

# Articles

## Electron-Rich Thienylene–Vinylene Low Bandgap Polymers

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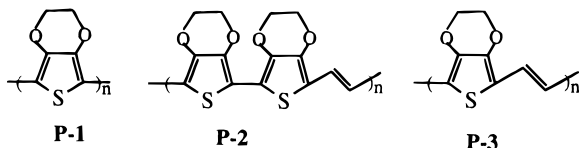
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A series of alternating copolymers of 2,5-(3,4-ethylenedioxy)thiophene and 1,2-vinylene with well defined repeat unit ratios were synthesized and characterized electrochemically and spectroscopically. By increasing the vinylene to thiophene ratio from 0:1 to 0.5:1 to 1:1 along the polymer backbone, the bandgap of the resulting polymers were reduced systematically as clearly evidenced by absorption spectroscopy. The 1:1 copolymer exhibited an onset bandgap of 1.0 eV.

### Introduction

Conjugated polymers have attracted considerable attention during the past decade owing to a wide range of promising electrochemical, electronic and optical applications.<sup>1–4</sup> Recently, conjugated polymers with low bandgaps draw much attention because they potentially provide materials with high conductivities as well as desirable optical properties, such as high degrees of optical transparency or enhanced nonlinear responses. Much effort has been expended in synthesizing alkyl- and alkoxy-substituted polythiophenes with improved electronic properties. One of the most promising thiophene derivatives is poly(3,4-ethylenedioxythiophene) (**P-1**), because it shows a much lower bandgap, better



environmental stability, and higher conductivity than its parent polythiophene.<sup>5–7</sup>

Recent studies have suggested that copolymers with modified bandgaps can be obtained by combining repeat units of polymers with different bandgaps. One important approach to modify the bandgaps of polyaromatic systems is to incorporate vinylene linkages between the

aromatic rings.<sup>4,8,9</sup> This has been demonstrated by the poly(*p*-phenylene vinylene) (PPV) and poly(thienylene vinylene) (PTV) systems, which have lower bandgaps by about 0.3 eV than their parent polyphenylene and polythiophene, respectively.<sup>8</sup> The vinylene linkage not only reduces the bandgap of the copolymers but also acts as a “conjugated spacer” to reduce steric interactions on successive aromatic rings, therefore increasing the degree of coplanarity of the conjugated polymer backbones.

Preliminary reports on the preparation and properties of poly[bis(3,4-ethylenedioxy-2-thienyl) vinylene] (**P-2**)<sup>10,11</sup> and poly(3,4-ethylenedioxy-2,5-thienylene vinylene) (**P-3**)<sup>12</sup> have recently appeared. Here, we present a detailed study of the electrochemical and optical properties of **P-2** and **P-3**, together with **P-1** for comparison.

### Experimental Section

**Reagents.** Diethyl ether and tetrahydrofuran (THF) were freshly distilled from sodium benzophenone ketyl. Dichloro-[1,3-bis(diphenylphosphino)propane]nickel(II) (NiCl<sub>2</sub>dppp) was obtained from Strem Chemicals. Acetonitrile (anhydrous) was distilled over CaH<sub>2</sub> and stored over molecular sieves. Tetrabutylammonium perchlorate (TBAP, Fluka) was recrystallized from ethanol and dried at 70 °C on a vacuum line for 48 h. All other reagents were from Aldrich and purified by standard methods before use.

**Instrumental.** <sup>1</sup>H NMR spectra were obtained as solutions in deuterated chloroform and recorded on a Bruker 300 MSL FT-NMR spectrometer with TMS as internal reference. <sup>13</sup>C NMR spectra were referenced to the central peak of the CDCl<sub>3</sub> triplet at 77.0 ppm. Electrochemistry was carried out on an EG&G PAR Model 273 potentiostat/galvanostat. Electronic

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absorption spectra were recorded on Varian Cary 5 UV–vis–NIR spectrophotometer. Conductivity measurements were made using a dc four-in-line-probe method (compressed pellets).

**3,4-Ethylenedioxythiophene (1).** 3,4-Ethylenedioxythiophene was prepared by published procedures.<sup>5,6</sup> This monomer is now commercially available from Bayer.

**trans-1,2-Bis(3,4-ethylenedioxy-2-thienyl)vinylene (2).** 3,4-Ethylenedioxythiophene (**1**, 0.35 g 2.47 mmol) was dissolved in 10 mL of freshly distilled diethyl ether in an oven-dried round-bottom flask and cooled to 0 °C under nitrogen. *n*-Butyllithium (1.1 mL, 2.5 M in hexane) was added slowly via a syringe. Removing the ice bath, the resulting light yellow solution was allowed to stir for 15 min at room temperature. MgBr<sub>2</sub>·Et<sub>2</sub>O (1.6 g, 6.2 mmol) was added, and the suspension was stirred for ca. 1 h to give a yellow solution. Then, 0.13 g of *trans*-1,2-dichloroethylene (1.36 mmol) and ca. 3 mg of NiCl<sub>2</sub>-dppp in 5 mL of fresh distilled diethyl ether were added by a syringe. The reaction mixture was stirred at room temperature for 15 h, after which it was diluted with 100 mL of ether and washed with 60 mL of dilute HCl/H<sub>2</sub>O, 60 mL of water two times, and 30 mL of brine. The organic phase was dried over MgSO<sub>4</sub> and evaporated to give 0.35 g of an orange solid. The crude product was recrystallized from ethanol to give 0.25 g of orange crystals in a yield of 70%; mp 166–168 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 6.88 (s, 2H, CH=CH), 6.18 (s, 2H, ring H-5), 4.26 (t, 4H, OCH<sub>2</sub>), 4.22 (t, 4H, OCH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 141.96, 138.76, 117.28, 116.21, 97.22, 64.81, 64.68. Anal. Calcd for C<sub>14</sub>H<sub>14</sub>O<sub>4</sub>S<sub>2</sub>: C 54.18%, H 4.55%. Found: C 54.25%, H 4.35%. For an alternate synthesis and X-ray crystal structure see ref 16.

**Poly(3,4-ethylenedioxy-2,5-thienylene vinylene) (P-3).** P-3 was prepared according to a previously reported procedure.<sup>12</sup>

**Electrochemical and Optical Studies.** Electrochemical studies were conducted in a one-compartment three-electrode cell in an argon-filled drybox. Either a platinum electrode (0.02 cm<sup>2</sup>) or indium–tin oxide (ITO) glass was used as the working electrode (WE) with corresponding platinum wire or foil as counter electrodes. Potentials were measured against Ag/Ag<sup>+</sup> reference electrode (a silver wire immersed in a solution of 0.01 M AgNO<sub>3</sub>/0.1 M TBAP/CH<sub>3</sub>CN; ca. +0.34 V versus SCE). This solution was separated from the surrounding electrolyte by a glass frit.

Electrochemical polymerization was done by both galvanostatic and potentiostatic conditions, where current density was controlled at 1 mA/cm<sup>2</sup> for the former. Monomer concentration was 0.05 M. Neutral polymers were obtained by applying a potential of ca. –0.8 V (vs Ag/Ag<sup>+</sup>) until current decayed to the background level.

Redox behavior of electrochemically (oxidatively) polymerized polymers was evaluated by cyclic voltammetry by first reducing deposited polymers to their undoped state. Cyclic voltammetry of the polymers was carried out in monomer-free electrolyte at a sweep rate of 20 mV/s. Optoelectrochemical studies of polymer films on ITO were done in quartz cuvettes with a Ag wire as a quasi-reference electrode and a thick platinum wire (1 mm diameter) as a counter electrode. The potential was increased in steps of 50–100 mV, and the current was monitored and allowed to fall to the background level before the UV–vis–near-IR spectrum was taken.

## Results and Discussion

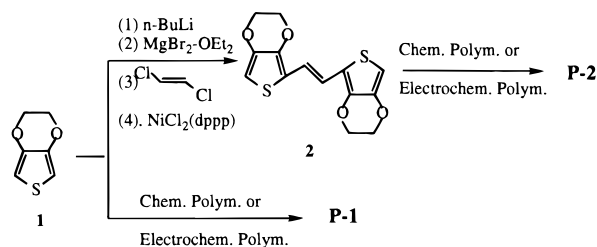
**Monomer and Polymer Synthesis.** A general but undetailed synthetic procedure for the preparation 3,4-ethylenedioxythiophene (**1**) was reported by Jonas et al.<sup>5</sup>

**Table 1. Electrochemical Oxidation<sup>a</sup> and Optical Data for Monomers 1 and 2**

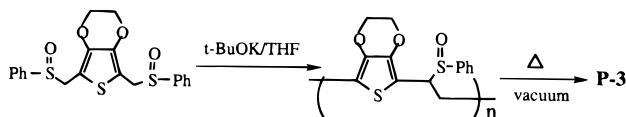
	<b>1</b>	<b>2</b>
$E_{\text{ox, onset}}^b$ (V)	0.65	0.27
$E_{\text{ox, peak}}^b$ (V)		0.40
$\lambda_{\text{max}}$ (nm)/CHCl <sub>3</sub>	270.0	363.0

<sup>a</sup> Potentials vs Ag/Ag<sup>+</sup> in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN. <sup>b</sup> Oxidation potential from cyclic voltammograms,  $E_{\text{ox, onset}}$  = onset oxidation potential,  $E_{\text{ox, peak}}$  = peak oxidation potential.

### Scheme 1. Synthesis of P-1 and P-2



### Scheme 2. Synthesis of P-3



A recent synthetic route was also reported by Pei et al.<sup>7</sup> *trans*-1,2-Bis(3,4-ethylenedioxy-2-thienyl)vinylene (**2**) was prepared utilizing the nickel–phosphine complex catalyzed Grignard coupling reaction developed by Tamao et al.<sup>13,14</sup> The one-pot coupling reaction between the Grignard reagent derived from 3,4-ethylenedioxythiophene (**1**) and *trans*-1,2-dichloroethylene provided orange crystalline compound **2** in good yield as outlined in Scheme 1. A similar route was reported by Soltzing et al.<sup>16</sup>

P-3 was recently synthesized by a precursor route via base-induced elimination of sulfoxide groups (Scheme 2).<sup>12</sup>

**Electrochemical Polymerization.** Owing to the presence of unsubstituted  $\alpha$ -positions on the thiophene rings of monomers **1** and **2**, the radical cation intermediates resulting from electrochemical oxidation can subsequently couple to form polymers P-1 and P-2. Figure 1 shows the multiscan cyclic voltammograms of monomers **1** and **2**. During the first anodic scan, **1** and **2** exhibited a single oxidation peak owing to formation of the monomer radical cation. The broad cathodic processes and anodic processes at lower potential, which increase in intensity with the number of scans, resulted from conducting polymer film growth. As shown in Table 1, the monomer oxidation peak potential ( $E_{\text{ox, peak}}$ ) and onset oxidation potential ( $E_{\text{ox, onset}}$ ) were found to decrease by ca. 0.4 V on going from **1** to **2**. This implies that the radical cation resulting from monomer **2** is more stable than that of monomer **1** and therefore can be formed at a lower oxidation potential. Also, the electronic absorption maximum of monomer **2** was observed to be red-shifted from monomer **1** by ca. 100 nm owing to the extended conjugation in monomer **2** versus monomer **1**.

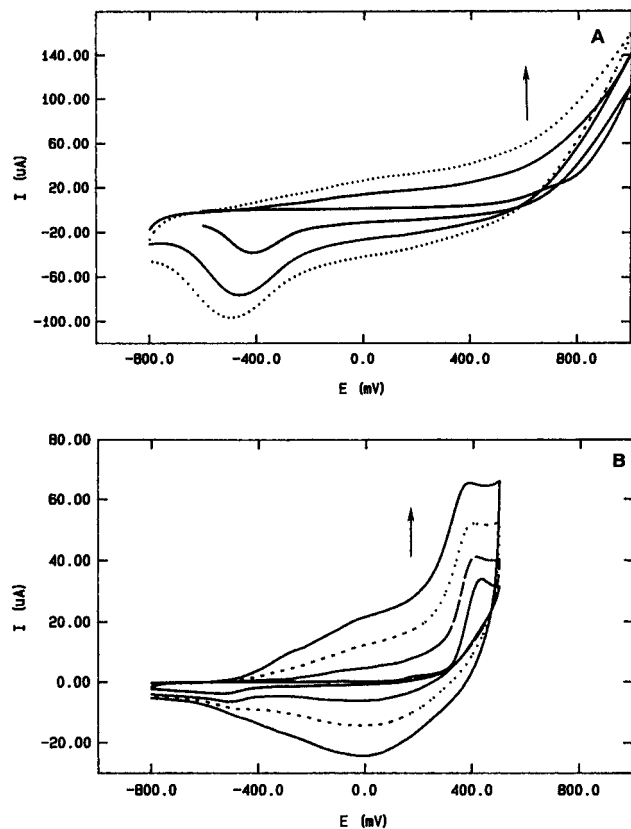
**Electrochemical Properties.** To elucidate the effect of a vinylene group on the electronic structure of these copolymers, the redox properties of polymers were subsequently characterized by cyclic voltammetry (CV).

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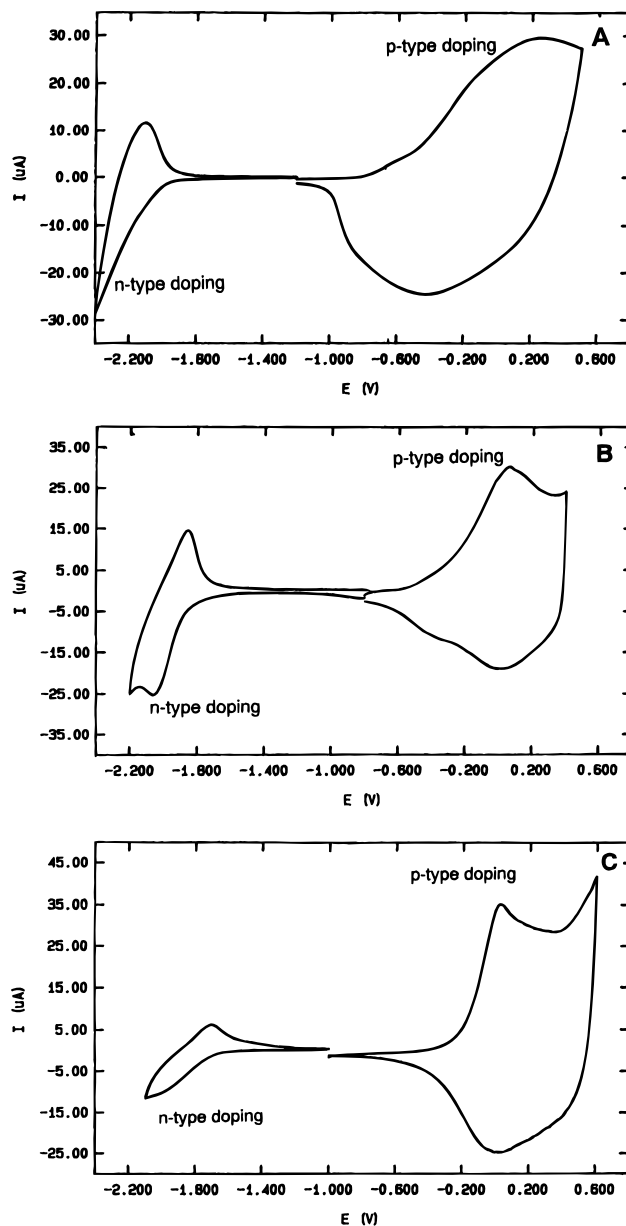
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**Figure 1.** Multicyclic voltammograms of monomers **1** and **2** (20 mV/s) in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> acetonitrile solution (V vs Ag/Ag<sup>+</sup>): (A) monomer **1** at 1st, 3rd, and 5th scan; (B) monomer **2** at 1st, 3rd, 5th, and 7th scan.

The electrochemically deposited polymers (**P-1**, **P-2**) on a Pt electrode were subsequently characterized in monomer-free 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN electrolyte solution. **P-3** was cast on a Pt electrode from a solution of its precursor polymer and then subsequently converted thermally to the conjugated polymer.<sup>12</sup> Figure 2A–C shows the redox properties of polymers **P-1**, **P-2**, and **P-3**, respectively, as determined from their cyclic voltammograms. Both p- and n-doping processes are reversible in the electrolyte solution employed. Therefore, electrochemically determined bandgaps, derived from either the difference between onset potentials ( $E_{g,onset} = E_{pa,onset} - E_{nc,onset}$ ) or half-wave potentials ( $E_{g1/2} = E_{p1/2} - E_{n1/2}$ ) for oxidation and reduction of polymers can be deduced. The electrochemical characteristics of these polymers are summarized in Table 2. With a vinylene group incorporated between every second thiophene ring (**P-2**), a decrease in bandgap ( $E_{g1/2}$ ) of ca. 0.12 eV was found on going from **P-1** to **P-2**. Furthermore, by increasing the vinylene to thiophene ratio from 1:2 (**P-2**) to 1:1 (**P-3**), the bandgap ( $E_{g1/2}$ ) of **P-3** decreased by another 0.11 eV relative to that of **P-2**. Hence, the vinylene linkage helps to reduce the bandgaps of the copolymers systematically. Similarly to the trend of half-wave potential derived bandgaps, the onset bandgap ( $E_{g,onset}$ ) of **P-2** is reduced by 0.17 eV relative to **P-1** owing to the insertion of the vinylene linkage. Contrary to the observation in half-wave potential derived bandgaps, the onset bandgap of **P-3** increased by 0.1 eV relative to that of **P-2**. This apparent contradiction arises because **P-2** is electrochemically polymerized and directly deposited on electrodes; however, **P-3** is chemically polymerized and cast



**Figure 2.** Cyclic voltammograms (20 mV/s) of polymer films on Pt electrodes in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> acetonitrile solution (V vs Ag/Ag<sup>+</sup>): (A) **P-1**, (B) **P-2**, and (C) **P-3**.

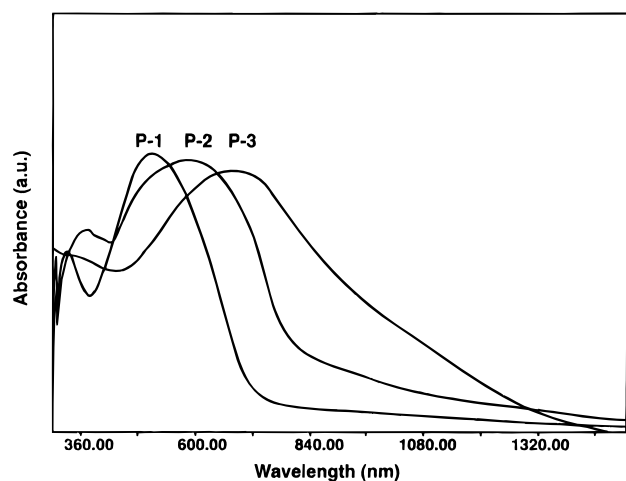
onto electrodes as a neutral polymer from an organic solvent. **P-2** and **P-3** synthesized by different methods may have significantly different morphologies and charge/mass transport characteristics. So they will have different initial electrochemical responses, where onset potential is somewhat dependent on the scanning rate of potential. Thus, a more accurate measure, in this case, of relative bandgaps is provided by the  $E_{g1/2}$  data. All polymer films (**P-1**, **P-2**, **P-3**) are highly stable in both the p-type and n-type doped state in the electrolyte solution under inert atmosphere and can be cycled for more than 30 times without degradation in peak intensity. The cathodic and anodic peak current heights vary linearly with the sweep rate, indicating that the redox-active species are anchored to the electrode surface to form good polymer modified electrodes.<sup>15</sup>

**Optical Properties.** To elucidate the effect of vinylene linkage on bandgaps and to compare the results obtained from electrochemical characterization, polymers **P-1**, **P-2**, and **P-3** were also characterized by

**Table 2. Electrochemical<sup>a</sup> and Optical Data for Polymers**

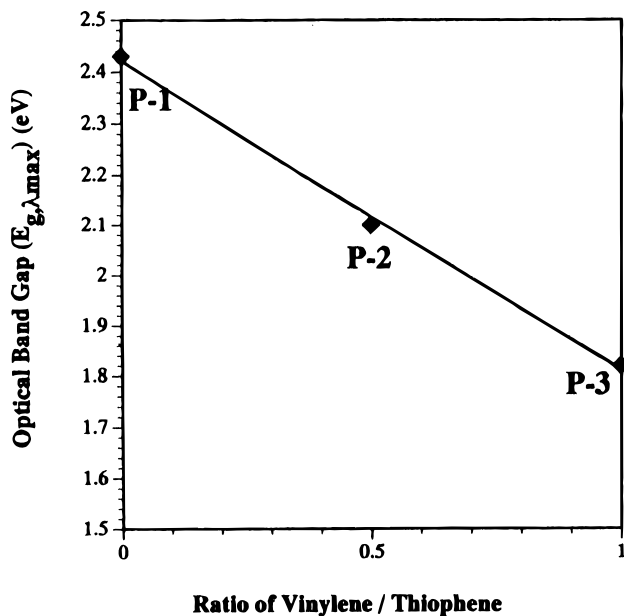
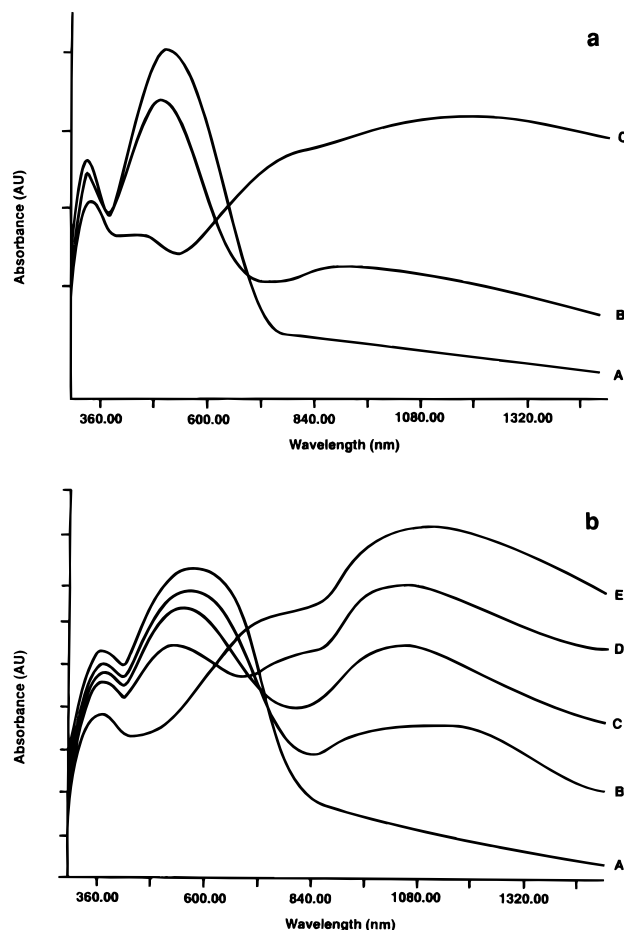
	P-1	P-2	P-3
from CV			
$E_{pa}$ , onset (V) <sup>b</sup>	-0.60	-0.55	-0.40
$E_{p1/2}$ (V) <sup>c</sup>	-0.10	0.00	0.00
$E_{nc}$ , onset (V) <sup>d</sup>	-1.94	-1.72	-1.67
$E_{n1/2}$ (V) <sup>e</sup>	-2.18	-1.96	-1.85
$E_g$ , onset (eV) <sup>f</sup>	1.34	1.17	1.27
$E_{g1/2}$ (eV) <sup>g</sup>	2.08	1.96	1.85
from UV–vis–NIR			
$E_{g,edge}$ (nm/eV) <sup>h</sup>	720/1.72	840/1.48	~1240/1.0
$E_{g,\lambda_{max}}$ (nm/eV) <sup>i</sup>	510/2.43	590/2.10	680/1.82
conductivity (S/cm)	8.3 <sup>j</sup>	20.0 <sup>j</sup>	2.0 <sup>k</sup>

<sup>a</sup> Potentials vs Ag/Ag<sup>+</sup> in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN. <sup>b</sup> Onset oxidation potential for p-doping. <sup>c</sup> Average of anodic and cathodic peak potentials for p-doping. <sup>d</sup> Onset reduction potential for n-doping. <sup>e</sup> Average cathodic and anodic peak potentials for n-doping. <sup>f</sup> Onset bandgap derived from  $E_{pa,onset} - E_{nc,onset}$ . <sup>g</sup> Bandgap derived from  $E_{p1/2} - E_{n1/2}$ . <sup>h</sup> Bandgap derived from the low energy optical absorption edge from the UV–vis spectrum. <sup>i</sup> Bandgap derived from the absorption peak maximum in the UV–vis spectrum. <sup>j</sup> Four-probe measurement on pressed pellets, polymer from chemical polymerization (FeCl<sub>3</sub>) and doped by FeCl<sub>3</sub>. <sup>k</sup> Four-probe measurement on pressed pellet, polymer made by precursor route and doped by FeCl<sub>3</sub>.

**Figure 3.** UV–vis–near-IR spectra for polymer films of **P-1** and **P-2** on ITO and **P-3** on quartz.

electronic absorption spectroscopy. Figure 3 shows the UV–vis–near-IR spectra of the polymer films (**P-1**, **P-2**, **P-3**). Both the bandgaps from onset absorption edge ( $E_{g,onset}$ ) and absorption maximum ( $E_{g,\lambda_{max}}$ ) for the neutral polymers are tabulated in Table 2. The absorption maximum of **P-2** (590 nm) is red-shifted by 80 nm relative to that of **P-1** (510 nm) by inserting a vinylene linkage between every second thiophene ring. By increasing the vinylene to thiophene ratio from 1:2 (**P-2**) to 1:1 (**P-3**), the absorption maximum of **P-3** (680 nm) is further red-shifted by another 90 nm relative to that of **P-2**. The shift in absorption maxima from **P-1** to **P-2** to **P-3** are consistent with the trend in the half-wave derived bandgaps ( $E_{g1/2}$ ) obtained from electrochemical methods. Polymers **P-2** and **P-3** exhibit some of the lowest bandgaps among the thienylene vinylene polymers thus far observed.

In Figure 4, a plot of the optical bandgaps determined from absorption maxima ( $E_{g,\lambda_{max}}$ ) as a function of vinylene to thiophene ratio are presented. A highly linear relationship (correlation coefficient of 0.997) was obtained. The optical bandgap ( $E_{g,\lambda_{max}}$ ) of **P-2** decreased by 0.3 eV with insertion of one vinylene between two

**Figure 4.** Optical bandgaps ( $E_{g,\lambda_{max}}$ ) vs ratio of vinylene to thiophene along polymer backbone.**Figure 5.** Optoelectrochemical spectra of **P-1** and **P-2** films on ITO glass in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> acetonitrile solution during electrochemical oxidation (V vs Ag wire): (a) for **P-1** at potentials of (A) 0.4 V, (B) 0.9 V and (C) 1.0 V; (b) for **P-2** at potentials of (A) -0.6 V, (B) 0.2 V, (C) 0.3 V, (D) 0.4 V, and (E) 0.6 V.

thiophene rings. Addition of one more vinylene group further reduced the bandgap of polymers by another 0.3 eV (from **P-2** to **P-3**). A highly linear relationship is also observed using  $E_{g1/2}$  data plotted versus vinylene

content. These data present a clear demonstration of linear tunability of bandgaps of copolymers which can be achieved by simply varying in a regular way the vinylene to thiophene ratio along the polymer backbones.

Optoelectrochemical methods were also employed to study the changes in band structure of the polymers during oxidation (p-type doping). Polymer films for optoelectrochemical analysis were electrochemically polymerized on ITO glass and subsequently washed with CH<sub>3</sub>CN and placed in a quartz cuvette with a counter and reference electrode. The polymers were fully reduced to the neutral state, and an initial UV-vis-near-IR absorption spectrum was obtained. The potential was stepped in 50–100 mV intervals, obtaining absorption spectra at each step, until the polymer was completely oxidized. A series of UV-vis-near-IR spectra on polymers **P-1** and **P-2** are shown in Figure 5a,b, respectively. Figure 5a,b shows typical characteristics of conjugated polymers. As the potential increases, the absorption peaks at 510 nm for **P-1** and 590 nm for **P-2** decrease, while new broad peaks beyond 1000 nm appear simultaneously, which is consistent with the formation of delocalized cationic charge carriers. Owing to much reduced absorption energy in the visible region, thin (less than 1000 nm) polymer films (**P-1** to **P-3**) on ITO are highly transparent in the doped state.

These polymers can be easily doped by ferric chloride. The four-probe conductivities on pressed pellets of doped polymers show values between 2 and 20 S/cm (Table 2). The doped polymers are highly conductive, and as such, they may be useful as transparent polymer electrode materials.

In conclusion, we have presented a predictable way to modulate electrochemical and optical properties of alkoxy-substituted polythiophenes by controlling their molecular architecture. By increasing the vinylene to thiophene ratio in a regular fashion along the polymer backbones, the bandgaps of the resulting polymers are reduced monotonically. These bandgaps are directly proportional to the composition of the repeat units. Thus, low bandgap materials (down to ca. 1.0 eV for onset bandgap) have been obtained with polymers comprising alternating ethylenedioxythiophene and vinylene groups. These materials obtained by this approach are potentially suitable for applications in transparent conducting electrodes for displays and transparent conducting composites for antistatic application.

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