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 polypophthiophene. Several other heterocycles, like indole [1], benzo-thiophene [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⁺ (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 cm²) for voltammetry and a 1 cm² platinum plate or 1.4 cm x 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
OH 3

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 (CH₂Cl₂ with TBAP as supporting electrolyte), a well defined wave A at +1.05 V (c = 1 × 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 of 1.04 × 10⁻¹ M. At 5.42 × 10⁻¹ 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 CH₂Cl₂ [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.

The cyclic voltammetry (CV) from −1 V to +1.4 V of 1 × 10⁻³ M SIN in CH₂Cl₂ 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 ip,ℓ/ip,rs (ip = 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 oxidized at the same potential as the monomer. After several subsequent CVs a small anodic peak appears at about +0.8 V, due to a thin electrocyclic 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 CH₂Cl₂ 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