

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

European Polymer Journal xxx (2004) xxx–xxx

EUROPEAN  
POLYMER  
JOURNAL[www.elsevier.com/locate/europolj](http://www.elsevier.com/locate/europolj)

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

A. Benyoucef<sup>a</sup>, F. Huerta<sup>b</sup>, J.L. Vázquez<sup>a</sup>, E. Morallon<sup>a,\*</sup><sup>a</sup> Dept. de Química Física, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain<sup>b</sup> Dept. de Ingeniería Textil y Papelera, Universidad Politécnica de Valencia, Paseo Viaducto 1, E-03801 Alcoy, Spain

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

### 10 Abstract

11 The electrochemical homo-polymerization of *o*-, *m*- and *p*-aminobenzoic acids has been performed on Pt electrodes  
12 in perchloric acid aqueous medium by cyclic scanning of the potential. Different limit potentials were employed to  
13 obtain thin polymeric films. When the switching potential was extended beyond the respective monomer oxidation  
14 peak, a rather degraded material was obtained. In situ FTIR spectroscopy has been used to characterize the redox  
15 response of films synthesized at the lower potential limits. Characteristic absorption features related with benzenoid  
16 and quinoid rings and different types of C–N bonds suggest the presence of redox processes similar to those undergone  
17 by the parent compound polyaniline. In addition, the existence of a chemical interaction between –COOH and –NH–  
18 groups in the reduced state of the three homopolymers studied can be suggested. Carbon dioxide has been detected at  
19 potentials higher than 1.0 V (RHE) irrespective of the polymeric material, thus indicating its degradation.  
20 © 2004 Published by Elsevier Ltd.

21 *Keywords:* Aminobenzoic acid; Electropolymerization; Cyclic voltammetry; in situ FTIR spectroscopy

### 23 1. Introduction

24 Organic conducting polymers can be switched revers-  
25 ibly between their conducting and insulating redox  
26 states through electrochemical oxidation/reduction pro-  
27 cesses [1]. Such reactions induce the exchange of coun-  
28 ter-ions with the electrolytic medium in order to  
29 preserve the electroneutrality of the organic film. In par-  
30 ticular, it is known that the electrochemical oxidation of

polyaniline (Pani) from the leucoemeraldine insulating 31  
form to the emeraldine conducting form is associated 32  
with the penetration of electrolyte anions within the 33  
polymer matrix [2]. It is expected that a number of fu- 34  
ture applications of Pani take advantage of this ex- 35  
change ability. However, the commercial use of this 36  
material is limited by its poor processability and low 37  
operation pH range inherent to the pristine polymer 38  
[1–3]. 39

In order to obtain a more processable material that 40  
can be dissolved in common solvents, or even in aqueous 41  
medium, the modification of the Pani chemical structure 42  
is necessary by, for instance, the introduction of some 43

\* Corresponding author. Tel.: +34965909590; fax:  
+34965903537.

E-mail address: [morallon@ua.es](mailto:morallon@ua.es) (E. Morallon).

44 hydrophilic groups [1,3]. There exist two synthesis routes  
45 to achieve the chemical modification. On the one hand, a  
46 pristine Pani can be prepared through the chemical poly-  
47 merization of the aniline monomer and, subsequently,  
48 the desired chemical modification of the polymer can  
49 be performed, see for example [4,5]. A second possibility  
50 is the direct synthesis of the material by chemical (or  
51 electrochemical) polymerization of the adequate substi-  
52 tuted aniline monomer [6-8]. It has been reported that  
53 both procedures can yield more soluble materials,  
54 although the conductivity of the modified polymers de-  
55 creases significantly, even by several orders of magni-  
56 tude, compared with that of Pani [4,8-10].

57 The modification of the chemical structure of Pani  
58 has been also employed to widen the pH range within  
59 which the polymer is electrochemically active. It is  
60 known that, for the original polymer, the electroactivity  
61 is restricted to solutions of very low pH because a high  
62 protonation degree at the imine nitrogen atoms is  
63 needed [11]. In this way, the insertion of acidic groups  
64 in the polymer backbone could change the micro-envi-  
65 ronment of the imine centers, shifting the local pH to  
66 lower values. This hypothesis has deserved some critical  
67 comments [8], although it seems supported by the exper-  
68 imental result showing that Pani modified with either  
69 sulfonic or carboxylic substituents is able to keep par-  
70 tially its electroactivity in solutions of pH 7 and 10,  
71 respectively [4,8]. It is also worth mentioning that, addi-  
72 tionally, the insertion of these kind of substituents re-  
73 sults in the modification of the ion exchange properties  
74 of the film: sulfonated or carboxylated polyanilines are  
75 known to act as *self-doped* Pani derivatives [10]. In these  
76 materials, the anionic groups bonded to the hydrocar-  
77 bon chain can compensate the positive charges gener-  
78 ated along the polymer backbone during the oxidation  
79 processes. Consequently, the anions of the electrolyte  
80 do not penetrate the film and the excess of positive  
81 charge is eliminated by the expulsion of protons out of  
82 the organic matrix.

83 Despite the extensive literature dealing with the syn-  
84 thesis and characterization of sulfonated polyanilines,  
85 few papers pay attention to their parent carboxylated  
86 derivatives [12-21]. In addition, most of those reports  
87 are devoted to the study of the copolymers formed by  
88 either chemical or electrochemical polymerization of  
89 anilines and *o*-aminobenzoic acid (anthranilic acid)  
90 [12,13,15,17,21]. A comparison between the homopoly-  
91 mers synthesized electrochemically from *o*-, *m*- and  
92 *p*-aminobenzoic acids was reported for the first time by  
93 Thiemann and Brett [18,19]. The polymerization was  
94 carried out on glassy carbon and ITO electrodes and  
95 several *ex situ* characterization techniques were em-  
96 ployed. They concluded that homopolymers derived  
97 from aminobenzoic acids are short-chain polymeric  
98 materials with a voltammetric behavior different from  
99 that displayed by polyaniline. Unfortunately, and prob-

ably due to the slow rate of electropolymerization, the  
100 IR characterization of the homopolymers was not done.  
101 The spectroscopic study was limited to *ex situ* IR mea-  
102 surements of the copolymers formed from *o*-, *m*- and  
103 *p*-aminobenzoic acids with aniline for reactant ratios  
104 of 1:1.  
105

106 The present contribution aims to characterize homo-  
107 polymers of aminobenzoic acids at the molecular level  
108 and in the electrochemical environment by means of a  
109 powerful technique such as the *in situ* FTIR spectros-  
110 copy. Since this characterization tool allows to obtain  
111 vibrational information from very small amounts of  
112 material, it is believed that it could serve as an improved  
113 alternative to obtain direct spectroscopic information  
114 from polyaminobenzoic acids. In this way, the *in situ*  
115 FTIRS method could allow the problems associated to  
116 the copolymerization of polyaminobenzoic acids with  
117 aniline to overcome.

## 2. Experimental

118

119 The monomers employed for the polymerization  
120 reaction were of reagent grade supplied by Merck. The  
121 electrolytic medium used for the synthesis and the elec-  
122 trochemical characterization of the polymeric materials  
123 was 0.1 M HClO<sub>4</sub> in ultrapure water (18.2 MΩ cm).  
124 The *in situ* FTIR experiments were also carried out in  
125 perchloric acid aqueous solutions but using either  
126 99.9%-D D<sub>2</sub>O (Aldrich) or 18.2 MΩ cm H<sub>2</sub>O as solvents.

127 The working electrode for the voltammetric study  
128 was a spherical polycrystalline platinum electrode with  
129 an area of about 4 mm<sup>2</sup>. For the *in situ* spectroscopic  
130 characterization, the polymers were grown up on a mir-  
131 ror-polished platinum disk electrode. The counter elec-  
132 trode was a platinum wire in all cases. All potentials  
133 were measured against a reversible hydrogen electrode  
134 (RHE) immersed in the working solutions through a  
135 Luggin capillary. The bare Pt working electrode was  
136 thermally cleaned and subsequently protected from the  
137 laboratory atmosphere by a droplet of ultrapure water.  
138 Then, it was transferred to the working solution which  
139 was previously deaerated by bubbling N<sub>2</sub>. Cyclic vol-  
140 tammograms were recorded at 50 mV s<sup>-1</sup> and at room  
141 temperature. After polymerization, the working elec-  
142 trode was extracted from the electrochemical cell, thor-  
143 oughly rinsed with water to remove any attached  
144 monomer species and transferred to a clean background  
145 solution containing 0.1 M HClO<sub>4</sub> (free of any monomer)  
146 to be characterized by voltammetric or spectroscopic  
147 techniques.

148 A Nicolet Magna 850 spectrometer was employed for  
149 the *in situ* FTIR experiments. The spectroelectrochemi-  
150 cal cell was provided with a prismatic CaF<sub>2</sub> window be-  
151 veled at 60°. The interferograms were acquired with the  
152 working electrode surface pressed against this window

153 and were collected at  $8 \text{ cm}^{-1}$  resolution. The final spectra  
154 are presented in the usual form  $\Delta R/R$ , for which, positive-going  
155 (upward) bands are related with vibrational modes that disappear (or become inactive) at the sample  
156 potential. On the contrary, negative-going (downward)  
157 bands are displayed when the related vibration mode develops (or becomes active) at the sample potential.  
158  
159

### 160 3. Results and discussion

#### 161 3.1. Electrochemical study

162 The electrochemical polymerization of the three  
163 aminobenzoic acid isomers was carried out in 0.1 M  
164  $\text{HClO}_4$  solutions containing, respectively, 10 mM of  
165 the corresponding monomer. The platinum working  
166 electrode was immersed in the polymerization media at  
167 a controlled potential of 0.06 V in order to avoid the initial  
168 oxidation of the monomeric species. Fig. 1(a) shows

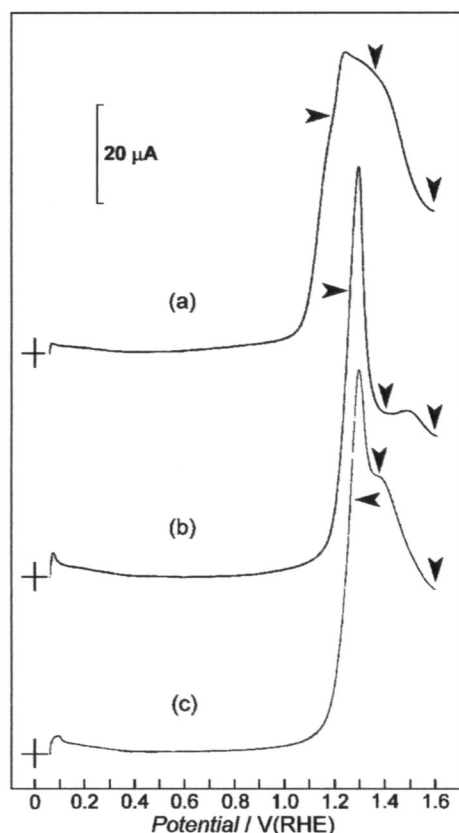


Fig. 1. Linear sweep voltammograms recorded for a Pt electrode in 0.1 M  $\text{HClO}_4$  during the electrochemical oxidation of: (a) *o*-aminobenzoic acid; (b) *m*-aminobenzoic acid; (c) *p*-aminobenzoic acid. Scan rate  $50 \text{ mV s}^{-1}$ . Monomer concentration 10 mM in all cases.

a single potential excursion performed between 0.06 V  
169 and 1.6 V in solutions containing *o*-aminobenzoic acid. 170  
The onset of its oxidation occurs at around 1.05 V 171  
and, after displaying a shoulder, the current reaches a 172  
maximum at 1.24 V. After this peak has been surpassed, 173  
an overlapped voltammetric wave of lower intensity is 174  
also recorded. Finally, the current falls continuously until 175  
the upper potential limit is reached. This voltammetric 176  
behavior contrasts with that recorded, under the same 177  
experimental conditions, during the oxidation of 178  
*m*-aminobenzoic acid, Fig. 1(b), and *p*-aminobenzoic 179  
acid, Fig. 1(c). Firstly, the initial stages of the electro- 180  
chemical oxidation of the two latter species are shifted 181  
80 mV to more positive potentials with respect to the 182  
*o*-aminobenzoic isomer. Furthermore, the main anodic 183  
feature for these monomers peaks at around 1.3 V in 184  
both cases. This value represents a close to 50 mV positive 185  
shift in the absence of current shoulders. Finally, the 186  
existence of a second anodic maximum (similar to that 187  
recorded for the *ortho* isomer) peaked at 1.48 V for the 188  
*m*-aminobenzoic and at 1.38 V for the *p*-aminobenzoic 189  
acid isomer can be also observed in their respective vol- 190  
tammetric curves. 191

The fact that the *ortho*-substituted monomer is oxidized 192  
at lower potentials seems to reflect a higher stability of the 193  
*meta* and *para* substituted anilines compared to the former 194  
isomer. This seems to be supported by the results shown in 195  
Table 1, for which, the oxidation charge recorded under the 196  
voltammetric curves decreases in the order *ortho* > *para* > 197  
*meta*, thus pointing that the electrochemical reactivity 198  
increases oppositely, i.e. from the *meta* to the *ortho* 199  
isomer. It should be noted that, due to the slow rate of 200  
polymerization, the voltammetric charge measured for each 201  
curve corresponds essentially to the oxidation of the respective 202  
monomeric species, with negligible contribution of the poly- 203  
meric products. Thus, it would be expected that the polymer 204  
obtained from the *o*-aminobenzoic acid oxidation could reach 205  
higher thickness at identical polymerization times and limit 206  
potential. 207  
208

Poly(aminobenzoic acid) films have been synthesized 209  
by cyclic scanning of the potential between 0.06 V and 210  
three different switching potentials. This experimental 211  
strategy has been followed in order to assess the role 212

Table 1

Potentials for the onset of monomer oxidation, potentials of the anodic main peaks and voltammetric charge measured for the oxidation of *o*-, *m*- and *p*-aminobenzoic acids

	$E_{\text{onset}}$ (V)	$E_{\text{peak}}$ (V)	$Q_{\text{oxidation}}$ ( $\mu\text{C}$ ) <sup>a</sup>
<i>o</i> -Aminobenzoic acid	1.05	1.24	1680
<i>m</i> -Aminobenzoic acid	1.13	1.28	1230
<i>p</i> -Aminobenzoic acid	1.13	1.29	1540

<sup>a</sup> Calculated from 1.0 to 1.6 V and without double layer capacity correction.

213 played by the upper potential limit reached during the  
 214 synthesis in the electrochemical properties of the depos-  
 215 ited polymers. A higher potential limit in the CVs makes  
 216 it possible to synthesize larger amounts of material keep-  
 217 ing constant the number of sweeps done. However, the  
 218 use of very high potentials could affect the quality (elec-  
 219 troactivity, degradation level, etc.) of the obtained poly-  
 220 mer. Accordingly, it would be desirable to reach a  
 221 compromise between the polymerization rate and the re-  
 222 quired film quality. The switching potentials we have se-  
 223 lected are marked with arrows in Fig. 1 for each  
 224 monomeric species. The first upper potential limit was  
 225 located just before the respective first anodic peaks.  
 226 The second limit was set at around 1.4 V, that is after  
 227 the main anodic peak and, finally, the polymers were  
 228 also synthesized by scanning of the potential up to  
 229 1.6 V. The voltammetric response of poly(*o*-aminoben-  
 230 zoic acid) synthesized after 25 potential cycles up to  
 231 1.2 V (a), 1.37 V (b) and 1.6 V (c) are shown in Fig. 2.  
 232 Following the synthesis process, the electrodes coated  
 233 with the polymeric films were rinsed with water and then  
 234 immersed in the background electrolyte free of mono-

235 mer at 0.06 V. The electrochemical behavior of the films  
 236 was tested in the 0.06–1.0 V potential range. From the  
 237 voltammetric responses depicted in Fig. 2 it can be ob-  
 238 served that the potential limit of 1.2 V generates an  
 239 electroactive film with, at least, two distinct redox pro-  
 240 cesses. The first one appears at 0.48/0.42 V, which results  
 241 in a peak separation,  $\Delta E_p$  close to 60 mV; the second  
 242 process is observed at 0.73/0.57 V and gives a  
 243  $\Delta E_p = 160$  mV. This voltammetric profile contrasts with  
 244 those recorded for the polymers grown up to 1.37 V and  
 245 1.6 V, for which no redox response can be observed in  
 246 Fig. 2(b) and (c). From this result it can be inferred that  
 247 the potential cycling beyond the limit corresponding to  
 248 the main anodic peak at 1.24 V in Fig. 1(a) results in  
 249 the generation of non-electroactive poly(*o*-aminobenzoic  
 250 acid) films, probably as a consequence of their  
 251 degradation.

252 Fig. 3 shows the cyclic voltammograms recorded for  
 253 poly(*m*-aminobenzoic acid) for a similar experiment to  
 254 that shown in Fig. 2. The synthesis of the polymeric film  
 255 was concluded after 25 potential cycles up to 1.25 V (a),  
 256 1.4 V (b) and 1.6 V (c). Contrary to what is observed for

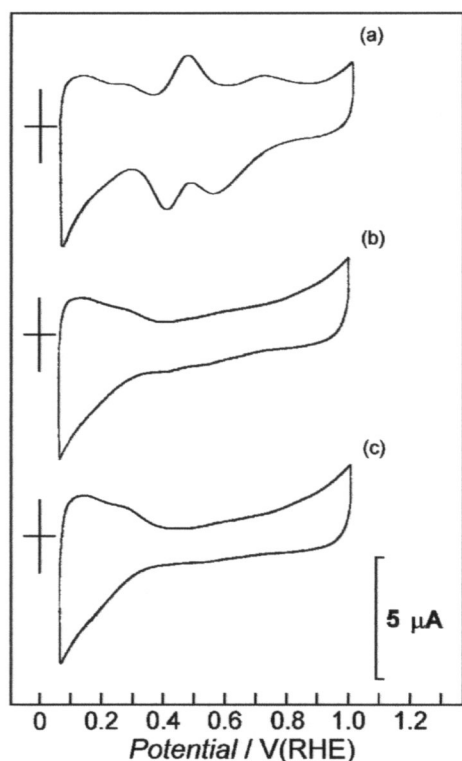


Fig. 2. Voltammetric response of poly(*o*-aminobenzoic acid) films in 0.1 M perchloric acid background solutions. Films deposited on a Pt electrode after 25 potential cycles in 0.1 M HClO<sub>4</sub> containing 10 mM *o*-aminobenzoic acid at the following potential limits: (a) 1.2 V; (b) 1.37 V; (c) 1.6 V. Scan rate 50 mV s<sup>-1</sup>.

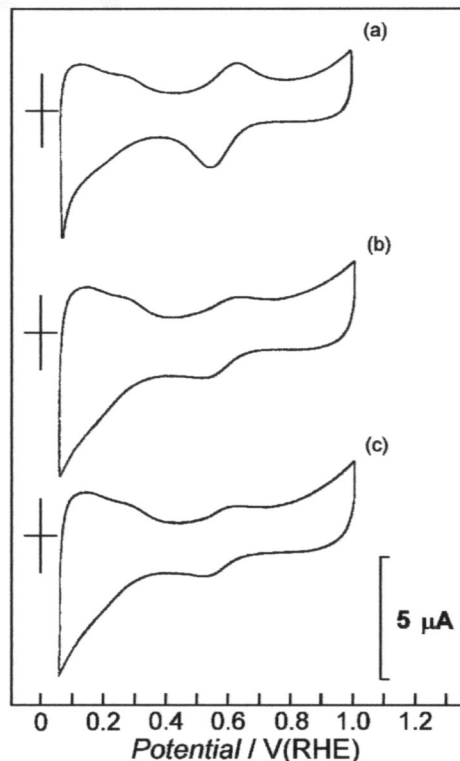


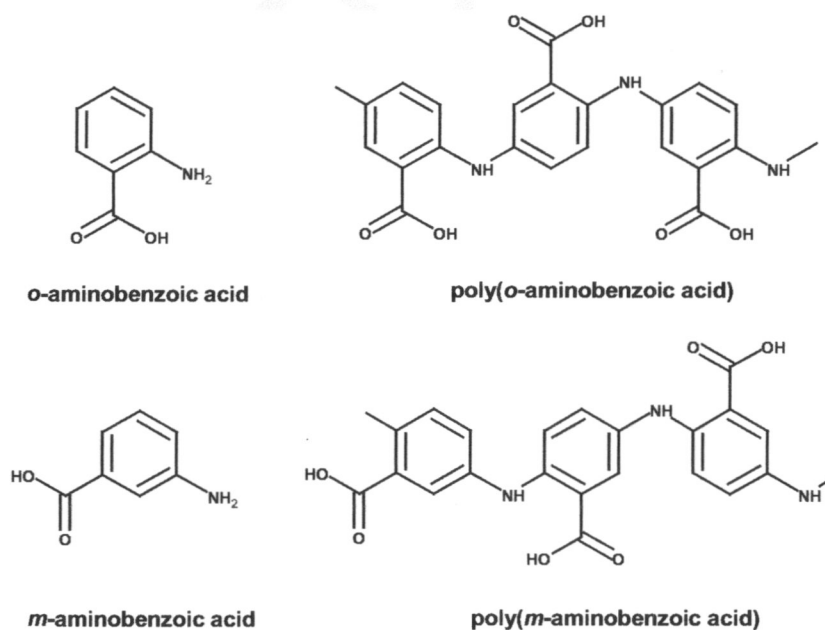
Fig. 3. Voltammetric response of poly(*m*-aminobenzoic acid) films in 0.1 M perchloric acid background solutions. Films deposited on a Pt electrode after 25 potential cycles in 0.1 M HClO<sub>4</sub> containing 10 mM *m*-aminobenzoic acid at the following potential limits: (a) 1.25 V; (b) 1.4 V; (c) 1.6 V. Scan rate 50 mV s<sup>-1</sup>.

257 the poly(*o*-aminobenzoic acid), the voltammetric curves  
 258 displayed a unique redox process at 0.64/0.53 V. Both  
 259 the peak separation,  $\Delta E_p = 110$  mV, and the middle po-  
 260 tential,  $E = 0.59$  V, are similar in the three cases. Addi-  
 261 tionally, the intensity of the redox peaks in Fig. 3  
 262 indicates that those poly(*m*-aminobenzoic acid) films  
 263 whose synthesis has been restricted at potentials lower  
 264 than that of the main anodic peak in Fig. 1(b) are more  
 265 electroactive. This is in agreement with the behavior of  
 266 the parent poly(*o*-aminobenzoic acid). The middle po-  
 267 tential value of the redox process of poly(*m*-aminoben-  
 268 zoic acid) is shifted around 140 mV to higher  
 269 potentials in relation to the first process recorded for  
 270 the parent polymer in Fig. 2. Such a result seems to indi-  
 271 cate that the polymer generated from the *meta* isomer is  
 272 considerably more difficult to oxidize than that derived  
 273 from the *ortho* species. This could be interpreted as a  
 274 consequence of the existence of different degradation  
 275 and branching levels, but also to the presence of polymer  
 276 chains with shorter length in poly(*m*-aminobenzoic  
 277 acid). In fact, assuming a head-to-tail coupling as the  
 278 main path to grow the polymeric chains, both the *ortho*  
 279 and *meta* isomers should produce polymers with quite  
 280 similar chemical structure: the *ortho* position with re-  
 281 spect to one carboxylate group at a given monomeric  
 282 unit (which is occupied by a nitrogen atom) would be lo-  
 283 cated in *meta* with respect to the carboxylate group of  
 284 the neighboring unit. This picture is the same for both  
 285 "ideally grown" polymeric chains, as can be clearly ob-  
 286 served in Scheme 1.

287 Finally, we have examined the redox behavior of 287  
 288 those films generated from the electrochemical polymer- 288  
 289 ization of *p*-aminobenzoic acid at 1.25 V, 1.37 V and 289  
 290 1.6 V. Since the *para* position is occupied in this mono- 290  
 291 meric species, the polymerization process should pro- 291  
 292 ceed either through the *ortho* or *meta* position, or by a 292  
 293 combination of both. Consequently, the chemical struc- 293  
 294 ture of the film formed is expected to be quite different 294  
 295 from that of poly(*o/m*-aminobenzoic acids). Fig. 4 shows 295  
 296 the voltammetric behavior recorded between 0.06 V and 296  
 297 1.0 V for the films obtained according to Fig. 1(c). 297  
 298 Again, only the polymeric material synthesized by cyclic 298  
 299 scanning of the potential up to 1.25 V displays a clear re- 299  
 300 dox process. In particular, the voltammetric profile 300  
 301 shows that the anodic part of the redox process seems 301  
 302 to be split into two overlapping peaks centered at 302  
 303 0.63 V and 0.73 V. On the contrary, the cathodic branch 303  
 304 of the cyclic voltammogram displays only a single peak, 304  
 305 which is centered at 0.57 V and involves an electrical 305  
 306 charge corresponding to, approximately, the sum of 306  
 307 the two anodic peaks (69.5  $\mu$ C for the oxidation and 307  
 308 69.3  $\mu$ C for the reduction cycle in the 0.5–0.9 V poten- 308  
 309 tial range). 309

### 3.2. In situ FTIR spectroscopic study 310

311 The previous voltammetric study suggests that only 311  
 312 small amounts of polymerization products can be iso- 312  
 313 lated on the surface of the Pt working electrodes from 313  
 314 the oxidation of aminobenzoic acid isomers. In spite of 314  
 315 this fact, the high sensitivity of the in situ FTIR spec- 315



Scheme 1.

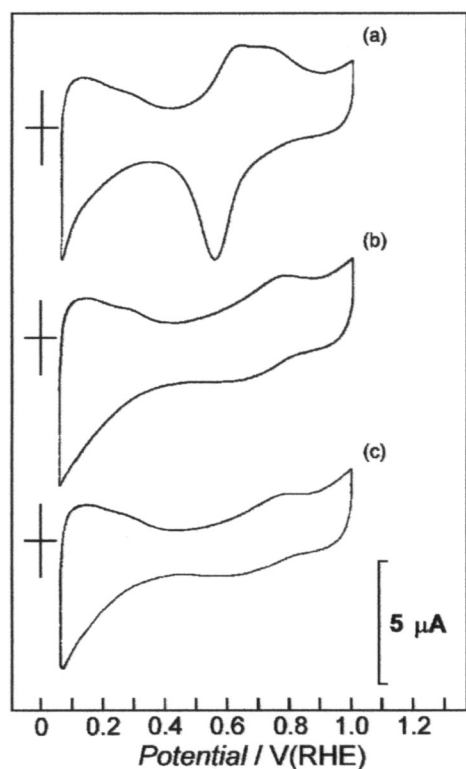


Fig. 4. Voltammetric response of poly(*p*-aminobenzoic acid) films in 0.1 M perchloric acid background solutions. Films deposited on a Pt electrode after 25 potential cycles in 0.1 M HClO<sub>4</sub> containing 10 mM *p*-aminobenzoic acid at the following potential limits: (a) 1.25 V; (b) 1.37 V; (c) 1.6 V. Scan rate 50 mV s<sup>-1</sup>.

316 troscopy technique allows to obtain vibrational spectra  
 317 of poly(*o*-aminobenzoic acid) with quite good S/N ratio.  
 318 Fig. 5 shows a set of in situ FTIR spectra obtained for a  
 319 Pt electrode covered with poly(*o*-aminobenzoic acid) in  
 320 0.1 M HClO<sub>4</sub> medium. Following the electropolymeriza-  
 321 tion process the filmed electrode was transferred to the  
 322 spectroelectrochemical cell which was free of any mono-  
 323 meric species. The electrode was then carefully pressed  
 324 against the prismatic CaF<sub>2</sub> window and a reference spec-  
 325 trum was acquired at 0.2 V. After that, the potential was  
 326 stepped sequentially to higher values (which are indi-  
 327 cated in Fig. 5) and a sample spectrum was acquired  
 328 at each potential. By referring each of the sample spectra  
 329 to the reference collected previously it is possible to fol-  
 330 low spectroscopically the redox transition undergone by  
 331 poly(*o*-aminobenzoic acid). The spectra of Fig. 5 display  
 332 several absorption bands whose intensities increase as  
 333 the potential is shifted to more positive values, thus  
 334 showing the progress of the oxidation processes with  
 335 the applied potential. Characteristic positive-going  
 336 bands are observed at 1676, 1505, 1310 and 1242 cm<sup>-1</sup>  
 337 which are indeed related with vibrational modes con-

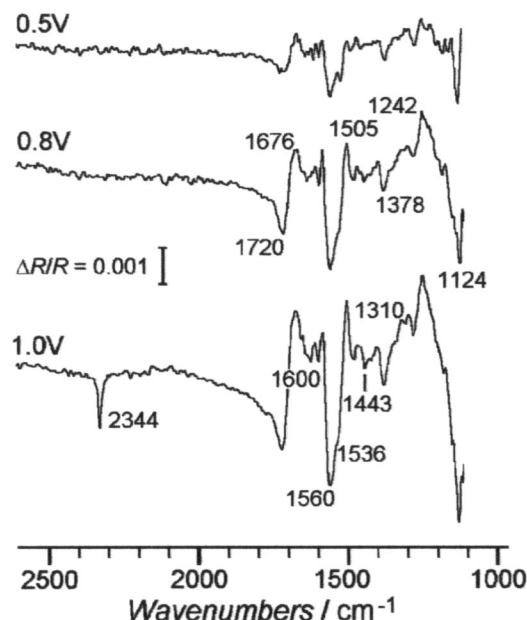
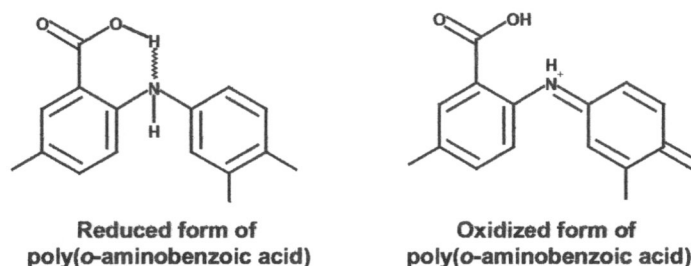


Fig. 5. In situ FTIR spectra collected during the oxidation of a poly(*o*-aminobenzoic acid) film in 0.1 M HClO<sub>4</sub> solution. Reference potential 0.2 V. Sample potentials indicated for each spectrum. 1000 interferograms were recorded at each potential. 8 cm<sup>-1</sup> resolution.

cerning to the reduced form of the polymer. Moreover,  
 downward bands which appear at 1720, 1600, 1560,  
 1536, 1443 and 1378 cm<sup>-1</sup> are related to vibrations com-  
 ing from the oxidized state of the polymer. It should be  
 noted the formation of carbon dioxide at 1.0 V (band at  
 2344 cm<sup>-1</sup>), which reveals the overoxidation (and degra-  
 dation) of the polymeric material at that potential. The  
 preservation of the carboxylic group in the chemical  
 structure of the polymer is evidenced by the presence  
 of the 1676 cm<sup>-1</sup> (reduced form) and 1720 cm<sup>-1</sup> (oxi-  
 dized form) absorption bands. The significant shift in  
 the peak frequency for this band upon oxidation (more  
 than 40 cm<sup>-1</sup> to higher energies) can be due to the exis-  
 tence of chemical interaction between the carboxylic and  
 the amino groups in the reduced state of poly(*o*-amino-  
 benzoic acid). It is well known that this kind of interac-  
 tion decreases considerably the C=O stretching  
 frequency of aryl carboxylic acids with amino or hydro-  
 xyl groups in the *ortho* position [22]. Thus, when the  
 polymer is oxidized, amine nitrogens transform into pro-  
 tonated imines and the C=O stretching frequency re-  
 turns to its characteristic value, which is higher than  
 1700 cm<sup>-1</sup>. This situation is illustrated in Scheme 2.

In order to facilitate the band assignments, the exper-  
 iment of Fig. 5 was reproduced in 0.1 M HClO<sub>4</sub>/D<sub>2</sub>O.  
 The use of D<sub>2</sub>O solvent allows the "mobile" acid H  
 atoms of poly(*o*-aminobenzoic acid) to be replaced by  
 D atoms (H/D ratio is about 0.001 in the electrolytic

338  
 339  
 340  
 341  
 342  
 343  
 344  
 345  
 346  
 347  
 348  
 349  
 350  
 351  
 352  
 353  
 354  
 355  
 356  
 357  
 358  
 359  
 360  
 361  
 362  
 363  
 364  
 365



Scheme 2.

366 medium). As a result, the amino and carboxyl groups of  
 367 the polymer will be deuterated whereas ring hydrogens  
 368 will remain unchanged. The spectra obtained in deuter-  
 369 ated water are displayed in Fig. 6. Here it is observed the  
 370 shift of several absorption features to lower energies. Ta-  
 371 ble 2 summarizes the peak frequencies observed for both  
 372 the reduced and oxidized states of the polymer and in-  
 373 cludes the proposed band assignments in both solvents.  
 374 Some remarkable features of the reduced state are that

Table 2

Assignments of the vibrational bands for the reduced and oxidized forms of poly(*o*-aminobenzoic acid) in acidic H<sub>2</sub>O and D<sub>2</sub>O solvents [14,16,17,22–24]

	Frequency (cm <sup>-1</sup> )		Assignments
	H <sub>2</sub> O	D <sub>2</sub> O	
Reduced state	1676	1660	Carboxylic acid (C=O) stretching
	1505	1489	Aromatic (C–C) stretching
		1372	(C–H) bending
	1310	1277	Benzenoid ring deformation
	1242	Benzenoid (C–N) stretching	
Oxidized state	1720	1702	Carboxylic acid (C=O) stretching
	1600	1599	Imine (C=N) stretching
	1560–30	1532	Quinoid ring (C=C) stretching
	1480–40	1435	Quinoid (>C–N=) stretching
	1378	1336	Intermediate order (C···N) stretching
	1124	1121	ClO <sub>4</sub> <sup>-</sup>

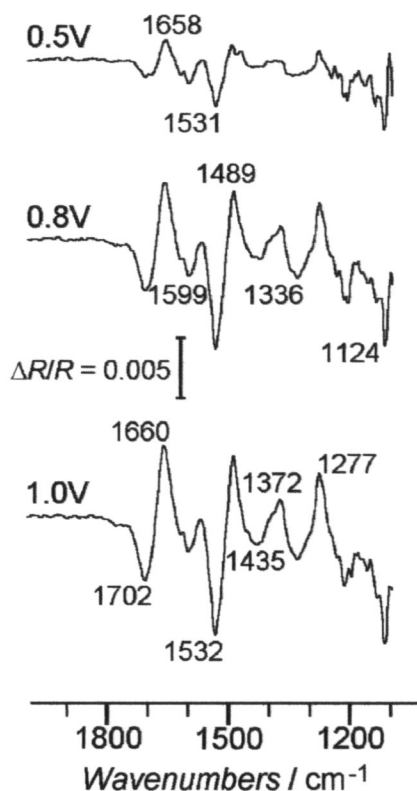


Fig. 6. In situ FTIR spectra collected during the oxidation of a poly(*o*-aminobenzoic acid) film in 0.1 M HClO<sub>4</sub>/D<sub>2</sub>O solution. Reference potential 0.2 V. Sample potentials indicated for each spectrum. 100 interferograms were recorded at each potential. 8 cm<sup>-1</sup> resolution.

both the carboxylic C=O and the aromatic C–C stretch- 375  
 ing vibrations are slightly red shifted upon deuteration, 376  
 whereas the effect of deuteration on the benzenoid ring 377  
 deformation and amine C–N stretching seems more sig- 378  
 nificant. Also, the broad positive-going absorption 379  
 peaked at 1372 cm<sup>-1</sup> in Fig. 6 which could be tentatively 380  
 associated with the C–H bending mode in benzenoid 381  
 rings, cannot be paired easily with any feature of the 382  
 spectra collected in H<sub>2</sub>O. An explanation of this result 383  
 can be that the 1400–1350 cm<sup>-1</sup> spectral region has sev- 384  
 eral contributions in H<sub>2</sub>O medium (from both the ox- 385  
 idized and reduced state of the polymer). In this way, 386  
 the disappearance of the 1372 cm<sup>-1</sup> mode is visible only 387  
 in D<sub>2</sub>O solvent, for which this frequency range is quite 388  
 free of perturbations. Regarding the oxidized form of 389  
 poly(*o*-aminobenzoic acid), the negative-going bands 390  
 observed in H<sub>2</sub>O and D<sub>2</sub>O can be easily paralleled. Thus, 391  
 imine (1600 cm<sup>-1</sup>) and quinoid ring C=C (doublet at 392  
 1536–1560 cm<sup>-1</sup>) stretching vibrations remain almost 393  
 unaltered upon deuteration. On the contrary, C–N 394  
 bonds with quinoid character which appear at around 395  
 1400 cm<sup>-1</sup> in H<sub>2</sub>O seem to be downshifted in D<sub>2</sub>O. 396

397 The negative-going band at  $1120\text{ cm}^{-1}$  which overlaps  
398 the quinoid C–H in-plane bending is clearly assigned  
399 to perchlorate anions, which penetrate the film to com-  
400 pensate the positive charges generated during the oxida-  
401 tion process. It should be noted that, in strongly acidic  
402 medium, the protonated carboxylic group is not able  
403 to balance the charge by itself.

404 The assignment of the characteristic vibrational  
405 bands for poly(*o*-aminobenzoic acid) facilitates the iden-  
406 tification of the absorption features in the spectra col-  
407 lected for poly(*m*-aminobenzoic acid). Fig. 7 shows a  
408 set of in situ FTIR spectra obtained in the  $1100\text{--}2500\text{ cm}^{-1}$   
409 spectral region for the latter material in a  
410 parallel experiment to that shown in Fig. 5. Similarly  
411 to poly(*o*-aminobenzoic acid), the presence of two differ-  
412 ent absorptions for the carboxylic C=O stretching  
413 vibration at  $1700\text{ cm}^{-1}$  (reduced) and  $1729\text{ cm}^{-1}$  (oxi-  
414 dized form) reveals the existence of chemical interaction  
415 between the –COOH and –NH groups in the reduced  
416 state of the polymer. Negative-going absorption bands  
417 in the vicinities of  $1550\text{ cm}^{-1}$ , which are ascribed to  
418 the formation of C=C structures, in addition to the dis-  
419 appearance of the C–C stretching mode at ca.  $1500\text{ cm}^{-1}$   
420 reveal the loss of aromatic character at the benzenoid  
421 rings and their transformation into quinoid centers as  
422 the potential is made more positive. Moreover, different  
423 C–N vibrational features related with amine, imine or  
424 intermediate order bonds can be also observed in this  
425 spectra. From the similarities found between the spectra

shown in Fig. 7 and those in Fig. 5, it can be concluded  
that, from an spectroscopic standpoint, the redox pro-  
cess of poly(*m*-aminobenzoic acid) is rather similar to  
that occurring in the parent poly(*o*-aminobenzoic acid).

426  
427  
428  
429  
430 Finally, Fig. 8 shows the in situ FTIR spectra col-  
431 lected during the anodic polarization of a Pt electrode  
432 covered with a poly(*p*-aminobenzoic acid) film. Charac-  
433 teristic infrared absorptions in the  $1200\text{--}1500\text{ cm}^{-1}$  and  
434 in the  $1650\text{--}2500\text{ cm}^{-1}$  spectral ranges are similar to  
435 those displayed by both poly(*o*-aminobenzoic acid) and  
436 poly(*m*-aminobenzoic acid). In particular, it is clear that  
437 the three polymeric films undergo a degradation reaction  
438 yielding  $\text{CO}_2$  (band at  $2344\text{ cm}^{-1}$ ) at potentials higher  
439 than  $1.0\text{ V}$ . Moreover, the chemical interaction between  
440 adjacent amino and carboxylic groups seems to be sup-  
441 ported by the bipolar character of the absorption centered  
442 at around  $1700\text{ cm}^{-1}$  which is due to the C=O  
443 stretching mode. However, an interesting difference ap-  
444 pears between the spectra of Fig. 8 and those of Figs.  
445 5 and 7. Contrary to its parent polymers, the spectra ob-  
446 tained during the oxidation of a poly(*p*-aminobenzoic  
447 acid) film are dominated by the vanishing of a vibra-  
448 tional mode at  $1609\text{ cm}^{-1}$ . Both the frequency and the  
449 positive character of this clear-cut band agree with the  
450 disappearance of either an N–H deformation vibrational  
451 mode of a primary aromatic amine or a C–C stretching  
452 of aromatic rings. The first possibility implies, necessar-  
453 ily, the presence of significant amounts of free amino  
454 groups in the chemical structure of this polymeric film.

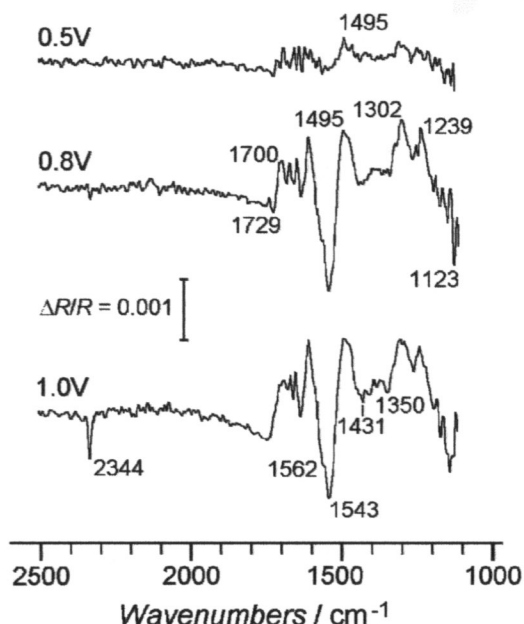


Fig. 7. In situ FTIR spectra recorded during the oxidation of a poly(*m*-aminobenzoic acid) film in  $0.1\text{ M HClO}_4$  solution. Reference potential  $0.2\text{ V}$ . Sample potentials indicated for each spectrum.  $1000$  scans at each potential.  $8\text{ cm}^{-1}$  resolution.

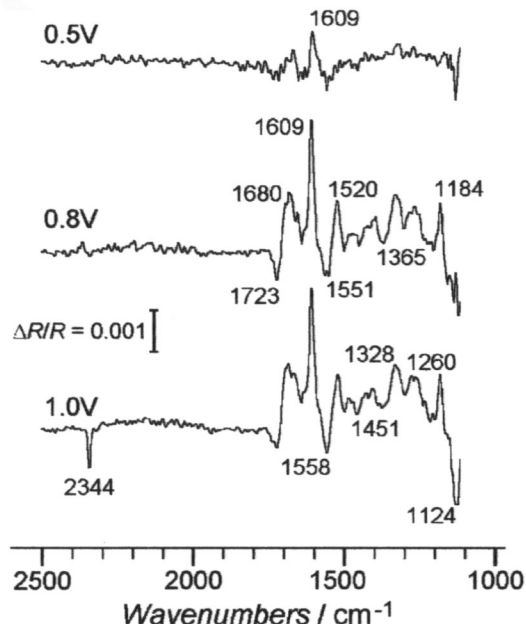


Fig. 8. In situ FTIR spectra recorded during the oxidation of a poly(*p*-aminobenzoic acid) film in  $0.1\text{ M HClO}_4$  solution. Reference potential  $0.2\text{ V}$ . Sample potentials indicated for each spectrum.  $1000$  scans at each potential.  $8\text{ cm}^{-1}$  resolution.



455 This would mean that poly(*p*-aminobenzoic acid) is  
 456 composed of large numbers of short-chain oligomeric  
 457 species (probably no longer than trimers or tetramers)  
 458 each one having a primary amino group at the end.  
 459 The second hypothesis means the existence of diverse  
 460 vibrational modes for the aromatic ring C–C stretching  
 461 because the transformation of benzenoid rings into  
 462 quinoid ones is indeed testified by the existence of a positive-going  
 463 band at  $1520\text{ cm}^{-1}$  and its coupled negative-going  
 464 band near  $1560\text{ cm}^{-1}$ . It is very difficult to ascertain  
 465 which hypothesis reflects the real situation but  
 466 experiments performed using  $\text{D}_2\text{O}$  as solvent have  
 467 revealed the presence of a positive-going feature with lower  
 468 intensity centered at  $1605\text{ cm}^{-1}$  (figure not shown).  
 469 Since the amine hydrogen atoms could be exchanged  
 470 with electrolyte deuterons, the result suggests that the  
 471  $1609\text{ cm}^{-1}$  vibrational mode should be better ascribed  
 472 to a C–C stretching of benzenoid rings.

473 Regarding the possible structure of poly(*p*-aminobenzoic  
 474 acid), the following points should be considered: (i)  
 475 carboxylic groups are electron withdrawing substituents  
 476 and deactivate the aromatic ring directing the substitution  
 477 to the position *meta* to them (this would yield an  
 478 *ortho*-substituted polymer with respect to the amino  
 479 group); (ii) it seems rather difficult for the *p*-aminobenzoic  
 480 acid monomer to undergo a *para* coupling reaction  
 481 similar to that found for polyaniline because IR spectroscopy  
 482 indicates that most of the carboxylic groups are kept in the  
 483 polymer structure after the polymerization. Then, the existence  
 484 of significant amounts of *para*-substituted chains has to be  
 485 discarded; (iii) on the other hand, the chemical interaction  
 486 between –COOH and –NH groups observed by in situ FTIR  
 487 spectroscopy would be only possible if both functionalities were  
 488 in the *ortho* position. As the latter hypothesis seems supported  
 489 by an experimental result, we propose that the preferential  
 490 growth of poly(*p*-aminobenzoic acid) could take  
 491 place via the incorporation of *p*-aminobenzoic mono-

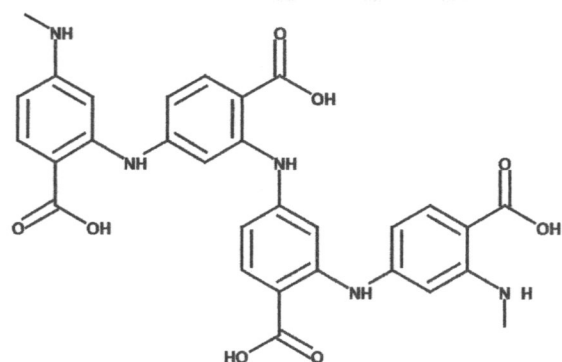
493 mers at the *ortho* position to the carboxylic group, as  
 494 shown in Scheme 3, although contribution of *meta*-  
 495 substituted rings to the real polymer structure cannot  
 496 be discarded.

#### 4. Conclusions 497

498 The electrochemical homo-polymerization of *ortho*,  
 499 *meta* and *para* aminobenzoic acid isomers has been per-  
 500 formed in strongly acidic medium on platinum elec-  
 501 trodes under similar experimental conditions. It has  
 502 been observed a strong effect of the switching potential  
 503 on the film quality (degradation level) for the three poly-  
 504 mers investigated. Those films generated at moderate  
 505 potentials (below the first anodic maximum) are more  
 506 electroactive.

507 In situ FTIR spectroscopy has revealed that the three  
 508 polymeric materials degrade yielding  $\text{CO}_2$  when submit-  
 509 ted at potentials higher than 1.0 V (RHE), at least if a  
 510 substrate of platinum is employed. This means that the  
 511 electrochemical synthesis is a process in which polymer-  
 512 ization and degradation reactions are coupled because  
 513 the lower potential limit required to produce the oxida-  
 514 tion of the monomeric species is around 1.1 V. The  
 515 unexpected low frequency observed for the C=O  
 516 stretching mode of –COOH in the reduced state of the  
 517 polymers strongly suggests that there exists a chemical  
 518 interaction (hydrogen bonding) between the carboxylic  
 519 and amino groups located in *ortho* position. When the  
 520 polymers are oxidized, the carboxylic group does not  
 521 interact and the C=O stretching frequency recovers  
 522 the characteristic value for a carboxylic acid.

523 Despite the different voltammetric response shown by  
 524 poly(*o*-aminobenzoic acid) and poly(*m*-aminobenzoic  
 525 acid), the spectroscopic results point that both polymeric  
 526 materials undergo very similar redox processes. This  
 527 suggests that the chemical structure of both polymers  
 528 could be similar, being the different voltammetric behav-  
 529 ior due to the existence of different chain lengths,  
 530 branching degree and degradation level. The compar-  
 531 ison between the in situ FTIR spectra obtained for  
 532 poly(*p*-aminobenzoic acid) and poly(*o/m*-aminobenzoic  
 533 acids) suggests that the oxidation process of the former  
 534 material involves a slightly different chemical transfor-  
 535 mation. This could be interpreted by the occurrence of  
 536 coupling of monomers at the *ortho* position to the amino  
 537 group, which would yield a polymeric structure some-  
 538 what different to that proposed for poly(*o/m*-aminoben-  
 539 zoic acids).



poly(*p*-aminobenzoic acid)

Scheme 3.

#### Acknowledgment 540

541 This work has been financed by the Spanish Ministe-  
 542 rio de Educación y Ciencia (projects MAT2001-1007

543 and MAT2004-01479) and by the Generalitat Valenci-  
544 ana (Grupos04/75).

#### 545 References

- 546 [1] Heeger AJ. *Angew Chem Int Ed* 2001;40:2591.  
547 [2] Salaneck WR, Lundstrom I, Haung WS, MacDiarmid AG.  
548 *Synth Met* 1986;13:291.  
549 [3] Gao Y, Smith P, Heeger AJ. *Synth Met* 1992;48:91.  
550 [4] Yue J, Epstein AJ. *J Am Chem Soc* 1990;112:2800.  
551 [5] Liu G, Freund MS. *Chem Mater* 1996;8:1164.  
552 [6] Shimizu S, Saitoh T, Uzawa M, Yuasa M, Yano K,  
553 Maruyama T, et al. *Synth Met* 1997;85:1337.  
554 [7] Watanabe A, Mori K, Iwabuchi A, Iwasaki Y, Nakamura  
555 Y, Ito O. *Macromolecules* 1989;22:3521.  
556 [8] Karyakin AA, Strakhova AK, Yatsimirsky AK. *J Electroanal Chem* 1994;371:259.  
557 [9] Wang X-H, Li J, Wang L-X, Jing X-B, Wang F-S. *Synth Met* 1995;69:147.  
558 [10] Huang WS, Humphrey BD, MacDiarmid AG. *J Chem Soc Faraday Trans* 1986;82:2385.  
561 [11] Malinauskas A. *J Power Source* 2004;126:214.  
562 [12] Chan HSO, Ng SC, Sim WS, Tan KL, Tan BTG. *Macromolecules* 1992;25:6029. 563  
564 [13] Chan HSO, Ng SC, Seow SH, Sim WS, Hor TSA. *J Thermal Anal* 1993;39:177. 565  
566 [14] Rao PS, Sathyanarayana DN. *Polymer* 2002;43:5051. 567  
568 [15] Wu M-S, Wen T-C, Gopalan A. *Mater Chem Phys* 2002;74:58. 569  
570 [16] Rivas BL, Sánchez CO. *J Appl Pol Sci* 2003;89:2641. 570  
571 [17] Yan H, Wang H-J, Adisasmito S, Toshima N. *Bull Chem Soc Jpn* 1996;69:2395. 571  
572 [18] Thiemann C, Brett CMA. *Synth Met* 2001;123:1. 573  
574 [19] Brett CMA, Thiemann C. *J Electroanal Chem* 2002;538-539:215. 574  
575 [20] Salavagione HJ, Acevedo DF, Miras MC, Motheo AJ, Barbero C. *J Polym Sci Part A Polym Chem* 2004;42:5587. 576  
577 [21] Nguyen MT, Díaz AF. *Macromolecules* 1995;28:3411. 578  
579 [22] Socrates G. *Infrared and Raman characteristic group frequencies*. Chichester: Wiley; 2001. 580  
581 [23] Louarn G, Lapkowski M, Quillard S, Pron A, Buisson JP, Lefrant S. *J Phys Chem* 1996;100:6998. 581  
582 [24] Ping Z, Nauer GE, Neugebauer H, Theiner J. *J Electroanal Chem* 1997;420:301. 583  
584 585