Communications to the Editor

Reversible *n*-Doping of Poly(nonylbithiazole) and Oligomeric Model Compounds. Application as a Li Battery Electrode

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Materials capable of being reversibly *n*-doped/undoped, that is, capable of undergoing reversible reduction/oxidation, are currently of interest in connection with supercapacitor technology and solid-state batteries,[1] in light-emitting electrochemical cells (LECs)[2] and diodes (LEDs),[3] in *p*–*n* junction devices,[4] and in electrochromic displays.[5] Electronically conducting polymers have properties that make them attractive for use in these applications. Their mechanical flexibility, light weight, and fast charge transport kinetics are superior to conventional solid-state ceramic and mixed conductors. Recently, a new class of conjugated polymers based on 4,4′-dialkyl-2,2′-bithiazoles (**1**) was reported.[6,7] Unlike most conjugated polymers, for example, PPV or poly(thiophenes), the poly(alkylbithiazoles) (PABTs)[8] have fast *n*-doping kinetics. Here we present the electrochemical, optical, and conductivity properties of electrochemically *n*-doped films of "poly(nonylbithiazole)" (PNBT, **1**, R = nonyl, $n \approx 52$) and perfomance of the polymer as the cathode of a Li/PNBT cell.

1, R = nonyl
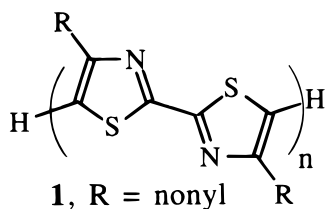
The cyclic voltammetry (CV) of short chain oligomers of **1** (*n* = 1, 2, 3, 5) have been obtained for comparison with the behavior of the polymer.[9] The monomer, NBT (**1**, *n* = 1), shows a quasi-reversible reduction in MeCN ($E_p^R = -2.44$ eV, $E_{p/2} = -2.36$, $\Delta E_p = 140$ mV, $i_c/i_a = 0.9$ at 100 mV/s sweep rate). In THF, the reduction of the monomer is less reversible and is at the edge of the solvent stability window. The dimer, (NBT)$_2$, shows two discernible reduction waves in THF (the oligomers and polymer are not soluble in MeCN) at $E_p^R = -2.34$ and -2.54 V and two well-defined, return oxidation peaks
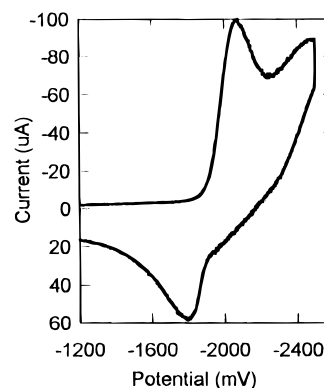

Figure 1. Cyclic voltammogram of PNBT in THF (0.1 M TBAF, supporting electrolyte).

at -2.36 and -2.11 V ($\Delta E_1 = 230$ mV and $\Delta E_2 = 180$ mV with the sweep rate = 100 mV/s). The trimer, (NBT)$_3$, has three poorly resolved reduction peaks at $E_p = -2.19$, -2.34, and -2.71 V, and three discernible reoxidation peaks at -2.67, -2.29, and -2.03 V ($\Delta E_p = 160$, 50, and 40 mV, respectively, at a sweep rate = 100 mV/s). This behavior mirrors the *oxidation* behavior of sexithiophene which shows three oxidation waves and gives a trication.[10] The pentamer, (NBT)$_5$, shows only two ill-resolved humps at -2.08 and -2.49 V, and the return oxidation peak is quite weak.

Thus, with increasing length of the oligomer, the reduction potential becomes more positive, but the effect begins to saturate. A graph of the first reduction peak potentials vs 1/*n* (*n* = number of bithiazole units) fits a straight line ($-E_p = 1.90 + 0.868/n$, $r = 0.9997$), except for the point associated with the monomer which falls below the line. The monomer may be more planar in solution than the higher oligomers and is therefore more easily reduced than the trend established by the latter would predict. The 1/*n* dependence of the reduction potential is not unexpected since the HOMO–LUMO gap of these oligomers also scales with 1/*n*,[6] and the reduction potential is related to the energy of the LUMO.

These electrochemical results suggest that one electron can be added per two thiazole rings in the oligomers. It has been reported that poly(methylthiophene) can be charged to 52%, that is, one electron per two thiophene rings,[11] but this level of doping is greater than that normally observed for *p*-doped poly(arylenes), where doping levels of 25% are typical (i.e., one electron removed per four aryl or heteroaryl rings).[12] Poly(acetylene) has been reported to be *n*-dopable to a level of 0.3 Li per CH unit,[13] but values of ≤0.1 Li/CH are more common.[12]

The CV of a solid film of the polymer, formed by evaporating a solution of the polymer on the electrode, is shown in Figure 1. The reduction peak occurs at $E_p = -2.16$ V (vs Fc/Fc$^+$) and the return oxidation peak is
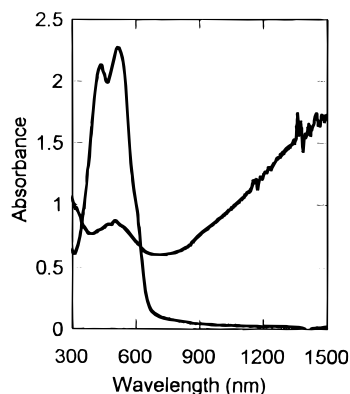
Figure 2. UV–vis spectra of PNBT film (a) at $V = 0.0$ V and (b) at $V = -2.0$V.
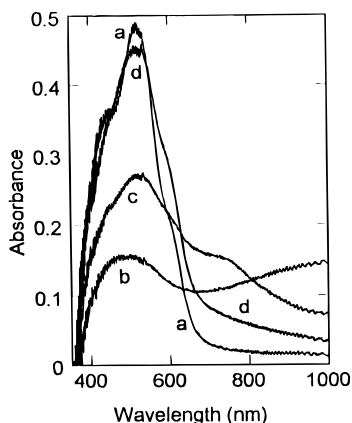

Figure 3. UV–vis spectra of PNBT at (a) $V = 0.0$ V, (b) $V = -2.0$V, (c) closed circuit discharge at $t = 2$ m, and (d) $t = 10$ m.

at -1.77 V at a 100 mV/s sweep rate. The reduction potential of the polymer suggests that only about three bithiazole units are in conjugation (assuming the $1/n$ correlation from the oligomers holds), and this estimate is approximately the same as that obtained from the correlation of λ_{max} with $1/n$.[6] The polymer electrode was stable to at least 500 cycles of reduction and reoxidation to the neutral species. This stability to redox cycling is a desirable property for the application to electrochemical devices. We have also observed that the color of the polymer film was dependent on the degree of electrochemical doping: the neutral polymer is orange and the fully reduced polymer is a transparent, light gray color. Figure 2 compares the UV–vis spectra of the neutral film and the fully reduced polymer at a potential of -2.0 V.[14] The peaks at 438 and 527 nm are due to two of the polymorphs[6] of PNBT, and these decrease in intensity and are replaced by an extremely broad absorption in the NIR due to "free carriers" as the polymer film is reduced. The conductivity of the n-doped material can be estimated from the molar absorption coefficient of the NIR absorption using the Drude equation, $K = (2\sigma\omega\mu_0)^{1/2}$, where K is the absorption coefficient (cm^{-1}), σ is the conductivity, ω is frequency, and μ_0 is the permeability of free space.[15] The value so calculated for σ is 26 S cm^{-1}.

Figure 3 shows the changes in the UV–vis spectra as the neutral, undoped PNBT (Figure 3a) was fully reduced at a potential of -2.0 V (Figure 3b). The doped film was then allowed to discharge by reducing the voltage back to 0.0 V. The spectrum in Figure 3c was taken after 2 min of discharge, and the one in Figure
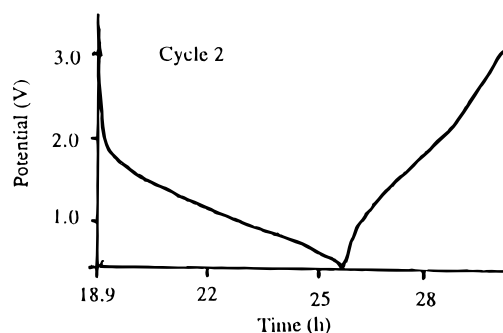

Figure 4. Potential–time plot of a discharge/charge cycle of a PNBT ||LiPF$_6$/EC/PC|| Li cell.

3d was after 10 min of discharge. The reduction/oxidation cycle occurs without detectable decomposition, but the morphology of the polymer film is affected in a manner similar to that caused by thermal annealing: the peak at 438 nm that arises from the disordered phase decreases in intensity relative to the peak at 527 nm and the shoulder at 619 nm. The latter two features are due to a highly ordered phase with planar, conjugated chains, and to $\pi-\pi$ stacked J aggregates of planar chains, respectively.[6] Apparently, the migration of the counterions in and out of the polymer film during doping and dedoping enhances the segmental motion of the polymer molecules, similar to that which occurs at higher temperatures, with the result that the polymer chains become aligned and crystallize.

Figure 4 shows the voltage profile of the PNBT polymer tested against a metallic Li electrode. The polymer was dissolved in CHCl$_3$ and mixed with a 3 wt % binder (EPDM, ethylene–propylene diene monomer) and 20 wt % carbon black. This slurry was cast onto Ni foil using the grooved blade technique and then dried at 110 °C under vacuum (10^{-3} Torr). A 5 cm^2 electrode was cut from the foil and placed in a cell against a 5 cm^2 Li electrode with a commercial separator (Cellguard 2400). The electrolyte was 0.8 M LiPF$_6$ in an ethylene carbonate–diethyl carbonate mixture (2:1 mol ratio). Charge–discharge cycling of the cell was performed with a Maccor battery cycler at a constant 10 μA current. The charge capacity of the PNBT electrode was 52 (mA h)/g. This corresponds to 0.81 electron per bithiazole unit, or 81% of the capacity expected on the basis of the CV study of the oligomers. Similar n-doping behavior was recently reported for poly(methylbithiazole), but the degree of reduction was not determined.[7]

These results show that bithiazole-based polymers are capable of reversible n-doping, with a maximum doping level of about one electron per bithiazole unit. Thus, the theoretical capacity of the unsubstituted polymer (**1**, R = H) is approximately 160 (mA h)/g. This capacity is comparable to that of (Li$_{0.1}$CH)$_x$ and greater than the usual capacities of common, p-dopable conjugated polymers.[12] The doped polymer is transparent in the visible region of the spectrum and exhibits metallic-like absorption in the NIR. The material was stable to 500 charge/discharge cycles.

Supporting Information Available: Cyclic voltammogram of (NBT)$_3$ and a graph of the first reduction peak voltage vs $1/n$ for (NBT)$_n$ (1 page).

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(8) PNBT: poly-5,5′-(4,4′-dinonyl-2,2′-bithiazole-diyl).

(9) Cyclic voltammograms were obtained with Princeton Applied Research potentiostat, model 173, interfaced to a PC computer with a program written by Dr. S. Paras, Department of Chemistry, The University of Michigan. The program provides the voltage ramp and handles data collection and manipulation. Solvent was dry THF, and the supporting electrolyte was tetrabutylammonium tetrafluoroborate (TBAF, 0.1 M). The concentration of the analyte was approximately 4 mM in bithiazole rings. The reported potentials are versus the ferrocene/ferricenium (Fc/Fc$^+$) couple, obtained by adding a crystal of ferrocene to the solution. The Fc/Fc$^+$ couple has a potential of $+400$ mV vs the NHE: Koepp, H. M.; Wendt, H.; Strahlow, H. Z. *Elektrochem.* **1960**, *64*, 483.

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(14) A polymer-coated ITO strip was used as the working electrode in the electrochemical cell (MeCN solvent, 0.1 M TBAF supporting electrolyte) which was constructed from a fused quartz optical sample cell. This assembly was placed in the beam of the spectrometer.

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