

Organic Chemistry of Polyanilines: Tailoring Properties to Technological Applications

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Abstract: The use of organic chemistry reactions to introduce additional functional groups on polyanilines is described. Among the reactions discussed are: electrophilic aromatic substitution, nucleophilic addition to the aromatic rings, nucleophilic substitution on the amine groups and reactions on pendant groups. The use of combinatorial chemistry techniques, by coupling of combinatorially synthesised diazonium salts with polyaniline, to produce a functionalized polyanilines library is also reviewed. The modification of polyaniline introduces or alters different properties of the materials: solubility, self-doping and redox coupled ion exchange. The tailoring of those properties to technical applications is therefore examined.

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. 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 through solubility of the conductive polymers in common solvents, including aqueous solutions. One of the promises of the conducting polymers is that, unlike inorganic metals and semiconductors, both the synthesis and chemical modification of organic materials offer unlimited possibilities. Soon enough it was recognized that few monomers render polymer chains with high conductivity. Two factors made difficult to produce truly conducting chains. On one hand the formation of high molecular weight polymer could be impeded by low reactivity of the monomer. On the other hand, conjugated polymer backbones could have low conductivity due to electronic and/or steric effects. This constrain is intrinsic and it remains unsolved to this day. On the other hand, synthetic obstacle to the synthesis of novel conducting polymers can be solved producing simple conducting backbones which are then post-modified. Another possibility is the copolymerization of non reactive monomers with more reactive monomers. However, the different reactivity of each comonomer results in a composition of the copolymer different to the ratio of comonomers in the feed and the formation of block copolymers. Moreover, since usually the reaction is carried

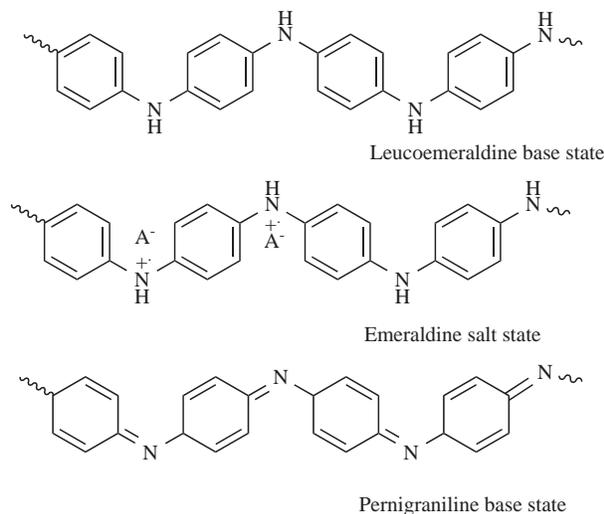
out to maximum conversion, a drift of composition occurs during reaction producing a mixture of different copolymers [4]. Both effects imply that the material has domains with different properties (e.g. conductivity) and the effective value of the property is different than the one observed in a homogenous material [5]. Another advantage is that the chain length of the modified polymer is similar to that of the parent polymer while copolymers have different chain lengths depending on the reactivity of the comonomers. Therefore, the influence of the chain length could be ruled out when considering new properties such as increased solubility.

Polyaniline (PANI) has attracted great attention because of its electronic, electrochemical and optical properties and especially good environmental and thermal stability [6-8]. The bad processability of the pristine polymer, make necessary to introduce a wide variety of functional groups on the polymer backbone. The synthetic problems are more acute in the case of polyanilines because the reactivity of the monomer is adversely affected by substitution, both in the ring and in the nitrogen, due to electronic and steric effects [9]. Therefore, unlike other conducting polymer families like polypyrroles and polythiophenes, it is only possible to obtain relatively high molecular weight polymer from a limited set of substituted anilines. Almost all the reactions are carried out with PANI in its insoluble solid form. An important point is how to know if the reaction has occurred and the structure of the modified polymer. To that effect, infrared spectroscopy is usually used because it is easily performed in solids [10]. Raman spectroscopy has also been used to that effect [11]. A more quantitative assessment of the degree of modification is usually made by X-ray photoelectron spectroscopy (XPS) [12], Electron dispersion-absorption (EDAX) [13], or plain chemical analysis [14]. Using those techniques it is possible to measure the degree of modification. This value is defined as the ratio between the moles of functional groups with respect to the moles of repetitive units in the polymer (aniline units in the case of PANI).

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ORGANIC CHEMISTRY REACTIONS

Polyaniline is a conducting polymer with a complex chemistry involving both electron and proton exchange [15]. In Scheme 1 are shown the three redox form of polyaniline in its most stable form at acidic pH ($1 < \text{pH} < 4$).



Scheme 1. Redox forms of polyaniline.

At that pH, emeraldine is its salt form with the imine units protonated. Increasing the pH more than 4 produce deprotonation of the imine units with removal of counterions. On the other hand, leucoemeraldine secondary aromatic amine units and pernigraniline imine units are less basic and remain unprotonated above pH ca. 1. At lower pH values, both forms become protonated with incorporation of counterions. Emeraldine state is the stable form in ambient conditions. The leucoemeraldine form can be produced by reduction with suitable reductants (e.g. phenylhydrazine) [16], and is easily oxidized to emeraldine in air. The pernigraniline form can be produced by oxidation with oxidants in basic or nonaqueous media [17]. It degrades in neutral or acid media, as described below. As it can be seen, leucoemeraldine state of PANI is an aromatic polyamine and will undergo reactions characteristic of aromatic groups (e.g. electrophilic aromatic substitution) and amines (nucleophiles in aliphatic and aromatic nucleophilic substitution, nucleophiles in nucleophilic addition to carbonyls, nucleophiles in nucleophilic acyl substitution) [18]. On the other hand, pernigraniline state has conjugated quinoimine units in the polymer backbone and will have the reactions of conjugated polar groups (nucleophilic addition, Michael reaction, Diels-Alder addition), like α,β -unsaturated carbonyls and quinones [19]. Emeraldine state has both types of functionalities could undergo both kinds of reactions. On the basis of the expected organic chemistry of the polyaniline backbone, different reactions have been studied.

Electrophilic Aromatic Substitution

Since most conducting polymers, with the significant exception of polyacetylene, contain activated aromatic rings it is possible to introduce substituents by electrophilic aromatic substitution. The method has been explored to modify polyanilines.

Sulfonation

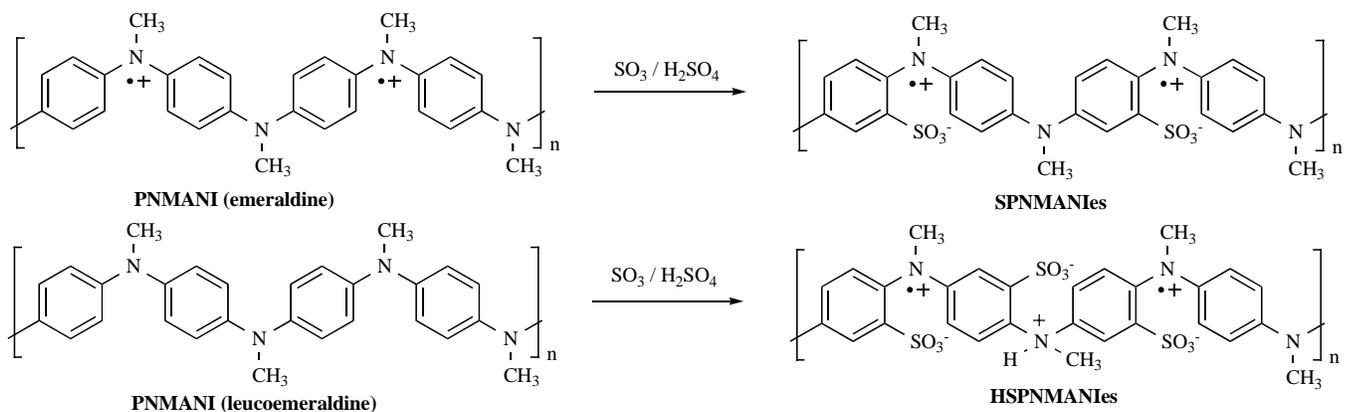
Epstein and co-workers synthesize a partially (up to 50 %) sulfonated polyaniline by sulfonation of emeraldine base, dissolved in concentrated sulfuric acid, with sulfur trioxide (SO_3) present in fuming sulfuric acid [20-24]. The resulting polymer (SPAN) is soluble in aqueous base and both the ion exchange during oxidation/reduction and the pH sensitivity were altered. The same group explore the use of other sulfonating methods, including heating the bisulfate salt of polyaniline and reaction with chlorosulfonic acid [25]. The synthetic process was patented [26]. It was found that fuming sulfuric acid and chlorosulfonic acid render the highest sulfonation degree. Other reports on the use of chlorosulfonic acid as sulfonating agent point out the need of and hydrolysis step [27]. Additionally, polymerization of aniline in acetonitrile with fluorosulfonic acid renders a sulfonated polyaniline [28]. Since the moiety subjected to sulfonation is the aromatic amine ring, the degree of sulfonation increases if a polyaniline containing 100 % of amine groups (leucoemeraldine state) is used as reactant. In that way up to 75 % of rings were found to be sulfonated [29]. It seems that 100 % sulfonation is not feasible because some oxidation of the leucoemeraldine occurs during sulfonation. Interestingly, the conductivity of the resulting polymer (HSPAN) is even higher than SPAN albeit lower than that of PANI. This result suggests that other factors than electronic and steric are responsible of the conductivity decrease. The resulting polymer is the only functionalized polymer which is commercially available [30]. Using the same methodology it is possible to sulfonate poly(N-methylaniline) to its partially sulfonated form (SPNMANIEs) and highly sulfonated form (Scheme 2).

The FTIR spectra of the product show characteristic bands of the $-\text{SO}_3^-$ group, such as the S=O stretching (1074 and 1016 cm^{-1}) and C-S stretching (622 cm^{-1}). Additionally, show a band at ca. 1650 cm^{-1} , assigned to $>\text{C}=\text{O}$ stretching which is related to the formation of quinones by chemical degradation of the chain. This observation is in agreement with the reported decrease in the molecular weight of PANI during electrophilic sulfonation due to hydrolysis in the harsh sulfonation conditions [31].

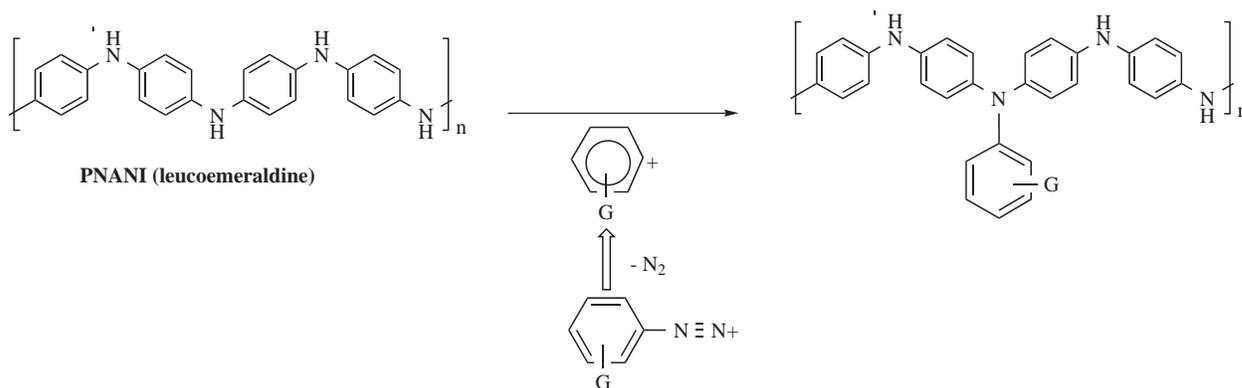
Coupling of Diazonium Salts with Polyaniline

The coupling of diazonium salts with PANI was investigated by Liu and Friend [32]. 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 ($1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4/\text{H}_2\text{O}$). In such conditions, they found evidence that the diazonium ion loses nitrogen, producing an aryl cation which is nucleophilically substituted by the amine of the PANI backbone (Scheme 3). Such substitution renders the modified polymer not electroactive.

To avoid the reaction on the nitrogen, we react diazonium ions with poly(N-methylaniline). We also used low temperature, to decrease the decomposition of the diazonium ion with nitrogen loss, and basic media, to increase the reactivity of the polyaniline backbone towards the weak electro-



Scheme 2. Synthetic routes of poly(N-methylaniline) sulfonation.



Scheme 3. Reaction of diazonium ion with polyaniline according to Liu & Freund.

phile. In that way 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 [33]. The proposed reaction is given in Scheme 4.

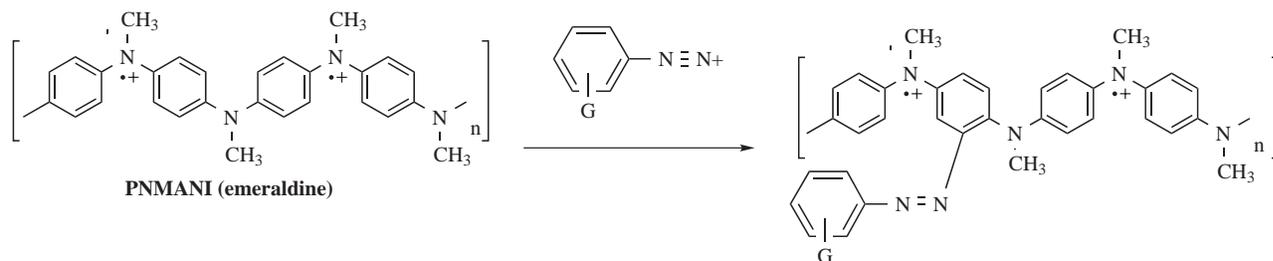
Similar products were obtained by coupling of other diazonium ions with PANI in basic media at low temperature. Zhang and coworkers also observed reaction of a diazo resin with PANI with retention of the azo groups and electroactivity [34]. We have shown that the same reaction could be made with 4-cyano-benzenediazonium salt. The modified polymer is soluble in common solvents, unlike PANI which is only soluble in concentrated acids and N-methylpyrrolidone. 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 [35] (Scheme 5).

The FTIR spectrum of the product reveals nearly total disappearance of the bands assigned to the cyano group indicating that azo linkages exist in the modified polymer. Addi-

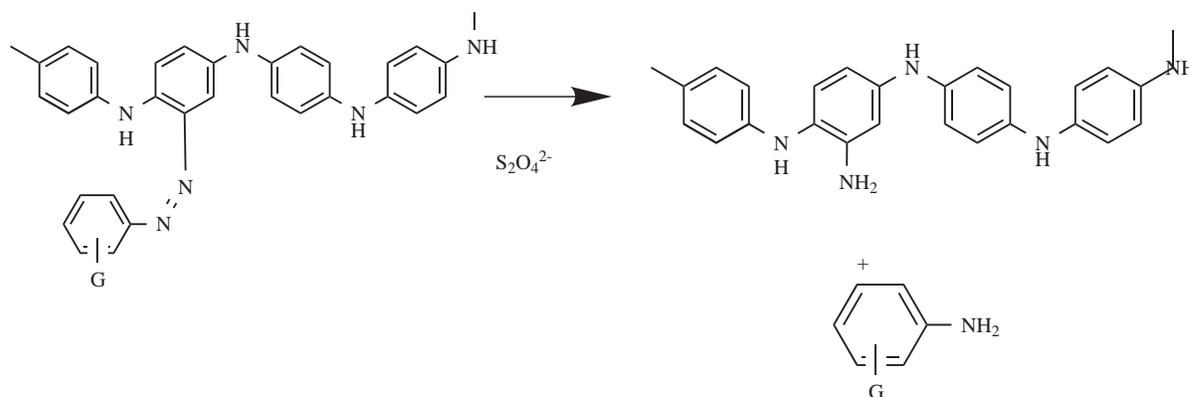
tionally, the solubility of the product is as low as polyaniline once eliminated the effect of the attached group. The modified polymers show conductivities lower than that of PANI, probably due to electronic and/or steric effect of the substituent group on the electron delocalization. However, the changes are relatively small. The successful synthesis of several modified polyanilines suggests that the method is general and it has been patented [36]. It should be note that dry diazonium salts are quite hazardous materials [37], therefore the reaction is carried out with the solution of the diazonium salt prepared just before its use.

Halogenation

The reaction of PANI with bromine yields brominated PANI, with a bromine content of bromine proportional to the concentration of bromine introduced in the reaction mixture (up to 59.1 wt %) [38]. The reaction reduces the conductivity of the polymer, as expected by electronic and steric effect of the covalently linked bromine atoms [39].



Scheme 4. Reaction of diazonium ion with Poly(N-methylaniline).



Scheme 5. Reductive degradation of azo linkages.

Nucleophilic Substitution Using the Amine Groups in PANI as Nucleophile

Amide Synthesis (Acyl Substitution)

Wrighton and coworkers described the nucleophilic reaction of PANI with substituted ethanoic anhydrides (Scheme 6). The reaction rate can be controlled by varying electrochemically the oxidation state of the polymer and/or the nature of the element present (X) on the methyl group [40]. While the leucoemeraldine state ($y=0$) is highly reactive, the emeraldine state ($y=0.5$) is almost unreactive. Conversely, the reactivity of the anhydride increases when electronegative elements (Cl, F) are used instead of H.

The ability to control the reaction electrochemically was used to selectively switch on and off the conductive path of an electrochemical transistor. A similar reaction occurs with sulfobenzoic anhydride [41]. In this case, an aromatic ring with a sulfonic group is attached to the polyaniline backbone. The polymer is soluble in pure water. A soluble polyaniline was also synthesized by modifying with a photolabile, acid-labile, and thermolabile *tert*-butoxycarbonyl (t-BOC). The group could be removed afterwards rendering polyaniline, giving the basis of a photolithographic process [42].

Amine Synthesis (Alkyl Substitution)

Polyaniline seems to have little reactivity as nucleophile in aliphatic nucleophilic substitution. However, it has been reacted with strained sultones to form polyanilines substituted in the nitrogen [43]. A more efficient reaction involves

initial conversion of the amine groups ($>NH$) to its amidure form ($>N^-$) by reaction with a strong base (e.g. NaH). The amidure form is then reacted with sultones [44]. In that way, sulfonic groups have been attached to the nitrogen of polyaniline by reaction with alkylsultones (Scheme 7). Subsequent work incorporates a benzene ring in the pendant group, producing poly(aniline-co-N-propylbenzenesulfonic acid) [45].

The resulting polymers present interesting properties towards electronic [46], and electroanalytical applications [47].

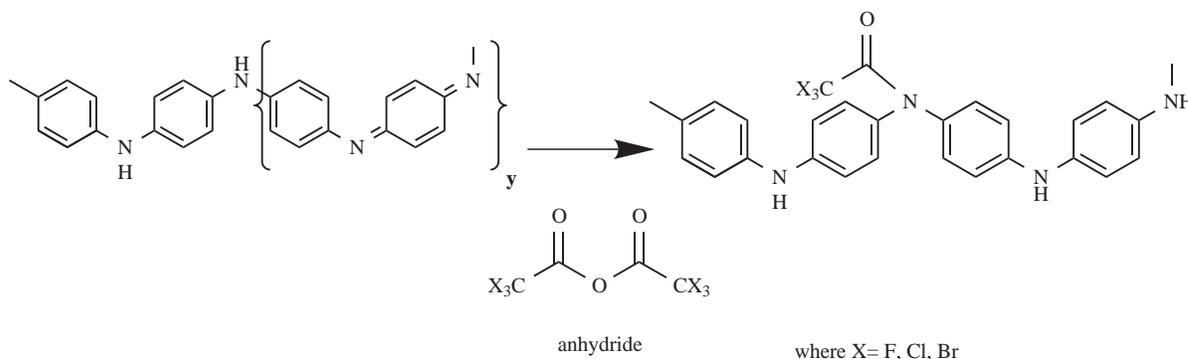
Reversible Nitrosation

The attack of NO^+ , formed by loss of water from protonated nitrous acid, on the amine groups PANI produces a red modified polymer (Scheme 8) [48].

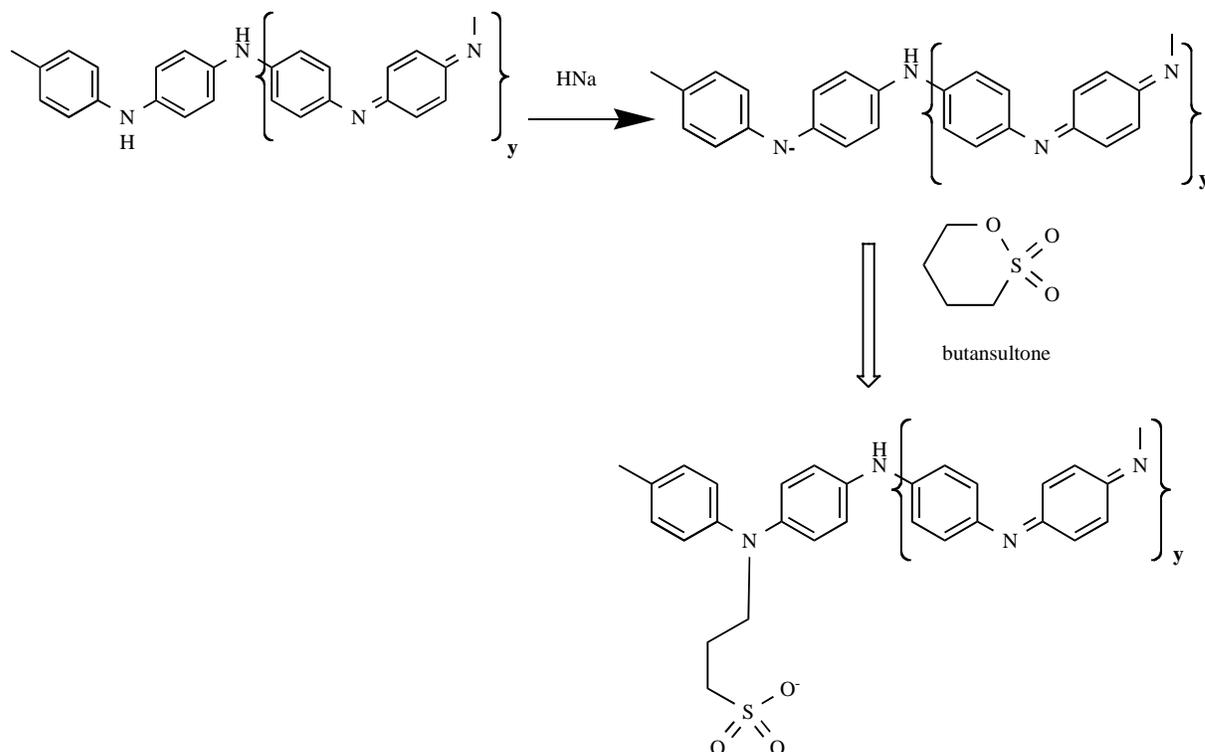
The obtained polymer, PANI-NO, is soluble in common solvents ($CHCl_3$, CH_2Cl_2 , $C_2H_4Cl_2$, secondary amines, DMSO, DMF), giving deep red solutions. By treatment with HCl vapours, the polymer is hydrolysed and the spectrum changes to one analogous to PANI (emeraldine salt form). The synthetic process has been patented [48]. The reversible nitrosation process could be used to develop a chemical or photochemical lithography of PANI (see below).

Nucleophilic Addition to Oxidized PANI

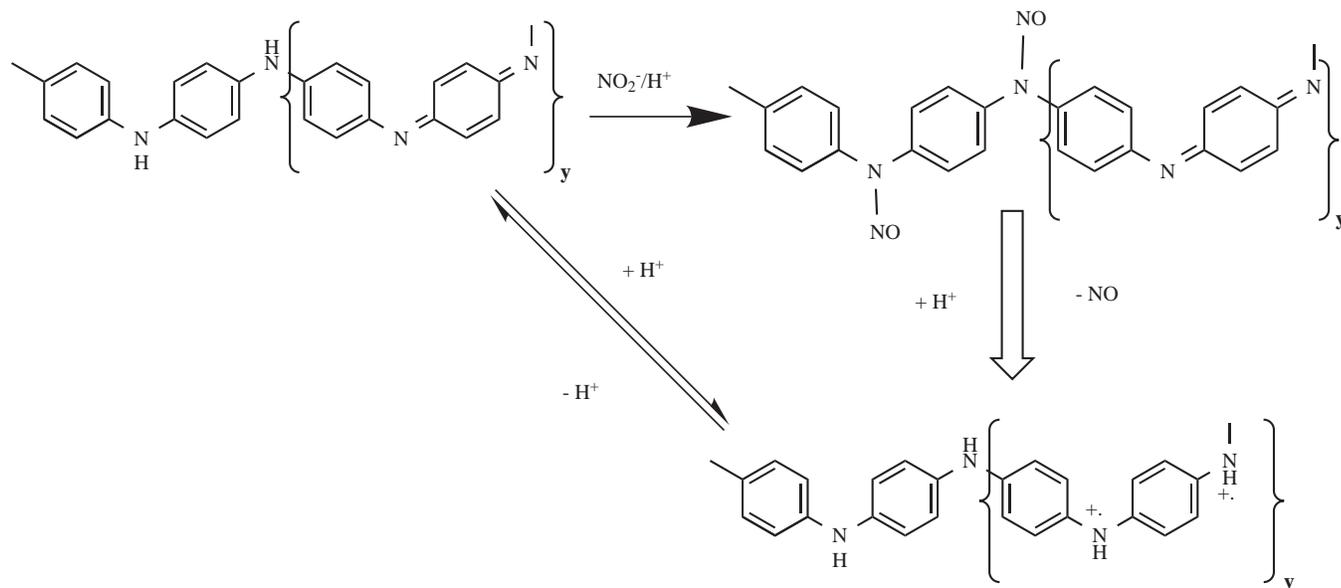
Nucleophilic addition of amines and thiols to quinonimine rings has been proposed as a powerful method to polyaniline post-modification by Han *et al.* [49, 50]. They



Scheme 6. Amide synthesis by reaction of anhydrides with polyaniline.



Scheme 7. Reaction of sultones with the amidure form of polyaniline.



Scheme 8. Reversible nitrosation of polyaniline.

showed that amines and thiols could be reacted to the quinonimine form of polyaniline. In that way, a self-doped polyaniline which is modified with a thiol containing a sulfinate group is produced [51]. Additionally, they found that the incorporation of butylthio substituents increase the conductivity of the parent polymer [52]. On the other hand, they showed that copolymerization of a substituted monomer (2-Butylsulfanyl-phenylamine) with aniline gives a polymer with less conductivity than polyaniline. This is likely due to the coexistence of conductive and non conductive domains.

This is the only case where reaction of PANI was performed also as a solution of its base form in N-methylpyrrolidone. In our laboratory, we have investigated the nucleophilic addition of sulfite ions [53], and other nucleophiles. Under proper conditions, up to 63% addition of sulfite 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 leucoemeraldine is not reactive. A possible explanation is that

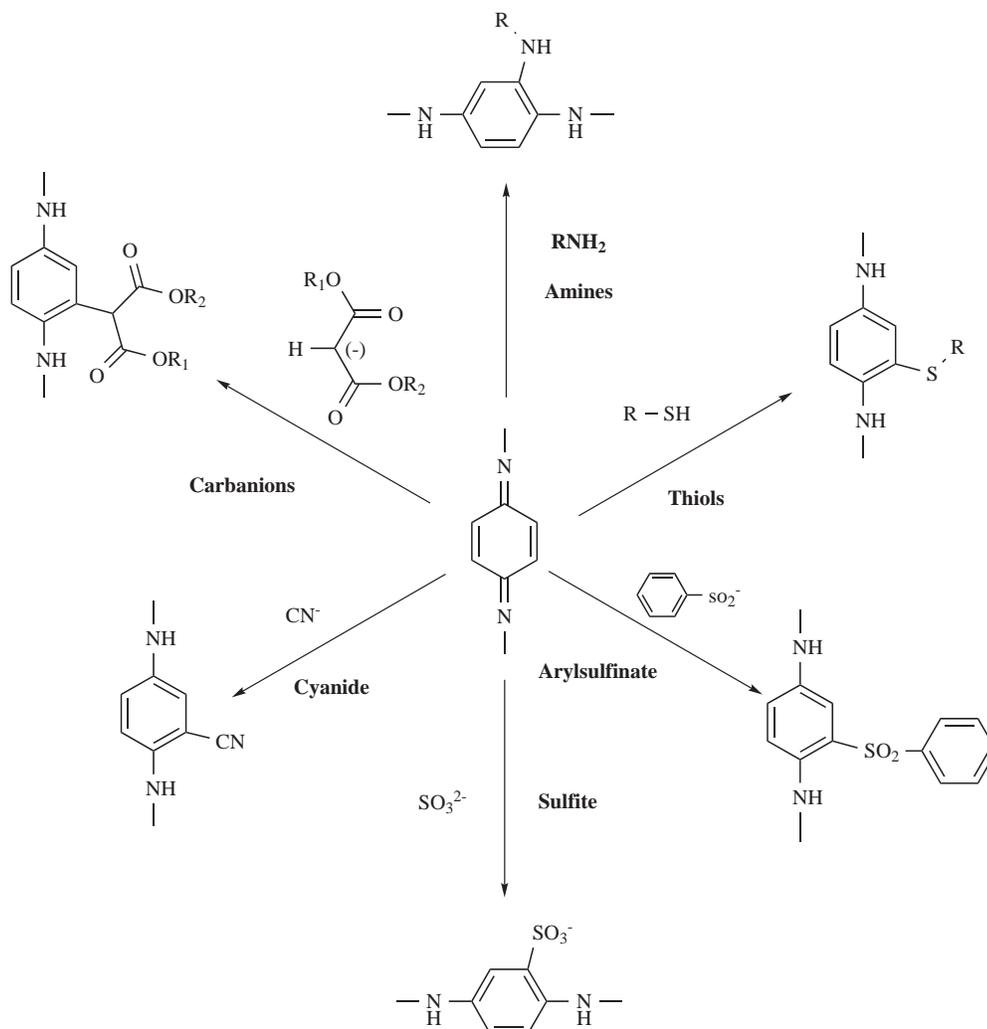
quinonimine units suffer nucleophilic attack with addition on the ring, as it is well known for low molecular weight quinonediimines [54]. The higher amount of quinonimine units in pernigraniline (100 %) than in emeraldine (50 %) accounts for its greater reactivity. The absence of those units in leucoemeraldine state makes it not reactive 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, sulfite ions (the nucleophile) become protonated too, making the results difficult to interpret. The method constitutes an alternative way to modify polyaniline by addition of nucleophiles to the oxidized polymer (Scheme 9) [55].

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 and miscibility with common polymers (e.g. PMMA) [56]. The product is soluble in basic media due to the formation of a polyanion with the carboxylate groups linked to the PANI backbone. The modi-

fied polymer is soluble in chloroform, probably due to the solvating effect of the covalently bonded ester group.

Addition of Sulfite Ions

Only the oxidised form of the polymer reacts, and the product is reduced during the reaction. Therefore, the reactivity could be controlled by the oxidation state of the polymer. Indeed, the mass increase of a polyaniline film during in-situ addition of sulfite ion, measured using Electrochemical Quartz Crystal Microbalance (EQCM) [57], occurs only when the potential is stepped from the reduced to the oxidised state [58]. Up to 50 % sulfonation can be achieved, under potential control. Ex-situ reflectance FTIR of the films confirms that sulfonate groups are incorporated to the film. The voltammetric response and the PBD signal are similar to that of SPANes [37]. The redox coupled ion exchange of the film is also modified, from a dominant anion process (in PANI) towards a dominant cation exchange (in SPANna) [35]. The synthetic process was patented [56]. The same addition of sulfite could be effected on PNMANI. The product shows bands characteristic of the $-\text{SO}_3^-$ group in the FTIR spectrum and a redox coupled ion exchange similar to that of SPNMANI. It is noteworthy that the band due to $>\text{C}=\text{O}$, present in SPNMANIes (see above) is absent in the sulfonated poly(N-methylaniline) pro-



Scheme 9. General pathway of nucleophilic addition to polyaniline.

duced by nucleophilic addition (SPNMANIna) suggesting that the later method is better because produces less degradation than electrophilic substitution with fuming sulfuric acid. The redox coupled ion exchange is altered (see below) [59]. The method represents a more environment friendly procedure than electrophilic substitution with sulfonating agents. Another advantage is was proved that the chain length is unaltered by the reaction, unlike electrophilic sulfonation where a decrease is observed [31].

Addition of Sulfinic Anions

The high reactivity of sulfite ion as nucleophile [58], suggests to test its organic derivatives: sulfinic acids. It is known that arenesulfinic acids could be used as nucleophiles to add to monomeric quinone diimines [60]. The simple synthesis of arenesulfinic acids from diazonium salts or arylsulfonyl chlorides should make this an easy route for incorporation of different organic functional groups to the PANI backbone. From the mechanistic point of view, arenesulfinic acids are protonated at higher pH (pK around 2.7 for arenesulfinic acids) [61], making possible to study the effect of pH without interference of changes in the nucleophile. Polyaniline (pernigraniline form) reacted with benzenesulphinate ion at pH = 3.9. The pKa of the quinonimine units in PANI [62], is in the order of 2-3 and the pKa of benzenesulfinic acid is 2.76. Benzenesulfinic acid, being neutral, should be less reactive as nucleophile than benzenesulfinate which has negative charge [63]. 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 sulfinate ions should be observed. The FTIR spectra of the reaction products of PANI (pernigraniline state) with benzenesulfinic acid at pH 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 and the sulfur to nitrogen (S/N) ratio obtained from chemical analysis indicate that the reaction smoothly decreases with pH between 4 and 8. As the reactive species (quinonimine unit and benzenesulfinate 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 [64].

Addition of Chloride Ions

It is known that polymerization of aniline in hydrochloric acid, at concentrations above 2 M, render a polyaniline containing covalently linked chlorine atoms [64]. The most likely mechanism involve the nucleophilic addition of chloride ions to the quinonimine units of polyaniline. Increasing the acid concentration increases the incorporation of chlorine atoms due to the increase of the nucleophile concentration and increase of the protonation degree of the polymer backbone [65].

Oxidative Degradation of Polyaniline by Water Nucleophilic Attack

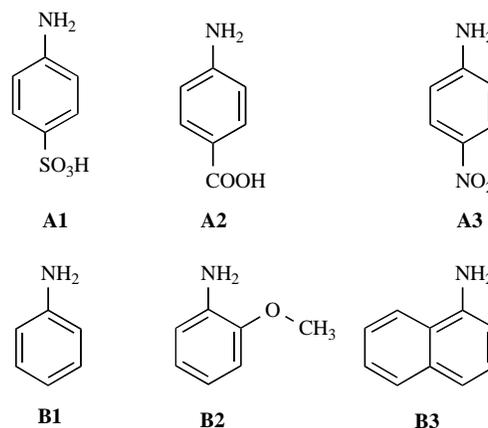
It is well known that polyanilines degrade in aqueous acid when are oxidized at the pernigraniline state. Indeed, boiling aniline in a oxidative acid solution is a laboratory procedure to produce p-benzoquinone. The mechanism of

degradation involves the nucleophilic attack of water, the only nucleophile present in sulfuric acid solution. Unlike the other nucleophiles, water attack at the positive nitrogen. It is noteworthy that the nucleophilic addition is the only reaction, in the best of our knowledge, which is specific of conducting polymers as extended conjugated chains.

Other Reactions

Combinatorial Coupling of Diazonium Salts with Polyaniline

As it can be seen above, one material (or few related materials) are synthesised and the properties studied. Such approach, usual in the field, makes the discovery of new materials rather slow and expensive. A method to overcome those limitations involves the combinatorial synthesis, coupled to high throughput screening of compounds. The method was initially developed to accelerate the discovery of pharmaceutical compounds [66], and have then been extended to the search of other organic compounds, materials [67] and polymers [68, 69]. Several compounds are produced through the reaction of several substrates with several reactants by the same reaction. The screening of properties is also made on the whole set of compounds produced and only those compounds with properties of interest are fully characterised. Combinatorial synthesis could be carried out in solution, but the simplicity of workout with immobilized substrates makes it the method of choice. Indeed, the solid phase synthesis has been used to synthesise conjugated molecules of precise length [70-72]. The low solubility of conducting polymers in most solvents makes them ideal to perform combinatorial chemistry reactions on the polymer. Recently, combinatorial reactions have been used to produce conjugated polymers with success [73]. To extend the method to conductive polymer modification, diazonium coupling with polyanilines (see above) was chosen as synthetic method [74]. This is due to the simplicity of the reaction, the possibility of combinatorial synthesis of the diazonium salt and the commercial availability of a variety of possible reactants (aromatic amines). The proposed combinatorial reaction requires the coupling of a diazonium salt, produced by diazotization of an aromatic amine (A), with another aromatic amine (B). The later has to be activated for electrophilic substitution. Taking this into account, the following aromatic amines were chosen for a first trial (Scheme 10).



Scheme 10. Aromatic amines used in the combinatorial synthesis of modified polyanilines.

It is possible to couple type A amines (non activated) with type B amines (activated) to produce azo dyes terminated in $-NH_2$. These azo dyes could be diazotized and coupled with PANI. The effectiveness of the diazonium salts coupling to PANI was tested using FTIR spectroscopy on the products. Most of the modified polymers are soluble in common solvents (Table 1), while unmodified polyaniline is insoluble in the same solvents.

Table 1. Solubilities (VS at Least 1% w/v, S at Least 0.1% w/v, I = Insoluble) of Combinatorially Modified Polyanilines (See Notation in Scheme 10)

Polymer	NH ₃ /H ₂ O	Acetone	Toluene	NH ₃ /iPrOH	CHCl ₃
PANI	I	I	I	I	I
A1-PANI	VS	I	I	VS	I
A2-PANI	VS	I	I	I	I
A3-PANI	I	S	I	I	I
B1-PANI	I	S	S	S	I
B3-PANI	I	S	I	I	I
B2-PANI	I	S	S	S	VS
A1B1-PANI	VS	I	I	S	I
A1B3-PANI	VS	S	I	I	I
A1B2-PANI	I	I	I	I	I
A2B1-PANI	S	S	I	I	I
A2B3-PANI	I	S	I	S	I
A2B2-PANI	S	I	I	I	I
A3B1-PANI	I	S	I	I	I
A3B2-PANI	I	S	I	I	I
A3B3-PANI	I	S	I	I	I

Thin films of combinatorially modified polyanilines could be produced from solutions in suitable solvents. Most of them are electroactive. While the conductivity of all the modified polyanilines is lower than that of unmodified PANI (Fig. 1), the decrease in conductivity is only of one order of magnitude. Such decrease is a reasonable trade-off for the improved solubility.

Grafting of Vinylic Monomers

It is possible to graft vinylic monomers by radical polymerization onto polyaniline [75]. In general, only the surface of the polymer structures is modified [76]. The treatment of polyaniline with ozone, or UV-irradiation, is an efficient way to produce radicals to that goal [77].

Nucleophilic Aromatic Substitution

In principle amine groups in polyaniline could act as nucleophiles in aromatic nucleophilic substitution [78]. However, secondary aromatic amines are poor nucleophiles. Preliminary results suggest that the reaction only gives a small modification percentage [79].

Reactions in Pendant Groups

Another strategy involves polymerization of substituted aniline, leaving reactive pendant groups which could be used to link functional groups.

Polyaniline Substituted with Aliphatic Amine Groups

A copolymer formed from aniline and *o*-aminobenzylamine (ABA) was electrochemically synthesized from a solution of ABA and aniline. Ferrocene carboxaldehyde (FcCp₂CHO) was then coupled to the copolymer by nucleophilic addition to the carbonyl, with formation of the Schiff base. The imine is reduced to the stable amine form, leaving the redox group attached to the polyaniline backbone (Scheme 11) [80]. The aliphatic primary amine groups are only reactive site for the addition reaction.

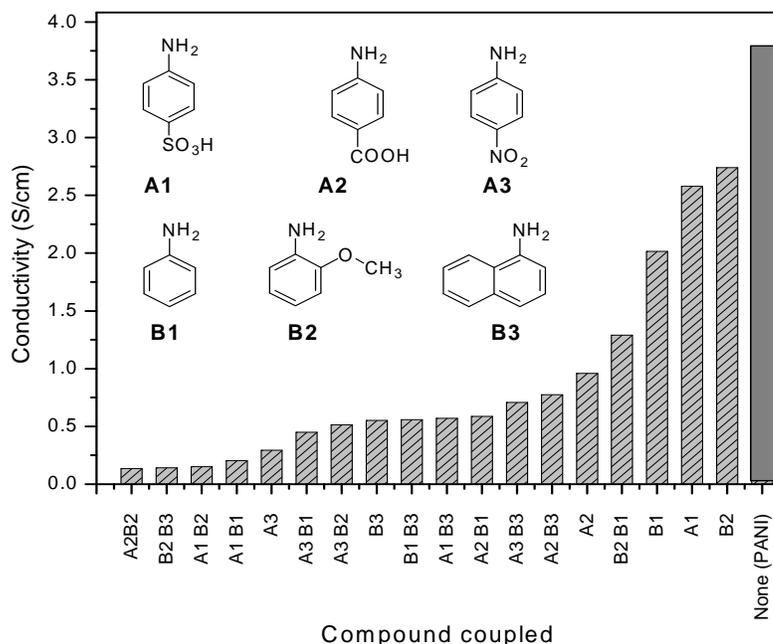
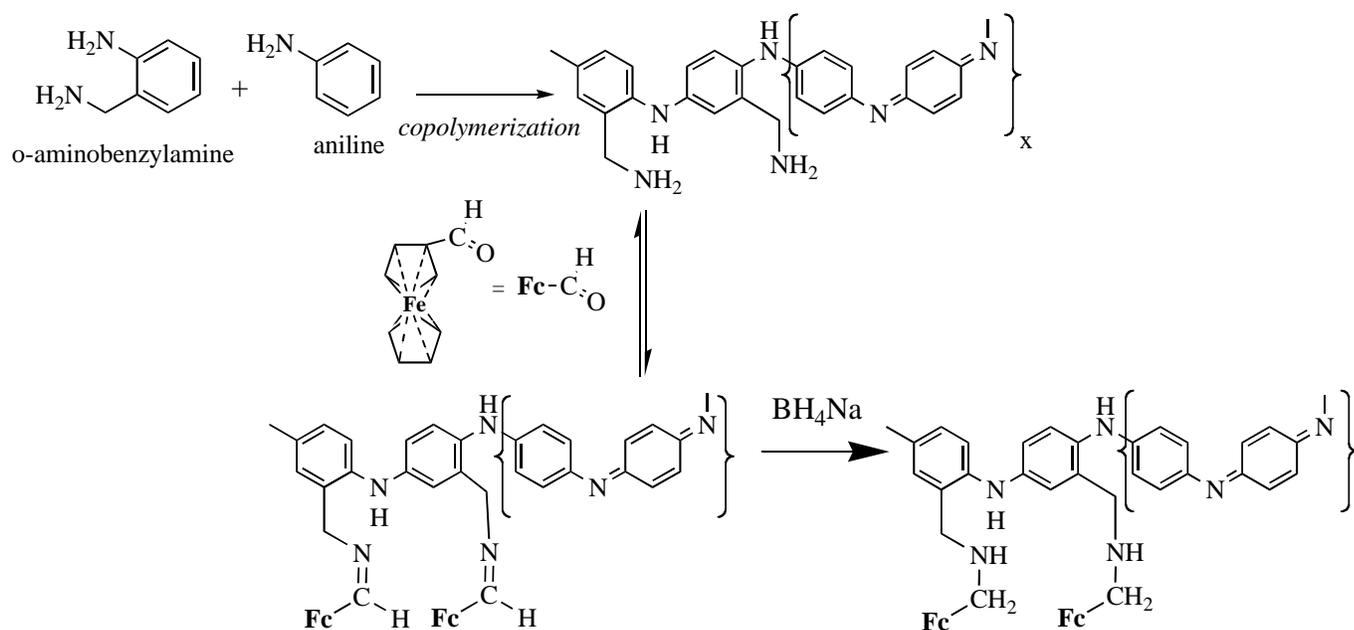


Fig. (1). Conductivities of polyaniline modified by coupling of diazonium salts prepared from combinatorially synthesized azo compounds. The dark grey bar at the left shows the conductivity of the unmodified polymer.



Scheme 11. PANI modification by reaction on the pendant aliphatic amine groups.

Polyaniline Substituted with Boronic Acids Groups

Wolfbeis and coworkers copolymerized aniline with anilineboronic acid, producing poly(aniline-co-anilineboronic acid) [81]. Fabre and coworkers homopolymerized anilineboronic acid, in the presence of fluoride [82], to produce a self-doped polyaniline. The copolymer and the homopolymer react easily with sacharides (e.g. D-fructose) to give specific complexes which could be hydrolyzed at low pH [83]. The monomer itself can be complexed with 3-anilineboronic acid and the oxidatively polymerized [84]. The pendant boronic acid group could be replaced by $-\text{OH}$, by reaction with H_2O_2 , or $-\text{I}$, by reaction with I_2 (Scheme 12) [85].

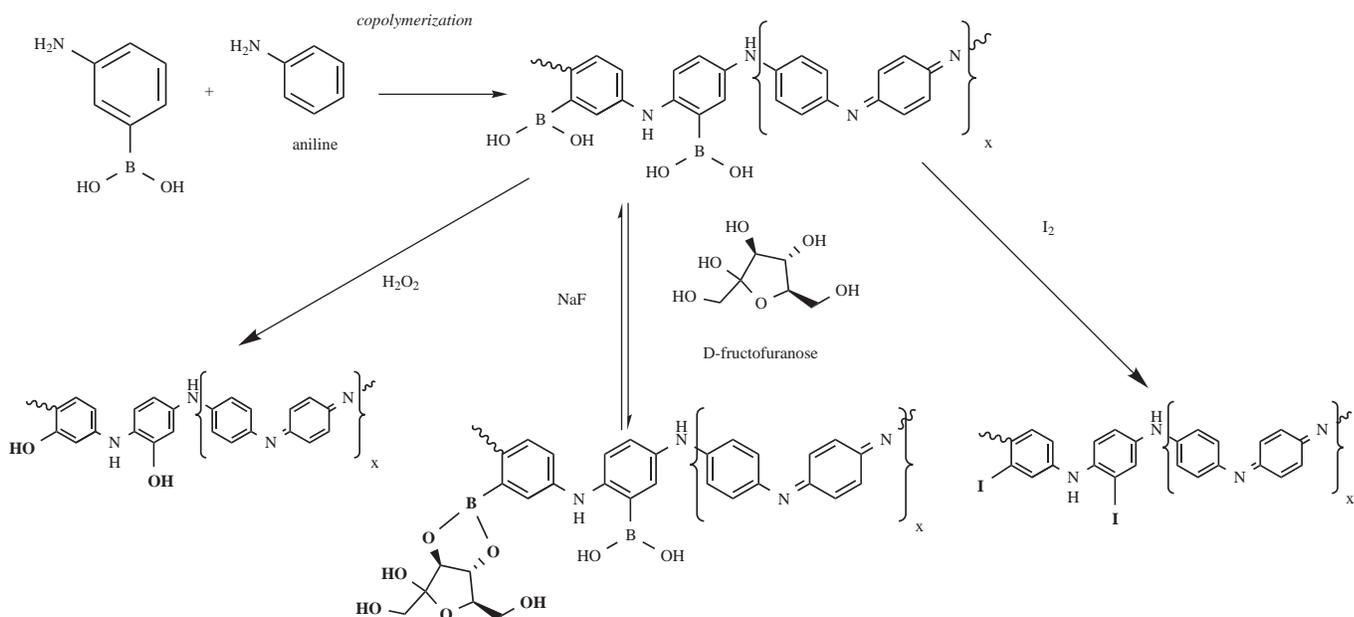
Polyaniline Substituted with Carboxylic Groups

Aniline substituted with one (aminobenzoic acids [86]) or two (aminophthalic acids [87]) carboxylic groups can be copolymerized with aniline to render electroactive copolymers. The copolymers could be thermally decarboxylated to form polyaniline [88]. The obvious reaction to form peptide chains using the pendant $-\text{COOH}$ groups has not been explored.

Novel Properties Incorporated and Application of Functionalized Polymers

Improvement in solubility by functionalization

As it was stated before, one of the main purpose of polyaniline modification is to make the polymer soluble in com-



Scheme 12. Reaction of polyanilines bearing boronic acid groups.

mon solvents. In that sense, incorporation of pendant groups produce two effects: increase the interaction of the polymer with the solvent through specific interactions (ion-dipole, dipole-dipole, hydrogen bonding) of the groups and decrease the chain to chain interactions through the steric effect of the groups. One of the most common functional groups linked to the polymer backbone is sulfonate ($-\text{SO}_3^-$). The group remains charged at acidic pH, creating strong ion-dipole interactions with water. Therefore, sulfonate bearing polyanilines like the sulfonated polyaniline are soluble in basic and neutral pH. However, in acid the amine and quinonimine groups are charged and compensate the negative charge of the sulfonate. Therefore, the zwitterions polymer has low solubility. Other anionic groups like $-\text{COO}^-$ and $-\text{PO}_3\text{H}_2^-$, also gives solubility but at acidic pH those groups are protonated and the solubility is reduced. Preliminary results in our group suggest that incorporation of easily protonated groups (e.g. pyridine) makes the polymer soluble in basic media. Nucleophilic addition of arylsulfonates makes polyaniline soluble in common solvents, like dimethylsulfoxide. It is likely that aryl substituents decrease the chain to chain interaction by steric effects. Therefore, using the combinatorial reaction with aryl diazonium ions should be possible to solubilize conducting polymers in different solvents.

Since the parent polymer (PANI) is insoluble in most solvents it possible to pattern PANI films using the different solubility of functionalized polyanilines. While such goal can be achieved by selective modification, those modification which can be reversed (N-nitrosation, reaction with t-BOC) has been used instead to pattern PANI films.

Applications of Reversible Functionalization Based on Solubility

Chemical Lithography of PANI

The increased use of conducting polymers for electronic and optoelectronic applications [89, 90], requires new patterning methods of conductive polymers [91]. Holdcroft and coworkers synthesized polythiophenes bearing pendant groups which can be hydrolyzed by acids [92], making it amenable to chemically amplified lithography. Similarly,

lithographic patterning of polyaniline has been achieved by changing the doping state of polyaniline (PANI) films using acid [93], or base photogenerators [94] 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 [95]. 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 [20, 21] or amine nitrogens [96]. However, the modified polymer usually presents inferior properties (e.g. conductivity) than the unmodified material [97]. If it would be possible to remove the group responsible for the increased solubility after the polymer has been processed (a traceless functional group), the material will retain its intrinsic properties during processing. Additionally, if group removal could be made chemically or photochemically driven, direct patterning of the film is possible. PANI amide formation/hydrolysis has been previously used to reversibly change PANI conductivity [98]. In that sense, the reversible N-nitrosation reaction could be used to devise a lithographic process of polyaniline [99] (Fig. 2).

First a PANI-NO coating was deposited onto a plastic plate (Fig. 2A) 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 (Fig. 2B). 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 (Fig. 2C) 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

The process is easily extended to photolithography using an acid photogenerator used to promote PANI-NO hydrolysis. It is known that poly(vinylchloride) (PVC) suffers deg-

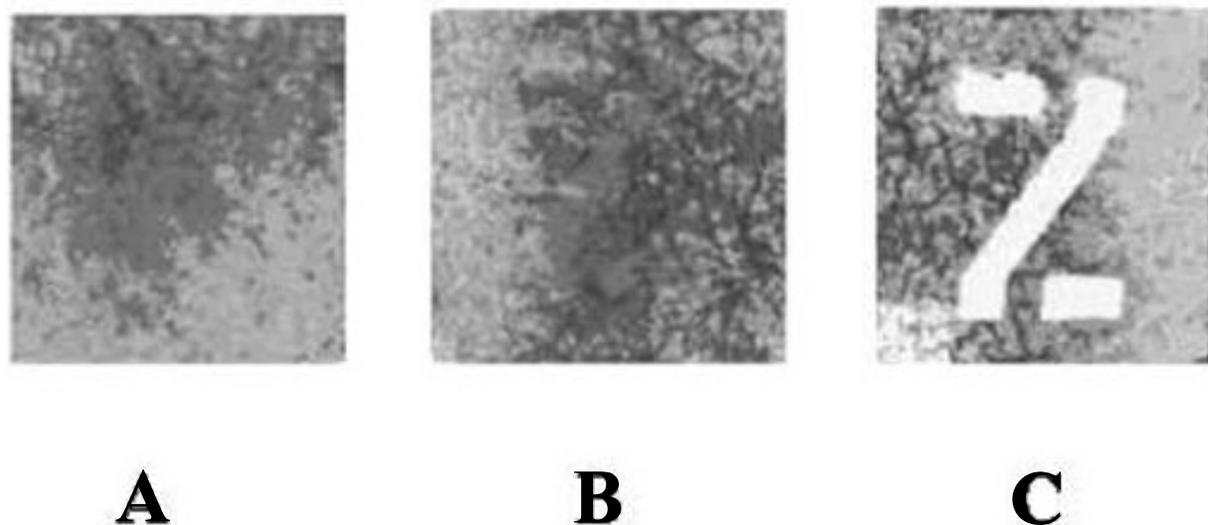


Fig. (2). Photographs taken during the steps of a chemical lithographic process of polyaniline based in reversible nitrosation.

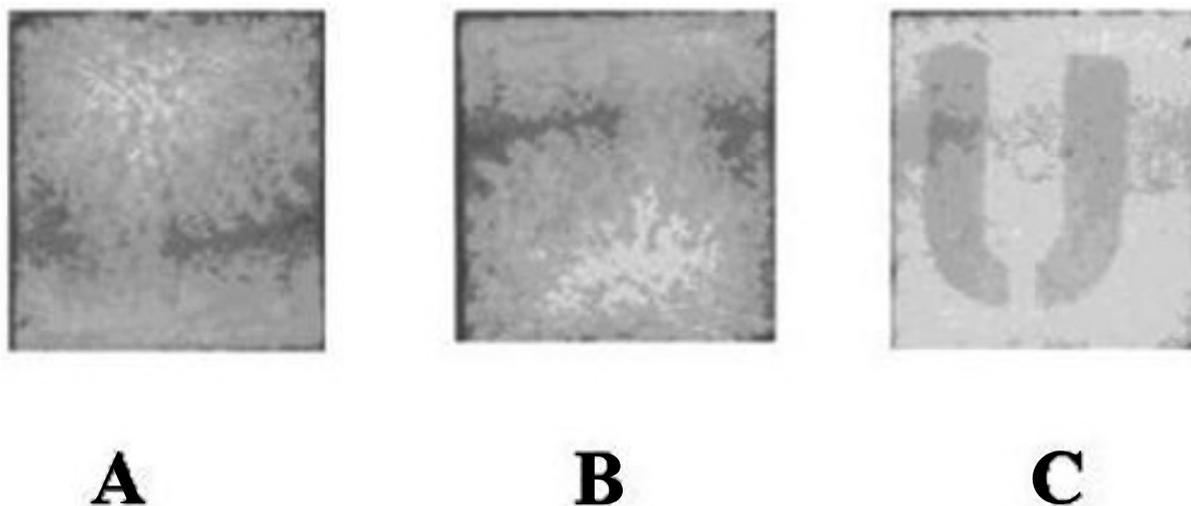


Fig. (3). Photographs taken during the steps of a photolithographic process of polyaniline based in reversible nitrosation and PVC photochemical dechlorination.

radation under UV irradiation, releasing HCl [100]. Therefore, PVC could be used as a polymeric acid photogenerator. In Fig. (3) are shown the images of a plastic plate covered with nitrosated polyaniline and PVC (Fig. 3A). After irradiation with UV light (250 nm) through a mask (letter U), the PVC degrades and releases HCl which hydrolyses the PANI-NO film (Fig. 3B) 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 (Fig. 3C) [101]. A FTIR spectrum of the layer has the same spectrum that of emeraldine salt. The lithographic method has been patented [102].

Self-Doping of Conducting Polymers by Functionalization

Uncharged conducting polymers are semiconducting [103]. To achieve conductivity, a certain amount of charge has to be injected into the polymer matrix [104]. The process, in loose analogy with inorganic semiconductors, has been called “doping”. Injection of negative charge (reduction) produces n-doped material and injection of positive charge (oxidation) gives p-doped conducting polymer. Since the polymer matrix is charged, an equivalent amount of counterions (e.g. anions in p-doping) have to be present to balance the charge. The presence of mobile counterions could be deleterious because they can be lost by washing or evaporation, react with the polymer, decompose, etc. Therefore, polymers containing the counterions covalently linked to the polymer backbone could have desirable properties. Such materials are called self-doped conducting polymers [105]. Self-doped conducting polymers present conductivity insensitive to the external concentration of ions. Self-doped conducting polymers have higher energy capacity, when used battery materials, than externally doped conducting polymers [106]. The reason is that a so called “rocking chair” battery [107], can be built using a self-doped polymer and an active metal (e.g. Li), where the metal cations are transferred reversibly between cathode and anode during charging/discharging of the battery. Therefore, the amount of solvent required to dissolve the electrolyte ions is significantly diminished. Incorporation of anionic groups by

chemical post-modification is an excellent method to achieve self-doping, as it has been shown for polyanilines [108]. The self-doping effect is directly linked to the changes in the redox coupled ion exchange (below). An interesting development is the synthesis of polymers which can be switched between self-doped and non-self-doped form by hydrolysis of a sacharide-boronate polyaniline [109].

Alteration of the Redox Coupled Ion Exchange by Modification

By introduction of anionic groups in the polymer backbone, the redox coupled ion exchange should be altered. A reduced conducting polymer, neutral, which become oxidized have to insert anions to maintain film electroneutrality. On the other hand, a self-doped conducting polymer will bear negative charges (due to the fixed anionic groups) in its reduced state which are compensated by cations. Upon oxidation, positive charges are developed in the polymer, which are compensated by the fixed anionic groups. Therefore, cations are expelled upon oxidation. As it can be seen the redox coupled ion exchange will change drastically by linkage of anionic groups to the backbone chain. In-situ measurements of the redox coupled ion exchange are always necessary since the mere presence of negative charges inside the film does not assure the self-doping mechanism in every condition [110].

Sulfonated Polyaniline. One easy way to alter the ion exchange mechanism implies fixing negative charges to the polymer backbone. In all cases, the ion exchange is altered. In aqueous media, both redox steps present negative deflection on oxidation. This suggests that both redox processes involve proton expulsion, being the negative charge compensated by the covalently linked anions. It is interesting to note that EQCM data show decreasing frequency (increasing mass) during oxidation. These results could indicate that anions are inserted during oxidation, in contrast to the PBD results. However, a more detailed study using different anions and cations show that the mass increase is independent on the mass of the anion and depends on a 10% on the mass of the cation present in the electrolyte. This effect suggests that anions are not involved and only a 10% of cations (other

than protons) are exchanged at pH=1. The observed mass increase is likely to be due to a counter flux of solvent (water) occurring when the protons are expelled on oxidation. PBD also reveal proton exchange during both redox processes in the copolymer of aniline with aminosulfonic acid. The results were confirmed using EQCM [111]. In nonaqueous media, both redox process in SPAN show a dominant cation flux [112]. This is surprising since the sulfonating degree (50 %) is lower than the 100 % necessary to compensate for all the positive charge. It seems apparent that solution counterions (ClO_4^-) form ion pairs with sulfonate and lithium, being retained upon polymer reduction. The mechanism was confirmed by EQCM. Similar results were observed when a small pH electrode was used to monitor the redox coupled proton exchange of a SPAN film [24]. A comparison between polyaniline sulfonated in the ring (SPAN) and polyaniline sulfonated in the nitrogen (PAPSAH), reveal that protons are the dominant species in the redox coupled ion exchange of SPAN while in PAPS AH, the participation of anions also occurs, with a contribution strongly dependent on anion size [113].

Sulfonated Poly(*N*-Methylaniline). The electrophilic substitution of -H by $-\text{SO}_3\text{H}$ in PNMANI could generate a polymer with different ion exchange properties. Indeed, the PBD signal for HSPNMANIes, recorded along the cyclic voltammogram reveals only cation (proton) expulsion during both oxidation processes [114]. These results indicate that the fixed anionic groups are used to compensate the positive charge produced during oxidation and protons have to move out of the polymer. Such behaviour is strikingly different to that of PNMANI. A similar behaviour is also observed with SPNMANIes and SPNMANIna.

Building Blocks of Electrostatically Self-Assembled Multilayers by Functionalization

Layer by layer self assembly into multilayers is one the most useful tools to produce novel nanostructures [115, 116]. Conducting polymer functionalization could introduce anionic and cationic groups linked to the polymer backbone. Those groups could be used to self-assemble multilayers containing conducting polymers. Indeed, sulfonated polyaniline containing multilayers were built using different non conducting polycations [117-119]. Sulfonated polyaniline was also self-assembled with dendrimers [120], and redox proteins (cytochrome-c) [121]. PAPS AH was also self-assembled into multilayers [122]. We have explored the possibility to self-assemble polyanilines modified by coupling with diazonium salts (negatively charged) with a cationic polyelectrolyte (poly(diallyldimethylammonium chloride), PDAMAC) [123]. The procedure was extended, using polyaniline modified with pyridine groups (positive charges), to the self assembly of multilayers only containing functionalized polyaniline. Cytochrome c was also self-assembled onto photochemically patterned SPAN [124].

Stabilization of Carbon Nanotubes Dispersion/solution by Wrapping with Functionalized Conducting Polymers

Another use of soluble functionalized conducting polymers is the dispersion/solubilization of carbon nanotubes. Carbon nanotubes are intrinsically insoluble in common solvents and immiscible with common polymers [125]. The low solubility is due to weak interaction with solvent molecules and

strong π - π , and dispersive interaction between individual nanotubes. A quite similar effect exists in conjugated polymers due to similar interactions. However, they interact strongly with conducting polymers by π - π interactions between the extended conjugations. Therefore, soluble conducting polymers could be used to disperse efficiently carbon nanotubes in common solvents [126], including water [127]. Carbon nanotubes and conducting polymers could be combined to create materials with new properties. Multiwall carbon nanotubes (MWNTs) were solubilized by interaction with sulfonated polyaniline (SPAN), which was prepared by in situ polymerization of aniline onto the nanotubes, followed by sulfonation with chlorosulfonic acid in an inert solvent and hydrolysis in water [128]. In a related work, single wall carbon nanotubes (SWNT) were made soluble by covalent linking of poly(*m*-aminobenzene sulfonic acid) [129, 130]. The solubility of functionalized polyanilines in various solvents, obtained by combinatorial functionalization (see above), could be then extended to the dispersion/solubilization of carbon nanotubes by polymer wrapping. Moreover, the wrapped nanotubes could also be used as building blocks for self-assembled multilayers [123].

CONCLUSIONS

Organic chemistry of conducting polymers is a field of research of increasing interest. Different chemical reactions can be used to functionalize polyaniline and improve the properties of the parent polymer. In the case of other conducting polymers, only nucleophilic addition has been explored suggesting that other reactions could be used to modify polypyrrole, polythiophene and related polymers. Additionally, combinatorial chemistry could be extended to other conducting polymers besides polyaniline. Both the modified polymers and the modification process itself have interesting technological applications. Other reactions, like nucleophilic aromatic substitution or Diels-Alder cycloaddition of polyaniline should be explored.

In the case of polypyrrole and polythiophenes, some reactions already explored for polyaniline should be investigated. Based on the data discussed above, nucleophilic addition seems to be the most interesting reaction for classic organic synthesis. On the other hand, coupling of diazonium salts produced using combinatorially synthesized amines seems to be the best route to the combinatorial synthesis of modified polymers. Since heterocyclic moieties are highly reactive towards electrophilic substitution [131], the coupling with diazonium ion (a weak electrophile) is feasible. Other reactions, like electrophilic sulfonation are likely to be accompanied of decrease of chain length due to polymer degradation.

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ABBREVIATIONS

PANI	=	Polyaniline. Usually emeraldine state (50% oxidation)
SPAN	=	Sulfonated polyaniline. Used usually for emeraldine base sulfonated by

- aromatic electrophilic substitution up to 50% sulfonation degree. However, it has also been used to name the copolymer of aniline and o-aminosulfonic acid
- HSPAN = Highly sulfonated polyaniline. leucoemeraldine base sulfonated by aromatic electrophilic substitution with fuming sulfuric acid up to 75% sulfonation degree
- SPANes = Sulfonated polyaniline. emeraldine base sulfonated by aromatic electrophilic substitution up to 50% sulfonation degree
- SPANna = Sulfonated polyaniline. Polyaniline sulfonated by nucleophilic substitution with sulfite ions
- PNMANI = Poly(N-methylaniline)
- SPNMANIes = Sulfonated poly(N-methylaniline). Poly(N-methylaniline) sulfonated by aromatic electrophilic substitution up to 50% sulfonation degree
- SPNMANIna = Sulfonated poly(N-methylaniline). Poly(N-methylaniline) sulfonated by nucleophilic substitution with sulfite ions
- HSPNMANIes = Sulfonated poly(N-methylaniline). Poly(N-methylaniline) (leucoemeraldine) sulfonated by aromatic electrophilic substitution up to 75% sulfonation degree
- PAPSAH = Poly(aniline-co-N-propanesulfonic acid aniline). Polyaniline modified by reaction with NaH, followed by reaction with propanesultone
- PVF = Poly(vinylferrocene). Redox polymer with electroactive ferrocene units pendant of a polyethylene chain.
- PANI-NO = Nitrosated polyaniline. PANI treated with nitrite ions in acid media
- PVC = Poly(vinylchloride)
- PMMA = Poly(methylmethacrylate).
- PDAMAC = Poly(diallyldimethylammonium chloride)
- MWNT = Multiwall carbon nanotubes
- SWNT = Single wall carbon nanotubes

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