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Effect of chemical functionalization on the electrochemical properties of conducting polymers. Modification of polyaniline by diazonium ion coupling and subsequent reductive degradation

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ABSTRACT

The electrochemical properties of polyaniline (PANI) can be altered by coupling the polymer with aryldiazonium ions. The ions are synthesized by diazotization of aromatic primary amines (1-aminoanthraquinone, sulphadiazine and 4-cyanoaniline) bearing functional groups which are then linked to the polyaniline backbone. All materials produced are electroactive, suggesting that the reaction involves coupling of the diazonium ion with the aromatic rings and not nucleophilic substitution by the aminic nitrogen of PANI on the aryl cations. The electrochemical properties of the modified polymers are different to those of PANI, likely due to electronic and steric effects of the attached groups. Reductive degradation of the azo linkages, using dithionite ion, removes the attached moieties leaving primary amino groups attached to the polyaniline backbone. In that way, the effect of the attached groups on the electrochemical properties of PANI is eliminated. FTIR spectroscopy measurement of the different polymers supports the proposed mechanism. Using the method a polymer containing redox (anthraquinone) groups, which could be used for charge storage, is obtained. Additionally a material containing sulphadiazine moieties, which can be released in vivo by bacterial activity, is also produced. The molecule is a well-known sulfa drug with bacteriostatic activity. The reaction sequence seems to be of general application to modify polyanilines, by attaching functional groups, and then to produce a PANI backbone bearing primary amino groups. Evidence is presented on the kinetic control of attached group removal.

1. Introduction

The ability to control the properties of materials, such as conducting polymers, is of paramount importance to develop technological applications [1]. Among the conductive polymers, polyaniline (PANI) is one of the most stable, and this property, together with its reasonable electrical conductivity and interesting redox properties associated with the chain heteroatom, make it one of the most attractive conductive polymers [2]. The usual way to produce new intrinsically conducting polymers (ICP) involves the synthesis or acquisition of a monomer, homopolymerization or copolymerization, followed for detailed study of the polymer properties [3]. Another, less explored, route to produce materials with varying properties involves post modification of already synthesized, and well characterized, conducting polymers. This can be done by different way, such as covalent bonding to the polymer backbone [4–6].

Liu and Freund showed that aryldiazonium ions react with polyaniline by nucleophilic substitution of the amine groups in the polyaniline backbone on the aryl cations [7]. The authors performed a reaction of thin films of PANI, in its reduced state, with 4-substituted benzenediazonium salts in acid solution. From XPS studies they deduced that a polymer backbone with aryl groups linked to the nitrogen is produced. The polymer produced is not electroactive, likely due to the electronic and steric effect of the group attached to the amine nitrogen. The measurement of charge, from the cyclic voltamograms of the films taken during reaction, showed that film electroactivity decreases during reaction. Since the reaction is fast, the process is controlled by mass transfer of the diazonium salt. Therefore, the reaction front moves from the polymer/solution interface towards the substrate/polymer interface. The oxidized (emeraldine) form of PANI was found unreactive.

On the other hand, we have shown that polymer with azo linkages linked to the ring of the backbone can be obtained from the reaction of 4-sulfobenzenediazonium ion with poly(N-methylaniline) (emeraldine form) at low temperature in basic media. It was shown that this polymer is soluble in aqueous basic media and was electroactive [8]. The method has been extended by us to produce a variety of modified polyanilines by linking of new

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functional groups to the polymer backbone [9,10]. Since the modification involves the formation of azo linkages, the incorporation of the new functional group can be mainly reversed by degradative reduction of the azo group. In the present communication, the capability of the procedure to introduce different functionalities, and to remove chemically the attached is demonstrated.

2. Experimental

2.1. Materials

Aniline (Merck) was distilled under reduced pressure prior to use. 1-aminoanthraquinone (Merck), p-cyanoaniline (Aldrich) and sulphadiazine (Aldrich) were used as received. All aqueous solutions were prepared with twice distilled water. All the other reagents were of analytical quality. All potentials were measured versus the saturated calomel electrode (SCE).

2.1.1. Electrochemical synthesis of PANI thin films

The electrochemical synthesis of PANI was performed on glassy carbon electrodes (ca 1 cm^2) by cycling (35 cycles) between −0.15 V and +0.8 V vs SCE at 50 $mV\,s^{-1}$ in a solution consisting of 0.1 M aniline in 1 M HCl. To initiate the polymerization, 3 cycles were initially performed between −0.15 V and +0.9 V vs SCE. After polymerization, the films were then washed with 1 M HCl solution for ca 10 min to eliminate remaining monomer and soluble by-products. The films were then dried by blowing dry N_2.

2.1.2. Chemical synthesis of PANI

Chemical synthesis of PANI was performed as described previously [11]. An aqueous solution of $(NH_4)_2S_2O_8$ was added slowly to a solution of 0.1 M of aniline dissolved in HCl 1 M. The ratio of oxidant to monomer was 1:1. The reaction was carried out in a reactor (1 l) immersed in a water–ice bath to keep the external temperature around 0 °C. After the polymer was formed, it was filtered and washed with 1 M HCl solution. Then the polymer was immersed for 24 h in a solution of NH_4OH (1 mol dm^{-3}), filtered and washed with the same solution. The polymer was dried under dynamic vacuum at room temperature for 24 h.

2.1.3. Chemical modification of PANI

The modification consists in the chemical coupling of diazonium ions with PANI dispersed in basic media (TRIS® solution of pH 8) [12]. The diazonium salt was prepared as described in the literature [13]. A solution of the appropriate amine (e.g. 1-aminoanthraquinone) was diazotized by reaction with $NaNO_2$ in acid media (1 M HCl). The mole ratio of the amine to $NaNO_2$ was 1:1. In a typical coupling reaction 0.1 g (1.0 mmol of monomer units) of the polymer were stirred in 50 ml of TRIS® solution (pH 8) and 50 ml of diazonium salt containing 5 mmol of salt were added. This reaction was carried out, at temperatures below 5 °C, for 2 h. The chemical modification of PANI thin film was performed in a similar way. A thin film of PANI was immersed in a TRIS® buffer solution (pH 8), containing 5×10^{-3} mol dm^{-3} of the diazonium salt, at temperatures below 5 °C, during 2 h. To maintain the temperature, an ice bath was used.

2.1.4. Degradative reduction of the azo linker

In order to remove the attached functional groups, modified polyanilines were treated with a strong reducing agent: sodium dithionite ($Na_2S_2O_4$), which is known to reductively degrade the azo linkage, forming primary amino groups [14]. The films, or the powdered form of the previously modified polymers, were immersed in an aqueous hot (∼50 °C) solution, containing 0.05% (w/v) g of $Na_2S_2O_4$ for different time periods (see Section 3). Then the polymers were washed with water and 1 M HCl, and dried under dynamic vacuum.

2.2. Polymer characterization

2.2.1. Spectroscopy

Fourier Transform Infrared Spectroscopy measurements were performed in a Nicolet Impact 400 spectrometer. FITR spectra of PANI and modified polyanilines were obtained using the pellet method. In the case of films, the electrode was scratched with a metal spatula and the polymer obtained was mixed with KBr. The ratio of polymer to KBr used was 1:10. After mixing, the powder was made into pellets by pressing for 15 min at ca. 1500 MPa.

2.2.2. Cyclic voltammetry

The electrochemical experiments were performed using a GAMRY PC4/750 potentiostat controlled by a personal computer. A conventional three electrode call was used with carbon aerogel as counter electrode and a saturated calomel electrode (SCE) as reference electrode. Glassy carbon (GC) electrodes were used as working electrodes. The electrode surface was polished with alumina powder (down up 1 μm particle size). The electrochemical measurements were carried out in an aqueous solution of 1 M HCl, and all voltammograms were recorded at a scan rate of 50 $mV\,s^{-1}$.

3. Results and discussion

3.1. Functionalization with anthraquinone groups

The first experiments consisted in a chemical modification of PANI powder and its subsequent reaction with $Na_2S_2O_4$. In Fig. 1 are shown the FTIR spectra of: (a) PANI, (b) PANI modified by coupling with the diazonium salt of 1-aminoanthraquinone (PANI-AQ), and PANI-AQ treated with dithionite for 1 h.

The spectrum of PANI shows all characteristic band of the polymer: at 1588 cm^{-1} (assigned as C=C stretching of the quinoid rings), 1496 cm^{-1} (C=C stretching of benzenoid rings), 1306 cm^{-1} (C—N stretching mode) and 1164 cm^{-1} (ring stretching, N=Q=N, Q representing the quinoid ring) [15]. The spectrum of modified PANI shows additional bands at 1652 cm^{-1} (assigned to C=O stretching in the anthraquinone), 1563 cm^{-1} and 1043 cm^{-1} (assigned to vibrations of the naphthalene ring), suggesting that the anthraquinone group is linked to the PANI backbone. A weak band

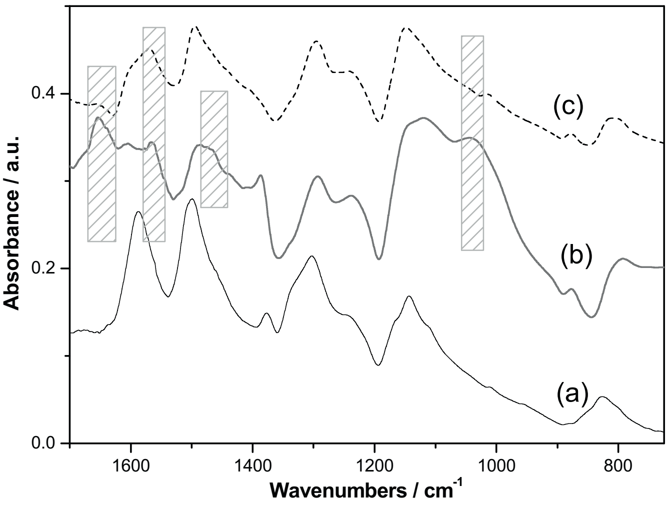
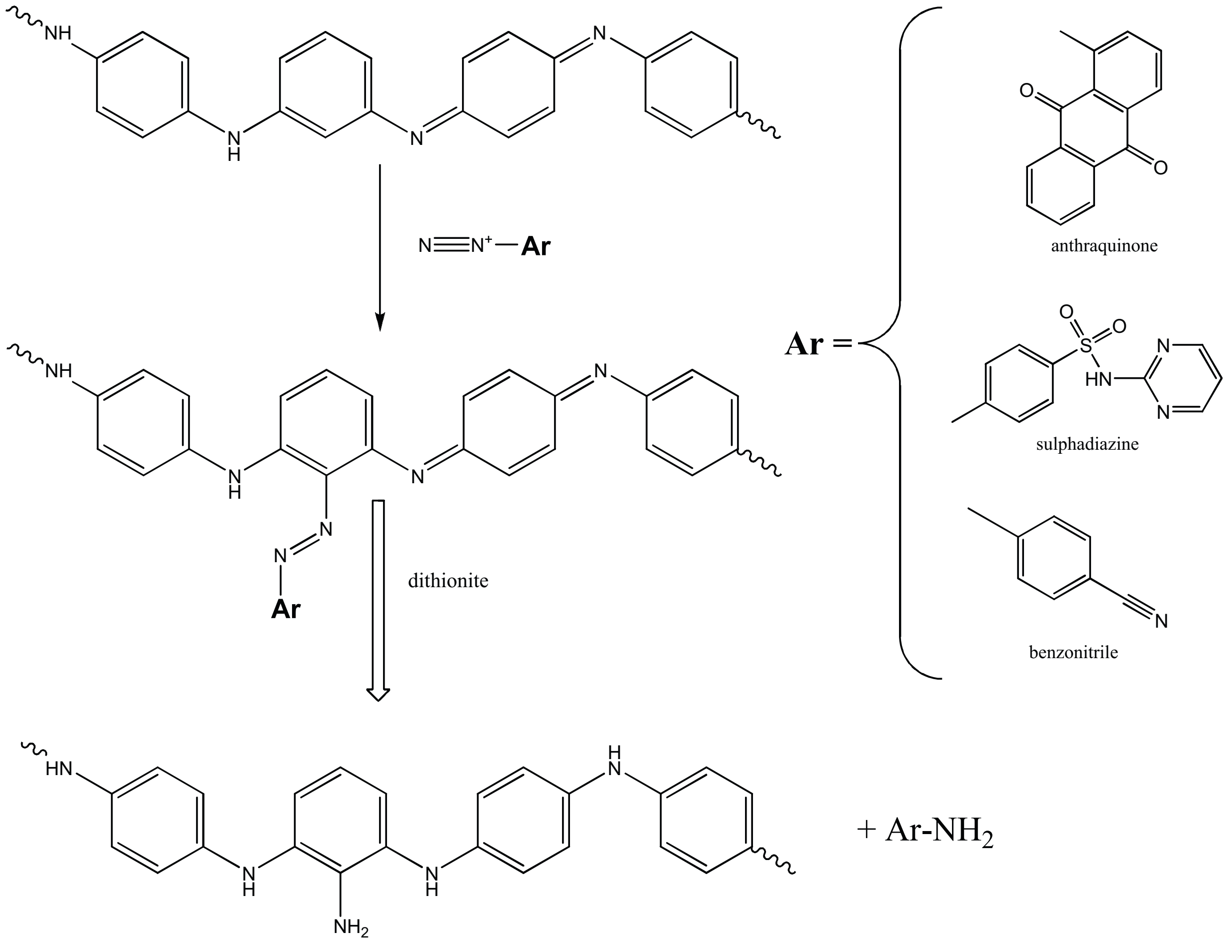


Fig. 1. FTIR spectra of polyanilines. (a) unmodified polyaniline; (b) polyaniline modified by reaction with the diazonium salt of 1-aminoanthraquinone; (c) the modified polymer shown in (b) treated during 1 h with dithionite ion solution.



Scheme 1. Reaction of incorporation and elimination of functional groups.

at 1463 cm^{-1} is also present, assigned to the stretching of azo bond (asymmetric azo bond) [16], suggesting that the linkage occurs by diazonium coupling to the amine rings with retention of the azo (—N=N—) group. It is important to note that in the reaction conditions (0 °C and pH 8) the stability of diazonium salt is high and can attack the activated amine ring giving azo linkages, without decomposition into aryl cations.

The FTIR spectrum of the modified polyaniline, treated with sodium dithionite, shows the same bands than PANI (Fig. 1c), suggesting that reductive degradation by dithionite removes the attached anthraquinone moieties. From this evidence, we propose a mechanism of diazonium salt coupling to the polyaniline backbone, described in Scheme 1. Polyaniline (in its emeraldine base form, stable at pH 10) is then reacted with an aromatic diazonium salt (reaction I), to give a modified polyaniline which has functional groups linked to the polymer backbone by azo linkages. The presence of the attached functional groups will incorporate new properties to the material and alter the intrinsic electronic properties of the polyaniline backbone due to electronic and/or steric effects. The attached functional group can be removed by degradative reduction of the azo group (reaction II). The product of reaction II should have electronic properties more similar to those of polyaniline because the only structural difference is the presence of amino groups attached to the polyaniline backbone.

To test the hypothesis that most of the effect of the attached group on the electrochemical response can be removed by reductive degradation, we studied the electrochemical properties of polyaniline at different stages of the reactions described in Scheme 1. In Fig. 2 are shown the cyclic voltammograms of the polymer films at the different reaction stages. The voltammogram of PANI (Fig. 2, black line) shows a clear peak at ca. 0.2 V vs SCE, characteristic of PANI electroactivity. After treatment of the film with the diazonium salt of 1-aminoanthraquinone (AQ), a modified polymer is produced: PANI-AQ. The cyclic voltammogram (Fig. 2, grey

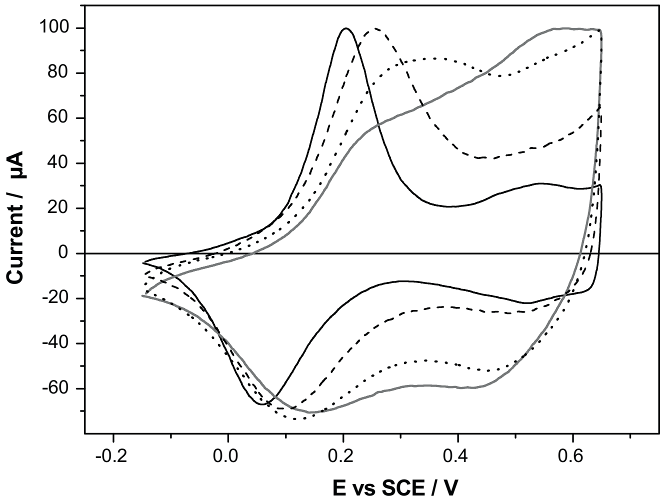


Fig. 2. Cyclic voltammograms of an unmodified polyaniline film (black line), modified with anthraquinone groups (grey line) and the later treated with dithionite ion at different times: 15 min (dotted line) and 1 h (dashed line). Scan rate = 50 mV s^{-1}. Electrolyte = 1 mol dm^{-3} HCl solution.

line) presents a similar redox system than PANI, albeit shifted to more anodic potential due to the steric effect of the attached groups. Additionally, a new redox peak due to the hydroquinone/quinone redox process is present at ca. 0.55 V vs SCE, which is related with the incorporation of the anthraquinone moieties into the polymer.

The charge storage in PANI occurs by redox conversion of diamine to quinonimine rings in the polymer backbone. In the PANI-AQ, such mechanism should remain active, as it occurs when non electroactive groups are attached (see below), but additional charge can be stored trough the conversion of hydroquinone to quinone moieties in the attached moiety. Therefore, the specific energy of the polymer will be higher than polyaniline, when the material is used as a battery or supercapacitor electrode [17]. An important parameter in such application is the cycling stability. Lifetime tests shows that PANI-AQ loss only 5% of redox charge when subjected to 2000 cycles in the conditions used to measure the cyclic voltammogram depicted in Fig. 2. Therefore, the modified polymer has enough stability for charge storage applications.

When the modified polymer (PANI-AQ) is treated with NaS_2O_4, the azo linkages should be degraded. The shape of the voltammogram changes revealing a decrease of the peak due to quinone and a relative increase of the peak due to PANI. This is apparent in Fig. 2, where it shown the response when the film was treated by 15 min (dotted line) and 1 h (dashed line) with dithionite. It is evident that 15 min treatment does not convert all the film into the final form. On the other hand, after 1 h, no further change in the voltammogram was observed. The difference suggests that the relative amount of functional groups present in the polymer can be tuned by controlled degradation of the azo linkages.

All the films obtained by reaction of PANI with different diazonium ions show clear electroactivity, in contrast with the results of Liu and Freund [7], indicating that, in our reaction conditions, the amine nitrogen in polyaniline remains unaffected. It is noteworthy that they do not observe any reaction of emeraldine state of PANI with diazonium salts, in clear contrast with our data. The difference is probably due to the use of acid media for the reaction by Liu and Freund [7]. It is noteworthy that the reaction mechanism proposed by Liu and Freund [7], renders a polymer bearing triphenylamine groups which would be unaffected by dithionite treatment. Therefore, the fact that reductive degradation removes the attached groups strongly supports the hypothesis that azo linkages are produced by coupling of PANI with diazonium salts in basic media, as described in Scheme 1.

As it is described in Scheme 1, the final product should not be polyaniline but the PANI backbone with amino groups attached to it. The presence of those groups could explain the small differences of the voltammogram of the final product with that of PANI (Fig. 2). However, it seems that the steric and/or electronic effect of those groups is significantly weaker than bigger groups linked by azo groups. Spectroscopic evidence for the presence of those groups in the final polymer product will be presented below.

3.2. Functionalization with sulphadiazine groups

The same method can be used to introduce other functional groups to the polyaniline backbone. In Fig. 3 are shown the cyclic voltammograms of the unmodified PANI (full line), PANI modified with the diazonium salt of sulphadiazine (grey line) and the one obtained when the modified film is treated with dithionite (dotted line). As it can be seen both redox process of PANI (leucoemeraldine to emeraldine and emeraldine to pernigraniline conversion) are altered by the incorporation of the sulphadiazine moiety. The steric and/or electronic effect of the attached group shifts the redox peak for the leucoemeraldine to emeraldine redox transition to more positive potentials. At the same time the potential for the emeraldine to pernigraniline transition shifts to less positive potential. This is a well-known effect when functional groups are attached to the aromatic rings of the polyaniline backbone [18].

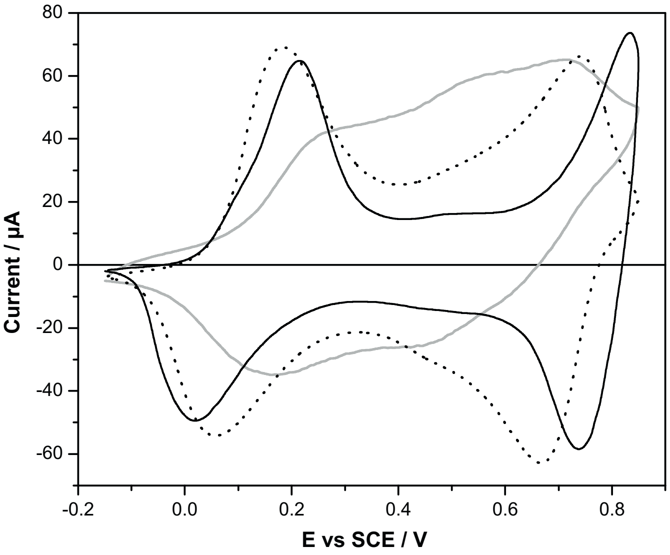


Fig. 3. Cyclic voltammograms of an unmodified polyaniline film (black line), modified with sulphadiazine moieties (grey line). The dotted line shows the CV of the modified polymer treated with dithionite ion during 1 h. Scan rate = 50 mV s^{-1}. Electrolyte = 1 mol dm^{-3} HCl solution.

On the other hand, treatment with dithionite of the functionalized film induces the degradative reduction of the azo linkage group, restoring most of the polymer electrochemical properties and making the cyclic voltammogram very similar to that of unmodified PANI. However, the final product is not PANI but the polymer backbone modified with amino groups (Scheme 1). The presence of those groups explains the relatively small differences observed in the voltammograms (Fig. 3).

The FTIR spectra of the polymers at different stages of the reactions are shown in Fig. 4. By comparison of the spectrum of the polymer before (a) and after treatment with the diazonium salt of sulphadiazine (b), it is apparent that a new band appears at ca. 1326 cm^{-1} and 960 cm^{-1} which could be assigned to the vibrations of the O=S=O group [15].

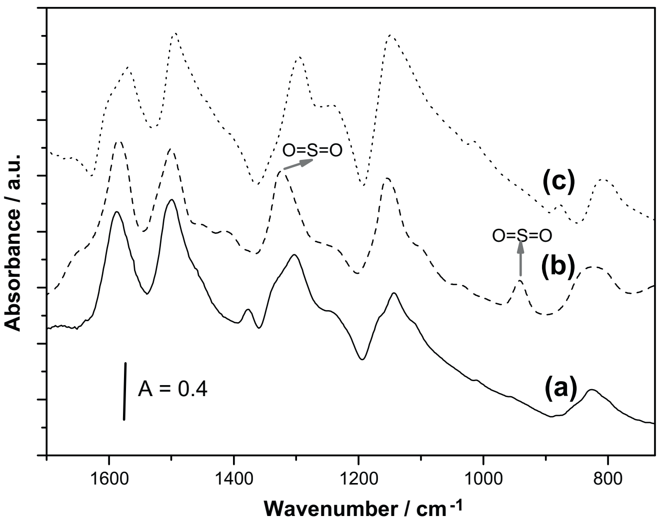


Fig. 4. FTIR spectra of polyanilines. (a) Unmodified polyaniline; (b) polyaniline modified by reaction with the diazonium salt of sulphadiazine; (c) the modified polymer shown in (b) treated during 1 h with dithionite ion solution.

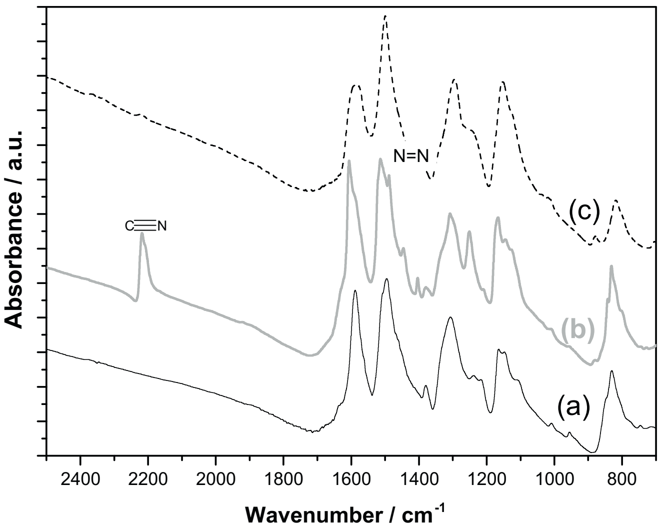


Fig. 5. FTIR of PANI (black line, a), PANI-CN (grey solid line, b), and PANI-CN treated with sodium dithionite solution (black dashed line, c).

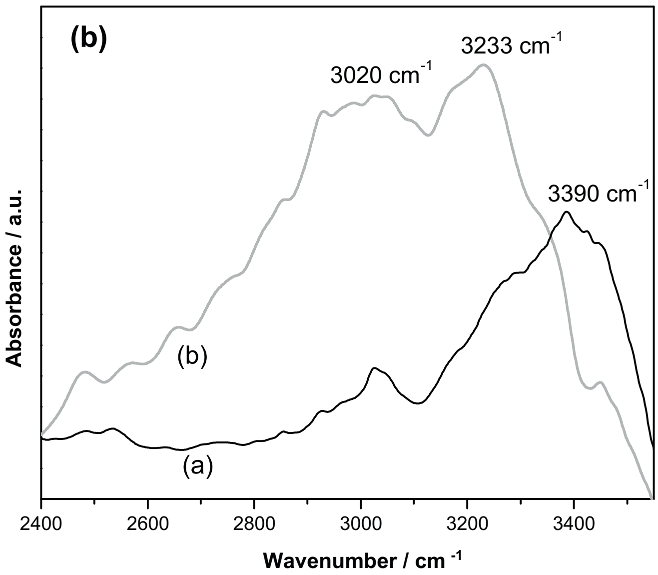


Fig. 6. FTIR of PANI (black line, a) and PANI-CN treated with sodium dithionite (grey line, b) in the higher wavenumbers region (2400–3550 cm^{-1}).

The possibility to remove the sulphadiazine groups by degradative reduction of the functionalized polymer has technological interest since the released molecule is a well-known bacteriostat [19]. The drug can be released from modified polyaniline by the action of reductive bacteria present in human intestines [20,21]. Additionally, the alteration of the polymer electrochemical response upon biological reductive degradation could be used to sense the azoreductase enzymatic activity [22].

3.3. Functionalization with benzonitrile groups

To further evaluate if the modification procedure is of general use, we studied the modification of PANI with the diazonium salt of 4-cyanoaniline (PANI-CN), followed by reaction with $Na_2S_2O_4$. In Fig. 5 are shown the spectra of PANI (a), PANI-CN (b) and PANI-CN treated with sodium dithionite (c). The PANI spectra shows all characteristic band of the polymer at 1588 cm^{-1} (assigned as C=C stretching of the quinoid rings), 1496 cm^{-1} (C=C stretching of benzenoid rings), 1306 cm^{-1} (C—N stretching mode) and 1164 cm^{-1} (ring stretching, N=Q=N, Q representing the quinoid ring) [15]. Additionally to the bands due to PANI polymer backbone, the modified PANI spectrum shows new bands at 2218 cm^{-1} (assigned to C≡N stretching), at 1251 cm^{-1} and at 544 cm^{-1} (assigned to a combination of C≡N in-plane bending and out of plane bending of the aromatic ring) which are all characteristic of the —C≡N group [15]. A new band at 1488 cm^{-1} is also present, assigned to the stretching of the —N=N— bond (asymmetric azo bond). On the other hand, the FITR spectra of PANI-CN treated with sodium dithionite (Fig. 5c)), shows mainly the bands previously assigned to PANI.

However, it has been proposed (Scheme 1) that reductive degradation of the azo linkages in functionalized PANI renders a polyaniline backbone with $-NH_2$ groups in the ortho position to the secondary amine group in PANI backbone. To test that, we measure the FTIR spectrum of PANI-CN, treated with sodium dithionite, at the high wavenumber region (4000–2000 cm^{-1}), where N—H stretching bands are usually observed (Fig. 6).[1] For comparison, the same measurement was carried out with unmodified PANI.

As it can be seen, broad bands at ca. 3020 cm^{-1} and 3230 cm^{-1} are present in the polymer subjected to diazonium ion coupling and further reductive degradation. The bands can be assigned to $-NH_3^+$ stretching [23], related with the presence of primary amino groups in the modified polymer. As it can be seen, in polyaniline only a weak band at ca. 3020 cm^{-1} is observed in the same region, together with a stronger band at ca. 3390 cm^{-1}. The former could be due to the presence of primary amine groups at the end of polyaniline chains and/or ramifications [24]. The band at ca. 3390 cm^{-1} can be assigned to the >NH stretching in the more abundant secondary amine groups of polyaniline monomer units [23]. The presence of the strong absorptions related with the presence of primary amine groups in the polymer modified by diazonium coupling and then reductively degraded, agrees with the structures proposed in Scheme 1.

It has been shown that modified polyanilines, bearing primary amino groups, could be used to link molecules bearing redox moieties by simple reactions with the amino group [25]. The reactions described here could be a simple way to introduce primary amino groups on the polyaniline backbone.

To study the electrochemical response of PANI-CN, aniline was electrochemically polymerized onto a glassy carbon electrode. The cyclic voltammogram of PANI is shown in Fig. 7 (solid line). The film was then treated with the diazonium salt of p-cyanoaniline. In the voltammogram of PANI-CN, shown in Fig. 7 (grey line), a clear shift in the oxidation and reduction potential of the polymer can be seen, due to the electronic and steric effect of the attached benzonitrile ($-C_6H_4CN$) group. After treatment of this film with dithionite, the electrochemical response (Fig. 7, dashed line) becomes similar to that of PANI.

While the cyclic voltammograms of different modified polymers are shown in different potential ranges, the stability of the polymers towards electrochemically induced degradation seems quite similar. The ranges of measurement were chose to show better the modification effect.

No noticeable difference was observed between FTIR spectra taken of powder PANI modified by the described reaction or PANI films modified by the reaction and scratched off the electrode. While more data is needed to ascertain that the reaction occurs evenly trough the whole polymer layer, we did not find evidence of more reaction on the polymer/solution interface. It should be reminded that polyaniline films on electrodes, made in the conditions described in the experimental part, are less than

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[1] The suggestion by a reviewer to investigate that spectrum region is gratefully acknowledged.

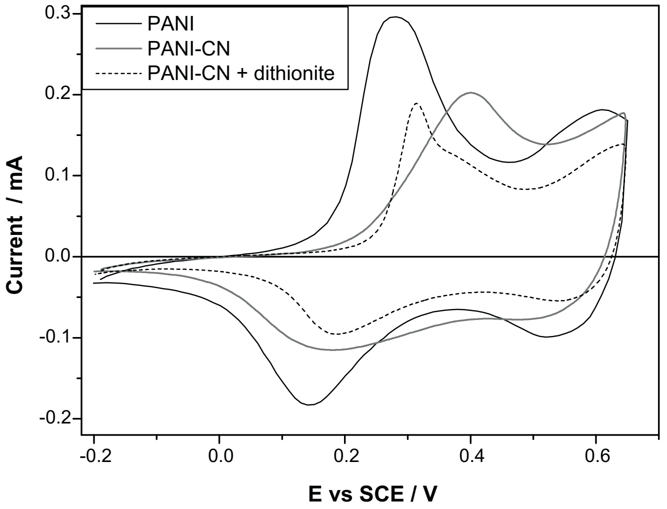

Fig. 7. Cyclic voltammograms of PANI (solid line), PANI-CN (grey line) and PANI-CN treated with dithionite (dashed line). Scan rate = 100 mV s^{-1}. Electrolyte = 1 mol dm^{-3} HCl solution.

100 nm thick [26]. Even considering a quite low diffusion coefficient (10^{-11} cm^2 s^{-1}), the time for the diazonium ion to penetrate trough the whole layer would be less than a minute. Therefore, the reaction should occur uniformly trough the whole polymer layer. On the other hand, the degree of reductive degradation can be controlled by the time of reaction.

4. Conclusions

The successful incorporation of azo linkages by coupling polyaniline with diazonium ion and the elimination of the attached group by degradative reduction of the azo linkage supports the mechanism of diazonium ion coupling with the aromatic rings in polyaniline, with formation of azo linkages. The data suggests that, at least in the experimental conditions described here, the reaction mechanism proposed by Liu and Freund [7], is not operative. Accordingly, while the electrochemical response is modified by the diazonium coupling and also by reductive degradation, all polymer materials remain electroactive. The possibility of attaching to and then releasing functional groups from the polyaniline backbone seems to be an easy method to control the electrochemical properties of polyaniline films and/or to tailor de degree of incorporation of functional groups to the polymer backbone. In that way, novel properties such as additional charge storage or the ability to release drugs inside living bodies could be incorporated. Additionally, the whole reaction sequence depicted in Scheme 1 seems an easy way to introduce primary amino groups into the polyaniline backbone. Those amino groups could then be used as anchoring sites to attach more complex molecules, such as enzymes [27].

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References

[1] G.G. Wallace, G.M. Spinks, P.R. Teasdale, L.A.P. Kane-Maguire, Conductive Electroactive Polymers: Intelligent Polymer Systems, CRC Press, Boca Raton, 2008.
[2] J. Huang, Pure Appl. Chem. 78 (2006) 15.
[3] W. Yin, E. Ruckenstein, Macromolecules 33 (2000) 1129.
[4] X.-L. Wei, Y.Z. Wang, S.M. Long, C. Bobeczko, A.J. Epstein, J. Am. Chem. Soc. 118 (1996) 2545.
[5] G.M. Morales, H.J. Salavagione, D.E. Grumelli, M.C. Miras, C.A. Barbero, Polymer 47 (2006) 8272.
[6] J. Balach, C.V. Ortiz, D.O. Peralta, D.F. Acevedo, M.C. Miras, C.A. Barbero, Mol. Med. Chem. 12 (2007) 21.
[7] G. Liu, M.S. Freund, Chem. Mater. 8 (1996) 1164.
[8] G.A. Planes, G.M. Morales, M.C. Miras, C. Barbero, Synth. Met. 97 (1998) 223.
[9] C. Barbero, H.J. Salavagione, D.F. Acevedo, D.E. Grumelli, F. Garay, G.A. Planes, G.M. Morales, M.C. Miras, Electrochim. Acta 49 (2004) 3671.
[10] M.C. Miras, D.F. Acevedo, N. Monge, E. Frontera, C.R. Rivarola, C.A. Barbero, Open Macromol. J. 2 (2008) 58.
[11] J. Stejskal, R.G. Gilbert, Pure Appl. Chem. 74 (2002) 857.
[12] D.F. Acevedo, H.J. Salavagione, M.C. Miras, C.A. Barbero, J. Braz. Chem. Soc. 16 (2005) 259.
[13] A.I. Vogel, A.R. Tatchell, B.S. Furniss, A.J. Hannaford, P.W.G. Smith, Vogel's Textbook of Practical Organic Chemistry, 5th ed., Prentice Hall, New York, 1996.
[14] H. Zollinger, Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments, Wiley, John & Sons, New York, 1996.
[15] G.A. Planes, J.L. Rodríguez, M.C. Miras, G. García, E. Pastor, C.A. Barbero, Phys. Chem. Chem. Phys. 12 (2010) 10584.
[16] G. Socrates, Infrared Characteristic Group Frequencies, John Wiley & Sons, New York, 1994.
[17] N. Oyama, T. Tatsuma, T. Sato, T. Sotomura, Nature 373 (1995) 598.
[18] R.M.Q. Mello, R.M. Torresi, S.I. Córdoba de Torresi, E.A. Ticianelli, Langmuir 16 (2000) 7835.
[19] R.J. Henry, Bacteriol. Rev. 7 (1943) 175.
[20] A.J. Ryan, J.J. Roxon, A. Slvayavirojana, Nature 219 (1968) 854.
[21] K.-T. Chung, S.E. Stevens, C.E. Cerniglia, Crit. Rev. Microbiol. 18 (1992) 175.
[22] F. Rafii, W. Franklin, C.E. Cerniglia, Appl. Environ. Microbiol. 56 (1990) 2146.
[23] E. Pretsch, J. Seibl, W. Simon, T. Clerc, Tables of Spectra Data for Structure Determination of Orgánic Compouns, 2nd ed., Springer-Verlag, Berlin, 1989.
[24] E.A. Ponzio, R. Echevarria, G.M. Morales, C. Barbero, Polym. Int. 50 (2001) 1180.
[25] D. Raffa, F. Battaglini, J. Electroanal. Chem. 504 (2001) 120.
[26] C. Barbero, R. Kötz, J. Electrochem. Soc. 141 (1994) 859.
[27] M. Skompska, M.J. Chmielewski, A. Tarajko, Electrochem. Commun. 9 (2007) 540.