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Influence of Sulfur Oxidation on the Absorption and Electronic Energy Levels of Poly(thienothiophene) Derivatives

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Two poly(thienothiophene) derivatives containing thieno[3,2-b]thiophene-4,4-dioxide unit were synthesized by Pd-catalyzed Stille coupling method. They were poly(3,6-dihexyl-thieno[3,2-b]thiophene-4,4-dioxide vinylene) (**P2**) and poly(2,5-diyl-3,6-dihexyl-thieno[3,2-b]thiophene-4,4-dioxide)-*co*-(2,5-diyl-thiophene) (**P4**). Poly(3,6-dihexyl-thieno[3,2-b] thiophene vinylene) (**P1**) and poly(2,5-diyl-3,6-dihexyl-thieno[3,2-b] thiophene)-*co*-(2,5-diyl-thiophene) (**P3**) were synthesized for comparison with **P2** and **P4**. After sulfur oxidation on the thienothiophene units, the absorption peaks of the polymer solutions were red-shifted from 540 nm of **P1** to 625 nm of **P2** and from 445 nm of **P3** to 520 nm of **P4**. The absorption peaks of the polymer films were red-shifted more significantly from 542 nm of **P1** to 630 nm of **P2** and from 480 nm of **P3** to 564 nm of **P4**. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels also decreased a lot after the sulfur oxidation. In comparison with **P1**, the LUMO and HOMO energy levels of **P2** decreased by 0.59 and 0.35 eV, respectively. The levels were 0.87 and 0.39 eV lower in the LUMO and HOMO energy levels of **P4** than in that of **P3**.

1. Introduction

In recent decades, conjugated organic and polymer materials have been the focus of great research activity mainly because of their interesting electronic and optoelectronic properties. They are being investigated for a variety of applications, including organic field-effect transistors (OFETs),[1,2] polymer solar cells (PSCs),[3–12] organic light-emitting diodes (OLEDs),[13] and so on. The hole mobility of the OFETs based on conjugated organic polymers has reached 1.4 cm²/(V s),[14] and the power conversion efficiency of the polymer solar cells (PSCs) has reached over 5%.[9–12] It is very important to tune the absorption, hole mobility, and energy levels of the conjugated polymers to suitable values for getting high-performance OFETs and PSCs. OFETs based on many small molecules containing fused thiophenes show good hole mobility because of good π stacking of the fused thiophenes in solid state.[15–17] Many conjugated polymers containing fused thiophene rings have also been synthesized[18–22] and have been used as active layer in OFETs.[18–21] Open-circuit voltage of the PSCs is related to the difference between the highest occupied molecular orbital (HOMO) energy level of the conjugated polymer donor and the lowest unoccupied molecular orbital (LUMO) energy level of the fullerene derivative acceptor.[23] Short-circuit current of the PSCs is related to the hole mobility of the conjugated polymer and the electron mobility of the fullerene derivatives as well as to the absorption of the conjugated polymer to sunlight and so forth. For improving the power conversion efficiency of the PSCs, it is very important to broaden absorption, increase hole mobility, and properly decrease HOMO energy level of the conjugated polymer donor materials.

In our previous work, we fabricated the OFET device on the basis of poly(3,6-dihexyl-thieno[3,2-b]thiophene vinylene); the hole mobility of the device reached 0.032 cm²/(V s).[24] Miguel and Matzger synthesized some thieno[3,2-b]thiophene oligomers and thieno[3,2-b]thiophene-4.4-dioxide oligomers; after sulfur oxidation of the thieno[3,2-b]thiophene unit, the absorption of the molecules was red-shifted.[25] Zhang et al. also synthesized some polymers on the basis of S,S-dioxide thienylenevinylene; these polymers possess longer wavelength absorption and lower LUMO and HOMO energy levels.[26]

For broadening the absorption band and decreasing the electronic energy levels of the polymers, we synthesized two poly(thieno[3,2-b]thiophene-4,4-dioxide) derivatives (**P2** and **P4**) and two poly(thieno[3,2-b]thiophene) derivatives (**P1** and **P3**) as shown in Scheme 1. **P2** and **P4** are the corresponding polymers of **P1** and **P3** after sulfur oxidation on the thienothiophene unit. The sulfur oxidation makes the absorption peaks of the polymer solutions red-shifted from 540 nm of **P1** to 625 nm of **P2** and from 445 nm of **P3** to 520 nm of **P4**. The absorption peaks of the polymer films are red-shifted more significantly from 542 nm of **P1** to 630 nm of **P2** and from 480 nm of **P3** to 564 nm of **P4**. In addition, the energy levels are 0.87 and 0.39 eV lower in the LUMO and HOMO energy levels of **P4** in comparison with **P3**. The results indicate that the sulfur oxidation is an efficient way to red-shift the absorption band and to decrease the electronic energy levels of the polythiophene derivatives.

2. Experimental Section

2.1. Materials. 2,5-Dibromo-3,6-dihexyl-thieno[3,2-b]thiophene (monomer **1**) was synthesized by the method used in the literature.[22] The monomers 2,5-bis(tributylstannyl)thiophene and (*E*)-1,2-bis(tributylstannyl)ethane were synthesized as reported in the literature.[5] All other reagents and solvents

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SCHEME 1: Molecular Structures of P1−P4

P1   P2   P3   P4
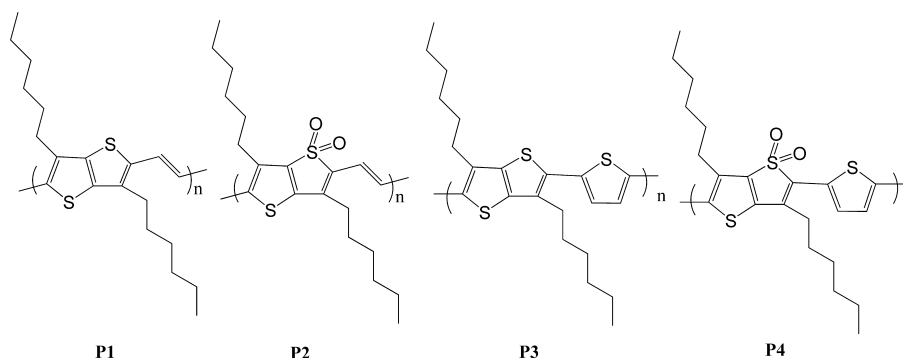
were purchased commercially as analytical-grade quality and were used without further purification.

2.2. Measurements. ^{1}H NMR spectra were measured on a Bruker DMX-400 spectrometer. Chemical shifts of the ^{1}H NMR were reported in ppm relative to the singlet of CDCl$_3$ at 7.26 ppm. Splitting patterns were designated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broaden). Absorption spectra were taken on a Hitachi U-3010 UV−vis spectrophotometer. Photoluminescence (PL) spectra were measured using a Hitachi F-4500 spectrophotometer for the polymer solutions in chloroform (analytical reagent) at 25 °C and for the polymer films on quartz plates spin-coated from the polymer solutions in chloroform. Molecular weight of the polymers was measured by gel permeation chromatography (GPC) method, and polystyrene was used as a standard. Thermogravimetric analysis (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. Polymer thin films were formed by drop-casting 1.0 μL of the polymer solutions in tetrahydrofuran (THF) (analytical reagent, 1 mg/mL) onto the working electrode and then were dried in the air.

2.3. Synthesis. The synthetic routes of 2,5-dibromo-3,6-dihexyl-thieno[3,2-b]thiophene-4,4-dioxide (monomer **2**) and the polymers are shown in Scheme 2. All starting materials, reagents, and solvents were carefully purified, and all procedures were performed under an air-free atmosphere.

2,5-Dibromo-3,6-dihexyl-thieno[3,2-b]thiophene-4,4-dioxide (Monomer 2). In a three-necked 250 mL flask, 4.68 g (0.01 mol) of 2,5-dibromo-3,6-dihexyl-thieno[3,2-b]thiophene (**1**) and 100 mL of dichloromethane were added. Nine grams of meta-chloroperoxybenzoic acid in 50 mL dichloromethane was added to the reaction mixture. Then, the mixture was stirred overnight at room temperature and was poured into 250 mL of water. The organic was extracted with dichloromethane. The combined organic layer was washed with brine and water and was dried over anhydrous MgSO$_4$. After the solvent was evaporated, monomer **2** was obtained by separation with silica gel column chromatography and elution with dichloromethane. E/I: m/z = 498. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 2.73(t, 2H), 2.48(m, 2H), 1.73(m, 2H), 1.63(m, 2H), 1.38(m, 12H), 0.89(t, 6H).

Synthesis of the Polymers. The mixture of monomer **1** or monomer **2** (1 mmol) and 2,5-bis(tributylstannyl)thiophene or (*E*)-1,2-bis(tributylstannyl)ethane (1 mmol) was 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 10 min, and then 15 mg of Pd (PPh$_3$)$_4$ was added. After

SCHEME 2: Synthetic Routes of the Monomers and Polymers
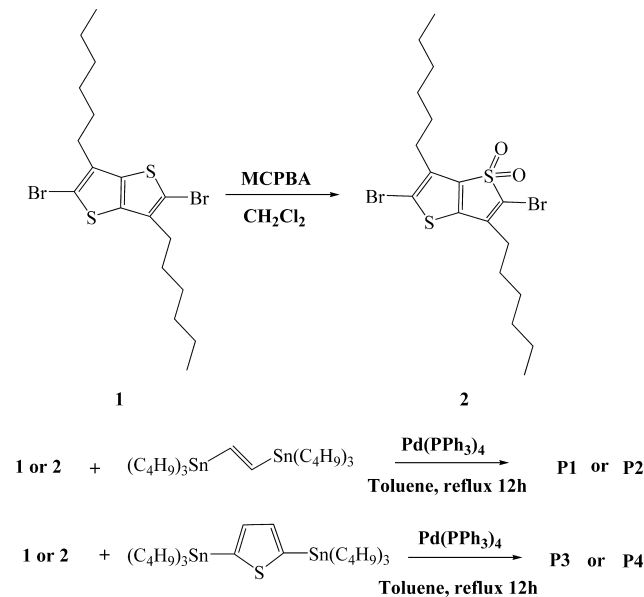
another flushing with argon for 20 min, the reactant was heated to reflux for 12 h. The reagents were cooled to room temperature. Then, the polymer was precipitated by the addition of 50 mL methanol and was filtered through a Soxhlet thimble. The precipitate was then subjected to Soxhlet extraction with methanol, hexane, 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.

P1. GPC: M_w = 32K; M_n = 28K; M_w/M_n = 1.13. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.15−6.99 (br, 2H), 2.79 (m, 4H), 1.74 (m, 4H), 1.38 (m, 12H), 0.93 (t, 6H). Elemental analysis for (C$_{20}$H$_{28}$S$_2$)n. Calculated: C, 72.29%; H, 8.72%; S, 19.28%. Found: C, 72.18%; H, 8.43%; S, 18.96%.

P2. GPC: M_w = 33K; M_n = 17K; M_w/M_n = 1.95. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 6.95 (d, 1H), 6.60 (d, 1H), 2.85 (t, 2H), 2.60 (t, 2H), 1.78 (m, 4H), 1.35 (m, 12H), 0.91 (t, 6H). ^{13}C NMR (CDCl$_3$, 400 MHz) δ (ppm): 142.84, 138.89, 114.86, 31.60, 29.20, 22.64, 14.20. Elemental analysis for (C$_{20}$H$_{28}$S$_2$O$_2$)n. Calculated: C, 65.93%; H, 7.69%; S, 17.58%; O, 8.79%. Found: C, 65.80%; H, 7.32%; S, 17.03%; O, 8.12%.

P3. GPC: M_w = 37K; M_n = 25; M_w/M_n = 1.48. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) 7.22−7.02 (d, 2H), 2.78 (t, 4H), 1.80 (m, 4H), 1.36 (m, 12H), 0.90 (t, 6H). Elemental analysis

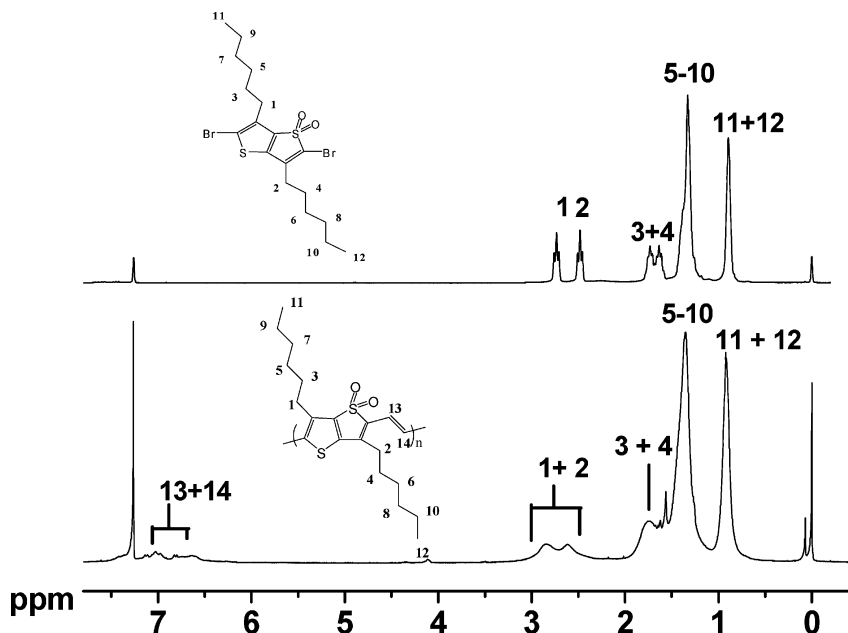Poly(thienothiophene) Derivatives

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Figure 1. ^{1}H NMR spectra of monomer **2** and polymer **P2**.

for $(C_{22}H_{28}S_3)_n$ Calculated: C, 68.04%; H, 7.22%; S, 24.74%. Found: C, 67.65%; H, 6.49%; S, 23.84%.

P4. GPC: M_w = 8K; M_n = 18; M_w/M_n = 2.12. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.72 (d, 1H), 7.17 (d, 1H), 2.97 (t, 2H), 2.76 (t, 2H), 1.80 (m, 4H), 1.36 (m, 12H), 0.90 (t, 6H). ^{13}C NMR (CDCl$_3$, 400 MHz) δ (ppm): 141.67, 137.79, 123.53, 115.00, 31.60, 30.69, 29.20, 28.75, 22.64, 14.20, 13.73. Elemental analysis for $(C_{22}H_{28}S_3O_2)_n$ Calculated: C, 62.86%; H, 6.67%; S, 22.86%; O, 7.62%. Found: C, 62.23%; H, 6.02%; S, 22.62%; O, 6.83%.

3. Results and Discussion

3.1. Synthesis of the Monomers and Polymers. The four polymers were synthesized by Stille coupling of monomer **1** or monomer **2** and 2,5-bis(tributylstannyl)thiophene or (*E*)-1,2-bis(tributylstannyl)ethane, respectively, as shown in Scheme 2. The ^{1}H NMR spectra of monomer **2** and **P2** are shown in Figure 1. The hydrogens numbered 1 and 2 in the thieno[3,2-b]thiophene ring positions are at 2.73 and 2.48 ppm; the other hydrogen positions are analyzed as shown in Figure 1. In the ^{1}H NMR spectrum of **P2**, there is a peak at 2.83 ppm (peak 1) which is attributed to the hydrogen numbered 1 in the thieno[3,2-b]thiophene-4,4-dioxide rings of **P2** (see the molecular structure inserted in Figure 1). The molecular weight of monomer **2** and the elemental analysis results of **P2** and **P4** confirm that there is only one sulfur oxidized in the thienothiophene ring. All the polymers are random polymers and are readily soluble in common organic solvents such as toluene, chloroform, and THF.

3.2. Thermal Analysis. Thermal stability of the four polymers was investigated with thermogravimetric analysis (TGA) in N$_2$ inert atmosphere as shown in Figure 2. The decomposition temperatures based on 5% weight loss of **P1**, **P2**, **P3**, and **P4** are at 314, 259, 209, and 313 °C, respectively. The thermal stability of the four polymers is good enough for the optoelectronic applications.

3.3. 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 3a depicts the UV−vis absorption spectra of the polymer solutions in chloroform. In comparison with the UV−vis absorption
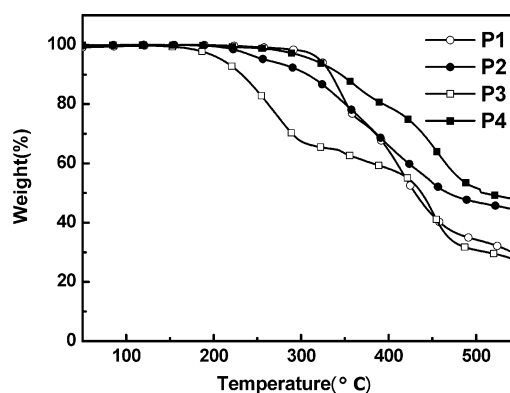

Figure 2. TGA plots of the polymers with a heating rate of 10 °C/min under inert atmosphere.

spectrum of **P1**, the S,S-dioxide structure in the thieno[3,2-b]thiophene unit of **P2** makes the UV−vis absorption peak of the polymer solution red-shifted greatly. The absorption peak is red-shifted by 87 nm from 538 nm of **P1** to 625 nm for **P2**. The same phenomenon was also observed between **P3** and **P4**. The absorption peak is red-shifted by 75 nm from 445 nm of **P3** without the S,S-dioxides to 520 nm for **P4** with the S,S-dioxides.

Figure 3b shows the UV−vis absorption spectra of the polymer films on quartz plates. The absorption peaks of the polymer films are more or less red-shifted in comparison with those of their corresponding solutions, which is a common phenomenon for the conjugated polymers and which results from the intermolecular and intramolecular interactions of the conjugated polymers in the solid state. For **P1** and **P2**, the red-shift from solution to film is less (ca. 4−5 nm) indicating that the intermolecular and intramolecular interactions of polymers **P1** and **P2** are weaker in the solid state. For **P3** and **P4**, the red-shift from solution to film is greater (ca. 35−44 nm) implying that the intermolecular and intramolecular interactions of polymers **P3** and **P4** are much stronger in the solid state. The red-shift is also associated with additional planarization, which is an intramolecular event. Obviously, the copolymeri-
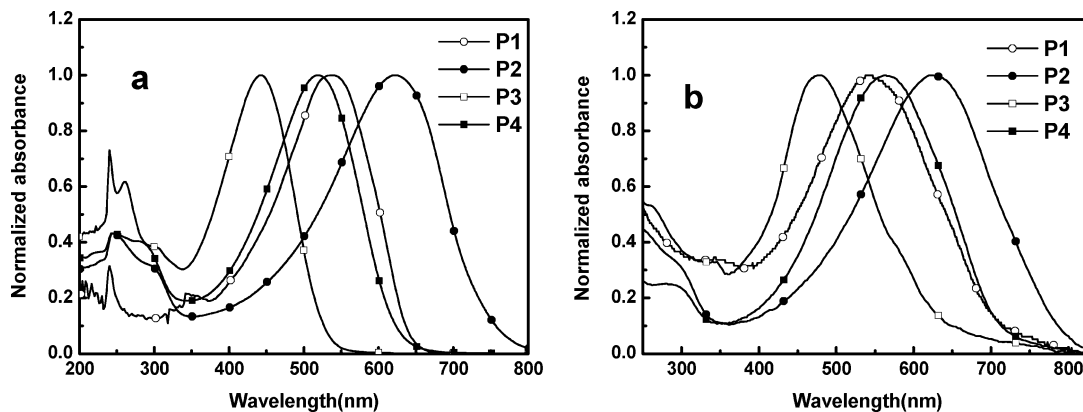
Figure 3. Normalized absorbance of (a) the polymer solutions in chloroform and (b) the polymer films on quartz plate.
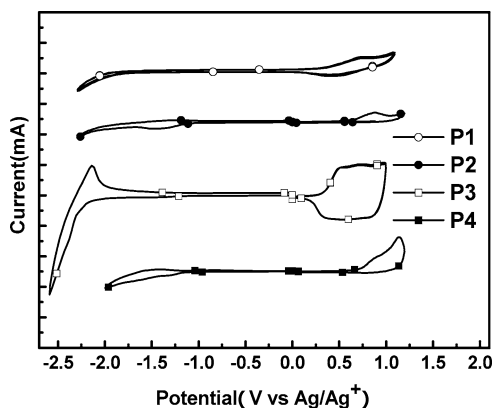

Figure 4. Cyclic voltammograms of the polymer films on Pt electrode in 0.1 mol/L Bu$_4$NPF$_6$, CH$_3$CN solution with a scan rate of 100 mV/s.

3.4. Electrochemical Properties. The electrochemical properties are among 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 by cyclic voltammetry.

Figure 4 shows the cyclic voltammograms (CVs) of the polymer films on Pt disk electrode. After the sulfur oxidation in **P2** and **P4**, the onset of the oxidation potentials and the onset of the reduction potentials are positively shifted, and the reversibility of the p-doping/dedoping (oxidation/rereduction) processes at positive potential range becomes poorer. There are reversible oxidation/rereduction current peaks in the CVs of **P1** and **P3**, but the oxidation process of **P2** and **P4** is irreversible.

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[27]

$$E_{HOMO} = -e(\phi_{ox} + 4.71)(eV)$$
$$E_{LUMO} = -e(\phi_{red} + 4.71)(eV)$$
$$E_g^{EC} = e(\phi_{ox} - \phi_{red})(eV)$$

where the units of φ_{ox} and φ_{red} are V versus Ag/Ag$^+$. The electrochemical properties and the electronic energy levels of the polymers calculated from the onset redox potentials are listed in Table 1. The LUMO and HOMO energy levels of **P2** dropped by 0.59 and 0.35 eV, respectively, compared with that of **P1**, and the electrochemical energy gap of **P2** is narrower by 0.24 eV than that of **P1**. The LUMO and HOMO energy levels of **P4** decreased by 0.87 and 0.39 eV, respectively, in comparison with that of **P3**, and the electrochemical energy band gap of **P4** is narrower by 0.48 eV than that of **P3**. The results indicate that the sulfur oxidation of thieno[3,2-b]thiophene decreases the LUMO and HOMO energy levels and reduces the energy band gap of the polymers.

zation with thiophene units in **P3** and **P4** enhanced the intermolecular and intramolecular interactions of the polymers in comparison with the polymers of **P1** and **P2**, which are copolymerized with the vinylene units in their main chain.

The influence of the sulfur oxidation on the absorption spectra of the polymer films is similar to that of the polymer solutions. There is an 88 nm red shift of the absorption peak of the polymer films from **P1** (at 542 nm) without the S,S-dioxides in the thieno[3,2-b]thiophene unit to that of **P2** (at 630 nm) with the S,S-dioxides in the thieno[3,2-b]thiophene unit. Also, the red-shift of the film absorption peak is 84 nm from **P3** (at 480 nm) without the S,S-dioxides in the thieno[3,2-b]thiophene unit to that of **P4** (at 564 nm) with the S,S-dioxides in the thieno[3,2-b]thiophene unit. Obviously, after the sulfur oxidation, the absorption peaks of the poly(thienothiophene) derivatives are red-shifted greatly both for the polymer solutions and for films. The absorption edges of the polymer films are 700 nm for **P1**, 803 nm for **P2**, 653 nm for **P3**, and 707 nm for **P4**.

TABLE 1: Electrochemical Onset Potentials and Electronic Energy Levels of the Polymer Films

	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]
P1	0.33/−5.04	−1.74/−2.97	2.07	1.77
P2	0.68/−5.39	−1.15/−3.56	1.83	1.54
P3	0.33/−5.04	−2.04/−2.67	2.37	1.90
P4	0.72/−5.43	−1.17/−3.54	1.89	1.75

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

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4. Conclusion

Three new poly(thienothiophene) derivatives, poly(3,6-di-hexyl-thieno[3,2-b]thiophene-4,4-dioxide vinylene) (**P2**), poly(2,5-diyl-3,6-dihexyl-thieno[3,2-b]thiophene)-*co*-(2,5-diyl-thiophene) (**P3**), and poly(2,5-diyl-3,6-dihexyl-thieno[3,2-b]thiophene-4,4-dioxide)-*co*-(2,5-diyl-thiophene) (**P4**), were synthesized by Pd-catalyzed Stille coupling method. The absorption spectra and the electrochemical cyclic voltammograms of the polymers together with poly(3,6-dihexyl-thieno[3,2-b]thiophene vinylene) (**P1**) were measured. The effect of the sulfur oxidation in the thienothiophene units on the absorption and electronic energy levels of the polymers was studied by comparison of their absorption and electrochemical properties of **P2** and **P4** with those of **P1** and **P3**. After sulfur oxidation, the absorption peaks of **P2** and **P4** red-shifted by ca. 75~88 nm than their corresponding polymers **P1** and **P3**, the energy band gap decreased by ca. 0.15−0.33 eV, the LUMO energy levels decreased by ca. 0.59−0.87 eV, and the HOMO energy levels decreased by ca. 0.35−0.39 eV. The results indicate that the sulfur oxidation on the thienothiephene unit is an effective way to reduce the band gap, red-shift the absorption peaks, and decrease the LUMO and HOMO energy levels of the poly(thienothiophene) derivatives.

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