

A New, General Approach to Tuning the Properties of Functionalized Polythiophenes: The Oxidative Polymerization of Monosubstituted Bithiophenes

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Received March 9, 1998

A new synthetic approach to functionalized polythiophenes utilizing 4-substituted 2,2'-bithiophenes is described. The general utility of this approach is illustrated by the preparation of the representative poly(4-substituted 2,2'-bithiophenes) (where substituent = octyl, hydroxymethyl, carboxy, carbomethoxy, or acetoxyethyl). The use of monofunctionalized bithiophenes as monomers has a number of advantages over traditional 3-substituted thiophene precursors. These advantages include direct oxidative polymerization of electron-poor monomers, selective oxidative polymerization in the presence of oxidatively sensitive side chains, polymerization without oxidative degradation of the backbone, and production of polymers with decreased side-chain density. The combination of these advantages allows the facile oxidative polymerization of monomers containing a large variety of functional groups. The reduction in side-chain density results in polymers with increased effective conjugation lengths as evidenced by their improved electrical and optical properties.

Introduction

The optical and electronic properties of conjugated organic polymers are of considerable fundamental and technological interest. Applications that have been demonstrated for these materials include their use as batteries, sensors, electrochromic devices, and field effect transistors.^{1–8} A potential advantage of utilizing conjugated polymers in such applications is the ability to tune the properties of the polymer at the molecular level. Tuning is typically accomplished through synthetic modification which permits the incorporation of side-chain functionalities.^{4–9} Although judicious selection of side chains can result in enhanced polymer characteristics (e.g., increased solubility,^{6–11} chain self-alignment,^{11–13} or ionic/molecular recognition^{6–9,13–15}), the steric and/or electronic effects introduced by the side

chains often hinder polymerization or adversely affect polymer properties.^{4–11} To rationally design polymers with tunable, well-defined electrical and optical properties, new synthetic methods must be developed which allow control of the number, position, and type of side chains present in the polymer.^{6–8}

The need for new synthetic methods that allow incorporation of a wide range of functional side chains has been widely recognized.^{6–8} The structural and electronic properties of many desirable substituents are often incompatible with conventional synthetic approaches. Desirable functional groups include alkyl chains, ionizable substituents, alcohols, and ethers, as well as more exotic functionalities such as amino acids and chiral substituents.^{5–20} The addition of alkyl chains to the β -position of the thiophene ring results in soluble and melt-processible polymers.^{6–12} Ionizable side chains (e.g., sulfonates or carboxylates) provide internal charge compensation¹⁶ (or self-doping)^{5,6,17,18} and impart water solubility, a desirable property for technical applications due to increasing restrictions on the use of organic solvents.⁵ Alcohol- or ether-containing side chains could potentially control cation transport properties in solid-state batteries, ion-selective electrodes, or mem-

- (1) Kaner, R. B.; MacDiarmid, A. G. *Sci. Am.* **1988**, 258 (2), 106.
- (2) Yam, P. *Sci. Am.* **1995**, 273 (1), 82.
- (3) Tourillon, G. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; p 350.
- (4) (a) Waltman, R. J.; Diaz, A. F.; Bargon, J. *J. Electrochem. Soc.* **1984**, 131, 1452. (b) Waltman, R. J.; Bargon, J. *Can. J. Chem.* **1986**, 64, 76.
- (5) Nguyen, M. T.; Leclerc, M.; Diaz, A. F. *Trends Polym. Sci.* **1995**, 3, 186.
- (6) Roncali, J. *Chem. Rev.* **1992**, 92, 711.
- (7) Schopf, G.; Kossmehl, G. *Adv. Polym. Sci.* **1997**, 129, 1.
- (8) Garnier, F. *Angew. Chem., Int. Ed. Engl.* **1989**, 28, 513.
- (9) Roncali, J.; Garreau, R.; Delabouglise, D.; Garnier, F.; Lemaire, M. *Synth. Met.* **1989**, 28, C341.
- (10) Chen, T. A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, 117, 233.
- (11) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, 58, 904.
- (12) McCullough, R. D.; Jayaraman, M. *J. Chem. Soc., Chem. Commun.* **1995**, 135.
- (13) McCullough, R. D.; Ewbank, P. C.; Loewe, R. S. *J. Am. Chem. Soc.* **1997**, 119, 633.
- (14) Swager, T. M.; Marsella, M. J. *Mater. Res. Soc. Symp. Proc.* **1994**, 328, 263.

- (15) Andersson, M.; Ekeblad, P. O.; Hjetberg, T.; Wennerström, O.; Inganäs, O. *Polym. Commun.* **1991**, 32, 546.

- (16) Bäuerle, P.; Gaudl, K. U.; Wurthner, F.; Saricitei, N. S.; Neugebauer, H.; Mehring, M.; Zhong, C.; Doblhofer, K. *Adv. Mater.* **1990**, 2, 490.

- (17) (a) Patil, A. O.; Ikenoue, Y.; Basecu, N.; Colaneri, N.; Chen, J.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1987**, 20, 151. (b) Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, 109, 1858. (c) Ikenoue, Y.; Saida, Y.; Kira, M.; Tomozawa, H.; Yashima, H.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1694.

- (18) Aldissi, M. *Mol. Cryst. Liq. Cryst.* **1988**, 160, 121.
- (19) Casa, C. D.; Bertinelli, F.; Bizzarri, P. C.; Salatelli, E. *Adv. Mater.* **1995**, 7, 1005.

- (20) Pohjakallio, M.; Sundholm, G. *Synth. Met.* **1993**, 55–57, 1590.

branes.^{6-9,14,19-21} Chiral functionalities such as amino acids are of interest for use in materials capable of molecular recognition and asymmetric electrosynthesis.^{6-9,15}

We are currently interested in developing general synthetic routes to functionalized polythiophenes based upon the use of *monosubstituted bithiophene* monomers. Although bithiophene-based monomers have been underutilized in the past, monosubstituted bithiophenes offer important advantages over the more commonly employed thiophene precursors. By limiting the number of side chains, the monomers and the resulting polymers are less affected by the electronic influence and structural nature of the side-chain functionality. This attenuation of side-chain influence allows the incorporation of a large variety of side chains without hindering the polymerization process or sacrificing the desirable properties of the resulting polymeric materials. This has been recently demonstrated in our report of a new water-soluble polythiophene, poly(4-carboxy-2,2'-bithiophene).²² The functionalized polythiophenes presented here are representative of the types of side-chain functionalities that are compatible with our synthetic approach, and more elaborate side chains can be easily envisioned.

The electronic effects of side-chain functionalities are attenuated in monosubstituted bithiophenes. For substituted thiophenes, on the other hand, the choice of possible side chains is limited by these electronic effects.⁴⁻⁸ For example, the incorporation of strong electron-withdrawing groups such as carboxylates is difficult because these substituents increase the potential for oxidation of the monomer and destabilize the resulting radical cation.^{4,6} This destabilization increases the radical cation's reactivity toward alternate reaction pathways at the expense of radical cation coupling reactions responsible for chain growth.⁴ A number of strategies have been investigated to allow the polymerization of monomers containing strong electron-withdrawing groups.^{16,17,23-28} These include insulating the thiophene ring from the electron-withdrawing group through the use of an alkyl linker,^{16,17,23} balancing the effect of the electron-withdrawing group with an electron-donating group,^{24,25} and the use of chemical coupling routes which are less affected by the withdrawing nature of the substituent.^{27,28} The use of monosubstituted bithiophenes allows facile oxidative polymerization because the delocalization of the π electrons stabilizes the radical cation intermediate to a greater extent than the destabilization induced by the electron-withdrawing group.

The decreased side-chain density of poly(4-substituted 2,2'-bithiophenes) results in fewer steric interactions

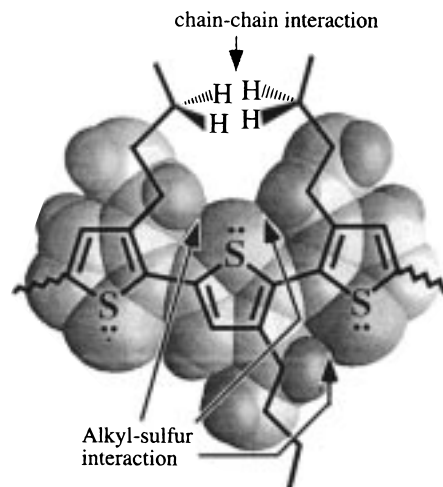


Figure 1. Steric interactions induced by the addition of side chains. The space-filled model (molecular mechanics, SYBYL force field) of the polythiophene backbone and the initial side-chain methylenes was constructed using SPARTAN (Wavefunction, Inc.).

known to reduce polymer chain planarity and limit conjugation length.^{6-11,29-35} As depicted in Figure 1, these steric effects include interactions between alkyl chains as well as sulfur-alkyl steric repulsions. For example, the irregular ring couplings of regiorandom poly(3-alkylthiophenes) result in a loss of conjugation caused by both of these types of steric effects. In polymers of symmetrical dialkylbithiophenes, interactions between alkyl chains are eliminated, but sulfur-alkyl steric repulsions are still present and are pronounced due to the high number of head-to-head couplings in these polymers.^{6,29-32} Regioregular head-to-tail poly(3-alkylthiophenes)^{10,11} lack the undesirable head-to-head couplings, but sulfur-alkyl steric interactions are still present. The use of monosubstituted bithiophenes removes interactions between chains and reduces the number of sulfur-alkyl interactions, thus resulting in more extended conjugation lengths. Similar effects have been observed in poly(3',4'-dibutyl-2,2':5',2''-terthiophene),³³ poly(3-alkyl-2,2'-bithiophenes),^{34,35} and regioregular, random copolymers of thiophene and 3-alkylthiophene¹² (Chart 1).

We report herein new general synthetic routes to functionalized polythiophenes derived from 4-substituted 2,2'-bithiophenes. We additionally describe how this synthetic strategy facilitates oxidative polymerization of substituted monomers and decreases the side-chain density on the polymer. Specifically, the strategy allows *direct* oxidative polymerization of electron-deficient

(21) Welzel, H.-P.; Kossmehl, G.; Schneider, J.; Plieth, W. *Macromolecules* **1995**, *28*, 5575.

(22) Rasmussen, S. C.; Pickens, J. C.; Hutchison, J. E. *Macromolecules* **1998**, *31*, 933.

(23) Bartlett, P. N.; Dawson, D. H. *J. Mater. Chem.* **1994**, *4*, 1805.

(24) Demanze, F.; Yassar, A.; Garnier, F. *Adv. Mater.* **1995**, *7*, 907.

(25) Demanze, F.; Yassar, A.; Garnier, F. *Macromolecules* **1996**, *29*, 4267.

(26) Curtis, M. D.; McClain, M. D. *Chem. Mater.* **1996**, *8*, 936.

(27) (a) Masuda, H.; Kaeriyama, K. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 461. (b) Masuda, H.; Kaeriyama, K. *Synth. Met.* **1995**, *69*, 513.

(28) Pomerantz, M.; Yang, H.; Cheng, Y. *Macromolecules* **1995**, *28*, 5706.

(29) Souto Maior, R. M.; Hinkelmann, K.; Eckert, H.; Wudl, F. *Macromolecules* **1990**, *23*, 1268.

(30) Zagórska, M.; Kulszewicz-Bajer, I. *Synth. Met.* **1991**, *45*, 385.

(31) Lapkowski, M.; Zagórska, M.; Kulszewicz-Bajer, I.; Koziel, K.; Pron, A. *J. Electroanal. Chem.* **1991**, *310*, 57.

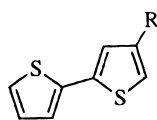
(32) Zagórska, M.; Krische, B. *Polymer* **1990**, *31*, 1379.

(33) Wang, C.; Benz, M.; LeGoff, E.; Schindler, J. L.; Allbritton-Thomas, J.; Kannewurf, C. R.; Kanatzidis, G. *Chem. Mater.* **1994**, *6*, 401.

(34) (a) Andersson, M. R.; Pei, Q.; Hjertberg, T.; Inganäs, O.; Wennerström, O.; Österholm, J. E. *Synth. Met.* **1993**, *55-57*, 1227. (b) Pei, Q.; Inganäs, O.; Gustafsson, G.; Granström, M.; Andersson, M.; Hjertberg, T.; Wennerström, O.; Österholm, J. E.; Laakso, J.; Järvinen, H. *Synth. Met.* **1993**, *55-57*, 1221.

(35) Masuda, H.; Kaeriyama, K.; Suezawa, H.; Hirota, M. *J. Polym. Sci. A: Polym. Chem.* **1992**, *30*, 945.

Chart 1



R = H (BT)	COOH (BT-CO ₂ H)
C ₈ H ₁₇ (BT-C ₈)	COOCH ₃ (BT-CO ₂ Me)
CH ₂ OH (BT-C ₁ OH)	(CH ₂) ₂ OCOCH ₃ (BT-C ₂ -Ac)

monomers or monomers that have competing oxidative side reactions. Polymers comprising these types of monomers have previously been prepared only by indirect methods.^{27,28} The optical spectroscopy and electrical conductivity measurements reported in this study demonstrate the efficacy of our strategy for enhancing optical and electronic properties of polythiophene by reducing the side-chain density. Finally, the different reactivities of the unsubstituted α positions of these monomeric precursors allow the production of regioregular polymers³⁶ utilizing the synthetic approaches of Rieke¹⁰ and McCullough.¹¹

Experimental Section

Monomeric 4-substituted 2,2'-bithiophenes were prepared as previously reported.³⁷ Anhydrous ferric chloride (Alpha-Aesar Organics) was used as received. Chloroform used in the chemical polymerizations (J. T. Baker spectroscopic grade) was dried over 4-Å molecular sieves prior to use. All other solvents were reagent grade and were used as received.

Unless otherwise noted, NMR spectra were obtained in CDCl₃ using a Varian 300-MHz spectrometer and referenced to the chloroform signal. FT-IR data was obtained using a Nicolet Magna 550 spectrometer. Samples were prepared as KBr pellets or as films drop-cast on either KBr plates or Teflon tape.³⁸ UV-vis spectroscopy was performed on a Perkin-Elmer Lambda 6 spectrophotometer using samples prepared as dilute CHCl₃, DMSO, or H₂O solutions in quartz cuvettes or as thin films cast on glass.

Molecular weight distributions of the polymers were determined by gel permeation chromatography (GPC) utilizing a bank of three columns (Waters HR0.5, HR1, and HR3). Polymers were eluted with DMF or THF and detected using a Waters 996 photodiode array detector and a Waters 410 differential refractometer. Polystyrene standards (Aldrich) were used for calibrating the GPC columns for hydrodynamic volume vs elution time.

2,2'-Bithiophene (BT). BT was obtained as a byproduct of the substituted bithiophene syntheses and purified by repeated sublimation. All data agree with previously reported values.³⁹ Mp: 32–33 °C. ¹H NMR (CDCl₃): δ 7.02 (2H, dd, J = 5.1, 3.6 Hz), 7.18 (2H, dd, J = 3.6, 1.2 Hz), 7.21 (2H, dd, J = 5.1, 1.2 Hz). ¹³C NMR (CDCl₃): δ 124.0, 124.5, 128.0, 137.6.

General Procedure for Chemical Polymerization. Chemical polymerization was accomplished utilizing modifications of the methods of Sugimoto et al.⁴⁰ The desired monomer (1–3 mmol) was dissolved in dry chloroform (100 mL), followed by the addition of anhydrous FeCl₃ (6 mol equiv). The mixture was allowed to stir under N₂ for 24 h, poured into CH₃OH (300 mL), and stirred vigorously for 30 min. The resulting dark precipitate was collected by vacuum filtration and air-dried. The polymer was dedoped and iron salts were removed by

Soxhlet extraction (CH₃OH) for 24 h with a color change of the polymer to deep red-brown.⁴¹ The polymeric product was then filtered and dried under vacuum at 70 °C.

Solubility. Quantitative solubility was determined as follows. The polymer sample (10–20 mg) was heated gently in an appropriate solvent for a few minutes and allowed to cool to room temperature. The suspension was filtered through a filter frit containing a preweighed piece of Whatman no. 50 hardened filter paper and washed with excess solvent. The filter paper containing the insoluble fraction was then dried at 100 °C under vacuum for at least 2 h before mass determination. In addition, the solvent was removed from the soluble portion by rotary evaporation and the fraction dried and weighed in a manner similar to that used for the insoluble fraction.

Poly(2,2'-bithiophene) (BT)_n. Yields were 90–95%. Solubility: completely insoluble. IR (KBr): 3059, 2921, 2853, 1489, 1313, 1108, 1019, 831, 786, 727, 688 cm⁻¹.

Poly(4-octyl-2,2'-bithiophene) (BT-C₈)_n. Chemical polymerization was accomplished as described above, with the addition of a second Soxhlet extraction (hexanes) to remove a small amount of oligomeric material. Yields were 70–75%. Solubility: partially soluble in chloroform, methylene chloride, and THF. IR (insoluble fraction, KBr): 2920, 2850, 1500, 1454, 1384, 1179, 1055, 827, 787, 720 cm⁻¹. IR (CHCl₃-soluble fraction, film): 2924, 2855, 1500, 1457, 1384, 1064, 829, 791, 722 cm⁻¹. ¹H NMR (CDCl₃): δ 0.87 (6H, br s), 1.26 (20H, overlapping resonances), 1.60 (2H, br s), 1.68 (2H, br s), 2.52 (2H, br s), 2.76 (2H, br s), 7.06 (6H, br s). Molecular weight (GPC, THF): M_w = 11 370; DP = 23; PDI = 1.8.

Poly(4-acetoxyethyl-2,2'-bithiophene) (BT-C₂-Ac)_n. Yields were 90–95%. Solubility: partially soluble in chloroform, methylene chloride, THF, and DMF. IR (insoluble fraction, KBr): 2950, 2109, 1740, 1452, 1363, 1212, 1030, 980, 835, 792, 750 cm⁻¹. IR (CHCl₃-soluble fraction, film): 3067, 2959, 1739, 1501, 1462, 1437, 1388, 1368, 1238, 1038, 836, 791, 754 cm⁻¹. ¹H NMR (CDCl₃): δ 2.07 (6H, br s), 2.91 (2H, br s), 3.13 (2H, br s), 4.26 (2H, br s), 4.36 (2H, br s), 7.10 (6H, br s). ¹³C NMR (CDCl₃): δ 21.0, 28.3, 28.7, 63.7, 63.9, 124.5 (v br), 125.2, 126.5, 127.0, 128.4, 131.3, 134.5, 135.3, 135.6, 136.1, 137.0, 136.8, 137.5, 137.6, 138.8, 170.9, 171.0. Molecular weight (GPC, DMF): M_w = 83043; DP = 74; PDI = 4.5.

Poly(4-carboxy-2,2'-bithiophene) (BT-CO₂H)_n. Chemical polymerization was accomplished as described above, with the addition of a second Soxhlet extraction (THF) to remove a small amount of oligomeric material. Yields were 65–70%. Solubility: partially soluble in DMF; soluble in DMSO and aqueous base. IR (protonated form, KBr): 3433, 3010, 2927, 2865, 1679, 1429, 1189, 1136, 1047, 845, 789 cm⁻¹. IR (Na⁺ salt, Teflon tape): 3345, 3086, 3062, 2923, 2852, 1575, 1457, 1430, 1352, 844, 776 cm⁻¹. ¹H NMR (DMSO-*d*₆): δ 7.36 (4H, br s), 7.56 (1H, br s), 8.20 (1H, br s), 13.08 (2H, br s). To obtain a sample for GPC and to increase sample concentration for ¹³C NMR, the polymeric sample was fractionated by gently heating the polymer in DMF, filtering, and removing the DMF via rotary evaporation. This DMF-soluble fraction consisted of approximately 70% of the initial sample and exhibited increased solubility in DMSO. ¹³C NMR (DMSO-*d*₆): δ 124.2, 124.9, 125.6, 126.2, 126.7, 129.1, 130.5, 132.5, 132.8, 133.6, 133.9, 135.2, 135.6, 136.7, 137.9, 139.4, 163.2, 163.7. Molecular weight (GPC, DMF): M_w = 51515; DP = 111; PDI = 2.2.

Poly(4-carbomethoxy-2,2'-bithiophene) (BT-CO₂Me)_n. Chemical polymerization was accomplished as described above, with the addition of a second Soxhlet extraction (CHCl₃) to remove a small amount of oligomeric material. Yields were 80–85%. Solubility: completely insoluble. IR (KBr): 2944, 1710, 1434, 1368, 1308, 1204, 1129, 992, 846, 792, 773, 731 cm⁻¹.

Hydrolysis of (BT-CO₂Me)_n to (BT-CO₂H)_n. To obtain a soluble sample for GPC analysis, hydrolysis of the methyl ester was performed. The polymer (BT-CO₂Me)_n (90 mg) was

(36) Rasmussen, S. C.; Straw, B.; Hutchison, J. E. *Polym. Prep.* **1998**, *39*, 87.

(37) Rasmussen, S. C.; Pickens, J. C.; Hutchison, J. E. *J. Heterocycl. Chem.* **1997**, *34*, 285.

(38) Oberg, K. A.; Palleros, D. R. *J. Chem. Educ.* **1995**, *72*, 857.

(39) Crisp, G. T. *Synth. Commun.* **1989**, *19*, 307.

(40) Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635.

(41) Soxhlet extraction with CH₃OH completely removed all Fe impurities as indicated by XPS.

added to 40 mL of 25% NaOH and heated at reflux with stirring for 17 h. The mixture was allowed to cool to room temperature and diluted with water to completely dissolve the polymer salt. The solution was acidified with 10% HCl and stirred for several minutes to promote aggregation. The resulting red precipitate was collected by vacuum filtration. Characterization by UV-visible and IR spectroscopy indicated complete hydrolysis to **(BT-CO₂H)_n**. Molecular weight (GPC, DMF): $M_w \geq 150\,000$, $DP \geq 741$.

Poly(4-hydroxymethyl-2,2'-bithiophene) (BT-C₁OH)_n. Yields were 75–80%. Solubility: completely insoluble. IR (KBr): 3443, 2923, 2850, 2825, 1641, 1438, 1191, 1089, 836, 802 cm^{-1} .

Electrochemistry. Electropolymerization and cyclic voltammetry (CV) experiments were performed on a Bioanalytical Systems BAS 100B/W electrochemical analyzer. All measurements were made at a sweep rate of 100 mV/s. CVs of the bithiophene monomers were carried out in a three-electrode cell consisting of a platinum disc working electrode, a platinum wire auxiliary electrode, and a Ag/Ag⁺ reference electrode. Millimolar solutions of the monomers were prepared by dissolution in CH₃CN dried over 4-Å molecular sieves. The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate (TBAPF₆) dried overnight under vacuum at 100 °C. The solutions were deoxygenated by sparging with argon prior to each scan and blanketed with argon during the scans. The platinum disc working electrode was polished with 0.05-mm alumina and washed well with deionized water and dry CH₃CN prior to each scan.

Electropolymerizations were carried out in the cell described above, substituting a silver wire quasireference electrode for the Ag/Ag⁺ electrode. Solutions consisted of monomer (0.10 M) dissolved in anhydrous propylene carbonate (Aldrich) stored over 4-Å molecular sieves. The supporting electrolyte was 0.03 M TBAPF₆, and solutions were argon sparged and blanketed as described above. The films were grown at a constant potential of 1.3 V. The polymer-coated electrode was then removed, washed well with CH₃CN, and placed in a cell containing a fresh 0.10 M TBAPF₆/CH₃CN solution. CVs were measured as described above for the monomers.

Conductivity. Measurements were taken using a Signatone four-point probe (tungsten carbide tips) connected to a Solartron SI 1287 electrochemical interface. Measurements were taken by sourcing current (20–200 mA) and measuring potential. All samples exhibited a linear Ohm's law response. Samples were prepared by placing the polymer (as either powder or free-standing film) in an evacuated chamber followed by exposure to I₂ vapor for approximately 30 min. Excess I₂ was removed by additional evacuation for 5–10 min. Powder samples were then pressed into pellets with a force of 3800 psi for 10 min and exposed to I₂ a second time. Sample thicknesses ranged from 0.052 to 0.710 mm.

Results

Polymerization. The 4-substituted 2,2'-bithiophenes investigated readily undergo oxidative polymerization using conventional chemical or electrochemical methods. Chemical polymerization of disubstituted bithiophenes has previously been reported to be problematic, and extensive modifications of the Sugimoto procedure⁴⁰ are necessary for its success.³² No such difficulties were observed for the monosubstituted bithiophenes, and their chemical polymerization provides a simple process for the preparation of large-scale quantities, thus allowing thorough characterization. Unlike derivatized thiophenes, the monosubstituted bithiophenes undergo electrochemical polymerization without oxidative degradation⁴² and allow convenient examination of the effect of the number and type of side chains on the redox properties of the monomeric and polymeric bithiophenes.

Table 1. Solubility and Selected Infrared Data for Polymeric Bithiophenes^a

polymer	fraction (%)	ν_1 and ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_4 (cm^{-1})
(BT)_n	insoluble (100)	831 (1.0)	786 (6.0)	727 (1.0)
(BT-C₈)_n	soluble (30)	829 (1.0)	791 (3.0)	722 (0.7)
	insoluble (70)	827 (1.0)	787 (2.3)	720 (0.5)
(BT-C₂Ac)_n	soluble (80)	836 (1.0)	791 (2.7)	754 (0.9)
	insoluble (20)	837 (1.0)	792 (1.6)	749 (2.3)
(BT-COOH)_n	soluble ^b (100)	845 (1.0)	789 (2.3)	735 (1.0)
(BT-COOMe)_n	insoluble (100)	846 (1.0)	792 (1.7)	731 (1.9)
(BT-C₁OH)_n	insoluble (100)	834 (1.0)	795 (1.9)	

^a Infrared spectra of soluble fractions were obtained from drop-cast CHCl₃ films. Spectra of insoluble fractions were obtained from KBr pressed pellets. ν_1 = ring def. of 2,3,5-substituted ring. ν_2 = ring def. of β CH in 2,4-substituted ring. ν_3 = ring def. of 2,5-substituted ring. ν_4 = ring def. of α CH in 2,4-substituted ring or CH₂ rock. Values in parentheses are ratios of relative intensities. ^b Solubility in DMSO. IR data obtained from KBr pressed pellet.

Solubility. The solubilities of **(BT-C₈)_n**, **(BT-C₂Ac)_n**, and **(BT-CO₂H)_n** were quantified in either CHCl₃ or DMSO and are given in Table 1. In addition, the alkali metal salts of **(BT-CO₂H)_n** are completely soluble in water. The polymers **(BT-CO₂Me)_n** and **(BT-C₁OH)_n** are insoluble in either common organic solvents or aqueous base. However, extended heating of **(BT-CO₂Me)_n** in aqueous NaOH results in hydrolysis to **(BT-CO₂H)_n** to give soluble samples.

Gel Permeation Chromatography (GPC). The soluble fractions of the polymers **(BT-C₈)_n**, **(BT-C₂Ac)_n**, and **(BT-CO₂H)_n** were analyzed by GPC to determine the corresponding molecular weights (M_w) and polydispersity index (PDI).⁴³ GPC analysis of the polymer **(BT-CO₂Me)_n** was accomplished after hydrolysis to **(BT-CO₂H)_n**. All samples studied gave trimodal distributions. With the exception of **(BT-C₈)_n**, the M_w of all samples were greater than 50,000 Daltons. GPC analysis of **(BT-C₈)_n** gave a $M_w = 11370$, corresponding to approximately 23 bithiophene units or 46 thiophene rings. All other samples gave a degree of polymerization (DP) of over 70. The M_w of the **(BT-CO₂H)_n** obtained from the hydrolysis of **(BT-CO₂Me)_n** was too large to be accurately determined with the present GPC column configuration and is therefore reported as $\geq 150\,000$ Da.

FT-IR Spectroscopy. All polymers were examined by FT-IR spectroscopy to qualitatively determine the proportion of α,α to α,β coupling during chemical polymerizations. The relevant transitions are given in Table 1. All the IR spectra display a band near 790 cm^{-1} (ν_3) characteristic of the aromatic C–H out-of-plane bend attributed to the unsubstituted rings of poly(2,5-thiophene).^{3,6,44} In addition, the functionalized polymers also exhibit single transitions (ν_1) between 827 and 846 cm^{-1} corresponding to the aromatic CH out-of-plane bends characteristic of a poly(2,5-thiophene) containing monosubstituted rings.^{45,46} The parent unsubstituted polymer **(BT)_n** displays two bands near 730 (ν_4) and 830 cm^{-1} (ν_2) corresponding to the C–H out-

(43) (a) The molecular weights in this study are reported versus polystyrene standards. In some cases, the molecular weights found by GPC using polystyrene standards either underestimate^{43b} or overestimate^{43c} the actual molecular weight of the polymer. (b) Pomerantz, M.; Tseng, J. J.; Zhu, H.; Sproull, S. J.; Reynolds, J. R.; Uitz, R.; Arnott, H. J. *Synth. Met.* **1991**, *41–43*, 825. (c) Yue, S.; Berry, G. C.; McCullough, R. D. *Macromolecules* **1996**, *29*, 933.

(44) Sanechika, K.; Yamamoto, T.; Yamamoto, A. *J. Polym. Sci.: Polym. Lett.* **1982**, *20*, 365.

(42) Krische, B.; Zagórska, M. *Synth. Met.* **1989**, *28*, C257.

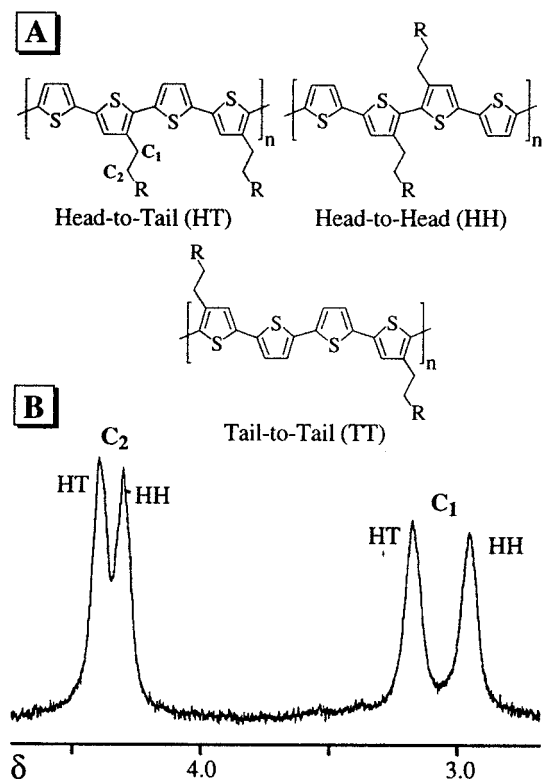


Figure 2. The three regiochemical diads of poly(4-substituted-2,2'-bithiophenes) (A) and the methylene region of the ^1H NMR of poly(4-acetoxyethyl-2,2'-bithiophene) (B).

of-plane bend for poly(2,4-bithiophene), indicating that some α,β coupling had occurred during polymerization.^{3,6,44} Although ν_1 would mask ν_2 in the functionalized polymers, it is possible to see that similar α,β coupling has occurred as indicated by a third transition (ν_4) located between 720 and 754 cm^{-1} . The polymer (**BT-C₁-OH**)_n containing hydroxymethyl functionalities is the single exception and displays no transitions corresponding to α,β coupling.

The ν_2 and ν_4 transitions of the soluble and insoluble fractions of polymers (**BT-C₈**)_n and (**BT-C₂-Ac**)_n were compared to determine if the insoluble material was a result of increased α,β defects. For (**BT-C₈**)_n, this was complicated by the fact that the CH_2 rock transition also appears at 720–725 cm^{-1} .^{45,46} However, the spectra of the soluble and insoluble fractions of (**BT-C₈**)_n show no noticeable differences. The spectrum of the insoluble fraction of (**BT-C₂-Ac**)_n indicates a sizable increase in α,β coupling in comparison to the spectrum of the soluble fraction.

NMR Spectroscopy. The ^1H NMR spectra of (**BT-C₈**)_n and (**BT-C₂-Ac**)_n each exhibit a single peak in the aromatic region corresponding to the ring protons of the mono- and unsubstituted rings. The spectra also exhibit two sets of peaks (2.52, 2.76 ppm for (**BT-C₈**)_n; 2.91, 3.13 ppm for (**BT-C₂-Ac**)_n) corresponding to the C_1 -methylenes of the polymer side chains. The appearance of two sets of peaks is attributed to regiorandom coupling that results in two distinct chemical environments within the polymer sample (Figure 2). Integration of the two

Table 2. UV–Vis and Conductivity Data for Monomeric and Polymeric Bithiophenes^a

compd	monomer λ_{max} (nm)	polymer		σ ($\Omega^{-1}\text{cm}^{-1}$)
		λ_{max} (nm, solution)	λ_{max} (nm, film)	
BT	304		475 ^b	84.5
BT-C₈	308	454	520	14.1 ^c
BT-C₂Ac	308	455	520	18.5 ^c
BT-COOH	304	455 ^d	475 ^e	3.6 $\times 10^{-3}$
BT-COOLi⁺	305	450 ^f	475 ^g	
BT-COONa⁺	305	453 ^f	475 ^g	
BT-COOCs⁺	305	454 ^f	475 ^g	
BT-COOMe	303	444 ^h	462 ^h	9.0 $\times 10^{-4}$

^a Spectra were obtained from room-temperature CH_2Cl_2 solutions or drop-cast films from CHCl_3 on glass. Conductivities were determined with a four-point probe on I_2 -doped pressed pellets. ^b Roncali, J. *Chem. Rev.* **1992**, *92*, 711. ^c Measured as freestanding film. ^d Measured in DMSO. ^e Drop-cast from DMSO on glass. ^f M^+ salt measured in 0.1 N MOH. ^g M^+ salt drop-cast from ethanolic 0.01 N MOH. ^h Oligomeric fraction isolated by CHCl_3 extraction.

proton signals indicates an approximate 1:1 ratio of head-to-head vs head-to-tail coupling. Likewise, the C_2 -methylenes of the side chains also appear as sets of two peaks (1.60, 1.68 ppm for (**BT-C₈**)_n; 4.26, 4.36 ppm for (**BT-C₂-Ac**)_n). Both polymers exhibit peaks corresponding to the remaining protons of their respective side chains, although no more peak doubling is observed due to regiorandom coupling.

The ^1H NMR spectrum of the carboxylate polymer (**BT-CO₂H**)_n also indicates regiorandom coupling. Two singlets of equal integration at 7.56 and 8.20 ppm are observed for the proton of the substituted thiophene ring.²⁸ In addition, the spectrum exhibits broad singlets at 13.08 ppm corresponding to the acid proton and at 7.36 ppm for the protons of the unsubstituted ring.

The presence of regiorandom coupling within these polymers is confirmed by ^{13}C NMR spectra which exhibit two sets of four peaks for each of the two thiophene rings, as well as multiple peaks for the corresponding side-chain carbons. For example, the spectrum of the carboxylate polymer (**BT-CO₂H**)_n shows two distinct $\text{C}=\text{O}$ peaks at 163.2 and 163.7 ppm. The $\text{C}=\text{O}$'s in the acetoxyethyl side chains of polymer (**BT-C₂-Ac**)_n also appear as two peaks (at 170.9 and 171.0 ppm) even though they are four atoms removed from the polymer backbone. The terminal methyl group does appear as a single peak. No peaks attributable to end groups or defects were observed in either the ^1H or ^{13}C spectra of the polymers studied.

UV–Vis Spectroscopy. The monomeric bithiophenes and their corresponding polymers were examined by UV–vis spectroscopy (Table 2). These experiments probe the effect of the type and number of various substituents upon the mean conjugation length. The absorbance maximum (λ_{max}) for all the bithiophene monomers fall within a narrow range of wavelengths between 303 and 308 nm. Upon polymerization, the λ_{max} values show an expected shift to longer wavelengths resulting from the more conjugated polymer backbone. The λ_{max} values for the polymers were all approximately 455 nm, with the exception of the carbomethoxy containing polymer (**BT-CO₂Me**)_n which exhibits a transition at 444 nm.⁴⁷ The optical spectra

(45) Zerbi, G.; Chierichetti, B.; Inganäs, O. *J. Chem. Phys.* **1991**, *94*, 4646.

(46) Winokur, M. J.; Spiegel, D.; Kim, Y.; Hotta, S.; Heeger, A. J. *Synth. Met.* **1989**, *28*, C419.

(47) This exception is most likely due to the fact that the only soluble portion of this polymer is oligomeric in nature.

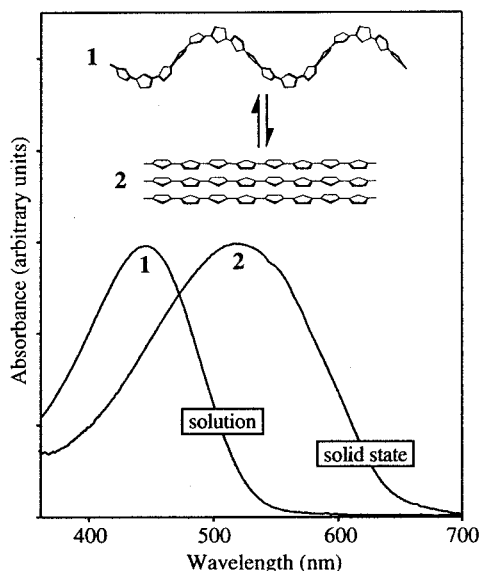


Figure 3. Solution and solid-state UV-vis spectra of $(\text{BT-C}_2\text{-Ac})_n$. Spectra were measured in CHCl_3 or as a drop-cast film on glass. Structures **1** and **2** represent stylized conformations of the polymers in solution and in the solid state.

Table 3. Electrochemical Data for Monomeric and Polymeric Bithiophenes^a

compd	monomer			polymer	
	$E_{\text{ox}1}$ (V)	$E_{\text{ox}2}$ (V)	$E_{\text{ox}3}$ (V)	$E_{\text{ox}1}$ (V)	$E_{\text{ox}2}$ (V)
thiophene	1.95			0.44	0.68
BT	1.04	1.41	1.69	0.57	0.77
BT-C₈	1.00	1.44	1.63	0.56	0.78
BT-C₂Ac	1.04	1.45	1.69	0.60	0.77
BT-COOH	1.20	1.50	1.64	0.70	1.04
BT-COOMe	1.19	1.58	1.65	0.70	1.09
BT-C₁OH	1.02	1.58 ^b		0.74	

^a All potentials vs. Ag/Ag^+ . Voltammetric data were measured in argon-sparged CH_3CN with 0.1 M TBAPF₆ as supporting electrolyte. Monomeric samples were prepared as millimolar solutions. Polymer samples were measured as films electropolymerized onto a platinum disc electrode. ^b Broad oxidation.

of the polymeric samples were also measured as thin films on glass substrates. In comparison to the solution spectra, the transitions in the solid state are red-shifted due to an intrachain coil-to-rod conformational change between solution and the solid state which results in extended delocalization (Figure 3).^{48–50} The solid-state λ_{max} values are much more side chain dependent than the solution spectra and range from 462 to 520 nm depending on the steric nature of the side chain.

Electrochemistry. Cyclic voltammetric data for the bithiophenes and their polymers are given in Table 3. All of the monomeric bithiophenes exhibit a well-defined irreversible oxidation wave (Figure 4) presumably corresponding to the formation of the radical cation. Scanning to higher positive potentials results in two consecutive broad oxidation waves. Since coupling of the radical cations is rapid ($\tau < 10^{-5}$ s),⁵¹ these broad waves most likely correspond to overoxidation⁴² of coupled products as opposed to further monomer oxida-

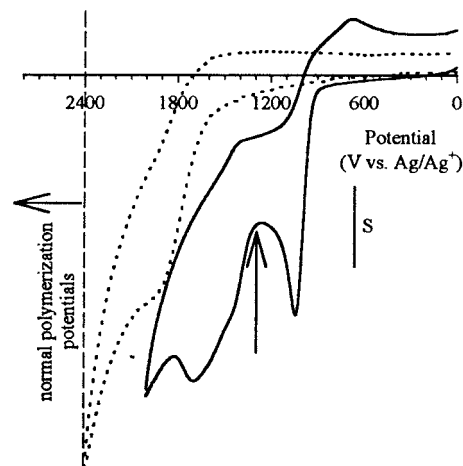


Figure 4. Cyclic voltammograms of **BT-C₂-Ac** (solid line, $S = 8$ mA) and thiophene (broken line, $S = 20$ mA). Voltammograms were measured as millimolar solutions in argon-sparged 0.1 M TBAPF₆/ CH_3CN at a scan rate of 100 mV/s. The vertical arrow indicates the potential used for the polymerization of the 4-substituted 2,2'-bithiophenes.

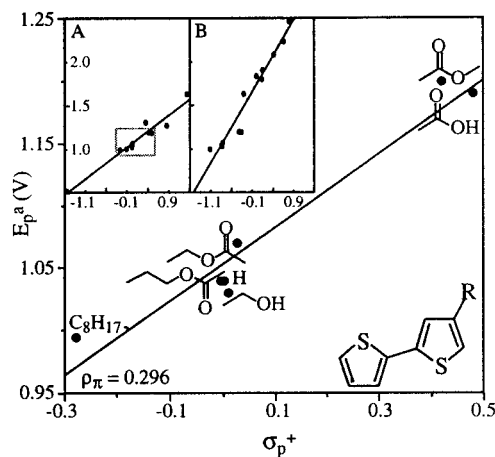


Figure 5. Hammett plot of 4-substituted 2,2'-bithiophenes. The inset plots show the combination of these data with the previous data for 3,3'-disubstituted 2,2'-bithiophenes (A) and 3-substituted thiophenes (B).

tions. The peak potentials (E_{pa}) of the first oxidation fall within a narrow range between 1.0 and 1.2 V vs Ag/Ag^+ , and they vary depending on the electronic effect of the substituent.

These variations in the oxidation potential correlate well with the respective Hammett substituent constants σ_{p}^+ of the monomeric bithiophenes as shown in Figure 5. The shifts in E_{pa} are dependent on the polar, steric, and mesomeric effects exerted by the substituents as described by the Hammett-Taft equation:

$$E = \rho_{\pi}\sigma^+ + S$$

where $\rho_{\pi}\sigma^+$ describes the polar-mesomeric parameters and S accounts for the steric factors.^{4,25,52} In the case of low or comparable steric interactions due to the substituents (i.e., S is constant), linear relationships are found between E_{pa} and σ_{p}^+ . The plot of the first oxidation wave potential ($E_{\text{ox}1}$, Table 3) for the monosubsti-

(48) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci. B: Polym. Phys.* **1987**, *25*, 1071.

(49) Chen, S.-A.; Ni, J.-M. *Macromolecules* **1992**, *25*, 6081.

(50) Inganäs, O.; Salaneck, W. R.; Österholm, J. E.; Laakso, J. *Synth. Met.* **1988**, *22*, 395.

(51) Audebert, P.; Hapiot, P. *Synth. Met.* **1995**, *75*, 95.

(52) Zuman, P. *Substituent Effects in Organic Polarography*; Plenum Press: New York, 1967.

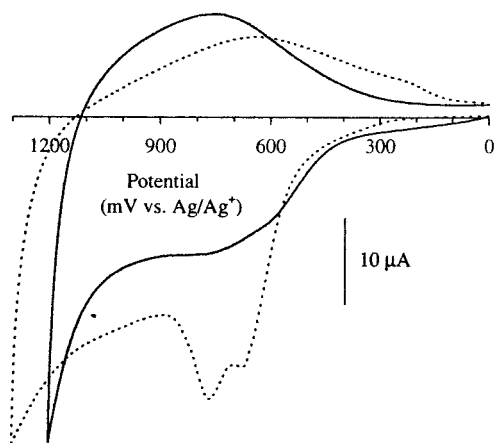


Figure 6. Cyclic voltammograms of $(\text{BT-C}_2\text{-Ac})_n$ films produced through electrochemical deposition (solid line) and by drop-casting a polymer sample prepared by chemical oxidation (broken line). Voltammograms were measured using a platinum disc working electrode ($A = 0.02 \text{ cm}^2$) in $0.1 \text{ M TBAPF}_6/\text{CH}_3\text{CN}$ at a scan rate of 100 mV/s .

tuted bithiophenes vs σ_p^+ gives $\rho_\pi = 0.296$ as illustrated in Figure 5. A similar correlation has been previously reported for a series of 3,3'-disubstituted 2,2'-bithiophenes ($\rho_\pi = 0.382$).²⁵ The difference between the values of ρ_π for the mono- and disubstituted bithiophenes may be due to the small data set for our series. For example, combination of the two data sets gives a linear fit with $\rho_\pi = 0.367$, as shown in Figure 5 (inset A).

The more commonly studied 3-substituted thiophenes have also been fitted to their corresponding Hammett constants ($\rho_\pi = 0.80$).⁴ In our series, the unsubstituted ring of the bithiophenes can be thought of as a substituent rather than as part of the parent structure, thus allowing treatment of this series as disubstituted thiophenes. Treating this series as such allowed combining of our data set with the previously reported 3-substituted thiophenes to give a linear fit with $\rho_\pi = 0.819$, as shown in inset B of Figure 5.

Electropolymerization of the monomeric bithiophenes yielded polymer films with a shiny black or coppery appearance when viewed on the platinum disc working electrode. In general, the films appeared to be quite uniform and fairly robust. Under a microscope ($40\times$), the polymer films from $(\text{BT-CO}_2\text{H})_n$ have a smooth, homogeneous surface morphology that is independent of film thickness. Preliminary tapping mode AFM studies were performed on $(\text{BT-CO}_2\text{H})_n$ films electropolymerized on ultraflat, template-stripped gold.⁵³ Investigation of the surface morphology gave an rms roughness of $0.5\text{--}1.0 \text{ nm}$ for a $10\text{--}20 \text{ \AA}$ thick film ($5 \mu\text{m}^2$ section). An approximate 10-fold increase in the film thickness gave a roughness of $1.0\text{--}2.0 \text{ nm}$.

Cyclic voltammograms obtained for electropolymerized thin films generally show two broad oxidation waves and one broad reduction wave (Figure 6 and Table 3). Peak potentials for the first oxidative wave range from 0.57 to 0.70 V . Peak potentials for the second wave range from 0.77 to 1.09 V . The exception is the hydroxymethyl-containing polymer $(\text{BT-C}_1\text{-OH})_n$ which exhibits only a single wave at approximately 0.74

V. As with the oxidation of the monomers, the potentials for oxidation of the polymers vary depending on the electronic contribution of the substituent, but all are higher than the measured potentials of 0.44 and 0.68 V for polythiophene.

Conductivity. The conductivities of the I_2 -doped poly(4-substituted 2,2'-bithiophenes) were measured with a four-point probe (Table 2). For comparison, the parent polymer $(\text{BT})_n$ was measured under identical conditions, giving a conductivity of 84.5 S/cm . Previously reported conductivities of chemically prepared $(\text{BT})_n$ are $3\text{--}17 \text{ S/cm}$.^{6,54–56} The samples used for the previously reported measurements, however, were measured directly from the FeCl_3 polymerization/doping reaction and not subjected to any further purification. In addition, we have found that the redox properties of the polymer are highly dependent on the purity of the monomer used. In the case of BT , repeated sublimation gave electropolymerized films that were oxidized at lower potentials. The functionalized polymers $(\text{BT-C}_8)_n$ and $(\text{BT-C}_2\text{-Ac})_n$ could be cast from CHCl_3 to give freestanding films. After doping, the films of the two polymers gave conductivities of 14.1 and 18.5 S/cm , respectively. Attempts to cast freestanding films of $(\text{BT-CO}_2\text{H})_n$ resulted only in powdery deposits. All remaining samples were measured as pressed pellets, with the exception of $(\text{BT-C}_1\text{-OH})_n$ which would not compress adequately to form a pellet suitable for measurement.

Discussion

The oxidative polymerization of 4-substituted 2,2'-bithiophenes provides access to a new class of functionalized polythiophenes and provides a number of synthetic advantages over the analogous polymerization of 3-substituted thiophenes. These advantages include the facile polymerization of monomers containing either strong electron-withdrawing groups or groups which are oxidatively sensitive and the polymerization of monomers without overoxidation. These new derivatized polymers exhibit unexpected regiochemistry, which could be used as a probe into the mechanism of chemical oxidative polymerization. The partially functionalized polymers exhibit improved optical and electronic properties over fully functionalized analogues.

Oxidative Polymerization. All derivatized bithiophenes investigated readily undergo oxidative polymerization using conventional chemical or electrochemical methods. The use of monosubstituted bithiophenes has a number of advantages over the more conventional substituted thiophenes. Due to the increased delocalization of the bithiophene monomer, the electronic effect of the functionality on the oxidation potential is greatly attenuated. This effect is clearly illustrated by the Hammett plot shown in Figure 5. In comparison to standard 3-substituted thiophenes (Figure 5, inset B), the slope of the monosubstituted bithiophenes is less ($\rho_\pi = 0.296$ vs 0.800). In fact, for these bithiophenes the difference in E_{pa} between the electron-donating octyl group and the electron-withdrawing carboxylate group is only 200 mV . The weaker dependence is not due to any change of the oxidation process since addition of

(54) Roncali, J.; Garnier, F.; Lemaire, M.; Garreau, R. *Synth. Met.* **1986**, *15*, 323.

(55) Ruckenstein, E.; Park, J. S. *Synth. Met.* **1991**, *44*, 293.

(56) Zotti, G.; Schiavon, G. *Synth. Met.* **1990**, *39*, 183.

(53) Wagner, P.; Hegner, M.; Güntherodt, H.-J.; Semenza, G. *Langmuir* **1995**, *11*, 3867.

our data as "disubstituted" thiophenes does not change the slope (ρ_n) of the thiophene plot, indicating that these bithiophenes obey the same linear free energy relationship as the previously reported substituted thiophenes. The fact that we reduce the effect of the side-chain functionality while retaining the ability to form the necessary active radical cation allows us to readily produce a wide variety of functionalized polythiophenes.

An illustrative example of the attenuation of side-chain electronic effects is the ability to oxidatively polymerize monomeric bithiophenes containing strong electron-withdrawing groups. The polymerization of thiophenes with strong electron-withdrawing groups is limited.^{4,6} However, the facile oxidative polymerization of analogous monosubstituted bithiophenes is possible because the delocalization of the π electrons over the bithiophene stabilizes the radical cation intermediate to a greater extent than the destabilization induced by the electron-withdrawing group. This stabilization results in much lower potentials for monomer oxidation, as illustrated by comparing the potential of 3-carboxythiophene (2.28 V vs SSCE)⁴ to the potential of **BT-CO₂H** (1.50 V vs SSCE).⁵⁷ Due to the stabilizing effect of the second thiophene ring, such derivatized bithiophenes polymerize at potentials less positive than thiophene itself.⁴

The polymerization of thiophenes containing oxidatively sensitive functionalities is also problematic due to competing oxidative side reactions. An example of this type of functionality is the benzylic-like alcohol in 3-thiophenemethanol. Benzylic alcohols oxidize at approximately 1.9 V vs Ag/Ag⁺ to the corresponding aldehyde and carboxylic acid.⁵⁸ Attempts to polymerize 3-thiophenemethanol (by sweeping 0–2 V) have only been successful at high concentrations, and even then polymerization was hindered by the competing growth of a passivating layer suggestive of an unconjugated polymer.²⁰ In contrast, polymerization of **BT-C₁-OH** occurs readily even at dilute concentrations, and no passivation of the electrode was observed. The decreased potential for oxidation of the bithiophene monomer allows polymerization at potentials below that of the alcohol functionality, thus avoiding complicating side reactions.

At higher potentials (~1.8 vs Ag/AgCl) most conjugated polymers undergo an overoxidation process which destroys the electroactivity of the material.⁴² The onset of this overoxidation can start as low as 1.3–1.5 V. Thiophene monomers are usually polymerized at potentials above 2 V, which means that polymerization and overoxidation are competing processes during the production of polythiophenes. However, the greater delocalization over the bithiophenes allows these monomers to polymerize below the overoxidation potentials of the resulting polymers, thereby allowing polymer growth without simultaneous decomposition.

Oxidation of the electropolymerized films of poly(4-substituted 2,2'-bithiophenes) occurs at potentials com-

parable to that of the parent (**BT**)_n. However, all of the polymers studied showed higher potentials (by ~130 mV) than polythiophene. It has been suggested previously that the difference in redox potentials between polythiophene and (**BT**)_n is due to the formation of a less conjugated polymer for (**BT**)_n. The reasoning is that either the increased stabilization of the **BT** monomer results in a lower degree of polymerization or the decreased selectivity between α and β positions results in a greater amount of α,β coupling.^{6,54} Analysis (GPC, UV-vis, and IR) of our polymeric samples prepared via chemical oxidation indicates polymers of high molecular weight which are highly conjugated and contain a low amount of α,β coupling. Cyclic voltammograms of these chemically prepared polymers (as solvent-cast films) do not show E_{pa} 's at potentials any lower than those of the electropolymerized samples (Figure 6).⁵⁹ The fact that these chemically and electrochemically prepared samples have similar potentials for oxidation suggests that the differences in redox properties between polythiophenes and polybithiophenes are not due to a decrease in conjugation.

Regiochemistry. The polymeric samples produced via chemical oxidation (FeCl₃) are composed of predominantly α,α coupling. Examination of the thiophene C–H region in the IR spectra indicates that the level of defects (i.e., α,β coupling) is equal to or below that of the parent (**BT**)_n. The lack of any visible α -H's in the ¹H NMR spectra also supports α,α coupling.

The ¹H NMR also provides information regarding the regioregularity of the ring couplings. As shown in Figure 2A, the asymmetrical bithiophenes can couple in a head-to-tail (HT), head-to-head (HH), or tail-to-tail (TT) fashion. The HT and HH couples produce different chemical environments for the side-chain methylenes resulting in different chemical shifts for these two types of side chains (Figure 2B). Integration of these peaks allows determination of the ratio of coupling types. In all poly(4-substituted 2,2'-bithiophenes) studied, the integrals corresponding to HT and HH couplings were equal. For a sufficiently long polymer chain the HH:TT ratio is 1:1. Thus, the overall ratio of HT:HH:TT is 1:1:1 and the polymeric sample is completely regiorandom. Although one-third of the couples formed during polymerization are HH couples, each couple is the addition of a monosubstituted *b*thiophene. Therefore, the total HH content is only ~17% of all the thiophene–thiophene linkages within the polymer backbone. Similar results have been reported for poly(4-butoxy-4'-decyl-2,2'-bithiophene).⁶⁰

Under similar polymerization conditions, asymmetrical 3-alkylthiophenes show a preference for HT coupling (70–80%).^{7,61,62} This selectivity is thought to be due to a localization of the radical cation at one of the asymmetrical α positions. Therefore, the more asymmetrical structure of the bithiophenes might be expected to show an even stronger HT preference. In an effort to better

(57) (a) The measured potential of 1.20 V vs Ag/Ag⁺ was converted to SCE^{57b} and then to SSCE^{57c} to allow comparison. (b) Larson, R. C.; Iwanoto, R. T.; Adams, R. N. *Anal. Chim. Acta* **1961**, *25*, 371. (c) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; John Wiley & Sons: New York, 1980.

(58) Mayeda, E. A.; Miller, L. L.; Wolf, J. F. *J. Am. Chem. Soc.* **1972**, *94*, 6812.

(59) The resulting potential is very dependent on the casting conditions of the film. Thin, highly uniform films gave the best results. Other films resulted in higher oxidation potentials.

(60) Faid, K.; Cloutier, R.; Leclerc, M. *Macromolecules* **1993**, *26*, 2501.

(61) Leclerc, M.; Diaz, F. M.; Wegner, G. *Makromol. Chem.* **1989**, *190*, 3105.

(62) Mao, H.; Xu, B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 1163.

understand the regiorandom coupling in the bithiophene system, we investigated the relative π spin densities of the α positions utilizing density functional theory (DFT, DN^{*} basis set)⁶³ for the necessary calculations. As expected, both 3-alkylthiophenes and 4-alkyl-2,2'-bithiophenes exhibited asymmetrical spin densities at the α positions, and this difference in spin densities was *greater* in the bithiophene series. The lack of any regioregularity in the poly(4-alkyl-2,2'-bithiophenes) despite the greater differences in spin density is unexpected and suggests a difference in the mechanism of chain growth compared to the polymerization of 3-alkylthiophenes. Further investigation of the chemical polymerization process and full details of the theoretical calculations will be published elsewhere.⁶⁴

Optical Properties. All of the poly(4-substituted 2,2'-bithiophenes) studied are highly conjugated, as evidenced by their low-energy UV-vis transitions (Table 2). In all cases, the reduction in side chains results in decreased steric interactions and increased conjugation in comparison to the fully substituted analogues. For example, (BT-C₈)_n exhibits maxima at 455 nm in solution and 520 nm in the solid state in comparison to 436 nm and 505–510 nm for regiorandom (70–80% HT) poly(3-octylthiophene).^{11,61,65} In fact, the solid-state maxima are directly comparable to the maxima reported by McCullough for regioregular (<98% HT) poly(3-octylthiophene).¹¹ This is even more remarkable if one considers the additional HH couplings (~17%) in (BT-C₈)_n.

The increase in conjugation for the monosubstituted bithiophenes is more dramatic in polymers containing sterically encumbered side chains such as branched functionalities. Analogous to (BT-C₈)_n, (BT-C₂-Ac)_n exhibits transitions at 455 nm in solution and 520 nm in the solid state. In comparison, fully functionalized polythiophenes containing similar ester-derivatized side chains exhibit higher energy solution transitions (400–420 nm) with little or no decrease in energy upon transition to the solid state.^{66–68} This illustrates the powerful effect of reduced sterics through reduction of side-chain density.

In solution, polythiophenes are thought to adopt a coiled structure with interruptions of conjugation caused by various rotations around the single bonds between thiophene units.^{48–50,69} These rotational defects are termed "conformons" and are thought to be either soft conformons, where the rotation is distributed over several monomers, or a wormlike model in which the rotation is distributed over all monomers.^{49,50} Theoretical studies have predicted a 34° twist between thiophene units for the wormlike model.⁷⁰ The polybithiophenes

in solution exhibit UV-vis transitions at approximately 455 nm and are independent of side-chain contributions. The fact that these solution maxima do not change with side chain suggests that, in these polymers, the coiled structure is not greatly affected by the side-chain functionality. However, the fact that our solution maxima are of lower energy than those of analogous poly(3-alkylthiophenes) suggests that the reduction in side-chain density reduces the degree of twist between monomeric units.

In the transition from solution to solid state, polythiophenes are thought to undergo a coil-to-rod transition producing extended chains of coplanar thiophene rings.^{48–50,69} This conformational change coupled with interchain interactions in the solid state results in increased electronic delocalization and a shift of the UV-visible transition to lower energy (Table 2 and Figure 3). Unlike the solution maxima, the solid-state maxima of the polybithiophenes are side chain dependent. This is most evident in the polymers (BT-CO₂H)_n and (BT-CO₂Me)_n which contain branched side chains that could hinder a coplanar configuration in the solid state.⁷¹ Similar effects have been reported for polythiophenes containing branched alkyl side chains.^{6,72} The fact that the poly(4-substituted 2,2'-bithiophenes) exhibit lower energy solid-state transitions than their fully functionalized analogues suggests that the reduction in side chains allows the polymers to adopt a more extended coplanar configuration in the solid state.

Conductivity. The measured conductivities of the I₂-doped polymers are comparable or higher than the reported values for the fully functionalized analogues. For example, doped (BT-C₈)_n exhibited a conductivity of 14.1 S/cm, which compares well with the commonly reported values for poly(3-octylthiophene) (1–30 S/cm, although conductivities as high as 90 S/cm have been reported).^{6,61,65,72,73} In addition, the higher value of 18.5 S/cm measured for (BT-C₂-Ac)_n is a remarkable improvement over previously prepared polythiophenes containing ester-derivatized side chains.^{66,68} Both of these polymeric samples also compare favorably with the previously reported poly(3-alkyl-2,2'-bithiophenes) (alkyl = octyl, 10 S/cm, butyl or dodecyl, 2–4 S/cm).^{34,35} The much lower values measured for (BT-CO₂H)_n and (BT-CO₂Me)_n are similar to the conductivity reported for carboxy-functionalized poly(3-alkylthiophenes) (3.3 × 10⁻³ S/cm)¹⁶ and are improved in comparison to that of poly(3-carbomethoxythiophene) (5 × 10⁻⁵ S/cm).²⁷ The values of these two samples suggest low doping levels and are possibly due to some instability of the doped state as reflected by their increased oxidation potentials.²²

Conclusion

A new class of functionalized polythiophenes, poly(4-substituted 2,2'-bithiophenes), can be obtained through the *direct* chemical or electrochemical oxidation of

(63) Modeling was accomplished using SPARTAN version 4.1.2 (Wavefunction, Inc.). Initial structures were calculated using molecular mechanics (SYBYL force field) followed by geometry optimization and spin population analysis using DFT.

(64) Rasmussen, S. C.; Hutchison, J. E. (manuscript in preparation).

(65) Pomerantz, M.; Tseng, J. J.; Zhu, H.; Sproull, S. J.; Reynolds, J. R.; Uitz, R.; Arnott, H. J. *Synth. Met.* **1991**, *41–43*, 825.

(66) (a) Lee, C.; Kim, K. J.; Rhee, S. B. *Synth. Met.* **1995**, *69*, 295. (b) Lee, C.; Kim, K. J.; Rhee, S. B. *Mol. Cryst. Liq. Cryst.* **1994**, *247*, 31.

(67) Kang, T. J.; Kim, J. Y.; Kim, K. J.; Lee, C.; Rhee, S. B. *Synth. Met.* **1995**, *69*, 377.

(68) Casa, C. D.; Andreani, F.; Bizzarri, P. C.; Salatelli, E. *J. Mater. Chem.* **1994**, *4*, 1035.

(69) Daoust, G.; Leclerc, M. *Macromolecules* **1991**, *24*, 455.

(70) Thémans, B.; Salaneck, W. R.; Brédas, J. L. *Synth. Met.* **1989**, *28*, C359.

(71) A distorted structure for these polymers is also supported by the blue shift of the C–H thiophene out-of-plane bend (ν_1 , Table 1) in the IR spectra.^{45,46}

(72) Roncali, J.; Garreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706.

(73) Ciprelli, J. L.; Clarisse, C.; Delabouglise, D. *Synth. Met.* **1995**, *74*, 217.

4-substituted 2,2'-bithiophenes. This general synthetic approach reduces the number of undesirable side-chain interactions, thus increasing the conjugation length, and allows the facile incorporation of a variety of functionalized side chains. Despite the decrease in density of solubilizing side chains, most of the resulting polymers exhibit good solubility in a variety of organic solvents, as well as increased optical and electronic properties as evidenced by their low-energy UV-visible transitions and good conductivities.

The new functionalized polythiophenes presented here are representative of the types of side-chain functionalities that are compatible with our synthetic approach, and the production of polymers containing more elaborate side chains is in progress. In addition, the different reactivities of the unsubstituted α positions of these monomeric precursors allows the use of the synthetic approaches of Rieke¹⁰ and McCullough¹¹ to produce regioregular polymers.³⁶ Preliminary success in producing regioregular poly(4-octyl-2,2'-bithiophene)

has resulted in solution UV-vis transitions of approximately 510 nm (compared to 455 nm for regiorandom samples). Further work to optimize the production of regioregular poly(4-octyl-2,2'-bithiophene) and to apply this methodology to other side-chain functionalities is underway.

Acknowledgment. Support for this work was provided by the National Science Foundation (NSF-CAREER (CHE-9702726) to J.E.H.), the Camille and Henry Dreyfus Foundation, and the University of Oregon. Partial support of the Materials Characterization Laboratory was provided by the National Science Foundation (DMR-9601813 and CHE-9512185). We thank Drs. Julie Haack and Carlos Bustamante for their assistance in the AFM studies and Dr. Mark Lonergan for his assistance with the GPC and conductivity measurements.

CM980150X