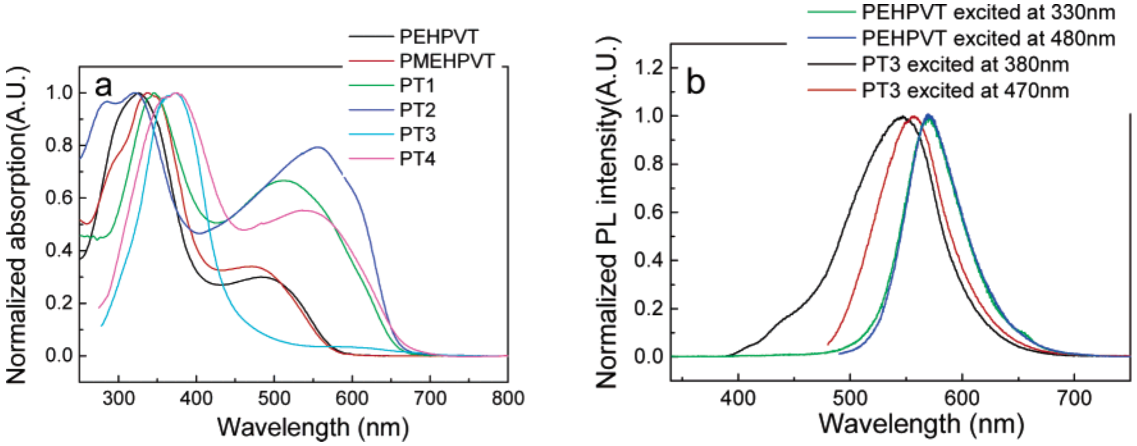


Figure 3. (a**)** Normalized absorption spectra of the polymer solutions in chloroform with the concentration of ca. 0.1 mg/mL. (b**)** PL spectra of PEHPVT (green line, excited at 330 nm, and blue line, excited at 480 nm) and PT3 (black line, excited at 380 nm, and red line, excited at 470 nm), in chloroform solution with a concentration of 10 μg/mL.

The UV−vis absorption spectra of PEHPVT and PMEHPVT solutions (see Figure 3a) indicate that the electron donor substituents (methoxy) on the conjugated side chain of PMEHPVT have little influence on the visible region absorption but have an obvious influence on the UV absorption of the polymer solution. (The UV absorption peak of PMEHPVT is 19 nm red-shifted in comparison with that of PEHPVT.) In comparison with the UV−vis absorption spectrum of P3OPT (poly(3-(4-octylphenyl)thiophene) solution (peaked at 467 nm[24]), the absorption of PEHPVT and PMEHPVT main chains red-shifted, which indicates a lower $\pi-\pi^*$ transition energy or a lower band gap of the two polymers. The lower band gap of the P3PVTs could be attributed to the extended conjugation system of the polymers benefited from the coplanarity of the phenylene unit in the side chain and the thiophene unit in the main chain through the linkage of the vinyl bond.

With increasing the length of side chains of the polymers, the absorption of side chains red-shifted from 324 nm (for PEHPVT) to 373 nm (for PT3), but the absorption of main chains is weakened greatly. To enhance the absorbance of main chains in the visible region, the content of main chains in the whole macromolecules should be increased, so PT1 and PT4 were designed and synthesized. As expected, the absorbance of main chains for PT1 and PT4 was increased greatly (see Figure 3a). In addition, the main-chain absorption of PT1 red-shifted greatly in comparison with PEHPVT. Obviously, the lessening of the steric hindrance in PT1 could be the reason for the red-shift.

We also measured the PL spectra of the polymers in solution, excited at the two wavelengths corresponding to the two absorption peaks; for example, PEHPVT was excited at 330 and 480 nm. Interestingly, as shown in Figure 3b, the PL spectra of PEHPVT excited at the two wavelengths are the same, which indicates that there is a thorough intramolecular energy transfer of the excitons from the conjugated side chains to the main chains when the polymer was excited by 330 nm. The phenomenon was also observed for the other P3PVTs, except PT3. The PL spectrum of PT3 excited at 380 nm shows a main peak at ca. 540 nm with a weak shoulder peak at ca. 440 nm. The 540 nm PL peak is quite close to the PL peak excited at 470 nm. The PL spectra of PTs indicate that although the absorbance of the main chains is much weaker than that of the side chains (see Figure 3a); when it was excited at 380 nm, a majority of the excitons on the side chains were still transferred to the main chains.

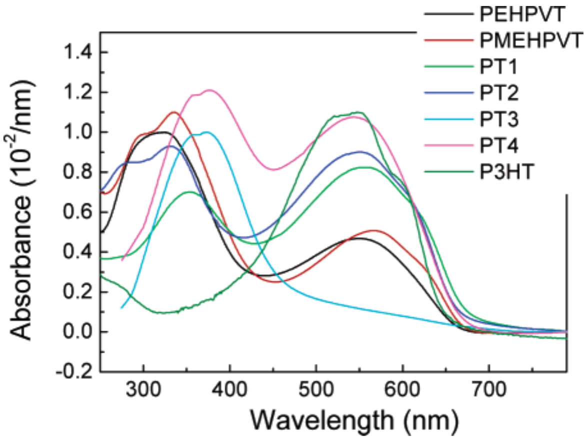


Figure 4. Absorption spectra of the polymer films spin-coated from tetrahydrofuran solution. (for PT3, the absorbance is reduced to one-third).

2.4. UV−vis Absorption Spectra of the Polymer Films. For most of the applications of conjugated polymers, such as photovoltaic cells and photodetectors, the absorbance of the polymer thin films, especially the absorbance in the visible region, is an important parameter. Figure 4 shows the absorbance of the polymer films with the unit of 10^{-2} per nm thickness, and Table 1 lists the peak absorbance values of the polymers corresponding to their UV and visible absorption peaks. In comparison with the PEHPVT film, the PMEHPVT film shows stronger absorbance, and the same is PT2 in comparison with PT1. These results indicate that the polymer absorbance can be enhanced by the substitution of auxochrome groups on the conjugated side chains. In addition, in comparison with the absorption spectra of the polymer solutions, the UV absorption peaks of the PEHPVT and PMEHPVT films remain the same, while their visible absorption peaks red-shifted by 30 and 50 nm, respectively. The red-shift of the $\pi-\pi^*$ transition of the polymer films should be due to the strong interaction between the polymer chains in the solid films.

For the convenience of discussion, we will discuss the effect of molecular structure on the absorbance of the visible peak and UV peak separately. For the most important visible absorption peak corresponding to the absorption of polymer main chains, it can be seen from Figure 3b that the absorbance of PEHPVT and PMEHPVT with every thiophene units attached with the conjugated side chains is weak, and that of PT3 with double length of its conjugated side chains is the weakest. The absorbance is enhanced and improved greatly for the copolymers

Table 1. Optical Absorption and Cyclic Voltammetric Results of the Polymer Films

	λ_{max} (nm)/absorbance (10^{-2}/nm)[a]		integral area[b]	optical E_g[c] (eV)	E_{red}(V)/LUMO[e] (eV)	E_{ox}(V)/HOMO[e] (eV)	electrochemical E_g (eV)
	side chain	main chain					
PEHPVT	328/0.99	550/0.47	0.95	1.85	−1.79/−2.91	0.23/−4.93	2.01
PMEHPVT	336/1.09	566/0.50	1.04	1.80	−1.76/−2.94	0.21/−4.91	1.97
PT1	356/0.70	560/0.82	1.73	1.82	−1.82/−2.88	0.28/−4.98	2.10
PT2	330/0.93	552/0.90	1.83	1.81	−1.62/−3.08	0.19/−4.89	1.81
PT3	371/3.10	544/0.33	0.75		−1.91/−2.79	0.31/−5.11	2.22
PT4	380/1.21	544/1.07	2.51	1.82	−1.82/−2.88	0.30/−5.10	2.12
P3HT		549/1.10	1.76	1.88			

[a] This value was obtained from dividing the maximum absorbance in visible region by the thickness of film. [b] Integral area of the absorbance of per nanomerter thick films in visible region. [c] The optical band gap was obtained from the empirical formula $E_g = 1240/\lambda_{edge}$, in which the λ_{edge} is the onset value of absorption spectrum in long wave direction.

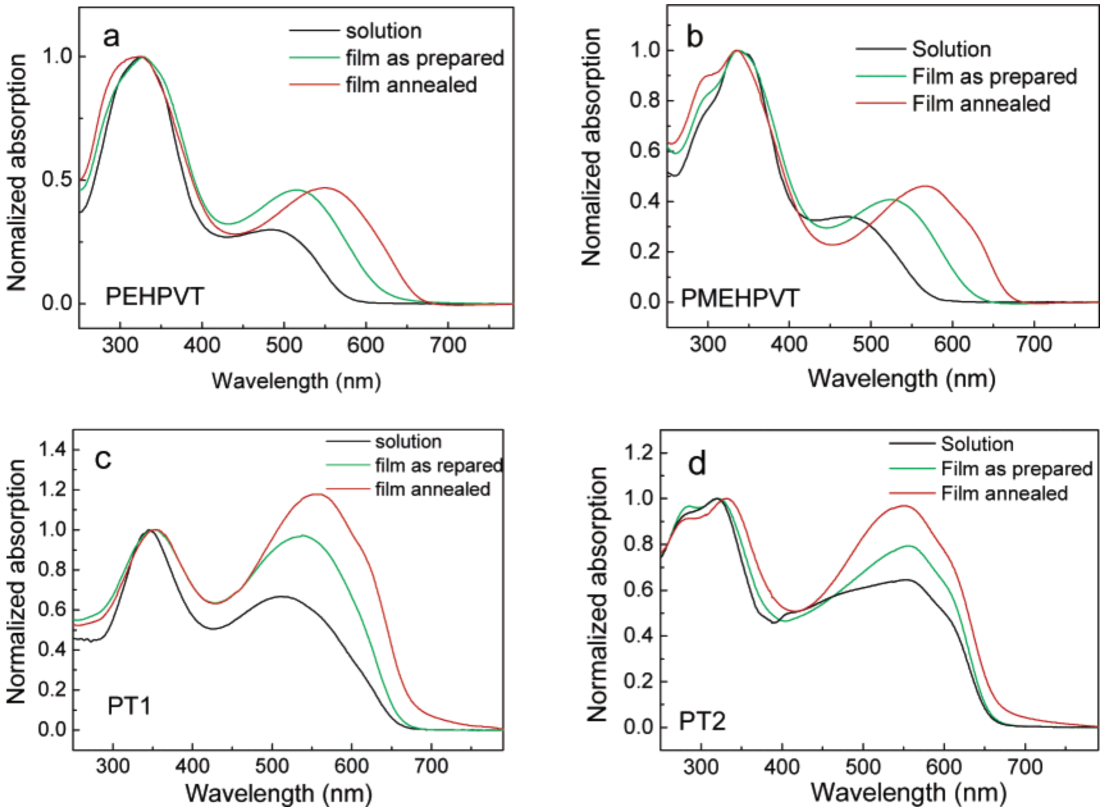


Figure 5. Absorption spectra of PEHPVT (a), PMEHPVT (b), PT1 (c), and PT2 (d) solutions in chloroform (red line), solid film (green line), and the annealed film at 130 °C for 10 min under an inert atmosphere (red line).

of thiophenes with and without the conjugated side chains, such as PT1, PT2, and PT4. For example, the peak absorbance of PEHPVT at 545 nm is only 0.47×10^{-2}/nm, while that of PT4 at 540 nm increased to 1.07×10^{-2}/nm, which is quite close to that of P3HT (see Table 1). Obviously, the steric hindrance of the big side chains and the lower concentration of the main chains in comparison with the side chains are responsible for the weak absorbance in the visible region for the polymers of PEHPVT, PMEHPVT, and PT3.

For the absorbance in the UV region, PEHPVT and PMEHPVT possess strong absorbance peaks at ca. 330 nm; PT3 shows the strongest peak absorbance (3.1×10^{-2}/nm), and its UV absorption peak red-shifted to 371 nm. For polymer PT4, the absorption peak further red-shifted to 380 nm, and the absorbance remains a moderate value of 1.21×10^{-2}/nm at 380 nm. For increasing light harvest to improve the power conversion efficiency of the polymer solar cells, strong absorbance and broad absorption of the conjugated polymers are both needed. Comparing the absorption spectra (see Figure 4) of PT4 with P3HT, which is the best polymer used in the polymer solar cells at present, it can be seen that PT4 has a much broader absorption than P3HT in the visible region, especially in the range from 380 to 480 nm. The integral area of the absorption spectra of PT4 and P3HT in the visible region is about 2.51 and 1.76, respectively (which is also listed in Table 1); the former is much greater than the latter. Obviously, PT4 should be a promising material for the application in polymer solar cells.

2.5. Thermal Annealing Effect of PEHPVT and PMEHPVT Films. As mentioned above, the visible absorption spectra of PEHPVT and PMEHPVT films red-shifted obviously in comparison with their solution. Very interestingly, the visible absorption peak of the polymer films red-shifted further to 540 nm for PEHPVT and 566 nm for PMEHPVT, while the UV absorption peaks remain unchanged after the films were treated at 130 °C for 10 min, as shown in Figure 5a,b. After the thermal annealing, the band gap of the two polymers calculated from their absorption edge is 1.85 and 1.80 eV, respectively. This phenomenon was also observed in some other polythiophene derivatives. For example, when the film of regioregular poly[3-(4-octylphenyl)thiophene] (P3OPT) was thermally annealed or treated in chloroform vapor, its band gap reduced from 2.1

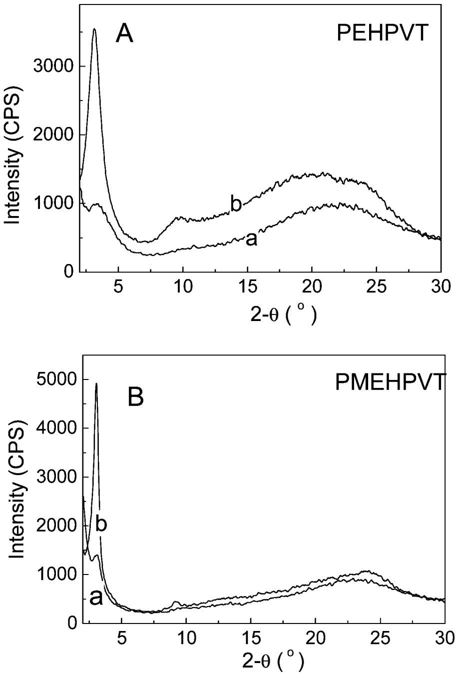


Figure 6. XRD patterns of PEHPVT (A) and PMEHPVT (B) powder, which was precipitated from THF solution by the addition of methanol and well dried under vacuum: as-prepared samples (line a) and the samples after thermal annealing at 130 °C for 30 min (line b).

to 1.85 eV, along with significant increase of structure ordering.[25]

Why the absorption in visible region of the annealed PEHPVT and PMEHPVT films could red-shift so much and the absorption in UV region remains unchanged? We propose that, in every thiophene unit of the polymer main chains of the as-prepared polymer films, the phenylene−vinyl side chain may keep in a plane with thiophene, but the whole polymer main chain and the aggregation state of the as-prepared polymer film were not in the lowest energy state. When the film was thermally annealed, the macromolecular chains of the polymer could realign, and then the conjugation effect could be enhanced. So the band gap of the polymers, which determines the absorption of the $\pi-\pi^*$ transition of the main chain, could be decreased after the thermal annealing. For PEHPVT and PMEHPVT, we do find such ordering transformation after the thermal annealing from XRD measurement, which will be discussed in the following.

Figure 6 shows the XRD patterns of the PEHPVT and PMEHPVT samples. The as-prepared powder samples of PEHPVT and PMEHPVT exhibited weak diffraction at $2\theta = 3.50°$ and 3.42°, respectively (corresponding to interlayer *d*-spacing: 2.52 nm for PEHPVT and 2.49 nm for PMEHPVT), and the annealed samples of PEHPVT and PMEHPVT exhibited enhanced diffraction at $2\theta = 3.14°$ and 3.04°, respectively (corresponding to the *d*-spacing: 2.81 nm for PEHPVT and 2.90 nm for PMEHPVT). The XRD results indicate that the heat treatment helps the polymer main chains realign, and an ordering structure forms. Obviously, after the P3PVTs (PEHPVT and PMEHPVT) were thermally annealed, effective conjugation length of the polymers was prolonged, which results in the band-gap reduction.

The XRD patterns of the P3PVTs are not as sharp as that of the regioregular P3HT (rr-P3HT),[26] which indicates that the ordering of the lamella structure of the P3PVTs is less than that of the rr-P3HT. Probably, the branched side chains in the P3PVTs hinder the packing of the polymer main chains. Therefore, after alternate copolymerization of the thiophene units with and without the conjugated side chains, such as PT1 and PT2, the steric hindrance of the big side chains of the polymer is reduced, so the as-prepared film of PT1 shows lower band gap than PEHPVT. After being thermally annealed, the absorption of PT1 and PT2 films only red-shifted a little, as shown in Figure 5c,d. For PT3 and PT4, there is almost no annealing effect on the absorption spectra of the polymer films.

2.6. Electrochemical Properties. Electrochemical cyclic voltammetry (CV) is often performed for determining the HOMO and LUMO levels of the conjugated polymers.[27] Figure 7 shows the cyclic voltammograms of the phenylene−vinyl-substituted PTs films on Pt electrode in 0.1 mol/L Bu_4NPF_6, CH_3CN solution. It can be seen that there are reversible p-doping/dedoping (oxidation/rereduction) processes at positive potential range and n-doping/dedoping (reduction/reoxidation) processes at negative potential range for all the polymers. The cyclic voltammograms of PEHPVT for continuous 10 repeated cycles are shown in Figure 7a. After 10 cycles of the potential scan, the reproducibility of the cyclic voltammograms is very good, which definitely verifies the reversibility of the p-doping/dedoping and n-doping/dedoping processes. For the application of conjugated polymers to electrochemical capacitors (ECCs), the reversible p-doping and n-doping processes are both needed. Poly(3-phenylthiophene) and its derivatives are an important kind of material in ECCs because of their good p-doping and n-doping reversibility.[28] The reversible p-doping and n-doping properties of the polymers studied here indicate that the polymers could also be promising materials for ECCs.

From the onset oxidation potentials (E_{ox}) and the onset reduction potentials (E_{red}) of the polymers, HOMO and LUMO energy levels as well as the energy gap of the polymers were calculated according to the equations[29]

$$\mathrm{HOMO} = -e(E_{ox} + 4.71)\ (\mathrm{eV});$$
$$\mathrm{LUMO} = -e(E_{red} + 4.71)\ (\mathrm{eV});$$
$$E_g^{ec} = e(E_{ox} - E_{red})\ (\mathrm{eV})$$

where the units of E_{ox} and E_{red} are V vs Ag/Ag$^+$. The values obtained are listed in Table 1. E_{red} of PT2 is positively shifted by 0.2 V in comparison with that of PT1, indicating that introducing a nitro group into the conjugated side chain in PT2 results in the easier reduction of the polymer. The result is reasonable for the effect of the electron-withdrawing nitro group on the electronic properties of the conjugated polymer chains. In the CV curve of PT3, two p-doping processes can be seen, which may be attributed to the oxidation of conjugated main chains and conjugated side chains (the second oxidation peak could be corresponding to oxidation of the side chains).

3. Conclusion

Six polythiophene derivatives with phenylene−vinylene conjugated side chains were synthesized and characterized. The absorption spectra of the polymers show two absorption peaks located in UV and visible region, where the visible absorption peak is attributed to the $\pi-\pi^*$ transition of the conjugated main chains while the UV absorption peak comes from the conjugated side chains. By doubling the conjugation length of the phenylene−vinylene side chains and reducing the concentration of the conjugated side chains, we synthesized PT4, which possesses a strong and broad absorption in the visible region from 380 to 650 nm.

For the polymer films of PEHPVT and PMEHPVT where every thiophene units are attached with a conjugated side chain,

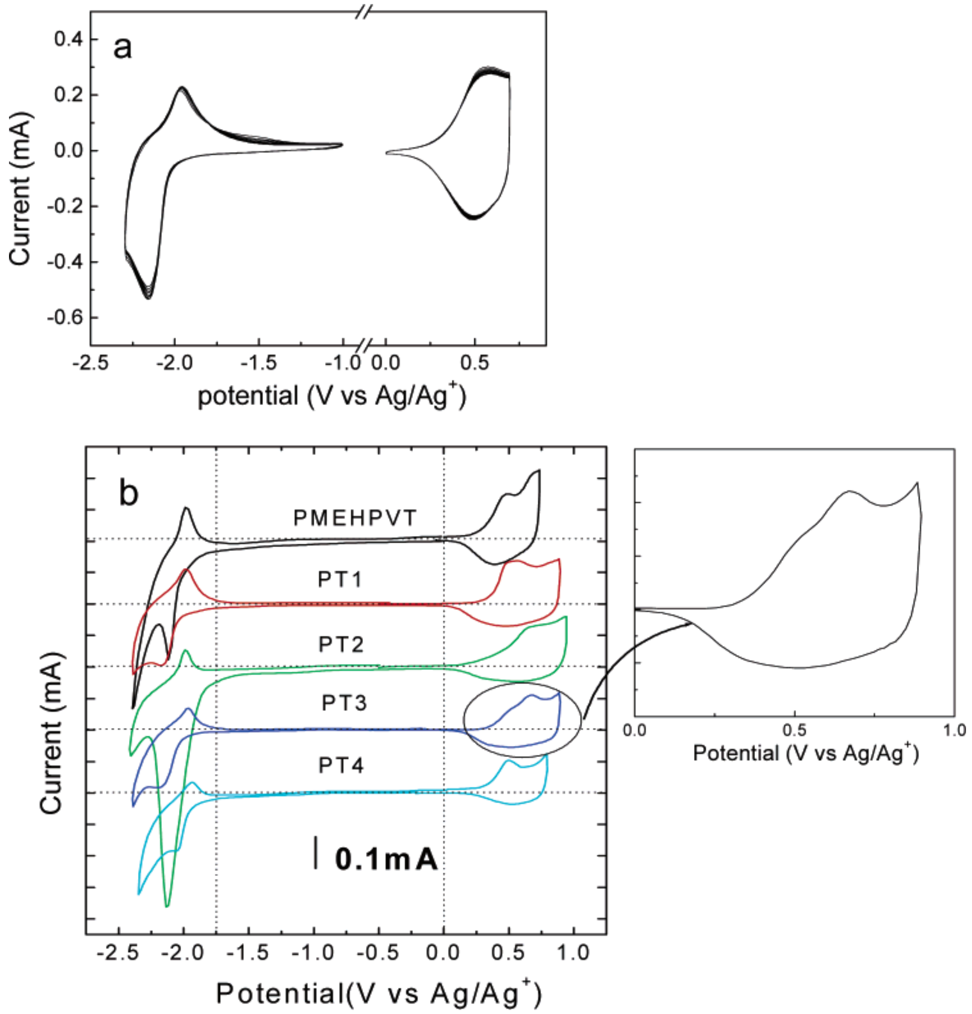


Figure 7. Cyclic voltammograms of (a) PEHPVT and (b) PMEHPVT, PT1 to PT4 films on platinum electrode in 0.1 mol/L Bu_4NPF_6, CH_3CN solution.

a thermochromic phenomenon was observed. The absorption spectra red-shifted, and the band gap of the polymers is reduced after thermal annealing at 130 °C for 10 min. XRD results reveal that the ordering structure of the two polymers was enhanced and their interlayer *d*-spacing expanded after the annealing. The steric hindrance of the big side chains and realignment of the macromolecular chains are responsible for the thermal annealing effect of the polymers.

The results of the cyclic voltammetry display that the p-doping/dedoping and n-doping/dedoping processes of all six polymers are reversible. The HOMO and LUMO energy levels and energy gap of the polymers were calculated from the electrochemical measurements. E_{red} of PT2 with a nitro group attached to its conjugated side chain is positively shifted by 0.2 V in comparison with that of PT1 without the nitro group substituent, indicating that introducing the electron-withdrawing nitro group on the conjugated side chains could result in the easier reduction of the polymer.

4. Experimental Section

Materials. *n*-Butyllithium (2.88 mol/L) in hexane and methylmagnesium bromide were purchased from Alfa Asia Chemical Co. Ni(dppp)Cl_2 was obtained from Aldrich Chemical Co. and used as received. Tetrahydrofuran was dried over Na/benzophenone ketyl and freshly distilled prior to use. *N*,*N*-Dimethylformamide, 1-bromooctane, thiophene, and 3-methylthiophene were dried over molecular sieves and freshly distilled prior to use. The other materials were common commercial grade and used as received.

Characterization. ^1H NMR and ^{13}C NMR spectra was 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. The molecular weight of polymers was measured by the GPC method, and polystyrene was used as a standard. TGA measurement was performed on a Perkin-Elmer TGA-7. X-ray diffraction (XRD) patterns were recorded by a Rigaku D/max-2500 diffractometer operated at a 40 kV voltage and a 200 mA current with Cu Kα radiation. 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_4NPF_6)−acetonitrile solution.

Synthesis of 4-(2-Ethylhexyloxy)benzaldehyde, 1. 4-Hydroxybenzaldehyde (12.2 g, 0.10 mol) was dissolved in 100 mL of DMF. 1-Bromo-2-ethylhexane (19.3 g, 0.10 mol) and K_2CO_3 (13.8 g, 0.10 mol) were added into the solution. The solution was stirred and heated to reflux for 4 h and then poured into cool water. The mixture was extracted with ether, and the organic layers were collected, washed with water, and dried over anhydrous $MgSO_4$; the removal of solvent gave a crude product. Distillation under vacuum gave 17 g (0.073 mol, yield 73%) of colorless 4-(2-ethylhexyloxy)-benzaldehyde. GC-MS: $m/z = 234$. ^1H NMR (δ, $CDCl_3$): 9.87 (s, 1H), 7.71 (d, 2H), 6.96 (d, 2H), 3.85 (d, 2H), 1.75 (m, 1H), 1.46−1.33 (m, 8H), 0.92 (t, 6H). Calculated for $C_{15}H_{22}O_2$: C = 76.88; H = 9.46; found C = 76.77; H = 9.50.

3-Methoxy-4-(2-ethylhexyloxy)benzaldehyde, 2. Compound **2** was prepared by the same procedure as that in the synthesis of compound **1**, but 4-hydroxy-3-methoxybenzaldehyde (15.2 g, 0.10 mol) was used instead of 4-hydroxybenzaldehyde. Distillation under vacuum gave 21.6 g (0.082 mol, yield 82%) of colorless 3-methoxy-4-(2-ethylhexyloxy)benzaldehyde. GC-MS: $m/z = 264$. ^{1}H NMR (δ, $CDCl_3$): 9.76 (s, 1H), 7.41 (d, 1H), 7.32 (s, 1H), 6.85 (d, 1H), 3.96 (d, 2H), 3.75 (s, 3H), 1.76 (m, 1H), 1.76−1.33 (m, 8H), 0.92 (t, 6H). Calculated for $C_{16}H_{24}O_3$: C = 72.69; H = 9.15; found: C = 72.70; H = 9.20.

2,5-Dibromo-3-methylthiophene, 3. 3-Methylthiophene (10.78 g, 0.11 mol) was dissolved in chloroform and acetic acid (80 mL: 80 mL) in a 500 mL one-necked flask equipped for stirring. *n*-Bromosuccinimide (39.16 g, 0.22 mol) was added to the solution in one portion, and the solution was stirred for 2 h. Then the solution was poured into water and extracted with chloroform; the organic extracts were washed with water three times and with $NaHCO_3$(aq) twice. The organic layer was dried over anhydrous $MgSO_4$, and the removal of solvent gave a crude product. Distillation under vacuum gave 24.0 g (0.94 mol, yield 85%) of colorless 2,5-dibromo-3-methylthiophene. GC-MS: $m/z = 254$. ^{1}H NMR (δ, $CDCl_3$): 6.78 (s, 1H), 2.51 (s, 3H). Calculated for $C_5H_4Br_2S$: C = 23.46; H = 1.58; Br = 62.44; S = 12.53; found: C = 23.40; H = 1.60; Br = 62.30; S = 12.63.

2,5-Dibromo-3-bromomethylthiophene, 4. Compound **4** was prepared by reacting 2,5-dibromo-3-methylthiophene (12.8 g, 50 mmol) with *N*-bromosuccinimide (8.9 g, 50 mmol) in 100 mL of carbon tetrachloride (CCl_4). A small amount of benzoyl peroxide was added as an initiator. The mixture was refluxed for 3 h. The completion of the reaction was indicated by the appearance of succinimide on the surface of the solution. The organic layer was washed with water and dried over anhydrous $MgSO_4$. Distillation under vacuum gave 13.9 g (41 mmol, yield 83%) of colorless 2,5-dibromo-3-bromomethylthiophene. GC-MS: $m/z = 332$. ^{1}H NMR (δ, $CDCl_3$): 6.42 (s, 1H), 4.56 (s, 2H). ^{13}C NMR ($CDCl_3$, 300 MHz, δ/ppm): 142.71, 134.53, 115.12, 113.12, 21.44.

2,5-Dibromo-3-{2-[4-(2-ethylhexyloxy)phenyl]−vinyl}thiophene, 5. Compound **4** (3.35 g, 10 mmol) and phosphorous acid triethyl ester (1.66 g, 10 mmol) were put in a flask and heated to 160 °C for 2 h. The product of (2,5-dibromothiophen-3-ylmethyl)-phosphonic acid diethyl ester was obtained and used directly without any purification. GC-MS: $m/z = 358$.

(2,5-Dibromothiophen-3-ylmethyl)phosphonic acid diethyl ester was dissolved in 20 mL of DMF. Under an ice−water bath, $NaOCH_3$ (0.6 g in 10 mL of DMF) was added into the solution. Then compound **1** (2.34 g, 0.01 mol) was added dropwise to the solution. After 30 min, the solution was poured into cold water and extracted with ether. The organic layer was washed with water and then dried over anhydrous $MgSO_4$, filtered, and concentrated. Purification was carried out via silica gel column chromatography, using petroleum ether as the eluent. After concentration, compound **5** was obtained as pale yellow oil (2.82 g, yield 60%). GC-MS: $m/z = 470$. Purity (by GC-MS) >98%. ^{1}H NMR (δ, $CDCl_3$): 7.49 (d, 2H), 7.39 (d, 2H), 7.21 (s, 1H), 7.01 (d, 1H), 6.87 (d, 1H), 3.89 (d, 2H), 1.75 (m, 1H), 1.46−1.33 (m, 8H), 0.92 (t, 6H). ^{13}C NMR ($CDCl_3$, 300 MHz, δ/ppm): 156.87, 140.21, 133.43, 131.22, 127.49, 127.81, 127.01, 126.89, 115.23, 114.67, 113.38, 110.55, 76.98, 40.33, 30.90, 29.78, 24.98, 23.45, 14.09, 12.89. Calculated for $C_{20}H_{24}Br_2OS$: C = 50.86; H = 5.12; Br = 33.84; O = 3.39; S = 6.79; found: C = 50.77; H = 5.16; Br = 33.81; S = 6.66%.

2,5-Dibromo-3-{2-[3-methoxy-4-(2-ethylhexyloxy)phenyl]−vinyl}thiophene, 6. The same procedure was performed as that described above in the synthesis of compound **5**, except that compound **2** was used instead of compound **1**. Another pale yellow oil of compound **6** was obtained. GC-MS: $m/z = 500$. Purity (by GC-MS) >99%.^{1}H NMR (δ, $CDCl_3$): 7.55 (d, 1H), 7.47 (s, 1H), 7.40 (d, 1H), 7.22 (s, 1H), 7.05 (d, 1H), 6.83 (d, 1H), 3.94 (d, 2H), 3.75 (s, 3H), 1.76 (m, 1H), 1.76−1.33 (m, 8H), 0.91 (t, 6H). ^{13}C NMR ($CDCl_3$, 300 MHz, δ/ppm): 150.34, 140.41, 135.62, 134.78, 127.49, 126.45, 120.89, 117.93, 115.34, 113.18, 112.45, 78.70, 39.53, 29.78, 25.12, 23.41, 14.11, 12.23. Calculated for $C_{21}H_{26}Br_2O_2S$: C = 50.21; H = 5.22; Br = 31.82; O = 6.37; S = 6.38; found: C = 50.10; H = 5.27; Br = 31.77; S = 6.38%.

2,5-Bis(tributylstannyl)thiophene, 7. Thiophene (8.4 g, 0.10 mol) was dissolved in 60 mL of THF in a well-dried flask under the protection of nitrogen. *n*-Butyllithium (73 mL, 0.21 mol, 2.88 M in hexane) was added dropwise (caution: a great deal of gas evolved), and the solution was stirred at reflux for 1 h. Tributylchlorostannane (70 g, 0.21 mol) was added in one portion at room temperature. After 12 h, the solution was poured into 100 mL of cool water. The organic layer was separated, and the aqua layer was extracted by ether. The organic layers were collected and dried over anhydrous $MgSO_4$; the removal of solvent gave a crude product. Distillation under vacuum (0.1 mmHg/220 °C), 35 g (0.053 mol, yield 53%) of 2,5-bis(tributylstannyl)thiophene was obtained. GC-MS: $m/z = 664$. Purity (by GC-MS) >96%. ^{1}H NMR (δ, $CDCl_3$): 7.34 (s, 2H), 1.60 (m, 12H), 1.39 (m, 12H), 1.09 (m, 12H), 0.91 (t, 18H). Calculated for $C_{28}H_{56}SSn_2$: C = 50.78; H = 8.52; found: C = 50.12; H = 8.75.

4-Hydroxy-3-nitrobenzaldehyde, 8. 4-Hydroxybenzaldehyde (0.2 mol, 24.4 g) was put into a flask, and glacial acetic acid (50 mL) was added. Under the ice−salt bath, fuming nitric acid (0.2 mol) was dropped into the flask below 0 °C. After the addition of nitric acid, the ice−salt bath was removed, and the reactants were stirred for 2 h at room temperature. Then, the mixture were poured into cracked ice. The solid was filtered and washed by a little ice−water. After being recrystallized from alcohol, 20.1 g (0.12 mmol, yield 61%) of 4-hydroxy-3-nitrobenzaldehyde was obtained. GC-MS: $m/z = 167$. ^{1}H NMR (δ, $CDCl_3$): 9.87 (s, 1H), 8.75 (s, 1H), 8.03 (d, 1H), 7.52 (d, 1H), 4.90 (s, 1H). Calculated for $C_7H_5NO_4$: C = 50.31; H = 3.02; N = 8.38; found: C = 50.25; H = 3.12; N = 8.29.

4-(2-Ethylhexoxy)-3-nitrobenzaldehyde, 9. 4-Hydroxy-3-nitrobenzaldehyde (16.7 g, 0.10 mol) was dissolved in 100 mL of DMF. 1-Bromo-2-ethylhexane (19.3 g, 0.10 mol) and K_2CO_3 (13.8 g, 0.10 mol) were added into the solution. The solution was stirred and heated to reflux for 4 h and then poured into cool water. The mixture was extracted with ether, and the organic layers were collected, washed with water, and dried over anhydrous $MgSO_4$; the removal of solvent gave a crude product. Purification was carried out via silica gel column chromatography, using petroleum ether/ethyl acetate (1:5 v/v) as the eluent. After concentration, 22.6 g (0.081 mol, yield 81%) of colorless 4-octyloxy-benzaldehyde was obtained. GC-MS: $m/z = 279$. ^{1}H NMR (δ, $CDCl_3$): 9.97 (s, 1H), 8.77 (s, 2H), 8.06 (d, 1H), 7.22 (d, 1H), 4.03 (d, 2H), 1.98 (m, 1H), 1.30−1.10 (m, 8H), 0.95 (t, 6H). Calculated for $C_{15}H_{21}NO_4$: C = 64.50; H = 7.58; N = 5.01; found C = 64.45; H = 7.60; N = 4.96.

2,5-Dibromo-3-[2-(4-(2-ethylhexyloxy)-3-nitrophenyl)−vinyl]thiophene, 10. The same procedure and workup were performed as that described above in the synthesis of compound **5**, except that compound **9** (0.01 mol) was used instead of compound **1**. Purification was carried out via silica gel column chromatography, using petroleum ether/ethyl acetate (1:10 v/v) as the eluent. After concentration, a yellow oil of compound **10** (6.1 mmol, yield 61%) was obtained. GC-MS: $m/z = 517$. ^{1}H NMR (δ, $CDCl_3$): 7.99 (d, 1H), 7.69 (quadruple, 1H), 7.32 (d, 1H), 7.23 (d, 1H), 7.11 (d, 1H), 6.90 (s, 1H), 4.05 (d, 2H), 1.58 (m, 1H), 1.48−1.33 (m, 8H), 0.94 (m, 6H). ^{13}C NMR ($CDCl_3$, 300 MHz, δ/ppm): 158.21, 142.32, 134.01, 133.22, 131.54, 127.75, 124.67, 121.90, 115.43, 115.89, 110.55, 74.55, 40.31, 30.98, 29.56, 24.12, 23.45, 14.11, 13.21. Calculated for $C_{20}H_{23}Br_2NO_3S$: C = 46.44; H = 4.48; Br = 30.89; N = 2.71; O = 9.28; S = 6.20; found: C = 46.32; H = 4.56; Br = 30.56; N = 2.70; S = 6.12.

2,5-Dibromo-3-(4-methylstyryl)thiophene, 11. The same procedure and workup were performed as that described above in the synthesis of compound **5**, except 4-methylbenzaldehyde (0.05 mol) was used instead of compound **1**. After being recrystallized from ethanol, 14.5 g (40.5 mmol, yield 81%) of colorless needle crystals of compound **11** was obtained. GC-MS: $m/z = 356$. ^{1}H NMR (δ, $CDCl_3$): 7.40 (d, 2H), 7.19 (d, 2H), 7.21 (s, 1H), 6.96 (d, 1H), 6.87 (d, 1H), 2.37 (s, 3H). Calculated for $C_{13}H_{10}Br_2S$: C = 43.60; H = 2.81; Br = 44.63; S = 8.95; found: C = 43.58; H = 2.85; Br = 44.53; S = 8.87.

Table 2. Elemental Analysis, Molecular Weight, and TGA Results of the P3PVTs

	elemental analysis (%) calculated/found				mol wt by GPC		
	C	H	O	S	M_n	PDs	onset point by TGA (°C)
PEHPVT	76.88/75.57	7.74/7.70	5.12/5.10	10.26/9.87	29K	2.3	280
PMEHPVT	73.64/72.00	7.65/7.60	9.34/8.96	9.36/9.29	22K	2.1	270
PT1	72.59/71.56	6.36/6.30	4.20/4.12	16.85/16.66	54K	2.3	342
PT2	64.91/64.12	5.45/5.46	11.28/10.98	15.07/14.97	62K	1.6	350
PT3	81.11/78.78	7.29/7.10	−	7.73/7.57	4.3K	2.4	355
PT4	−/72.67	−/6.67	−	−/19.65	52K	1.6	360

3-(4-(Bromomethyl)styryl)-2,5-dibromothiophene, 12. Compound **12** was prepared by reacting compound **11** (14.24 g, 40 mmol) with *N*-bromosuccinimide (7.12 g, 40 mmol) in 60 mL of carbon tetrachloride (CCl_4). A small amount of benzoyl peroxide was added as an initiator. The mixture was refluxed for 3 h. The completion of the reaction was indicated by the appearance of succinimide on the surface of the solution. The reactant was washed by warm water five times, and then the solvent was evaporated under reduced pressure. The solid was recrystallized in 50 mL of ethanol. 14.7 g (34 mmol, yield 85%) of colorless needle crystals was obtained. GC-MS: $m/z = 434$. ^{1}H NMR (δ, $CDCl_3$): 7.47 (d, 2H), 7.39 (d, 2H), 7.19 (s, 1H), 6.99 (d, 1H), 6.88 (d, 1H), 4.51 (s, 3H). ^{13}C NMR ($CDCl_3$, 400 MHz, δ/ppm): 140.01, 137.17, 135.43, 133.46, 131.10, 129.01, 129. 30, 127.78, 126.89, 126.60, 115.21, 112.34, 34.72. Calculated for $C_{13}H_9Br_3S$: C = 35.73; H = 2.08; Br = 54.86; S = 7.34; found: C = 35.69; H = 2.10; Br = 54.76; S = 7.44.

3-(4-(4-(2-Ethylhexyloxy)styryl)styryl)-2,5-dibromothiophene, 13. The same procedure and workup were performed as that described above in the synthesis of compound **5**, except that compound **12** (4.34 g, 0.01 mol) was used instead of compound **4**. Purification was carried out via silica gel column chromatography, using petroleum ether/ethyl acetate (1:30 v/v) as the eluent. After concentrated, a yellow solid of compound **13** (4.34 g, 7.6 mmol, yield 76%) was obtained. GC-MS: $m/z = 572$. ^{1}H NMR (δ, $CDCl_3$): 7.50 (s, 4H), 7.48 (d, 2H), 7.23 (s, 1H), 7.12 (d, 1H), 7.02 (d, 1H), 6.99 (d, 1H), 6.93 (d, 2H), 6.91 (d, 1H), 3.89 (d, 2H), 1.59 (m, 1H), 1.47−1.33 (m, 8H), 0.94 (m, 6H). Calculated for $C_{28}H_{30}Br_2OS$: C = 58.55; H = 5.26; Br = 27.82; O = 2.79; S = 5.58; found: C = 58.25; H = 5.35; Br = 27.72; S = 5.60.

Synthesis of PEHPVT, PMEHPVT, and PT3 Using the Grignard Metathesis Method. These three polymers were prepared by the same method. At the protection of prepurified nitrogen atmosphere, monomer **5** or **6** or **13** (3 mmol) was dissolved in freshly distilled THF (20 mL, resulting in a 0.15 mol/L solution). To this solution was added methylmagnesium bromide (1.67 mL, 1.8 mol/L in THF). The mixture was heated to reflux for 1 h, and during the refluxing Ni(dppp)Cl_2 (16 mg, 1 mol %) was added. After refluxing for 30 min, another Ni(dppp)Cl_2 (16 mg, 1 mol %) was added again. After 30 min, the reactant was poured into 100 mL of methanol and then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and THF. The polymer was recovered from the THF fraction by rotary evaporation. The solid was dried under vacuum for 1 day. Elemental analysis, molecular weight, and TGAresults of the three polymers are summarized in Table 2.

Synthesis of PT1, PT2, and PT4 Using Stille Coupling Reaction. These polymers were prepared by the same procedure. 1 mmol of compound **5** or **10** or **13** was put into a three-neck flask, and 20 mL of degassed toluene was added under the protection of argon. The solution was flushed with argon for 10 min, and then 10 mg of $Pd(PPh_3)_4$ and 1 mmol of 2,5-bis(tributylstannyl)thiophene were 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 polymer was precipitated by addition of 50 mL of methanol and then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. Polymer was recovered from the chloroform fraction by rotary evaporation as solid. The solid was dried under vacuum for 1 day. For preparation of these three polymers, the yields of the polymerization reactions were about 30−50%. Elemental analysis, molecular weight, and TGA results of the three polymers are also summarized in Table 2.

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