Synthesis and Characterization of a Conducting Organomain Group Polymer, Poly[bis((3,4-ethylenedioxy)-2-thienyl) sulfide]: A Heteroaromatic Relative of Poly(*p*-phenylene sulfide)

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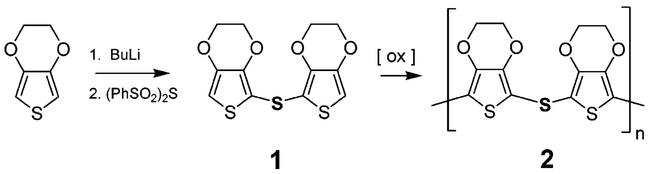
A contemporary theme in polymer science is the introduction of inorganic elements into polymer backbones, either as wholly inorganic polymers or as "hybrid" materials combining organic and inorganic moieties.[1] This strategy has been particularly attractive in the arena of conjugated organic polymers, in which the novel electronic features inherent in these systems can be modulated by incorporation of nonorganic components into the backbone. One approach has been to incorporate transition-metal-based species into the backbone of conjugated polymers, leading to conjugated "metallopolymers".[2] Alternatively, multicomponent systems from combinations of organic and main group substrates are possible. Polyaniline and its derivatives are arguably the best known examples.[3] Other π-conjugated/main group polymers have incorporated other elements such as boron,[4] silicon,[5] phosphorus, and arsenic.[6] Among group 16 elements, poly(*p*-phenylene sulfide) (PPS) derivatives have attracted attention because of the inherent robustness of the parent polymer.[7] The electrical properties of other vinyl[8] or heteroaryl[9] sulfides have been described but are poorly characterized; the stability of the oxidized (doped) forms of these polymers is poor, thereby hindering their further study or development. Herein we present the synthesis and properties of a new hybrid polymer based on 3,4-ethylenedioxythiophene[10] (EDOT) moieties linked by divalent sulfur. This polymer exhibits excellent electrochemical stability as well as anomalously high conductivity for a formally nonconjugated polymer.

Bis(3,4-ethylenedioxy-2-thienyl) sulfide (**1**) was prepared by lithiation of EDOT followed by treatment with bis(phenylsulfonyl) sulfide. Cyclic voltammetry of **1** showed an oxidation at +1.2 V vs Ag/Ag$^+$ that was irreversible, as expected for α-unsubstituted thiophenes. Repeated electrochemical cycling between 0 and +1.5 V led to new peaks at potentials cathodically shifted relative to monomer **1** and concomitant formation of a dark film. These observations are indicative of electropolymerization of **1** at the α carbons of each EDOT moiety to give polymer **2** (Scheme 1).

Cyclic voltammograms of as-deposited **2** in fresh (monomer-free) solutions show a broad oxidation process at ca. +600 mV vs Ag/Ag$^+$. The peak current was found to be linearly dependent on scan rate (Figure 1), indicative of a surface-bound species. The doping/dedoping process of **2** is fully reversible: repeated cycling several hundred times did not lead to any detectable change in the electrochemical cyclic behavior. This stability arises from a combination of two factors: the generally excellent electrochemical characteristics of EDOT-based polymers and the demonstrated stabilizing effect of terminal −SR groups on the oxidation of thiophene oligomers.[11] This electrochemical stability contrasts the behavior of (chemically) doped PPS, which leads to irreversible changes via cross-linking processes.[7c,d]

Scheme 1



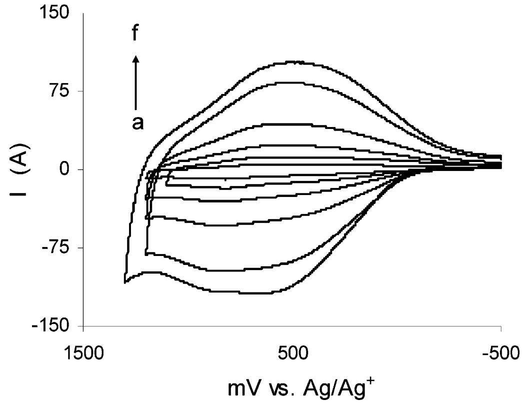


Figure 1. CV of films of **2** at different scan rates: (a) 0.05, (b) 0.1, (c) 0.2, (d) 0.4, (e) 0.8, and (f) 1 V/s.

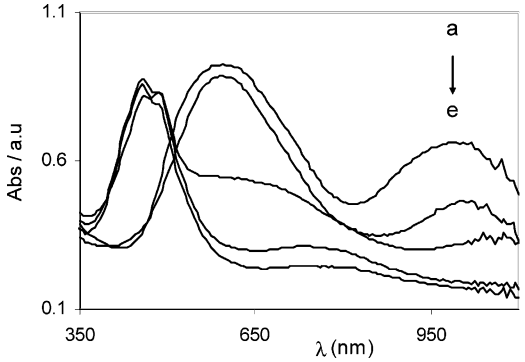


Figure 2. Electronic spectra of **2** at different potentials: (a) +1.3, (b) +0.5, (c) +0.2, (d) +0, and (e) −0.2 V vs Ag/Ag$^+$.

The spectroelectrochemical properties of films of polymer **2** were examined on an ITO electrode (Figure 2). In the oxidized state the polymer is deep blue with absorption maxima at 605 and 1020 nm. As the potential is lowered, these peaks gradually disappear and are replaced by two maxima at 455 and 484 nm, giving rise to a yellow/orange film. The two maxima probably arise as a result of vibronic fine structure. Collectively, these spectroscopic features *qualitatively* mimic those found in PPS:[7c] The neutral polymer has its principal absorption at 315 nm, and upon doping new transitions are observed at 1033 and 1378 nm. However, unlike PPS

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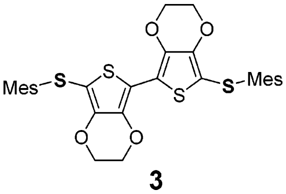
the coloration/decoloration process in **2** is fully reversible, as anticipated on the basis of the electrochemical stability noted above. This stability is in fact comparable to that seen in derivatives of poly(EDOT) itself,[10,14] although the nature of the electrochromism in the two systems is complementary to one another: In poly(EDOT) derivatives, the *neutral* form is intensely blue due to it being a low-band-gap conjugated polymer, whereas upon doping it becomes nearly transparent with its sub-gap transition in the IR region.

Insights into the electronic structure of polymer **2** can be gained by comparison to compound **3**,[11] which is a useful model for **2** because it contains a biEDOT flanked by sulfurs. The longest wavelength absorption of neutral **3** is at 362 nm, considerably blue-shifted compared to **2**. We take this as evidence for strong intra- and/or interchain electronic coupling of the biEDOT units in polymer **2**, despite the fact that the electroactive units are not formally conjugated with one another. Moreover, the electronic spectrum of the radical cation of **3** has absorption maxima at 920 and 512 nm, values that are also blue-shifted compared to polymer **2**. Further evidence for the presence of significant interactions between the biEDOT units in **2** is gleaned by comparison of its electrochemical behavior with that of **3**: The latter has two well-defined oxidation processes at +0.57 and +0.94 (vs SCE) whereas the CV of **2** consists of a single but broad oxidation process.



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Conductivity studies of films of **2** were carried out in situ using the interdigitated electrode method.[12] The conductivity rises with increasing potential, reaches a maximum at +0.79 V, and then decreases (see Supporting Information). This behavior is consistent with redox type conductivity, in comparison to the behavior of conventional conjugated polymers, in which a plateau of high conductivity over a relatively large potential window is seen. The maximum conductivity of **2** was determined to be 1.5×10^{-3} S cm^{-1}. This moderately high conductivity is despite the fact that **2** is formally a nonconjugated polymer. The reasons for this are not clear, although intra- or interchain contributions could both be important; the latter are known to be viable charge transport processes even in the absence of intrachain contributions.[13]

In summary, we have prepared a new PPS-like polymer incorporating biEDOT units linked by a sulfide bridge and discovered surprisingly good charge transport characteristics. There are a large number of alternating copolymers based on EDOT-X-EDOT type monomers.[10,14] All of these are π-conjugated systems with either organic spacers or coordination compounds. Herein we have described an EDOT-S-EDOT monomer that is easy to make and has excellent charge transport and electrochromic properties, despite the absence of a fully conjugated backbone. The origins of these properties are currently under investigation. This system can also be considered as a prototype for other π-conjugated/main group systems linked via electron-donating heteroatoms (e.g., N,O) that are easy to prepare and exhibit excellent materials properties.

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Supporting Information Available: Details of the synthesis and characterization of **1** and electrochemical data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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