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Poly(3,4-ethylenedioxyselenophene)

Asit Patra,[†] Yair H. Wijsboom,[†] Sanjio S. Zade,[†] Mao Li,[†] Yana Sheynin,[†] Gregory Leitus,[‡] and Michael Bendikov*,[†]

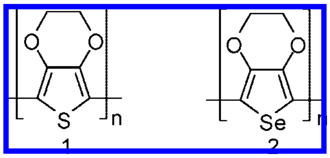
Department of Organic Chemistry and Chemical Research Support Unit, Weizmann Institute of Science, Rehovot 76100, Israel

Received March 24, 2008; E-mail: michael.bendikov@weizmann.ac.il

Since the discovery of highly conductive iodine-doped polyacetylene,[1] conducting polymers[2] have become a rapidly growing field in chemistry. However, despite significant efforts, the types of conducting polymers are limited to polythiophenes, polypyrroles, polyacetylenes, polyphenylenes, poly(*p*-phenylene vinylene)s, and a few others. Given the similarity between thiophene and selenophene rings, and considering that selenium analogues of tetrathiafulvalene (TTF), such as tetramethyltetraselenafulvalene (TMTSF) and bis(ethylenedithio)tetraselenafulvalene (BETS), have been shown[3] to be even better organic superconductors than TTF derivatives, it is surprising that very little is known about polyselenophenes and no highly conductive polyselenophene was reported.[4,5] Theoretical studies[6] indicate that polyselenophenes should have a lower band gap than polythiophenes. Polyselenophenes are also expected to have some advantages over polythiophenes, such as having lower oxidation and reduction potentials,[6] being easier to polarize (since the selenium atom is more easily polarized than sulfur), and being more suited to interchain charge transfer (which should be facilitated by intermolecular Se•••Se contacts).

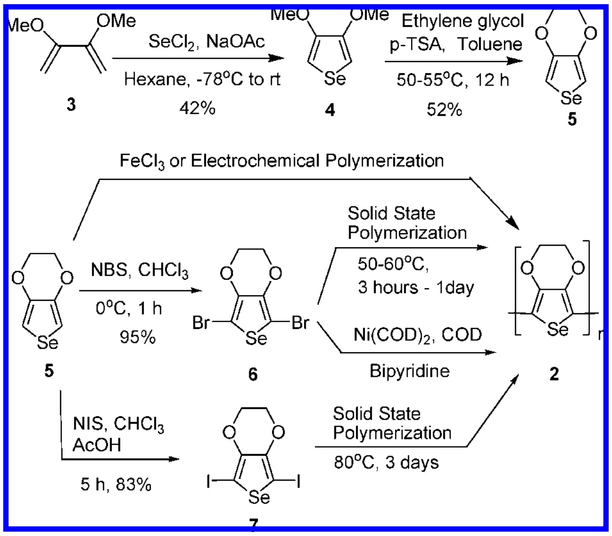
All previous reports[4,5] indicate that the conductivities of doped polyselenophenes range from 10^{-4} to 10^{-1} S cm^{-1}, which is significantly lower than the conductivity of doped polythiophenes (up to 1000 S cm^{-1}).[7] Until now, this low conductivity and the lack of a well-defined electrochemical response by polyselenophenes have prevented their study and application.[4,5] The unavailability of synthetic methodologies for the synthesis of substituted selenophene-based monomeric precursors is another reason why polyselenophenes remained practically unexplored. We presume that the low conductivity and poor electrochemical behavior of polyselenophenes result from their instability during oxidative polymerization and that a polymer with high conductivity and well-defined electrochemistry could be obtained if appropriate monomeric precursors and mild polymerization conditions could be found.

Taking into account the many advantages of poly(3,4-ethylenedioxythiophene)[8] (PEDOT; **1**) compared to other conductive polymers, we decided to concentrate our study on its selenium analogue and here report the synthesis and study of the first highly conductive polyselenophene, namely, poly(3,4-ethylenedioxyselenophene) (PEDOS; **2**).[9]



To prepare PEDOS, we first developed a new and efficient synthetic strategy for the preparation of 3,4-ethylenedioxyselenophene (EDOS; **5**, Scheme 1).[10] The selenophene ring was constructed, for the first time,[11] by cycloaddition of **3** with freshly prepared $SeCl_2$[12] in the presence of NaOAc.[13] Transetherification of **4** with ethylene glycol in the presence of a catalytic amount of *p*-toluenesulfonic acid (*p*-TSA) produced EDOS (52% yield). Chemical polymerization of EDOS using 4 equiv of $FeCl_3$ in acetonitrile at 60 °C for 18 h led to formation of completely insoluble PEDOS with a good yield.[14] Unlike PEDOT, PEDOS prepared by oxidative polymerization with $FeCl_3$ shows a low conductivity of about 0.002 S cm^{-1}, which we tentatively attribute to the oxidative polymerization of EDOS producing defects in the conjugation of the polymer chain due to chemical modification of some selenophene rings caused by oxidation. We have also successfully polymerized DBEDOS (**6**) by transition-metal-mediated polymerization (using $Ni(COD)_2$, COD, and 2,2-bipyridyl), leading to clean formation of PEDOS in good yield (Scheme 1).

Scheme 1. Synthesis of PEDOS (**2**)



In order to obtain highly conductive PEDOS, we used a recently developed solid-state polymerization[15] method requiring mild polymerization conditions. 2,5-Dibromo-3,4-ethylenedioxyselenophene (DBEDOS; **6**, Scheme 1), obtained from bromination of EDOS with NBS, was easily polymerized within 5−6 h under slight heating (55 °C) or within several days at room temperature. White crystals of DBEDOS slowly transformed to blue-black crystals with a metallic luster that retained the morphology of the starting material (Figure 1). However, SEM analysis showed that the structure of crystal was destroyed due to evaporation of bromine (Figure 1). The resulting bromine-doped PEDOS is completely insoluble in common organic solvents and has a strong ESR signal. As-obtained PEDOS has a high conductivity of about 3−7 S cm^{-1} measured in a pressed pellet. The conductivity value is close to that of

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[†] Department of Organic Chemistry.
[‡] Chemical Research Support Unit.

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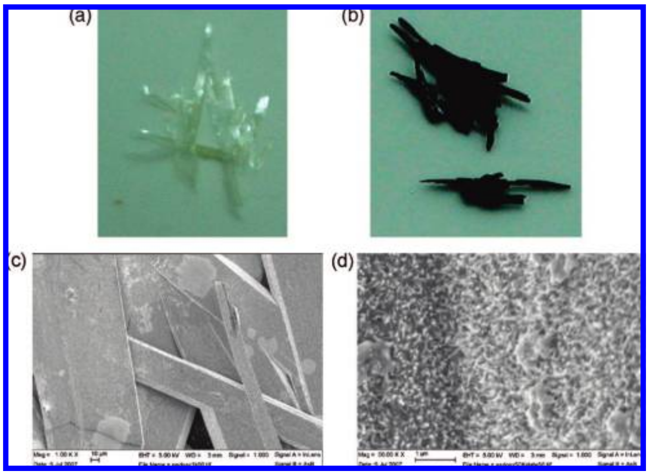

Figure 1. Photographs of (a) crystals of DBEDOS (**6**); (b) PEDOS obtained on heating the DBEDOS crystals at 50 °C for 24 h. SEM pictures of the surface of PEDOS (**2**) obtained by solid-state polymerization with (c) a 10 μm scale bar; (d) a 1 μm scale bar.

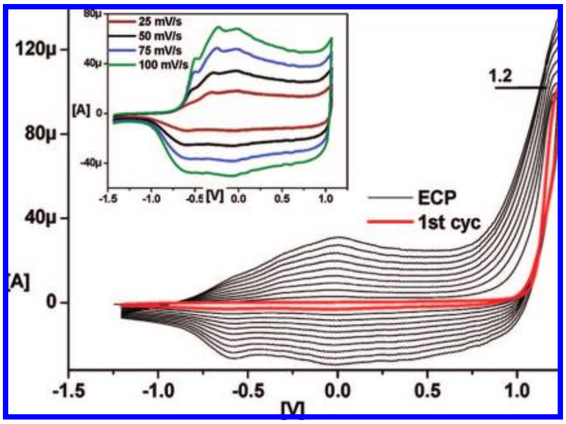

Figure 2. Multisweep electropolymerization of EDOS on a Pt electrode in acetonitrile at 50 mV s^{-1}. (Inset) Cyclic voltammetry of PEDOS produced in monomer-free acetonitrile.

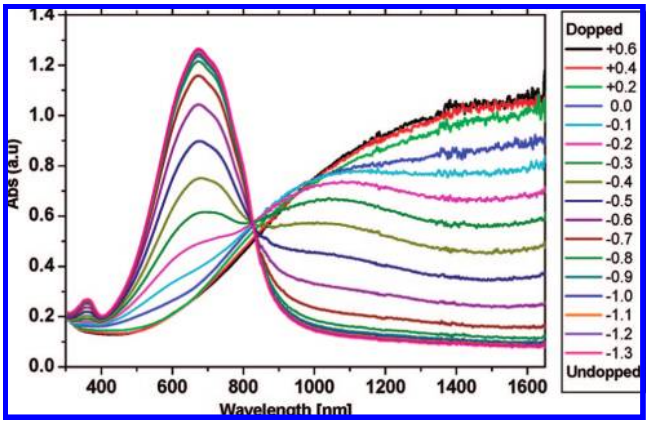

Figure 3. Spectroelectrochemistry of PEDOS as a function of the applied potential between +0.6 and −1.3 V in propylene carbonate.

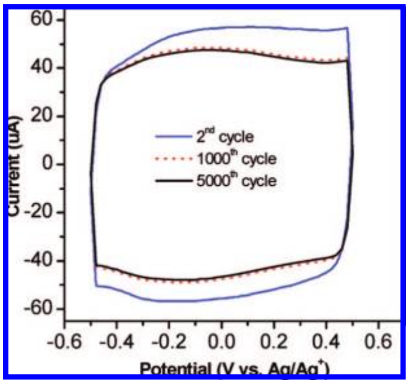

Figure 4. CV of PEDOS films after 2nd, 1000th, and 5000th cycle in MeCN solution.

similarly prepared PEDOT measured by the same method. Similarly, 2,5-diiodo-3,4-ethylenedioxyselenophene (DIEDOS; **7**, Scheme 1), prepared from iodination of EDOS with NIS, was polymerized within 3 days at 80 °C. As-prepared polymer from compound **7** (which includes iodine as a dopant) shows an even higher conductivity of about 30 S cm^{-1} measured in a pressed pellet. The well-ground doped PEDOS synthesized from **6** was dedoped by treatment with hydrazine hydrate in acetonitrile. In contrast to PEDOT, neutral PEDOS is easily doped by air. A sample of the dedoped polymer exposed to air showed a conductivity of about 0.1−0.5 S cm^{-1} measured in a pressed pellet. When dedoping of PEDOS synthesized from **6** and conductivity measurements were done under argon atmosphere, the resulting material has conductivity below 10^{-3} S cm^{-1}. MALDI MS analysis of dedoped PEDOS synthesized from **6** showed weight fragments corresponding to at least up to the 20-mer. The actual molecular weight of the polymer might be significantly higher since high molecular weight ions might be less volatile under MS conditions. By comparison, MALDI MS spectra of PEDOT prepared by solid-state polymerization showed peaks up to the 13-mer.[15b]

X-ray crystallographic analysis of **6** (Figure S1 in Supporting Information) reveals intermolecular Br−Br and Br−Se distances of 3.68 and 3.57 Å, respectively, which are within the van der Waals radii of Br (1.85 Å) and Se (1.90 Å). These interactions may play a role in the expulsion of bromine atoms and concomitant C−C bond formation between selenophene units. The interplane distance between the DBEDOS molecules is 3.64 Å.

The kinetics of the solid-state polymerization of DBEDOS was studied by differential scanning calorimetry (DSC). Heating of the monomer at different temperatures (50−80 °C) below its melting point results in exothermic polymerization (Figure S3 in Supporting Information). The measured reaction enthalpy is 18.5 kcal mol^{-1}, which is 4 kcal mol^{-1} higher than the reaction enthalpy for the solid-state polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT).[15b] The measured activation energy for solid-state polymerization of DBEDOS is 27.5 kcal mol^{-1}, which is practically the same as for DBEDOT[15b] (27.1 kcal mol^{-1}). Extrapolation of the Arrhenius plot to 20 °C predicts a half-life time for DBEDOS of about 21 days (compared to 70 days for DBEDOT),[15b] which qualitatively fits the observation of polymerization of the material at room temperature. Comparison of the DSC data shows that DBEDOS polymerizes at a temperature that is about 20 °C lower than that for DBEDOT.[12,15b]

The EDOS monomer presents two irreversible anodic peaks at 1.22 and 1.75 V in cyclic voltammetry (CV) measurements (Figure S7 in Supporting Information).[16] The first oxidation potential is lower than that of EDOT, which oxidizes at 1.4 V under the same conditions. Under repeated CV cycles, EDOS undergoes smooth polymerization to produce an insoluble PEDOS film on the surface of the working electrode (Figure 2). The electrochemical behavior of PEDOS synthesized by solid-state polymerization was also investigated and shows a similar CV trace to PEDOS as obtained using the electrochemical polymerization (Figure S8 in Supporting Information).

The spectroelectrochemistry of PEDOS film obtained on an ITO electrode is shown in Figure 3. The spectroelectrochemically measured band gap of PEDOS (assigned as the onset of the $\pi-\pi^*$ transition) is 1.4 eV (876 nm) and λ_{max} is 673 nm. The color of PEDOS ranges from deep-blue in the neutral state, with CIE of 0.19, 0.21 at -1.3 V, to transmissive gray in the doped state with CIE of 0.29, 0.31 at 0.4 V. So, PEDOS is an excellent candidate for transparent electrodes due to its transparence in the doped state. Formation of polarons is observed at around 1050 nm (compared to a similar peak at around 900 nm for PEDOT), while the bipolarons peak after 1600 nm. PEDOS films are highly stable during spectroelectrochemical measurements between -1.3 and $+0.6$ V (Figure 3). PEDOS films were cycled 5000 times between -0.5 and 0.5 V (Figure 4). The total charge decrease between the initial and 5000th cycle was less than 17%. It should be noted that most of this decrease occurred during the first 1000 cycles, with only a 1% decrease in total charge between the 1000th and 5000th cycles. The high stability of the PEDOS films is comparable to the stability of PEDOT[17] films. The high stability of doped PEDOS together with its transparency as a film is important for its future applications in electrochromic devices.

The measured band gap of PEDOS (1.4 eV) is in excellent agreement with the calculated value of 1.66 eV. The band gap of PEDOT (measured under similar conditions as those used for PEDOS) is 1.6 eV, by 0.2 eV higher than that of PEDOS,[8] while the calculated band gap for PEDOT is 1.84 eV. The HOCO and LUCO levels for PEDOS at $k = 0$ are -3.45 and -1.79 eV, respectively. For comparison, the HOCO and LUCO levels of PEDOT at $k = 0$ are -3.54 and -1.69 eV, respectively. Both polymers also have similar calculated valence and conduction bandwidths. The optimized geometries of both polymers are very similar, and they have a planar backbone. The major difference between the structures of PEDOS and PEDOT is the calculated interring C−C bond length, which is 1.425 and 1.434 Å for PEDOS and PEDOT, respectively. All calculations were performed using Gaussian 03 program at the PBC/B3LYP/6-31G(d) level.[12]

In conclusion, we have synthesized the first highly conductive polyselenophene by taking advantage of a novel method for efficiently contracting the selenophene ring. PEDOS shows a low band gap (1.4 eV), very high stability in the oxidized state, and a well-defined spectroelectrochemistry. We have demonstrated that solid-state polymerization could be a viable route for the synthesis of highly conductive polyselenophenes. We have shown that polyselenophenes are excellent candidates for application as transparent conducting surfaces. Applications of PEDOS in electrochromic devices and studies of other polyselenophenes are currently underway in our laboratory.

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Supporting Information Available: Experimental procedure, spectral data, CIF file, detailed electrochemistry and the optoelectrochemical spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) One attempt to prepare PEDOS by chemical polymerization of EDOS using $FeCl_3$ has been reported earlier.[4b] However, the reported polymer was soluble in organic solvents, and the onset of UV absorption was more than 200 nm smaller than reported in this paper (λ_{max} reported in ref 4b is by 79 nm smaller than reported in this paper). This indicates the presence of only relatively short oligomer chains. The electrochemically prepared polymer was also claimed; however, its characterization was limited, and our results indicate that the PEDOS reported in this paper has better conjugation than the material reported in ref 4b.

(10) EDOS (**5**) was previously synthesized in five steps.[4b] Detailed experimental procedures were not reported.

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