# Synthesis and Electronic Properties of Poly(2-phenylthieno[3,4-b]thiophene): A New Low Band Gap Polymer

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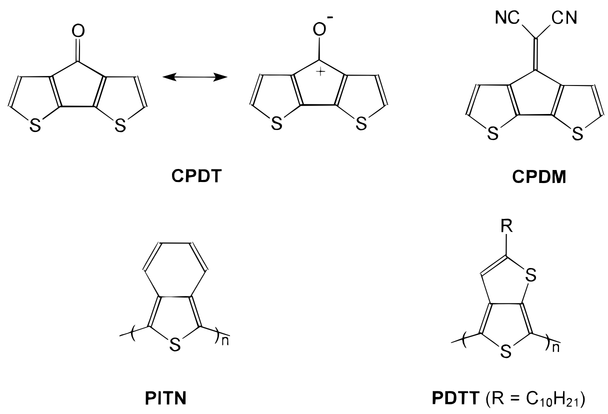

**Figure 1.** Low $E_{\text{gap}}$ monomers and polymers.

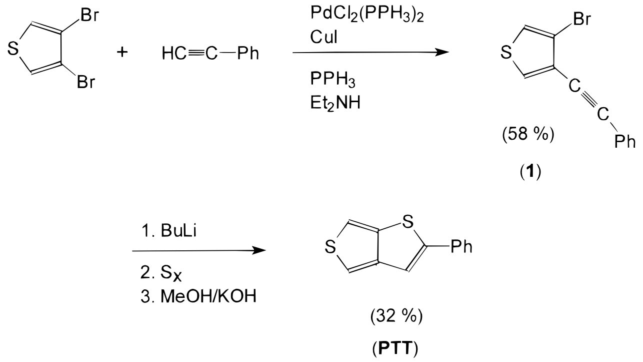

**Figure 2.** Synthetic scheme for PTT.

A major research thrust in the field of conducting polymers is the design and synthesis of low band gap ($E_{\text{gap}}$) materials, and several approaches have been recently reviewed by Roncali[1] and Pomerantz.[2] One of these employs the reduction of aromatic character,[3] which yields a smaller highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) separation. A model for this approach is based on the nonaromatic, 12$\pi$ electron system, 4H-cyclopenta[2,1-b:3,4-b′]dithiophen-4-yl cation, which is approximated by one of the resonance structures of cyclopenta[2,1-b:3,4-b′]dithiophen-4-one (CPDT) (Figure 1). The polymer derived from CPDT exhibited an $E_{\text{gap}}$ of ca. 1.2 eV.[4] The utility of this concept was extended by the synthesis of cyclopenta[2,1-b;3,4-b′]dithiophen-4-dicyanomethylene (CPDM), which incorporates the more strongly electron withdrawing moiety dicyanomethylene.[5] This derivative afforded a polymer with an $E_{\text{gap}}$ of ca. 0.8 eV and pointed the direction to further lowering of the HOMO−LUMO separation.

A second approach to lowering the $E_{\text{gap}}$ in polythiophenes relies on enhancing the quinoid character of the backbone and was first illustrated by polyisothianaphthene (PITN),[6] which exhibits an $E_{\text{gap}}$ of ca. 1 eV, i.e., much lower than that of the parent polythiophene, ca. 2 eV (Figure 1). Since only one of the aromatic rings of PITN can accommodate an aromatic sextet, the relative resonance energies of benzene (36 kcal/mol) and thiophene (29 kcal/mol) drive the aromaticity into the benzene ring, thus forcing the quinoid resonance form into the thiophene moiety. Alkyl,[7] alkoxy,[8] and halide[9] derivatives of PITN have also been reported, but a lower $E_{\text{gap}}$ has not been realized.

This concept has been extended to fused heteroaromatics with the synthesis of poly(2-decylthieno[3,4-b]-thiophene) (PDTT, R = $C_{10}H_{21}$), which displays an $E_{\text{gap}}$ of ca. 1.2 eV and a $\lambda_{\max}$ value of 1.68 eV[10] (Figure 1). Molecular orbital calculations on the parent compound, poly(thieno[3,4-b]thiophene) (R = H), predicted $\lambda_{\max}$ values of 1.54 and 1.63 eV for the aromatic and quinoid resonance forms,[11] respectively, and are in good agreement with the observed value for PDTT.

Recent work in our laboratories has focused on the structure/property relationship of poly(3-phenylthiophene)s. The extended conjugation of the phenyl group lowers the oxidation potential of the monomers compared to that of thiophene, and the redox properties of the resulting polymers can be varied by introducing substituents onto the phenyl ring.[12,13] We were interested in developing a synthetic methodology that combined the strategies of poly(3-phenylthiophene)s with PDTT to ultimately yield a series of substituted poly(2-phenylthieno[3,4-b]thiophene)s. The synthesis and electronic properties of the parent poly(2-phenylthieno[3,4-b]thiophene) (PTT) are reported in this paper.

PTT was synthesized in two steps, as shown in Figure 2. First phenylacetylene was coupled to 3,4-dibromothiophene using $PdCl_2(PPh_3)_2$ in the presence of CuI and $PPh_3$ with diethylamine as the solvent. Purification by column chromatography (silica gel with hexane as the eluent) afforded **1** as an oil in a 58% yield.[14] Next,

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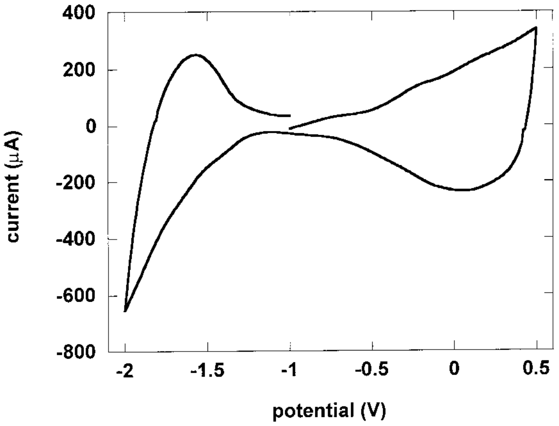

**Figure 3.** Cyclic voltammagrams of poly(PTT) deposited on Pt using $Me_4N\ CF_3SO_3$ (0.2 M in acetonitrile) as the supporting electrolyte, a carbon counter electrode, and a $Ag/Ag^+$ reference electrode at a scan rate of 50 mV/s.

**1** was converted to PTT in one-pot by treatment with butyllithium in diethyl ether at −78 °C, followed by the addition of sulfur. After being stirred for 1 h, the reaction was allowed to warm to ambient temperature and the diethyl ether was removed under reduced pressure. The reaction flask was then charged with a methanol solution of KOH and refluxed for 16 h. Purification by chromatography (silica gel with 1:3 chloroform:hexane as the eluent) afforded PTT in a 32% yield.[15]

Electrochemical polymerization by repetitive cyclic voltammetry was carried out from an acetonitrile solution of PTT (sat.) with tetramethylammonium triflate (0.2 M) as the supporting electrolyte using a Pt button working electrode (0.017 $cm^2$), a carbon counter electrode, and a $Ag/Ag^+$ reference electrode. The first scan (from −0.8 to +1.1 V at a scan rate of 20 mV/s) displayed an irreversible wave with a peak at 0.9 V, indicative of monomer oxidation followed by coupling. Subsequent scans exhibited an increase in the current with each scan, showing good polymerization and that the underlying polymer is conductive. The modified electrode was removed from the growth solution, rinsed with acetonitrile, and placed into fresh electrolyte for further experiments. Cyclic voltammetry on poly(PTT) showed broad redox waves for both the p- and n-doping cycles (Figure 3) but clearly illustrated the low band gap nature of this polymer. Estimation of the $E_{gap}$ from the onset of oxidation (−0.50 V) and from the onset of reduction (−1.35 V) yielded an approximate value of 0.85 eV, placing poly(PTT) among the lowest $E_{gap}$ polymers reported to date. Due to the broadness of the redox waves, this estimation is only approximate but was consistent with the optical $E_{gap}$ value obtained for the polymer (vide infra). Repeated cycling of this polymer in the p-doping region, 100 cycles from −1.0 to +0.5 V, showed no loss of charge capacity.

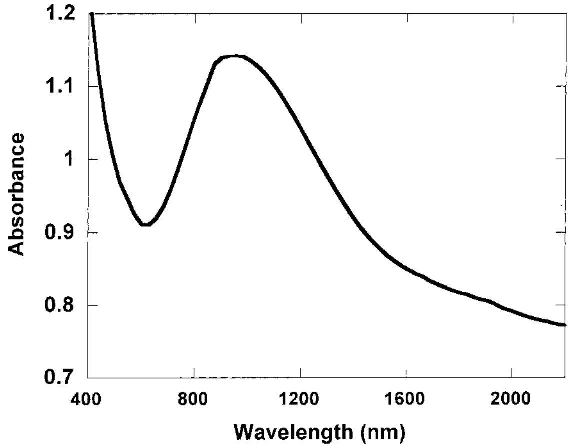

**Figure 4.** Absorption spectrum of poly(PTT) deposited on ITO-coated Mylar by repetitive CV using $Me_4N\ CF_3SO_3$ (0.2 M in acetonitrile) as the supporting electrolyte, a carbon counter electrode, and a $Ag/Ag^+$ reference.

Poly(PTT) was grown onto ITO-coated Mylar (Altair O, Southwall Technologies) for spectroanalysis by repetitive CV under similar conditions as the cyclic voltammetry experiments. The resulting spectrum is shown in Figure 4. Since the spectrum of the neutral film did not reach zero, tangents were drawn to the long wavelength and the baseline of the spectrum, with the intersection of these tangents taken as the $E_{gap}$. This intersection resulted in an approximate $E_{gap}$ of ca. 0.82 eV, in good agreement with the value obtained from cyclic voltammetry. The polymer exhibits a $\lambda_{max}$ value of 1.30 eV, which is significantly lower than both PDTT and that calculated for the parent compound poly(thieno[3,4-b]thiophene), attesting to the beneficial effect of the phenyl substituent in poly(PTT).

In summary, a new low band gap polymer, poly(2-phenylthieno[3,4-b]thiophene), has been synthesized. Its $E_{gap}$ of ca. 0.85 eV places it among the lowest reported to date. Subsequent research with this system will evaluate the effect that substituents on the phenyl moiety have on the electronic properties, and this material will be evaluated for electrochemical capacitor applications.

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(14) IR (neat): 3109, 2218, 1598, 1484, 1442, 1336, 985, 788, 754, 689 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.55 (q, $J = 3.5$ Hz, 2H), 7.49 (d, $J = 3.5$ Hz, 1H), 7.34 (t, $J = 3.5$ Hz, 3H), 7.25 (d, $J = 3.5$ Hz, 1H) (ppm). $^{13}C$ NMR (500 MHz, CDCl3): $\delta$ 131.65, 128.70, 128.53, 128.40, 128.38, 128.33, 124.52, 122.92, 122.72, 113.78, 92.16, 82.72 (ppm).

(15) Mp = 186 °C. MS: calculd 216.2 found 216. IR (KBr): 3099, 1479, 1436, 823, 754, 690 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.62 (d, $J = 8$ Hz, 2H), 7.40 (t, $J = 7$ Hz, 2H), 7.33 (t, $J = 8$ Hz, 1H), 7.30 (d, $J = 3$ Hz, 1H), 7.2 (d, $J = 3$ Hz, 1H), 7.18 (s, 1H) (ppm). $^{13}C$ NMR (500 MHz, CDCl3): $\delta$ 149.88, 147.87, 138.26, 134.76, 128.85, 128.45, 126.14, 112.37, 112.03, 110.67 (ppm).