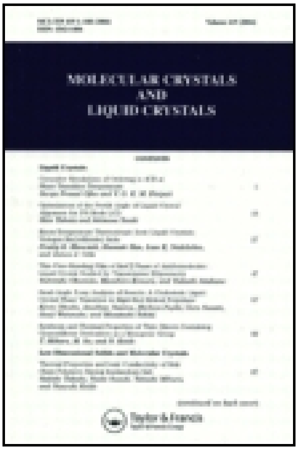

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Optical and Electrical Characterization of Polymers Obtained by Electro-Oxidation of [1] Benzothieno [3,2-b] Indole Derivatives

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OPTICAL AND ELECTRICAL CHARACTERIZATION OF POLYMERS OBTAINED BY ELECTRO-OXIDATION OF [1] BENZOTHIENO [3,2-b] INDOLE DERIVATIVES

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Abstract New polymers have been produced by electrochemical oxidation of monomers derived from [1] benzothieno [3,2-b] indole. Acid-base equilibria involving heterocyclic nitrogen and protons produced by electrolysis have been detected. The spectra of polymer films deposited on ITO electrodes show bands in the visible and NIR regions. The electrical conductivity ranges from 10^{-6} to 10^{-4} S cm^{-1} , depending on the substance and the preparation conditions, and increases with the temperature.

Keywords : [1] benzothieno [3,2-b] indole, electro-oxidation, electropolymerization, electrical conductivity, absorption spectra.

INTRODUCTION

The preparation of polymeric materials by electrochemical oxidation of [1] benzothieno [3,2-b] indole (TNI) and some of its derivatives has been the object of previous papers.[1–4]

Keeping in mind the interesting electronic features of TNI, it seemed important to characterize from this point of view the polymers so obtained, the electrical properties of which appeared, from a preliminary approach, to be worthy of attention.

The results of this study are presented and discussed in this paper. In particular, the conditions of the electrochemical preparation and their changes during the electrolytic process have been taken into consideration in order to better understand the electrical behaviour of the oxidized polymers.

EXPERIMENTAL

Semiconducting polymers have been synthesized by electrochemical oxidation of the following monomers: [1] benzothieno [3,2-b] indole (TNI) (Ferrania S.p.A.), N-allyl-TNI (ATNI) (home made), N-vinyl-TNI (VTNI) (home made) and 7-methyl-TNI (MTNI) (home made).

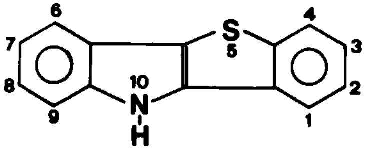

FIGURE 1 TNI

The syntheses of the polymers by oxidation of these monomers on a Pt electrode in methylene chloride (Merck p.a.), with 0.1 M tetrabutylammonium perchlorate (TBAP) (Fluka) as a supporting electrolyte, have been reported elsewhere.

The electrical conductivities of the oxidized materials, obtained as dark powders, have been measured on compressed pellets (2 tons), having a diameter of 0.5 cm and with a thickness between 150 and 700 μm, using a two probe method. Platinum or gold discs were used as electrodes. A Keithley 230 and a Keithley 195A were used as a voltage source and a current meter respectively. The measurements have been performed at a pressure of 10^{-4} Pa in an evacuable thermostatable cell. Transient measurements were done by using the apparatus shown in ref. 5.

The electronic spectra of the oxidized polymers deposited on ITO (indium tin oxide) electrodes have been recorded by a Perkin Elmer Lambda 9 UV-VIS-NIR spectrophotometer.

RESULTS AND DISCUSSION

[1] Benzothieno [3,2-b] indole (TNI) and some of its derivatives have been electrochemically polymerized in methylene chloride at different potentials depending on the molecular structure of the monomer.[1-4]

The synthesis of these oxidized oligomers or polymers by anodic electrolysis involves a progressive growth of reaction products, associated with acid-base equilibria, due to hydrogen ions produced by the coupling of radical cations on the hetercyclic nitrogen. These equilibria are rate determining steps for electro-oxidation processes of condensed species. As a consequence, by changing monomer concentration and time of electrolysis, in spite of the substantial uniformity of the elemental analyses, it is possible to obtain products for a given monomer having different conformations as well as different molecular weights and consequently different electrical properties.

Another important parameter is the voltage applied to the electrode. A higher content of supporting electrolyte (TBAP) has been found in the electrolysis products obtained at relatively high anodic potential ($E_a >$ + 1.2V) with respect to experiments performed at less anodic potentials.

The electrical conductivity equilibrium values of the oxidized polymers of TNI and derivatives are reported in Table I.

TABLE I Conductivity equilibrium values of oxidized polymers.

Polymer	Electrical conductivity (S cm^{-1})	Initial monomer concentration (M)	Voltage applied vs SCE (V)
poly(TNI)	8.3×10^{-6}	5×10^{-3}	2.0
poly(N-allyl-TNI)	1.2×10^{-6}	5×10^{-3}	2.0
poly(N-vinyl-TNI)	2.0×10^{-5}	5×10^{-3}	1.2
poly(7-methyl-TNI)	2.8×10^{-4}	5×10^{-3}	1.2

These values, however, are strongly influenced by the preparation conditions, in particular by the monomer concentration, the electrode potential, and the acidity changes during the electrolytic process.

In the case of TNI, for instance, the conductivity of the polymeric material obtained during the first time interval of electrolysis (0-4 hours) is about 20 times higher than that of the polymer produced in a later time interval of the process (8-12 hours), as evidenced in Table II.

This is probably due to the decrease of monomer concentration and the increase of the acidity of the medium during the electrolysis.

Another feature of these polymers is the decrease of the electrical conductivity observed immediately after the application of the electric field. A steady conductivity value is generally obtained after some minutes. In the figures 2 and 3 the behaviours of poly(TNI) and poly (VTNI) are reported for different values of applied voltage.

The electrical conductivity increases with increasing temperature, showing an activated behaviour, as shown in Figure 4, where the Arrhenius plot for poly(VTNI) is reported. For this polymer the activation energy of the process is 0.7 eV, as expected in the case of semiconducting materials.

Analogous behaviour is shown by the other polymers.

TABLE II Specific conductivity values of poly(TNI) samples obtained, as a non-coherent film on a Pt electrode or as a powder in the electrolytic cell, during the electrolysis of 0.0597M TNI in methylene chloride (0.1M TBAP), anodic potential: 1.2-1.4 V (vs SCE).

Sample	Electrolysis time (hours)	Specific conductivity ($S\ cm^{-1}$)
Film	0 - 4	2.43×10^{-3}
Powder	0 - 4	1.42×10^{-3}
Film	4 - 8	4.55×10^{-4}
Powder	4 - 8	7.40×10^{-4}
Film	8 - 12	6.58×10^{-5}
Powder	8 - 12	1.00×10^{-4}

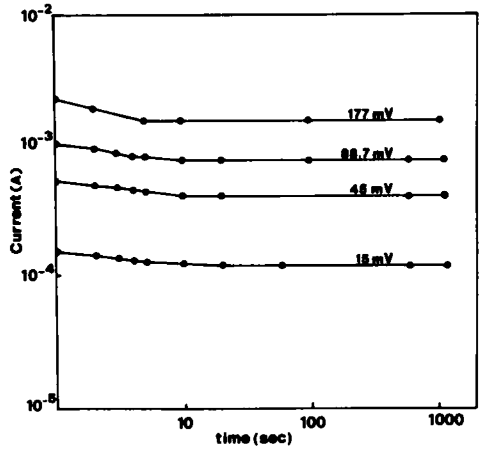

FIGURE 2 Current vs time logarithmic plot at different applied voltages for poly(TNI).

The electronic spectra of the oxidized polymers are characterized by two intense absorption bands in the visible region and one very broad band in the NIR region. The spectrum of a film of poly(VTNI), deposited onto an ITO electrode from a solution of VTNI in methylene chloride, is shown in Figure 5. In this spectrum the absorbance of ITO has been subtracted. Further studies are in progress in order to define any correlation between the activation energy of the dark conductivity and the energy of the absorption bands of the oxidized polymers.

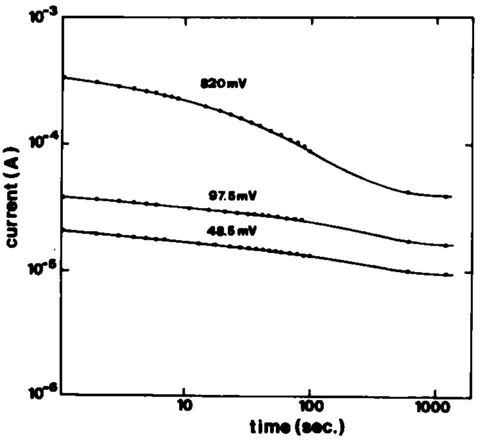

FIGURE 3 Current vs time logarithmic plot at different applied voltages for poly(VTNI).[5]

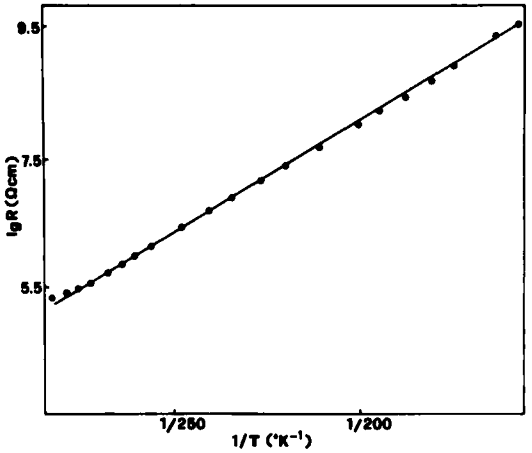

FIGURE 4 Arrhenius plot for electrical conductivity of poly(VTNI) from which an activation energy of 0.7 eV has been calculated.

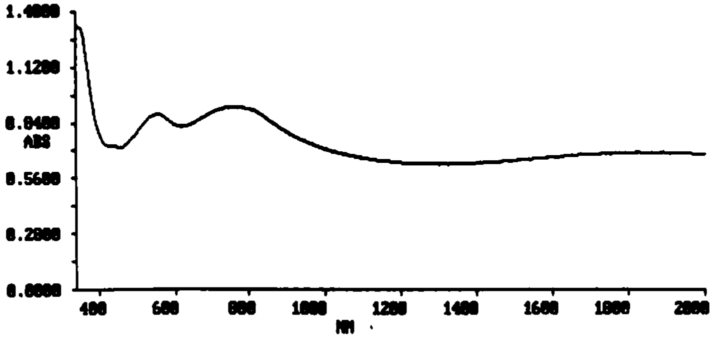

FIGURE 5 Electronic spectrum of a film of poly(VTNI) deposited on ITO from VTNI in methylene chloride by flowing 50 millicoulombs.

CONCLUSIONS

The polymers obtained by anodic electrolysis of TNI and some of its derivatives show electrical conductivity ranging roughly from 10^{-6} to 10^{-4} S cm^{-1}.

It should be remarked that, for a given monomer, the specific conductivity of the corresponding oxidized polymer decreases during the electrolytic process. Moreover, an activated behaviour for the conductivity has been observed.

In conclusion, when dealing with the electrical conductivity of oxidized polymer obtained by electrochemical methods, the following factors must be taken into consideration:

1 - the preparation method and the eventual changes in the medium during the preparation itself (if possible, buffered solutions should be employed);

2 - the nature of the polymer : powder or film;

3 - the method used for the electrical measurement; transient measurements outline electrical conductivity changes in the time range of more than one order of magnitude, caused by modifications of the electrodes and depending on the electric field supplied to the sample during the measurements.

Frequency response analyses for the identification of the electrochemical processes active at the sample-electrode interfaces are in progress. By these measurements it should be possible to distinguish between electronic and ionic conductivity and to produce evidence of the faradic currents at the electrode-sample interfaces.

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