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Polythiophene Films Containing Anthraquinone Groups

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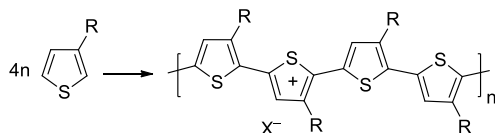
ABSTRACT

The monomer, 3-(3-thienyl)prop-1-yl-9,10-anthraquinone-2-carboxylate (**5**) was prepared by reacting 9,10-anthraquinone-2-carbonyl chloride with 3-(3-thienyl) propanol. Electrochemical polymerisation of (**5**) at a platinum electrode was achieved in acetonitrile. Electrochemical behaviour of (**5**) and the resulting greenish blue polymer, poly(**5**), have been examined by cyclic voltammetry in acetonitrile containing TPAB. These films were quite stable to repetitive scanning between 0 and -1.35 V. The neutral, hydrophobic poly(**5**) films show some resistance to swelling in acetonitrile and are not stable at potentials more negative than -1.55 V.

1. Introduction

Electrochemical syntheses of conducting polythiophenes [1-4] and polypyrroles [4] have received considerable attention [1-8]. There are many reports on electrochemical preparation of 3-substituted polythiophene films and their various applications (e.g., devices such as field-effect transistors, chemical and biochemical sensors) [1-8]. Molecular hybrid films were obtained by incorporating gold nanoparticles into 3-substituted polythiophene films [9]. Recently, poly[3-(2-anthraquinone)-2,5-thiophene] was synthesized by chemical oxidation of the monomer using FeCl_3 [10]. Unlike pyrrole-based polymers, some 3-substituted polythiophene derivatives can be dissolved in common organic solvents, allowing workers to characterize and process these polymers [11,12].

Thiophene and 3-substituted or 3,4-disubstituted thiophenes can be electropolymerized at a Pt electrode to give a coating of the corresponding oxidized polymer. It is formed by linking the 2nd and 5th positions (i.e., linking α , α' positions) of the thiophene derivative and one in every four thiophene moieties is positively charged as shown in Scheme 1.



Scheme 1: Electrochemical polymerisation of 3-substituted thiophenes; X⁻ is the counter anion of the electrolyte

Polythiophene fractions can be reduced to neutral non-conducting polymers. Neutral polythiophenes can be further reduced to obtain cation doped, negatively charged polymers at potentials below -1.5 V. 3-Substituted polythiophenes with long pendent redox groups in the polymer backbone can act as electron mediators. Electrodes modified with poly(pyrrole-anthraquinone) films [13] catalyze the reduction of

dioxygen, due to the rapid redox reaction between reduced anthraquinone units and dioxygen [14]. Electron transfer between a bare Pt electrode and dioxygen is much lower at the same potential. Therefore, it is of interest to synthesize a thiophene-based monomer containing an anthraquinone group and to investigate its electro-polymerization and electrochemical behavior of the resulting polymer. In this article, we report the synthesis of (**5**), electro polymerization of (**5**) at a Pt electrode and the electrochemical behaviour of the resulting polymer, poly(**5**).

2. Methodology

Elemental analysis was carried out on a Perkin-Elmer PE-240 automatic analyzer. IR spectra were recorded on Perkin-Elmer model 598 and 983G IR spectrometers, using KBr discs unless otherwise stated. Mass spectral data were obtained using a VG updated MS902 spectrometer operating at 70 eV. NMR spectra were recorded at 250 MHz using a Bruker WH250 instrument. The chemical shifts are in ppm with respect to TMS and coupling constants are in Hz.

9,10-anthraquinone-2-carboxylic acid and 3-thiophenecarboxaldehyde were purchased from Sigma-Aldrich. 3-(3-Thienyl) propionic acid (**2**) was prepared from 3-thiophenecarboxaldehyde according to a literature procedure [15] and some characterizing data for (**1**) and (**2**) are given.

3-(3-Thienyl) acrylic acid (1)

Prepared in 89% yield, m.p. $152-153$ °C (lit. [15], m.p. 151 °C). $^1\text{H NMR}$ (δ , CDCl_3): 6.27 (1H, d, J(HH) 15.8 Hz, CHC=O), 7.34 (2H, m, ThH), 7.54 (1H, t, J(HH) 1.34 Hz, ThH), 7.78 (1H, d, J(HH) 15.9 Hz, CH=). Mass m/z (%): 154 (M^+ , 100), 137 (27), 112 (27), 111 (14) and 109 (29). IR ν_{max} (KBr): 3084 (broad), 1676, 1623 and 1284 cm^{-1} .

3-(3-Thienyl) propionic acid (2)

Prepared in 81% yield, m.p. 53-55 °C, (lit. [15], m.p. 62-62.5 °C). ¹H NMR (δ, CDCl₃): 2.68 (2H, t, J(HH) 7.5 Hz, ThCH₂), 2.97 (2H, t, J(HH) 7.5 Hz, CH₂), 6.97 (2H, m, ThH), 7.25 (1H, m, ThH). Mass m/z (%): 156 (M⁺, 73), 111 (63) and 97(100).

3-(3-Thienyl) propanol (3)

3-(3-Thienyl) propionic acid (4.9 g) and excess lithium aluminium hydride (4.5 g) were refluxed in tetrahydrofuran (150 mL) for 7 h. After cooling, the solution was filtered, evaporated to dryness and then vacuum distilled to give (3) as a colorless oil (3.4 g, 76%), b.p. 62-63 °C/0.15 mm. ¹H NMR (δ, CDCl₃): 1.87 (2H, m), 2.20 (1H, s, OH), 2.71 (2H, t, J 7.6 Hz, CH₂Th), 3.64 (2H, t, J 6.5 Hz, CH₂O), 6.93 (2H, m, ThH), and 7.23 (1H, m, ThH). Mass m/z (%): 142 (M⁺, 30), 123 (11), 111 (20), 98 (100) and 97 (84). IR ν_{max} (liquid): 3332, 3100, 2937, 2864 and 1054 cm⁻¹.

9,10-Anthraquinone-2-carbonyl chloride (4)

9,10-Anthraquinone-2-carboxylic acid (2 g, 7.9 mmol) was refluxed in thionyl chloride (10 mL) for 7 h. Excess thionyl chloride was removed and the product was recrystallized from benzene to give yellow plates (1.85 g, 86%). m.p. 147 °C. ¹H NMR (δ, CDCl₃): 7.87 (2H, m, H⁷ and H⁶), 8.34 (2H, m, H⁸ and H⁵), 8.45 (2H, m, H³ and H⁴), 9.02 (1H, s, H¹). Mass m/z (%): 272 (M+2, 4), 270 (M⁺, 12), 235 (M-Cl, 100) and 151(30). IR ν_{max} (KBr): 1740, 1670, 1580 and 1210 cm⁻¹.

3-(3-Thienyl)prop-1-yl 9,10-anthraquinone-2-carboxylate (5)

3-(3-Thienyl) propanol (0.16 g, 1.1 mmol), 9,10-anthraquinone-2-carbonyl chloride (0.27 g, 1.0 mmol) and pyridine (0.1 g, 1.3 mmol) in dichloromethane (20 mL) were stirred for 3 h. The solution was filtered; the filtrate was washed with water, dried over anhydrous sodium sulphate and then solvent was removed. The residue was recrystallized from methanol/dichloromethane to yield (5) as pale-yellow plates (0.25 g, 67%). m. p. 103-105 °C. Found: C, 67.5; H, 4.2, calcd. (%) for C₂₂H₁₆SO₄·0.25CH₂Cl₂: C, 67.2; H, 4.2. ¹H-NMR (CDCl₃, TMS): δ 2.17 (2H, m, CH₂), 2.84 (2H, t, J(HH) 7.6 Hz, Th-CH₂), 4.44 (2H, t, J(HH) 6.5 Hz, CH₂O), 7.00 (2H, m, ThH), 7.27 (1H, m, ThH), 7.84 (2H, m, ArH), 8.37 (4H, m, ArH) and 8.93 (1H, s, ArH). Mass m/z (%): 376 (M⁺, 4), 15 (12), 124 (ThCH₂CH=CH₂, 100) and 97 (ThCH₂⁺, 27). IR ν_{max} (KBr): 1712, 1669, 1590, 1278, 1245 and 703 cm⁻¹.

Film preparation

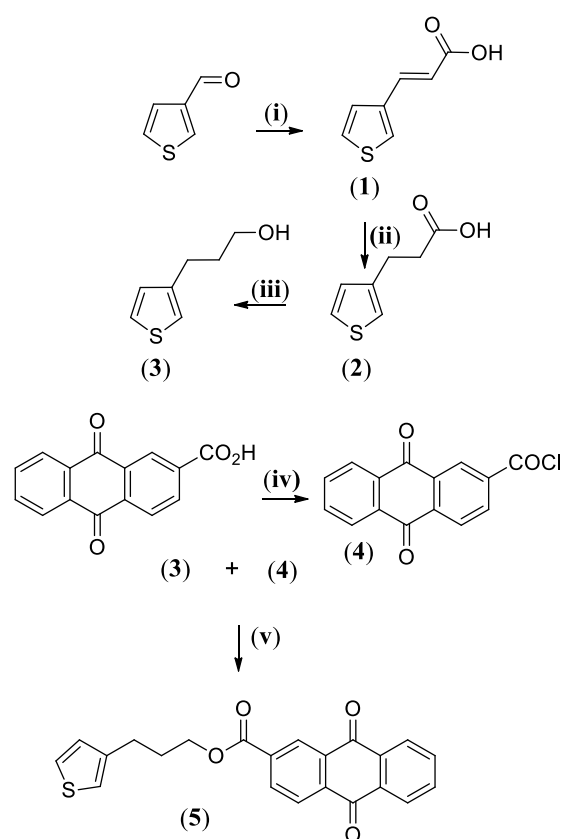
All electrochemical studies were performed in a three-electrode, one compartment cell. The potentiostat was a PAR-176 model, controlled through an Apple-IIe computer. The working electrode was a Pt sphere (diameter 1-2 mm) sealed in a glass mounting. A Pt wire was used as the counter electrode. All potentials are quoted with respect to saturated sodium chloride calomel electrode (SSCE). The solution was degassed by passing dry oxygen-free nitrogen for 10-20 min and experiments were done under a nitrogen atmosphere. The acetonitrile (Aldrich, HPLC grade) was dried over CaH₂. Tetrapropylammonium

tetrafluoroborate (TPAB) was dried under vacuum at 100-120 °C for two days.

The films of poly(5) were obtained on Pt spheres by controlled potential oxidation of (5) in acetonitrile containing TPAB at 1.65 V. These modified electrodes were washed thoroughly with acetonitrile and transferred to a fresh acetonitrile solution containing the electrolyte for cyclic voltametric experiments.

3. Results and Discussion**Preparation of the monomer**

The reaction conditions used for the preparation of the monomer (5) are summarised in Scheme 1. Perkin reaction of 3-thiophenecarboxaldehyde with malonic acid gave 3-(3-thienyl) acrylic acid (1) in 89% yield.



Scheme 1: (i) malonic acid; (ii) Na/Hg; (iii) LiAlH₄; (iv) SOCl₂; (v) pyridine

Compound (1) was converted into 3-(3-thienyl) propionic acid (2) in 81% by reducing (1) with sodium amalgam. Reduction of (2) with LiAlH₄ afforded the corresponding alcohol (3) as a colorless oil in 76% yield. The acid chloride (4) was prepared in 86% yield by reacting 9,10-anthraquinone-2-carboxylic acid with thionyl chloride. The monomer (5) was obtained as pale-yellow plates in good yield by reacting (3) with (4).

Electrochemical behaviour of (5) and poly(5)

Cyclic voltammetry of (5) (1.6 mM) in acetonitrile containing 0.1 M TPAB showed two reversible

electron transfer reactions at $E^{\circ} = -0.80$ and -1.36 V for the $(5)/(5)^{-}$ and $(5)^{-}/(5)^{2-}$ redox couples respectively (Figure 1). The oxidation of the thiophene moiety gave an irreversible peak ($E_{pa} = 1.85$ V).

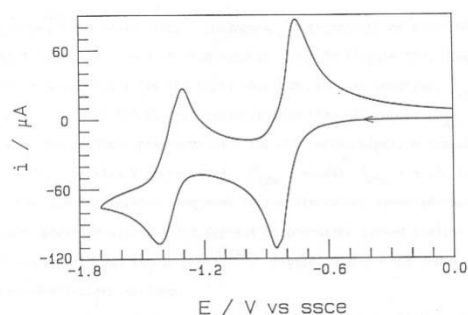


Figure 1: Cyclic voltammogram of poly(5) (1.6 mM) at a Pt electrode (area = 0.116 cm²) in acetonitrile containing 0.1 M TPAB. Scan rate = 0.1 V s⁻¹.

Greenish blue coloured coatings of poly(5) were obtained on Pt spheres by controlled potential oxidation of (5) (5.5 mM) solution in acetonitrile containing a TPAB (0.1 M) at 1.65 V. The colour of the neutral film is reddish yellow. No dark coloured soluble products were formed at the anode during the constant potential oxidation so we believe that all of the oxidised monomer is converted to polymer poly(5). The current passed during the polymerisation reached a plateau value and the thickness of the poly(5) film formed could be regulated by controlling the time of polymerisation. Figure 2 shows the redox behaviour of the polythiophene residue of poly(5) in the anodic zone. These peaks are reversible with a similar shape as poly(3-alkylthiophene) derivatives [12].

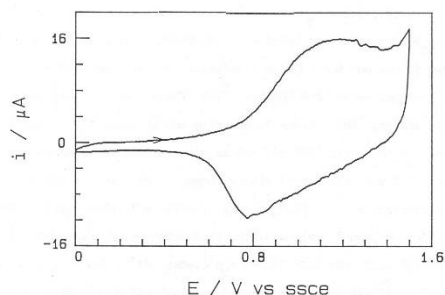


Figure 2: Cyclic voltammogram of a film of poly(5) on Pt (area = 0.155 cm²) in acetonitrile containing 0.1 M TPAB. Scan rate = 0.1 V s⁻¹. Film prepared by passing 8.7 mC cm⁻² at 1.65 V.

In the cathodic zone, where the anthraquinone groups are active, the poly(5) films showed quite different cyclic voltammograms compared to those of their polypyrrole analogue [13]. A typical cyclic voltammogram of a "broken-in" poly(5) film between 0 and -1.55 V in acetonitrile containing 0.1 M TPAB is shown in Figure 3. The cathodic peak potential for the first electron transfer reaction, E_{1pc} , is -1.24 V, which is 390 mV more negative than that of monomer ($E_{1pc} = -0.85$ V). The cathodic peak potential for the second electron transfer reaction, E_{2pc} , is -1.4 V as expected from the behaviour of the monomer. For the corresponding anodic waves,

the peak potentials are $E_{1pa} = -0.84$ V and $E_{2pa} = -1.36$ V.

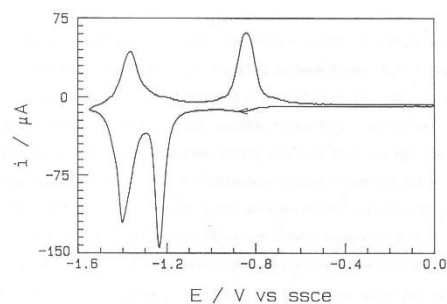


Figure 3: Cyclic voltammogram of a film of poly(5) on Pt (area = 0.135 cm²) in acetonitrile containing 0.1 M TPAB. Scan rate = 0.08 V s⁻¹. Film prepared by passing 10.75 mC cm⁻² at 1.65 V.

The anthraquinone moiety in the polypyrrole [13] backbone showed similar electrode potentials as its monomer for the first and second electron transfer reactions. It seems with the polythiophene backbone that there is a barrier for the first electron transfer which could be associated with a considerable film resistance due to poor swelling of the hydrophobic neutral poly(5) in acetonitrile which restricts the motion of cations into the film. A search for related phenomena in the literature revealed that electrodes modified with a thick deposit of phenazine show similar widely separated anodic and cathodic peaks [16].

In the potential range 0 to -1.55 V, the poly(5) film was found to be unstable and green coloured material diffused away from the electrode. Because of this the anodic peak heights and the amounts of charge under the anodic curves are less than the corresponding cathodic ones. On repetitive scanning, the film on the electrode was destroyed within 6-7 cycles and E_{1pc} slowly moved 20-50 mV towards less negative potentials.

The reduction and cation doping of neutral polythiophene [17-19] have been observed at negative potentials. In fact, application of potentials more negative than -1.5 V with respect to SCE to polythiophene films resulted in the degradation of the film [18,19]. The deterioration of the poly(5) films at very negative potentials might be due to the incorporation of a large number of cations into the film as a result of the reduction of both the neutral polythiophene backbone and the anthraquinone moieties.

By working at less negative potentials, we were able to avoid this decomposition of the films. Figure 4a shows the cyclic voltammogram obtained for poly(5) in acetonitrile containing 0.1M TPAB when potential is cycled between 0 and -1.35 V. Under these conditions, the film required a "breaking-in" period of 3-5 cycles. An ill-defined cathodic peak with a corresponding anodic peak was observed for the electron transfer reaction. On continuous cycling between 0 and -1.35 V, well-defined cathodic and anodic peaks were developed (Figure 4b). $E_{1pa} = -0.81$ V, thus peaks widely separated ($\Delta E = 402$ mV).

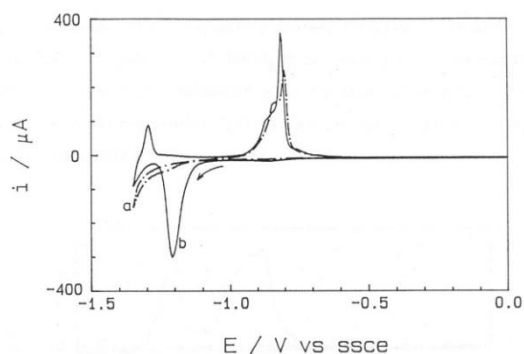


Figure 4: Cyclic voltammogram of a film of poly(5) on Pt (area = 0.135 cm²) in acetonitrile containing 0.1M TPAB. Scan rate = 0.08 V s⁻¹.

a) 1st scan; b) 6th scan after continuous scans. Film prepared by passing 10.75 mC cm⁻² at 1.65 V.

This activity was maintained only during repetitive scanning. After a few minutes of rest at 0V, the original ill-defined cyclic voltammogram was observed on the next scan and the “breaking-in” process had to be repeated. This behaviour indicated that poly(5) has a poor swelling ability in acetonitrile. These films were quite stable to repetitive scanning between 0 and -1.35V and the charge under the cathodic peak (q_c) decreased slowly (0.3% per cycle).

4. Conclusions

We have successfully prepared a thiophene derivative (5) containing a pendent anthraquinone group at the 3-position. These hydrophobic poly(5) films show some resistance to swelling in acetonitrile and the cathodic peak potential due to the first electron transfer is more negative than that of monomer. These films were quite stable to repetitive scanning between 0 and -1.35 V but are not stable at potentials more negative than -1.35 V.

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