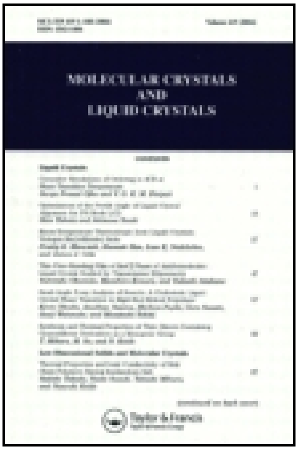

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Photoelectrochemistry of Poly (2, 5-Thienylene)-Coated Electrodes

Gianni Zotti [a], Gilberto Schiavon [a] & Giuliano Mengoli [a]
[a] 1st.Polarografia C.N.R., 35100, Padova, (Italy)

Version of record first published: 20 Apr 2011.

To cite this article: Gianni Zotti , Gilberto Schiavon & Giuliano Mengoli (1985): Photoelectrochemistry of Poly (2, 5-Thienylene)-Coated Electrodes, Molecular Crystals and Liquid Crystals, 121:1-4, 341-344

To link to this article: http://dx.doi.org/10.1080/00268948508074887

Mol. Cryst. Liq. Cryst. 1985, Vol. 121, pp. 341-344
0026-8941/85/1214-0341/$10.00/0

Printed in the United States of America

PHOTOELECTROCHEMISTRY OF POLY(2,5-THIENYLENE)-COATED ELECTRODES

GIANNI ZOTTI, GILBERTO SCHIAVON and GIULIANO MENGOLI
Ist.Polarografia C.N.R., 35100 Padova (Italy)

Abstract The photoelectrochemical behaviour of poly(2,5-thienylene)(PT) films electrodeposited onto platinum electrodes was studied in aqueous solution. PT displays a p-type semiconductor character (positive photovoltages and cathodic photocurrents) with high quantum yields (up to ca.8%) and good stability even under high power illumination. The dependence of photoresponses on bias voltage, illumination intensity, film thickness and redox potentials of various redox couples was investigated.

INTRODUCTION

The unusual conducting properties displayed by coniugated polymers typified by trans-polyacetylene (PA) prompted investigation on the semiconducting properties of these materials and on their possible utilization as solar absorbing materials in thin-film photovoltaic devices[1]. Poly(2,5-thienylene)(polythiophene,PT) appears to be a good alternative to PA because of its higher chemical stability and very easy electrochemical preparation[2,3], although its estimated E_g value is higher (2.0 vs. 1.5 eV for PA).

The photovoltaic properties of PT which, from a very recent solid state study[4], appear to be quite promising, were here investigated in a liquid-junction arrangement consisting of thin films (20-1000 nm) electrodeposited on platinum[3] and immersed in aqueous solution containing appropriate redox couples.

RESULTS AND DISCUSSION

PT films, when illuminated with white light (ca.100 mWcm^{-2}) in O_2 saturated 0.1M LiOH solution, display reductive photocurrents (ca. 0.24 mAcm^{-2} at -1.0 V vs.SCE) with applied potentials in the range 0.2 ÷ -1.0 V (fig.1, for a 200 nm film). The photocurrents (i_{ph}) do not show time-dependent phenomena, are very stable and are superimposed on a negligible dark current (ca.5 μAcm^{-2} at -1.0 V). Photovoltages of ca.+0.3 V ($V_{light}-V_{dark}$; 0.55 V as $V_{light}-E_{redox}$, see table) are shown (fig.2). Their dependence on incident light power (W) is logarithmic in the range 0.5-50 mWcm^{-2}.

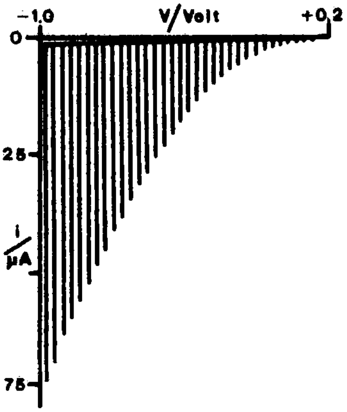

FIGURE 1

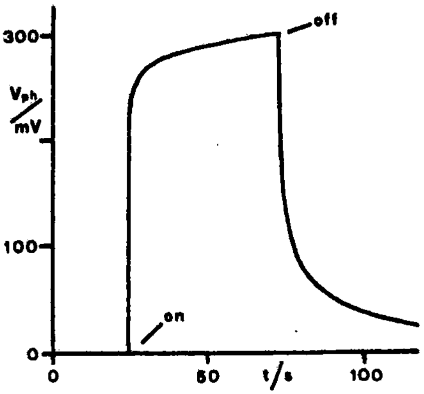

FIGURE 2

The photocurrent, whose action spectrum matches the absorption spectrum of PT (full and dashed curves respectively in fig.3), increases with film thickness (fig.4) up to a value which is constant in the 100-1000 nm range. A maximum monochromatic quantum yield (Φ) of 8% is achieved at -1.0 V. Also, a linear dependence of i_{ph} on W is observed in the range 0.5-50 mWcm^{-2}. The relatively high Φ values cannot be ascribed to O_2 doping, though O_2 appears to act as a trapping agent. In fact, using other depolarizers under N_2, very similar i_{ph}/V curves, with different onset potentials (V_{on}, see table) were recorded. The photovoltages U_{ph}, expressed as differences between the

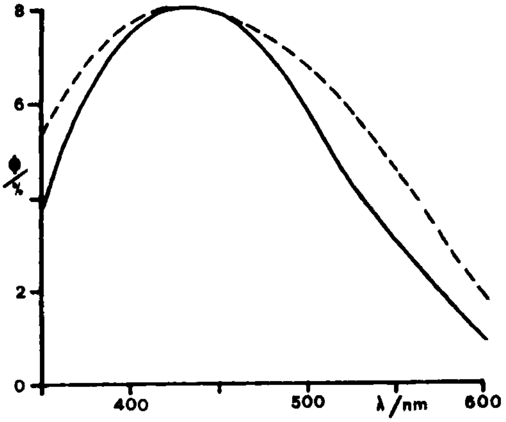

FIGURE 3

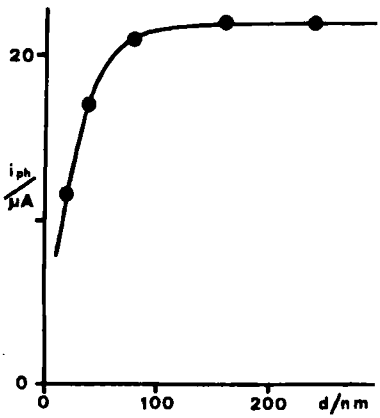

FIGURE 4

voltage measured under maximum illumination at the PT electrode and the potential of the redox couple (see table), are linearly related to E_{redox}[5], allowing extrapolation of a zero-photovoltage potential of 0.25 V. Couples with $E_{redox} > 0.25$ V, such as $Fe^{3+/2+}$ and I_2/I^-, do not show photovoltaic effects.

TABLE Photocurrent onset potentials (V_{on}) and photovoltages (U_{ph}, see text) for PT with various redox couples.

couple	E_{redox}/V vs.SCE	V_{on}/V vs.SCE	U_{ph}/V
$MV^{2+}/MV^{+\cdot}$	-0.66	-0.10	0.86
AQD/H_2AQD[a]	-0.60	0.30	0.85
O_2/HO_2^-	-0.30	0.20	0.55
Q/H_2Q	0.05	-	0.20
$Fe(CN)_6^{3-/4-}$	0.18	0.05	0.03
I_2/I^-[b]	0.28	-	0.00

(a) AQD=2,6-anthraquinone disulphonate; Q=benzoquinone.

(b) 0.1M $LiClO_4$.

The results can be rationalized if PT is viewed as a p-type semiconductor with an optical bandgap of 2.0 eV and absorption coefficient $> 10^5$ cm^{-1} for photon energies $>$ 2.0 eV[6]; in this view, the above reported value of 0.25 V for the zero-photovoltage potential may be assumed as the "flatband potential" of the system. The dependence of the photocurrent on film thickness indicates that the charge carriers are generated and separated over most of the absorption lenght without appreciable follow-up recombination. However, the low quantum yields point to the low efficiency of the carrier generation step. As may be seen from the exponential form of the i_{ph}/V relationship, the applied electric field assists in carrier generation from the initially formed or trapped excitons.

REFERENCES

1. J.Tsukamoto, H.Ohigashi, K.Matsumura and A.Takahashi, Synt.Met., 4, 177 (1982); B.R.Weinberger, M.Akhtar and S.C.Gau, ibid., 4, 187 (1982); J.Kanicki,S.Bouè and E. Vander Donckt, Mol.Cryst. Liq.Cryst., 83, 319 (1983).
2. G.Tourillon and F.Garnier, J.Electroanal.Chem., 135, 173 (1982); K.Kaneto,K.Yoshino and Y.Inuishi, Jap.J.Appl.Phys.,21,L567(1982).
3. R.J.Waltman, J.Bargon and A.F.Diaz,J.Phys.Chem., 87, 1459 (1983).
4. S.Glenis, G.Horowitz, G.Tourillon and F.Garnier; Thin Solid Films, 111, 93 (1984).
5. G.A.Chamberlain and R.E.Malpas, Faraday Discuss.Chem.Soc., 70, 299 (1980).
6. K.Kaneto,K.Yoshino and Y.Ynuishi, Solid State Comm.,46,389 (1983).