

## Effect of electron-withdrawing type substituents in the polyaniline ring on the electrical conductivity

C. O. Sánchez (✉), C. J. Bustos, D. A. Mac-Leod Carey

Instituto de Química, Universidad Austral de Chile, Avda. Los Laureles s/n,  
Campus Isla Teja, Casilla 567, Valdivia, Chile,  
e-mail: [christiansanchez@uach.cl](mailto:christiansanchez@uach.cl)

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### Summary

Poly(ethyl 3-aminophenyl formate), poly(ethyl 3-aminophenyl acetate) and poly(ethyl 3-aminophenyl propionate) were synthesized in 1 M HCl media from respective monomers using ammonium persulphate as oxidizing. The polymers were characterized by FT-IR, UV-vis and <sup>1</sup>H-NMR spectroscopy. The effect of electron-withdrawing on the electrical conductivity of polyaniline, was studied. The electron-withdrawing group (ester) bond to the aniline ring affects the formation of charge carriers and electrical conductivity of polymers, therefore, at various bond lengths of the aniline ring, the electron-withdrawing effect decreases and a polymer with electrical conductivity from the semi-conduction order is obtained.

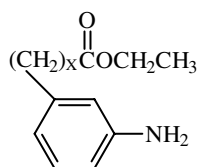
### Introduction

Polyaniline is referred to a set of polymers that have diverse redox states and only one of them, called polyemeraldine has good electrical conductivity in doped state. This polymer is of easy preparation, it has good stability [1,2] and it is a unique polymer that increases its electrical conductivity in the presence of acids [3-5]. Polyemeraldine is a conductive material of great interest in scientific and technological areas, It has been studied in rechargeable batteries [6,7], diodes and transistors [8-10] and electrocatalytic reactions [11]. However, the processability and poor mechanical properties are disadvantages for its use in the technological area. The processability of polyemeraldine can be improved by diminution of the melting temperature and by increases of solubility. The solubility can be increased by the incorporation of substituents in the aniline ring, therefore, the electrical conductivity strongly decreases towards polyemeraldine[12-16]. The effect of substituents in polyemeraldine on the electrical conductivity is not well known yet.

Derivatives of polyaniline with alkyl type substituents as methyl, propyl, hexyl, hidroxi-ethyl, dimethyl, methoxy have similar spectroscopy properties to polyemeraldine, which include absorption in the UV-vis region, associated to benzenoid-diamine groups, quinoid-diimine groups and charge carriers such as polarons and/or bipolarons [14-21]. In those cases the electrical conductivity decreases to 10<sup>-4</sup>-10<sup>-6</sup> S/cm<sup>-1</sup> towards polyemeraldine. On the contrary, substituents in

the polyaniline ring such as, dihalo, carboxylic acid, acetic acid and propionic acid have some different spectroscopy properties to those of polyemeraldine. In those cases, the absorptions in the UV-vis of quinoid-diimine groups are of small intensity against the absorption benzenoid-diamine groups and, also the band of charge carriers, such as bipolaron does not appear in those spectra. The reported electrical conductivity of the previously mentioned derivatives is considered to be of an insulator, less than  $10^{-9} \text{ Scm}^{-1}$  [12,13,22,23].

The effect of substituents in polyaniline on the electrical conductivity is not yet clear. We have been looking at the problem considering the substituents in the ring of aniline as electron-donating or electron-withdrawing. In this context, the aim of this article is to report polyaniline functionalized by etoxi-carbonyl groups with different number of methylene connected to the aniline ring.



X = 0, 1, 2

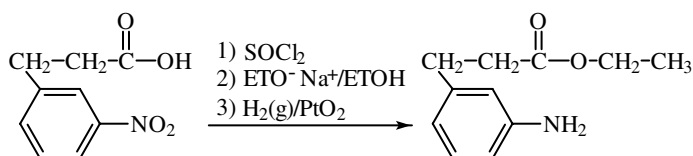
The methylene group is a weak electron-donating and the etoxi-carbonyl group is electron-withdrawing, both properties are combined in the side group of the polymer to study their effect in the absorption spectra and, on electrical conductivity of polymers. Moreover, the synthesis and characterization of new polymers are reported.

## Experimental

IR spectra were obtained from KBr pellets on a FT-IR Nexus Nicolet spectrophotometer. UV-vis spectra were recorded in UV 500 Unicam, using DMF as the solvent in 1cm cell.

## Synthesis of monomer

Ethyl 3-aminophenyl formate ( $x=0$ ) was obtained from Sigma-Aldrich, and used without further purification. Ethyl 3-aminophenyl acetate ( $x=1$ ) was synthesized by us and reported in a previous paper [24]. Ethyl 3-amino phenyl propionate ( $x=2$ ) was synthesized from 3-nitrophenyl propionic acid [23] according to scheme 1 and described as following:



Scheme 1

(0.80 g, 4.10 mmol) 3-nitrophenyl propionic acid was refluxed under stirring by 5 h with thionyl chloride (2.10 g, 17.8 mmol), vacuum distilled the excess of thionyl

chloride and the product was cooled in an ice/water bath (8°C) and then 0.57 g of sodium etoxide in ethylic alcohol mixture, prepared by dissolution of 0.34 g sodium in 3.5 mL ethylic alcohol was slowly added. The mixture was shaken until a red oil was formed (30 min), then it was washed with 2 mL water, 10 mL aqueous solution NaHCO<sub>3</sub> 8%, and with water again several times until the washing water reached pH=6. The product was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, dissolved again in CH<sub>2</sub>Cl<sub>2</sub> and separated by column Flash chromatography with Silica Gel and eluted with CH<sub>2</sub>Cl<sub>2</sub>. The second eluted product corresponded to ethyl 3-nitro phenyl propionate (0.58 g, 67% yield).

PtO<sub>2</sub> 0.016 g (catalizer Adams) and 5 mL ethylic alcohol were added to ethyl 3-nitro phenyl propionate 0.36 g (1.61 mmol). The mixture was hydrogenated at 10-15 at. at 100-145°C for 4.5 h, cooled at room temperature, filtered, ethylic alcohol removed by rotary vapour equipment resulting in an orange-colour oil. The product was purified by column Flash preparative chromatography filled with Silica Gel, eluted with CHCl<sub>3</sub> (approx. 20 mL, 15 fractions), and ethylic ether/CH<sub>2</sub>Cl<sub>2</sub> (1:2 v/v) (approx. 40 mL, 10 fractions), then the fractions N° 12-20, were pooled together and purified again by one sheet chromatography with Silica Gel F<sub>254</sub> and eluted with ethylic ether/CH<sub>2</sub>Cl<sub>2</sub> (1:8, v/v). Fraction with R<sub>f</sub>=0.35 is the liquid orange colour product of ethyl 3-amino phenyl propionate separated with ethylic ether from sheet: 0.067 g, 22% yield. <sup>1</sup>H NMR: 1.25 ppm (t, 3H, CH<sub>3</sub>), 2.65 ppm (t, 2H, CH<sub>2</sub>), 2.80 ppm (t, 2H, CH<sub>2</sub>), 3.6 ppm (s, 2H, NH<sub>2</sub>), 4.1 ppm (q, 2H, CH<sub>2</sub>), 7.1 ppm (t, 1H, aromatic), 6.4-6.6 ppm (m, 3H aromatic).

### Polymerization

The polymers were synthesized using persulphate as oxidizing agent in HCl 1M media, according to the classic method for polyemeraldine preparation.

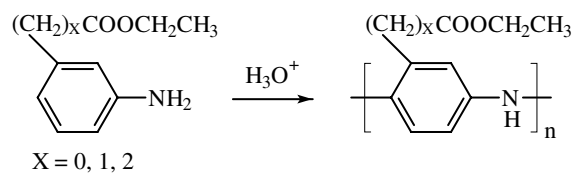
*Poly(ethyl 3-aminophenyl formate)*, X=0: 0.40 g monomer x=0 were dissolved in 2 mL HCl 1M, then added an aqueous solution of 0.62 g K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> dissolved in 3 mL HCl 1M. The mixture was stirred for 1 day at room temperature, filtered and washed with HCl 1M and methylic alcohol. 0.05 g of the polymer was obtained and, result soluble in methylic alcohol.

*Poly(ethyl 3-aminophenyl acetate)*, X=1: 0.40 g monomer x= 1 were dissolved in 2 mL HCl 1M, then added an aqueous solution of 0.56 g (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> dissolved in 3 mL HCl 1M. The mixture was stirred at room temperature for 1 day, filtered and washed with HCl 1M and methylic alcohol. 0.07 g of the polymer was obtained and, resulted not very soluble in DMSO and DMF.

*Poly(ethyl 3-aminophenyl propionate)*, X=2: 0.07 g monomer x=2 was dissolved in 0.9 mL HCl 1M, then was added to the aqueous solution, 0.078 g (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> dissolved in 1.2 mL HCl 1M. The mixture was stirred at room temperature for 1 day, filtered and washed with HCl 1M. 0.0082 g the polymer was obtained and, resulted soluble in DMSO and DMF.

### Results and discussion

The poly(ethyl 3-aminophenyl formate), x=0; poly(ethyl 3-aminophenyl acetate), x=1 and poly(ethyl 3-aminophenyl propionate), x=2, were synthesized in 1M HCl media according to scheme 2.



Scheme 2

Figure 1 shows the FT-IR spectra of the three polymers. In spectra polymers  $x=0,1$  the band at  $1717\text{ cm}^{-1}$  was assigned to the stretching carbonyl groups, while the bands at  $1577\text{ cm}^{-1}$  ( $x=0$ ) and at  $1617\text{ cm}^{-1}$  ( $x=1$ ) were assigned to the C=N and C=C stretching of the quinoid-diiimine units. The bands at  $1508\text{ cm}^{-1}$  ( $x=0$ ) and  $1487\text{ cm}^{-1}$  ( $x=1$ ) were assigned to the C=C stretching of the benzenoid diamine units. In both spectra ( $x=0,1$ ) show a broad band centred between  $3371\text{ cm}^{-1}$  and  $3414\text{ cm}^{-1}$ , which were assigned to the stretching of amine groups. In those spectra the bands quinoid-diiimine units and benzenoid-diamine units are of almost equal intensity, indicating that the polymers backbones contains similar populations of quinoid and benzenoid units. The aliphatic bands C-H of stretching asymmetry are observed at  $2981\text{ cm}^{-1}$ ,

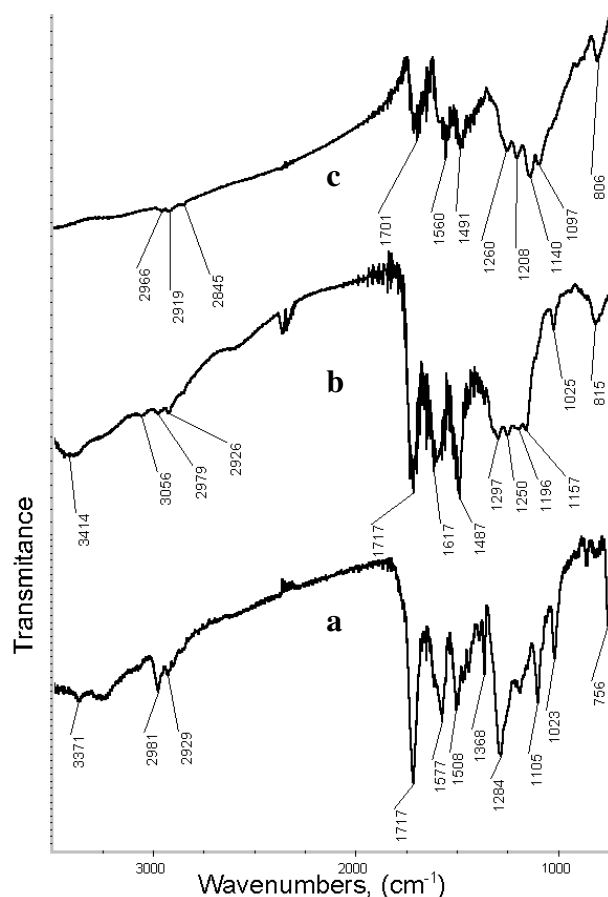


Figure 1: Spectra FT-IR of polymers, a) X=0, b) X=1, c) X=2

2929  $\text{cm}^{-1}$  ( $x=0$ ) and at 2979  $\text{cm}^{-1}$ , 2926  $\text{cm}^{-1}$  ( $x=1$ ). In the spectrum of polymer  $x=2$  the band at 1701  $\text{cm}^{-1}$  was assigned to the stretching, of the carbonyl group, the band at 1560  $\text{cm}^{-1}$  assigned to the stretching C=C, C=N of quinoid-diimine groups and the band at 1491  $\text{cm}^{-1}$  was assigned to the stretching C=C of benzenoid-diamine units. In this spectrum the region between 3600-2500  $\text{cm}^{-1}$  is somehow different to the other spectra. In this case the broad band of great intensity covers the NH stretching band and it was attributed to the presence of charged amine or imine species, thus indicating that the polymer  $x=2$  is obtained much more doped than others polymers [25-27].

The doping level of polymers is shown in table 1. If the length of side chain increases by methylene groups, then the aniline ring is affected by electron-donating groups and the polymer with greater a doping level is obtained.

Table 1: Doping level of polymers

Polymer	Cl/N
X=0	0.15
X=1	0.18
X=2	0.38

Figure 2 shows the  $^1\text{H-NMR}$  spectra of polymers  $x=0,2$  measured in  $\text{DMSO-d}_6$ . It was not possible to obtain the graph of the sample of polymer  $x=1$ , due to its low solubility in deuterated solvent. In spectrum for polymer  $x=2$ , (figure 2a) the signals

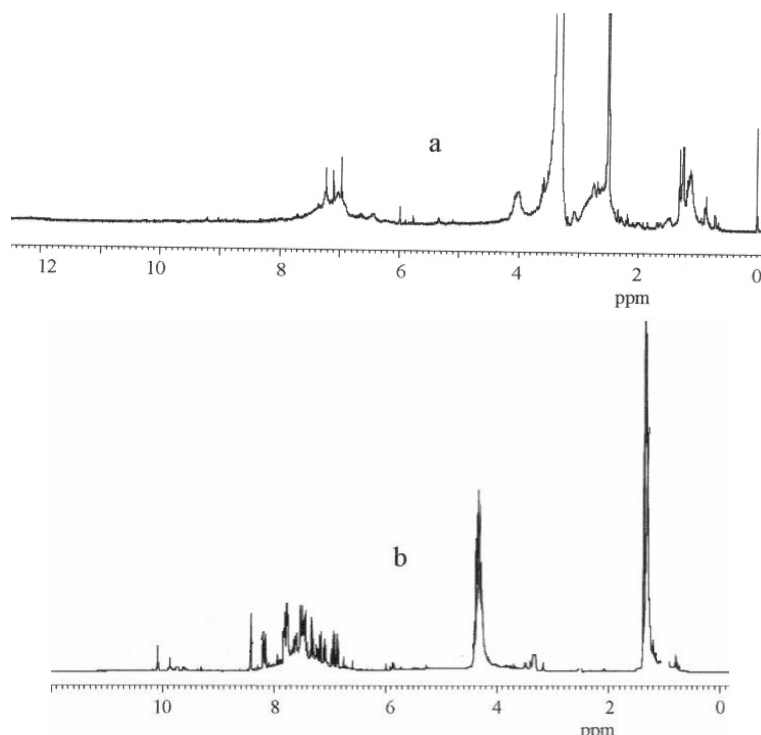


Figure 2:  $^1\text{H-NMR}$  spectra of polymer a) X=2, b) X=0

at 2.6 ppm and 3.3 ppm, are attributed to hydrogen resonances of DMSO (solvent) and water molecules respectively, which are difficult to eliminate from the polymer. Those two picks partially overlap the signals of the side chain methylene groups of the polymer.

The broad signal centred at 1.2 ppm was assigned to the hydrogen methyl of the ester group, while the signals centred at 4.1 ppm and 7.1 ppm were assigned to the resonances of the hydrogen amine and aromatic hydrogen, respectively. The integral signals of hydrogen methyl and aromatics are in the ratio  $H_{\text{CH}_3}/H_{\text{aromatic}} = 25.52/26.22 = 0.97$  indicating that in polymer  $x=2$ , the ester groups of polymer side chains are not hydrolysed in the aqueous acid conditions of polymerization. This is confirmed in the spectrum, since hydrogen resonances of proton acid of carboxylic group do not appear. However, in spectrum  $^1\text{H-NMR}$  of polymer  $x=0$  (figure 2b), the signal at 9.8 ppm was assigned to hydrogen acid of carboxylic acid groups. The integrals of hydrogen carboxylic acid and methyl signals are in the ratio  $H_{\text{COOH}}/H_{\text{CH}_3} = 0.17/7.76 = 0.022$  indicating that 2.2% of ester groups were hydrolyzed in the reaction media. The signals at 1.3 ppm, 4.4 ppm and 7.5 ppm were assigned to the hydrogen resonances of methyl, methylene and aromatic groups, respectively. The integrals of signals methyl and methylene groups are according to the side chain etoxi groups. The low percentage of hydrolysis (2.2 % for polymer  $x=0$  and 0% for polymer  $x=2$ ), is an important result showing that the oxidation reaction of monomers and the formation of polymer is more much favoured than the hydrolysis reaction of the ester group in acidic conditions.

Figure 3 shows the absorption spectra of polymer,  $x=0$ ,  $x=1$ ,  $x=2$  in DMF. All the spectra are different, the absorption bands in the UV region were assigned to the electronic  $\pi-\pi^*$  transition of the phenyl rings in the polymer backbones. In the Visible region it is necessary to emphasize the maximum absorption at 600 nm of polymer  $x=2$ , those absorptions are attributed to quinoid-diimine groups of the polymer backbone, and its intensity and broad form of those band is typically similar to the quinoid band of polyemeraldine [17,28,29]. The band absorption at higher wavelength (blue region) is attributed to charge carriers (bipolaron) localized in the polymer[30,31]. Therefore, the polymer  $x=2$  can be considered in an intermediate

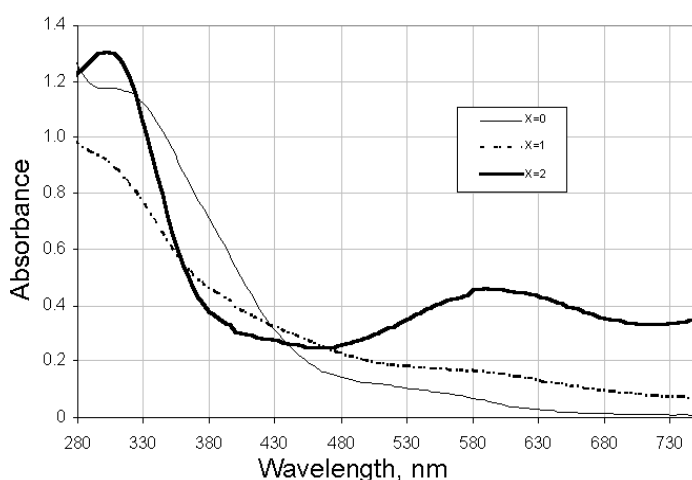


Figure 3: Spectra absorption in solution of polymer: X = 0, 1, 2

redox state and partially doped. The electrical conductivity for polymer  $x=2$  is  $10^{-6} \text{ Scm}^{-1}$ , while that for polymer  $x=0,1$  is less than  $10^{-9} \text{ Scm}^{-1}$ . The semi-conductor regime of the polymer  $x=2$ , can also be observed by its green colour such as polyemeraldine.

On the other hand, it has been described in literature that monomers of substituted-aniline with electron-withdrawing groups, such as nitro, ciano and sulfonic acid are not polymerized in acid media [32,33], and substituted-aniline by electron-donating groups, such as methyl, propyl, hexyl,  $\alpha$ -hidroxi-ethyl, dimethyl, methoxi groups are polymerized in acid media thus resulting in a polymer with electrical conductivity of a semiconduction order [14-21]. According to the previous results it is possible to combine both properties, electron-donating and electron-withdrawing, to obtain a polymer with improved electrical conductivity. To do this it is necessary that electron-withdrawing is at a distance of the aniline ring of at least three bonds. Thus, the two methylene groups, which are weak electron-donors, connected to the aniline ring favour the polymerization reaction, doping, and, consequently the formation of charge carriers in the derived polyaniline.

Considering the reactivity of ester groups, it is possible that other derivatives with electrical conductivity of the semi-conduction order of magnitude can be obtained by substituting etoxi groups of ester group by other groups such as, alcoxi and amines with different length of methylene chain. These results will be later reported.

## Conclusions

News derivatives of polyaniline were synthesized and characterized. It is possible to combine electron-donating and electron-withdrawing groups on the side chain of aniline ring for that polymers with electrical conductivity of a magnitude of the order of the semiconduction can be obtained. Derivatives of polyaniline with electron-donating (methylene) favors the formation of charge carries and consequently the electrical conductivity.

We think that other electron-withdrawing groups such as Nitro, Ciano, Sulphonic acid, etc could be at least three bonds distant from the aniline ring, for that its monomers can be polymerized and conductivities of the semiconduction order can be obtained.

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