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A Second Look at Polythieno[3,4-*b*]pyrazines: Chemical vs Electrochemical Polymerization and Its Effect on Band Gap

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The optical and electronic properties of conjugated polymers (CPs) are of considerable fundamental and technological interest. Applications demonstrated for CPs include their use in batteries, sensors, electrochromic devices, LEDs, and field effect transistors.[1,2] The advantage of utilizing CPs in such applications is the ability to tune properties at the molecular level via synthetic modification.[2] This ability is of the utmost importance for their efficient application. Soluble, stable systems are required, and the desirable properties are dependent on the extent of conjugation. Increased conjugation lowers the band gap, resulting in an enhancement of the thermal population of the conduction band and increasing the number of intrinsic charge carriers. In addition, the lower oxidation potentials associated with narrow band gaps result in stabilization of the corresponding doped (i.e., oxidized) state.[3] Thus, the ability to control polymer properties is the key to the production of technologically useful materials.

One method of tuning polymer properties is the annulation of aromatic rings to the repeat units, which has been found to be a powerful approach to the production of low band gap materials.[3] An excellent example of such materials is polythieno[3,4-*b*]pyrazines (pTPs, Figure 1).[4−7] We report herein the first electropolymerization of pTPs resulting in band gaps as low as 0.66 eV. As far as we are aware, this represents one of the lowest reported band gaps for a simple homopolymeric conjugated polymer.[8]

Interest in pTPs began in 1990 when theoretical band gap calculations predicted a value of 0.70 eV,[4] less than half that of polythiophene (2 eV).[2] Shortly thereafter, Pomerantz and co-workers prepared pC$_6$TP through the oxidative polymerization[2b] of 2,3-dihexylthieno[3,4-*b*]pyrazine using FeCl$_3$ as a chemical oxidant and determined its band gap to be 0.95 eV.[5,6]

In the pursuit of new metalated conjugated polymers, we turned to pTPs when it was observed that the polymer's s-trans conformation should provide a suitable cleft for metal chelation directly to the backbone (Figure 1).[7b] With this in mind, the known pTP studies were reevaluated, as FeCl$_3$ polymerizations could result in the complicating factor of iron binding. In fact, Pomerantz stated that even after prolonged attempts to dedope the polymer, an EPR signal was still observed, indicating that the material was paramagnetic.[5] *This reported observation could be explained in terms of* Fe^{3+}*chelation by the polymer, which common dedoping techniques would then be unable to remove.* To ensure the production of metal-free samples, the electropolymerization of various thieno[3,4-*b*]pyrazines[9] was investigated and compared to samples prepared via chemical methods using FeCl$_3$.

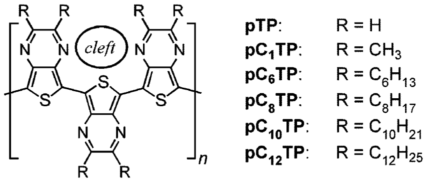

Figure 1. Poly(2,3-disubstituted thieno[3,4-*b*]pyrazine)s.

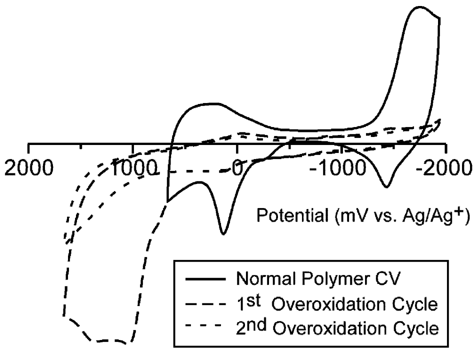

Figure 2. Cyclic voltammograms illustrating normal and overoxidation cycles of poly(2,3-dioctylthieno[3,4-*b*]pyrazine) (pC$_8$TP).

Polythiophene electropolymerizations have been heavily studied,[2] but only a single report of the failed electropolymerization of pC$_1$TP could be found in the literature, which was attributed to the quenching of the radical cation by the pyrazine ring.[10] We have found, however, that this is not the case and that the difficulty lies in the fact that pTPs are highly susceptible to overoxidation. This process is a common problem among conjugated polymers at higher potentials (∼1.8 V vs Ag/AgCl), which results in the destruction of the electroactivity of the polymeric material and can compete with electropolymerization.[11] In the case of pTPs, we have found that overoxidation can begin at potentials below 1.0 V (Figure 2) and competes much more strongly with polymerization than in the case of other polymers such as polythiophene. Therefore, polymerization attempts at higher potentials (∼2.0 V) resulted in the overoxidation of the polymer as it was being formed and thus no polymer deposition.

By using the lower oxidation potential of the dialkyl monomers (ca. 1.35 V vs 1.55 V for the parent)[9] and keeping applied potentials as low as possible (∼1.4 V), we have been able to successfully grow dialkyl-functionalized pTP films (Figure 2 and Table 1). These films are purple-black in appearance and are relatively soluble in organic solvents such as CHCl$_3$ or THF. Cyclic voltammograms of thin films typically exhibit two successive oxidations of the neutral pTP. The oxidations of the pC$_1$TP occur at much lower potentials than typical polythiophenes (ca. 0.50 V),[2] and both oxidations occur before the first oxidation of the analogous poly(isothianaphthene) (∼0.095 V).[3] As can be seen in Table 1, the predominant oxidation wave shifts to higher potentials with increasing side chain length. This can be attributed to increased side chain induced steric interactions, causing decreased conjugation and an increase in the oxidation potential.

In addition to these oxidative processes, the films also undergo reduction at fairly negative potentials. This

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Table 1. Electrochemical and Optical Data for Electrochemically Polymerized Poly(2,3-dialkylthieno[3,4-*b*]pyrazine)s

polymer	E_{pa} (V)[a]	E_{pc} (V)[a]	λ_{max}[b]	band gap[c] (eV)
pC$_1$TP	−0.15, 0.07	−1.49	1275	0.66
pC$_6$TP	−0.22, 0.13	−1.63	1365	0.69
pC$_8$TP	−0.28, 0.13	−1.75	1410	0.69
pC$_{10}$TP	0.23	−2.08	1400	0.67
pC$_{12}$TP	0.23	−2.05	1260	0.79

[a] V vs Ag/Ag$^+$. [b] Solid state in nm. [c] Optical.

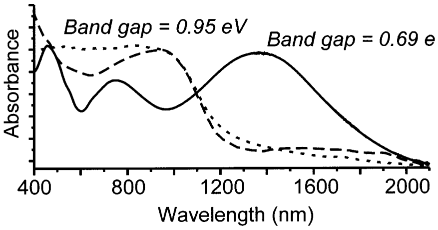

Figure 3. Solid-state vis−NIR spectra of chemically (− − −, original, ref 5; - - -, reproduced) and electrochemically polymerized (—) poly(2,3-dihexylthieno[3,4-*b*]pyrazine) (pC$_6$TP).

reduction process is stable for all species studied with the exception of pC$_1$TP. In this case, reduction causes an irreversible chemical change, resulting in a film of light yellow color. While the peak potentials seem to be somewhat dependent on side chain length, the onset of the oxidative and reduction processes does not change much throughout the series, with the difference corresponding to ∼0.70−0.80 eV. The polymer voltammograms remain stable and reproducible through at least 10 repetitive cycles.

Samples have also been successfully grown on ITO slides, thus allowing investigation of the solid-state optical properties of these polymers. As shown in Table 1, the onset of the low-energy absorptions corresponds to optical band gaps of 0.66−0.79 eV, agreeing with both the electrochemical measurements and the previously reported theoretical value.[4]

To make a fair comparison of the electropolymerized films to the previous chemically polymerized materials, pC$_6$TP was prepared via FeCl$_3$ polymerization followed by extensive purification via methanol washes and Soxhlet extraction with hydrazine. A comparison of the solid-state vis−NIR spectrum of pC$_6$TP originally reported by Pomerantz[5] and our spectra of both chemically and electrochemically polymerized pC$_6$TP is shown in Figure 3. The onsets of both of the FeCl$_3$ polymerized films are nearly identical and give similar band gap values (0.95 eV). The lowest energy absorption of the electropolymerized film, however, is drastically red-shifted, resulting in a much lower band gap.

The spectral differences are thought to be due to a combination of iron incorporation via the natural tridentate clefts of the polymer backbone (Figure 1) and overoxidation by the high oxidizing potential of FeCl$_3$ (∼2.1 V in CHCl$_3$). Computational modeling has shown that the binding of this cleft would have a size and geometry similar to those of terpyridine, and pK_a studies have shown that the basicity of the thieno[3,4-*b*]pyrazine nitrogens is equivalent to normal pyrazines.[9] While the basicity of the thiophene sulfur is typically very low, it has been shown that stable η^1-thiophene complexes can be obtained if the thiophene is incorporated into a multidentate ligand containing stronger binding sites.[12] Analysis of FeCl$_3$ polymerized pC$_6$TP samples by ICP-AAS indicated an iron concentration of ∼0.6 wt %, corresponding to ∼1 iron center for every 33 polymer repeat units. Although this seems a relatively small percentage, it must be remembered that the only additional ligands available during polymerization would be the original Cl$^-$ anions, and thus each iron center could be expected to occupy two tridentate clefts. Such a binding motif could be accomplished either by two different orthogonal polymers binding a single center or via backbiting in which a single chain loops back on itself to allow two binding sites to access a single metal center. Such a backbiting structure would result in significant backbone twisting, causing reduced conjugation and an increase in the band gap.

In conclusion, highly conjugated materials with very low band gaps can be produced via electropolymerization, providing steps are taken to limit overoxidation. In contrast, the metal-binding ability of pTPs makes polymerization via FeCl$_3$ problematic.

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Supporting Information Available: Experimental conditions for polymerizations, electrochemistry, spectroscopy, and computations. This material is available free of charge via the Internet at http://pubs.acs.org.

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