

Poly(dithieno[3,4-*b*:3',4'-*d*]thiophene): a New Transparent Conducting Polymer

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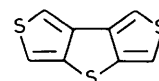
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Electropolymerization of dithieno[3,4-*b*:3',4'-*d*]thiophene leads to a new transparent conducting polymer with electrical conductivity of 1.0 S cm⁻¹, while the reduced species is highly opaque in the visible spectral range owing to the strong $\pi \rightarrow \pi^*$ electronic absorption at 590 nm.

All the conducting polymers based on heteroaromatic monomer units¹ are highly absorbing in the oxidized (conducting) and in the reduced (insulating) state apart from poly(isothianaphthene).² Here we report on the preparation and the characterization of a new transparent conducting polymer based on the monomer unit of dithieno[3,4-*b*:3',4'-*d*]thiophene (1).³

The electropolymerization was performed in a two-compartment cell at room temperature with platinum electrodes at

a constant current of 1 mA cm⁻². The monomer was dissolved (0.03 M) in acetonitrile with LiClO₄ as electrolyte (0.1 M); the



(1)

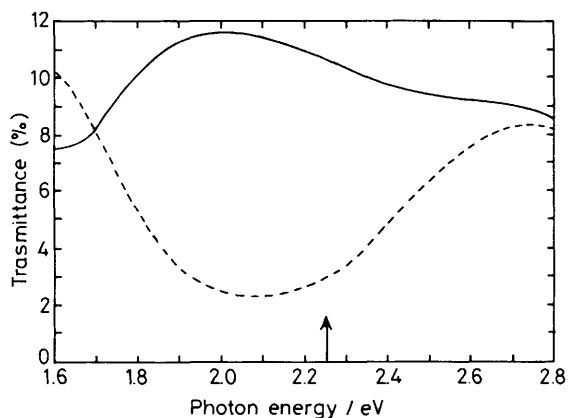


Figure 1. *In situ* electronic spectra of the poly(dithieno[3,4-*b*:3',4'-*d*]thiophene) deposited on ITO glass. The dashed line represents the reduced (insulating) form and the full line represents the reversibly oxidized (conducting) form. The maximum wavelength sensitivity of the eye at 550 nm (green) is indicated by the arrow.

oxidation potential remained constant at 1.04 V vs. standard calomel electrode (S.C.E.) during the electropolymerization.

Elemental chemical analysis shows that the degree of doping of the as-grown oxidized polymer was of one ClO_4^- ion every three monomer units.

However, the i.r. absorption of the reduced polymer, electropolymerized on silicon substrates, is rather similar to that of poly(dithieno[3,2-*b*:2',3'-*d*]thiophene).⁴ The lowest $\pi \rightarrow \pi^*$ electronic absorption, whose peak is at 590 nm in the neutral polymer (*c.f.* 460 nm in the parent polythiophene),⁴ implies an increased degree of π -electron delocalization.

Electrical conductivity measurements were performed on a 'test pattern' made of four gold electrodes, separated by a 33 μm gap, deposited by photolithographic techniques on a silicon oxide substrate.⁵ The polymer was electrochemically grown on the 'test pattern' until it filled the gap between the gold electrodes. Electrical conductivity was measured by the standard four points technique giving a specific conductivity of 1.0 S cm^{-1} .

A strong electrochromic effect is observed in the visible spectral range by reversibly doping and undoping the as-grown polymer on indium tin oxide (ITO) glass substrates in propylene carbonate and LiClO_4 . While the reduced (insulating) polymer is opaque, the oxidized (conducting) polymer is colourless and highly transparent. The overall effect is shown in Figure 1 which shows the *in situ* spectra of the oxidized and the reduced forms of the same film (about 1 μm thick) of polymer in the visible spectral range; the two forms may be reversibly switched from one to the other by the application of an appropriate voltage. It should be noted that the transmittance changes by an order of magnitude at the wavelength of the maximum response of the eye at 2.25 eV (550 nm).

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