



# Electrosynthesis and characterisation of poly(safranine T) electroactive polymer films

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## ABSTRACT

The phenazine safranine T has been electropolymerised by potential cycling at carbon film electrodes in nitrate-containing solutions at different pH: 2.0, 5.5, and 7.0, as well as from chloride solution, pH 5.5. The electroactive polymer obtained, poly(safranine T), has been analysed by cyclic voltammetry in different electrolyte solutions and its morphology examined using scanning electron microscopy. The surface coverage was calculated and found to be the highest for the film formed in chloride solution, pH 5.5, with  $8.7 \text{ nmol cm}^{-2}$ . The other films had lower coverages, from 5.3 to  $7.8 \text{ nmol cm}^{-2}$ , and are similar to those obtained for other phenazine dye polymers. Although the fastest polymerisation occurred in solutions at pH 5.5, the best electrochemical properties resulted from electropolymerisation at pH 2.0. Analysis of the cyclic voltammograms showed that in most cases the electrochemical processes at the polymer coated electrodes are limited by surface reactions. Scanning electron microscopy data confirmed the results obtained by cyclic voltammetry and showed that the most compact film was obtained in chloride solution.

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## 1. Introduction

Polymer films possessing conductive properties have become attractive for many purposes since the electrosynthesis of polyaniline [1,2]. Many other semiconducting polymer films have been reported, in particular polypyrrole, polyphenols, polythiophene [3,4], as well as polymer films electrodeposited from substituted monomers [3–6]. Some of these polymers also exhibit electrocatalytic properties and they have been widely applied in the preparation of different sensing surfaces [3,7].

A special interest is that of polymers with direct charge transport properties and which can therefore serve as redox mediators [3,7]. Such films can be formed from azines, particularly various phenazines, by electropolymerisation of their monomers [7,8]. The most-used azines for this purpose, as polymeric mediator, that have been reported so far are azur A [9,10], methylene blue [7,11–17], methylene green [7,12,13,17], neutral red [7,12–18], brilliant cresyl blue [12,13], phenothiazine [12,13], toluidine blue [7,12,13], and phenosafranine [19,20].

Safranine T (ST), 3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride (Fig. 1), is a water-soluble red-coloured phenazine-type dye used in the textile, pharmaceutical, paper and cosmetic industries [21] and as a marker in biological processes [22]. This dye, like many phenazine dyes, is difficult to degrade due to its complex structure and one of the ways to achieve this is electrochemical degradation [21].

The application of the dye monomer as a mediator in a biosensing system with nitrite and nitrate reductase has been reported [23].

A redox polymer containing safranine has been prepared by a chemical procedure [24]. The amine groups present in safranine O were condensed with poly(methacryloylchloride) in dry dimethylformamide and allowed to reflux for a few days; the product was then precipitated by addition of water to the reaction mixture. A structure of the product was not given, but cross-linking due to reaction of both amino groups in safranine O molecules was seen as being possible. The important role of counterion diffusion during the polymer redox processes was demonstrated.

In other work, a polysafranine dye derivative poly[5-phenyl-7-(N,N-diethylamino) phenazinium] chloride, was prepared by decomposition of the diazonium salt of 3-amino[5-phenyl-7-(N,N-diethylamino) phenazonium] chloride, and was used as a levelling component for electrodeposited copper coatings [25].

The chemical oxidative polymerisation of safranine and phenosafranine using peroxydisulfate initiator has been recently reported together with structural characterisation of the oligomers formed by Fourier transform infrared, Raman and ultraviolet spectroscopies [26]. Safranine, dissolved in dilute hydrochloric acid, was oxidized by addition of ammonium peroxydisulfate at room temperature to give, as product after 24 h, a dark red insoluble precipitate suspended in the colourless aqueous medium. The polymerisation mode was determined to be coupling of the monomer molecules to give oligomeric-type structures with a molecular mass of several thousand, corresponding to about 20 monomer units. Some parameters of the polysafranine obtained were determined: conductivity  $6.2 \times 10^{-10} \text{ S cm}^{-1}$ ; density  $1.34 \text{ g cm}^{-3}$ ;

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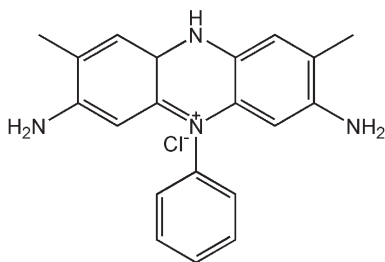


Fig. 1. Chemical structure of safranin T (3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride).

molecular weight,  $M_w$ , 45,000; soluble in *N*-methylpyrrolidone and dimethylsulfoxide [26].

Carbon film electrodes are attractive supports for mediator-based sensors because they are cheap, easy to produce, small and are adaptable as disposable or short-term use sensors or biosensors [27–29]. They have properties similar to those of glassy carbon and after electrochemical pre-treatment have a large potential window and low background current [30]. Recently, electrochemical enzyme biosensors on carbon film electrode supports have been investigated using various poly(azine) dyes – poly(neutral red), poly(methylene blue) and poly(methylene green) – for measurements in complex matrices [14–18].

The present work aims to study the electrochemical polymerisation of ST in different media and characterise the polymer films obtained using cyclic voltammetry and scanning electron microscopy.

## 2. Experimental details

### 2.1. Materials and reagents

Safranin T was obtained from La Chema (Czech Republic). KCl was from Reachim (Russia),  $\text{HNO}_3$  and HCl were from Sigma,  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$  were purchased from Riedel-de Haen (Germany). All solutions were analytical grade purity and were used as obtained without any further purification. Purified water (conductivity  $\leq 1 \mu\text{S cm}^{-1}$ , DEMIWA 10rosa system, Watek, Czech Republic) was used for preparation of all solutions.

### 2.2. Electrode preparation

Cylindrical carbon film electrodes were made from carbon film resistors of diameter 1.5 mm and length 6 mm (resistance  $\sim 1.5 \Omega$ ). The electrode preparation protocol is described elsewhere [30,31]. The exposed electrode geometric area was  $\sim 0.20 \text{ cm}^2$ . Prior to first use, the electrodes were electrochemically pre-treated by cycling the applied potential between 0.0 and +1.0 V vs. Ag/AgCl in 0.1 M  $\text{KNO}_3$  solution for not less than 10 cycles, until stable cyclic voltammograms were obtained.

Poly(safranin T) (PST) films were obtained by electrochemical polymerisation, cycling the applied potential from  $-0.8$  to  $1.2$  V vs. Ag/AgCl at scan rate  $50 \text{ mV s}^{-1}$  in the polymerisation solution containing 0.5 mM ST, and different electrolytes: 10 mM  $\text{HNO}_3$  + 100 mM  $\text{KNO}_3$  (S1), 50 mM phosphate buffer (pH 5.5) + 100 mM  $\text{KNO}_3$  (S2), 50 mM phosphate buffer (pH 7.0) + 100 mM  $\text{KNO}_3$  (S3), or 50 mM phosphate buffer (pH 5.5) + 100 mM KCl (S4). The polymer films obtained from the polymerisation solutions S1, S2, S3 and S4 will be referred to as PST1, PST2, PST3 and PST4, respectively.

### 2.3. Instruments

A three-electrode electrochemical cell was used for electrochemical measurements. It contained a PST-coated carbon film working electrode, a platinum foil as counter electrode, and an Ag/AgCl/sat.

KCl electrode served as reference. Electrochemical measurements were performed using a computer-controlled BAS Epsilon potentiostat/galvanostat analyser running with DigiSim software (BAS, West Lafayette, IN, USA).

The pH measurements were carried out with a Mettler Toledo pH-meter.

The surfaces of the samples were examined using an EVO 50EP (Carl Zeiss SMT AG, Germany) scanning electron microscope. All observations were carried out with a secondary electron (SE) detector in high-vacuum mode at 15 kV accelerating voltage.

## 3. Results and discussion

### 3.1. Electropolymerisation of safranin T

ST was polymerised electrochemically by cycling the applied potential from  $-0.8$  to  $1.2$  V vs. Ag/AgCl 18 times in solutions of different composition in order to find the best polymerisation conditions. Since it is known that  $\text{NO}_3^-$  catalyses the polymerisation of some phenazine derivatives such as neutral red and methylene blue [12], potassium nitrate electrolyte solutions were used at different pH: 2.0 (S1), 5.5 (S2), and 7.0 (S3). At higher pH, in strongly alkaline media, ST does not form a stable polymer, the same happens with neutral red [12]. Potentiodynamic mode was chosen because it is simple to observe film growth by following the changes in cyclic voltammograms. The potential window has been chosen in order to follow the peaks of the redox processes of monomer/polymer ( $\sim -0.55$  V vs. Ag/AgCl) and irreversible monomer oxidation (between 0.9 and 1.0 V) and the position of these peaks varied only

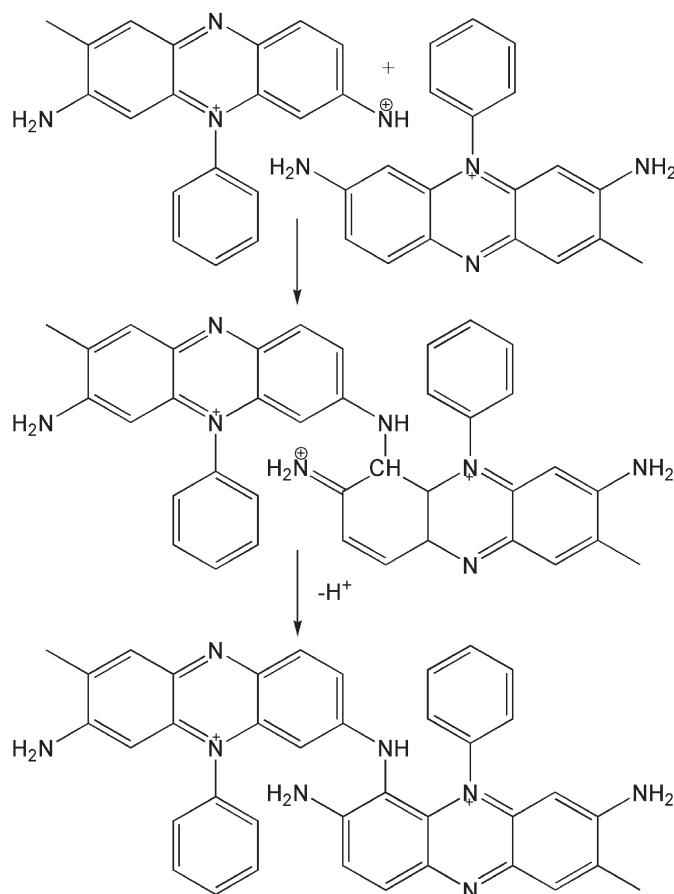
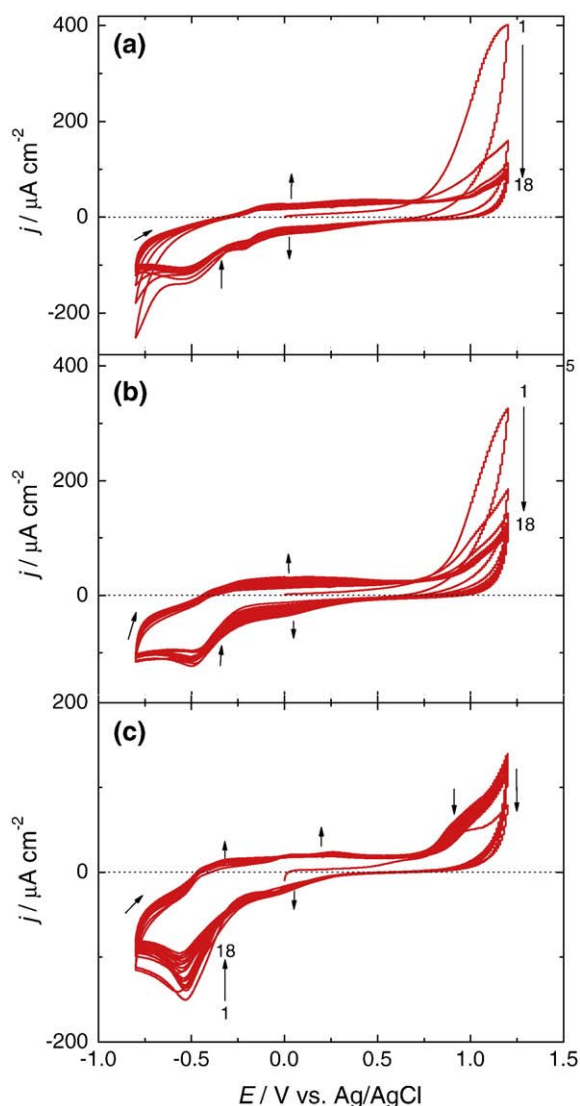


Fig. 2. Mechanism of dimer formation from safranin T.



**Fig. 3.** Cyclic voltammograms recorded during the polymerisation of ST from different solutions containing 0.5 mM ST and (a) 10 mM  $\text{HNO}_3$  + 100 mM  $\text{KNO}_3$  (pH 2.0), S1; (b) 50 mM phosphate buffer (pH 5.5) + 100 mM  $\text{KNO}_3$ , S2; (c) 50 mM phosphate buffer (pH 7.0) + 100 mM  $\text{KNO}_3$ , S3. Scan rate  $50 \text{ mV s}^{-1}$ .

slightly with changes in solution pH. Therefore, the same potential window for electrochemical polymerisation was chosen in all cases.

Polymerisation occurs via formation of dications and their reaction with other monomer molecules, together with deprotonation, as presented in Fig. 2. Dications are obtained in the reactions of the radicals formed during electrochemical oxidation by reaction with ST monomers [26]. The dimers formed can then react with other monomer molecules or dimers to increase chain length and form oligomers and polymer chains. Since deprotonation is involved, the polymerisation rate may vary with solution pH.

Further investigations in order to determine if the polymer was linear or cross-linked were not performed, but judging from the data of dimerisation in Ref. [26] a cross-linked polymer would be expected. However, it can be supposed that, as in the case of many other electrochemically obtained polymers, such as polyaniline [32] or poly(neutral red) [33], linear and/or cross-linked structures of PST can be obtained depending on the deposition conditions, i.e. potentiostatic or potentiodynamic deposition conditions.

Cyclic voltammograms illustrating the electropolymerisation of ST are presented in Fig. 3. All voltammograms show two redox couples

and one irreversible oxidation, similar to what was obtained in Ref. [21] at Pt electrodes. The first redox couple at  $-0.5 \text{ V}$  is the redox process for  $\text{ST}_{\text{ox}}/\text{ST}_{\text{red}}$ , as found for neutral red [33]. In all cases the reduction peak decreases with the number of cycles due to changes to the surface after polymerisation; however, the oxidation peak height increases, thus showing the formation of the polymer film. This redox couple was found to be the best defined in S3 solution. The second, less well-defined redox couple, appears at  $\sim 0 \text{ V}$  due to doping and dedoping of the film. These peaks increased in height with the number of cycles which confirmed growth of the film with insertion/extraction of counterions. A further reduction wave at  $-0.25 \text{ V}$  in acidic solution also decreases in size with the number of cycles, which indicates that the  $\text{ST}_{\text{ox}}/\text{ST}_{\text{red}}$  reduction process occurs in two steps. The final oxidation peak at  $\sim +1.0 \text{ V}$  is due to irreversible oxidation of the monomer. This peak decreases in size with the number of cycles and shifts towards more positive potentials due to changes during the polymerisation and to local changes of pH at the electrode surface, similar to what is observed at poly(neutral red) (PNR) [12–18], azur A [10], and toluidine blue [12,13,34].

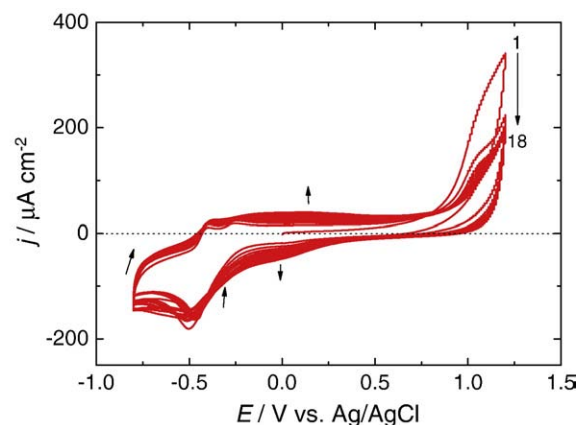
The fastest film formation was obtained from polymerisation solution S2 (phosphate buffer solution, pH 5.5, with potassium nitrate), Fig. 3b, because deprotonation of dimers and oligomers was faster at this pH (Fig. 2). Similar optimum polymerisation conditions have been observed when polymerising neutral red [7,12–18].

In order to demonstrate the influence of nitrate ions in electro-synthesis, potassium nitrate was replaced by potassium chloride in the best electropolymerisation solution (S2), that is S4 (50 mM phosphate buffer solution, pH 5.5 + 100 mM KCl) was used as polymerisation solution. The redox peaks were better defined in this case as seen from Fig. 4, probably due to the smaller counter anion, which penetrates the polymer film more easily. However, the growth of the PST4 film, observed from the CVs, was rather similar to that from nitrate solution (Fig. 3b).

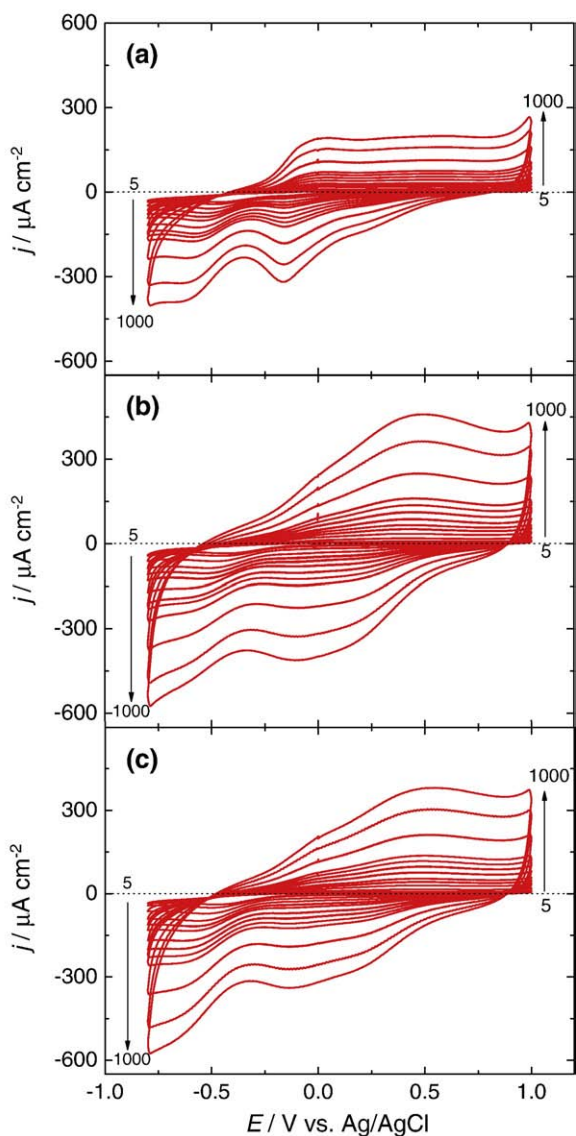
The surface coverage was calculated from the charge under the reduction peak at  $\sim -0.5 \text{ V}$  for all polymer films obtained in  $\text{KNO}_3$  (KCl in the case of PST4) solution, and was found to be  $7.8 \text{ nmol cm}^{-2}$  of monomer units for PST1,  $7.0 \text{ nmol cm}^{-2}$  for PST2,  $5.3 \text{ nmol cm}^{-2}$  for PST3, and the highest surface coverage was obtained for the film polymerised from chloride solution, PST4, at  $8.7 \text{ nmol cm}^{-2}$ .

### 3.2. Electrochemical characterisation of poly(safranin T)

All types of PST film (PST1, PST2, PST3, and PST4), obtained by electropolymerisation as described in the previous section, were examined electrochemically by cyclic voltammetry in 0.1 M  $\text{HNO}_3$ ,



**Fig. 4.** Cyclic voltammograms recorded during the polymerisation of ST from solutions containing 0.5 mM ST and 50 mM phosphate buffer (pH 5.5) + 100 mM KCl, S4. All other conditions as in Fig. 3. Scan rate  $50 \text{ mV s}^{-1}$ .



**Fig. 5.** Cyclic voltammograms recorded in 0.1 M  $\text{HNO}_3$  of PST films, electropolymerised from (a) S1, (b) S2, and (c) S3. Scan rates: 5, 10, 25, 50, 75, 100, 150, 200, 250, 300, 500, 750, and 1000  $\text{mV s}^{-1}$ .

0.1 M  $\text{KNO}_3$ , 0.1 M KCl and phosphate buffer pH 3.5–7.0 in order to investigate their electrochemical stability and redox behaviour.

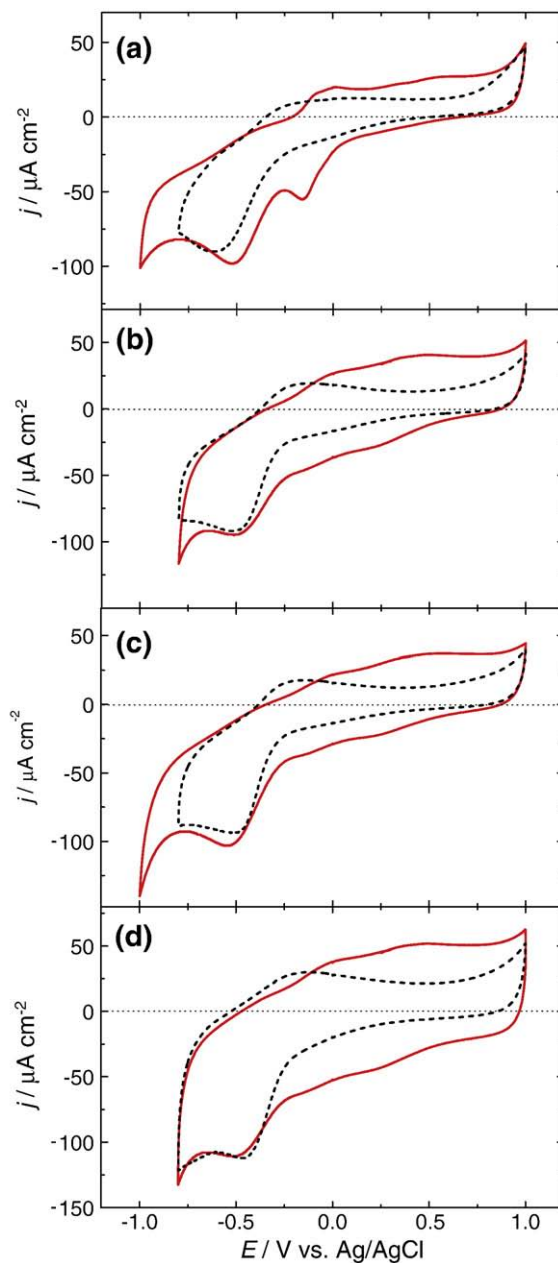
**Fig. 5** presents cyclic voltammograms at different scan rates in 0.1 M  $\text{HNO}_3$  solution. The PST1 film, made in acidic solution (S1), exhibited the best-defined redox peaks even at high scan rates, as seen from **Fig. 5a**. The dependence of peak current was linear with the square root of the potential scan rate. The slopes of the lines were 2.7 and  $-7.9 \mu\text{A cm}^{-2} \text{mV}^{-1/2} \text{s}^{1/2}$  for oxidation and reduction, respectively. These data show that surface processes controlled the total electrochemical reaction, most probably the absorption of counter ions and doping of the film.

PST2 and PST3 exhibited similar behaviour in nitric acid solution in the potential range from  $-0.8$  to  $1.0$  V vs. Ag/AgCl, **Fig. 5b,c**. A redox couple was observed at  $-0.5$  V for  $\text{PST}_{\text{ox}}/\text{IPST}_{\text{red}}$ , which becomes misshapen at high scan rates, so that the quantitative dependence of peak current on scan rate could not be evaluated. The second redox couple was broad and turned into two-redox-wave peaks at high scan rates. It is probable that the charge compensation by counter anion and cation is separated at high scan rates.

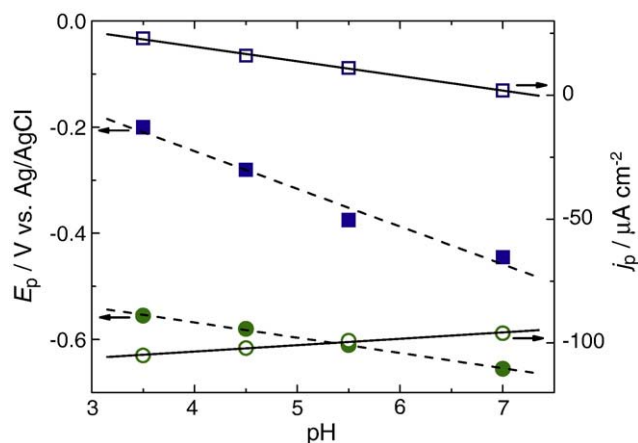
PST4 films in nitric acid exhibited a similar behaviour to PST2 (not shown) except that redox currents were higher, probably due to thicker films.

In  $\text{KNO}_3$  solution, all films exhibited less-well defined cyclic voltammograms, particularly at high scan rates. This is probably due to a lesser ability of  $\text{K}^+$  to penetrate the polymer film than  $\text{H}^+$ , as observed in the case of PNR [35]. Moreover, there were even less-well-defined peaks of the films at different scan rates in KCl solution than in  $\text{KNO}_3$  which confirms the fact that  $\text{NO}_3^-$  is a better counter anion than other monovalent anions, as occurs with other phenazine polymers [7,12].

**Fig. 6** compares CVs at the different types of PST film in  $\text{HNO}_3$  and  $\text{KNO}_3$  solutions, and in HCl and KCl in the case of films electropolymerised from S4, which confirm the above deductions of easier charge compensation by  $\text{H}^+$  than by  $\text{K}^+$ , since the redox peaks are always better defined in acid than in neutral solutions.



**Fig. 6.** Cyclic voltammograms of PST films electropolymerised from (a) S1, (b) S2, (c) S3, and (d) S4 recorded in 0.1 M  $\text{HNO}_3$  (0.1 M HCl in (d)) (—), and 0.1 M  $\text{KNO}_3$  (0.1 M KCl in (d)) (---). Scan rate 50  $\text{mV s}^{-1}$ .



**Fig. 7.** Dependence of  $PST_{ox}/PST_{red}$  peak potential,  $E_p$ , and peak current density,  $j_p$ , on solution pH in 50 mM phosphate buffer solution. Squares indicate oxidation and circles reduction; filled symbols refer to  $E_p$  and unfilled symbols to  $j_p$ .

PST2 films, chosen owing to the best definition of the redox peaks, were subjected to potential cycling in phosphate buffer at different pH values from 3.5 to 7.0 in order to investigate the variation of peak potential and peak current with pH. A linear dependence of peak potential as well as of peak current on pH was obtained, see Fig. 7. However, the slopes were different for reduction and oxidation processes:  $-4$  and  $2 \mu A cm^{-2} pH^{-1}$  for oxidation and reduction current, respectively, and  $-76 mV pH^{-1}$  for oxidation and  $-27 mV pH^{-1}$  for the variation of reduction peak potential. These latter values suggest that an equal number of electrons and protons was involved in the oxidation process; however, the reduction process is more complicated since the electron:proton ratio was 2:1, that can be attributed to the release of a counter anion that occurs during this reaction [30]. Square wave voltammetry studies (not shown) were performed to calculate the number of electrons involved in the electrode reactions. At some films it was not possible to estimate the number of the electrons from the peak width at half height, since monomer and polymer oxidation/reduction formed a double peak. Therefore, the

dependence of peak potential on the logarithm of square wave frequency was applied according to Ref. [36]:

$$\frac{E_p}{\log f} = \frac{2.3RT}{\alpha nF} \quad (1)$$

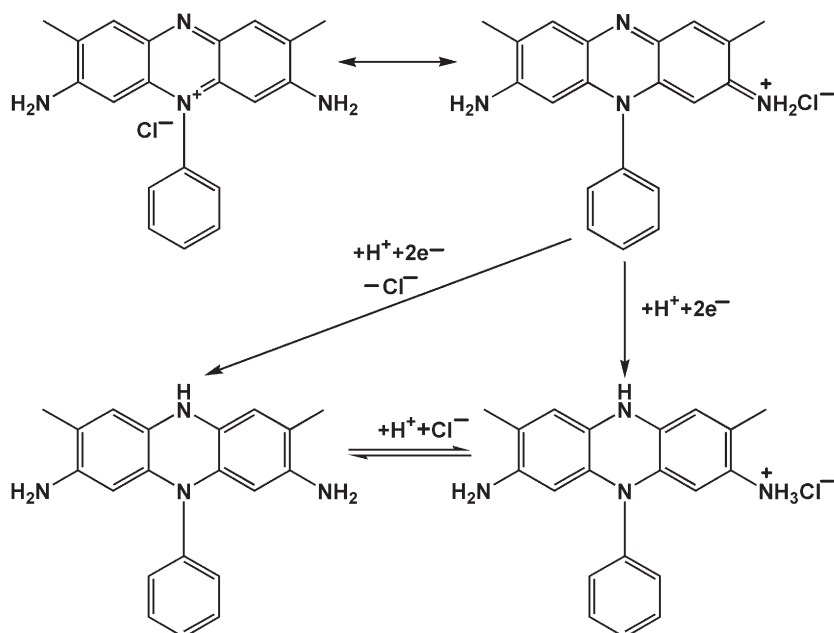
From this, it was found that 2 electrons took part in both the oxidation and reduction electrochemical reactions. Taking into account the variation of peak potential with pH, this corresponds to two protons in the oxidation and one in the reduction.

Since ST is a phenazine compound, the redox mechanism is probably similar to that of either neutral red [37,38] or phenosafranin [39], and is referred to in Ref. [26] for the dimeric species. The monomer and polymer redox mechanism can be similar, as assumed with poly(neutral red), since the monomer and polymer redox peaks overlap [16,37]. A possible scheme, analogous to that in Ref. [37] for neutral red, is given in Fig. 8. This scheme shows how the monomer reduction and oxidation reactions can be different, if the protonation of the amine group in the newly-produced reduced species is relatively slow, but that of the ring nitrogen is fast in the pH range tested. The protonation can be regarded as the rate-determining process, since the movement of counter anions is likely to be significantly slower. In the polymer, some breaking and formation of bonds between amine groups and adjacent aromatic rings can also be invoked [26].

### 3.3. Surface characterisation of poly(safranin T)

All four PST films were characterised by scanning electron microscopy. In order to identify better the PST films an image of a bare carbon film was taken prior to coating it with the polymer, Fig. 9a. The bare carbon film has a non-uniform rough surface structure having some "hills" and "valleys" (not shown).

The PST1 film looked rather smooth and followed the morphology of the carbon film substrate surface as observed from cyclic voltammetry. Furthermore, at high amplification the polymer coating appeared to reduce the substrate roughness (Fig. 9b). The PST2 film had a different surface morphology and did not follow the contours of the substrate surface so precisely (Fig. 9c) and appeared to form clusters at some points. A similar PST film was obtained following electropolymerisation from S3 (Fig. 9d), but appeared smoother than PST2 at low



**Fig. 8.** Possible mechanism of electrochemical redox reactions of ST.

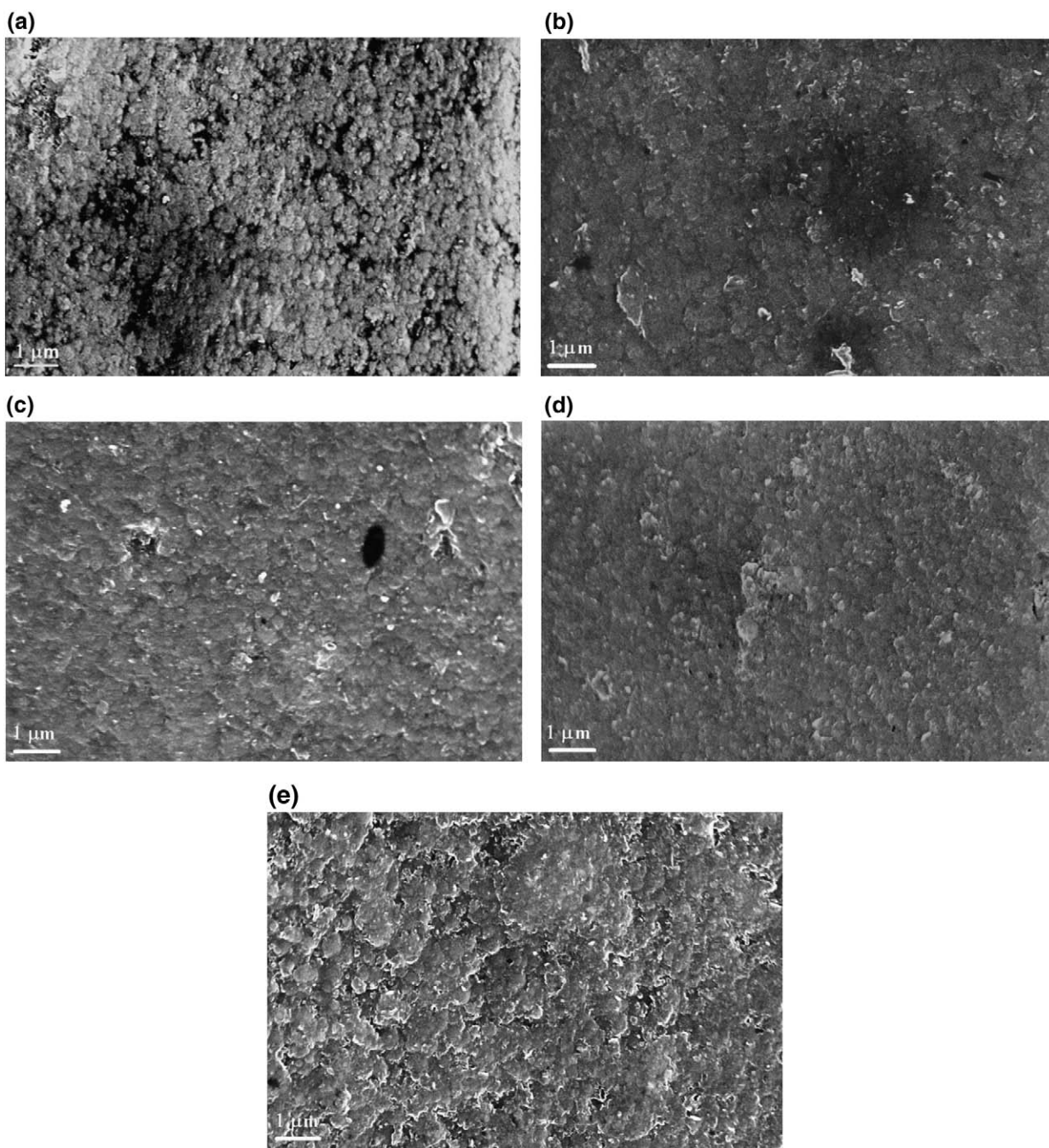


Fig. 9. Scanning electron microscopy images of (a) bare carbon film and of PST films electropolymerised from 0.5 mM ST: (b) PST1; (c) PST2; (d) PST3; (e) PST4.

magnification. However, a totally different surface morphology was observed for PST4 films, prepared in KCl solution, Fig. 9e. This film was thicker than the previous ones and it consisted of overlapping layers, like in mica's cross-section. This film was not smooth and had some fissures. None of the films studied had features in the shape of nanowires that are sometimes observed, for example in the case of PNR electropolymerised from strongly acidic media (pH 1.0,  $H_2SO_4$ ) on the Pt substrate [37].

The results obtained using scanning electron microscopy support the data from cyclic voltammetry as well as from the calculated surface coverage.

#### 4. Conclusions

PST has been obtained by electropolymerisation of ST on carbon film electrodes by potential cycling in nitrate solutions at different

pH: 2.0, 5.5, and 7.0, as well as from chloride solution, pH 5.5. The best electropolymerisation in terms of current growth with the number of cycles of the film observed by cyclic voltammetry was found to be in chloride solution, pH 5.5.

The films obtained were characterised using cyclic voltammetry and scanning electron microscopy. Although the polymerisation was best from solutions at pH 5.5, the better electrochemical properties were from PST film electropolymerised from solution at pH 2.0. The electrochemical behaviour of the films was similar to those of the other poly(phenazines) and a redox mechanism is proposed similar to that at poly(neutral red); in most cases the electrochemical process at the polymer-coated electrode is limited by surface reactions. Scanning electron microscopy data confirmed the results obtained by cyclic voltammetry and the most compact film was obtained from chloride solution.

Applications of this polymer in sensors and biosensors as have occurred with other azine-type polymers can be expected in the future.

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