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Highly Conjugated, Water-Soluble Polymers via the Direct Oxidative Polymerization of Monosubstituted Bithiophenes

Seth C. Rasmussen, Jason C. Pickens, and James E. Hutchison*

Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon 97403

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Introduction. The functionalization of conjugated polymers is a powerful method for tuning the properties of these materials.[1−3] Derivatization with ionizable groups provides internal charge compensation[4] (or self-doping[3,5]) as well as imparts water solubility.[3] New synthetic methods that permit tuning of polymer properties are desirable for a number of potential technological applications, including batteries, sensors, and electrochromic devices.[3,6,7]

We report a new carboxylate derivatized polythiophene, poly(4-carboxy-2,2′-bithiophene) obtained through the *direct* chemical or electrochemical oxidation of 4-carboxy-2,2′-bithiophene[8] (**1**). The utility and advantages of preparing functionalized polythiophenes from 4-substituted-2,2′-bithiophenes are presented. This new approach reduces undesirable side chain interactions and allows facile incorporation of strong electron-withdrawing side chains.

Although the derivatization of conjugated polymers allows tuning the properties of these materials, it can also result in unwanted steric and electronic interactions. Substitution of the thiophene ring with alkyl chains results in soluble and melt-processible polymers.[1,9−15] However, steric effects introduced by the side chains can reduce backbone planarity, thus limiting conjugation.[9b,10] Such steric effects (Figure 1) include interactions between alkyl chains as well as sulfur−alkyl steric repulsions. For example, regiorandom poly(3-alkylthiophenes) exhibit both of these effects due to the irregular ring couplings. Alkyl−alkyl interactions are eliminated in symmetrical poly(dialkylbithiophenes), but sulfur−alkyl steric repulsions are pronounced due to the high number of head-to-head couplings in these polymers.[10,11] Regioregular head-to-tail poly(3-alkylthiophenes)[9] lack head-to-head couplings, but still suffer sulfur−alkyl interactions. Studies by McCullough et al. suggest that decreasing the side chain density in regioregular random copolymers of thiophene and 3-alkylthiophene leads to more extended conjugation.[12] Similar effects have been observed in poly-(3′,4′-dibutyl-2,2′:5′,2″-terthiophene)[13] and poly(3-alkyl-2,2′-bithiophenes).[14]

The addition of side chains can also introduce complicating electronic interactions. For example, the functionalization of polythiophenes with strong electron-withdrawing groups (e.g., carboxylates) is limited because these substituents are known to increase the potential for monomer oxidation and destabilize the resulting radical cation.[1,2] This destabilization increases the radical cation's reactivity toward alternate reaction pathways at the expense of radical cation coupling reactions responsible for chain growth.[2] A number of strategies have been investigated to allow the polymerization of monomers containing strong electron-withdrawing groups.[6,7,15−17]

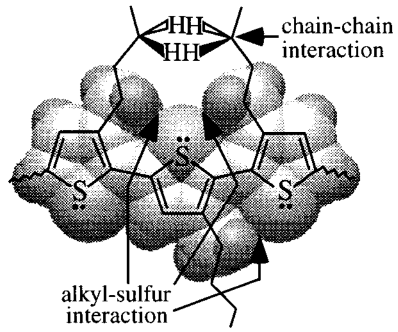
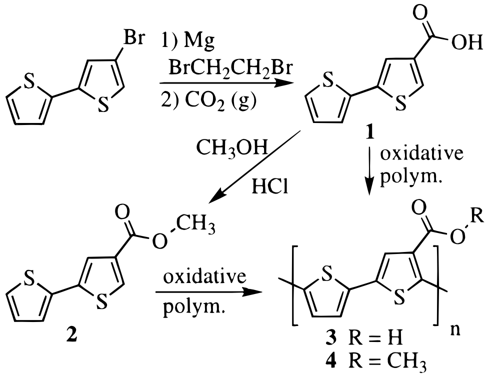


Figure 1. Side chain induced steric interactions. Space-filled model (molecular mechanics, SYBYL force field) was constructed using SPARTAN (Wavefunction, Inc.).

Scheme 1



Results and Discussion. Chemical polymerization of **1** using anhydrous $FeCl_3$ occurs in high yields (65−70%) producing polymeric samples of **3** that are soluble in DMSO, DMF, or aqueous base.[18a] GPC indicates molecular weights corresponding to a degree of polymerization ($\overline{DP}$) of 114 (228 thiophene rings). A considerable fraction (~15%) elutes as a higher molecular weight peak ($\overline{DP}$ = 690 or 1380 thiophene rings).[18b] The methyl ester **2** was also polymerized using $FeCl_3$ to produce **4**, followed by hydrolysis with aqueous NaOH to yield **3** (Scheme 1). The spectral properties of **3** produced by either route are identical.

The IR spectra exhibit transitions at 845 and 789 cm^{-1} corresponding to aromatic CH out-of-plane bends characteristic of a poly(2,5-thiophene) containing mono- and unsubstituted rings. No evidence of significant branching or cross-linking was observed. A C═O stretch was observed at 1679 cm^{-1} for the protonated polymer and at 1575 cm^{-1} for its corresponding salts. The ^1H NMR spectrum exhibits a singlet at 13.08 ppm corresponding to the acid proton, a broad singlet at 7.36 ppm for the protons of the unsubstituted thiophene ring, and singlets at 7.56 and 8.20 ppm for the proton of the substituted thiophene ring. The appearance of two peaks for this proton is attributed to regiorandom coupling that results in two distinct chemical environments within the polymer.[17] The peak integrations

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* To whom correspondence should be addressed. E-mail: hutch@oregon.uoregon.edu.

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Table 1. Electrochemical and Spectroscopic Data[a]

	$\lambda_{\max}^{\text{solution}}$ (nm)	$\lambda_{\max}^{\text{film}}$ (nm)	$E_{\text{ox}}(1)$ (V)	$E_{\text{ox}}(2)$ (V)
4-carboxy−2,2′-bithiophene, **1**	304		1.20	1.64
4-carbomethoxy−2,2′-bithiophene, **2**	303		1.19	1.58
poly(4-carboxy−2,2′-bithiophene), **3**	455[b]	475[c]	0.70	1.04
polymeric salts of **3**: Li^+	450[d]	475[e]		
Na^+	453[d]	475[e]		
Cs^+	454[d]	475[e]		
poly(4-carbomethoxy−2,2′-bithiophene), **4**	444	462	0.70	1.09
poly(3-carboxythiophene), Na^+ salt[f]	433[d]			
poly(methyl thiophene−3-carboxylate)[g]	423	443		
poly(hexyl thiophene−3-carboxylate)[h]	423[i]	447		

[a] Spectra obtained as $CHCl_3$ solutions or films on glass. E_p *vs* Ag/Ag^+. Voltammetric data were measured in 0.1 M $CH_3CN/(TBA)PF_6$ at 100 mV/s. Samples were prepared as mM solutions or as films electropolymerized onto a Pt disk electrode. [b] In DMSO. [c] From DMSO. [d] In H_2O. [e] From H_2O. [f] Reference 16b. [g] Reference 16a. [h] Reference 17. [i] In THF.

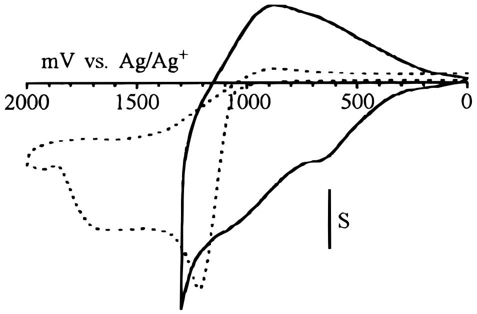

Figure 2. Cyclic voltammograms of 1 (···, S = 50 μA) and polymer 3 (—, S = 20 μA) in CH_3CN/0.10 M $(TBA)PF_6$ at a scan rate of 100 mV/s (Pt disk working electrode, A = 0.02 cm^2).

suggest a 1:1 ratio of head-to-head vs head-to-tail coupling. The presence of regiorandom coupling is confirmed by the ^{13}C NMR spectrum, which exhibits two sets of four peaks for each of the thiophene rings and two distinct C=O peaks at 163.2 and 163.7 ppm. No peaks attributable to endgroups or defects were observed in either the ^1H or ^{13}C spectra.

The UV−visible data are given in Table 1. In solution, polymer **3** exhibits a $\pi-\pi^*$ transition at 455 nm in DMSO and at 452 nm in H_2O as its Na^+ salt. Although poly(thiophene-3-propionic acid) has recently been reported to exhibit ionochromic behavior,[19] the polymeric salts of **3** exhibited no appreciable shifts in the solution or solid-state spectra[20] as a result of the change of the cation from Li^+ to Na^+ to Cs^+ (Table 1). In the solid state, polymer films of **3** cast from DMSO show maxima at 475 nm, constituting a 20 nm red-shift from the solution spectrum. The decreased degree of conjugation within these films compared to polythiophene ($\lambda_{\max}$ = 480 nm)[1] can be attributed to the amount of head-to-head coupling, as well as the steric hindrance resulting from the branched nature of the side chain.[1,21] Solid-state films of the polymeric salts exhibit maxima at 475 nm.

The electrochemical data for **1** and polymer **3** are listed in Table 1. As shown in Figure 2, the bithiophene **1** exhibits first a narrow irreversible peak at approximately 1.20 V, presumably corresponding to the formation of the radical cation,[22] followed by a broad oxidation. Because coupling of the radical cations is rapid ($<10^{-5}$ s),[23] this broad oxidation likely corresponds to overoxidation[24] of the resulting coupled products. The fact that oxidative coupling occurs at less positive potentials than overoxidation allows polymerization without simultaneous decomposition.[24]

Polymerization of **1** at constant potential (1.3 V vs Ag/Ag^+) results in smooth, dark polymeric films of **3**.[25] A typical cyclic voltammogram of **3** is shown in Figure 2 (solid line). The initial oxidative wave occurs at 0.70 V, followed by a second oxidation at 1.04 V. The shift of the oxidation waves to higher potential in comparison to polythiophene[1] can be attributed to the electronic effect of the carboxylate chains. The increase in current following the second oxidation is due to the onset of polymer overoxidation.[24] Potential cycling between the doped and undoped states (0−1.3 V) indicates that these polymeric films are electrochemically stable and exhibit only a gradual loss (~10% after 50 cycles at 100 mV/s) of current response.

Poly(4-carboxy-2,2′-bithiophene) was oxidatively doped upon exposure to oxidants such as $FeCl_3$, I_2, and Br_2, as evidenced by a color change of the polymer from red to dark purple/black. Doped solutions of the polymer can be formed by dissolution in concentrated sulfuric acid. Doping results in a decrease in the intensity of the $\pi-\pi^*$ transition at 455 nm and the formation of a broad transition centered at approximately 1075 nm. This near-IR absorption is analogous to absorptions seen for bipolaronic transitions of highly doped polythiophene.[26,27] Measurements of pressed pellets ($FeCl_3$ doped) gave conductivities of $\sim 10^{-4}\ \Omega^{-1}\ cm^{-1}$. Further doping with I_2 gave conductivites of $1.6 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, similar to values reported for other carboxylate functionalized polythiophenes.[4] This level of conductivity suggests a low doping level in comparison to the sulfuric acid solutions and may be due to instability of the doped state. Although the solid-state spectra indicate an optical band gap comparable to that of polythiophene (~2 eV), the higher oxidation potential of **3** suggests a greater instability of its doped state.

The polymerization of **1** and **2** illustrates a new approach to functionalized polythiophenes utilizing monosubstituted bithiophenes. The facile oxidative polymerization of electron-deficient bithiophenes occurs because delocalization within the π system stabilizes the radical cation to a greater extent than it is destabilized through induction. This stabilization results in much lower oxidation potentials for substituted bithiophenes compared to analogous functionalized thiophenes. For example, the oxidation potential of 3-carboxythiophene is 2.28 V vs SSCE,[2] whereas the potential of **1** is 1.50 V vs SSCE.[28] Due to the stabilizing effect of the second thiophene ring, the derivatized bithiophenes polymerize at potentials less positive than thiophene itself.[2]

The lower density of side chains in poly(4-substituted-2,2′-bithiophenes) allows retention of the desirable characteristics of functionalization (i.e. solubility, stability, etc.), but reduces unwanted steric interactions. Despite the decrease in solubilizing side chains, poly-

(4-carboxy-2,2′-bithiophene) is soluble in DMF and DMSO in its protonated form and is completely water soluble as its various deprotonated salts. The reduction in side chain interactions results in polymeric samples that are highly conjugated as evidenced by the low energy transitions exhibited in their solution and solid-state UV−visible spectra. This is well illustrated by comparing the spectral data of the polymers **3** and **4** with the related sodium salt and methyl ester of poly(3-carboxythiophene) which have been recently synthesized via chemical coupling.[16] In comparison to these fully substituted polymers, the polymers **3** and **4** contain half as many side chains and display a 20 nm increase in the $\pi-\pi^*$ transitions of their solution and solid state spectra (Table 1). This degree of effective conjugation has been previously seen only in carboxylate-functionalized systems which use a long alkyl spacer to separate the carboxylate from the polymer backbone.[4] In addition, polymer **3** exhibits a 50 nm red-shift (425 vs 475 nm) in comparison to the related water-soluble sulfonated polythiophenes.[5]

Experimental Section. Monomeric bithiophenes **1** and **2** were prepared as previously reported.[8] Anhydrous $FeCl_3$ (Alfa-Aesar Organics) was used as received. Chloroform and CH_3CN (J. T. Baker spectroscopic grade) were dried over 4 Å molecular sieves prior to use.

Chemical Polymerizations. To the monomeric bithiophene (1−3 mmol in 100 mL of dry $CHCl_3$) was added anhydrous $FeCl_3$ (6 mol equiv). The mixture was allowed to stir under N_2 for 24 h, poured into CH_3OH (300 mL), and stirred for 30 min. The dark green precipitate was collected by vacuum filtration and air-dried. Dopants were removed by Soxhlet extraction (CH_3OH) for 24 h.[29] Extraction with THF for an additional 24 h removed small amounts of oligomeric material before the polymer was dried under vacuum at 70 °C (yields 65−70%). Polymer **3** was then fractionated by gently heating the polymer in DMF, filtering, and removing the DMF via rotary evaporation. The DMF-soluble fraction (~70% of the isolated sample) exhibited increased solubility in DMSO (>30 mg/mL). ^{1}H 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). ^{13}C 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. IR (KBr): 3433, 3010, 2927, 2865, 1679, 1429, 1189, 1136, 1047, 845, 789 cm^{-1}. IR (Na$^+$ salt, Teflon): 3345, 3086, 3062, 2923, 2852, 1575, 1457, 1430, 1352, 844, 776 cm^{-1}.

NMR spectra were obtained as DMSO-d_6 solutions using a Varian 300 MHz spectrometer and referenced to the DMSO signal (^{1}H, 2.49 ppm; ^{13}C, 39.5 ppm). FT-IR samples were prepared as KBr pellets or as films drop-cast on Teflon. Samples for UV−vis spectroscopy were dilute DMSO, H_2O, or H_2SO_4 solutions, or thin films on glass.

Cyclic voltammograms (CVs) of monomers were performed in a three-electrode cell (Pt disk working, Pt wire auxiliary, and Ag/Ag$^+$ reference electrodes). Monomer solutions (5−10 mM) were prepared in CH_3CN containing 0.10 M tetrabutylammonium hexafluorophosphate ((TBA)PF_6). Solutions were deoxygenated by sparging with Ar and were blanketed with Ar during the scans. The Pt disk was polished with 0.05 μm alumina and washed well with deionized H_2O and dry CH_3CN prior to each scan.

Electropolymerizations were carried out in the cell described above, substituting a Ag wire quasi-reference electrode for the Ag/Ag$^+$ electrode. Solutions consisted of monomer (0.10 M) dissolved in anhydrous propylene carbonate (Aldrich, dried over 4 Å molecular sieves) containing 0.03 M (TBA)PF_6. Solutions were Ar 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 CH_3CN, and placed in a cell containing a fresh 0.10 M (TBA)PF_6/CH_3CN solution. CVs were measured as described above for the monomers.

Conductivity measurements were obtained with a Signatone four-point probe connected to a Keithley 236 Source Measure unit. Samples were doped in 0.1 M $FeCl_3$/nitromethane for ~2 h, filtered under N_2, and pressed (3800 psi for 10 min) into pellets (0.08−0.10 cm thick). Further doping was accomplished in a closed chamber with I_2 crystals.

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Supporting Information Available: Text giving further characterization data for polymer **3** and a figure showing the UV−vis spectra (1 page). See any current masthead page for ordering and Internet access instructions.

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(18) (a) The solubility of polymer **3** is ~4 mg/mL in DMSO and ~15 mg/mL in aqueous base. (b) Molecular weights of the DMF-soluble fraction were measured vs polystyrene standards on a Waters gel permeation chromatography system utilizing a bank of three columns (Waters HR0.5, HR1, and HR3) to give a trimodal distribution resulting in a $\bar{M}_w$ of 52 000 and PDI of 2.2.

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