Synthesis, Properties and Aplications of Functionalized Polyanilines

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Novos polímeros condutores funcionalizados foram sintetizados a partir de modificações das reações de acoplamento polianilina-diazônio, adição nucleofílica e N-nitrosação. O acoplamento de diazônio fornece polímeros modificados que são eletroativos e solúveis em solventes comuns. Adição nucleofílica também pode ser usada para modificações da polianilina. Polímeros modificados pela adição de tióis, carbânions e ácidos arilsulfínicos são apresentados. A adição nucleofílica de ácidos arilsulfínicos à polianilina oxidada mostrou ser controlada pelos estados de oxidação e/ou protonação do polímero. A N-nitrosação de polianilina também é possível, produzindo material solúvel em solventes comuns. Esta reação pode ser revertida por tratamento ácido. A reação de nitrosação reversível foi usada para controlar processos litográficos e fotolitográficos de deposição de padrões de PANI.

Novel functionalized conductive polymers are synthesised using modification reactions of polyaniline: diazonium coupling, nucleophilic addition and N-nitrosation. Diazonium salt coupling with polyaniline renders modified polymers which are soluble in common solvents and electroactive. Nucleophilic addition could also be used to modify polyaniline. Modified polymers produced by addition of thiols, carbanions and arylsulphinic acids are described. The nucleophilic addition of arylsulphinic acids to oxidized polyaniline is shown to be controlled by the oxidation and/or protonation state of the polymer. It is also possible to N-nitrosate polyaniline producing a material soluble in common solvents. The reaction could be reversed by acid treatment. The reversible nitrosation reaction is used to design lithographic and photolithographic processes to deposit PANI patterns.

Keywords: conductive polymers, synthesis, lithography, conductivity, processability

Introduction

Polymers have been traditionally considered as insulators.[1] However, since the discovery by Shirakawa, Heeger and MacDiarmid that the conductivity of polyacetylene increases significantly upon doping with electron acceptors,[2] a large effort has been devoted to make new intrinsically conductive polymers (ICP) and/or improving the properties of those materials.[3] Conductive polymers could have a variety of applications: corrosion protection coatings and conductive coatings for antistatic and/or RF shielding purposes.[3] An obvious requirement to produce such coatings is processability trough solubility of the conductive polymers in common solvents, including aqueous solutions.

The usual way to produce functionalized conductive polymers involves the synthesis or acquisition of a monomer its homopolymerization or copolimerization, followed with a detailed study of the polymer properties. Another, less explored, route to produce materials with varying properties, involves post modification of, already synthesised and well characterised, conducting polymers. This can be done by means of covalent bonding of the functional group to the polymer backbone.[4] A simple way to do that is to polymerize anilines substituted with functional groups of interest. However, inductive and steric effects could make the monomer difficult or impossible to polymerize.[5] A way to overcome such limitation consists in the controlled modification of the polymer backbone by synthetic reactions on the whole polymer. Indeed, it has been shown that is possible to modify polyaniline by different reactions. Wrighton and coworkers describe the nucleophilic reaction of PANI with trifluoracetic anhydride where the reaction rate could be controlled by varying the electrochemical potential of the polymer.[6] The electrochemical control of the modification reaction allows

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to produce electrochemical transistors with varying properties. It was also shown that sulfonate groups can be linked to PANI backbone by sulfonation of the polymer [7] to give partially (50% or 75%) sulfonated polymer (SPAN).

Examples of three novel modification pathways: diazonium ion coupling, nucleophilic addition and nitrosation, will be described.

Experimental

Materials

Aniline (Merck) was purified by distillation at reduced pressure. Sulphite and bisulphite (Riedel de Haen) were used as received. All aqueous solutions were prepared with twice distilled water. All other reagents were of analytical quality.

Polymer reactants

Polyaniline (emeraldine form) was prepared, as described in the literature,[8] by oxidation of aniline (0.1 mol L^{-1}) in 1 mol L^{-1} HCl with ammonium persulphate (equimolar) at temperatures below 5 °C. The temperature was monitored during the polymerization. When the reaction was completed, after the maximum of temperature has occurred, the polymer was filtered out under suction and washed with 1 mol L^{-1} HCl solution (0.5 L) and water (1 L). The polymer was then converted into its base form by stirring for 24 hs in a 0.1 mol L^{-1} NH_4OH solution. The emeraldine base form (50% oxidation) used in all reactions had an intrinsic viscosity [η] of 1.12. Pernigraniline base (100% oxidation) was prepared, freshly before use, by oxidation of emeraldine base with ammonium persulphate (1%) at neutral pH for 15 min.[9] It was used without drying to avoid degradation, which involves reduction to the nigraniline state (75% oxidation). A solution of the material in N-methylpyrrolidone shows an ultraviolet-visible spectrum characteristic of pernigraniline.[10] Leucoemeraldine base form (0% oxidation) was obtained by reduction of emeraldine base with phenylhydrazine in basic aqueous media, followed by washing and drying in oxygen free environment.

Methods

Elemental analysis

Chemical analysis by combustion were performed using a Carlo Erba EA 1108 microanalyzer at INQUIMAE (Buenos Aires, Argentina). The samples were dried under vacuum during 72 h before measurement. The instrument was standardised using benzenesulphonamide in the same run.

Spectroscopy

To obtain the ultraviolet-visible spectra, clear solutions were prepared by dissolving the polymers in adequate solvents (e.g. $C_2H_3Cl_3$). The spectra were taken in 1 cm path length quartz cells using a diode array UV-vis spectrophotometer (HP 8452A).

Fourier Transform Infrared Spectroscopy (FTIR) measurement of chemically prepared polymers were performed on the polymer dried under vacuum at ambient temperature by 48 h. The polymers were mixed with KBr and pellets for transmission measurements were prepared. The spectra were taken in an Impact 400 FTIR spectrometer (Nicolet) with a resolution of 4 cm^{-1}, using 200 scans.

Electrochemistry

Electrochemical measurements were carried out in a conventional three electrode cell, controlled by a computerised potentiostat (GAMRY PC4). All potentials are quoted against the saturated calomel electrode (SCE).

Diazonium ion coupling to PANI

The amines were diazotized with sodium nitrite and concentrated HCl in an ice bath. PANI was suspended in TRIS® buffer (pH 8) and mixed with the diazonium salt solution in an ice bath. The solid was filtered under vacuum and washed first with 1 L of 1 mol L^{-1} HCl solution and then with 1 L distilled water. The products were filtered out of the mixture under vacuum and dried (dynamic vacuum for 48 h).

Nucleophilic addition

0.05 L of a solution 0.5 mol L^{-1} of the nucleophile and 0.5 g of the base polymer in aqueous (buffer pH 4) or ethanol are mixed and heated to reflux in a water bath during 2 h. The reaction mixture is left to cool, filtered and washed with successive portions (0.500 L) of H_2O, 1 mol L^{-1} NH_4OH and 1 mol L^{-1} HCl. Then, the product is dried under dynamic vacuum for 24 h.

N-nitrosation reaction

PANI-NO was prepared reacting emeraldine base with sodium nitrite (1 mol L^{-1}) in 1 L mol L^{-1} HCl solution during 1 h at 20 °C.[11] After reaction, the polymer was

washed with water and 0.1 mol L^{-1} NH$_4$OH solution. The polymer was then dried under dynamic vacuum for 48 h at room temperature and stored in a dessicator. Up to 43% of N-nitrosation was obtained. Solutions of PANI-NO were prepared by dissolution of the solid in acid-free solvents. This was achieved treating previously the solvent (e.g. CHCl$_3$) with anhydrous K$_2$CO$_3$. The solutions have to be stored in the dark to avoid formation of acid by solvent photodegradation.

Results and Discussion

Coupling of diazonium salts with polyaniline

The coupling of diazonium salts with PANI was investigated by Liu and Friend.[12] They performed the reaction by treating electrochemically produced PANI films with diazonium salts. They found that the reaction only occurs with the films in reduced state. As the reaction is performed inside the electrochemical cell, the reaction media was acidic (1 mol L^{-1}H$_2$SO$_4$/H$_2$O). In such conditions, they found evidence that the diazonium ion loses nitrogen and substitutes on the amine nitrogen of the PANI backbone. Such substitution renders the modified polymer not electroactive.

On the other hand, by reaction of 4-sulphobenzene-diazonium ion with poly(N-methylaniline) at low temperature in basic media we obtained a modified polymer with azo linkages to the rings of the polymer backbone. The product was soluble in aqueous basic media and electroactive.[13] As it will be shown, similar products could be obtained by coupling of other diazonium ions with PANI in basic media at low temperature. The proposed reaction for the synthesis of the diazonium salt and subsequent reaction with polyaniline is given by Scheme 1:
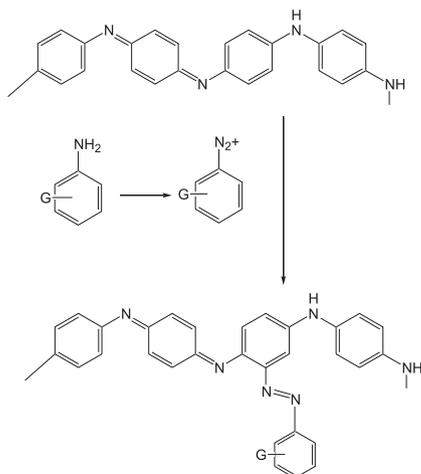
Scheme 1. Reaction pathway of diazonium coupling to polyaniline.

The FTIR spectra of modified polyaniline (4CNAZOPANI), produced by reaction of PANI with 4-cyano-benzenediazonium salt, is shown in Figure 1.
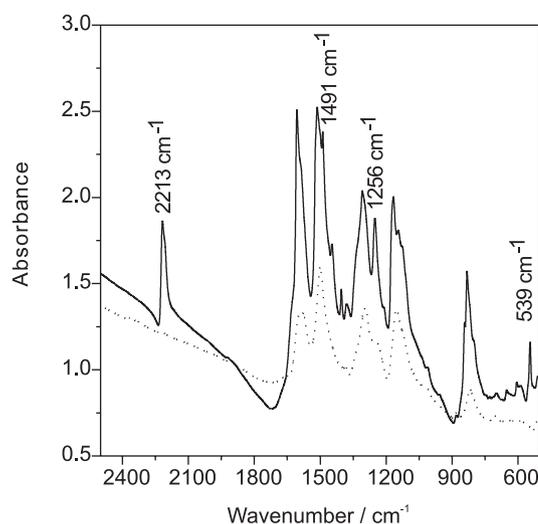

Figure 1. FTIR spectrum of polyaniline modified by reaction with 4-cyano-benzenediazonium salt (black line). A spectrum of un-modified polyaniline is shown for comparison (dotted line). The spectra were taken by transmission of the polymer dispersed in KBr pellets with 200 scans and 4 cm^{-1} resolution.

As it can be seen, all bands due to the PANI backbone are present, together with bands at 2213, 1491, 1256 and 539 cm^{-1}. The band at 2213 cm^{-1} could be assigned to the stretching of cyano group.[14] The band at 1491 cm^{-1} is assigned to stretching of aromatic azo group. This band is only active in infrared when aromatic rings with different polarity are linked to the azo group, as it is the case here. The band at 539 cm^{-1} is characteristic of cyano substituted aromatics and could be assigned to a combination band of the out of plane bending of the aromatic ring and the bending of the cyano group. The band at 1256 cm^{-1} has not been assigned in the literature but it is present in aromatic nitriles.[15]

The modified polymer is soluble in common solvents (Table 1), unlike PANI which is only soluble in concentrated acids and N-methylpyrrolidone.

The UV-Vis spectra of the modified polymer show bands at 269 and 367 nm and a broad weak band at ca. 850 nm. The band at 298 nm is attributed to the $\pi \rightarrow \pi^*$ transition of the aniline rings.[16] The band at 367 nm is likely to be due to the n$\rightarrow\pi^*$ transition in the radical cation of the polymer,[17] while the broad weak band is due to the polaron absorption. To check the polymer electroactivity, thin films were deposited by evaporation of the solvent from its solution in CHCl$_3$. The cyclic voltammogram of a typical film, in acid media, is shown in Figure 3. As it can be seen, the conversion of leucoemeraldine to emeraldine occurs at *ca*. 0.4 V sce.

The potential is shifted to more positive values, compared with the same process in PANI,[18] due to electronic and steric effects of the azo substituyent in the rings.[19]
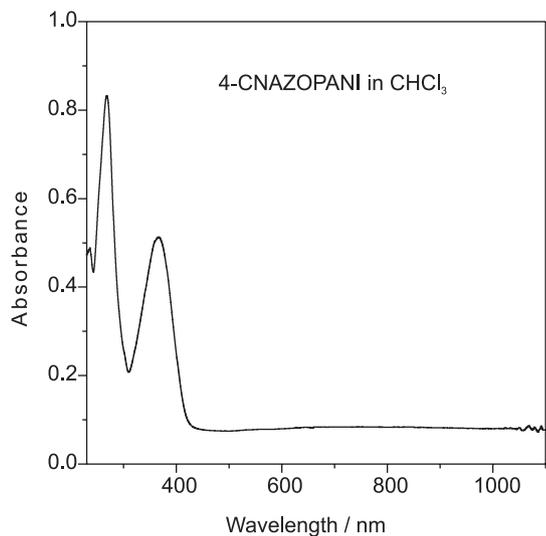

Figure 2. UV-visible spectrum of the modified polymer (4CNAZOPANI) in CHCl$_3$.
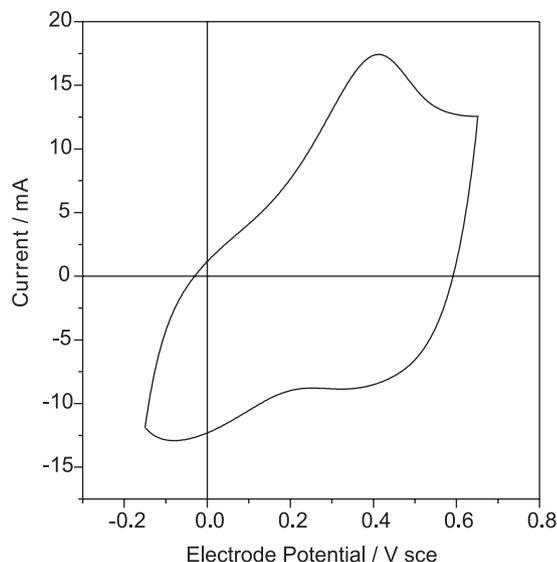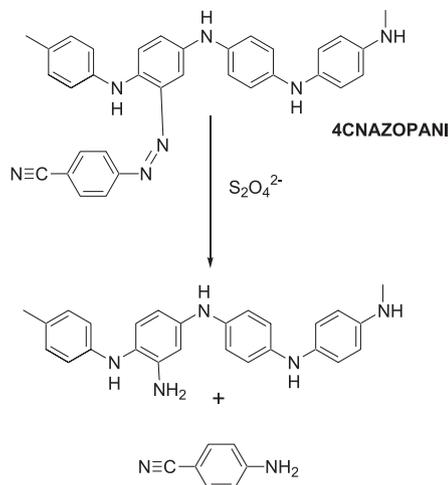

Figure 3. Cyclic voltammogram of a 4CNAZOPANI film deposited onto glassy carbon. Solution = 1 mol L^{-1} HCl, Scan rate = 50 mV/s, A = 1 cm^2.

To corroborate that the reaction occurs through azo linkages, the modified polymer was treated with sodium dithionite. In that way, the azo linkages should be reductively degraded [20] (Scheme 2).

Scheme 2. Reductive degradation of azo modified polyaniline (4CNAZOPANI).

The FTIR spectrum (not shown) reveals nearly total disappearance of the bands assigned to the cyano group indicating that azo linkages exist in the modified polymer.

In Table 1 are described the solubilities of several modified polyanilines, obtained using this synthetic method.
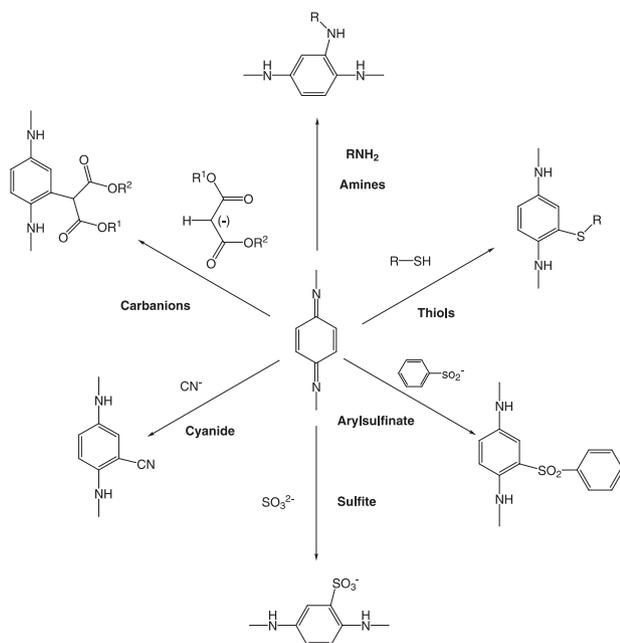
The modified polymers show conductivities lower than that of PANI (Table 1), probably due to electronic and/or steric effect of the substituent group on the electron delocalization. However, the changes are relatively small. The successful synthesis of several modified polyanilines suggests that the method is general.

Nucleophilic addition to oxidized PANI

Nucleophilic addition of amines and thiols to quinonimine rings has been proposed as a powerful method to polyaniline post-modification.[21] In our laboratory, we

Table 1. Solubilities[a] and conductivities of modified polyanilines

Amine used to modify PANI	NH$_3$/H$_2$O	Acetone	Toluene	NH$_3$/iPrOH	CHCl$_3$	σ (S/cm)
None (PANI)	I	I	I	I	I	3.78
4-aminobenzoic acid	VS	I	I	I	I	0.96
4-nitroaniline	I	S	I	I	I	0.29
Aniline	I	S	S	S	I	2.01
2-metoxianiline	I	S	I	I	I	2.74
4-cyanoaniline	I	S	I	S	S	0.41
1-naphtylamine	I	S	S	S	VS	0.55

[a] (VS = 1% m/v, S = 0.1% m/v, I = insoluble).

have investigated the nucleophilic addition of sulphite ions[22] and other nucleophiles.[23] Under proper conditions, up to 63% addition of sulphite ions with formation of self-doped polyaniline, is observed. A mechanism was proposed to account for the effect of polymer oxidation state and solution pH on the reaction rate. The pernigraniline state is more reactive than emeraldine while leucomeraldine is not reactive. A possible explanation is that quinonimine units suffer nucleophilic attack with addition on the ring, as it is well known for low molecular weight quinonediimines.[24] The higher amount of quinonimine units in pernigraniline (100 %) than in emeraldine (50 %) accounts for its greater reactivity. The absence of those units in leucoemeraldine state makes it unreactive to nucleophilic addition. The results also suggest that decreasing the pH makes the reaction faster. It has been rationalized taking into account that protonation of the quinonimine units (pH 2-3 for emeraldine) would make them more reactive to nucleophilic attack. However, in the range of pH where quinonimine units become protonated, sulphite ions (the nucleophile) become protonated too, making the results difficult to interpret. We have also observed that sulphite ions are more reactive than neutral thiols or amines, in agreement with their relative reactivities as nucleophiles, as measured by the Grunwald-Winstein relationship.[25]

The method constitutes an alternative way to modify polyaniline by addition of nucleophiles to the oxidized polymer (Scheme 3).[26]

In that way, polyaniline could be easily modified by nucleophilic addition giving polymers containing different moieties linked to the polymer backbone. The modification changes the properties of the polymer increasing the solubility in common organic solvents[27] and miscibility with common polymers (e.g. PMMA).[28]

As an example we show the FTIR spectra of nucleophilic addition products (Figure 4). The addition of a thiol (Figure 4a) produces a material which spectra have new bands, additional to those of PANI, at 1659, 1221 and 503 cm^{-1}. The band at 1659 cm^{-1} could be assigned to the stretching of the >C=O group in the carboxilate moiety. The band at 1221 cm^{-1} is assigned to the C-O stretching in the carboxilate group, while the band at 503 cm^{-1} could be assigned to the C-S stretching in the
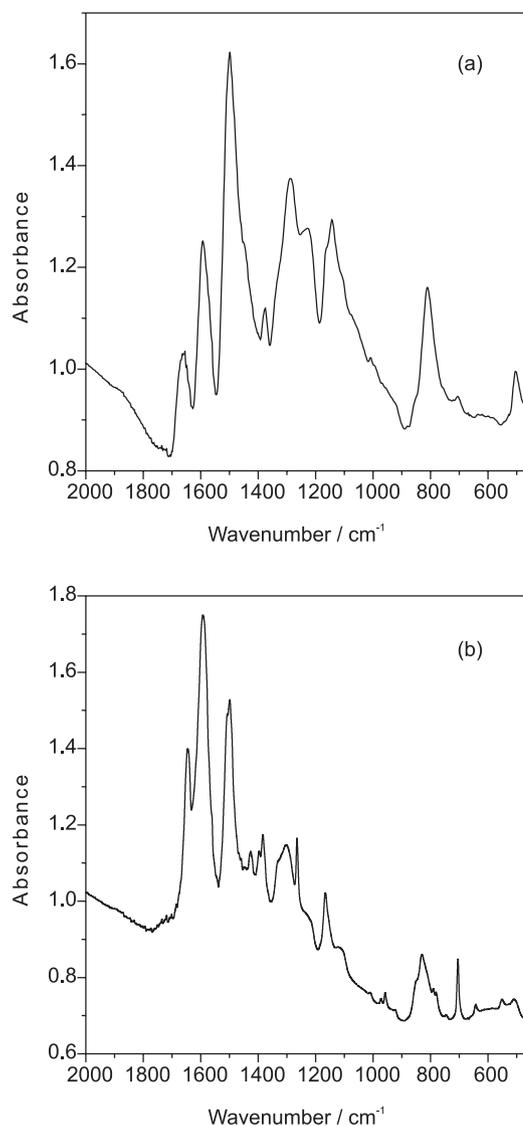

Figure 4. FTIR spectra of the products of nucleophilic addition to polyaniline. (a) addition of a thiol (thiolactic acid), (b) addition of a carbanion (diethylmalonate).

Scheme 3. Reaction pathways of nucleophilic addition to polyaniline.

modified polymer. The product is soluble in basic media due to the formation of a polyanion with the carboxilate groups linked to the PANI backbone.

The FTIR spectrum of the reaction product with a preformed carbanion is shown in Figure 4b. As it can be seen the spectrum has new bands at 1646 cm, 1263 and 706 cm^{-1}. The band at 1646 cm^{-1} and 1263 cm^{-1} are assigned to the C=O and C-O stretching, respectively, in the ester group. The band at 703 cm^{-1} is assigned to the C-H bending in the α hydrogen of the incorporated malonate. The modified polymer is soluble in chloroform, probably due to the solvating effect of the covalently bonded ester group.

The nucleophilic reaction follows the mechanism depicted in Scheme 4:
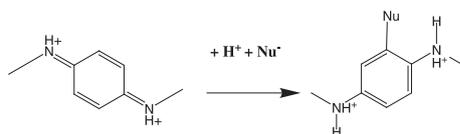
Scheme 4. Mechanism of nucleophilic addition.

As it can be seen, only the oxidized moiety reacts, and the product is reduced during the reaction. Therefore, the reactivity can be controlled by the oxidation state of the polymer. The high reactivity of sulphite ion as nucleophile[29] lead us to test its organic derivatives: sulphinic acids. We choose the arylsulphinic acids that are readily accessible and chemically stable. It is known that arylsulphinic acids could be used as nucleophiles to add to monomeric quinone diimines.[30] The simple synthesis of arylsulphinic acids from diazonium salts or arylsulphonyl chlorides should make this an easy route for incorporation of different organic functional groups to the PANI backbone. While the nucleophilic addition of sulphite only constitutes an alternative procedure to obtain sulphonated polyaniline, the addition of sulphinic acids could produce materials not easily synthesised by other routes. From the mechanistic point of view, arylsulphinic acids are protonated at higher pH (pK around 2.7 for arylsulphinic acids)[31] making possible to study the effect of pH without interference of changes in the nucleophile.

Polyaniline (pernigraniline form) reacted with benzenesuplhinate ion at pH 3.9 as described in the experimental part. In Figure 5 are shown the spectra of the product and that of PANI (leucomeraldine salt form) for comparison. In the product spectrum there are vibrational bands that could be assigned to the PANI backbone and new bands at 1330, 1089, 586 and 566 cm-1 due to S=O and C-S vibrations.[32] Additionally there are new bands at 1446, 1089, 724, 756 y 688 cm-1 which are present in the FTIR spectrum of benzenesulphonamide and/or

phenylsulphone,[33] but they have not been assigned, in the literature, to defined vibrations.
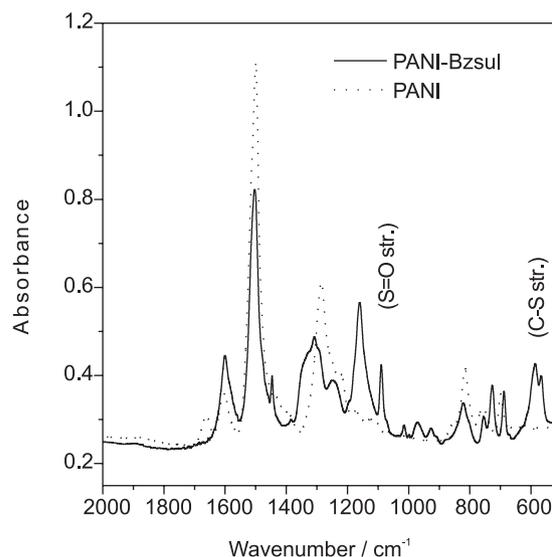

Figure 5. FTIR spectrum of polyaniline modified by nucleophilic addition of benzenesulphinic acid. An spectrum of unmodified polyaniline (dotted line) is shown for comparison.

It has been shown that the degree of nucleophilic addition of sulphite ion to PANI increases with decreasing pH. This was understood based on the protonation of the quinonimine units. The protonated form is more reactive, therefore the reaction rate increases at lower pH. However, a more quantitative analysis wasprecluded due to the two protonation constants of sulphite ion which could also affect the reaction rate. The pKa of the quinonimine units in PANI[34] is in the order of 2-3 and the pKa of benzenesulphinic acid is 2.76. Benzensulphinic acid, being neutral, should be less reactive as nucleophile than benzenesulphinate which has negative charge.[35] Therefore the mechanism could be quite complex at pH below 4. On the other hand, working at pH above 4, no effect of the protonation of quinonimine or sulphinate ions should be observed.

The FTIR spectra of the reaction products of PANI (pernigraniline state) with benzensulphinic acid at different pH are shown in Figure 6a.

As it can be seen the spectra at pH below 5 show clear indication of the reaction (new bands, reduced polymer, low conductivity band) while at pH 8 the reaction seems minimal. Both the ratio of the band at 1600 cm^{-1} with respect to the band at 1500 cm^{-1} (Figure 6b) and the sulphur to nitrogen (S/N) ratio obtained from chemical analysis (Table 2) indicate that the reaction smoothly decreases with pH between 4 and 8.

As the reactive species (quinonimine unit and benzenesulphinate ion) are unchanged in that range of

pH, another mechanism should be operative. A likely explanation is that proton incorporation during addition determines the pH dependence. At pH 8 the concentration
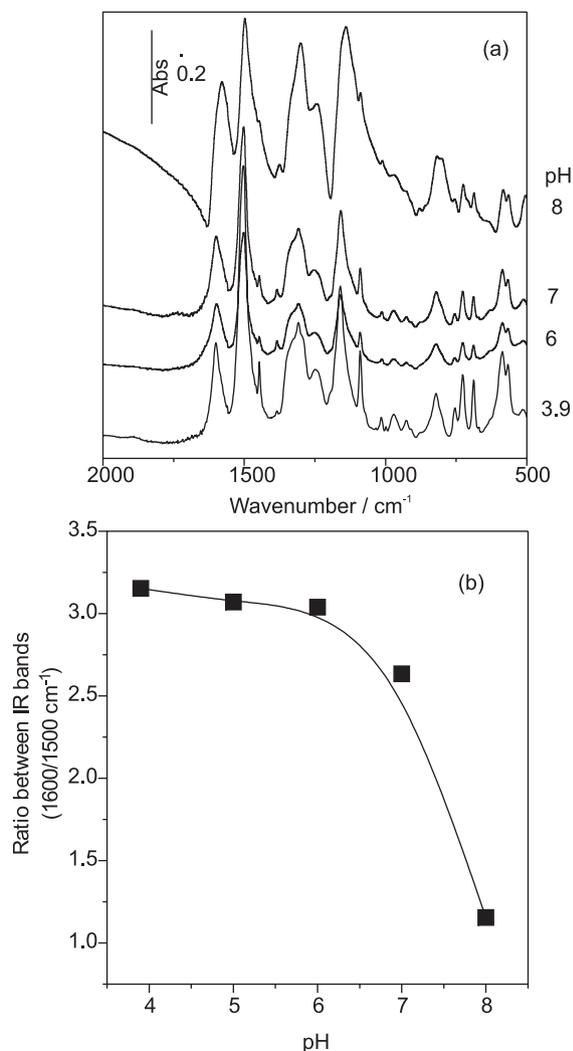
of proton is too low to allow a significant reaction rate. This is in agreement with the pH effect observed in monomeric quinonediimines.[36]

Reversible nitrosation

The N-nitrosation of nitrite on PANI produces a polymer soluble in common solvents[37] (Scheme 5). FTIR spectrum of the product (Figure 7) shows bands characteristic of polyaniline (emeraldine base) and new bands occurring at 1508 cm^{-1} (str. -N=O), 1034 cm^{-1} (str. -N-N-) and 757 cm^{-1} (def. -N-N=C),[38] indicating formation of N-nitrosated polyaniline.

The obtained polymer, PANI-NO, is soluble in common solvents (CHCl$_3$, CH$_2$Cl$_2$, C$_2$H$_4$Cl$_2$, secondary amines, DMSO, DMF), giving deep red solutions.

The UV-visible spectra of polymer solutions in dichloromethane and dimethyslufoxide are shown in Figure 8. Bands at 298 nm (4.15 eV) and 495 nm (2.50 eV)
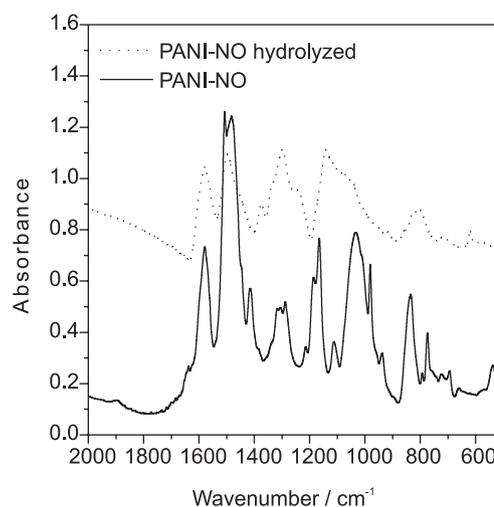

Figure 6. (a) FTIR spectra of polyaniline modified by nucleophilic addition of benzenesulphinic acid at different pHs; (b) Ratio between the intensity of the bands at ca. 1500 and 1600 cm^{-1}.

Figure 7. FTIR spectra of nitrosated polyaniline (PANI-NO), before (full line) and after (dotted line) hydrolysis.

Table 2. Effect of pH and oxidation degree of the polymer reactant on the modification degree (S/N ratio) and reduction (measured by the ratio of IR bands)

Polymer	Polymer Oxidation degree	Reaction pH	Ratio of intensity (bands at 1500 cm-1 and 1600 cm-1)	Modification degree[a]
Pernigraniline base (PN)	100 %	—	0.95	0
Emeraldine base (EB)	50 %	—	1.13	0
Leucoemeraldine base (LB)	0 %	—	4	0
LE + C6H5SO2-	0 %	3.9	3.9	0.03
EB + C6H5SO2-	50 %	3.9	1.50	0.17
PN + C6H5SO2-	100 %	3.9	3.15	0.43
PN + C6H5SO2-	100 %	6.0	3.03	0.42
PN + C6H5SO2-	100 %	7.0	2.63	0.38
PN + C6H5SO2-	100 %	8.0	1.15	0.11

[a] obtained from S/N (chemical analysis).

can be seen. The band at 298 nm is attributed to the $\pi \rightarrow \pi^*$ transition of the aniline ring.[39] The band at 495 nm is assigned to the excitation from HOMO of the benzenoid rings (π_b) to the LUMO of the quinoid rings (π_q) in the quinoneimine units.[40]

To compare with polyaniline, spectra were measured in N-methylpyrrolidone (Figure 9), where both polymers are soluble. The spectrum of PANI-NO solution in NMP presents two bands at 316 nm (3.92 eV) and 490 nm (2.52 eV). The UV band occurs at 327 nm in PANI, indicating an hypsochromic shift in PANI-NO for the $\pi \rightarrow \pi^*$ transition due to the NO group. The band in the visible region shifts to higher energy with respect to PANI in NMP (630 nm, 1.96 eV)[36] to 490 nm (2.52 eV) in PANI-NO probably due the electron withdrawing effect of the NO group.

Similar spectra were obtained in thin films (Figure 10).

By treatment with HCl vapours, the polymer is hydrolysed and the spectrum changes to one analogous to PANI (emeraldine salt form).

Several applications of the modified polymer could be envisioned. As examples we describe the chemical lithography and photolithography of polyaniline via reversible nitrosation

Chemical lithography of PANI

The increased use of conducting polymers for electronic and optoelectronic applications,[41] requires new patterning methods of conductive polymers.[42] Holdcroft and coworkers synthesized polythiophenes bearing pendant groups which can be hydrolyzed by acids,[43] making it amenable to chemically amplified lithography. Similarly, lithographic
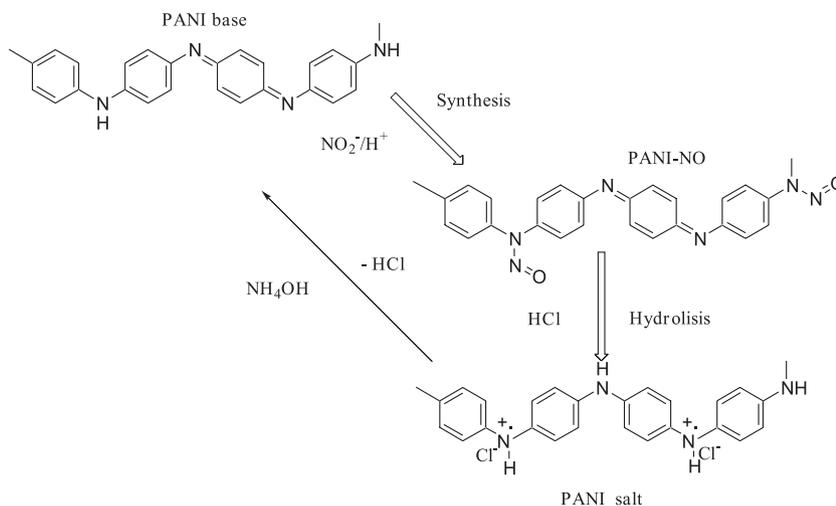
Scheme 5. Reaction scheme of N-nitrosated polyaniline synthesis and hydrolysis.
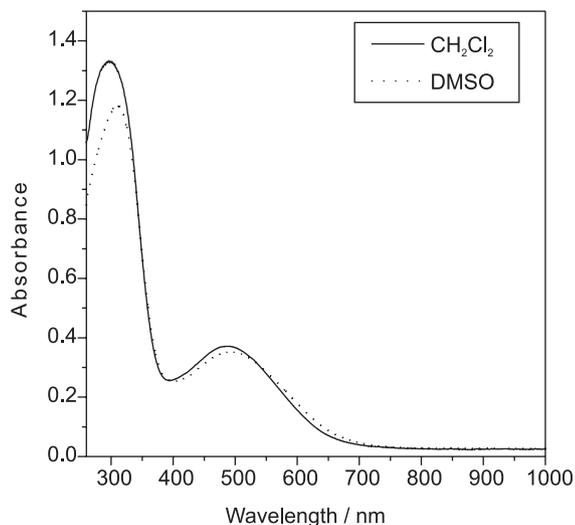
Figure 8. UV-Visible spectra of PANI-NO in dichloromethane (CH$_2$Cl$_2$, full line) and dimethylsulfoxide (DMSO, dotted line).
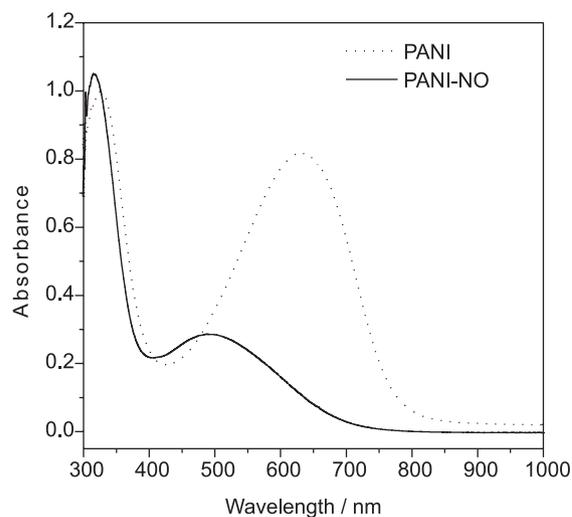
Figure 9. UV-Visible spectrum of PANI-NO solution in N-methylpyrrolidone(full line). A spectrum of polyaniline (dotted line, emeraldine base) is shown for comparison.
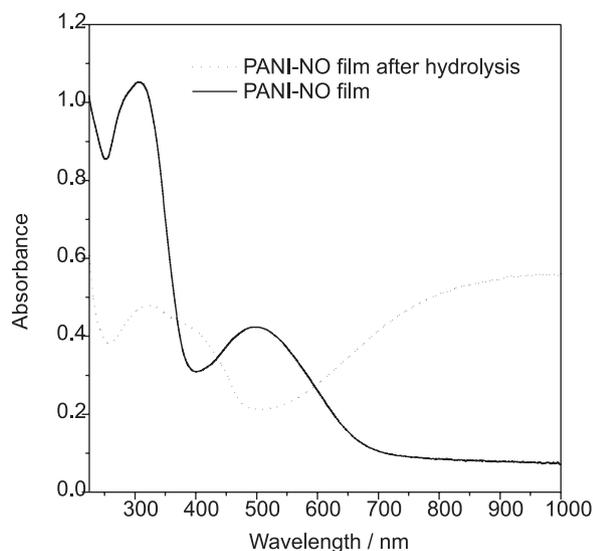
Figure 10. UV-Visible spectra of PANI-NO thin films on quartz, before (full line) and after (dotted line) hydrolysis.

patterning of polyaniline has been achieved by changing the doping state of polyaniline (PANI) films using acid[44] or base photogenerators[45] which could alter the solubility of the polymer changing its protonation state. The polymer has to be deposited from the few solvent in which PANI is soluble, like N-methylpyrrolidone.[46] If PANI could be made soluble in common organic solvents or water, it could be deposited from them. Such increased solubility has been achieved by covalent binding of functional groups to the backbone rings[47] or amine nitrogens.[48] However, the modified polymer usually presents inferior properties (e.g. conductivity) than the unmodified material.[49] If it would be possible to remove the group responsible for the increased solubility after the polymer has been processed (a traceless functional group),[50] the material will retain its intrinsic properties during processing. Additionally, if group removal could be chemically or photochemically driven, direct patterning of the film is possible. PANI amide formation/hydrolysis has been previously used to reversibly change PANI conductivity.[51]

In that sense, the reversible N-nitrosation reaction could be used to devise a lithographic process of polyaniline[52] (Figure 11).
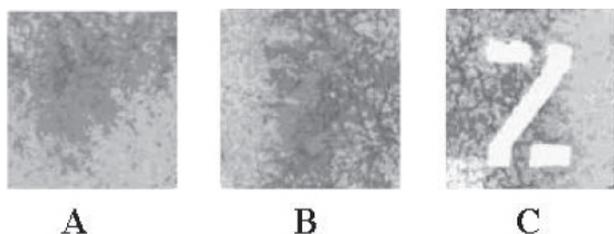

Figure 11. Photographs taken during the steps of a chemical lithographic process of polyaniline based in reversible nitrosation.

First a PANI-NO coating was deposited onto a plastic plate (Figure 11A) from its solution in CH_2Cl_2. Then, the red film was covered with a metal mask and an image of a protective layer was produced by spraying a solution of an inert polymer (PMMA) through the mask.

The plate was then exposed to HCl vapors. The PANI-NO layer hydrolyzes into PANI except in the protected region, leaving a positive image of the mask in PANI-NO surrounded by a PANI salt region (Figure 11B).

The plate is then washed with CH_2Cl_2 removing the protective layer together with the unexposed PANI-NO leaving a negative image of the mask (Figure 11C) in PANI salt. The exposed region is conductive while the unexposed region shows high resistivity (> 100 Mohms), suggesting that PANI-NO has been completely removed.

Photolithography of polyaniline via reversible nitrosation

The process is easily extend to photolithography using an acid photogenerator used to promote PANI-NO hydrolysis.

It is known that poly(vinylchloride) (PVC) suffers degradation under UV irradiation, releasing HCl.[53] Therefore, PVC could be used as a polymeric acid photogenerator.

In Figure 12 are shown the images of a plastic plate covered with nitrosated polyaniline and PVC (Fig. 12A). After irradiation with UV light (250 nm) trough a mask (letter U), the PVC degrades and releases HCl which hydrolyses the PANI-NO film (Figure 12B) leaving a positive image of PANI. After separation from the PVC film and washing with CH_2Cl_2, the PANI-NO is removed and only the positive image of PANI remains (Figure 12C). A FTIR spectrum of the layer has the same spectrum that of emeraldine salt.
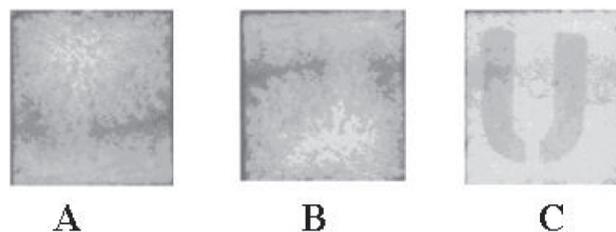

Figure 12. Photographs taken during the steps of a photolithographic process of polyaniline based in reversible nitrosation and PVC dehydrochlorination promoted by ultraviolet light.

Conclusions

Coupling of diazonium ions with polyaniline renders modified polymers which are soluble and electroactive. Polyaniline can be easily modified by nucleophilic

addition giving polymers with increased solubility in common solvents, including aqueous solutions. The extent of nucleophilic addition of arylsulphinic acids is controlled by the oxidation and protonation state of the polyaniline.

N-nitrosation of PANI can be easily accomplished by reaction with nitrous acid. The reaction can be reversed by acid treatment. Reversible N-nitrosation could be used to develop chemical lithographic and photolithographic processes to deposit polyaniline patterns.[7]

Acknowledgements

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