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Soluble polyanilines obtained by nucleophilic addition of arenesulphinic acids

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Abstract

Polyaniline powder and films can be modified by nucleophilic addition of arenesulphinic acids to oxidized forms of polyaniline. The FTIR spectra of modified polymers suggest the formation of sulphone and/or sulphonamide moieties linked to the polymer backbone. The modification degree increases with the increasing of the oxidation state of the polymer. The addition decreases significantly at pH above 7. It is proposed a mechanism of nucleophilic addition, which explains the effect of the oxidation state of the polymer and pH of the solution. The modification increases the solubility of the polymers in common organic solvents. The modification reaction seems to provide a simple pathway to the incorporation of organic moieties to polyaniline backbone.

Keywords: Conducting polymers; Polyaniline; Nucleophilic addition

1. Introduction

Polyaniline (PANI) has attracted great attention because of its electronic, electrochemical and optical properties and especially good environmental and thermal stability [1–6]. The low processability of the pristine polymer make necessary the introduction of a wide variety of functional groups on the polymer backbone. A simple method to introduce functionalities is the polymerization of anilines substituted with functional groups of interest. However, inductive and steric effects could make the monomer difficult or impossible to polymerise [7]. 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 it is possible to modify polyaniline by different reactions. Wrighton and co-workers described the nucleophilic reaction of PANI with trifluoracetic anhydride, where the reaction rate was controlled by varying the oxidation state of the polymer electrochemically [8]. Liu and Freund modified PANI by electrophilic attack of an arene cation to the nitrogen, controlling the degree of reaction by diffusion of reactants inside the film [9]. Also, it has been reported that sulphonate groups can be linked to the PANI backbone by sulphonation of the polymer to give partially (50% or 75%) sulphonated polymer (SPAN) [10]. We have shown that diazonium salts coupling could also be used to introduce functionalities in poly(*N*-methylaniline) (PNMANI) [11]. Electrophilic nitrosation was also employed to modify PANI, rendering it soluble in common solvents [12].

Han et al. have proposed the nucleophilic addition of amines and thiols to the quinonimine rings as a powerful method to polyaniline post-modification [13]. In our laboratory, we have investigated the nucleophilic addition of sulphite ions [14] and other nucleophiles [15]. Under proper conditions, a sulphonation degree up to 63% can be obtained,

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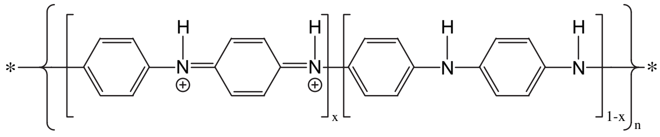


Scheme 1. General formula of polyaniline in different redox states: leucoemeraldine ($x = 0$), emeraldine ($x = 0.5$) and pernigraniline ($x = 1$).

producing a self-doped polyaniline. Also, a mechanism for the nucleophilic addition, which explained the effect of the oxidation state of PANI and the electrolyte pH, was proposed. The pernigraniline ($x = 1$ in Scheme 1) state is more reactive than emeraldine ($x = 0.5$ in Scheme 1) while leucoemeraldine ($x = 0$ in Scheme 1) is unreactive. It has been suggested that quinonimine units suffer nucleophilic attack with addition on the ring, as it is well known for low molecular weight quinonediimines [16]. Then, the difference in reactivity between the forms leucoemeraldine, emeraldine, and pernigraniline could be explained with the ratio quinonid/benzenoid units in the polymer. In addition, it was observed that the reaction rate increases as the pH of the electrolyte decreases. This fact has been rationalized taking into account that the quinonimine units are protonated at that pH range (given a pK_a of 2–3 for emeraldine), being more reactive to the nucleophilic attack than the unprotonated ones. However, in the range of pH where quinonimine units become protonated, the sulphite ions (the nucleophile) become also protonated making the interpretations of the results more complex. Moreover, we have 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 [17].

The high reactivity of sulphite ion as nucleophile leads us to test its organic derivatives: the sulphinic acids. We choose the arenesulphinic acids that are readily accessible and chemically stable. It is well known that arenesulphinic acids can be attached to monomeric quinone diimines through nucleophilic attack [18].

The simple synthesis of arenesulphinic acids from diazonium salts or arenesulphonyl chlorides [19] allows us to generate a wide range of compounds, which can be incorporated 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 which cannot be synthesized by other procedures. From the mechanistic point of view, arenesulphinic acids are protonated at higher pH (pK around 2.7 for arenesulphinic acids) [20] making possible to study the effect of pH below 4 without producing chemical changes to the nucleophile.

2. Experimental section

Aniline (Merck) was purified by distillation at reduced pressure. Benzenesulphinic and toluenesulphinic acids (Aldrich) were used as received. All aqueous solutions were prepared with twice distilled water. All other reagents were analytical quality.

2.1. Elemental analysis

Elemental analysis was made using a Carlo Erba EA 1108 microanalyzer at INQUIMAE (Buenos Aires, Argentina). The samples were dried under vacuum for 72 h before the measurement. The instrument was standardized using benzenesulphonamide in the same run.

2.2. Spectroscopy

To obtain the UV–vis spectra, clear solutions were prepared by dissolving the polymers in the solvent (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) transmission measurements of chemically prepared polymers were performed in KBr pellets.

FTIR measurements of polymer films onto platinum electrodes were made by reflection–absorption. The measurements were performed using a SpectraTech specular reflectance accessory with an incidence angle of 70°. The polymer films were deposited on polished Pt plates and the bare Pt plate was used to record the background. The sensitivity of the FTIR measurement improves when the film is in the reduced state. To maintain the redox state of the polymer, the electrode is extracted from the electrolyte solution under potential control and rapidly flushed with dry nitrogen. All the FTIR measurements were carried out in a Nicolet Impact 400 FTIR with a resolution of 4 cm^{-1}.

2.3. Electrochemistry

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

2.4. Polymer reactants

Polyaniline (emeraldine form) was prepared, as described in the literature [21], by the oxidation of aniline (0.1 M) in HCl (1 M) with ammonium persulphate (equimolar) at temperature 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 and washed with HCl (1 M) solution and water. The polymer was then converted into its base form by stirring for 24 h in a NH_4OH (0.1 M) solution. The emeraldine base form (50% oxidation) used in all reactions had an intrinsic viscosity ([η]) of 1.12 (measured in concentrated sulphuric acid solution). Pernigraniline base (100% oxidation) was prepared freshly before use by the oxidation of emeraldine base with ammonium persulphate (1%) at neutral pH for 15 min [22]. The polymer was used without drying to avoid degradation and further reduction to the nigraniline state (75% oxidation) [22]. A solution of the material in *N*-methylpyrrolidone showed an UV–vis spectrum characteristic of pernigraniline [23]. Leucoemeraldine base form (0% oxidation) was obtained by reduction of emeraldine base with phenylhydrazine in basic aqueous media, followed by washing and drying in an oxygen-free environment.

Polyaniline films on Pt or glassy carbon electrodes were produced by cycling (50 cycles) the base electrode in aniline aqueous solution (0.1 M aniline/1 M HCl) between −0.2 and 0.8 V_{SCE} at a scan rate of 25 mV/s as described before [24]. The electropolymerization was carried out at 0 °C to avoid degradation reactions. The film was washed with HCl (1 M) and water and then immersed in a benzene solution to be modified.

Poly(*N*-methylaniline) was prepared by oxidation of *N*-methylaniline with ammonium persulphate in HCl (1 M) solution [25]. The polymer was treated in the same way as PANI. PNMANI (pernigraniline) state was synthesized by an analogous procedure to those used for the pernigraniline state of PANI.

2.5. Nucleophilic reactions

2.5.1. Reaction of pernigraniline with benzenesulphinic acid

50 ml of benzenesulphinic acid in buffer solution (0.5 M; pH as described in the text) was mixed with 0.5 g of wet pernigraniline and heated in a water bath for 2 h. The reaction mixture was left to cool, filtered and washed with successive portions of H_2O, NH_4OH (1 M) and HCl (1 M). Then, the product was dried under dynamic vacuum for 24 h.

2.5.2. Reaction of pernigraniline with toluenesulphinic acid

50 ml of 0.5 M toluenesulphinic acid in a 1:1 mixture of phthalate buffer (0.25 M, pH = 3.9) and 95% ethanol (added to increase solubility). The solution was mixed with ca. 0.5 g of wet pernigraniline and heated in a water bath for 2 h. The reaction mixture was left to cool, filtered and washed with successive portions (500 ml) of H_2O, NH_4OH (1 M) and HCl (1 M). Then, the product was dried under dynamic vacuum for 24 h.

2.5.3. Reaction of PNMANI (pernigraniline state) with benzenesulphinic acid

A 25 ml solution of benzenesulphinic acid in biphthalate buffer (0.5 M; pH = 3.9) was mixed with 0.166 g of PNMANI (pernigraniline state). The reaction mixture was refluxed for 2 h. Then the solution was filtered and the solid washed sequentially with 250 ml portions of H_2O, NH_4OH (1 M) and HCl (1 M).

2.5.4. Reaction of PANI-modified electrodes with benzenesulphinic acid

The reaction with benzenesulphinic acid was carried out by subjecting the PANI-modified electrode to a potential cycling, between −0.2 and 0.45 V at 25 mV/s, in a 0.2 M solution of benzenesulphinic acid at pH = 1.5 (using 1 M KCl as supporting electrolyte and adjusting the pH using HCl).

3. Results and discussion

3.1. Nucleophilic reactions

3.1.1. Nucleophilic addition of arenesulphinates to PANI

Polyaniline (pernigraniline form) reacted with benzenesulphinate ion at pH = 3.9 as described in Section 2.5. Fig. 1 shows the FTIR spectra of the product and PANI (leucoemeraldine form). The product (PANI-BzSul) spectrum displays characteristic vibrational bands of the PANI backbone and new bands at 1330, 1309, 1159, 1089, 586 and 566 cm^{-1} due to SO_2 vibrations (see Table 1) [26]. Additionally there are other bands at 724, 756 and 688 cm^{-1} that are present in the FTIR spectrum of benzenesulphonamide and/or phenylsulphone but have not been assigned, in the literature, to defined vibrations [27].

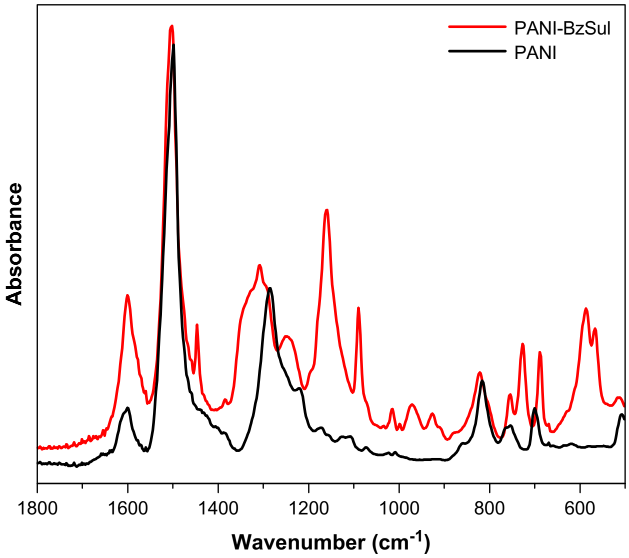


Fig. 1. FTIR spectra of PANI modified by nucleophilic addition of benzenesulphinic acid and PANI-leucoemeraldine.

Table 1
Assignment of IR bands in PANI-BzSul (PANI modified by nucleophilic addition of benzenesulphinate) and PANI-leucoemeraldine salt

Wavenumber (cm^{-1})		Assignment	
PANI	PANI-BzSul	Bond	Vibration
1596	~1600	C–C	Str. quinonoid ring
1496	~1500	C–C	Str. benzenoid ring
	1450	C–C	Str. mono-substituted aromatic ring
	1330 (sh) and 1309	SO_2	Asymmetric str. (sulphonamides and sulphones)
1280	1280 (sh)	C–N	Str. in benzenoid ring
1218	1240	C–H	In plane bending of 1–4 ring
	1159 and 1089	SO_2	Symmetric stretching (sulphones and sulphonamides)
817	815	C–H	Out of plane deformation
	586, 566	SO_2	Deformation in sulphones

Table 2
Elemental analysis data of polyaniline modified by nucleophilic addition of benzenesulphinate under various conditions

Method	pH	Elemental content (wt%)						Formula
		C	N	H	S	O[b]	S/N[c]	
PANI-BzSul (Theoretical)[a]	–	67.06	8.69	4.38	9.93	9.94	0.5	$C_{18}N_2H_{14}S_1O_2$
LE + $C_6H_5SO_2^-$	3.9	69.18	13.00	4.77	0.89	12.16	0.03	$C_{12.42}N_2H_{10.20}S_{0.06}O_{1.64}$
EB + $C_6H_5SO_2^-$	3.9	74.20	11.33	5.05	4.55	4.87	0.18	$C_{15.27}N_2H_{12.39}S_{0.35}O_{0.75}$
PB + $C_6H_5SO_2^-$	3.9	64.28	8.83	4.17	8.78	13.94	0.44	$C_{16.98}N_2H_{13.12}S_{0.87}O_{2.76}$
PB + $C_6H_5SO_2^-$	6	64.14	8.78	4.19	8.43	14.46	0.42	$C_{17.04}N_2H_{13.26}S_{0.84}O_{2.88}$
PB + $C_6H_5SO_2^-$	7	65.62	9.25	4.30	8.03	12.80	0.38	$C_{16.54}N_2H_{12.92}S_{0.76}O_{2.42}$
PB + $C_6H_5SO_2^-$	8	76.72	9.04	3.51	2.34	8.39	0.12	$C_{19.79}N_2H_{10.79}S_{0.23}O_{1.63}$

[a] Assuming a polymer modification of 50%.
[b] Polymer modification by difference.
[c] Polymer modification by molar ratio.

Elemental analysis of the product (Table 2) suggests an empirical formula with 44% of modification: $-([C_6H_4NH]_{0.56}-[C_6H_3NH(SO_2C_6H_5)]_{0.44})-$.

Similar results were obtained when toluenesulphinic acid was used as nucleophile, indicating that the addition is a general reaction for the incorporation of groups to the PANI backbone.

3.1.2. *Nucleophilic addition of benzenesulphinate to PNMANI*

While in the case of sulphite ion only addition on the ring is possible, it is known that quinonimines can react with arenesulphinates to produce modification in the ring and the nitrogen atoms [18].

To check that the addition occurs in the ring, we tested the reaction of arenesulphinates with a polymer whose nitrogen center is blocked by a methyl group: poly(*N*-methylaniline) (PNMANI). The FTIR spectra of the product (PNMANI-BzSul) (Fig. 2) compared with the parent polymer shows new bands (1446, 1159, 1089, 756, 724, 688, 586 and 566 cm^{-1}), which are similar to those found in PANI-BzSul. The asymmetric stretching of sulphones is not observed due the strong absorption of PNMANI in the range of 1200–1380 cm^{-1}. This result indicated that the reaction is possible in the ring without addition at the nitrogen. However, the latter type of addition should not be excluded for PANI.

3.1.3. *Effect of oxidation state on the nucleophilic addition of benzenesulphinate to PANI*

It has been shown that the nucleophilic addition increases when the oxidation state of the polymer increases from emeraldine to pernigraniline [13,14]. The high quinonid/benzenoid ratio in the pernigraniline form of PANI increases the reaction rate for two reasons. The concentration of the quinonimine units increases and the interaction between neighbouring quinonimine makes them more reactive towards nucleophilic addition.

To test the effect of the oxidation state of PANI on the addition, the reaction was carried out with leucoemeraldine, emeraldine and pernigraniline at the same pH (3.9). Looking at the intensity of the new bands, in the IR spectra of the products (Fig. 3), it can be seen that very little or no addition

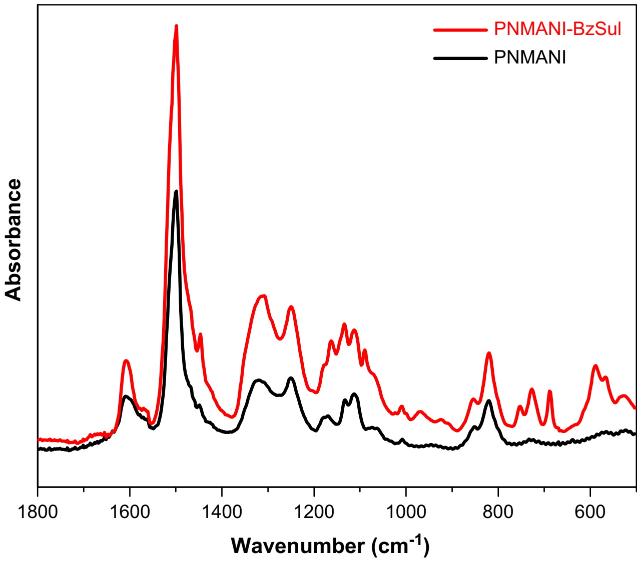


Fig. 2. FTIR spectra of PNMANI and PNMANI modified by nucleophilic addition of benzenesulphinic acid.

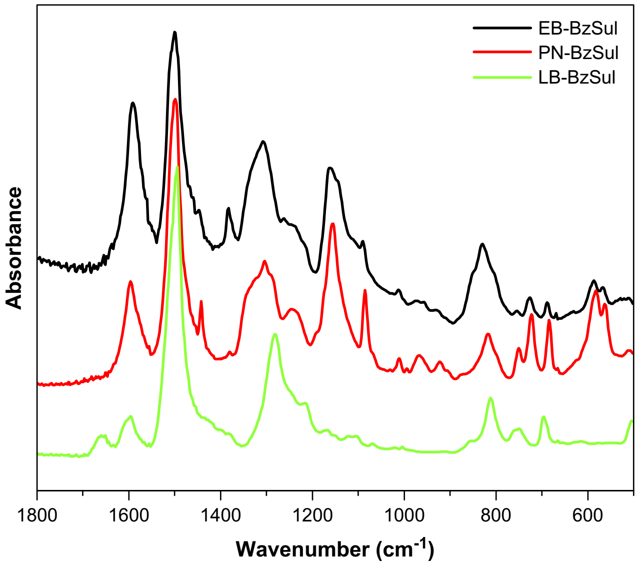


Fig. 3. FTIR spectra of (a) leucoemeraldine, (b) emeraldine, and (c) pernigraniline forms of PANI modified by nucleophilic addition of benzenesulphinic acid.

occurs with the leucoemeraldine form. The addition of sulphinate to the emeraldine base form was also noticeably lower than those observed in pernigraniline (Fig. 3). Accordingly, elemental analysis of the products indicates 18% of modification for the addition to emeraldine in comparison with 44% for the addition to pernigraniline and only 3% for leucoemeraldine (Table 2).

As descried above [13–15], the quinonimine units in the reactant polymer are converted to amine units upon reaction. Therefore, the product should be more reduced than the original polymer. It has been proposed that the ratio of the band at ca. 1500 cm^{-1} (assigned to the aromatic ring stretching of the benzenoid units, B) to the band at ca. 1600 cm^{-1} (assigned to the aromatic ring stretching, corresponding to quinoid units, Q), both normalized with background absorption, can be used as indication of the oxidation state of PANI and substituted polyanilines [1,28].

Table 3 shows the B/Q ratio for the modified polymers and polyaniline in different oxidation states. It is observed that the product is more reduced when the reactant is more oxidized precluding a redox mechanism to explain the observed changes. Furthermore, the intensity of the free carrier absorption band at >2000 cm^{-1} (data not shown) also decreases after reaction, indicating formation of a less oxidized polymer.

3.1.4. Effect of pH on the nucleophilic addition of benzenesulphinate to PANI

It has been shown that the degree of nucleophilic addition of sulphite ion to PANI increases as the pH decreases [13–15]. This behaviour was explained based on the protonation of the quinonimine unit. The protonated form is more reactive; therefore the reaction rate increases at lower pH. However, a more quantitative analysis is precluded due to the protonations of sulphite ion, which may also affect the reaction rate. The pK_a of the quinonimine units in PANI [29] is in the order of 2–3 and the pK_a of benzenesulphinic acid [19] is 2.76. The benzenesulphinic acid should be less reactive as nucleophile than the benzenesulphinate ion, which has negative charge [30]. Therefore, the mechanism can be quite complex at pH below 4, whereas 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 benzenesulphinic acid at different pH are shown in Fig. 4. Here, it can be noted that the spectra at pH below 7 show clear evidences of successful reaction (new bands, reduced polymer, low conductivity band) while in those realized at pH = 8 the reaction seems minimal. Indeed, both the B/Q (Fig. 5) and the S/N ratio obtained by chemical analysis (Table 3) indicate that the reaction smoothly decreases at pH between 4 and 8. It should be noticed that in this range of pH, the reactive species (quinonimine unit and benzenesulphinate ion) remain chemically unchanged. A possible explanation is that the pH dependence is determined by the proton incorporation during the addition. At pH = 8 the concentration

Table 3
Effect of pH and oxidation degree of the reactant polymer on the modification degree (S/N ratio) and reduction (measured by the ratio of the intensity in the IR bands at 1500 cm^{-1} and 1600 cm^{-1})

Polymer	Oxidation degree (%)	pH	B/Q ($In_{1500\ cm^{-1}}/In_{1600\ cm^{-1}}$)	Degree of modification[a]
Pernigraniline base (PB)	100	–	0.95	0
Emeraldine base (EB)	50	–	1.13	0
Leucoemeraldine base (LB)	0	–	4	0
LB + $C_6H_5SO_2^-$	0	3.9	3.9	0.03
EB + $C_6H_5SO_2^-$	50	3.9	1.50	0.18
PB + $C_6H_5SO_2^-$	100	3.9	3.15	0.44
PB + $C_6H_5SO_2^-$	100	6.0	3.03	0.42
PB + $C_6H_5SO_2^-$	100	7.0	2.63	0.38
PB + $C_6H_5SO_2^-$	100	8.0	1.15	0.11

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

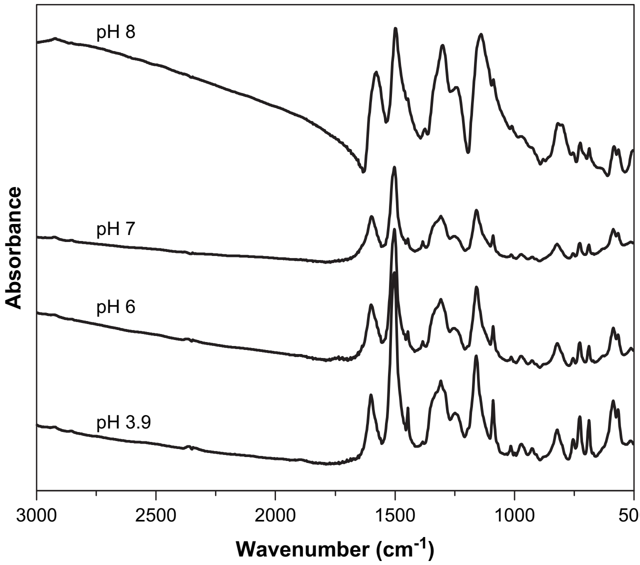


Fig. 4. FTIR spectra of PANI modified by nucleophilic addition of benzenesulphinic acid to pernigraniline form in a reaction media at different pH (see caption in figure).

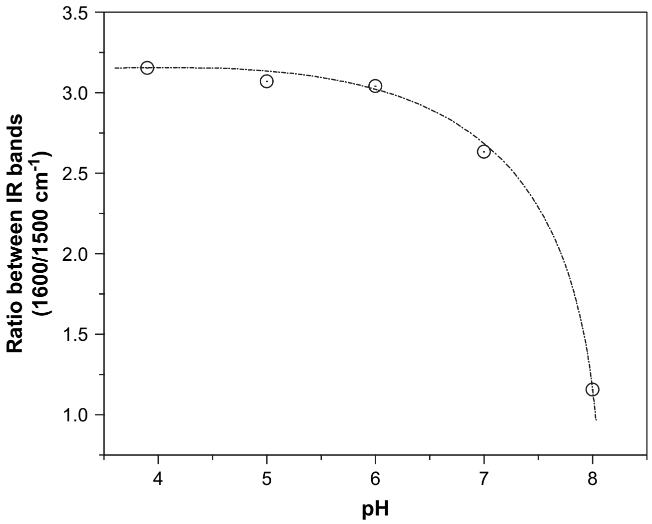


Fig. 5. Variation of the B/Q ratio with the pH of the reaction mixture.

of proton is too low to allow a significant reaction rate. This is in agreement with the pH effect observed in monomeric quinonediimines [16].

The modification of PANI with toluenesulphinate gives similar products.

3.2. Mechanism of the nucleophilic addition of arenesulphinate to polyanilines

According to the observed effects of the oxidation state and pH on the addition efficiency, a mechanism for the nucleophilic addition can be proposed where the reaction goes through two pathways rendering isomers containing sulphonamide and/or sulphone units (Scheme 2, compounds **I** and **II**, respectively).

The sulphone/sulphonamide ratio (product of each competitive pathway) decreases abruptly with increasing the pH for the nucleophilic addition of benzenesulphinate ions to quinonediimines [16]. At pH = 8, only sulphonamide is observed. This has been rationalized by assuming that in the addition of arenesulphinates to quinonimine (in the ring) a general acid catalysis by acid phosphate salts is operative, in agreement with the mechanism proposed for sulphite addition [15]. On the other hand, the pathway involving addition on the nitrogen to produce sulphonamide is independent of the pH, therefore should be preferred when the proton concentration is reduced. In our case, when the proton concentration decreases, the whole addition efficiency decreases. Thus, while both reaction pathways are possible, the dominant reaction occurring during nucleophilic addition of arenesulphinic acids to PANI is the formation of sulphone linked to the polymer backbone. This statement agrees with the result for the addition to PNMANI, which renders sulphone.

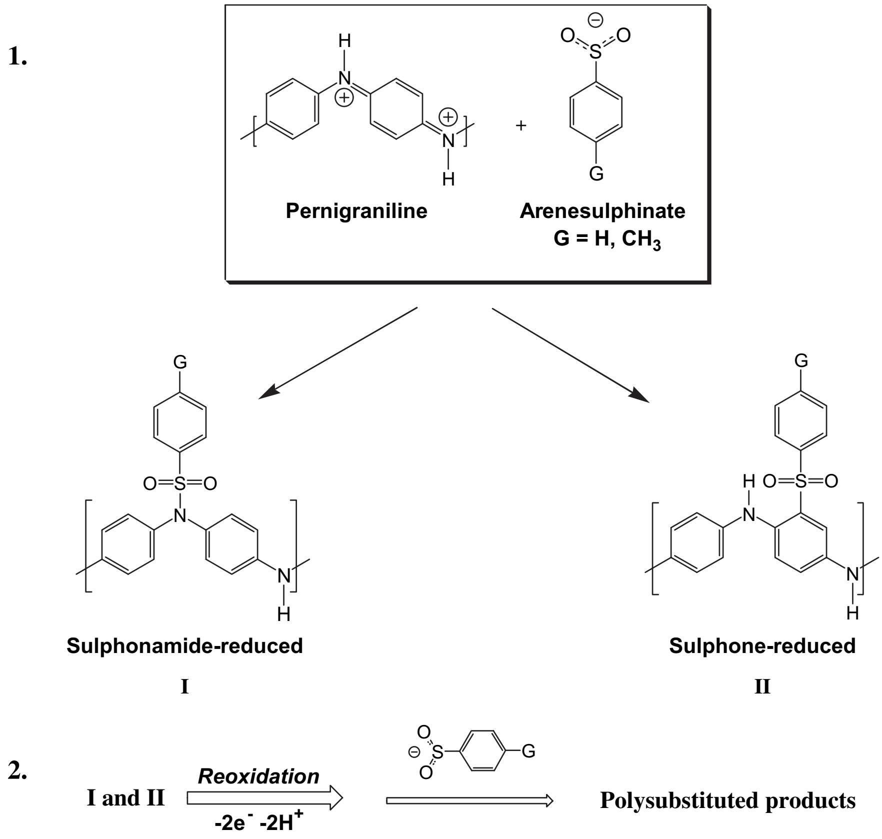
Additional evidence to the mechanism shown in Scheme 2 comes from an attempted hydrolysis of PANI-BzSul. Treatment of PANI-BzSul, obtained at pH = 3.9, with 10% NaOH for 6 h in a water bath shows little change in the FTIR spectra (not shown). If a significant amount of sulphonamide would be present it would be hydrolyzed back to PANI, altering the FTIR spectrum, while the sulphone should not be affected [31].

3.3. Properties of the polymer

3.3.1. Solubility

While PANI is only soluble in strong acids (e.g. concentrated sulphuric acid) [32], strong hydrogen bonding solvents (e.g. *N*-methylpyrrolidone) [33] or needs the aid of surfactive counterions [34,35], PANI-BzSul is soluble in common organics solvents (Table 4).

Another way to show the solubility behaviour of PANI-BzSul in different solvents is Teas [36] graph (Fig. 6). This map clearly illustrates the improvement in the processability of the modified polymer compared with PANI, only soluble in *N*-methylpyrrolidone (circled point in Fig. 6). The expanded oval in the graph is related with the fact that different factors intervene in the improved solubility.



Scheme 2. Mechanism of arenesulphinic nucleophilic addition to polyaniline.

Table 4
Solubility of PANI modified by nucleophilic addition of benzenesulphinic acid (44% of modification)

Solvent	Solubility
Methanol	Not soluble
Ethanol	Not soluble
Water	Not soluble
Chloroform	Soluble[a]
1,2-Dichloroethane	Soluble[a]
Trichloroethylene	Soluble[a]
N-methylpyrrolidone	Soluble[a]
Acetonitrile	Slightly soluble[b]
DMSO	Soluble[a]
DMF	Soluble[a]
Dichloromethane	Soluble[a]

[a] 0.5 g/100 ml or higher.
[b] 0.01 g/100 ml.

The increase of solubility in organic solvents by substitution is a general phenomenon which has been observed in several substituted polyanilines (e.g. poly(*o*-methoxyaniline)) [37]. A possible explanation of the increased solubility involves the solvation of the pendant group and/or the disruptive effect of the bulky pendant group on the interchain interaction, allowing the interaction between the solvent and individual chains.

The products obtained using emeraldine at pH = 3.9 or pernigraniline at pH = 8 show low solubility in common solvents indicating, as it was shown before for sulphonated polyaniline [38], that a certain degree of modification is necessary to induce solubility.

3.3.2. Optical spectra

The solubility of the polymer in organic solvents allows us to study the optical absorption of polymer solutions. The UV–vis spectra of PANI-BzSul dissolved in trichloroethylene show bands at 326 nm (3.79 eV) and 620 nm (1.99 eV) (Fig. 7). The band at 326 nm is attributed to the $\pi \rightarrow \pi^*$ transition of the aniline ring [39] and the band at 620 nm is assigned to the "exciton" transition of the quinone and has been related to intrachain hopping [40]. This band is absent in reduced state (leucoemeraldine) of the polymer. The UV–vis spectra of solutions in the range of $10^{-3}\%$ to $5 \times 10^{-3}\%$ follow the Lambert–Beer law. Thus it is possible to calculate weight percentage extinction coefficients of $\alpha = 197.76\ (\%\text{w/v})^{-1}$ at 326 nm and $\alpha = 61.38\ (\%\text{w/v})^{-1}$ at 620 nm. To express the values as molar absorptivity (ε) we consider chromophore as a ring with 0.5 benzenesulphone units, obtaining a molar mass of 160.5 g/mol. The extinction coefficient values are $\varepsilon = 3174\ \text{M}^{-1}$ at 326 nm and $\varepsilon = 985\ \text{M}^{-1}$ at 620 nm. The values correspond to forbidden transitions and are lower than those measured for sulphonated polyaniline ($\varepsilon = 5400\ \text{M}^{-1}$ at 313 nm and $\varepsilon = 3200\ \text{M}^{-1}$ at 563 nm) [39]. In order to compare with PANI, spectra of both polymers were taken in DMF and NMP. The spectra of PANI in DMF (Fig. 8) show two bands in the UV region (286 nm and 321 nm) while PANI-BzSul

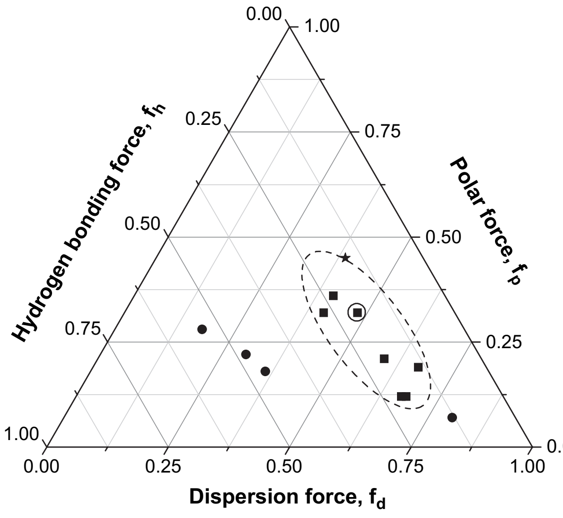


Fig. 6. Teas graph for PANI modified by nucleophilic addition of benzenesulphinic acid (44% of modification) using data from Table 4. (■) Soluble 0.5 g/100 ml or higher, (★) 0.01 g/100 ml, (●) not soluble, (- - -) polymer solubility window.

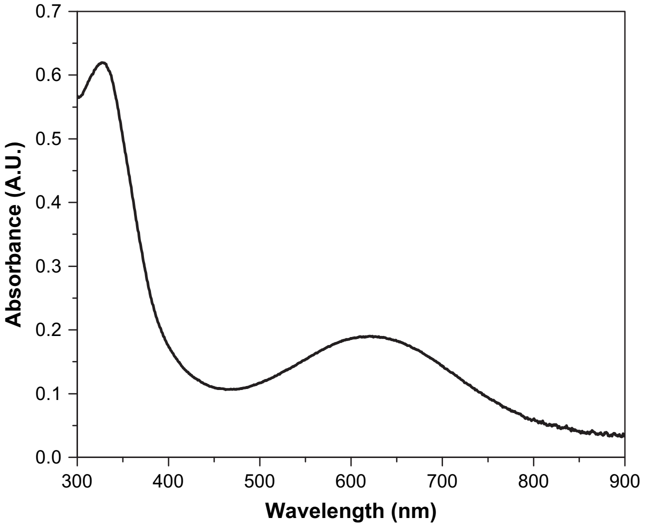


Fig. 7. UV–vis spectrum of a PANI-BzSul solution in trichloroethylene.

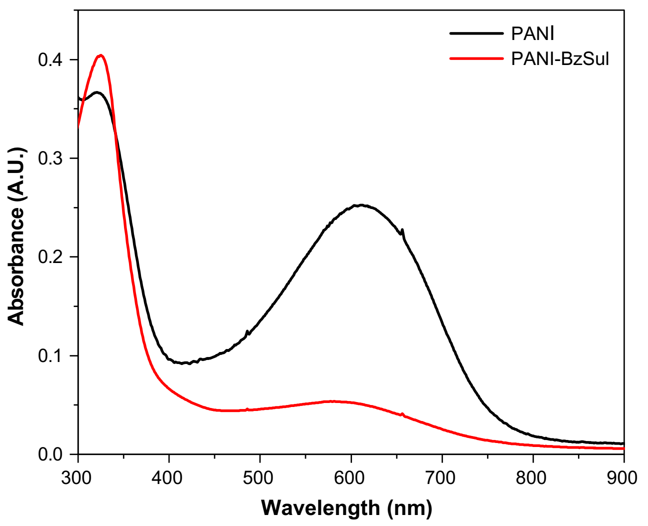


Fig. 8. UV–vis spectra of PANI and PANI-BzSul solutions in DMF.

Table 5
UV–vis spectroscopy maxima of PANI and PANI-BzSul solutions

Solvent	PANI (nm)	PANI-BzSul (nm)	Dielectric constant[a]
DMF	610, 321, 289	593, 325	37
NMP	635, 328	590, 330	32
C_2HCl_3	–	621, 330	3.4

[a] Ref. [17].

presents only one (320 nm). The exciton band in PANI appears at 610 nm, while for PANI-BzSul it shows up to higher energy (593 nm). The absorbance maxima of PANI and PANI-BzSul in C_2HCl_3, DMF and NMP are described in Table 5. The table shows that the exciton band shifts to lower energy when the dielectric constant (k) of the solvent is decreased from DMF ($k = 37$) or NMP ($k = 32$) to C_2HCl_3 ($k = 3.4$) (Table 5). In the case of PANI, a strong shift occurs between NMP and DMF that could not only be attributed to the change of polarity, but to a stronger hydrogen bonding of the >N–H groups in PANI with the >C=O groups in NMP [41]. These results suggest that the interaction between the solvent and the electronic conjugated chain (backbone) is weaker in the case of PANI-BzSul. This is in agreement with the fact that solvents with lower dielectric constant are unable to interact with PANI strongly enough to solubilize it but could dissolve PANI-BzSul through interaction with the pendant aromatic rings.

3.3.3. Electrochemistry

Reoxidation of the polymer using oxygen [14] or electrochemical in situ oxidation [42] allows increasing the modification degree (Scheme 2, step 2). Due to the fact that benzenesulphinic acid is stable in the pH range where PANI is electroactive ($pH < 4$), it is possible to reoxidize electrochemically the polymer in situ, gaining control over the modification process in general.

Fig. 9 shows the cyclic voltammogram of pristine PANI and the electrochemically modified PANI films. The films were modified cycling between −0.2 and 0.45 V_{SCE}.

The voltammograms show that the peak potential shifts anodically upon nucleophilic addition. It is likely that a combination of inductive (electron withdrawing) and steric effect (reducing the planarity of the polymer chain) increases the oxidation potential of the redox units, resembling the behaviour reported for sulphonated polyaniline [10,24].

The product of the electrochemically catalyzed modification was tested by FTIR (reflection–absorption). The spectra of polyaniline film deposited on Pt after treatment show new bands due to the presence of sulphone (and probably sulphonamide), similar to those obtained by chemical modification (Table 1). The polymer film at the potential used for the modification is less oxidized than the emeraldine state of PANI. However, the film is effectively modified because the amount of quinonimine units is regenerated continuously by reoxidation, maintaining the concentration of quinonimines almost constant during the reaction (Scheme 2, step 2). As it was described in Section 2, the potential used for oxidation was chosen to be less anodic than required for benzenesulphinic acid oxidation. The fact that polyaniline could be modified in situ by electrochemical reoxidation at a potential where unnoticeable reaction would occur with a polymer with the corresponding degree of oxidation means that modification could be driven but also controlled electrochemically.

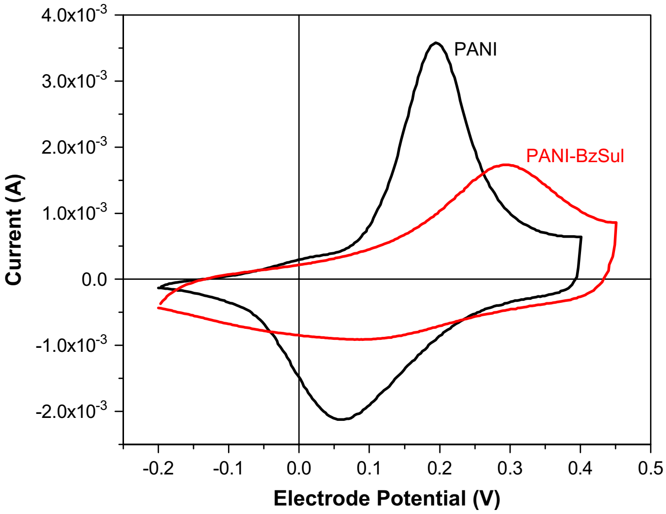


Fig. 9. Cyclic voltammograms of PANI-BzSul film on a glassy carbon electrode and unmodified PANI film on the same electrode. Electrolyte = 1 M HCl. Scan rate = 50 mV/s.

4. Conclusions

Polyaniline could be easily modified by nucleophilic addition of arenesulphinic acids giving polymers containing sulphone and, less likely, sulphonamide moieties linked to the polymer backbone. The modification changes the properties of the polymer increasing the solubility in common organic solvents. The process could be driven and controlled electrochemically. The modification procedure described here introduces new functionalities and effectively changes the solubility of the polymer and it can be used to electrochemically etch PANI films with defined patterns. A PANI film is protected by a poly(methylmethacrylate) (PMMA) film, patterned by spraying [12]. The film is then subjected to electrochemical oxidation inside a cell containing arylsulphinate ion. The unprotected region reacts with the sulphinate ion becoming soluble in common solvents (e.g. $CHCl_3$). Washing with the same solvent removes the modified film and the PMMA, leaving a positive image of the mask in PANI [43].

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