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Electrochemical polymerization of N-methyl-10,10-dimethylphenazasiline

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N-methyl-10,10-dimethylphenazasiline (SIN) was polymerized by electrochemical oxidation at + 1.3 V in methylene chloride. Acid-base equilibria in solution between the heterocyclic nitrogen and the protons produced by the coupling reaction were detected. The oxidized polymer deposits on platinum or ITO electrodes to give strongly adherent and electrochromic coatings.

1. Introduction

The electrochemical oxidation of organic heterocycles is a promising method for the preparation of new polymers with chemical, electrical and mechanical properties of interest for technological application. Important examples are, in this respect, polypyrrole and polythiophene. Several other heterocycles, like indole [1], benzothiophene [1], carbazole [2] etc., have been subsequently polymerized, but the investigations have been generally focused on the oxidation of small molecules, probably because, in these cases, films of oxidized polymers are more easily obtained and characterized.

Nevertheless, by means of the electrolytic condensation of more complex molecules, new materials, useful for technological applications, can be obtained. In previous papers [3, 4, 5] the electrochemical preparation of polymers derived from thionaphthene-indole (TNI), a heterocycle with two different heteroatoms, have been reported. The oxidized products are, in these cases, black powders which, when electrolytically reduced to neutral compounds, show high electrical photoconductivity [6]. Also in this paper we report a study on the electrochemical oxidation and polymerization of a heterocyclic compound with two different heteroatoms: N-methyl-10,10-dimethylphenazasiline (SIN, Fig. 1), with a molecular structure very similar to that of phenothiazine. This work is part of an investigation of the electrochemical oxidation and polymerization of several heterocycles containing a fourth group atom (Si, Ge, Sn) and S or N as a second heteroatom. As the chemical and physical properties of the polymers produced by electrooxidation of heterocyclic compounds depend on the nature of the heteroatoms, this investigation is expected to increase the knowledge of the conducting polymers as materials with non-usual optical and electrical properties.

2. Experimental details

SIN was synthesized from 2,2′4,4′-tetrabromo-N-methyl-diphenylamine and dichloro(dimethyl)silane, according to the Wassermann procedure [7]. The mass-spectrum of the product confirmed its purity and gave an interesting fragmentation pattern: the ion $SiN^{+}\cdot$ (m/z = 239) and its onefold demethylated fragment (m/z = 224), also present in spectra of similar heterocycles [8], are responsible for the most intense peaks.

Purification of the solvent (methylene chloride, Merck 'pro analysi') and of the supporting electrolyte (tetrabutylammonium perchlorate, TBAP, Fluka 'purum') and description of the electrochemical apparatus are reported elsewhere [5].

As a reference a saturated calomel electrode (SCE) was used, to which all the electrode potentials are referred. Unless otherwise stated, the working electrode was a spherical platinum microelectrode (1.92 cm^2) for voltammetry and a 1 cm^2 platinum plate or 1.4 cm × 1.4 cm glass plate coated with indium tin oxide (ITO) for electrolysis. All the electrochemical experiments were carried out at room temperature (about 22° C) under argon atmosphere.

The mass-spectra of the monomer and polymer were obtained with a VG ZAB2F spectrometer at 70 eV

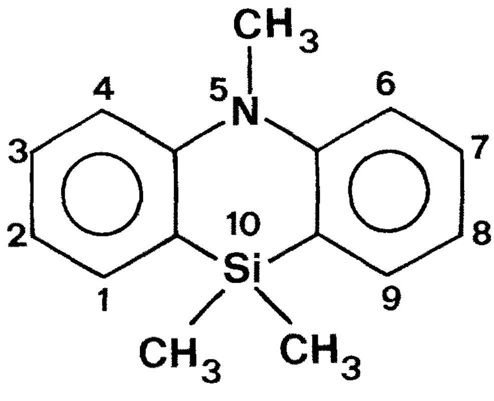


Fig. 1. N-methyl-10,10-dimethylphenazasilane (SIN).

(200 μA) and at different source temperatures (150–300° C). The samples were introduced into the mass-spectrometer by means of a direct insertion probe.

UV-visible-NIR spectra were recorded using a Perkin Elmer Lambda 5 spectrophotometer.

3. Results and discussion

3.1. *Electrochemical and spectrophotometric experiments on the monomer. Preparation of oxidized polymer*

The diffusion layer renewal voltammetry (DLRV) of SIN shows, in the potential range accessible for our solvent (CH_2Cl_2 with TBAP as supporting electrolyte), a well defined wave A at +1.05 V ($c = 1 \times 10^{-3}$ M, slope of the logarithmic plot = 43.5 mV), followed by a post-wave B, which is much more evident at higher concentrations (5×10^{-2} M) (Fig. 2a, d). The half-wave potential of A is very close to that of the anodic waves of many heterocycles with nitrogen as heteroatom, such TNI [9]. The ratio of the heights of the wave A of SIN and of the analogous monoelectronic wave of TNI is 1.2, at a monomer concentration 1.04×10^{-3} M. At 5.42×10^{-3} M the ratio increases to 1.8: then, at this concentration, the wave A of SIN is nearly bielectronic. At intermediate concentrations the number of electrons associated with the wave A is between 1 and 2. This behaviour, typical for an ECE process, was not observed in the case of phenothiazine, which shows one anodic wave, monoelectronic in many organic solvents, including CH_2Cl_2 [10, 11]. The anodic wave B, also detected in the voltammetry of TNI derivatives, has been attributed to the oxidation of protonated monomeric or oligomeric species, which are formed at the electrode owing to the high H^+ concentration due to the coupling between radical cations.

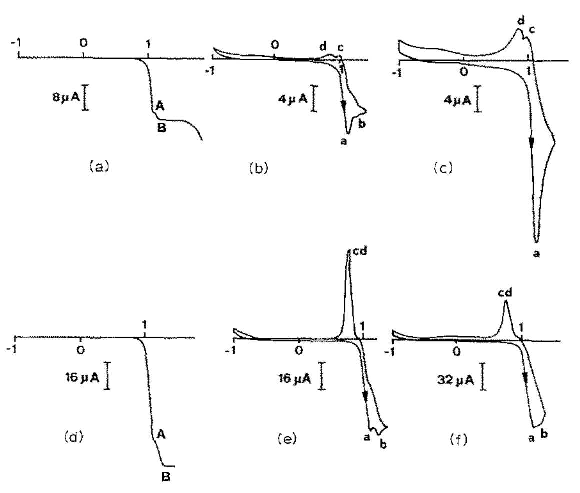


Fig. 2. DLRV of 1.04×10^{-3} M (a) and 5.42×10^{-3} M (d) SIN in CH_2Cl_2 (TBAP 0.1 M). CV of 1.04×10^{-3} M SIN at $v = 20$ mV s^{-1} (b) and at $v = 100$ mV s^{-1} (c), and of 5.42×10^{-3} M SIN at $v = 20$ mV s^{-1} (e) and $v = 100$ mV s^{-1} (f) in CH_2Cl_2; anodic limit = +1.4 V.

The cyclic voltammetry (CV) from −1 V to +1.4 V of 1×10^{-3} M SIN in CH_2Cl_2 shows (Fig. 2b,c) an anodic peak a at +1.09 V, closely followed by a small peak b at +1.24 V. Two small reversal cathodic peaks, c and d, increase enormously with increasing scan rate. The more cathodic peak, d, splits at high rates (100 mV s^{-1}), while, when the CV is run between −1 V to +1.8 V, it takes the form of an adsorption triangular peak. For 5×10^{-3} M solutions (Fig. 2e, f), the ratio $i_{p,a}/i_{p,b}$ (i_p = peak current) increases, while it decreases with increasing sweep rate. In this case, only one reversal cathodic peak, cd, appears, at +0.75–0.78 V. This big triangular peak is evidently due to the reduction of an adsorbed species and hides other smaller peaks that could be present in the same potential region; its height decreases slightly with increase of the sweep rate from 20 to 100 mV s^{-1}, owing to the smaller amount of adsorbable species produced during the oxidation sweep. The peaks a and b are connected with the formation of an oxidized adsorbable product. Taking also into account the ECE behaviour of wave A, the related kinetic process is probably linked to the reaction between radical cations to give dimers, which can be oxidixed at the same potential as the monomer. After several subsequent CV's a small anodic peak appears at about +0.8 V, due to a thin electrodic film of oxidizable condensed compounds.

Electrolyses at the anodic plateau potential (+1.3 V) show a behaviour similar to that observed, in the same experimental conditions, with TNI derivatives. The current decreases slowly up to a consumption of 1 electron per monomer unit, then remains nearly constant for a long time. During the electrolysis the sample turns blue and, for SIN concentrations higher than 5×10^{-3} M, after the flow of about 1 electron per monomer unit, a black coherent film of oxidized polymer begins to deposit on the platinum or ITO electrode.

It must be pointed out that the cation of SIN, formed in the primary event of the anodic oxidation, is a short lived radical, as shown by CV of SIN before electrolysis. In fact, pulse radiolysis experiments in CH_2Cl_2 show that the radical cation of SIN has a lifetime of some hundreds of picoseconds [12]. The suggested mechanism, which satisfactorily agrees with the electrolytic experiments, takes into consideration the gradual formation of condensed compounds. As scheme 1 shows, the species produced by electrolysis are: neutral dimer or oligomers, protonated neutral dimers or oligomers, dication dimers and radical cation dimers, besides oxidized oligomers which deposit on the electrode. While the neutral polymer is soluble in CH_2Cl_2, the oxidized poly(SIN) is insoluble and deposits on the electrode. It is possible that the soluble oxidized species are dimers, as observed in the electropolymerization of other monomers with similar molecular weight [13, 14].

Because, during the electrolysis, the solution becomes increasingly acidic, all the neutral species tend to be protonated on the heterocycle nitrogen and oxidation is possible only through a preceding deprotonation.

Mechanism of the electrolytic oxidation of SIN at +1.3 V in CH_2Cl_2 (D = dimer)

$$\mathrm{SIN} - e \longrightarrow \mathrm{SIN}^{+}\cdot \tag{1}$$

$$2\mathrm{SIN}^{+}\cdot \longrightarrow \mathrm{D} + 2\mathrm{H}^{+} \tag{2}$$

$$\mathrm{D} + \mathrm{H}^{+} \rightleftharpoons \mathrm{DH}^{+} \tag{3}$$

$$\mathrm{DH}^{+} + \mathrm{H}^{+} \rightleftharpoons \mathrm{DH}_2^{2+} \tag{4}$$

$$\mathrm{D} - e \longrightarrow \mathrm{D}^{+}\cdot \tag{5}$$

$$\mathrm{D} - 2e \longrightarrow \mathrm{D}^{2+} \tag{6}$$

$$\mathrm{D}^{+}\cdot + \mathrm{SIN}^{+}\cdot \longrightarrow \mathrm{Trimer}\ldots \tag{7}$$

$$\text{Neutral polymer} - xe \rightleftharpoons \text{Oxidized polymer} \tag{8}$$

Voltammograms and optical spectra recorded after electrolysis change if the solution is allowed to stand for some hours. The colour turns gradually from blue to green. DLRV run immediately after electrolysis show two cathodic waves (Fig. 3a), the wave C at about +0.9 V and the wave D at about 0 V, which is much higher than C. The wave D, as its potential suggests, can be attributed to the reduction of H^+, free or associated with neutral condensed compounds through a preceding deprotonation step. The wave C, the $E_{\frac{1}{2}}$ of which is very close to the oxidation potential of SIN, is probably due to the reduction of cations $D^{+}\cdot$ and D^{2+} and decreases rapidly after the end of electrolysis (Fig. 3b) owing to a reaction which consumes these oxidized species. The system of anodic waves AB is due to the oxidation of neutral oligomers, free or protonated through a preceding deprotonation.

CV carried out after electrolysis show several redox peaks (Fig. 3c, e, f), which, for an initial SIN concentration 1×10^{-3} M, at scan rate 100 mV s^{-1}, show the following peak potentials: α, +0.7 V; α', +0.65 V; β, +0.95 V; β', +0.9 V; γ, +1.15 V and δ, +1.02 V. An irreversible cathodic peak, ε, at $-0.1/-0.2$ V is also present. The attribution of each peak to a well defined electrode process is difficult. The peaks α, α', β, β' are proportional to the scan rate (v) and nearly triangle-shaped. This is evidence of adsorption phenomena at the electrode and agrees with the results of the CV of the monomer. At all the investigated scan rates the i_p of α is one half of the i_p of β and the i_p of α' is one half of the i_p of β'. Therefore, taking into account their potentials, these peaks can be attributed to the following electrode processes:

$$\mathrm{DH}^{+} \rightleftharpoons \mathrm{D} + \mathrm{H}^{+}$$

$$\mathrm{D} \rightleftharpoons \mathrm{D}_{\mathrm{ads}}$$

$$\alpha,\ \alpha'\,\mathrm{D}_{\mathrm{ads}} - e \longrightarrow \mathrm{D}^{+}_{\mathrm{ads}}\cdot$$

$$\beta,\ \beta'\,\mathrm{D}^{+}_{\mathrm{ads}}\cdot - e \longrightarrow \mathrm{D}^{++}_{\mathrm{ads}}$$

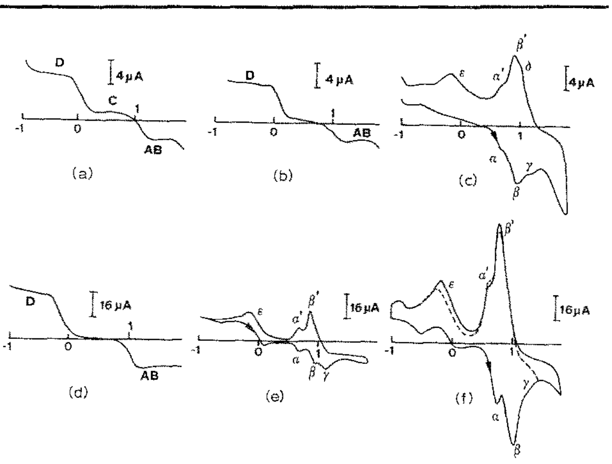


Fig. 3. DLRV of 1.04×10^{-3} M SIN in CH_2Cl_2 (TBAP 0.1 M) electrolyzed at +1.3 V (1.23 electrons per monomer), immediately after electrolysis (a).-DLRV (b) and CV at v = 100 mV s^{-1}, anodic limit = +1.8 V (c) of the same solution, 15 h after the electrolysis.-DLRV (d), CV at v = 20 mV s^{-1}, anodic limit = +1.8 V (e), CV at v = 100 mV s^{-1}, anodic limit = +1.8 V (f-full line) and at v = 100 mV s^{-1}, anodic limit = +1.4 V (f-dotted line) of 5.42×10^{-3} M SIN in CH_2Cl_2 (TBAP 0.1 M) electrolyzed at +1.3 V (0.9 electrons per monomer), 15 h after the electrolysis.

The processes connected with the peaks α and β can be ascribed to the formation of radical cations and dications, or, in other words, of the so called polarons and bipolarons. The potential of the peak β (+0.95 V) suggests that the oxidized species present in solution after electrolysis at +1.3 V, responsible in DLRV for the wave C, are almost exclusively dimers.

The peak γ is ascribable to an electron transfer of a non-adsorbed species and becomes more evident at low scan rates. Because its peak potential is very close to the potential of the anodic wave B of SIN, this may be due to the process:

$$\mathrm{DH}^{+} \rightleftharpoons \mathrm{D} + \mathrm{H}^{+}$$

$$\mathrm{D} - e \longrightarrow \mathrm{D}^{+}\cdot \quad \text{or} \quad \mathrm{D} - 2e \longrightarrow \mathrm{D}^{2+}$$

The peak δ appears after electrolysis of low concentrated solutions of SIN. Its interpretation is not completely clear, but it must be considered that in solution several condensed species are probably present, which, in their cationic form, can give reduction peaks at slightly different potentials. Less problematic is the attribution of the peak ε, corresponding to the wave D: because of its potential, the similarity to peaks of analogous systems and the detected acidity of the electrolyzed solution, it can be attributed to electron transfer involving the reduction of H^+, free (process a) or associated with neutral dimers or oligomers (process b):

$$H^+ - e \longrightarrow \tfrac{1}{2}H_2 \qquad \text{(a)}$$

$$DH^+ \rightleftharpoons D + H^+ \qquad \text{(b)}$$

$$H^+ - e \longrightarrow \tfrac{1}{2}H_2$$

In the electrolysis at +1.3 V, by increasing the amount of charge towards and beyond 2 electrons per monomer unit, the peak system α, α', β, β' becomes gradually less defined and β (with its corresponding cathodic peak) becomes the most important peak. The black oxidized polymer deposits on the electrode, the neutral polymer in solution grows bigger and the number of different oxidizable sites in the polymeric molecules increases with the formation of a big broad peak.

The visible-NIR optical spectrum of the electrolyzed system shows bands in three different regions: 450–500 nm, 620–630 nm and 900–1400 nm (Fig. 4). This spectrum, after the end of the electrolysis, changes with time, the colour turning from blue to green. These changes are probably due to the coupling of the cations, present in solution, to give condensed structures. Some hours later, the colour does not change further. As the voltammetric pattern (Fig. 3b, d) suggests that the green colour attained a long time after the end of the electrolysis is due to protonated dimer or oligomers, it can be inferred that the main absorption band at 620–630 nm (Fig. 4c) is due to such species. The bands around 500 nm may be ascribed to oxidized species, mainly dimers, owing to the solubility in CH_2Cl_2. In fact, in the electrolyzed solutions, these bands decrease with time, while they tend to be restored when the electrolysis is switched on again and a further production of oxidized species takes place (Fig. 4b). This behaviour of the 500 nm band is very similar to that of the voltammetric wave C, and this confirms that the wave C is connected to the reduction of oxidized soluble oligomers.

The nature of the bands in the NIR region is not fully understood. These have different intensity ratios at the different wavelengths in solutions containing either protonated or oxidized oligomers. Finally, the neutral oligomers do not show bands in most of the visible and NIR spectra, as may be demonstrated by shaking the green solutions with dilute aqueous NaOH.

3.2. *Spectrophotometric, voltammetric and mass spectrometric experiments on the oxidized poly-SIN films*

During the electrolyses of highly concentrated solutions, an oxidized film of oligomer is produced in the form of a strongly adherent film on platinum or ITO electrodes. The mass spectra of these products are shown in Fig. 5. At low source temperatures no signal was obtained. At higher temperatures (> 200° C) the mass spectra were characterized by the presence of pyrolysis products. As Fig. 5 shows, the degradation of the original compound depends strongly on temperature. The most significant ionic fragments agree with the suggested polymer structure and are given in Fig. 6.

The colour of the films changed with the degree of oxidation. In fact, they are yellow for the neutral material and green, deep green and finally black with increase of the electrode potential from −0.6 V to +1.9 V.

The CV in CH_2Cl_2 (0.1 M TBAP) of a film of ITO (Fig. 7) shows that, at different scan rates, v, the anodic peak current, i_{pa}, is nearly equal to the cathodic one, i_{pc}. By changing v from 10 to 50 mV s^{-1}, i_p tends to increase linearly with $\sqrt{v}$ for high v values, indicating a slow diffusion of the counterions, and with v for low v values ($v < 10$ mV s^{-1}), when this step becomes less significant.

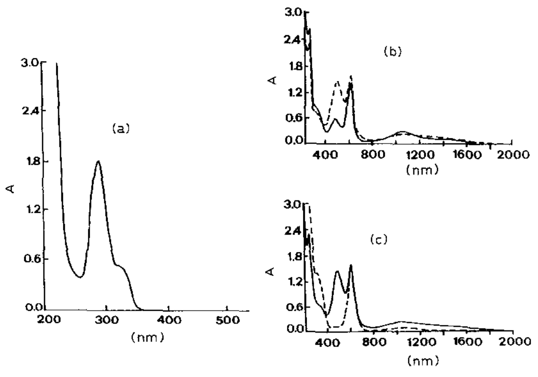


Fig. 4. (a) Absorption spectrum of 1.04 × 10^{-3} M SIN in CH_2Cl_2. Optical path: 0.1 cm. Molar absorbance: 5223 dm^3 mol^{-1} cm^{-1} at 324 nm; 17878 dm^3 mol^{-1} cm^{-1} at 286 nm. (b) (——) absorption spectrum of 5.42 × 10^{-3} M SIN in CH_2Cl_2 (TBAP 0.1 M) electrolyzed at +1.3 V (1.92 electrons per monomer) 15 h after the electrolysis; (— —) absorption spectrum of the same solution after a further electrolysis at +1.3 V (0.18 electrons per monomer). Optical path: 0.1 cm. (c) (——) absorption spectrum of 5.42 × 10^{-3} M SIN in CH_2Cl_2 (TBAP 0.1 M), electrolyzed at +1.3 V (2.1 electrons per monomer); (— —) the same solution after 11 days. Optical path: 0.1 cm.

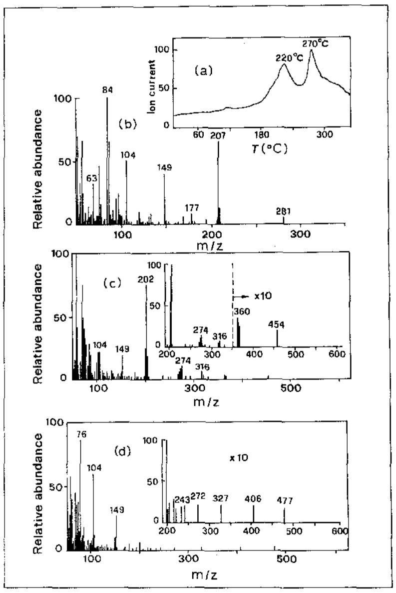


Fig. 5. Mass spectra of a film of oxidized polymer: (a) relative abundance of total ion current against source temperature. (b) (c) and (d) mass spectra at source temperature of 200° C, 250° C and 280° C respectively.

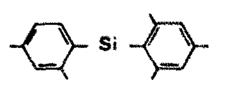
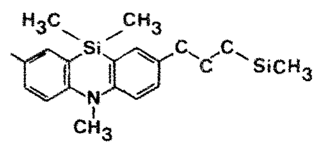
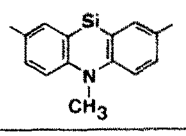
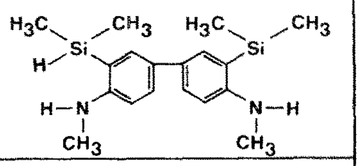
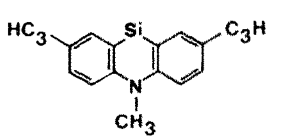
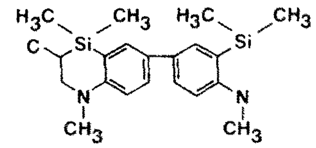
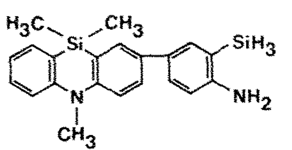
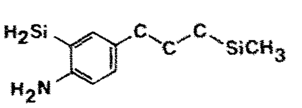
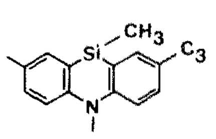
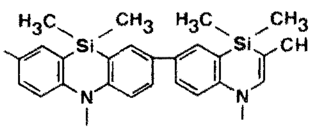
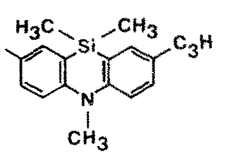
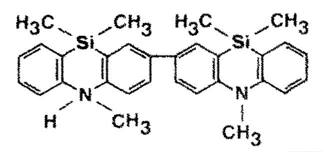
m/z	Empirical formula	Structure formula	m/z	Empirical formula	Structure formula
149	$C_{12}H_5$		272	$C_{18}H_{14}NSi$	274 − 2H
177	$C_{12}H_5Si$		316	$C_{19}H_{18}NSi_2$	
207	$C_{13}H_9NSi$		327	$C_{18}H_{27}N_2Si_2$	
281	$C_{19}H_{11}NSi$		360	$C_{21}H_{24}N_2Si_2$	 or 
202	$C_{10}H_{12}NSi_2$				
243	$C_{16}H_9NSi$		406	$C_{25}H_{22}N_2Si_2$	
274	$C_{18}H_{16}NSi$		477	$C_{30}H_{33}N_2Si_2$	

Fig. 6. The most important fragments detected in the mass spectra of a film of oxidized poly(SIN).

The anodic and cathodic peaks are almost symmetrical with reference to the formal E^0. Indeed, they have the same value of i_p and the same shape; moreover, by decreasing v, their peak potentials approach one another owing to the greater reversibility of the process, though the formal E^0 does not change (+0.95 V). This value is very similar to that deducible from E^p_{ox} (+1.04 V for peak β) and E^p_{red} (+0.81 V for peak β') shown by the CV of electrolyzed 5 × 10^{-3} M solutions at $v = 100\,mV\,s^{-1}$ (Fig. 3f), containing neutral protonated or non-protonated polymer and a small amount of oxidized dimer.

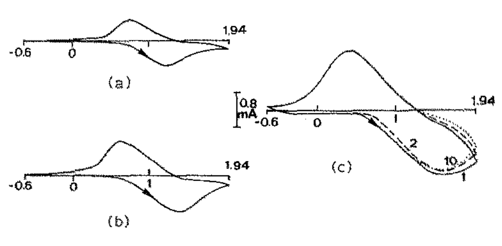


Fig. 7. CV in CH_2Cl_2 (TBAP 0.1 M), from −0.6 V to +1.94 V, of a 0.8 μm film of polymer obtained on ITO electrode by flowing 0.1 coulombs through 5.42 × 10^{-3} M SIN in CH_2Cl_2 (TBAP 0.1 M), electrolyzed at +1.3 V. The deposition of polymer has been done after the preliminary flow of 15 C. (a) $v = 10\,mV\,s^{-1}$; (b) $v = 20\,mV\,s^{-1}$; (c) $v = 50\,mV\,s^{-1}$ (1st, 2nd and 10th cycle).

At relatively high v ($50\,mV\,s^{-1}$, Fig. 7c), the voltammogram between −0.6 V and +1.94 V remains almost identical after 10 cycles, revealing good reversibility of the redox process. The amount of charge involved in the oxidation and reduction is the same and does not change significantly with change of v from 10 to $50\,mV\,s^{-1}$ (about 30 mC in the case of Fig. 7). Figure 8 shows the optical spectra of neutral and oxidized polymer films on ITO electrode. The neutral polymer was obtained by reducing for few minutes the polymer film at −0.6 V in CH_2Cl_2 (0.1 M TBAP) and the fully oxidized polymer was prepared by oxidizing the film at +1.94 V for the same time in the same medium. While the oxidized polymer

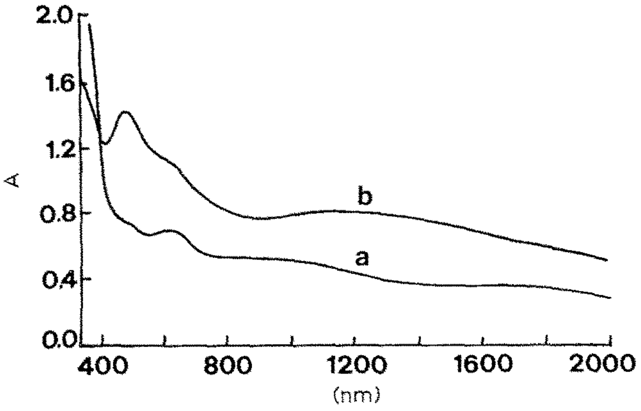


Fig. 8. (a) Absorption spectrum of neutral polymer film on ITO, obtained at −0.6 V and (b) of the oxidized polymer on ITO, obtained at +1.94 V. ITO absorbance has been subtracted.

absorbs strongly in the visible and NIR, the neutral material shows a smaller absorbance in the same spectral regions. The spectra show broad bands at 477–480 nm, 630 nm and about 1100 nm, already attributed, in the case of electrolyzed samples in solution, to oxidized and protonated dimers. From Fig. 8 it can be inferred that the two bands at about 500 nm and at 630 nm are respectively due to higher and lower degrees of oxidation at different sites of the polymer molecules. A fuller investigation of these spectra in relation to the oxidation level of the polymer is in progress.

4. Conclusions

The electrochemical oxidation of SIN shows several similarities to that of phenothiazine, which has the same molecular structure, apart from a sulphur atom in place of the $Si(CH_3)_2$ group. Phenothiazine, when oxidized electrochemically in hydroalcoholic medium, forms green polymers or oligomers which absorb at 630 and about 500 nm [15]. Likewise, the polymer films obtained by oxidation at the potential of the anodic wave of SIN show, in the visible region, two absorption bands at 620–630 nm and 470–480 nm. Therefore, it can be inferred that the substitution of S with the group $Si(CH_3)_2$ does not significantly influence the absorbance of the polymer in the visible region. The site of coupling, C=C or C=N, seems not to influence strongly the absorbance in the visible region; in fact, in the electropolymerization of phenothiazine a coupling involving nitrogen is very probable [15], while in the case of SIN the methyl group hinders the coupling in this position. However, the reactivity of the molecule changes by substituting S with $Si(CH_3)_2$. Indeed, while the radical cations of phenothiazine, produced by anodic electrolysis, can give rise to sulfoxide groups and interchain S–S bridges, this kind of reaction cannot occur in the case of SIN.

Another interesting result of this study is the detection of acid–base equilibria in solution between the heterocyclic nitrogen and the protons produced by the coupling reaction. These equilibria, already detected in the electrochemical oxidation of TNI derivatives in CH_2Cl_2 and of phenothiazines in acetonitrile [16, 17], are determining steps in the kinetics involved in the preparative anodic electrolyses and strongly influence the kind of soluble species produced. Indeed, the neutral oligomers, soluble in the organic solvent, can be protonated, so changing the optical spectrum.

Finally, the oxidized polymer, which is deep green or black in the case of thick and strongly oxidized films, deposits on platinum or ITO electrodes to give strongly adherent and electrochromic coatings. Studies are in progress to define their electrical and photoelectronic properties and their potential application in the construction of electronic devices.

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