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Poly(thieno[3,4-*b*]thiophene). A New Stable Low Band Gap Conducting Polymer

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Conducting polymers have generated considerable interest due to their potential broad applicability in numerous electronic devices. Presently, commercially available applications utilizing conductive polymers include antistatic coatings for electronic packaging,[1] organic light-emitting diodes,[2] electrochromic windows,[3] and volatile organic gas sensors.[4] These polymers are presently being investigated as potentials for molecular wires.[5−7]

The band structure of conducting polymers dictates their electrochemical and optical properties. The band structure can be tuned by altering either or both the electronic structure and sterics of the backbone. Of particular interest is the preparation of stable, low band gap conductive polymers. These materials have attracted much attention due to their high visible transmissivity in the conductive form and their ease at which they can be both p- and n-doped. The first low band gap (E_g) polymer reported was poly(isothianaphthene) (E_g = ca. 1.0−1.2 eV),[8,9] making the band gap approximately 1 eV lower than that of polythiophene. This has been attributed to the ability of the fused benzene ring to stabilize the quinoidal form of the polymer in the conductive state.[10] Despite this, the practical use of poly(isothianaphthene) became limited due to its environmental instability.

Several examples of conducting polymers derived from thieno[2,3-*b*]thiophene[11] and thieno[3,2-*b*]thiophene[12−17] have been reported. The chemical structures of these monomers are depicted in Figure 1. Although the electrochemical and chemical polymerization of 2-substituted thieno[3,4-*b*]thiophenes have been reported,[18,19] the polymerization of unsubstituted thieno[3,4-*b*]thiophene has not previously been accomplished. Herein we communicate the synthesis and preliminary characterization of poly(thieno[3,4-*b*]thiophene) as a potential low band gap conductor and electrochromic material.

Thieno[3,4-*b*]thiophene was prepared in accordance to literature procedure in multigram quantities[20] and characterized by nuclear magnetic resonance spectroscopy, gas chromatography−mass spectrometry, and both Raman and infrared spectroscopy. The monomer was dissolved in 0.1 M tetrabutylammonium perchlorate/acetonitrile solution to give a concentration of 10 mM monomer and was electrochemically polymerized using a three-electrode configuration with a platinum button working electrode (2 mm diameter), platinum flag counter electrode (1 cm^2), and a Ag/Ag$^+$ nonaqueous reference electrode (0.473 V vs standard hydrogen electrode as determined by calibration with a ferrocene solution).

The cyclovoltammetric growth of the polymer is displayed in Figure 2. The monomer exhibits a low oxidation potential with an onset at 0.9 V and a peak at 1.05 V. For comparison, the onset potential is ca. 0.1 V higher than that of pyrrole, and the peak potential is ca.0.2 V lower than that of 3,4-ethylenedioxythiophene. A low oxidation potential of the monomer is beneficial since degradative side reactions may be avoided during polymerization. Polymerization to form a conductive polymer is apparent from the current response increase in regular intervals at a lower redox potential upon repetitive scans.

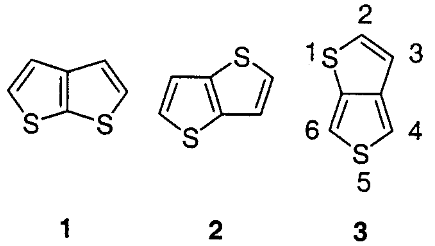

Figure 1. Chemical structures of thieno[2,3-*b*]thiophene (**1**), thieno[3,2-*b*]thiophene (**2**), and thieno[3,4-*b*]thiophene (**3**). Atom labels are shown for thieno[3,4-*b*]thiophene.

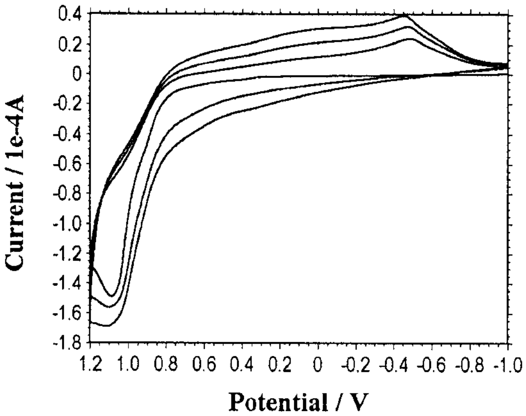

Figure 2. Electrochemical polymerization (100 mV/s) of thieno[3,4-*b*]thiophene in 0.1 M TBAP/ACN; 10 mM monomer concentration. Potential vs Ag/Ag$^+$ reference electrode (0.473 V vs SHE).

Poly(thieno[3,4-*b*]thiophene) was prepared at a constant potential of 1.2 V on an indium tin oxide (ITO)-coated glass plate and washed with ACN, and cyclic voltammetry was carried out in 0.1 M TBAP/ACN. Upon scanning at a rate of 50 mV/s from −0.8 to 0.8 V an onset for oxidation became apparent at −0.5 V with a half-wave potential at ca. 0.2 V (Figure 3). On top of this broad redox process was a sharp redox process present at $E^{1/2}$ of 0.3 V with 0.18 V peak-to-peak separation. This sharp redox process was not an artifact but was repeatable numerous times for thin films on both platinum and ITO. Presently, we do not understand the origins of this sharper redox process. We hypothesize that it is due to the redox process of discrete conjugated oligomers. Discrete units within the polymer structure could exist since the electrochemical polymerization of thieno[3,4-*b*]thiophene could afford a branched or cross-linked polymer. It should be noted that there are three α positions, positions 2, 4, and 6, accessible for coupling (see Figure 1).

Scan rate dependency was carried out on the conductive polymer at scan rates of 50, 100, 200, and 250 mV/s. The peak current for the reductive process of the polymer was found to scale linearly with the scan rate,

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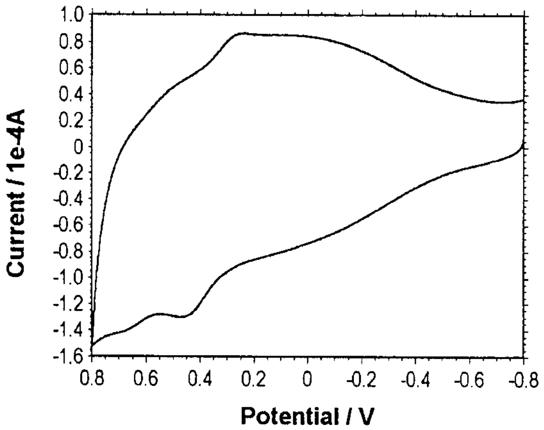

Figure 3. Cyclic voltammetry of a poly(thieno[3,4-*b*]thiophene) film on ITO glass at 50 mV/s in 0.1 M TBAP/ACN. Potential vs Ag/Ag^+ reference electrode (0.473 V vs SHE).

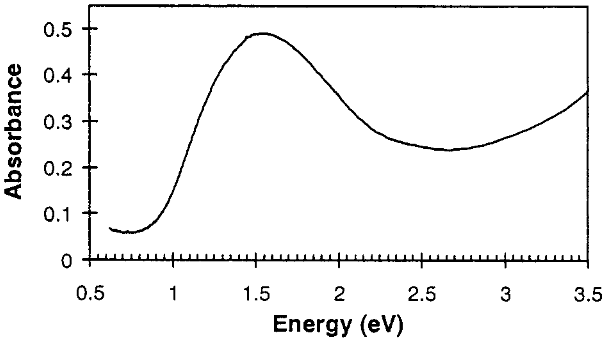

Figure 4. UV−vis−NIR spectrum of a 0.1 μm thick poly(thieno[3,4-*b*]thiophene) film on ITO glass. The film was electrochemically reduced at -0.8 V in 0.1 M TBAP/ACN, dipped in a solution of 0.1 M TBAP/ACN containing 0.2% hydrazine by volume, and air-dried before obtaining the spectrum.

indicating that the conductive polymer was adhered to the surface of the electrode.

A ca. 0.2 μm thick film, as measured by profilometry, of poly(thieno[3,4-*b*]thiophene) was prepared at 1.0 V from a 10 mM monomer/0.1 M TBAP/ACN solution on an ITO-coated glass slide. The polymer was reduced at -0.8 V and dipped into 0.1 M TBAP/ACN containing 0.2 vol % hydrazine, and the UV−vis−NIR spectrum (Figure 4) of the air-dried film was obtained. The onset for the valence to conduction band occurs at 0.85 eV (1459 nm) with a peak at 1.54 eV (804 nm), qualifying this material as a low band gap polymer.[21] This value is in excellent agreement with the values of 1.54 and 1.63 eV for the aromatic and quinoidal forms, respectively, as calculated by Hong and Marynick.[22] The band edge is approximately the same as that reported for poly(2-phenylthieno[3,4-*b*]thiophene)[19] and poly(2-decylthieno[3,4-*b*]thiophene-4,6-diyl).[18] Of further note, the absorption for the valence to conduction band for poly(thieno[3,4-*b*]thiophene resembles that reported for poly(2-pheylthieno[3,4-*b*]thiophene, not poly(2-decylthieno[3,4-*b*]thiophene-4,6-diyl), in that it has one broad absorption. The UV−vis−NIR spectrum reported for the insulating form of poly(2-decylthieno[3,4-*b*]thiophene-4,6-diyl) displayed two overlapping absorptions.[18]

The polymer is deep blue in the insulating form and transmissive tan in the p-doped state, making it a potential cathodically coloring material for use in electrochromic devices. Initial chronocoulometry experiments stepping the polymer between -0.8 V for 20 s and 0.6 V for 20 s, constituting a double potential step, on a platinum button show the polymer to have no calculable loss of electroactivity upon 200 double potential steps.

In conclusion, we have shown that the monomer thieno[3,4-*b*]thiophene undergoes facile electrochemical polymerization to yield a conductive polymer with a very low band gap of 0.85 eV, which is one of the lowest reported for conductive polymers to present.[18,21] Due to its stability and optical properties, poly(thieno[3,4-*b*]thiophene) is a potential material for electrochromic devices as a cathodically coloring material. With a band gap of 0.85 eV, we project that the n-doping process for this polymer will occur at ca. -1.35 V vs Ag/Ag^+. We will report the full spectroelectrochemical analysis, p- and n-doping cyclic voltammetry, n-doping stability, and structural characterization of poly(thieno[3,4-*b*]thiophene in the future.

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