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Low-oxidation-potential conducting polymers: alternating substituted *para*-phenylene and 3,4-ethylenedioxythiophene repeat units

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The effect of alkoxy substituents on the physical and electronic properties of a series of poly{1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-dialkoxybenzene}s is reported. Monomers containing methoxy, heptoxy, dodecyloxy and hexadecyloxy substituents were obtained from Negishi couplings in yields ranging from 42 to 83%. The methoxy, heptoxy and dodecyloxy monomers electropolymerized efficiently to form electroactive films, with irreversible monomer oxidation peak potentials ranging from +0.46 to +0.51 V *versus* Ag/Ag$^+$. The hexadecyloxy-substituted derivative exhibited a higher oxidation potential of +0.66 V and a slower rate of film formation owing to solubility of the oligomer. Cyclic voltammetry of the polymer films revealed reversible redox processes with quite low $E_{1/2,p}$ potentials ranging from −0.28 to −0.35 V. Band gaps of 1.75 eV for the methoxy-substituted polymer and 2.0 eV for the longer-chain-substituted polymers were determined from the onset of the π to π^* transition observed by optoelectrochemical techniques. Oxidative chemical polymerization of the dodecyloxy and hexadecyloxy monomers with ferric chloride, followed by reduction with ammonium hydroxide, produced slightly soluble polymers. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Fully conjugated polythiophenes and poly(*p*-phenylene)s have attracted significant attention owing to their electrical and optical properties and ease of derivatization. Solubility can be induced by introducing long alkyl substituents and, in some instances, an enhancement of ion transport rates during redox switching is observed[1–5]. In addition to improving solubility, alkoxy substituents lower the band gap by raising the energy of the valence-band electrons (destabilization of the highiest occupied molecular orbtial) along the conjugated chain[6–8]. These alkoxy substituents also decrease the oxidation potential of both the monomers and their polymers, allowing milder oxidative polymerization conditions, which results in fewer side reactions and more stable polymers.

Substitution at the 3- and 4-positions of thiophene monomers prevents β coupling during polymerization[9,10]. However, dialkyl substitution results in severe steric hindrance, decreasing conjugation[11]. While alkoxy substituents were expected to decrease steric hindrance and thus lower band gaps, long alkoxy substituents were found to lower conductivity as a consequence of repulsive interactions between adjacent side chains[3,12]. Monomers containing 3,4-dialkoxy substituents are also poorly reactive to oxidative polymerization because of stabilization caused by conjugation with the thiophene[9]. To eliminate these problems, an ethylenedioxy group can be attached at the 3- and 4-positions of the thiophene; in this way, the electron-donating benefits are maintained, and the steric effects are eliminated. Alkylenedioxy substituents are also too strained for a high level of conjugation with the thiophene ring, allowing them to polymerize easily.

The polymerization of 3,4-ethylenedioxythiophene (EDOT) as a route to a useful, highly conducting, and quite stable material has been the focus of considerable recent research efforts[9,13,14]. The polymer (PEDOT) exhibits a low band gap of 1.6 eV, allowing it to be used as a cathodically coloring electrochromic and a highly transmissive conductor. By incorporating a vinylene group into the polymer backbone, our group and others[15,16] have been able to lower the band gap of the resultant polymer, poly[*trans*-bis(3,4-ethylenedioxythienyl)vinylene], to 1.4 eV.

Polymers incorporating both bithiophene and phenylene moieties in the backbone have been developed in order to finely control optoelectronic properties on easily functionalized systems[6–19]. For example, poly[1,4-bis(2-thienyl)-2,5-dimethoxybenzene] exhibited a band gap of 2.2 eV, 0.5 eV lower than its dimethyl analogue[6]. By utilizing long alkoxy substituents, soluble regioregular polymers were obtained that could be cast to form free-standing films which, upon annealing, were highly crystalline and, in some instances, thermotropic[7].

By analogy with the thiophene-based systems, incorporation of EDOT into similar phenylene-containing polymers should yield lower gap materials that will form stable oxidized and conducting states. We find this to indeed be the case and have previously reported on a series of bis(EDOT)arylenes[15,20–22]. By combining the EDOT and dialkoxyphenylene units along the main chain, a very electron-rich, low-oxidation-potential system is created. We

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report here on a series 1,4-bis[2-(3,4-ethylenedioxythienyl)]-2,5-dialkoxybenzenes [BEDOT-B(OR)$_2$] which not only polymerize under mild oxidative conditions, but also undergo redox switching at extremely low potentials (≤ -0.3 V *versus* Ag/Ag$^+$).

EXPERIMENTAL

Materials

Hydroquinone, potassium hydroxide, iodomethane, 1-bromoheptane, 1-bromododecane, 1-bromohexadecane, bromine, n-butyl lithium (2.5 M in hexanes), magnesium bromide diethyl etherate, nickel (II) bis(diphenylphosphino)propane dichloride, tetrakis(triphenylphosphine) palladium (0), tetra-n-butylammonium bromide and perchloric acid were obtained from Aldrich Chemicals and used as-received. Zinc chloride was obtained from Aldrich Chemicals and flame dried under vacuum prior to use. 3,4-Ethylenedioxythiophene (EDOT) was obtained from AG Bayer and distilled prior to use. Carbon tetrachloride, concentrated ammonium hydroxide, concentrated hydrochloric acid, glacial acetic acid, diethyl ether, methanol, ethanol and benzene were acquired from Fisher Scientific and used as-received. Tetrahydrofuran (THF), acetonitrile and methylene chloride were purchased from Fisher Scientific and dried and distilled prior to use. Tetra-n-butylammonium perchlorate was prepared by reaction of tetra-n-butylammonium bromide with perchloric acid and recrystallized from ethanol prior to use[23].

Structural identification of monomers and polymers

Infra-red spectra were obtained with a Biorad/Digilab FTS-40 Fourier transform infra-red (*FT*i.r.) spectrophotometer with diffuse reflectance attachment on a powdered mixture of the sample with KBr. Nuclear magnetic resonance (n.m.r.) spectra were obtained in solution and recorded on a Gemini 300 *FT*n.m.r. or a VXR 300 *FT*n.m.r. spectrophotometer. Elemental analyses were obtained from Robertson Microlit Laboratories, Inc., Madison, NJ. High-resolution mass spectrometry (HRMS) was performed with a Finnigan MAT 95Q mass spectrometer.

Electrochemistry

Cyclic voltammetry was carried out with an EG & G Princeton Applied Research model 273 potentiostat/galvanostat employing a platinum button working electrode, a platinum plate counter electrode, and an Ag/Ag$^+$ reference electrode. The monomer concentration was 10 mM in each case, and the electrolyte was 0.1 M tetra-n-butylammonium perchlorate in acetonitrile or acetonitrile/methylene chloride. Electronic spectra were obtained with a Varian Cary 5E ultraviolet–visible–near infra-red (u.v.–vis.–n.i.r.) spectrophotometer. Experimental details have been reported previously[24].

Monomer synthesis

1,4-Dibromo-2,5-dihydroxybenzene (1). Hydroquinone (0.968 mol) was combined with glacial acetic acid (500 ml) and methylene chloride. A solution of bromine (1.88 mol) in methylene chloride (100 ml) was added dropwise over 2 h at room temperature. After approximately half the bromine was added, all solids had dissolved. The solution was stirred at room temperature for 15 h, at which time the precipitate was collected by filtration and dried under vacuum over NaOH pellets. Recrystallization from isopropanol yielded a white crystalline solid [m.p. 191–192°C, 42%]. ^{1}H n.m.r. (ppm): 9.94 (br), 7.03 (m).

1,4-Dibromo-2,5-dimethoxybenzene (2a). A solution of KOH (0.077 mol) in ethanol (100 ml) was added slowly with stirring to a solution of **1** (0.035 mol) in THF (200 ml) under argon. The solution was stirred at room temperature for 3 h, and then a solution of iodomethane (0.077 mol) in THF (100 ml) was added slowly with stirring. The mixture was stirred at 50°C for 24 h, then precipitated into water. The product was collected by filtration and recrystallized from ethanol to give a white crystalline solid [m.p. 144–147°C (lit.[25] m.p. 142–143°C), 86% yield]. ^{1}H n.m.r. (CDCl$_3$, ppm): 7.10 (s), 3.85 (s).

1,4-Dibromo-2,5-diheptoxybenzene (2b). Compound **2b** was synthesized according to the procedure described for **2a** using KOH (0.069 mol), **1** (0.033 mol) and 1-bromoheptane (0.069 mol). Recrystallization from ethanol gave a white clumped solid [m.p. 65–67 °C (lit.[7] m.p. 59–60°C), 90% yield]. ^{1}H n.m.r. (C$_6$D$_6$, ppm): 6.98 (s), 3.37 (t), 1.54 (m), 1.25 (m), 0.90 (t).

1,4-Dibromo-2,5-didodecyloxybenzene (2c). Compound **2c** was prepared according to the procedure described for **2a** using KOH (0.032 mol), **1** (0.016 mol) and 1-bromododecane (0.032 mol). Recrystallization from ethanol/benzene (3/1) resulted in a white crystalline solid [m.p. 75–77°C (lit.[7] m.p. 77–79°C), 57% yield]. ^{1}H n.m.r (CDCl$_3$, ppm): 7.18 (s), 4.00 (t), 1.88 (p), 1.53 (p), 1.32 (m), 0.98 (t).

1,4-Dibromo-2,5-dihexadecyloxybenzene (2d). Compound **2d** was prepared according to the procedure described for **2a** using KOH (0.151 mol), **1** (0.072 mol) and 1-bromohexadecane (0.151 mol). Recrystallization from chloroform resulted in a white fluffy solid [m.p. 87–89°C (lit.[7] m.p. 88–89°C), 88% yield]. ^{1}H n.m.r. (C$_6$D$_6$, ppm): 6.99 (s), 3.38 (t), 1.55 (q), 1.30 (m), 0.92 (t).

1,4-Bis[2-(3,4-ethylenedioxy)thienyl]-2,5-dimethoxybenzene (3a). n-Butyl lithium (0.0669 mol) was slowly added to a stirred solution of EDOT (0.0669 mol) in THF (75 ml) at −78°C under argon. The yellow solution was allowed to stir for 1 h. The lithiated EDOT was transferred by means of a cannula into a stirring solution of ZnCl$_2$ (0.0639 mol) in THF (75 ml) over a 15 min period. The mixture was stirred under argon for 1 h. The resulting EDOT–ZnCl was then slowly added to a solution of **2a** (0.0167 mol) and Pd(PPh$_3$)$_4$ (8.65×10^{-5} mol) in THF (50 ml). The bright yellow solution was stirred at 50°C under N$_2$ for 72 h. It was then cooled to ambient temperature and quenched by pouring the mixture into 1.5 M HCl. A large amount of tan solid precipitated upon contact with the acid. This was collected and washed with saturated NaH$_2$CO$_3$, then dried under vacuum. The product was purified by recrystallization from ethanol/benzene (3/1) followed by column chromatography (ethyl acetate/pentane, 1/1) to yield a pale green solid [m.p. 197–200°C, 42%]. Anal. calcd for $C_{20}H_{18}O_6S_2$: C, 57.4; H, 4.34; O, 22.94; S, 15.32. Found: C, 57.21; H, 4.29; S, 15.44. ^{1}H n.m.r. (C$_6$D$_6$, ppm): 7.97 (s), 6.34 (s), 3.63 (s), 3.48 (s). ^{13}C n.m.r. (CDCl$_3$, ppm): 149.95, 141.31, 138.73, 121.13, 113.28, 95.57, 97.58, 64.90, 64.37, 56.68. HRMS calcd for $C_{20}H_{18}O_6S_2$: 418.054; found: 418.048.

1,4-Bis[2-(3,4-ethylenedioxy)thienyl]-2,5-diheptoxybenzene (3b). Compound **3b** was prepared according to the procedure described for **3a** using EDOT (0.0352 mol), n-butyl lithium (0.0352 mol), zinc chloride (0.0352 mol), $Pd(PPh_3)_4$ (4.16 × 10^{-5} mol) and **2b** (0.00879 mol), resulting in a pale yellow, crystalline solid after recrystallization from ethanol/benzene (3/1) [m.p. 85–87°C, 83% yield]. Anal. calcd for $C_{32}H_{42}O_6S_2$: C, 65.50; H, 7.21; O, 16.36; S, 10.93. Found: C, 65.24; H, 7.18; S, 11.09. ^{1}H n.m.r. (C_6D_6, ppm): 8.10 (s), 6.36 (s), 4.0 (t), 3.5 (m), 1.85 (p), 1.46 (p), 1.23 (m), 0.87 (t). ^{13}C n.m.r. ($CDCl_3$, ppm): 148.79, 141.05, 138.41, 120.73, 113.30, 99.36, 99.24, 69.72, 64.73, 64.20, 31.71, 29.31, 29.03, 26.14, 22.55, 14.03. HRMS calcd for $C_{32}H_{42}O_6S_2$: 586.24; found: 586.24.

1,4-Bis[2-(3,4-ethylenedioxy)thienyl]-2, 5-didodecyloxybenzene (3c). Compound **3c** was prepared according to the procedure described for **3a** using EDOT (0.0331 mol), n-butyl lithium (0.0331 mol), zinc chloride (0.0331 mol), $Pd(PPh_3)_4$ (3.91 × 10^{-5} mol) and **3b** (0.00827 mol), resulting in a bright green, crystalline solid after recrystallization from ethanol/benzene (3/1) [m.p. 92–95°C, 79% yield]. Anal. calcd for $C_{42}H_{62}O_6S_2$: C, 69.38; H, 8.6; O, 13.2; S, 8.82. Found: C, 69.65; H, 8.68; S, 8.57. ^{1}H n.m.r. (C_6D_6, ppm): 8.11 (s), 6.37 (s), 4.06 (t), 3.5 (m), 1.86 (p), 1.51 (p), 1.28 (m), 0.93 (t). ^{13}C n.m.r. ($CDCl_3$, ppm): 149.04, 141.20, 138.50, 121.04, 113.60, 99.35, 69.91, 64.82, 64.28, 31.91, 29.68, 29.65, 29.43, 29.34, 26.26, 22.67, 14.06. HRMS calcd for $C_{42}H_{62}O_6S_2$: 726.399; found: 726.398.

1,4-Bis[2-(3,4-ethylenedioxy)thienyl]-2, 5-dihexadecyloxybenzene (3d). Compound **3d** was prepared according to the procedure described for **3a** using EDOT (0.0352 mol), n-butyl lithium (0.0352 mol), zinc chloride (0.0352 mol), $Pd(PPh_3)_4$ (4.16 × 10^{-5} mol) and **2d** (0.00879 mol), resulting in a bright yellow, amorphous solid after recrystallization from chloroform and column chromatography (ethyl acetate/pentane, 1/1) [m.p. 92–94°C, 79% yield]. Anal. calcd for $C_{50}H_{78}O_6S_2$: C, 71.55; H, 9.37; O, 11.44; S, 7.64. Found: C, 71.46; H, 9.29; S, 7.53. ^{1}H n.m.r. (C_6D_6, ppm): 8.11 (s), 6.37 (s), 4.06 (t), 3.52 (m), 1.88 (p), 1.52 (m), 1.31 (m), 0.91 (t). ^{13}C n.m.r. ($CDCl_3$, ppm): 149.04, 141.19, 138.54, 121.02, 113.62, 99.44, 69.93, 64.87, 64.37, 31.96, 29.74, 29.70, 29.65, 29.50, 29.45, 29.39, 26.31, 22.72, 14.14. HRMS calcd for $C_{50}H_{78}O_6S_2$: 838.53; found: 838.53.

Chemical polymerization

Poly{1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2, 5-didodecyloxybenzene} (4c). A solution of $FeCl_3$ (2.75 × 10^{-3} mol) in $CHCl_3$ (5 ml) was added dropwise to a stirring solution of **3c** (6.88 × 10^{-4} mol) in chloroform (15 ml). The black mixture was stirred under argon for 24 h, then added dropwise to rapidly stirring methanol (200 ml). The black solid was collected by filtration and washed with successive portions of methanol and water. The black powder was reduced by rapid stirring in concentrated ammonium hydroxide (75 ml) and $CHCl_3$ (75 ml) for 20 h. The red $CHCl_3$ solution was isolated, washed with water until neutral, and concentrated under reduced pressure. The solution was then precipitated into rapidly stirring methanol to yield a brick red powder that was collected by filtration and washed with methanol, then dried under vacuum. The resultant brick red powder was insoluble or very poorly soluble in a broad range of organic solvents, with highest solubility in $CHCl_3$.

Poly{1,4-bis[2-(3, 4-ethylenedioxy)thienyl]-2,5-dihexadecyloxybenzene} (4d). Compound **4d** was prepared according to the procedure described for **4c** using **3d** (2.98 × 10^{-4} mol) and $FeCl_3$ (2.98 × 10^{-4} mol to 5.96 × 10^{-4} mol), resulting in a poorly soluble, brick red powder.

RESULTS AND DISCUSSION

Monomer synthesis

The known compounds, 1,4-dibromo-2,5-dialkoxybenzenes (**2a–2d**), were synthesized by an alternative method to that used previously[6], allowing a reduction in the total number of synthetic steps as shown in *Figure 1*. 1,4-Dibromo-2,5-dihydroxybenzene (**1**) was prepared by bromination of hydroquinone in acetic acid/methylene chloride. Williamson ether synthesis was then used to

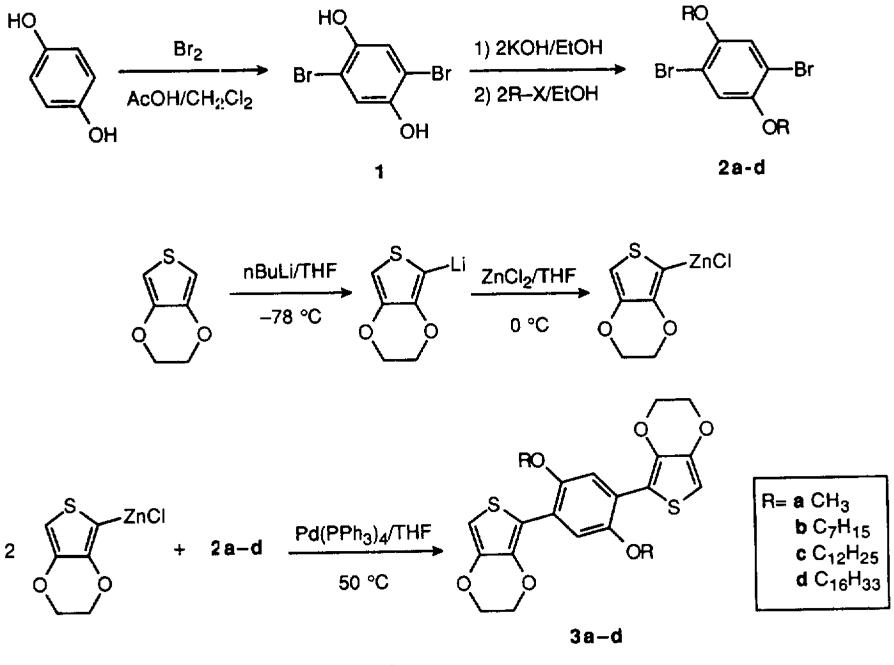
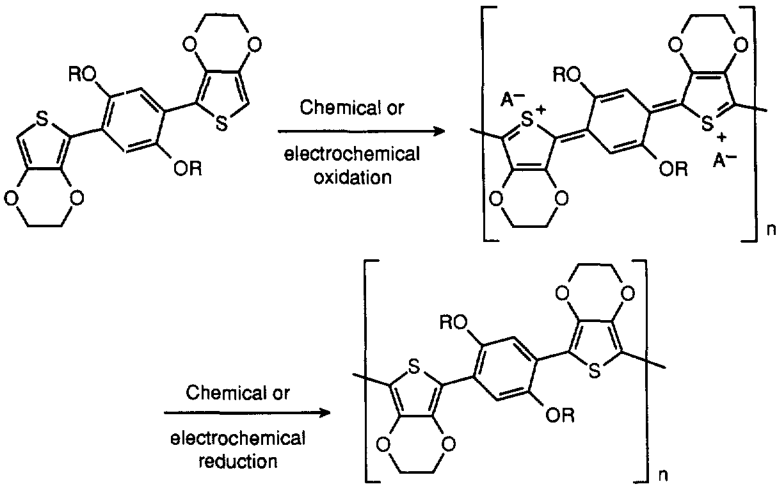


Figure 1 Synthesis of 1,4-bis(3,4-ethylenedioxythienyl)-2,5-dialkoxybenzene monomers



4a–d

Figure 2 Oxidative polymerization of 1,4-bis(3,4-ethylenedioxythienyl)-2,5-dialkoxybenzenes

prepare 1,4-dibromo-2,5-dialkoxybenzenes (**2a–2d**) by reaction of the dipotassium salt of **1** with the appropriate 1-haloalkane. The structure and purity of **2a–2d** were confirmed by ^{1}H n.m.r. and melting point.

Coupling of 2-bromothiophene with 1,4-dialkoxy-2,5-dibromobenzenes has been reported previously[5,6]. Attempts to couple the magnesium bromide derivative of EDOT with 1,4-dibromo-2,5-dimethoxybenzene (DBDMB) using nickel (II) bis(diphenylphosphino)propane dichloride ($NiCl_2$·dppp) were unsuccessful, probably due to the electron-donating methoxy substituents reducing the electrophilicity of the phenyl carbon *ortho* to the methoxy substituent.

The catalyst system was then changed, as shown in *Figure 1*, to utilize tetrakis(triphenylphosphine) palladium (0) [$Pd(PPh_3)_4$], which is thought to be less selective than nickel catalyst. This is typically attributed to the increased size of the palladium (so that coordination is less hindered) and the better leaving ability of the triphenylphosphine ligands[26,27].

Reaction of EDOT with butyl lithium, followed by reaction of the lithiated product with $ZnCl_2$, provided the organometallic for coupling. The resultant EDOT–ZnCl was then reacted with the desired 1,4-dialkoxy-2,5-dibromobenzene in the presence of $Pd(PPh_3)_4$ at 50°C under argon to produce the 1,4-bis(3,4-ethylenedioxythienyl)-2,5-dialkoxybenzene [BEDOT-B$(OR)_2$] (**3a–3d**). The monomers were obtained in reasonable yields (42–83%) and characterized by i.r., u.v.–vis., ^{1}H n.m.r., ^{13}C n.m.r., melting point, elemental analysis and HRMS. As expected, longer alkoxy chains resulted in decreased melting points (for example, the dimethoxy monomer **3a** melts at 197–200°C, while the diheptoxy monomer **3b** melts at 85–87°C) and decreased polarities (thin layer chromatography).

Electrochemical analysis and polymerization

The monomers **3a–3d** were electrochemically polymerized (*Figure 2*) in an argon atmosphere using 0.01 M monomer and 0.1 M tetrabutylammonium perchlorate (TBAP) in CH_3CN/CH_2Cl_2. The mixture of CH_2Cl_2 and CH_3CN was required for electropolymerization because the monomers were poorly soluble in CH_3CN. For all monomers, polymer film deposition in CH_2Cl_2 electrolyte alone was quite slow, probably due to solubility of the oligomers.

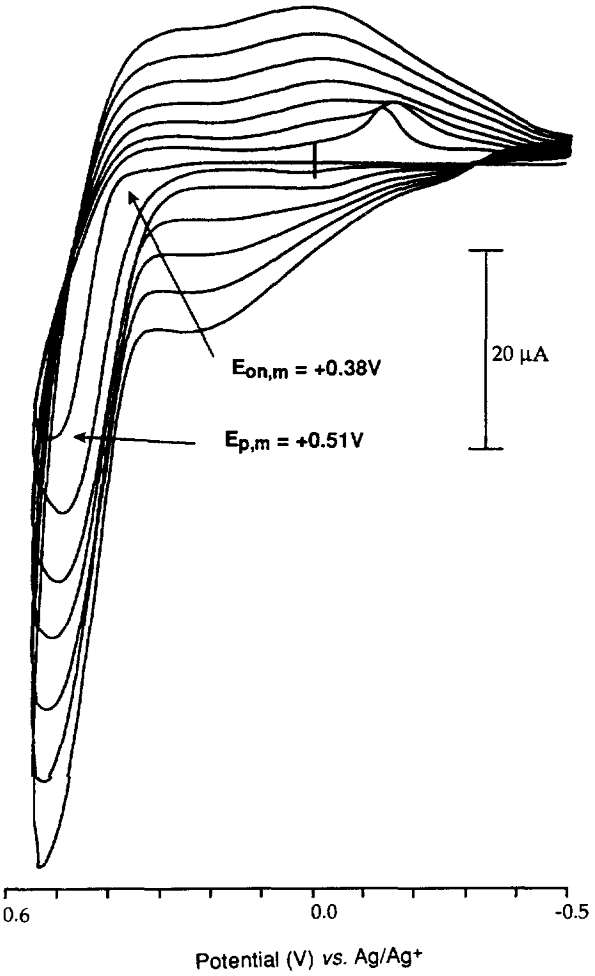


Figure 3 Repeated potential scanning electropolymerization of **3c** (0.01 M) carried out in 0.1 M TBAP in 60:40 CH_2Cl_2:CH_3CN at 100 mV s^{-1}

A solubility study was conducted to determine the minimum amount of CH_2Cl_2 needed to solubilize the monomers in CH_3CN. As expected, the longer the alkoxy substituent, the more CH_2Cl_2 was needed. For R = methyl, heptyl, dodecyl and hexadecyl, the ratios of CH_2Cl_2 to CH_3CN required were, respectively, 40:60, 50:50, 60:40 and 70:30.

Table 1 Electrochemical results for BEDOT-B(OR)$_2$ monomers and polymers

Monomer	$E_{on,m}$ (V)[a]	$E_{p,m}$ (V)	$E_{a,p}$ (V)	$E_{c,p}$ (V)	$E_{1/2,p}$ (V)	E_g (eV)
3a	+0.30	+0.46	−0.20	broad	[b]	1.75
3b	+0.32	+0.47	−0.28	−0.36	−0.32	1.95
3c	+0.38	+0.51	−0.25	−0.31	−0.28	2.03
3d	+0.41	+0.66	−0.30	−0.40	−0.35	[b]

[a] All potentials reported *versus* Ag/Ag$^+$
[b] Could not be determined

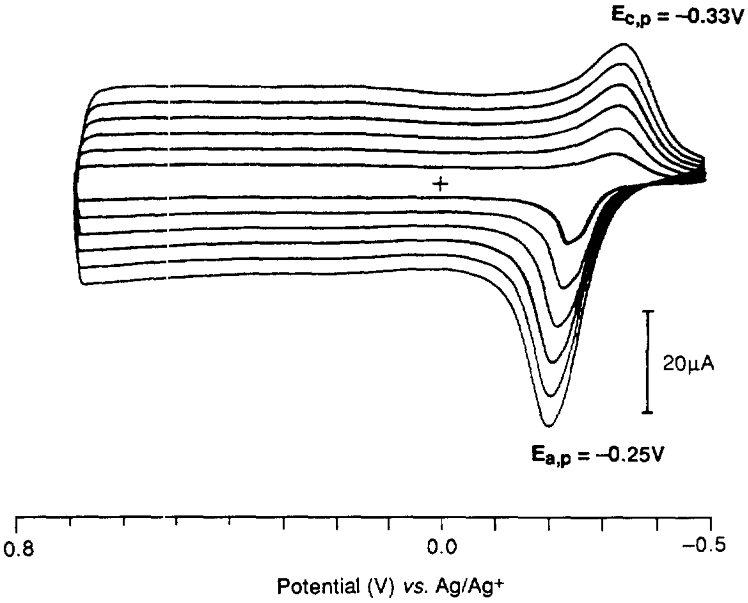


Figure 4 Cyclic voltammograms of **4c** at 50, 100, 150, 200, 250 and 300 mV s^{-1} carried out in 0.1 M TBAP in CH$_3$CN

Figure 3 shows multiple cyclic voltammograms for the repeated scanning electropolymerization of **3c**, which is representative for polymerization of **3a**–**3d**. During the first anodic scan, a single peak is observed for all monomers which corresponds to irreversible monomer oxidation at a bare metal electrode. For **3a**, the monomer oxidation ($E_{on,m}$) onsets at +0.30 V and a peak ($E_{p,m}$) is observed at +0.46 V *versus* Ag/Ag$^+$. All further electrochemical potentials will be reported with respect to this reference The $E_{p,m}$ values shown in *Table 1* are low relative to the analogous 1,4-bis(2-thienyl)-2,5-dialkoxybenzene monomers; for example, 1,4-bis(2-thienyl)-2,5-dimethoxybenzene exhibits an $E_{p,m}$ value 250 mV higher at +0.71 V. These low oxidation potentials are important as they are indicative of the ease with which the monomers are oxidized, and the electropolymerization can proceed with minimal side reactions.

With repeated potential scanning, thin, insoluble films of the polymers **4a**–**4d** form on the electrode surface. Cathodic redox processes at about +0.2 V and at 0.0 V are observed during reduction of the polymer and evolve in intensity with repeated scanning. On the anodic scans, polymer oxidation is seen to evolve at about +0.15 V, prior to further monomer oxidation and polymerization. The increase in current response with each scan indicates that effective electroactive polymer film deposition is occurring.

Films of polymers **4a**–**4d** were washed with CH$_2$Cl$_2$/CH$_3$CN and placed in a monomer-free 0.1 M TBAP/CH$_3$CN solution. Cyclic voltammograms of the polymers were obtained as a function of scan rate between 50 and 300 mV s^{-1}. For example, the cyclic voltammograms of polymer **4c**, which are representative of **4b**–**4d**, are shown in *Figure 4*. A linear increase in peak current for both the cathodic and anodic redox processes as a function of scan rate is observed and indicates that the film is electrode supported and electroactive[28].

It is evident that all of these polymers are converted into their doped forms remarkably easily. The half wave potentials ($E_{1/2,p}$) of the polymers are all very low (*Table 1*) as desired for polymers which are highly stable conductors. In fact, these switching potentials are the lowest we have ever observed for a thiophene-based conducting polymer. By comparison, poly[1,4-bis(2-thienyl)-2,5-dimethoxybenzene] exhibits much higher half wave potentials[8] at $E_{1/2,p}$ = +0.27 and +0.68 V. The low oxidation potentials of the EDOT polymers can be attributed to electron donation from the ethylenedioxy substituents along with the low steric requirements of the ethylenedioxy ring appended to the thiophene.

The cyclic voltammogram of polymer **4a** differs somewhat from those of polymers with longer alkoxy substituents. As shown in *Figure 5*, the redox switching occurs at a slightly higher potential (although still less than 0.0 V) and is significantly broadened. In addition, a second oxidative process begins at about +0.40 V and is reminiscent of the cyclic voltammetry (CV) response for the dialkoxy-substituted bis(2-thienyl)benzene polymers[6]. Interestingly, the CV response for **4a** is similar to the polymer electrochemistry that evolves during film growth for all of the polymers (compare *Figures 3, and 5*). On the other hand, during redox cycling of polymers containing longer alkoxy

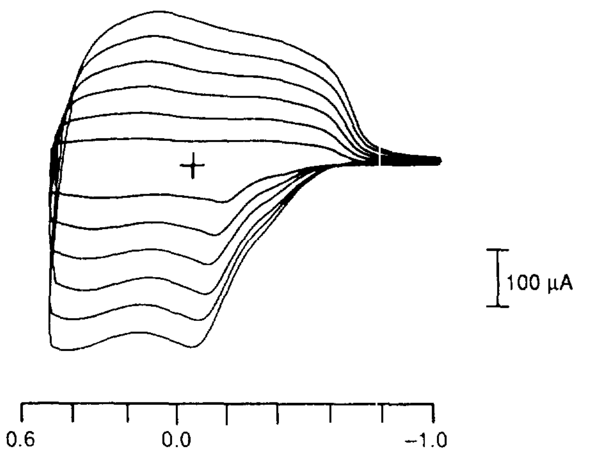


Figure 5 Cyclic voltammograms of polymer **4a** at 50, 100, 150, 200, 250 and 300 mV s^{-1} carried out in 0.1 M TBAP in CH_3CN

substituents, there is a distinct cathodic shift in the polymer redox (*Figure 4*). In these instances, we believe that the side chains play a role in relative charge carrier (polaron *versus* bipolaron) stability. The fact that the longer-chain alkoxy-substituted EDOT-based polymers under investigation here switch at such low potentials, suggests that these side chains are greatly assisting in charge transfer and stabilization of the fully doped species.

The low monomer and polymer oxidation potentials lead to fewer side reactions during polymerization and switching: thus more stable polymers are obtained. A relative measure of polymer stability was obtained by monitoring the loss in electroactivity, indicated by a decreased current response with repeated redox cycling. Polymer **4c** was cycled repeatedly between −0.5 and 0.0 V in monomer-free electrolyte solution. The loss in electroactivity was found to be a function of the solvent chosen for switching. When the solvent system was the same as that used for polymer growth (a 60:40 mixture of CH_2Cl_2:CH_3CN with 0.1 M TBAP), very little loss in current response was observed with repeated scanning; after 3100 scans, only 27% loss in electroactivity was observed. When **4c** was switched in 0.1 M TBAP/CH_3CN, the same electroactivity loss occurred in 50 scans. This disparity, which has been observed previously for polypyrroles[29], has been attributed to a solvent memory effect in the polymer. These polymers are swollen to some extent by solvent during film growth. Subsequent exposure to a poorer solvent system during switching leads to film collapse (and ultimately delamination from the electrode) and a reduction in electroactivity.

Of special interest in considering these polymers for electrode applications is the flat current response visible in *Figure 4* which extends to well beyond +0.7 V. This indicates that polymers **4b**–**4d** are stable over a broad potential window where they can be used as conductors. To determine the useful potential window for polymer **4c**, films were cycled to sequentially higher potentials in monomer-free electrolyte solution while monitoring the current response in 0.1 M TBAP/CH_3CN. As can be seen in *Figure 6*, the flat anodic response extends to beyond 1.0 V. A second oxidation process, attributed to polymer over-oxidation, begins above 1.0 V. As the second process occurs, the current response for the low-potential reversible redox process decreases. After scanning to +1.4 V, greater than 70% loss in the current response of the polymer oxidation peak at −0.20 V is observed.

Optoelectrochemistry

In order to determine the electronic band structure of

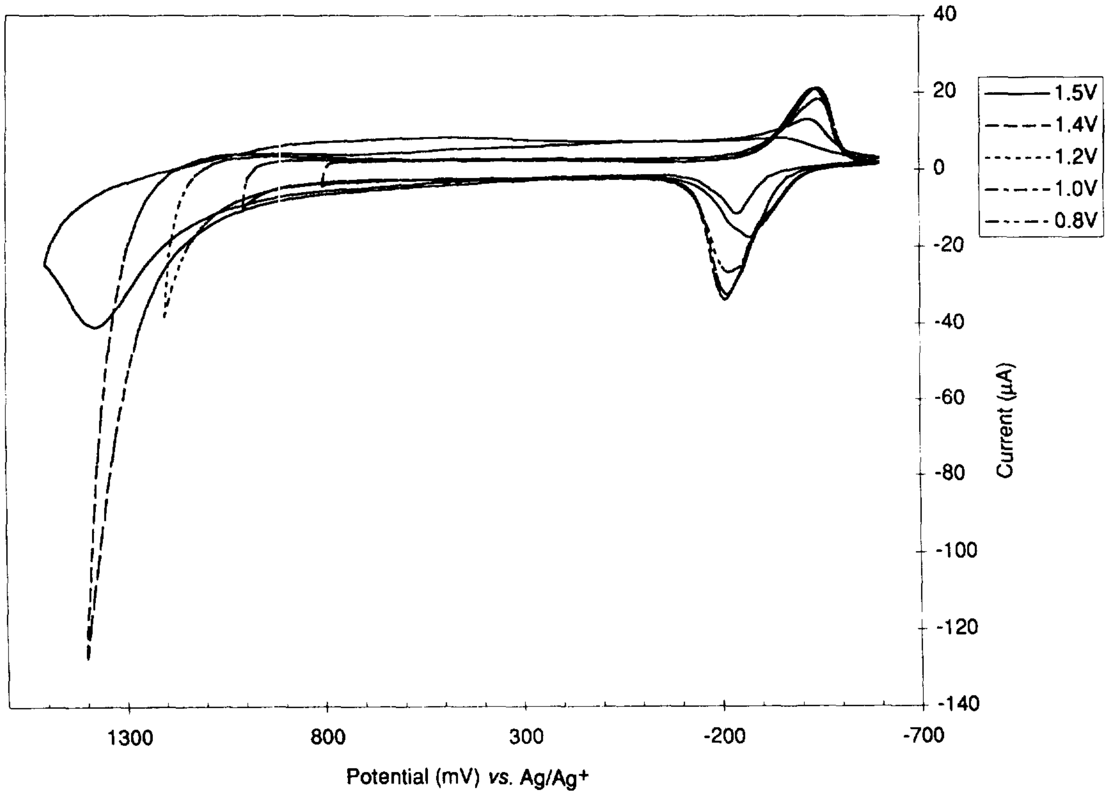


Figure 6 Cyclic voltammograms to subsequently higher switching potentials of polymer **4c** carried out in 0.1 M TBAP in CH_3CN at 100 mV s^{-1}

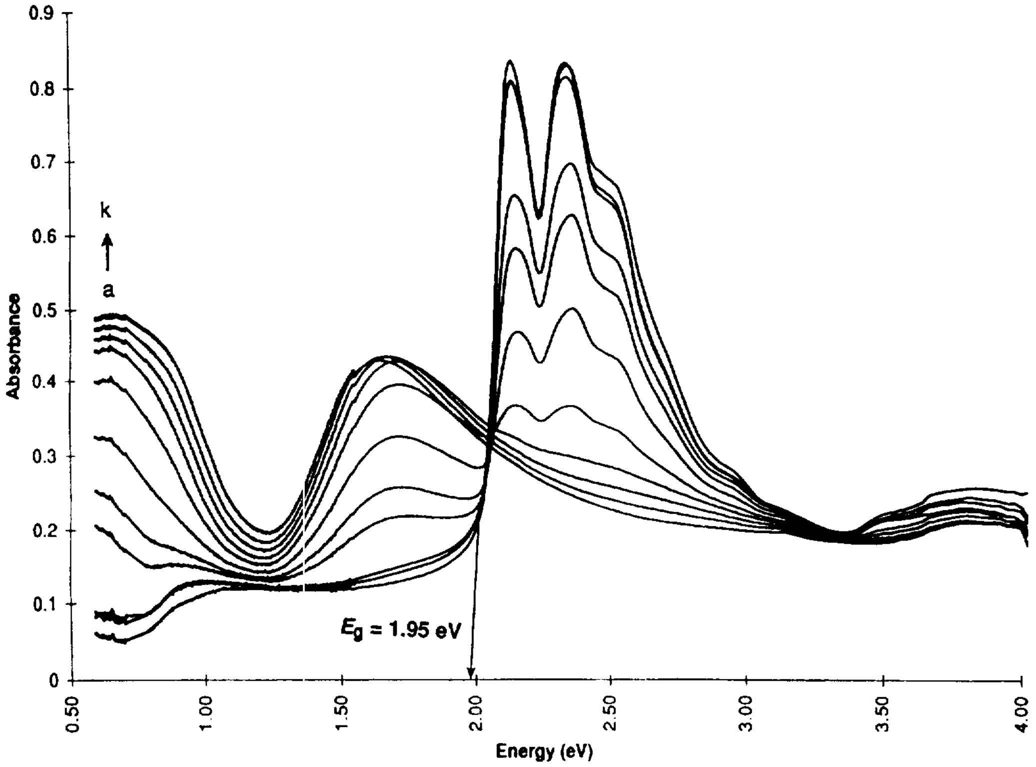
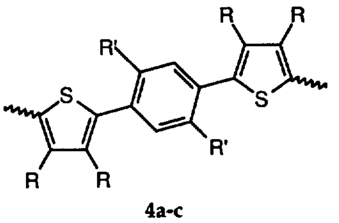


Figure 7 Optoelectrochemical analysis of **4b**: u.v.–vis.–n.i.r. spectra taken at ptentials of −0.40 (a), −0.30 (b), −0.20 (c), −0.10 (d), −0.08 (e), −0.04 (f), 0.00 (g), 0.10 (h), 0.20 (i), 0.30 (j) and 0.40 V (k) *versus* Ag/Ag$^+$

Table 2 Comparative band gaps for various conjugated polymers



4a-c

Compound	R	R′	E_g (eV)	Ref.
Polythiophene			2.0	32
Poly(*p*-phenylene)			3.0	33
Poly(3,4-EDOT)			1.6	12
PBTB-(Me)$_2$[a]	H	CH_3	2.7	6
PBTB[b]	H	H	2.2	6
PBTB-(OMe)$_2$[c]	H	OCH_3	2.2	6
PBEDOT-B[d]	OCH_2CH_2O	H	1.8	20
4a	OCH_2CH_2O	OCH_3	1.8	this work
4b	OCH_2CH_2O	OC_7H_{15}	2.0	this work
4c	OCH_2CH_2O	$OC_{12}H_{25}$	2.0	this work

[a] PBTB-(Me)$_2$ = poly[1,4-bis(2-thienyl)-2,5-dimethylbenzene]
[b] PBTB = poly[1,4-bis(2-thienyl)benzene]
[c] PBTB-(OMe)$_2$ = poly[1,4-bis(2-thienyl)-2,5-dimethoxybenzene]
[d] PBEDOT-B = poly{1,4-bis[2-(3,4-ethylenedioxy)thienyl]benzene}

polymers **4a–4c**, u.v.–vis.–n.i.r. spectra (310 to 2480 nm) were obtained as a function of applied potential. Polymer films were obtained by electropolymerization in the mixed solvent/electrolyte systems described earlier onto indium tin oxide (ITO) coated glass electrodes at a constant potential of +0.50 V. After washing to remove excess monomer and placing the film in a monomer-free electrolyte solution, spectra were obtained by incrementally stepping the potential between −0.4 and +0.4 V after an initial reduction at −0.8 V. During this stepwise oxidation, the polymers switched from a pale red reduced state to a deep blue oxidized state, with green observed at intermediate potentials.

A series of optoelectrochemical spectra for polymer **4b** is

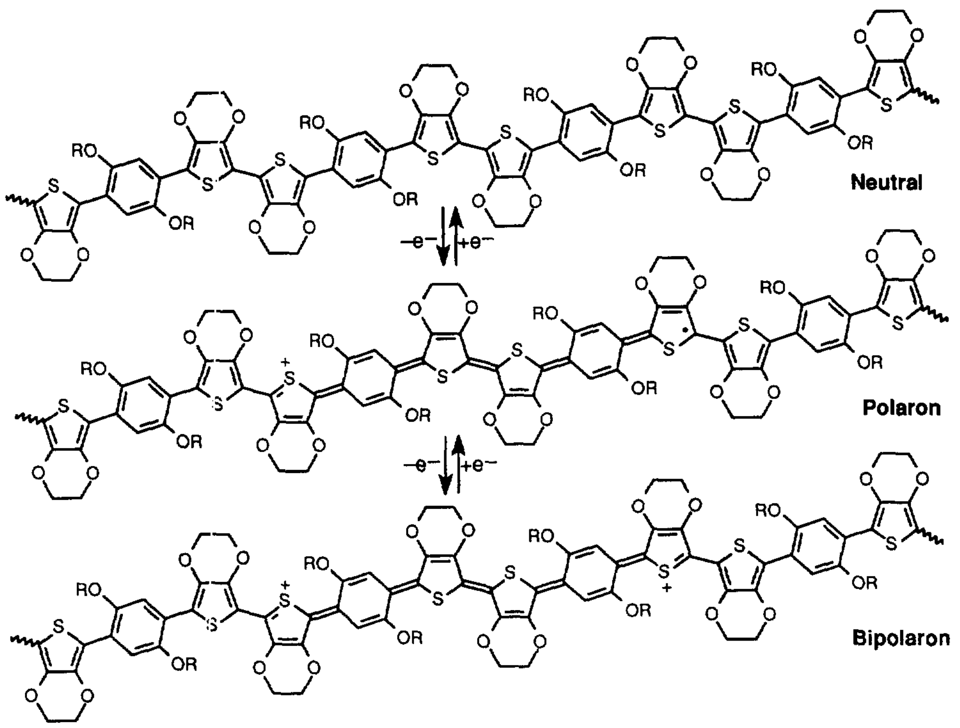


Figure 8 Reversible oxidation and reduction processes of poly[1,4-bis(3,4-ethylenedioxythienyl)-2,5-dialkoxybenzene]s

shown in *Figure 7*. At low potential (−0.4 V), the polymer is in its reduced (insulating) form and the electronic band gap (E_g, *Table 1*) can be determined from the onset of the π to π^* transition. In this state, the only significant absorption is due to the excitation of electrons from the valence band to the conduction band. The onset of the transition occurs at 1.95 eV for **4b**, with peaks at 2.10 eV and 2.35 eV and a shoulder at 2.45 eV. The splitting of the π to π^* absorption is commonly attributed to vibronic coupling of the π electrons of the polymer backbone[30]. Interestingly, this is observed only in the polymers (**4b** and **4c**) with longer alkoxy substituents; the dimethoxy polymer shows only a broad absorption, yet has a similar band gap. As the potential is increased, the polymer oxidatively dopes. The interband transition decreases in intensity, and two absorbances evolve at lower energies owing to the formation of bipolaronic species (*Figure 8*)[31]. This behaviour is consistent with the many thiophene-based conducting polymers that have been studied to date.

With the availability of the poly{1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-dialkoxybenzene}s, we can now compare the steric and electronic effects of substituent groups on electronic properties of these systems. *Table 2* shows E_g values for a series of related polymers. For poly[1,4-bis(2-thienyl)benzene], a band gap of 2.2 eV has been previously reported[6], which is intermediate to the band gaps of polythiophene[32] and poly(*p*-phenylene)[33]. Derivatization with methyl substituents in the 2- and 5-positions of the phenyl ring increases the band gap to 2.7 eV[6]. This can be attributed to steric effects; the methyl substituents decrease interaction between adjacent rings, decreasing the extent of conjugation.

When methoxy substituents are used instead of methyl substituents, the band gap is identical to that of the unsubstituted polymer (2.2 eV[6]); presumably, the steric effect of ring substitution is counteracted by electron donation from the ether groups. The addition of the ethylenedioxy bridge to the thiophenes in poly{1,4-bis[2-(3,4-ethylenedioxy)thienyl]benzene} (PBEDOT-B), to give four electron-donating substituents per monomer repeat unit, significantly decreases the band gap to 1.8 eV[20]. As with the analogous thiophene polymers, addition of methoxy groups to the internal phenylene ring does not have a net effect on the band gap. Increasing the alkoxy substituent length slightly increases the band gap (to 2.0 eV for heptoxy and dodecyloxy polymers), presumably owing to increased steric interactions.

Chemical polymerization

Ferric-chloride-induced oxidative polymerization[34] has been used previously to prepare poly[1,4-bis(2-thienyl)-2,5-dialkoxybenzene]s[7]. In those instances, chloroform-soluble polymers were obtained with alkoxy substituents R = $C_{16}H_{33}$ and $C_{20}H_{41}$, while R = $C_{12}H_{25}$ was insoluble. We find that EDOT derivatives typically have lower solubilities than their thienyl counterparts. Oxidative polymerization of either BEDOT-B($OC_{12}H_{25}$)$_2$ (**3c**) or BEDOT-B($OC_{16}H_{33}$)$_2$ (**3d**) using $FeCl_3$ (in concentrations ranging from one to four equivalents of $FeCl_3$) in chloroform and subsequent reduction in concentrated NH_4OH (*Figure 2*) produced very poorly soluble, brick red polymers.

The structures of the neutral polymers were studied by *FT*i.r. The vibration associated with the thiophene α-C–H stretch apparent in the monomers (*ca.* 3100 cm^{-1}) is absent in the polymers, while the vibrations of the phenylene C–H stretches remain. These results indicate that polymerization occurred through the thiophene α-carbon, as expected. It is not possible to discern whether the polymer was crosslinked through the phenylenes, because the phenylene C–H stretch would remain in the i.r. spectrum of partially crosslinked materials. Because of poor solubility, the focus of this work has been on the electrochemical and optoelectrochemical properties of the electrosynthesized polymers. Further studies of soluble bis(EDOT)-2,5-dialkoxybenzene polymers are under way and a full study will be published elsewhere.

CONCLUSION

A series of 1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-dialkoxybenzenes was synthesized by using palladium-catalysed cross-coupling reactions. These monomers were subsequently electrochemically polymerized to form electroactive poly{1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-dialkoxybenzene}s. All the monomers exhibited quite low oxidation potentials, and all the corresponding polymers exhibited polymer oxidation and reduction potentials well below 0.0 V *versus* Ag/Ag$^+$ as desired for stable conducting systems. Incorporation of the electron-donating ethylenedioxy group lowered the band gaps of the polymers compared with their thiophene analogues, with E_g = 1.75 eV for the methoxy-substituted polymer and 2.0 eV for the longer alkoxy-substituted polymers.

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