

# Electrochemical polymerisation of thiophene derivative induced by Lewis acid: Electrosynthesis of poly[(*R*)-(–)-2-(3'-thienyl)ethyl-(3',5''-dinitrobenzoyl)- $\alpha$ -phenylglycinate]

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## Abstract

Films of poly[(*R*)-(–)-2-(3'-thienyl)ethyl-(3',5''-dinitrobenzoyl)- $\alpha$ -phenylglycinate] were deposited on ITO electrodes by potentiodynamic, potentiostatic and galvanostatic methods using a (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBF<sub>4</sub>/CH<sub>3</sub>CN electrolyte system containing 20% boron trifluoride diethyl etherate. Polymerisation occurred as a charge dependent process at a potential of 1.4 V vs. Ag/Ag<sup>+</sup>(CH<sub>3</sub>CN). The surface morphologies of the films so-formed were examined using atomic force microscopy. The film deposited by the galvanostatic method displayed more homogeneous grain geometry and a larger superficial area than those formed by the other methods. Cyclic voltammetry revealed a well defined redox couple at the anodic region, attributable to polymer *p*-doping, and a poorly defined redox pair at the cathodic region, attributable to the reduction of the nitro group. The polymeric films obtained were yellow in colour ( $\lambda_{\max}$  425 nm) in the reduced state and light blue ( $\lambda_{\max}$  745 nm) in the oxidised state. © 2006 Elsevier Ltd. All rights reserved.

**Keywords:** Substituted polythiophenes; Conducting polymers; Atomic force microscopy

## 1. Introduction

Electrochemical polymerisation has proven to be an extremely valuable technique for the synthesis of inherently conducting polymers. Amongst the advantages offered by this method are: (i) the conducting film is formed on the working electrode in a one-step process, (ii) the amount of polymer deposited on the electrode may be controlled through regulation of the total charge passed through the cell, (iii) only small amounts of monomer are required, and (iv) highly accurate and precise data concerning the characteristics and properties of the electropolymerised material are available through integrated electrochemical studies [1].

Conducting polymers produced from thiophene derivatives are environmentally and thermally stable [2,3], and they also display high conductivities and acceptable chromic and fluorescent properties. Consequently, such films have potential application in the production of micro-electrical devices [4], including electrochromic devices [5], antistatic coatings [6], sensors [7,8], batteries [9] and solar cells [10,11].

However, a critical obstacle to the further development of novel advanced materials concerns the ability to control the structure, properties and function of the synthesised polymer [3]. With respect to the electrosynthesis of polythiophene and its derivatives, the high oxidation potential (>1.6 V vs. SCE) of the thiophene monomers in common organic media, such as acetonitrile (CH<sub>3</sub>CN), nitromethane or propylene carbonate, leads to the formation of poor quality conducting films. Moreover, the use of high potentials irreversibly damages the conjugated system through overoxidation [12–14].

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A major research challenge is, therefore, to reduce the oxidation potential of the monomer and, consequently, the band gap of the corresponding polymer.

A possible approach to this problem would involve the substitution of electron donating groups at the  $\beta$ -position of the thiophene ring of the monomer, giving rise to a decreased oxidation potential for both the monomer and the corresponding polymer [2,3]. It is reported that, compared with thiophene itself, higher quality films can be readily formed using  $\beta$ -substituted thiophenes, and that the corresponding polymers are more stable in the doped (conducting) states [2,15]. Moreover, modification of the monomer repeat unit, or substitution of functional groups on the polymer backbone, would permit control at the molecular level of the structure and physical properties of the polymer [16].

In contrast to the above, substrates derivatised with electron-withdrawing groups usually exhibit oxidation potentials higher than those of the unsubstituted monomer and produce polymer films of poor quality. This is especially so for monomers that contain nitro group substituents. Nevertheless, nitro groups are involved in the redox processes of the corresponding conducting polymers and, since such reduction utilises many electrons and is readily reversible [17], these polymers have potential application as electrochemical batteries in which charge storage would be of Faradaic nature [18]. Apparently, however, substitution of a monomer with strongly destabilising nitro groups inhibits electropolymerisation and prevents the formation of conducting polymer films [1,19]. It is likely that the presence of strong electron-withdrawing substituents in the monomer can stabilise the intermediate cation-radical sufficiently for it to diffuse away from the electrode thus precluding further reactions on the anode surface.

A second strategy by which good quality films of substituted polythiophenes may be prepared involves replacement of common organic media with a medium-strength Lewis acid, such as boron trifluoride diethyl etherate (BFEE) [12,20,21]. The facile formation of polymer films by direct anodic oxidation of appropriate monomers in an electrolyte containing BFEE has been demonstrated for both polythiophene [22–26] and its derivatives [27–29]. The onset of monomer oxidation occurred at a much lower potential in the presence of BFEE rather than in  $\text{CH}_3\text{CN}$  containing small inorganic anions (such as  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{PF}_6^-$ ), apparently by virtue of the interaction between the medium-strength Lewis acid and the aromatic monomers [12]. The strong electrophilic nature of BFEE catalyses the deprotonation of aromatic compounds at electrodes and dramatically decreases the oxidation potential of such compounds [26,30,31]. In the specific case of thiophene monomers [12,32], the formation of  $\pi$ -complexes with BFEE suppresses the resonance stability of the thiophene ring thus facilitating the loss of electrons from the ring [16].

Under such conditions, BFEE acts not only as solvent but also as the supporting electrolyte owing to its significant ionic conductivity ( $400 \mu\text{S cm}^{-1}$  for freshly distilled BFEE). However, in order to further improve the properties of electro-synthesised films of conducting polymers, mixed electrolytes consisting of BFEE with a strong acid or with another organic

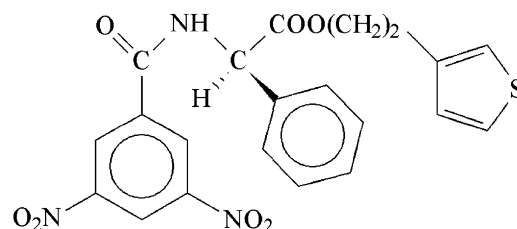


Fig. 1. Molecular structure of (*R*)-(-)-2-(3'-thienyl)ethyl-(3',5''-dinitrobenzoyl)- $\alpha$ -phenylglycinate (TDNB).

solvent have also been employed [33]. Thus, high quality films of poly(3-chlorothiophene) [34], poly(thianaphthene) [30] and poly(paramethylphenylene) [35] have been electro-synthesised in an electrolyte containing BFEE and sulphuric acid or trifluoroacetic acid, whilst films of poly(indole) and poly(thiophene) derivatives have been prepared using mixtures of BFEE and diethyl ether [1,31] or  $\text{CH}_3\text{CN}$  [32,36] in various proportions.

Previously, we have reported the synthesis of the monomers (*R*)-(-)- and (*S*)-(+)-2-(3'-thienyl)ethyl-(3',5''-dinitrobenzoyl)- $\alpha$ -phenylglycinates (TDNB; Fig. 1), their polymerisation in chloroform with  $\text{FeCl}_3$  as oxidising agent, and the characterisation of the resulting products [37]. In the present paper, we report the electrodeposition of films of poly(TDNB) by direct anodic oxidation of TDNB monomer in  $\text{CH}_3\text{CN}$  containing 20% BFEE, and describe detailed studies of the morphological, electrochemical and spectroscopic properties of the poly(TDNB) films so-produced.

## 2. Experimental

The deposition of poly(TDNB) films on indium tin oxide (ITO)/glass electrodes ( $1.0 \text{ cm}^2$ ,  $R_s \leq 10 \Omega \text{ cm}$ ; Delta Technologies) was performed in a single compartment cell using an Autolab PGSTAT20 galvanostat/potentiostat. In order to prevent the migration of water into the experimental system, a home-built non-aqueous  $\text{Ag}/\text{Ag}^+(\text{CH}_3\text{CN})$  reference electrode ( $+0.298 \text{ V vs. normal hydrogen electrode}$ ; Analion), isolated from the working solution by a Vycor<sup>®</sup> frit, was used for all experiments. A platinum wire (4.0 cm length, 0.25 mm in diameter) was used as the counter electrode. The monomer (*R*)-TDNB, synthesised as described previously [37], was employed at a concentration of  $0.05 \text{ mol L}^{-1}$  in a supporting electrolyte consisting of  $0.2 \text{ mol L}^{-1}$   $(\text{C}_4\text{H}_9)_4\text{NBF}_4$  (Merck) in freshly distilled  $\text{CH}_3\text{CN}$  ( $\text{H}_2\text{O} < 0.002\%$ ; Omnisolv), or in a mixed electrolyte system containing  $(\text{C}_4\text{H}_9)_4\text{NBF}_4/\text{CH}_3\text{CN}$ : BFEE (8:2, v/v).

Films were deposited using potentiodynamic [PDN;  $0.0 \leq E \leq 1.4 \text{ V vs. Ag}/\text{Ag}^+(\text{CH}_3\text{CN})$ ,  $\nu = 0.02 \text{ V s}^{-1}$ ], potentiostatic (PST;  $E_{\text{app}} = 1.4 \text{ V}$ ) or galvanostatic (GST;  $j = 0.7, 0.5$  and  $0.25 \text{ mA cm}^{-2}$ ) methods. Layers of different thickness were obtained by varying the number of voltammetric cycles performed (PDN), or by altering the potential/time (PST) or current/time (GST) parameters, in order to produce

a deposition charge ( $Q_{\text{dep}}$ ) between 30 and 60  $\text{mC cm}^{-2}$ . Deposited films were washed several times with  $\text{CH}_3\text{CN}$  to remove unreacted TDNB monomer and excess electrolyte. The morphological characteristics of the films were determined by atomic force microscopy (AFM) using a Shimadzu SPM-9500 J3 instrument in the contact mode with Olympus probes ( $\text{Si}_3\text{N}_4$ ). Spectroelectrochemical studies of the polymer film deposited on ITO were carried out in a solution of  $\text{LiClO}_4$  ( $0.1 \text{ mol L}^{-1}$ ) in  $\text{CH}_3\text{CN}$  by varying the potential within the range  $-2.0$ – $0.8 \text{ V}$ . Spectra were acquired in the range  $350 \leq \lambda \leq 800 \text{ nm}$  in tandem with the electrochemical measurements.

### 3. Results and discussion

#### 3.1. Electrodeposition of poly(TDNB) films

Initial attempts to produce poly(TDNB) films by electro-synthesis employed a  $(\text{C}_4\text{H}_9)_4\text{NBF}_4/\text{CH}_3\text{CN}$  solution as electrolyte. However, a series of cyclic voltammograms scanning the range  $0.0 \leq E_\lambda \leq 2.2 \text{ V}$ , with  $E_\lambda$  increasing in steps of  $0.100 \text{ V}$ , revealed that the TDNB oxidation did not occur (Fig. 2A). Further experiments, using PST method, showed no nucleation looping, making evident that the polymerisation process is not possible in this electrolyte/solvent system, in the potential range investigated. When BFEE (20%) was added to the  $(\text{C}_4\text{H}_9)_4\text{NBF}_4/\text{CH}_3\text{CN}$  electrolyte system, oxidation of

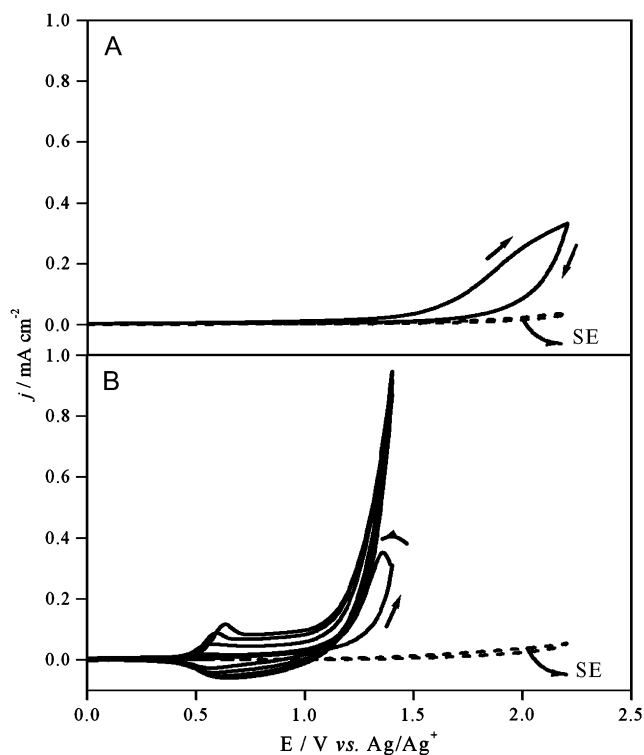


Fig. 2. Cyclic voltammograms ( $\nu = 0.02 \text{ V s}^{-1}$ ) of the potentiodynamic electrodeposition of poly(TDNB) on ITO electrodes using an electrolyte system consisting of (A)  $0.20 \text{ mol L}^{-1} (\text{C}_4\text{H}_9)_4\text{NBF}_4/\text{CH}_3\text{CN}$  and (B)  $0.20 \text{ mol L}^{-1} (\text{C}_4\text{H}_9)_4\text{NBF}_4/\text{CH}_3\text{CN}$  containing BFEE (20% by volume), film was deposited over 5 cycles ( $Q_{\text{dep}} = 53.5 \text{ mC cm}^{-2}$ ). SE = supporting electrolyte.

TDNB was initiated at about  $1.4 \text{ V}$  (Fig. 2B) and was accompanied by polymerisation, as confirmed by the presence of the nucleation loop in the reverse scan and by the cathodic peak at ca.  $0.55 \text{ V}$ , which was associated with poly(TDNB) reduction.

Cyclic voltammograms of the electrodeposition of poly(TDNB) film employing a PDN method involving 5 cycles are shown in Fig. 2B. Film formation was confirmed by the presence of polymer reduction/oxidation waves at  $0.55$ – $0.65 \text{ V}$ . The cyclic voltammograms showed a strong hysteresis between the positive and negative scans, and the shift in peak potentials provided information concerning the increase in electrical resistance in the polymer film and the overpotential required to overcome this resistance [38]. The integration of voltammetric charges revealed a logarithmic grow up of anodic scan which stabilises in the 5th cycle at  $\sim 14 \text{ mC cm}^{-2}$ , against  $\sim 3.0 \text{ mC cm}^{-2}$  for the cathodic scan, giving a  $Q_a/Q_c$  ratio of 4.8. Due to this charge ratio, the increase of net charge was still obtained during further cycles and resulted in very irregular films, that exhibited poor and undefined fractal deposits, according AFM images. Thus, at the 5th cycle, the net charge is  $\sim 40 \text{ mC cm}^{-2}$ .

The deposition of poly(TDNB) films using the PST method was performed by applying a potential ( $E_{\text{app}}$ ) of  $1.4 \text{ V}$  (chosen on the basis of the cyclic voltammograms shown in Fig. 2B) for 30–120 s in order to obtain  $Q_{\text{dep}}$  values that varied between 30 and  $60 \text{ mC cm}^{-2}$ .

Using the GST method, poly(TDNB) films were obtained at different deposition charges by employing current densities of 0.7, 0.5 and  $0.25 \text{ mA cm}^{-2}$ . High current densities ( $j > 0.5 \text{ mA cm}^{-2}$ ) provoked polymer overoxidation as indicated by the  $E$  vs. time curves shown in Fig. 3. More efficient deposition could be obtained using a current density of  $0.25 \text{ mA cm}^{-2}$ , which produced very homogeneous films that adhered well to the electrode surface.

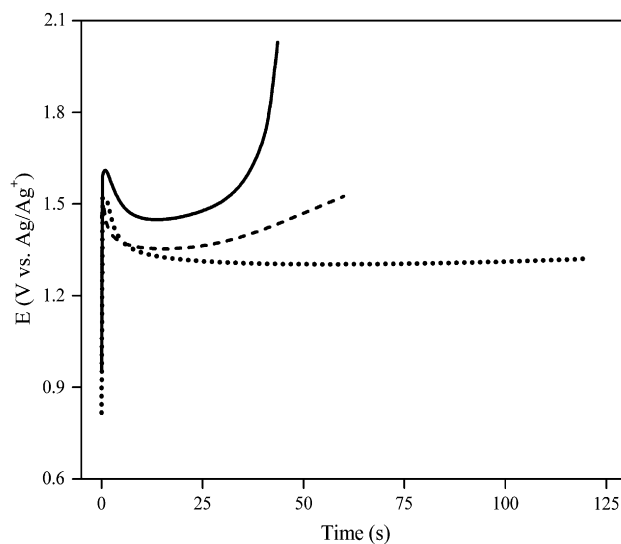


Fig. 3. Galvanostatic curves recorded during the deposition of poly(TDNB) films using the GST method with current densities of 0.7 (—), 0.5 (---) and  $0.25 \text{ mA cm}^{-2}$  (····).

### 3.2. Surface characteristics of poly(TDNB) films

The surfaces of the deposited poly(TDNB) films were mapped and their morphological parameters determined using an AFM technique. Measurements were performed *ex situ* using undoped films that had been washed with CH<sub>3</sub>CN after electrodeposition and then dried. Characteristic three-dimensional AFM images of films obtained by PDN, PST or GST deposition are shown in Fig. 4A–C, respectively, together with the corresponding Gaussian analyses of the film grain heights that were used to acquire square average roughness (RMS) and relative superficial area values as presented in Table 1.

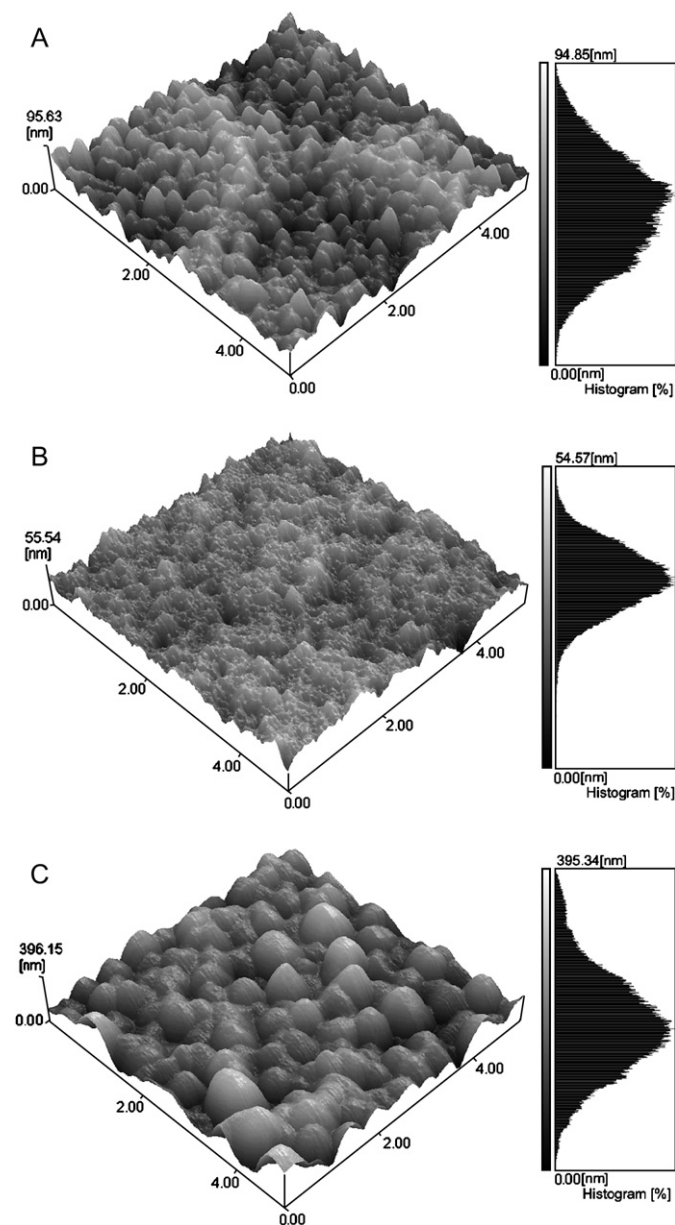


Fig. 4. Three-dimensional AFM images of poly(TDNB) films obtained using (A) the PDN method with  $Q_{\text{dep}} = 53.5 \text{ mC cm}^{-2}$ , (B) the PST method with  $Q_{\text{dep}} = 43.5 \text{ mC cm}^{-2}$ , and (C) the GST method with  $Q_{\text{dep}} = 45.0 \text{ mC cm}^{-2}$ . The right side insets show the corresponding Gaussian analysis of the grain height of the film.

Table 1

Values for RMS roughness and relative superficial area of poly(TDNB) films deposited by various electrochemical methods

Deposition method	Experimental conditions	$Q_{\text{dep}}$ ( $\text{mC cm}^{-2}$ )	RMS <sup>a</sup> (nm)	Relative surface area <sup>a</sup> ( $\mu\text{m}^2$ )
PDN	$0 < E < 1.4 \text{ V}$ , $\nu = 0.02 \text{ V s}^{-1}$	53.5	13.73	1.020
PST	$E_{\text{app}} = 1.4 \text{ V}$	43.5	5.85	1.006
GST	$j = 0.25 \text{ mA cm}^{-2}$	45.0	62.92	1.151

<sup>a</sup> RMS and RSA values calculated from the Gaussian analyses of the grain heights of the films (*cf.* Fig. 4).

The basic geometries of poly(TDNB) films deposited using the PDN or GST methods were similar in that both were composed of globular grains (Fig. 4A and C). However, films formed by GST deposition presented grains that were better defined and larger (mean radius *ca.* 400–700 nm) than those of PDN-produced films (mean radius *ca.* 200–500 nm). Clearly, the potential cycling inherent in the PDN method gives rise to a multi-nucleation process that results in a surface with small, but well-dispersed, grains. Films deposited using the PST method are much more compact when compared with others and exhibited “sponge-like” surfaces displaying absence of grain formation. It is likely that this morphology resulted from the overoxidation of polymer occasioned by the maintenance of a high potential (1.4 V) throughout the deposition time. These two morphology types are intrinsically linked to the electrochemical character of each deposited polymer, where the PST deposits presented lower quality for electrochemical devices, as observed in voltammetric response of quasi-hysteretic shape. The molecular level justify for the electrochemical behaviour and the compact morphology of PST method is cleavage of the  $\pi$ -conjugation [12–14].

### 3.3. Spectroelectrochemical properties of poly(TDNB) films

Cyclic voltammograms of the poly(TDNB) films were acquired using a LiClO<sub>4</sub>/CH<sub>3</sub>CN rather than a (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBF<sub>4</sub>/CH<sub>3</sub>CN electrolyte system, since the former generated a superior electrochromic response. Moreover, future electrochromic devices employing poly(TDNB) films will be assembled using a polymer electrolyte containing LiClO<sub>4</sub>.

The cyclic voltammograms showed single, well defined waves at the anodic region with an anodic peak ( $E_{\text{pa}}$ ) at  $0.67 \pm 0.04 \text{ V}$  and a cathodic peak ( $E_{\text{pc}}$ ) at  $0.59 \pm 0.01 \text{ V}$  (Fig. 5). This redox couple is attributed to the polymer *p*-doping process, and the difference between  $E_{\text{pa}}$  and  $E_{\text{pc}}$  ( $\Delta E_{\text{p}} \sim 0.081 \text{ V}$ ) indicates that the system displays quasi-reversible behaviour. Typically,  $\Delta E_{\text{p}}$  values for conducting polymers are between 0.15 and 0.20 V, and are assigned to structural reorganisation processes within the film [39,40].

A poorly defined redox pair associated with the reduction of the nitro group could be observed at the cathodic region of the cyclic voltammograms (Fig. 5). In CH<sub>3</sub>CN, nitro group reduction is considered to be reversible through a mechanism involving the generation of an anion radical and/or a dianion



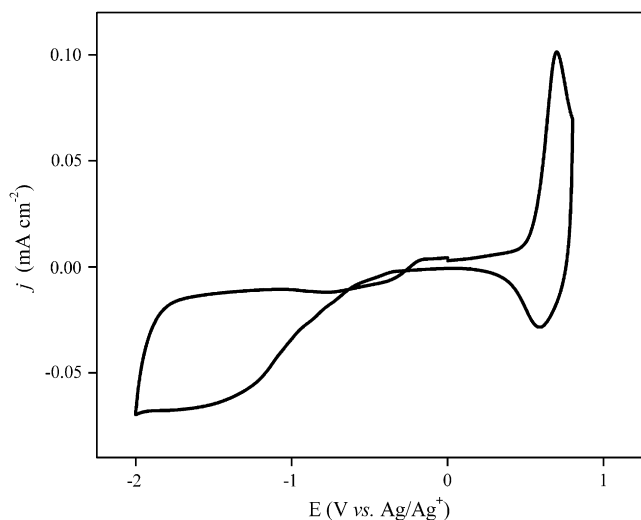


Fig. 5. Cyclic voltammogram ( $0.1 \text{ mol L}^{-1} \text{ LiClO}_4/\text{CH}_3\text{CN}$ ;  $\nu = 0.02 \text{ V s}^{-1}$ ) of a poly(TDNB) film deposited on an ITO electrode using the PDN method.

[17], but in the polymeric films the nitro group exhibited a capacitive behaviour within the potential range  $-2.0$  to  $-0.6 \text{ V}$ . Such behaviour can be related to polymer  $n$ -doping, in which the cation enters the polymeric structure to neutralise the negative charge formed during the reduction process.

The changes in the UV–vis spectrum of a poly(TDNB) film plotted as a function of the potential applied to the electrode during cyclic voltammetry are presented in Fig. 6. Poly(TDNB) films held at potential ( $E = 0.0 \text{ V}$ ) exhibited an electronic band gap (defined as the onset potential for  $\pi$ – $\pi^*$  transition) of *ca.*  $2.92 \text{ eV}$  and appeared yellow in colour with an absorbance band  $\lambda_{\text{max}}$  of  $425 \text{ nm}$ . The spectra of the

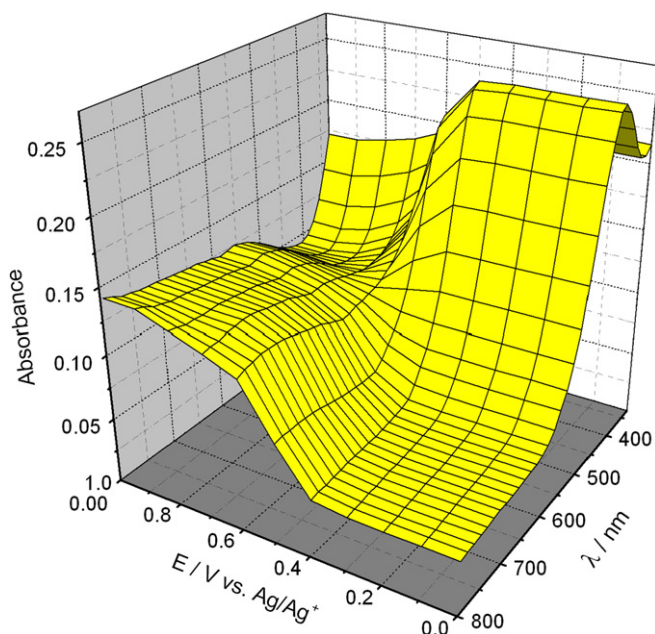


Fig. 6. Spectroelectrochemical characterisation ( $0.1 \text{ mol L}^{-1} \text{ LiClO}_4/\text{CH}_3\text{CN}$ ) of a poly(TDNB) film deposited on an ITO electrode using the PDN method showing absorbance as a function of the applied potential.

polymer obtained by chemical polymerisation of TDNB (using  $\text{FeCl}_3$ ) revealed a very near absorption band at  $423 \text{ nm}$  in the reduced state [37]. Following a stepwise increase in the applied potential, the intensity of the  $\pi$ – $\pi^*$  transition decreased and an absorbance broad band with  $\lambda_{\text{max}}$   $750 \text{ nm}$  ( $1.65 \text{ eV}$ ) became apparent indicating the evolution of polaron charge carriers [39]. The blue-like appearance of this polymer is revealed when the oxidation potential shifts to values above  $0.6 \text{ V}$ . This colour is obtained by the large plateau in the range  $500$ – $700 \text{ nm}$  during the oxidation process, as denoted in Fig. 6. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) Although, for potential above  $0.6 \text{ V}$  the electrochemical properties changed due to overoxidation.

#### 4. Conclusions

TDNB did not present any sign of polymerisation in the useful potential range allowed by the supporting electrolyte/solvent system used. On the other hand, the addition of a Lewis acid (BFEE) aid in the polymerisation process due the displacement of the oxidation potential of TDNB, attributed to the formation of  $\pi$ -complexes with BFEE. This fact opens opportunities for a very easy way to do polymerisation in a series of derivatised monomers not yet studied due to its high oxidation potential.

The comparison between the 3 methods of electrodeposition revealed that GST resulted in a better defined morphological structure, when compared with PDN and PST methods. This occurs due to the ability to control  $Q_{\text{dep}}$ , which is inherent to the method. Another advantage is the fine control of oxidation process, maintaining the potential safe enough to avoid overoxidation.

Cyclic voltammograms revealed a redox pair at the anodic region, related to polymer doping/un-doping, and a redox pair at the cathodic region, attributed to the reduction of the nitro groups present in the polymer. In the neutral state, poly(TDNB) films were yellow but became light blue-gray in the doped state. Through exploitation of their inherent electrochromism and  $p$ - and  $n$ -doping capacities, poly(TDNB) films may have potential application in the production of a range of optical and electrochemical devices. Once some possible applications of the polymer are considered, the chiral character of amino-acid linkage can also be useful as enantioselective inductor for asymmetric electrosynthesis or for specific sensors.

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