Short communication

Study of some pyrolysis–gas chromatography indexes for the differentiation among oxidation states of polyaniline[1]

S. Borrós*, E. Muñoz, I. Folch

Secció Ciència dels Materials, Institut Químic de Sarrià (Universitat Ramon Llull), Via Augusta 390, 08017 Barcelona, Spain

Abstract

A method has been developed to distinguish between two oxidation states of polyaniline (emeraldine and pemigraniline) using pyrolysis–high-resolution GC. Some tentative pyrolysis indexes are discussed here, as well as the relationship between the pyrolysis products and the polymer structures. This technique seems to be promising for this purpose. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Pyrolysis; Polyaniline; Emeraldine; Pernigraniline; Polymers

1. Introduction

Pyrolysis has been used for many years to study the decomposition of materials such as soils, rubber, etc. when exposed to a high temperature in a short time [1–3]. There are even official methods for the determination of the structure of such materials based on the pyrolytic process [4]. The coupling of pyrolysis to gas chromatography (especially when IR or mass spectrometry are used as detectors), provides valuable information about the component units and structural bonds of the compounds studied. It can also be used as a qualitative technique, by comparing the shape obtained from a known matrix used as standard, and the studied sample ('fingerprints pyrolysis').

Anyway, there are only a few studies concerning the application of pyrolytic analysis to polymeric conducting materials [5–8], all of them coupling directly the pyrolyser to an IR or mass spectrometer. In these studies, the products obtained from the oxidation of a mixture of compounds have been analysed in order to determine if the synthetic process has lead to a copolymer or a simple mixture of polymers. The data obtained, however, is not specific enough to allow the determination of the structure of the initial sample, because the spectra obtained (mass spectrum as well as infrared one) correspond to a mixture of the decomposition products.

The coupling of pyrolysis to a chromatographic system appears to be a useful alternative, for it allows the separation and individual identification of all the compounds formed, giving, thus, more structural information. Furthermore, it somehow allows the quantification of the ratio indexes among the different compounds obtained from the pyrolytic process.

The aim of our work is the study of pyrolysis

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*Corresponding author. Fax: +34 9 320 56266.

(Py)–GC as a suitable technique for the characterization of the oxidation states of polyaniline. This polymer has been known for more than a century, although its conducting properties were discovered at the end of the 1960s, and now it is one of the most widely studied (and well-known) conducting polymers. It may have many structures, depending on the synthetic process developed (it determines its oxidation state) and the conditions in which it is at the moment (mainly its degree of protonation). The different properties of polyaniline depend on the combination of its two different structural units, those shown in Fig. 1: (i) benzene rings joined by amine nitrogens, (ii) quinone rings joined by imine nitrogens.

The different combination of such units leads to an infinite number of possible structures depending on the oxidation potential of the polymerization agent, or the later treatment polyaniline is subjected to.

Anyway, only emeraldine salt form exhibits conducting properties, and that fact limits the development of industrial applications of polyaniline. Obviously, there is the need of a rapid and secure method to determine the oxidation state of the polymer.

As a matter of fact, when samples of different forms of polyaniline are pyrolyzed, the amount of each decomposition product is expected to vary depending on the oxidation state of the polymer, thus giving rise to different values on their pyrolytic indexes.

2. Experimental

The emeraldine form of polyaniline was obtained from the most typical synthetic process, that is, oxidizing a 1 *M* aniline solution in 1 *M* hydrochloric acid with ammonium persulfate [9–11]. From the polymer obtained in that way, the oxidation to pernigraniline was performed with *m*-chloroperbenzoic acid as described by Sun et al. [12].

The pyrolysis was performed in a CDS Pyroprobe 1000 (Chemical Data Systems, Oxford, PA, USA), applying to a sample of about 10 mg laid in a quartz tube (Kromxpek, Barcelona, Spain) into a platinum coil probe, a heating rate of 5°C/ms, up to 700°C, and standing at such a temperature for 10 s. The fragments obtained were then introduced in the chromatographic system.

The pyrolysis products were analyzed by using two different chromatographic systems, described below.

2.1. Py–high resolution (HR) GC-flame ionization detection (FID)

A Perkin-Elmer (Norwalk, CT, USA) Model 8700 chromatograph equipped with a Supelcowax 10 column (polyethyleneglycol), 30 m×0.32 mm, 0.25 μm. Pyrolysis products were introduced by a helium current of 105 kPa of pressure, in the splitter mode, using a splitter flow of 40 ml/min. During the first 2
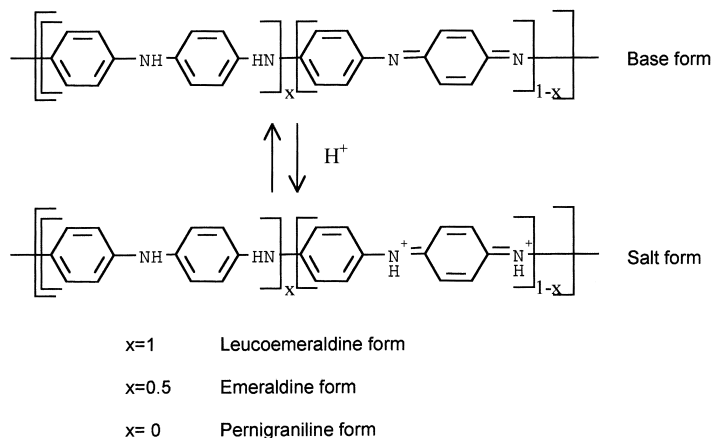

x=1   Leucoemeraldine form

x=0.5   Emeraldine form

x= 0   Pernigraniline form

Fig. 1. Different structures of polyaniline depending on its oxidation state, and protonation degree.

min, a cold trap of CO_2/acetone assured the concentration of all the compounds at the first turn of the chromatographic column. The temperature was held at 35°C for 2 min, then raised to 50°C by applying a ramp of 30°C/min, and to 240°C at 10°C/min. The final temperature was held for 30 min. The detection was by FID at 250°C.

The chromatograms obtained were recorded on a Waters Maxima 820 station, and integrated including the peaks marked with an asterisk (*) in Fig. 3. The results obtained were compared using the program Pirostel [13], developed in our Institute for the comparison and identification of pyrolysates. The areas of the peaks observed in the pyrograms are compared, by calculating their similarity coefficients.

2.2. Py–HRGC–MS

A Hewlett-Packard 5890 chromatograph equipped with a DB5 column, 40 m by a helium current at an initial pressure of 100 kPa. Pyrolysis products were injected in the splitter mode, using a splitter flow of 40 ml/min. The temperature was held at 30°C for 2 min, then raised to 60°C by applying a ramp of 30°C/min, and held there for 7 min and to 280°C at 8°C/min. The final temperature was held for 25 min. The detection was done using the mass spectrometer HP 5989 (electron impact ionization) at a temperature of 250°C. Identification was achieved by mass fragmentography in a mass range from 40 to 500 u, and library searches.

3. Results and discussion

Our study was started with the thermogravimetric analysis (TGA) of an emeraldine base sample, shown in Fig. 2, in order to determine the decomposition temperature of such a product. It can be seen that after an initial step of mass loss up to 100°C, mainly due to its moisture content, then the sample mass remains almost constant until about 450°C then leading to a 44% remaining at about 650°C.

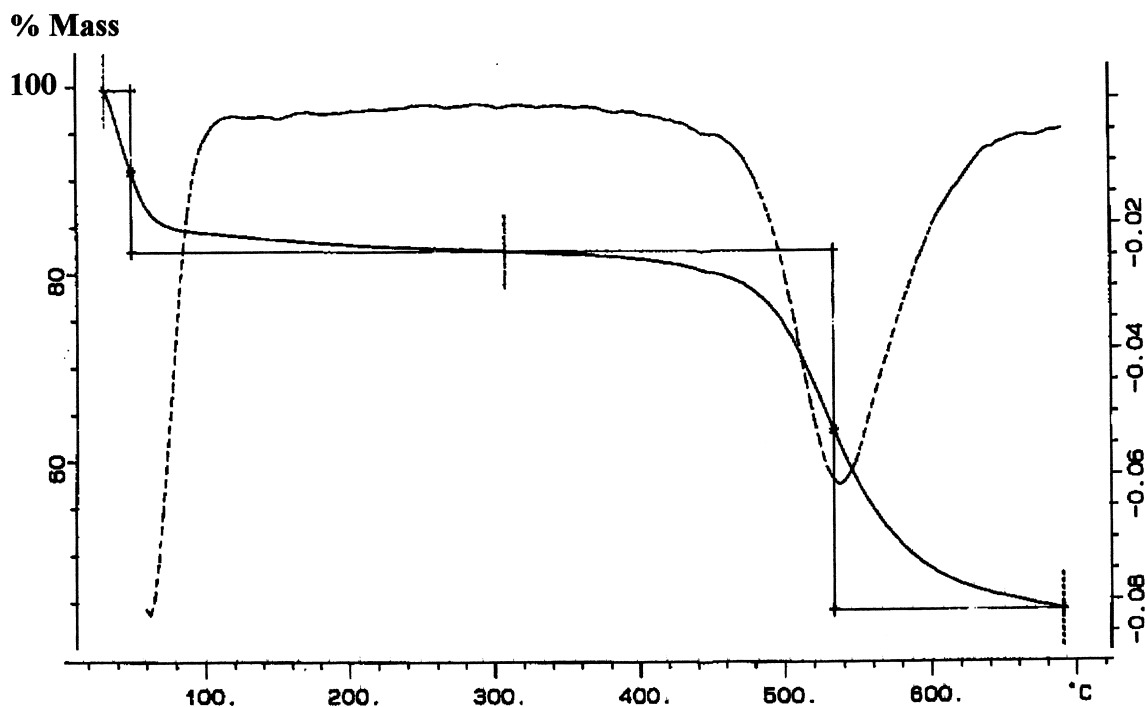According to this thermal analysis, it makes no

Fig. 2. Thermogravimetric analysis (TGA) of an emeraldine base sample. Mass losses are observed at 42 and 525°C.

sense to pyrolyze at a temperature lower than 650°C. On the other hand, previous studies in our group [14] showed that an increasing of the pyrolysis temperature of polymers from 700 to 1000°C lead to the decomposition of the polymer in a greater extent, to simpler compounds, and thus providing poor information about its structure. According to these considerations the pyrolysis temperature was fixed on 700°C.

3.1. Py–HRGC–FID: Similarity coefficients

The first pyrograms obtained showed important differences for the same samples, due to the volatile compounds remaining in the samples (rest of monomer, low molecular weight oligomers, or volatile compounds adsorbed from the atmosphere...). It was found that a desorption process of such volatile compounds was needed in order to obtain reproducible results when pyrolysis was applied to the sample. Therefore, the desorption process was assayed by applying a temperature of 270°C during a

period of 10 s before the pyrolysis process was applied. The desorption temperature was fixed according to the TGA analysis, for it is a non-critical temperature at which the sample mass remains constant.

The subsequent pyrograms were very similar, as is shown in Fig. 3 for two emeraldine samples, and in Fig. 4 for two pernigraniline samples. Anyway, unimportant differences can be observed among those different oxidation states.

As the visual comparison of the pyrograms obtained from each sample does not give much information about the different oxidation states of polyaniline, there is a need for an objective parameter that allows us for that purpose.

First of all, the similarity coefficients were calculated, by using the program Pyrostel for fingerprints analysis. Those coefficients are calculated on the basis of the percentage area represented by each peak in the chromatograms being compared. Therefore, all the pyrograms must have the same peaks, those considered as the fingerprints for the sample. In our
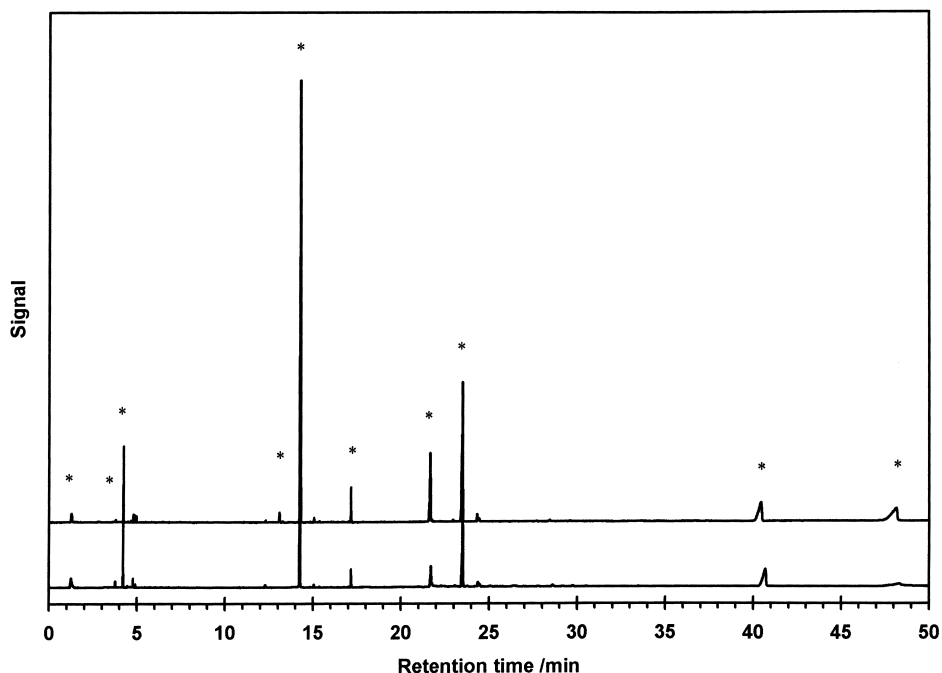

Fig. 3. Chromatograms obtained from two different samples of emeraldine base, after desorption and pyrolysis processes using the chromatographic method Py–HRGC–FID. The peaks marked with an (*) are those used in the similarity coefficients calculations.
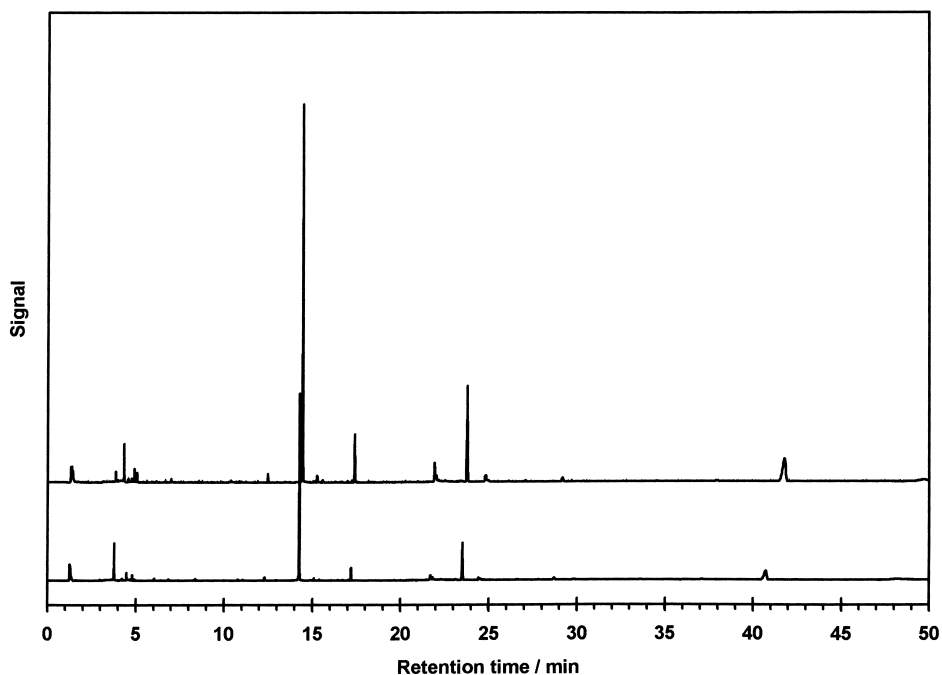
Fig. 4. Chromatograms obtained from two different samples of pernigraniline base (oxidized form of polyaniline), after desorption and pyrolysis processes using the chromatographic method Py–HRGC–FID.

analysis of polyaniline samples, the peaks used in the comparison are those remarked in the pyrograms shown in Fig. 3.

The results of the analysis of the different oxidation states of polyaniline showed a poor definition in the classification of the samples in their group. Emeraldine samples showed quite low similarity coefficients, always about 55%, and most of them in the same order or smaller than if those samples are compared to the pernigraniline ones. Pernigraniline samples, on the other hand, showed higher similarities (around 70%) between them, being the coefficients lower but very disperse (15–60%) when compared to the other oxidation states.

It can be seen that the similarity coefficients are too different when comparing equal samples, and, at the same time, too similar when comparing different kinds of samples. That fact may be due to the great number of compounds found in the pyrograms, some of them corresponding to small peaks. Little differences in the areas of those minor peaks can represent an important change in the global coefficient of the sample, or, on the other hand, differences in more

than one peak may compensate thus giving rise to a higher similarity coefficient.

3.2. Py–HRGC–MS: Indexes calculations

Anyway, the relationship observed among compounds corresponding to one or other structural units might show important differences when samples of different oxidation states are compared. According to the different structures of emeraldine and pernigraniline, we can expect that the area ratios among some pairs of peaks would be consistent with the different amounts of benzene and quinone units present in the samples.

Our group has identified the polyaniline fragments in a previous work, by using the chromatographic system Py–HRGC–MS described before, where a mass spectrometer is used as the detector. The pyrograms obtained from emeraldine and pernigraniline samples in these conditions (Fig. 5) have been used here to discuss the area ratios among different compounds obtained from the decomposi-
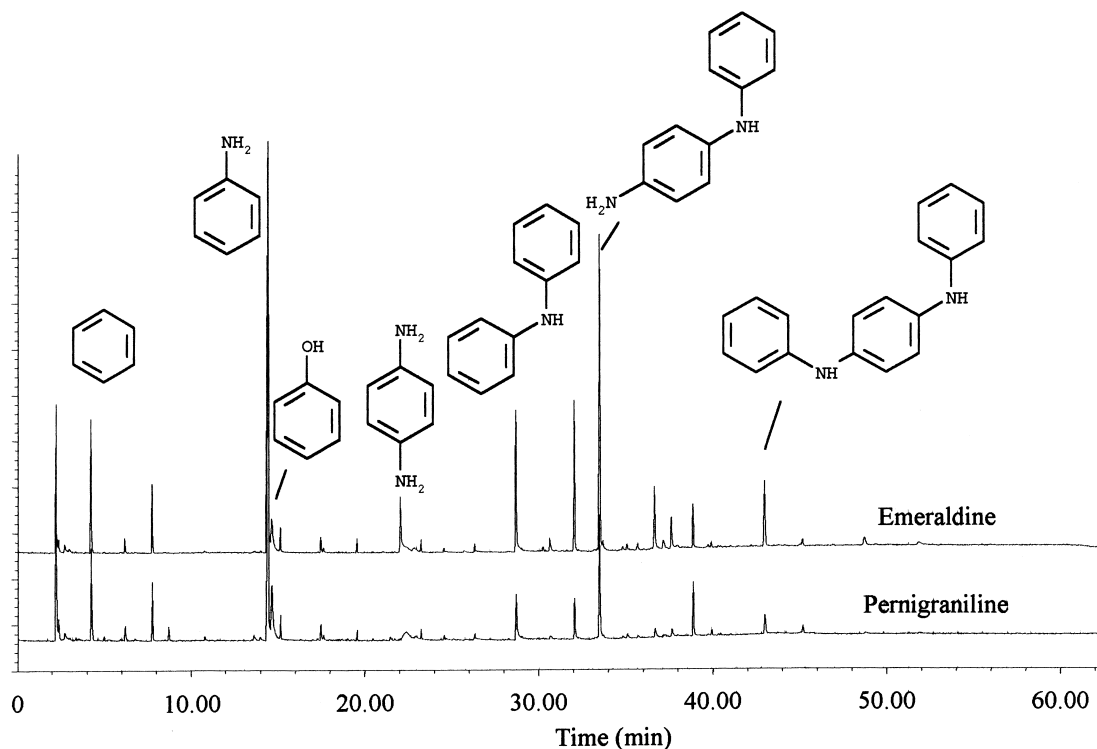
Fig. 5. Chromatograms obtained from an emeraldine and a pernigraniline base samples, after desorption and pyrolysis processes using the chromatographic method Py–HRGC–MS.

tion process. Some of the indexes obtained in this part of the work are presented in Table 1.

There are no differences for the emeraldine and pernigraniline samples when the indexes among benzene and aniline peaks are compared. This is not surprising, because they are the smallest units present in the polyaniline samples, and do not change whatever its oxidations state is.

The indexes among aniline and other greater oligomers, however, show interesting differences for the different oxidation states of the polymer. As the oligomers identified contain two or three aniline units in their reduced form, the ratios aniline vs. oligomer are greater for pernigraniline samples than for the emeraldine ones.

The index aniline vs. p-phenylenediamine is one-half greater for pernigraniline samples than for emeraldine ones, while aniline vs. diphenylamine and 4-aminodiphenylamine is twice for pernigraniline, as it contains two complete aniline units in the reduced form. When aniline vs. N,N'-diphenyl-1,4-benzenediamine (three monomer units) is calcu-

Table 1
Indexes obtained from selected pairs of peaks, according to the structure of the sample

Index	Emeraldine	Pernigraniline
Benzene vs. aniline	0.1662	0.1617
Aniline vs. phenol	7.8510	4.3553
Aniline vs. p-phenylenediamine	6.1386	9.1335
Aniline vs. diphenylamine	4.2241	8.6634
Aniline vs. 4-aminodiphenylamine	1.9937	4.4704
Aniline vs. N,N'-diphenyl-1,4-phenylenediamine	7.4915	20.4809

lated, the pernigraniline samples show a three-times higher index than emeraldine.

The increase in the series of indexes described above can be explained by the minor occurrence of the reduced units in the pernigraniline structure, and so the greater reduced oligomers have a lower probability of appearance in the pyrogram.

On the other hand, the index aniline vs. phenol is greater for emeraldine than for pernigraniline samples, because the oxidation of the final imine nitrogen obtained from the break of pernigraniline is easier than the amine nitrogens obtained from emeraldine.

4. Conclusion

Pyrolysis analysis of polyaniline samples has shown the polymer break giving place to aniline, benzene and diphenylamine, as well as other greater oligomers.

The comparison of global pyrograms does not allow the differentiation of the oxidation states of the polymer, based simply in a similarity coefficient, for the pyrograms are too different in the same group of samples, and too similar in different groups.

Anyway, the definition of some ratio indexes among pairs of peaks can lead to the differentiation of polyaniline samples in different oxidation states.

Acknowledgements

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