Poly(3,4-ethylenedioxypyrrole): Organic Electrochemistry of a Highly Stable Electrochromic Polymer

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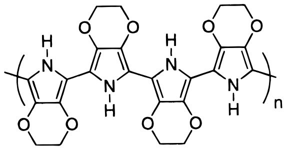
Electron-rich conjugated polymers are especially useful for the formation of stable conducting polymer complexes which can be switched between their oxidized (doped) and charge-compensated (neutral) states rapidly over many redox cycles.[1] These materials are represented by polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT)[2] and its derivatives. Of the many potentially useful properties afforded by these polymers (high conductivity, mechanical actuation, chemical sensing, etc.), molecular engineering of conjugated systems can be used to provide electrochromic materials[3,4] with a range of colors, a high degree of switching stability, and striking color contrasts between absorptive and transmissive forms. In the case of PEDOT, the 3,4-alkylenedioxy substitution pattern facilitates electrochemical polymerization by lowering the monomer oxidation potential ($E_{p,m}$) and directing polymerization through the 2- and 5-positions, yielding regiosymmetric polymers with a low degree of main chain imperfections. This is not the case with PPy, which exhibits structural defects arising from β couplings resulting in conjugation breaks.[5] Substitution of pyrrole at the β-positions prevents these unwanted couplings, leading to more regular materials. At the same time though, PPy exhibits a quite low oxidation potential (−0.2 V vs SCE, ca. −0.4 V vs Ag/Ag$^+$)[6] and can be formed as highly conductive (near metallic) and stable films,[7] and its redox properties are compatible in aqueous electrolytes, making it useful in biological systems.[8] It is evident that combination of the electron-rich pyrrole heterocycle with the 3,4-alkylenedioxy substituent in 3,4-ethylenedioxypyrrole (EDOP) should provide a stable conducting polymer (as reported in a single patent by Savage et al.[9]) and has been the focus of our recent efforts in electroactive polymers as aqueous compatible biomaterials.[10]

Here we communicate the first report of the organic electrolyte-based electropolymerization of EDOP and the unique electrochromic properties of the resultant poly(3,4-ethylenedioxypyrrole) (PEDOP) (**1**) films. PEDOP exhibits one of the lowest half wave potentials ($E_{1/2}$) for p-type doping of any conjugated polymer reported to date. In addition, this polymer switches between a bright red neutral form and a highly transmissive blue-gray doped/conducting form. While the electropolymerization of 3,4-dimethoxy-substituted pyrrole has been carried out,[11] the electrochromic properties of the corresponding polymers were not investigated.



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Similar to the synthesis of EDOT derivatives,[2] the preparation of EDOP involves a multistep procedure that is further complicated by the necessity of protecting the pyrrole nitrogen as reported by Merz et al.[12] Starting from dimethyl-*N*-benzyliminodiacetate, a five-step synthesis adopted from a previous procedure[12] afforded EDOP in 20% overall yield.

A 10^{-2} M solution of EDOP was polymerized by repeated potential scanning (20 mV/s) between −1.4 and +0.8 V vs Ag/Ag$^+$ (all further potentials are reported relative to this reference electrode) in 0.1 M $LiClO_4$/propylene carbonate (PC) using a standard three-electrode cell on a Pt button working electrode under an inert atmosphere. With a peak monomer oxidation potential ($E_{p,m}$) of +0.7 V, EDOP oxidizes 0.25 V more easily than EDOT and 0.5 V more easily than pyrrole, confirming its electron-rich character and allowing electropolymerization to proceed under quite mild conditions. During the polymerization, an electroactive polymer film forms quickly on the electrode surface. The resulting film is highly redox active, and free-standing films with electrical conductivities in excess of 80 S/cm have been prepared. PEDOP is one of the most easily oxidized conducting polymers reported to date as evidenced by the cyclic voltammetric results in Figure 1 showing an $E_{1/2}$ of −0.5 V vs Ag/Ag$^+$ (*Note: this corresponds to an* $E_{1/2}$ *of ca.* −0.3 *V vs SCE.*) For comparative purposes, the $E_{1/2}$ values for PEDOT and PPy are indicated at −0.25 and −0.4 V, respectively. In addition, Figure 1 shows the outstanding redox stability of PEDOP upon cycling, where only a limited decrease in the current response is observed compared to other conducting polymers after 2000 cycles between −1.67 and +0.33 V. Redox stability is a stringent requirement in numerous applications, such as the production of reliable electrochromic devices with long lifetimes.

In addition to raising the effective highest occupied molecular orbital (HOMO) level of the conjugated backbone, the presence of the 3,4-ethylenedioxy substituent on the pyrrole ring significantly decreases the band gap (taken as the onset of π to π* transition) of PEDOP, relative to PPy, by 0.65 eV to a value of 2.05 eV. Examination of the spectrum for the reduced polymer (−0.9 V) in the spectroelectrochemical series shown in Figure 2 shows it to have a remarkably sharp π to π* transition when compared to that of PPy. In fact, this spectrum is quite similar to that observed for PEDOT, yet translated to higher energy. This exemplifies the regiosymmetry enforced by the 2,5-linkages. Upon oxidation, the π to π* transition is fully depleted as a strong lower energy transition centered at about 0.75 eV in the near-infrared is induced. This near-infrared band reaches its maximum intensity at about −0.4 V. This further confirms the ease with which PEDOP can be converted to its oxidized form. Because of the low oxidation potential, air and moisture will not

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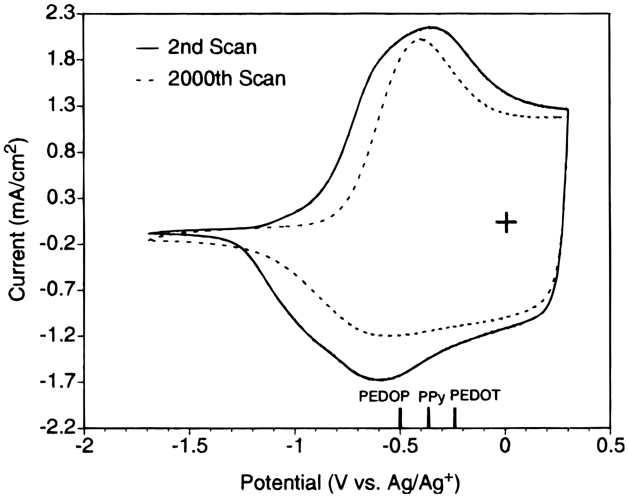

Figure 1. Cyclic voltammetry on a $\sim$1 μm thick film demonstrating long-term redox switching stability of PEDOP after repeated cycling (up to 2000 cycles) between -1.67 and $+0.3$ V vs Ag/Ag$^+$ at 20 mV/s.

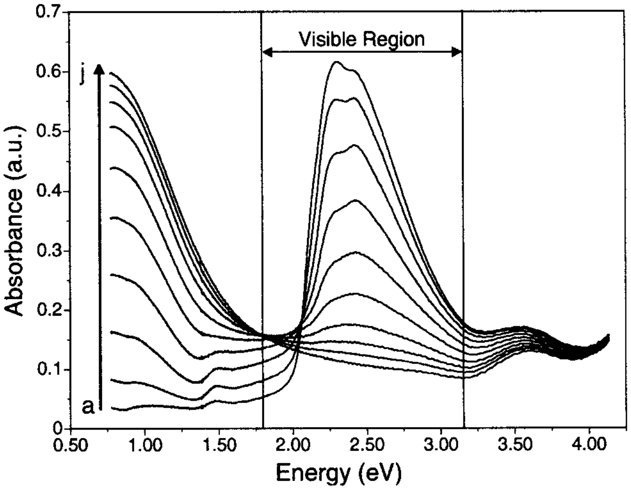

Figure 2. Spectroelectrochemistry of a $\sim$0.1 μm thick (50 mC/cm^2) PEDOP film in 0.1 M $LiClO_4$/PC at applied potentials of -0.87 to -0.37 V vs Ag/Ag$^+$: (a) -0.87, (b) -0.82, (c) -0.77, (d) -0.72, (e) -0.67, (f) -0.62, (g) -0.57, (h) -0.52, (i) -0.47, and (j) -0.37 V.

affect the electroactivity by redox processes, which should play an important role in yielding a very stable conductor.

As the applied potential is further increased incrementally up to +1.6 V above the $E_{1/2}$, the near-infrared band decreases only 30% in intensity. This result emphasizes the stability of PEDOP to overoxidation and is noteworthy since very few polymers remain electroactive over 2 V above their $E_{1/2}$.

Galvanostatic deposition of a thin film (ca. 220 nm) onto an indium tin oxide (ITO) coated glass substrate affords an extremely smooth transmissive light blue-gray coating (doped state) which can be switched to a bright red (neutral state). Such a color change has not been reported for other conjugated polymer systems, thus making it an attractive electrochromic material. These color changes were further investigated by colorimetry[13] using the CIE 1931 Yxy color space,[14] since precise color is required for the construction of electrochromic devices. The neutral state is a highly saturated red ($x = 0.57$, $y = 0.31$), while the doped state is a neutral blue-gray ($x = 0.34$, $y = 0.38$). Examination of the light transmission characteristics showed the neutral state to be quite absorptive with a relative luminance (% Y)[15] of only 11% while the more transmissive oxidized state exhibited a relative luminance of 53%.

In summary, the alkylenedioxy substitution pattern serves to enhance the electrochemical, optical, and electrochromic properties of the polypyrrole backbone in a manner that is analogous to that observed for PEDOT. We are presently exploiting the versatility of 3,4-alkylenedioxypyrrole chemistry through the preparation of numerous derivatives with optimized properties. Highly conducting and stable films, variable color electrochromic materials, and water-compatible electrode materials and conductors potentially useful in biological applications are but a few of the possibilities.

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Supporting Information Available: Synthesis of 3,4-ethylenedioxypyrrole (EDOP). This material is available free of charge via the Internet at http://pubs.acs.org.

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