# Preparation and Characterization of Conducting Polymers based on 1,3-Di(2-thienyl)benzo[*c*]thiophene

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An electroactive polymer with a bandgap of 1.7 eV has been obtained from the monomer 1,3-di(2-thienyl)benzo[*c*]thiophene.

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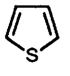
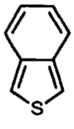
Copolymerization offers one of the more powerful ways of altering the physical properties of polymers. Polymers that possess segments of thiophene (**T**) and benzo[*c*]thiophene (**BT**) are expected to be particularly interesting since they would incorporate the steric and electronic characteristics of the parent homopolymers, polythiophene (**PT**) and polybenzo[*c*]thiophene (**PBT**).

**PT** has an aromatic ground state and adjacent rings are essentially coplanar.[1] **PBT** contains significant quinoid[2] character in its ground state and exhibits one of the lowest energy gaps ($E_{gap} \approx 1$ eV) for any conducting polymer.[3]

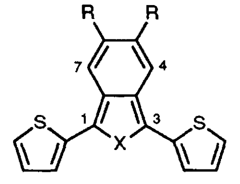
We report the synthesis and electrochemical behaviour of the monomer 1,3-di-(2-thienyl)benzo[*c*]thiophene (**TBT**, **1**, R = H, X = S) which yields a system that can formally be viewed



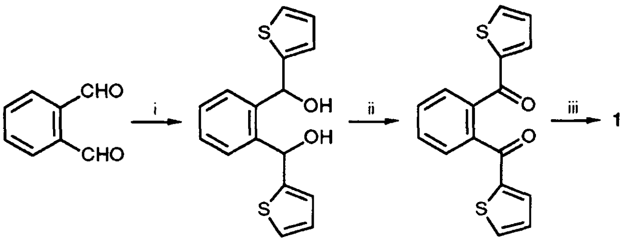
**T**



**BT**



**1** (**TBT**, R = H, X = S)



**Scheme 1** *Reagents and conditions*: i, 2-thienylmagnesium bromide, tetrahydrofuran (THF); ii, $CrO_3$, $H_2SO_4$, acetone; iii, $P_2S_5$, $NaHCO_3$, THF

as a copolymer of thiophene and benzo[*c*]thiophene. The spectroelectrochemical and electrical properties of this polymer are also described.

Previous theoretical calculations[4] on semiconductor superlattices containing the **T** and **BT** units predict a decrease in the energy gap from the polythiophene system ($E_{gap} \approx 2.1$ eV[5]) upon addition of benzo[*c*]thiophene units. Qualitative considerations[6] suggest that the effect will be proportional to the length of the **BT** block with the energy gap of the copolymer lying between the limits defined by the homopolymers ($E_{gap}{}^{PT} > E_{gap}{}^{PTBT} > E_{gap}{}^{PBT}$). One effect that is expected from the incorporation of thiophene units is the partial relief of steric interactions along the backbone, since these are essentially eliminated between adjacent thiophene units[1] and reduced for **BT–T** dyads. Molecular modelling calculations[7] (PRDDO) have shown that steric interactions between the sulfur and the hydrogens at the 4,7 positions in **BT** dimers would drive the adjacent rings out of coplanarity if they are in their aromatic form, achieving an energy minimum at 59°. We have performed MM2 calculations on this dimer (Chem3D Plus), arriving at a somewhat smaller dihedral angle, 43°, between the benzo[*c*]thiophene rings. The same routine applied to the monomer **TBT** predicts an even smaller dihedral angle, 36°, between adjacent rings. A further advantage of **TBT** is the expected increase in the monomer's stability since substituents in the 1,3-positions of the benzo[*c*]-fused heterocycles are known to stabilize these systems.[8]

Compound **1** was prepared in about 32% overall yield in a three-step synthesis (Scheme 1). Thus benzene-1,2-dicarbaldehyde was treated with 2-thienylmagnesium bromide (2 mol equiv.) to give the intermediate diol[9] which was oxidized to 1,2-di-(2-thenoyl)benzene and subsequently cyclized[10] with $P_2S_5$† to afford orange crystals of **1**, m.p. 100–102 °C.

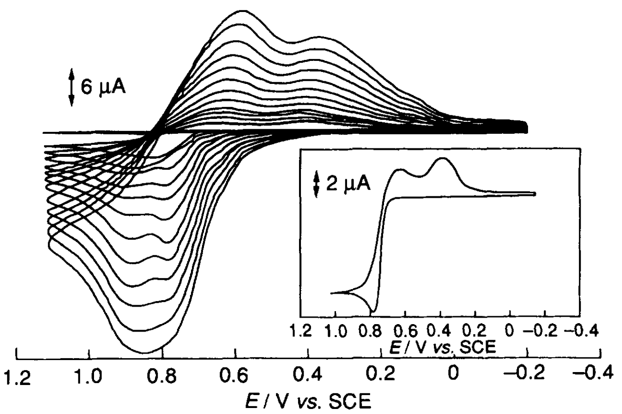


**Fig. 1** Repetitive cyclic voltammetry (100 mV $s^{-1}$) of **TBT** on Pt. Insert: first scan.

Repetitive cyclic voltammetry‡ of **1** shows a peak anodic potential, $E_{p,a}$, of 0.800 V *vs.* standard calomel electrode (SCE) on the first scan (Fig. 1, insert). This is >200 mV lower than the $E_{p,a}$ for 2,2′;5′,2″-terthienyl[11] and illustrates the pronounced effect one fused ring can have on the overall system. Upon further cycling, a second anodic wave appears at lower potentials characteristic of the electroactive polymer depositing on the surface of the electrode.

A polymer film grown onto an indium tin oxide (ITO) coated glass electrode was used in spectroelectrochemical measurements§ that allowed an estimation of the neutral polymer's energy gap. Fig. 2 displays the difference spectra as a function of doping. Two transitions appear at lower energies than the π–π* absorption of the neutral polymer ($\lambda_{max}$ 534 nm) for intermediate doping levels. The energy gap determined from these spectra at light doping levels was 1.7 eV. This experimental value fortuitously agrees with the compositionally adjusted linear combination of the energy gaps of the components (*i.e.*, 33% $E_{gap}{}^{PBT}$ + 67% $E_{gap}{}^{PT}$ = 1.67 eV).

The two-probe dc electrical conductivity[12] of compressed pellets of $I_2$-doped **PTBT** is $1.3 \pm 0.3 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$, comparable to that of similarly doped **PBT**.[3]

The dimethoxy derivative (**1**, R = OMe, X = S) has an $E_{p,a}$ of 0.9 V *vs.* SCE and also forms electroactive polymers. We have also prepared the isobenzofuran (**1**, X = O) and *N*-methylated isoindole (**1**, X = NMe) analogues[13] but these are considerably less stable than their sulfur counterpart and have resisted electrochemical polymerization in our hands.

In conclusion, an electroactive polymer incorporating a 2:1 ratio of thiophene and benzo[*c*]thiophene units has been prepared and has an energy gap that reflects this composition.

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† Satisfactory spectral characteristics were obtained. UV-VIS [hexane; $\lambda_{max}$(log ε): 427 nm (4.81) Analysis: Calc. (found): C, 64.4% (64.4); H, 3.4% (3.4).

‡ Cyclic voltammetry experiments were done using an EG & G PARC Model 173 potentiostat coupled to an EG & G PARC Model 175 universal programmer and a Nicolet 2090 digital oscilloscope interfaced to a microcomputer. The data were analysed using commercially available software (Waveform Basic, Blue Feather Software, Inc.). A two-compartment, three-electrode system was used, with a Pt disc (*ca.* 100 µm diam) working electrode, a graphite rod as the counter electrode and a $Ag/Ag^+$ (0.25 mol $dm^{-3}$ $LiBF_4$–acetonitrile) reference electrode. Experiments used 5 mmol $dm^{-3}$ solution of the monomer in 0.25 mol $dm^{-3}$ $LiBF_4$ in anhydrous acetonitrile.

§ Spectroelectrochemical measurements were made using a Perkin-Elmer Lambda 9 UV-VIS-NIR spectrophotometer interfaced to a microcomputer. Potentials were controlled by an EG & G PARC Model 179 potentiostat. The data were analysed using Spectra-Calc (Galactic Ind. Corp.). Polymer films were grown onto ITO-coated glass electrodes from 5 mmol $dm^{-3}$ monomer solutions in acetonitrile containing 0.25 mol $dm^{-3}$ $LiBF_4$. The films were rinsed with acetonitrile prior to being sealed in a cell consisting of aluminium counter and reference electrodes and the polymer film working electrode. Fresh acetonitrile–0.25 mol $dm^{-3}$ $LiBF_4$ was used as solvent–electrolyte system and all manipulations up to this point were conducted in a helium-filled glove box.

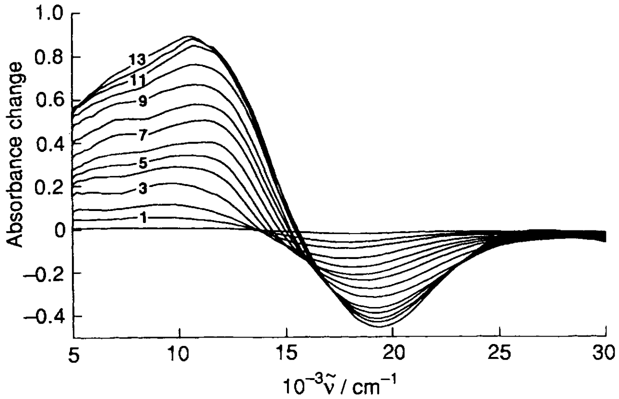

**Fig. 2** Absorption spectra for **PTBT** as a function of applied potential plotted as the difference from neutral polymer ($V_{\mathrm{appl}}$ = 0.0 V). The curves are for applied potentials ranging from 0.2 V (curve 1) to 0.8 V (curve 13) in 50 mV steps.

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