

Synthesis, electrochemical polymerization and properties of poly(2,5-di-(-2-thienyl)-pyrrole)

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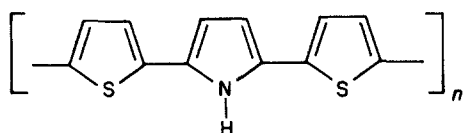
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Poly(2,5-di-(-2-thienyl)-pyrrole) obtained by electrochemical synthesis and doped with *para*-toluene sulphonate exhibits electrical conductivities between 10^{-8} and 10^{-1} S cm $^{-1}$. The conductivity of the polymer films changes with the concentration of the electrolyte and voltage used in the synthesis. The polymer films are found to be soluble in acetonitrile and acetone and exhibit a rough structure, characteristic of the conditions occurring during the synthesis.

(Keywords: thiophene-pyrrole copolymers; poly(2,5-di-(-2-thienyl)-pyrrole) synthesis; electrical conductivity; electrochemical synthesis; film structure; *para*-toluene sulphonate salt)

INTRODUCTION

During the last five years there has been a significant increase in research devoted to the synthesis and study of polymeric materials with the capacity of exhibiting either semiconducting or metallic properties. Although the concept of conductivity in organic polymers was postulated over forty years ago it is only relatively recently that conducting polymers have become a practical reality. A wide variety of polymers possessing conjugated backbones have now been shown to possess high electronic conductivities when doped with either donor or acceptor molecules. Polypyrrole²⁻⁴ and polythiophene⁵⁻⁷ have attracted considerable interest since they form oxidatively stable films with high conductivities and good mechanical properties. In this paper we report the electrochemical synthesis of poly(2,5-di-(-2-thienyl)-pyrrole) which has the structure:



By analogy with polypyrrole and polythiophene we may anticipate that this polymer, when anion doped, may exhibit a high electrical conductivity and this paper reports its preparation and physical properties.

EXPERIMENTAL

Synthesis of 2,5-di-(-2-thienyl)-pyrrole

The method of synthesis has been described by Wynberg and Metsalar⁸. An improvement in the yield was obtained by refluxing the intermediate 1,4-di-(-2-thienyl)-1,4-butane dione with ammonium acetate, acetic acid and acetic anhydride under a blanket of nitrogen for a period of twelve hours. The mixture was then poured

into distilled water and the resultant green solid was purified using an alumina column and ether as solvent. The product was pale yellow. The structure of the trimer was confirmed using micro analysis and infra-red and proton n.m.r. spectroscopy. The ¹³C n.m.r. spectra obtained at 62.9 MHz using a Bruker n.m.r. spectrometer with deuterochloroform as solvent gave characteristic resonances at 108.3, 121.0, 122.7, 127.6 and 135.4 ppm.

Electrochemical synthesis of poly(2,5-di-(-2-thienyl)-pyrrole)

The electrode used in the electrochemical synthesis was constructed by half coating a microscope slide with chromium and then overlaying this with gold. Polymerization was carried out using a three electrode electrochemical cell controlled by a Solatron 1186 electrochemical interface. A saturated calomel (SCE) electrode was used as reference and a silver wire acted as the counter electrode. Acetonitrile containing silver *para*-toluene sulphonate (0.0085–0.072 M) and the monomer 2,5-di-(-2-thienyl)-pyrrole (0.014–0.018 M) was used as the electrolyte. The solutions were thoroughly degassed by bubbling nitrogen through the electrolyte prior to polymerization. An inert atmosphere of nitrogen was maintained over the reaction mixture. Polymer films were grown at voltages from –0.5 to –0.2 V relative to the calomel electrode.

Analysis of polymer films

Thickness and surface roughness. A Dektak II1 surface profile analyser was used to examine the surface roughness and also determine the thickness of the films. A vertical resolution of 80 Å and a horizontal resolution of 1 μm was achieved with a probe load of 25 mg.

Microanalysis. Elemental analysis on the thicker films was used to determine the anion to trimer ratio. This analysis was based on determination of the carbon, hydrogen, sulphur and nitrogen ratios; *para*-toluene sulphonate being the anion.

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Conductivity measurements

The conductivity (σ) was determined from current-voltage curves obtained by measurement of a sandwich obtained by evaporation of a gold layer over the electrochemically deposited polymer. A four-point probe method was satisfactory for samples with low conductivity. The geometric surface area required for determination of the conductivity was defined by the area of overlap of the second evaporated gold layer. Samples of higher conductivity and thicker films were detached from the electrode, pressed into the form of a pellet, electrodes deposited and current voltage characteristics determined using a four-point method.

RESULTS AND DISCUSSION

Electrochemical synthesis

The electrochemical syntheses of the related compounds pyrrole and thiophene have been discussed by Street *et al.*² and Tourillon and Garnier⁵ respectively. In both cases they have established that the reaction is a two-electron process. Cyclic voltmetry on a 7 μm thick electrochemically deposited film of poly(2,5-di-(2-thienyl)-pyrrole) was performed using a solution of 0.1 M silver *para*-toluene sulphonate in acetonitrile as electrolyte (see Figure 1). Silver *para*-toluene sulphonate was used in this study because earlier investigations of films produced with pyrrole² have shown that incorporation of this anion yields highly conductive mechanically stable films. The cyclic voltamogram was reversible and consisted of four peaks, two of which are associated with oxidative and two with reductive processes. For the ideal experiment, the polymer film should be only a few hundred angstroms thick. Thick films are known² to lead to a broadening of the voltamogram peaks. Two of the peaks observed can be associated with the gold substrate used in the electrochemical polymerization. The effects of the substrate electrode on the cyclic voltamogram have been discussed previously and have no effect on the polymerization chemistry. The average of the forward and reverse peak potentials is known as the formal reduction potential of the redox couple. The number of electrons transferred in the electrode reaction (n) for a reversible couple can be determined from the separation of the peak potentials and a value of $n=0.139$ is observed; this is approximately a half of the equivalent value observed for pyrrole and suggests that the polymer is 14% oxidized. In poly(2,5-di-(2-thienyl)-pyrrole) approximately one in three pyrrole units will be in an oxidized form, in comparison with the value of one in four for polypyrrole. The curves are consistent with a two-electron reaction; however the uncertainty in the analysis as a consequence of the breadth of the peaks precludes further analysis.

Structure of poly(2,5-di-(2-thienyl)-pyrrole) films

The surfaces of the deposited films were examined optically and surface profiles obtained using a Dektak II 1 analyser. Regardless of whether the films were prepared as thin ($2 \times 10^4 \text{ \AA}$) or thicker films ($4 \times 10^6 \text{ \AA}$), the profiles were found to be very rough (see Figure 2). The films appear to be composed of a number of peaks and were visibly powdery. Tourillon and Garnier⁹ observed that electrochemically prepared polythiophene and substituted polythiophene is formed as a thick powdery deposit. Thin films, $1 \times 10^3 \text{ \AA}$ thick, were observed, using

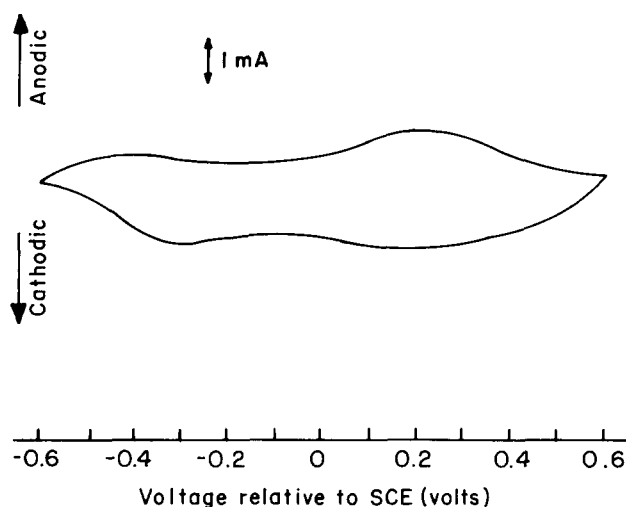


Figure 1 Cyclic voltamogram of poly(2,5-di-(2-thienyl)-pyrrole) doped with *para*-toluene sulphonate. The film thickness was 7.4 μm and the scan rate was 118 mV s^{-1} . Peak broadening is a consequence of the film's thickness

scanning electron microscopy (SEM), to be homogeneous, whereas thicker films, 0.5–1 μm , were no longer homogeneous. When the polymer thickness was increased to a few μm , powdery deposits rather than films were obtained.

Conductivity measurements

Variation of the salt concentration from $1 \times 10^{-3} \text{ M}$ to 0.1 M yields films with conductivities in the range 10^{-8} to 0.1 S cm^{-1} . Because of the rough texture of these thin films it was possible to examine these materials only in a low conducting form using the sandwich electrode configuration. Samples grown with electrolyte concentrations in the range 0.05 to 0.1 M were detached from the electrode, compressed into pellet form and exhibited conductivities in the range 0.02 to 0.1 S cm^{-1} . A typical current voltage curve is shown in Figure 3. The conductivity of the polymer films is observed to increase with concentration of salt used in the electrolyte, Figure 4, and the applied voltage (see Figure 5). Microanalysis of the polymer films indicates that the increased conductivity is paralleled by an increase in the concentration of incorporated anion.

It was observed that films grown under certain conditions (Table 1) were soluble in acetonitrile and acetone. The films were observed to be completely soluble at a concentration of 10% w/v. Evaporation of the solvent yields once more a black powder with essentially the same conductivity as the original film. A number of polymers capable of being doped to give highly conducting films have recently been prepared in soluble form; however as far as we are aware this is the first report of a soluble semi-conducting form of a conducting polymer system.

Spectroscopic properties

The visible and ultraviolet spectrum of the trimer was obtained, prior to electrochemical synthesis in acetonitrile (Figure 6) using a Perkin-Elmer fluorescence spectrometer. Since the polymer is soluble it was also possible to obtain its spectrum (see Figure 6). Polymerization produces a marked shift in the absorption maximum from 477 nm in the trimer to 516 nm in the polymer. The shift to higher wavelength is consistent with an increase in the conjugated chain length. The shift in the

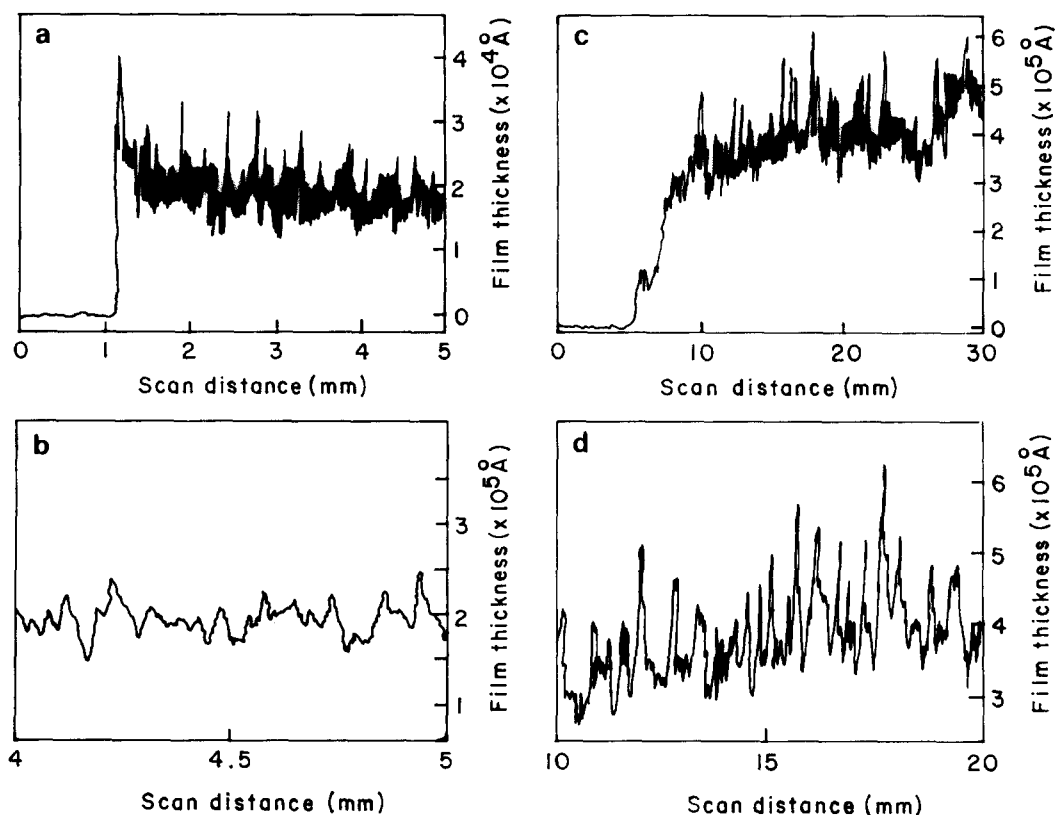


Figure 2 Typical surface profiles of poly(2,5-di-(2-thienyl)-pyrrole). Profiles (a) and (b) refer to a polymer thickness of $2 \times 10^4 \text{ \AA}$. Profiles (c) and (d) refer to a thicker $4 \times 10^5 \text{ \AA}$. The profiles show that the surface roughness is considerable and independent of the film thickness. Profiles (a) and (b) depict a scan across the width of a polymer film, whereas profiles (c) and (d) depict a scan along the length of the film. The relatively level initial portions of the profiles are for profile (a) the surface of the glass slide and for profile (c) the surface of the gold/chromium sandwich

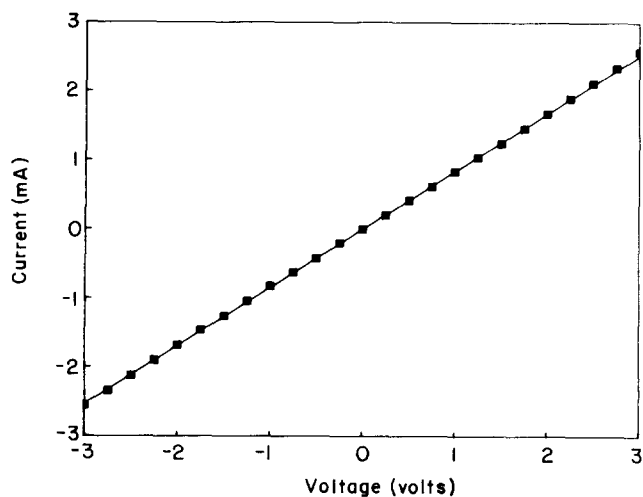


Figure 3 Typical plot of the current-voltage relationship for a film of poly(2,5-di-(2-thienyl)-pyrrole). Plots are linear over a wide voltage range

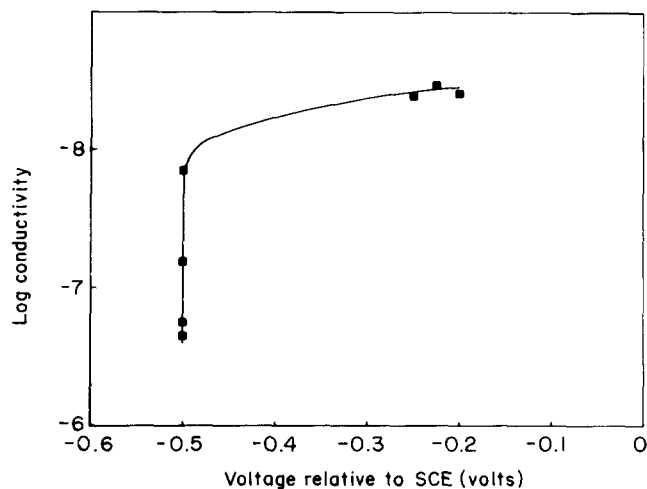


Figure 4 Plot of the log (conductivity) plotted against voltage relative to the standard calomel electrodes used in the electrochemical polymerization

Table 1 Film growing conditions and conductivity and solubility measurements

Film No.	Conductivity (S cm^{-1})	Voltage rel. to SCE (V)	[Trimer] (M)	[Salt] (M)	Solubility in	
					CH_3CN	CH_3COCH_3
1	5.61×10^{-8}	-0.500	0.018	0.0085	No	No
2	1.56×10^{-7}	-0.500	0.018	0.0085	No	No
3	4.46×10^{-8}	-0.500	0.018	0.0085	No	No
4	N/A	-0.368	0.018	0.018	No	No
5	7.16×10^{-7}	-0.500	0.014	0.014	No	No
6	2.55×10^{-6}	-0.200	0.014	0.072	Yes	Yes
7	2.48×10^{-6}	-0.250	0.014	0.072	Yes	Yes
8	2.96×10^{-6}	-0.225	0.014	0.072	Yes	Yes

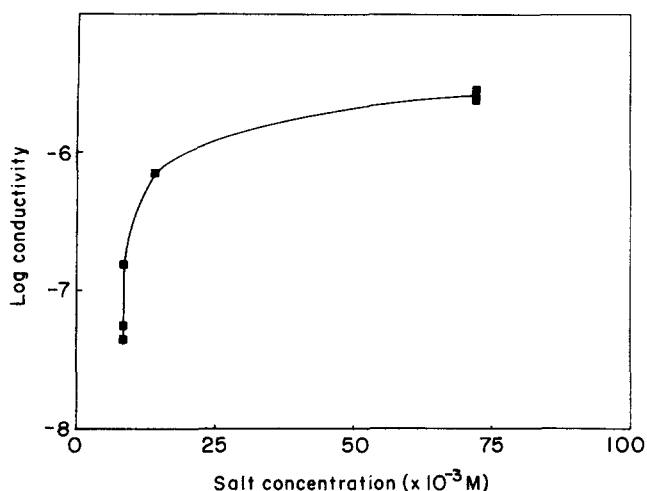


Figure 5 Plot of the log (conductivity) plotted against the concentration of the silver *para*-toluene sulphate salt in acetonitrile during the electrochemical preparation

absorption spectrum is consistent with the formation of a polymer with molecular weight of approximately 4000. Dramatic changes in the colour of the solution were observed with the addition of an aprotic donor such as chloroform.

The photoconductivity of a sandwich structure, in which the upper electrode had a thickness of between 800–1000 Å and was partially transmitting to light, was explored over a frequency range from 200 to 800 nm using a monochromated xenon light source. Despite the possible donor–acceptor properties of this polymer no significant photoconductivity was detected.

CONCLUSIONS

Poly(2,5-di-(2-thienyl)-pyrrole) can readily be synthesized electrochemically and is obtained under certain conditions in a soluble form. Despite the fact that it exhibits strong donor–acceptor spectral characteristics it does not show any marked photoconductivity. This study indicates the feasibility of the production of soluble conducting polymers.

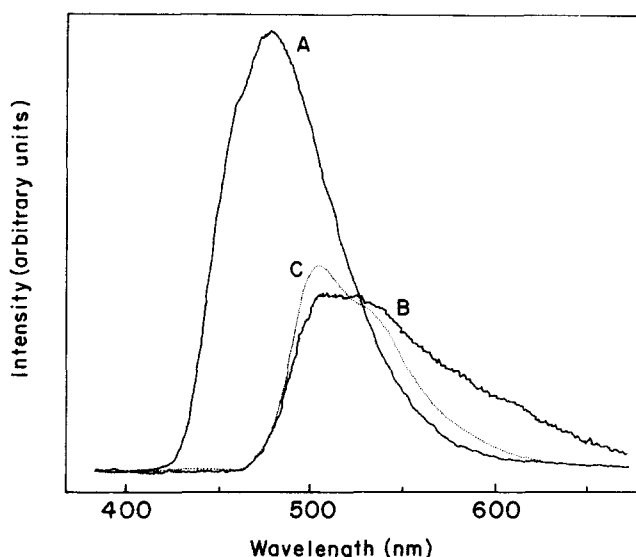


Figure 6 Visible-u.v. spectrum of the trimer and polymer. (A) refers to the emission spectrum of the trimer, 2,5-d-(2-thienyl)-pyrrole in acetonitrile, (B) refers to the emission spectrum of the polymer with incorporated *para*-toluene sulphate anion, (C) refers to the emission spectrum of the polymer in acetone. The trimer is observed to undergo photopolymerization

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