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In situ UV–vis and Raman spectroscopic studies of the electrochemical behavior of *N*,*N*′-diphenyl-1,4-phenylenediamine

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Abstract

The electrochemical behavior of the *N*,*N*′-diphenyl-1,4-phenylenediamine (B3) in acid solution has been investigated by in situ UV–vis and Raman spectroscopies. The electrogenerated species semiquinone form ($B3^{\bullet +}$) and monoprotonated structure of B3 ($B3^{+}$) have been characterized as the main products of B3 oxidation. The *N*,*N*′-diphenyl-1,4-benzoquinonediimine (B2Q1) species has also been characterized in B3 neutral solution and the $B3^{\bullet +}$ proton loss was attributed to proton absence in solution. Finally, a mechanism has been proposed concerning the electron and proton transfer that occurs during the oxidation process.

Keywords: Spectroelectrochemistry; Raman spectroscopy; Polyaniline; *N*,*N*′-Diphenyl-1,4-phenylenediamine; *N*,*N*′-Diphenyl-1,4-benzoquinonediimine

1. Introduction

Among the numerous conducting polymers, polyaniline has been extensively investigated in recent years due to its very stable electronic conducting state [1,2]. A few papers have discussed the relationship between its structure and physicochemical properties. However, our understanding is still fragmentary because of the complicated structural problems involved in the macromolecular aggregation.

The study of oligomeric compounds as a tool to understand the structure and behavior of polyaniline forms has been the subject of a number of papers [3–13]. In particular, this approach appears very convenient to investigate the interesting electrical properties of the conducting state [14]. Consequently, it was necessary to obtain information about the oxidation processes leading to the conducting form, the emeraldine salt, and to identify each formed species. If the conditions were known that favor the stabilization of these species, during the chemical and electrochemical synthesis, it would be easy to achieve a concise characterization of the nature of the charged defects created during the doping processes by spectroscopic techniques. Hence, this uncertainty justifies a more extended study of the mechanism of conductivity in these compounds.

Our study deals with the characterization of some oligomers of polyaniline, these compounds are schematized in Fig. 1.

The *N*,*N*′-diphenyl-1,4-phenylenediamine, Fig. 1(a), is referred to as B3 (for three benzene rings) in the following, but it is also referred to as a phenyl capped dimer (of polyaniline) in the literature. The characteristic, completely oxidized and deprotoned compound of *N*,*N*′-diphenyl-1,4-phenylenediamine is *N*,*N*′-diphenyl-1,4-benzoquinonediimine, or B2Q1, shown in Fig. 1(b). In Fig. 1(c) is presented the radical cation of B3, the semiquinone form ($B3^{\bullet +}$), after a simple oxidation of B3; in Fig. 1(d) the monoprotonated structure of B3 ($B3^{+}$) formed after the loss of two electrons from B3 followed by deprotonation is depicted.

The electrochemical behavior of B3 has been largely investigated in several studies [15–17]. In particular, its stable radical cation has been characterized by methods such as optical absorption [18,19]. However, further oxidized species are not well characterized. Previous papers attribute the form of B3 to the pH of the electrolyte, however, herein is presented an investigation of possible fully oxidized forms of B3 in neutral and acidic solutions. The vibrational features the electrogenerated B3 species are known to be very sensitive to their oxidation

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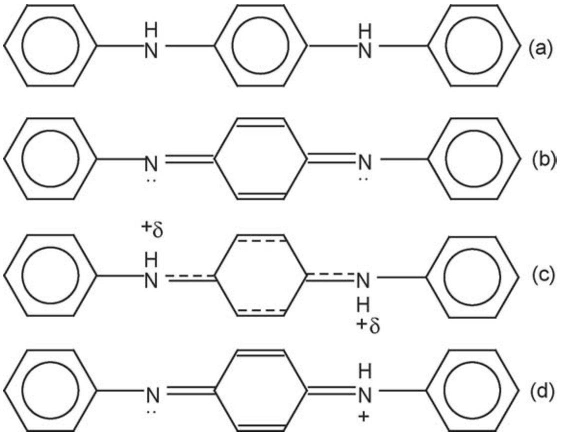

Fig. 1. Schematic structure of the model compounds studied: (a) B3, (b) B2Q1, (c) $B3^{\bullet+}$ and (d) $B3^{+}$.

state leading to a significant characterization of these materials by optical absorption and Raman scattering spectroscopies.

2. Experimental

For cyclic voltammetry a standard three-electrode cell was used. A platinum plate acted as the working electrode and a large platinum sheet was used for the auxiliary electrode. All potentials were determined with reference to an $Ag/AgNO_3$ 10^{-2} M + acetonitrile electrode. The cyclic voltammograms were obtained with a potentiostat–galvanostat PAR 273.

The UV–vis absorbance spectra were acquired with a Varian Cary 2300 spectrometer. These spectroelectrochemical studies were conveniently carried out in a transmission geometry cell using an indium tin oxide (ITO) optically transparent working electrode.

In situ Raman scattering spectra were recorded on a multichannel Jobin-Yvon T64000 type spectrometer connected to a CCD detector using 676.4 and 514.5 nm lines of krypton and argon ion lasers. All the experiments were carried out under a microscope to focus on the working electrode. The scattered radiation was collected with a backscattering geometry under a microscope.

The *N*,*N*′-diphenyl-1,4-phenylenediamine (B3) was purchased from Aldrich. The imine form of *N*,*N*′-diphenyl-1,4-phenylenediamine (B2Q1) was synthesized by oxidation of B3 [20].

Tetraethylammonium tetrafluoroborate (Et_4NBF_4), and diphenyl phosphate $[(C_6H_5O)_2P(O)OH]$, as acid, was used for supporting electrolyte. All these reagents were purchased from Aldrich without further purification.

3. Results and discussion

Cyclic voltammograms of the investigated oligomer obtained in different electrolytes are displayed in Fig. 2. Fig. 2(a) shows the cyclic voltammogram of 10^{-3} M phenyl capper dimer (B3) in acetonitrile with 10^{-1} M Et_4NBF_4. In the positive scan two oxidation peaks are observed at 0.15 and 0.55 V with corresponding cathodic current peaks at 0.10 and 0.48 V on scanning in the negative direction. According to Wolf et al. [21] this is a typical voltammogram of dimer B3 in the acetonitrile solution. The intensity of the second cathodic current peak, however, was found to critically depend on the presence of acid in the electrolyte. The cyclic voltammogram displayed in Fig. 2(b) was obtained of the oxidation and reduction of B3 in acidic medium. The solution for this study was 10^{-1} M Et_4NBF_4, 5×10^{-2} M of $[(C_6H_5O)_2P(O)OH]$ in acetonitrile containing 10^{-3} M of B3. Of these results, it can be concluded that those oxidation–reduction reactions in our potential ranges have an irreversible character. During the positive scan, two oxidation peaks are observed at 0.21 and 0.50 V with corresponding cathodic current peaks at 0.13 and 0.38 V on scanning in the negative direction. These results indicated that species formed during the second peak should be assigned to a chemical reaction or a degradation in neutral solution, causing the abnormality observed in the voltammogram. In acid solution this species was stable, and able to reduce on the electrode surface during the reduction process.

In order to characterize the electrogenerated species of B3, the in situ UV–vis absorption spectra obtained in acidic medium (10^{-1} M Et_4NBF_4 + 5×10^{-2} M $[(C_6H_5O)_2P(O)OH]$ in acetonitrile solution containing 10^{-3} M of B3) were recorded at different applied potentials. The absorption spectra were presented at the potentials for which the characteristic features of the cyclic voltammogram were observed.

Fig. 3 shows the in situ absorption spectra of B3 in acid medium. On scanning in the positive direction absorption bands

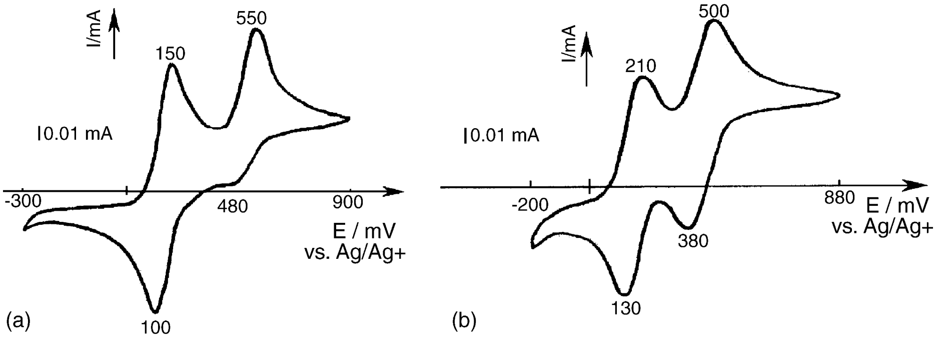

Fig. 2. Cyclic voltammogram of B3 (10^{-3} M) in a solution of: (a) 10^{-1} M Et_4NBF_4/CH_3CN and (b) 10^{-1} M Et_4NBF_4 + 5×10^{-2} M $[(C_6H_5O)_2P(O)OH]/CH_3CN$ (scan rate: 50 mV s^{-1}).