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Electrochemical behaviour of poly(thiophene–benzoquinone) films

James Grimshaw and Sarath D. Perera

Department of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG (Northern Ireland)

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ABSTRACT

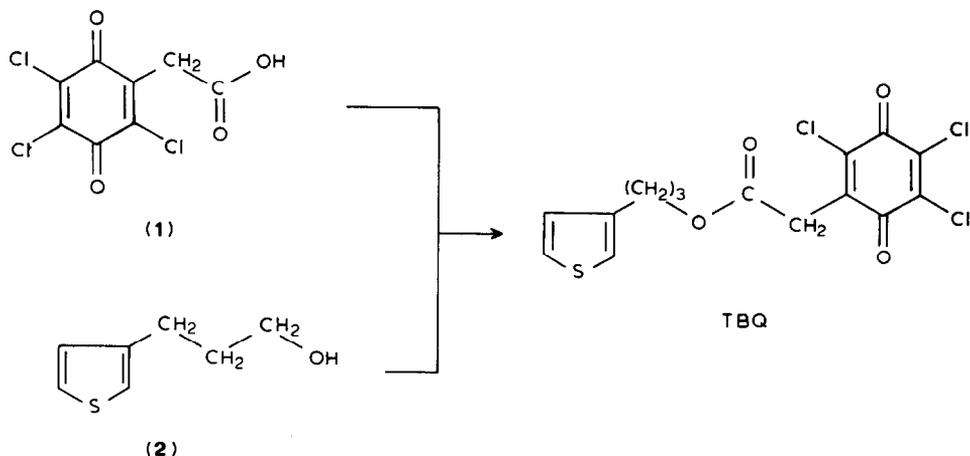
Poly(thiophene–benzoquinone) films were prepared on platinum spheres by electropolymerization of the monomer 1-[3-(3-thienyl)propyl]2,4,5-trichloro-3,6-dioxo-1,4-cyclohexadiene-1-acetate (TBQ) in acetonitrile. These films were studied mainly by cyclic voltammetry and chronoamperometry in acetonitrile containing tetraalkylammonium salts as the supporting electrolyte.

INTRODUCTION

Thiophene and β -substituted thiophenes can be polymerized by electrochemical oxidation at a platinum electrode from solutions in acetonitrile containing a trace of water [1–3]. Elemental analysis of the resulting polymers showed that one in every four thiophene moieties is positively charged and the film contains counter ions derived from the supporting electrolyte used [1,2]. In the absence of oxygen, polythiophene can be cycled repeatedly between the conducting oxidized and the non-conducting neutral state with little decomposition of the film [4]. This process is accompanied by a reversible colour change. Oxidized poly(3-methylthiophene) shows excellent conductivity up to 2000 S cm^{-1} [5].

Neutral polythiophene can be reduced at potentials below $-1.5 \text{ V vs. Ag/AgCl}$ to a negatively charged polymer that is cation doped [6]. This reversible process is accompanied by a colour change from red in the neutral state to green in the reduced state [6].

In the course of our work with N-substituted polypyrrole modified electrodes [7,8], we wanted to prepare a modified electrode with a redox group operating around 0 V vs. SSCE in order to extend the sequence of electroactive polypyrroles. 2,4,5-Trichloro-3,6-dioxo-1,4-cyclohexadiene-1-acetic acid (**1**) [9] has a E° value close to -0.1 V vs. SSCE . Attempts to prepare an ester between (**1**) and 1-(3-hydroxypropyl)pyrrole were unsuccessful and resulted in only a black solution, prob-



Scheme 1.

ably due to formation of the charge transfer complex. As an alternative we decided to prepare a thiophene derivative of (1) according to Scheme 1.

To our knowledge polythiophene films containing electroactive groups are not known in the literature. Even this trichlorobenzoquinone moiety has not previously been used as an electroactive group in modified electrodes.

EXPERIMENTAL

Preparation of monomer

3-(3-Thienyl)propionic acid [10] was reduced to 3-(3-thienyl)propanol (2) [11] in 76% yield with lithium aluminium hydride in THF. The alcohol was obtained as a colourless oil, b.p. 62–63°C/0.15 Torr (Lit. [11], b.p. 133°C/10 Torr). 2,4,5-Trichloro-3,6-dioxo-1,4-cyclohexadiene-1-acetic acid (1) was obtained as yellow needles, m.p. 158–161°C (Lit. [9], m.p. 168–171°C).

1-[3-(3-Thienyl)propyl]2,4,5-trichloro-3,6-dioxo-1,4-cyclohexadiene-1-acetate (TBQ)

3-(3-Thienyl)propanol (0.32 g, 2.2 mmol), compound (1) (0.54 g, 2.0 mmol) and 4-toluenesulphonic acid (30 mg) were refluxed in dry benzene for 18 h, using a Dean-Stark apparatus for azeotropic removal of the water formed. After cooling, the solution was filtered and solvent removed. The residue was chromatographed on silica using ether-light petroleum (b.p. 40–60°C) (1 : 1) to yield the ester (TBQ) as a yellow oil (0.42 g, 53%) which was crystallised from methanol + dichloromethane as yellow cubes, m.p. 57–58°C. Found: C, 45.4; H, 2.8. $C_{15}H_{11}O_4Cl_3S$ requires C, 45.7; H, 2.8%. 1H NMR ($CDCl_3$, TMS) δ : 1.98 (2 H, m), 2.69 (2 H, t, $J = 7.5$ Hz, Th- $\underline{CH_2}$), 3.78 (2 H, s, $\underline{CH_2CO}$), 4.15 (2 H, t, $J = 6.5$ Hz, O- $\underline{CH_2}$), 6.94 (2 H, m,

ThH), 7.25 (1 H, m, ThH). Mass spectrum m/e (%): 396 (M^{4+} , 1.3), 394 (M^{2+} , 3.6), 392 (M^+ , 3.2), 124 (100), 123 (62) and 97 (66). Ir (KBr) ν_{\max} : 1730, 1680, 1671 cm^{-1} .

Film preparation

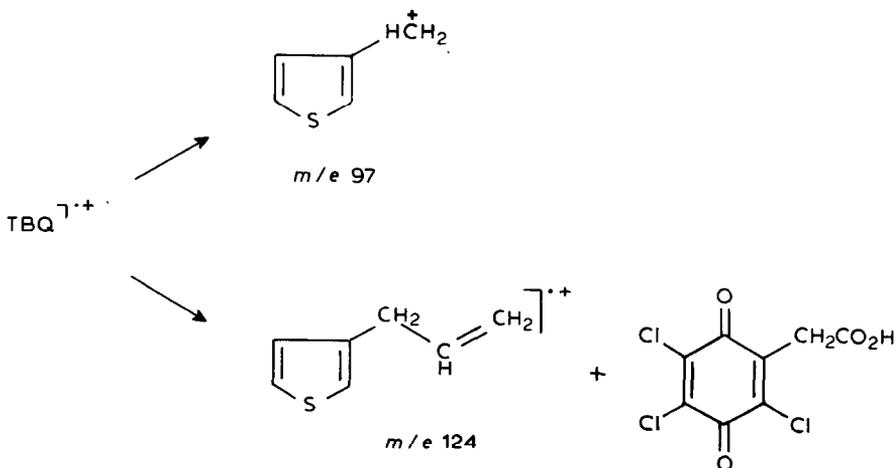
All electrochemical studies were performed in a three-electrode, one-compartment cell. The working electrode was a Pt sphere (diameter 1–2 mm), sealed in a glass mounting. A Pt wire was used as the counter electrode. All the potentials are quoted with respect to a saturated sodium chloride calomel electrode (SSCE). The solutions were degassed by bubbling (10–20 min) dry oxygen-free nitrogen. The acetonitrile (Aldrich, HPLC grade) was dried over calcium hydride. Tetrapropyl- and tetramethylammonium tetrafluoroborate were dried under vacuum at 100–120 °C for two days.

Films of poly(TBQ) were obtained on Pt spheres by controlled potential oxidation of 10 mM solutions of TBQ in acetonitrile containing either 0.1 M tetrapropyl or saturated tetramethylammonium tetrafluoroborate at 1.7 V vs. SSCE. The oxidised form of thick films is black in colour, the neutral form is red. Coloured soluble products were also formed during the polymerization process. Thus the amount of polymer deposited is not directly related to the amount of current passed. The formation of some soluble products made it difficult to achieve polymerization by repetitive cyclic voltammetry. The coated Pt spheres were transferred to a fresh solution of electrolyte in acetonitrile and were examined by cyclic voltammetry (CV) and chronoamperometry (CA).

RESULTS AND DISCUSSION

Behaviour of TBQ and poly(TBQ)

The structure of the monomer is confirmed by the spectral data. The mass spectrum is interpreted according to the bond fragmentations shown in Scheme 2.



Scheme 2. Mass spectral fragmentation of TBQ.

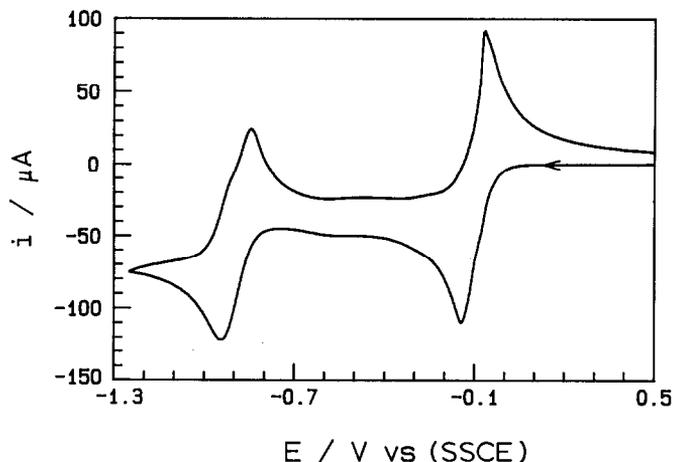


Fig. 1. Cyclic voltammogram of TBQ (2 mM) at a Pt electrode (area = 0.118 cm²) in acetonitrile containing 0.1 M tetrapropylammonium tetrafluoroborate. $\nu = 0.08 \text{ V s}^{-1}$.

Cyclic voltammetry of TBQ in acetonitrile containing 0.1 M tetrapropylammonium fluoroborate between +0.5 and -1.3 V vs. SSCE showed two reversible redox couples due to TBQ/TBQ^{•-} and TBQ^{•-}/TBQ²⁻ with $E^\circ = -0.098 \text{ V}$ and -0.91 V vs. SSCE respectively (Fig. 1). Cyclic voltammetry in the positive region showed an irreversible peak ($E_{\text{pa}} = 1.91 \text{ V}$) due to oxidation of the thiophene group.}

Poly(TBQ) films showed a reversible reduction wave (Fig. 2) at $E^\circ = -0.14 \text{ V}$ vs. SSCE for the TBQ/TBQ^{•-} couple. The cyclic voltammetry data at potentials

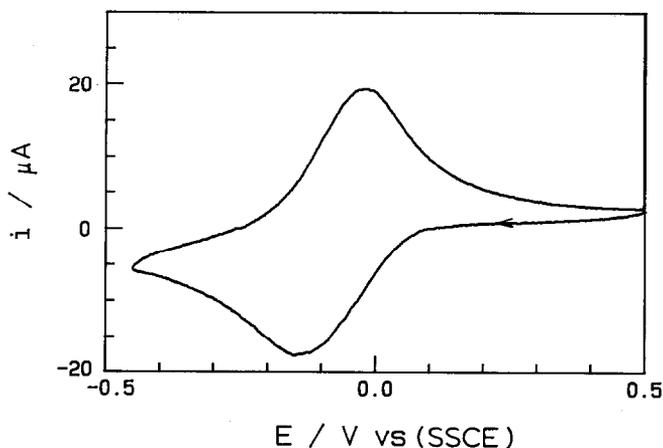


Fig. 2. Cyclic voltammogram of poly(TBQ) on Pt (area = 0.126 cm²) in acetonitrile containing 0.1 M tetrapropylammonium tetrafluoroborate. $\nu = 0.07 \text{ V s}^{-1}$. Film prepared by passing 54.3 mC cm⁻² at 1.7 V.

TABLE 1

Cyclic voltammetric data from a film of poly(TBQ) on Pt (area = 0.135 cm²) in acetonitrile containing tetrapropylammonium fluoroborate (0.1 M); i_{pc} is proportional to scan rate. Film prepared by passing 23.5 mC cm⁻² at 1.7 V vs. SSCE

$v/V s^{-1}$	$\Delta E_p/mV$	$-E^\circ/V$ vs. SSCE	$i_{pc}/\mu A$	$i_{pa}/\mu A$	$i_{pc}v^{-1}/mA s V^{-1}$	$q_c/\mu C$	$q_a/\mu C$
0.100	121	0.13	12.7	13.3	0.13	24	25
0.081	116	0.13	10.2	10.5	0.13	24	24
0.064	116	0.15	7.9	7.6	0.12	24	21
0.049	115	0.15	6.2	6.2	0.13	23	23
0.036	117	0.16	4.6	4.6	0.13	23	24
0.025	103	0.16	3.2	3.4	0.13	24	25
0.016	91	0.16	2.1	2.4	0.13	25	24

between +0.5 V and -0.45 V for a poly(TBQ) film in acetonitrile containing 0.1 M tetrapropylammonium tetrafluoroborate are collected in Table 1. Films showed a normal behaviour after a breaking-in period of one cycle. The charge under the cathodic and anodic waves (i.e. q_c and q_a) is roughly constant irrespective of the scan rate. The i_{pc}/v value is also approximately constant over the scan rate between 15 and 100 mV s⁻¹, indicating thin layer behaviour. Poly(TBQ) films behaved similarly in acetonitrile containing saturated tetramethylammonium tetrafluoroborate.

The stability of the poly(TBQ) films was examined by continuous cyclic voltammetry between +0.5 and -0.45 V. The charge under the cathodic peak decreased gradually by approximately 1.5% per cycle but the wave shape did not deteriorate.

A chronoamperometry experiment with a potential step from 0 to -0.45 V was carried out on freshly "broken-in" film in 0.1 M tetrapropylammonium tetrafluoroborate (Fig. 3). The data fitted reasonably well to the Cottrell plot (i vs. $t^{-1/2}$ curve) and calculated $D^{1/2}c$ values were in the range of 3 to 8 nmol cm⁻² s^{-1/2}.

A surprising aspect of the electrochemistry of films of poly(TBQ) is that we are unable to detect electron transfer on CV due to the process TBQ^{•-}/TBQ²⁻. This point is illustrated by the CV of poly(TBQ) given in Fig. 4a. No rise in the baseline corresponding to this second electron transfer step to poly(TBQ) was observed when the potential was scanned to -1.3 V vs. SSCE.

The Gibbs energy (taken as $-nFE^\circ$) for conversion of TBQ to its radical-anion within the polymer is greater by an amount 4 kJ mol⁻¹ than for the same process in acetonitrile and greater still, > 40 kJ mol⁻¹, for the conversion of the radical-anion to the dianion. An increase in the Gibb energy required for these reversible charging processes indicates that the polythiophene matrix is hydrophobic. Other phenomena due to interaction between the doping ion and the polymer matrix have been described in the oxidation of poly(thiophenes) [12,13]. Thus poly(thiophene) with a chiral 3-position side chain shows enantioselectivity for chiral anions [12]. Related

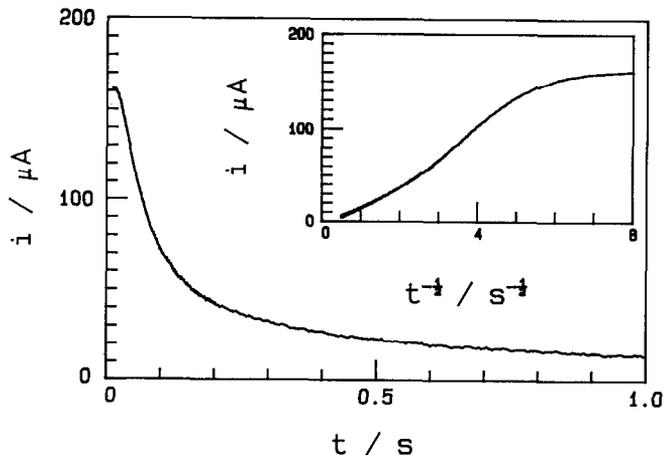


Fig. 3. Chronoamperometry of a film of poly(TBQ) on Pt (area = 0.126 cm²) in acetonitrile containing 0.1 M tetrapropylammonium tetrafluoroborate. Potential step 0 to -0.45 V. Film prepared by passing 54.3 mC cm⁻² at 1.7 V. Inset shows the Cottrell plot from which $D^{1/2}c = 3.8 \text{ mmol cm}^{-2} \text{ s}^{-1/2}$.

phenomena due to lipophilicity in 3-substituted poly(pyrroles) have been reported [13].

The electrochemical behaviour of polythiophene residues in the poly(TBQ) film was examined in acetonitrile containing 0.1 M tetrapropylammonium tetrafluoroborate, by cyclic voltammetry between 0 and +1.2 V (Fig. 5). The associated redox

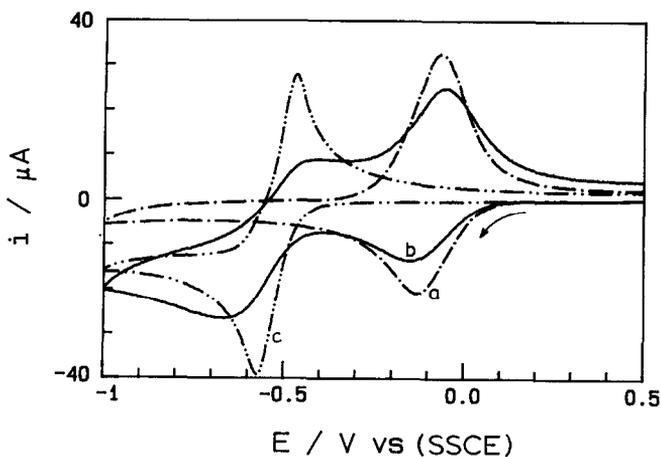


Fig. 4. (a) Cyclic voltammogram of Pt/poly(TBQ) electrode (area = 0.117 cm²) in acetonitrile containing 0.1 M tetrapropylammonium tetrafluoroborate. $v = 0.1 \text{ V s}^{-1}$. Film prepared by passing 45.5 mC cm⁻² at 1.7 V. (b) Cyclic voltammogram of above electrode in same electrolyte containing 1 mM 1,4-benzoquinone. $v = 0.1 \text{ V s}^{-1}$. (c) Cyclic voltammogram of 1 mM 1,4-benzoquinone in acetonitrile containing 0.1 M tetrapropylammonium tetrafluoroborate at a Pt electrode. $v = 0.1 \text{ V s}^{-1}$.

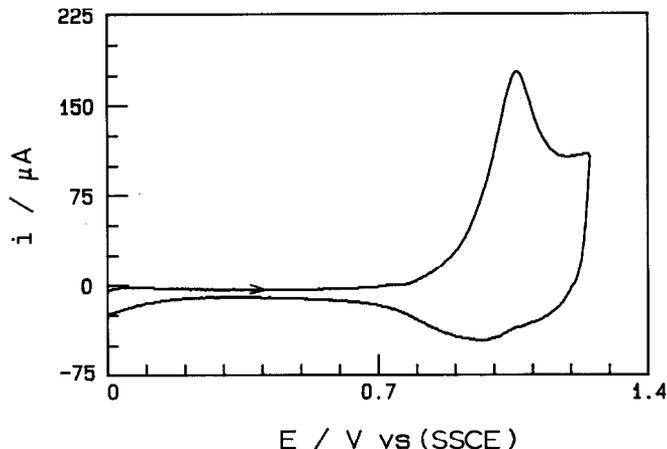


Fig. 5. Cyclic voltammogram of Pt/poly(TBQ) electrode (area = 0.123 cm²) in acetonitrile containing 0.1 M tetrapropylammonium tetrafluoroborate, $\nu = 0.1 \text{ V s}^{-1}$. Film prepared by passing 108 mC cm⁻² at 1.7 V.

couple is reversible with a sharp anodic peak ($E_{\text{pa}} = 1.06 \text{ V}$) and a broad cathodic peak. The shape of the cyclic voltammogram and the peak potentials are very similar to those of polythiophene [4]. Sometimes E_{pa} moved slightly towards more positive values on repetitive scanning. These results indicate that our poly(TBQ) films are electroactive at both more positive and more negative potentials.

We could demonstrate that 1,4-benzoquinone is reduced through the poly(TBQ) film at the usual potential for the benzoquinone/radical-anion couple (Fig. 4). The 1,4-benzoquinone radical-anion is reoxidised even though the film is at a potential where the TBQ units are present in the radical-anion form. Thus electron transfer to benzoquinone and from its radical-anion must occur either through pin-holes in the film where the supporting metal surface is exposed, or by diffusion of benzoquinone and its radical-anion through the thickness of the film.

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REFERENCES

- 1 G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, 135 (1982) 173.
- 2 K. Kaneto, K. Yoshino and Y. Inuishi, *Jpn. J. Appl. Phys.*, 21 (1982) 567.
- 3 A.J. Downard and D. Pletcher, *J. Electroanal. Chem.*, 206 (1986) 147.
- 4 R.J. Waltman, J. Bargon and A.F. Diaz, *J. Phys. Chem.*, 87 (1983) 1459.
- 5 J. Roncali, A. Yassar and F. Garnier, *J. Chem. Soc., Chem. Commun.*, (1988) 581.
- 6 M. Aizawa, S. Watanabe, H. Shinhara and H. Shinkawa, *J. Chem. Soc., Chem. Commun.*, (1985) 264.
- 7 J. Grimshaw and S.D. Perera, *J. Electroanal. Chem.*, 265 (1989) 335.

- 8 J. Grimshaw and S.D. Perera, *J. Electroanal. Chem.*, 278 (1990) 279.
- 9 E.P. Fokin and E.P. Prudchenko, *Zh. Org. Khim.*, 6 (1970) 91.
- 10 M.L. Mihailovic and M. Tot, *J. Org. Chem.*, 22 (1957) 652.
- 11 P. Cagniant and G. Merle, *C.R. Acad. Sci., Paris, Ser. C*, 267 (1968) 156.
- 12 M. Lemaire, D. Delabouglise, R. Garreau, A. Guy and J. Roncali, *J. Chem. Soc., Chem. Commun.*, (1988) 658.
- 13 D. Delabouglise, J. Roncali, M. Lemaire and F. Garnier, *J. Chem. Soc., Chem. Commun.*, (1989) 475.