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Pyrolysis–gas chromatography/mass spectrometry applied to the identification of different states of polyaniline

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Abstract

Pyrolysis–gas chromatography/mass spectrometry (Py–CG/MS) has been applied to study and compare the composition of two electrochemically synthesized polyaniline (PANI) forms: fully reduced leucoemeraldine (LE) and intermediately oxidized emeraldine (EM). The different PANI forms were electrochemically synthesized using cyclic voltammetry. They were dedoped by stirring for 24 h in ammoniacal solutions. Leucoemeraldine and emeraldine pyrograms presented differences in the relative intensity of their fragment signals. Emeraldine pyrograms presented a higher relative intensity of the signals associated to oxidized fragments (i.e. quinone imine) than leucoemeraldine pyrograms. On the other hand, polymer samples synthesized under different anodic potentials showed small differences, consistent with a higher degree of crosslinking at higher anodic potentials. The results obtained indicate that Py–GC/MS may be used for identification among different oxidation states in aryl amine polymers.

Keywords: Conducting polymer; Oxidation states; Cyclic voltammetry; Polymer structure

1. Introduction

Conducting polymers, in particular aryl amine polymers such as polyaniline (PANI) are proposed to be used for many applications [1–12]. Due to their potential applications and interesting characteristics, the electrochemistry of aryl amine polymers have been intensively studied [13–17]. The insulator/conductor transition observed during the oxidation from the fully reduced form leucoemeraldine (LE) to the partially oxidized one emeraldine (EM) (redox switching) has been extensively studied [14,18–20], but its details are not fully known yet.

Many of the interesting properties of PANI, such as electrochemomechanical changes [21,22] and photophysical behaviour [23], are closely related to their structure. Thus, in the study of the redox switching behaviour of polyaniline, structural analysis is an important aspect, which would help to elucidate the changes in polymer structure and their relationship to its physicochemical properties. Among the many different techniques applied to the study of polyaniline, mass spectrometry-related techniques have received little attention. Sauerland and Schindler [24] studied its structure using multiphoton ionization mass spectrometry, being able to identify the polymer building blocks. Stassen and Hambitzer [25] applied electrochemical thermospray mass spectrometry to investigate the electrosynthesis of PANI in acidic solutions. Recently, laser desorption ionization techniques, such as MALDI, have been applied to the analysis of PANI and similar compounds [26]. Pyrolysis–gas chromatography/mass spectrometry (Py–CG/MS) has previously been applied to chemically synthesized PANI [27], and only to the oxidized forms emeraldine and pernigraniline.

In this paper, pyrolysis–gas chromatography/mass spectrometry has been applied to study and compare the composition of two PANI forms: fully reduced leucoemeraldine and intermediately oxidized emeraldine, obtained electrochemically under different synthesis conditions. The chemical structures of both forms are shown in Fig. 1.

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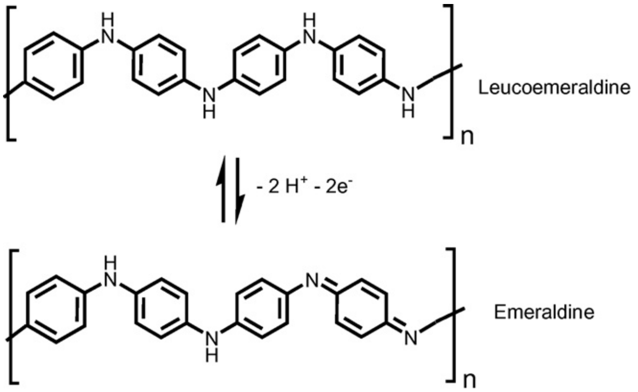


Fig. 1. Leucoemeraldine and emeraldine forms of polyaniline.

2. Materials and methods

2.1. Polymerization

PANI films were electrochemically synthesized from a 0.5 M aniline solutions in a 1.5 M sulphuric + 1.5 M perchloric acid mixture, by potential cycling at a scan rate of 0.05 V s^{-1} between 0.1 and an anodic limit, E_a, of 1.0 or 1.2 V, to study its influence on the resulting structure. Details of the procedure can be found in Ref. [22]. The polymerization was carried out in a standard electrochemical cell. A reversible hydrogen electrode (RHE) was used as the reference whereas a platinum foil was used as the auxiliary electrode, both placed in separate compartments. The working electrode was a platinum disk of 10 mm diameter. The electrode was polished with alumina, washed in an ultrasonic bath and rinsed thoroughly. The process was monitored through the anodic charge under the first anodic peak (between 0.3 and 0.5 V), Q_a, and it was stopped when $Q_a = 0.5\ C\ cm^{-2}$. About 45 cycles were needed for the electrosynthesis at E_a = 1.0 V and 10 when E_a = 1.2 V in order to obtain similar film thicknesses.

2.2. Preparation of different polyaniline forms

The working electrode coated with the synthesized polymer was soaked in an ammoniacal solution for 24 h in order to dedope it, thoroughly rinsed and dried. A 1 M NH_3 solution was used to obtain the polymer in the emeraldine form, whereas a 1 M NH_3 + 0.1 M hidroxylamine solution was used to obtain

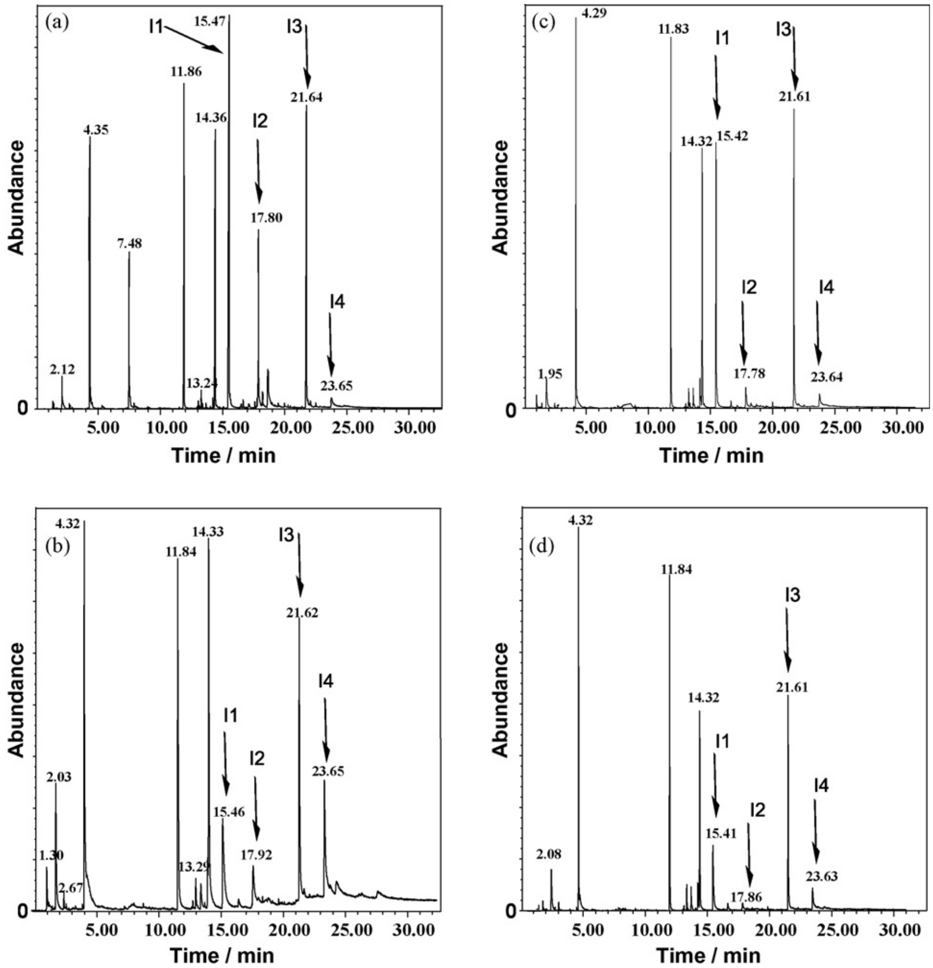


Fig. 2. Pyrograms of PANI in: (a) leucoemeraldine form synthesized with E_a = 1.0 V, (b) emeraldine form synthesized with E_a = 1.0 V, (c) leucoemeraldine form synthesized with E_a = 1.2 V and (d) emeraldine form synthesized with E_a = 1.2 V. The peaks signaled as I1, I2, I3, I4 correspond to the compounds listed in Table 1. Abundance scales are different in all the TICs.

the leucoemeraldine form. The polymer was then removed from the working electrode surface to be pyrolized.

2.3. Pyrolysis measurements

The pyrolysis experiments were performed with a Pyrolyzer PY2020 (Frontier Laboratories Ltd., Koriyama, Japan) directly attached to a GC–MS. The Pyrolyzer was composed of a plunger for the sample, the sample cup, a deactivated needle (into the injector) and a micro furnace. The pyrolysis was carried out with 0.4 mg samples at a temperature of 700 °C in order to analyze the basic polymer. The released pyrolyzates were analyzed on a GC–MS equipment (Agilent 6890) equipped with a DB5 capillary column (30 m length × 0.25 mm i.d. × 0.25 μm film thickness, J. & W. Scientific, Agilent, Palo Alto, USA).

The pyrolysis products were injected in the splitter mode using a temperature of 250 °C both at the interface and injector. The oven temperature was held at 50 °C for 1 min, and then raised to 100 °C by applying a ramp of 30 °C min^{-1} and when the temperature arrived to 100 °C, it was then increased to 300 °C heating at 10 °C min^{-1}. Finally, the temperature was held at 300 °C for 10 min. The detector consisted of an Agilent 5973 mass selective detector (EI at 70 eV) in the scan mode. The carrier gas used was helium with a flow of 1.5 ml min^{-1}.

3. Results and discussion

The total ion current (TIC) traces obtained by GC–MS analysis of the pyrolysates are reported in Fig. 2. These pyrolysates were generated by different states of PANI, obtained in different anodic limits (E_a = 1.0 or 1.2 V) during the electropolymerization. The different peaks in the leucoemeraldine and emeraldine pyrograms were identified as the aniline monomer, dimers, trimers and rearrangement products using different mass spectra libraries.

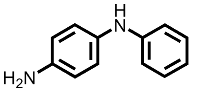
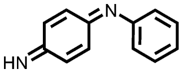
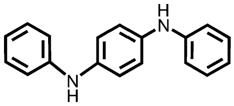
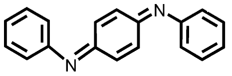
The peaks signalled in the pyrograms with arrows as I1, I2, I3, I4 were identified with the compounds indicated in Table 1. Compounds 1 and 3 belong, respectively, to the dimmer and trimmer totally reduced as they only present aminic nitrogens, whereas compounds 2 and 4 have iminic nitrogens and present quinone structures. These structures are only present in the oxidized forms of PANI.

Table 2
Intensity ratios of oxidized to reduced fragments

PANI form	Compounds	Intensity ox./ intensity red.
Leucoemeraldine (E_a = 1.0 V)	I1/I2	2.38
	I3/I4	13.55
Emeraldine (E_a = 1.0 V)	I1/I2	2.73
	I3/I4	1.34
Leucoemeraldine (E_a = 1.2 V)	I1/I2	6.50
	I3/I4	9.92
Emeraldine (E_a = 1.2 V)	I1/I2	6.36
	I3/I4	4.72

It is clear from Table 1 that compounds 1 and 3 are reduced fragments whereas 2 and 4 are oxidized fragments. In each pyrogram, the dimmers that belong to different PANI forms (compounds 1 and 2) were analyzed together comparing their intensity signal relation I1/I2 in the different polymer preparation conditions. The same procedure was performed for the trimmers, which were also compared to each other by their intensity signal relation I3/I4. The results obtained from this analysis are presented in Table 2. They show, as expected, that emeraldine forms present a greater proportion of fragments containing quinone imine groups than in leucoemeraldine forms. However, some of those fragments are still found in the reduced polymer, which indicates that a quantitatively reduced PANI is difficult to obtain, as it is already known. When comparing the polymers obtained using different anodic potential limits in the voltammetric electropolymerization, it is expected that at higher anodic potentials, a crosslinked polymer (through ortho coupling) will be obtained, due to the higher reactivity of the polymerization intermediates. However, no new fragments are observed for PANI prepared at E_a = 1.2 V compared to that at E_a = 1.0 V. This fact would indicate that the polymer synthesized at E_a = 1.0 V already has some crosslinking, and that at E_a = 1.2 V the degree of crosslinking is higher, but no different forms are present. In the results shown in Table 2 for the emeraldine form (E_a = 1.2) the ratio of quinone imine to amine fragments is lower than at E_a = 1.0 V.

Table 1
Identification of the signalled peaks in the pyrogram

Peak	Compound	Retention time (min)	Prominent ions
I1	 1	15.5	184 (M$^+$), 107, 166–$C_{12}H_{12}N_2$
I2	 2	17.8	182 (M$^+$), 91, 154–$C_{12}H_{10}N$
I3	 3	21.6	260 (M$^+$), 183, 167–$C_{18}H_{16}N_2$
I4	 4	23.6	258 (M$^+$), 128, 129–$C_{18}H_{14}N_2$

Due to the fact that polymer units with ortho coupling are more difficult to oxidize, the lower number of such fragments is consistent with the fact that at higher polymerization potentials more crosslinking is present in the polymer.

4. Conclusions

The pyrograms presented differences in the relative intensity of the signals associated to dimers and trimers according to their oxidation states. Emeraldine pyrograms presented a higher relative intensity of the signals associated to oxidized fragments (i.e. quinone imine) than leucoemeraldine pyrograms. The results are consistent with higher polymer crosslinking as the anodic polymerization potential is increased.

The results indicated that Py–GC/MS may be used for identification among different oxidation states in aryl amine polymers.

At the moment MALDI–MS analysis is being performed in order to compare the fragmentation patterns provided by the mass spectra of the native sample with the pyrolysis results.

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