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European Polymer Journal 41 (2005) 843–852

EUROPEAN
POLYMER
JOURNAL

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Synthesis and in situ FTIRS characterization of conducting polymers obtained from aminobenzoic acid isomers at platinum electrodes

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Received 17 September 2004; received in revised form 28 October 2004; accepted 28 October 2004

Abstract

The electrochemical homo-polymerization of *o*-, *m*- and *p*-aminobenzoic acids has been performed on Pt electrodes in perchloric acid aqueous medium by cyclic scanning of the potential. Different limit potentials were employed to obtain thin polymeric films. When the switching potential was extended beyond the respective monomer oxidation peak, a rather degraded material was obtained. In situ FTIR spectroscopy has been used to characterize the redox response of films synthesized at the lower potential limits. Characteristic absorption features related with benzenoid and quinoid rings and different types of C–N bonds suggest the presence of redox processes similar to those undergone by the parent compound polyaniline. In addition, the existence of a chemical interaction between –COOH and –NH– groups in the reduced state of the three homopolymers studied can be suggested. Carbon dioxide has been detected at potentials higher than 1.0 V (RHE) irrespective of the polymeric material, thus indicating its degradation.

Keywords: Aminobenzoic acid; Electropolymerization; Cyclic voltammetry; In situ FTIR spectroscopy

1. Introduction

Organic conducting polymers can be switched reversibly between their conducting and insulating redox states through electrochemical oxidation/reduction processes [1]. Such reactions induce the exchange of counter-ions with the electrolytic medium in order to preserve the electroneutrality of the organic film. In particular, it is known that the electrochemical oxidation of polyaniline (Pani) from the leucoemeraldine insulating form to the emeraldine conducting form is associated with the penetration of electrolyte anions within the polymer matrix [2]. It is expected that a number of future applications of Pani take advantage of this exchange ability. However, the commercial use of this material is limited by its poor processability and low operation pH range inherent to the pristine polymer [1–3].

In order to obtain a more processable material that can be dissolved in common solvents, or even in aqueous medium, the modification of the Pani chemical structure is necessary by, for instance, the introduction of some hydrophilic groups [1,3]. There exist two synthesis routes

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doi:10.1016/j.eurpolymj.2004.10.047

to achieve the chemical modification. On the one hand, a pristine Pani can be prepared through the chemical polymerization of the aniline monomer and, subsequently, the desired chemical modification of the polymer can be performed, see for example [4,5]. A second possibility is the direct synthesis of the material by chemical (or electrochemical) polymerization of the adequate substituted aniline monomer [6–8]. It has been reported that both procedures can yield more soluble materials, although the conductivity of the modified polymers decreases significantly, even by several orders of magnitude, compared with that of Pani [4,8–10].

The modification of the chemical structure of Pani has been also employed to widen the pH range within which the polymer is electrochemically active. It is known that, for the original polymer, the electroactivity is restricted to solutions of very low pH because a high protonation degree at the imine nitrogen atoms is needed [11]. In this way, the insertion of acidic groups in the polymer backbone could change the micro-environment of the imine centers, shifting the local pH to lower values. This hypothesis has deserved some critical comments [8], although it seems supported by the experimental result showing that Pani modified with either sulfonic or carboxylic substituents is able to keep partially its electroactivity in solutions of pH 7 and 10, respectively [4,8]. It is also worth mentioning that, additionally, the insertion of these kind of substituents results in the modification of the ion exchange properties of the film: sulfonated or carboxylated polyanilines are known to act as *self-doped* Pani derivatives [10]. In these materials, the anionic groups bonded to the hydrocarbon chain can compensate the positive charges generated along the polymer backbone during the oxidation processes. Consequently, the anions of the electrolyte do not penetrate the film and the excess of positive charge is eliminated by the expulsion of protons out of the organic matrix.

Despite the extensive literature dealing with the synthesis and characterization of sulfonated polyanilines, few papers pay attention to their parent carboxylated derivatives [12–21]. In addition, most of those reports are devoted to the study of the copolymers formed by either chemical or electrochemical polymerization of anilines and *o*-aminobenzoic acid (anthranilic acid) [12,13,15,17,21]. A comparison between the homopolymers synthesized electrochemically from *o*-, *m*- and *p*-aminobenzoic acids was reported for the first time by Thiemann and Brett [18,19]. The polymerization was carried out on glassy carbon and ITO electrodes and several ex situ characterization techniques were employed. They concluded that homopolymers derived from aminobenzoic acids are short-chain polymeric materials with a voltammetric behavior different from that displayed by polyaniline. Unfortunately, and probably due to the slow rate of electropolymerization, the IR characterization of the homopolymers was not done. The spectroscopic study was limited to ex situ IR measurements of the copolymers formed from *o*-, *m*- and *p*-aminobenzoic acids with aniline for reactant ratios of 1:1.

The present contribution aims to characterize homopolymers of aminobenzoic acids at the molecular level and in the electrochemical environment by means of a powerful technique such as the in situ FTIR spectroscopy. Since this characterization tool allows to obtain vibrational information from very small amounts of material, it is believed that it could serve as an improved alternative to obtain direct spectroscopic information from polyaminobenzoic acids. In this way, the in situ FTIRS method could allow the problems associated to the copolymerization of polyaminobenzoic acids with aniline to overcome.

2. Experimental

The monomers employed for the polymerization reaction were of reagent grade supplied by Merck. The electrolytic medium used for the synthesis and the electrochemical characterization of the polymeric materials was 0.1 M $HClO_4$ in ultrapure water (18.2 MΩ cm). The in situ FTIR experiments were also carried out in perchloric acid aqueous solutions but using either 99.9%-D D_2O (Aldrich) or 18.2 MΩ cm H_2O as solvents.

The working electrode for the voltammetric study was a spherical polycrystalline platinum electrode with an area of about 4 mm^2. For the in situ spectroscopic characterization, the polymers were grown up on a mirror-polished platinum disk electrode. The counter electrode was a platinum wire in all cases. All potentials were measured against a reversible hydrogen electrode (RHE) immersed in the working solutions through a Luggin capillary. The bare Pt working electrode was thermally cleaned and subsequently protected from the laboratory atmosphere by a droplet of ultrapure water. Then, it was transferred to the working solution which was previously deaerated by bubbling N_2. Cyclic voltammograms were recorded at 50 mV s^{-1} and at room temperature. After polymerization, the working electrode was extracted from the electrochemical cell, thoroughly rinsed with water to remove any attached monomer species and transferred to a clean background solution containing 0.1 M $HClO_4$ (free of any monomer) to be characterized by voltammetric or spectroscopic techniques.

A Nicolet Magna 850 spectrometer was employed for the in situ FTIR experiments. The spectroelectrochemical cell was provided with a prismatic CaF_2 window beveled at 60°. The interferograms were acquired with the working electrode surface pressed against this window and were collected at 8 cm^{-1} resolution. The final spec-