Synthesis, characterization, and properties of poly(2- and 3-aminophenol) and poly(2- and 3-aminophenol)-Cu(II) materials

B. L. Rivas (✉)[1], **C. O. Sánchez** (✉)[1], **J.-C. Bernede**(✉)[2], **P. Mollinié** (✉)[2]

(✉)[1] Department of Polymers, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile. brivas@ udec.cl

(✉)[2] Laboratoire de Phisique des matériaux pour L'Electronique, Faculté des Sciences et des Techniques de Nantes, 2 rue de la Houssiniere, BP 92208, F-44322 Nantes, Cedex 3, France.

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Summary

Poly(2-aminophenol) and poly(3-aminophenol) were synthesized from the respective monomers by using $CuCl_2$ x $2H_2O$ and ammonium persulfate as oxidizing agents in HCl(aq). The materials were characterized by FT-IR, X- ray electron spectroscopy (XPS), electron spin resonance (ESR) and nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, thermal stability, and electrical conductivity. The poly(2-aminophenol) presented a higher copper(II) content than that of poly(3-aminophenol), moreover as shown by ESR measurements, Cu appears homogeneously dispersed in the former, poly(2-amino phenol), while it seems not to be the case in the latter. The electrical conductivity did not depend on the conditions of synthesis as well as of the hydroxyl groups position. The results indicate that the polymers have several branched rings and their thermal stability increased by the presence of the copper ions into the polymer matrix.

Introduction

Transition-metal dispersed into modified polymer electrodes have been recently recognized to have potential applications in electrocatalysis. Electrodeposition of platinum into polyaniline (Pani) films with electrocatalytic applications in the oxidation of methanol has been reported [1]. Moreover, metal microparticles dispersed into the polymer on glassy carbon electrodes have been previously described as amperometric sensors in acidic and neutral media [2,3]. Pani-Co(II) acetate catalyzes the oxidation of different alkenes in the presence of molecular oxygen [4,5].

One way to incorporate the metal cations into polymers has been the functionalization by metallic complexes of bipyridyl type [6], porphyrins [7], tetraazaannulene [8], metallated cyclam [9]. These ligands are difficult to synthesize and need multi-step synthesis which is very expensive.

If the monomers are functionalized by small size donor groups, the resultant polymer would be able to interact with the metal ions. However, it is known that Pani is an insulator in alkaline media [10]. Casella and coworkers [11]

reported that Pani-Cu(II) films in alkaline media show electrocatalytic oxidative properties of several organic molecules, like aminoacids and carbohydrates.

This paper reports the synthesis of poly(2- and 3-aminophenols) which can incorporate copper by using $CuCl_2$ as oxidizing agent. Thus, the reduced form (or oxidized) of the oxidizing agent stay entrapped or through a complex into the polymer matrix. In this case, the incorporation of the metal ion is faster and cheaper.

Experimental

The monomers 2-aminophenol, 3-aminophenol (Merck, Germany) were purified by recrystallization from ethanol/$CHCl_3$.

FT-IR spectra were obtained from KBr pellets on a Magna Nicolet 550 spectrophotometer. The quantification (weight %) of the metals incorporated into the polymers was done by calcinating the solid sample, solubilizing with HNO_3 and determining the metal concentration by AAS using an Atomic Absorption Spectrometer, Perkin Elmer 3100.

Electrical conductivity was measured on an Elchema Electrometer, using pellets and the four probe method.

Thermograms were recorded under nitrogen with the Polymer Laboratories STA 625 Thermal Analyzer. The XPS spectra were recorded with a Leybold LHS-12 spectrometer. XPS data were obtained with the magnesium source radiation (1253.6 eV) operating at 10 KV and 10 mA and the pass energy was set to 50 eV. The quantification studies were based on the determination of the C1s, N1s, O1s, Cu2p3/2 peak areas. The polymer powder pressed on sheet, while the binding energy of the carbon-carbon bond taken as described previously [12], is 285 eV.

ESR experiments were performed at room temperature and 105K on a Bruker ER 200D spectrometer operating in X band mode at 9.416 GHz. The decomposition of ESR spectrum and the interpretation were made using the method described elsewhere [13-15]. Using the pole method integration [15] with a Gaussian or a Lorenztian (or a mixture of the two) line shape, the theoretical ESR signal can be computed yielding parameters of each distribution that can produce the signal after comparison with the experimental results.

Synthesis of polymers

Synthesis with ammonium persulfate: 6.0 g (55 mmol) of 2-aminophenol (or 3-aminophenol), were dissolved in 90 mL 1M HCl (45 mL in the case 3-aminophenol) at 22-25°C. 12.56 g (55 mmol) of ammonium persulfate dissolved in 60 mL 1M HCl (30 mL in the case 3-aminophenol) were added drop wise. The mixture reaction was stirred for 10 h, filtered and washed with 1M HCl. The products were dried at 50°C for 2 days under vacuum.

Synthesis with $CuCl_2$ x $2H_2O$: 6.0 g (55 mmol) of 2-aminophenol (or 3-aminophenol) were dissolved in 67 mL (40 mL for 3-aminophenol). 28.12 g (165 mmol) $CuCl_2$ x $2H_2O$ dissolved in 60 mL (35 mL for 3-aminophenol) of 1M HCl were added drop wise at 40°C. The mixture was stirred for 23 h (90 h for 3-aminophenol), filtered, washed with enough 1M HCl at 40°C, and dried under vacuum at 50° C until constant weight.

Results and discussion

Figures 1a, b, and c, show the FT-IR spectra of the polymers containing the hydroxyl group at positions 2- and 3. Both polymers are similar if the ammonium persulfate or copper(II) chloride are used as oxidizing agent.
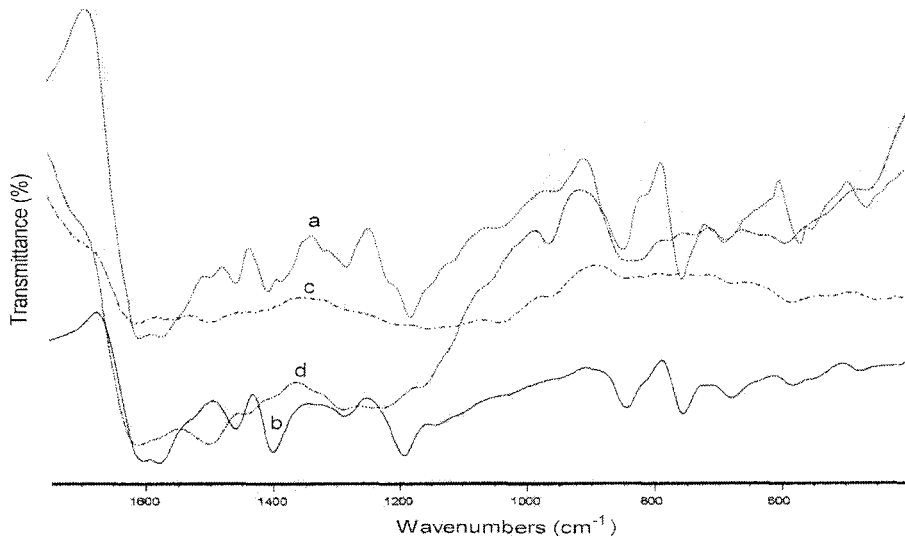

Figure 1. FT-IR spectra of poly(2-aminophenol) synthesized with a) ammonium persulfate, b) CuCl₂ x 2H₂O; poly(3-aminophenol) synthesized with c) ammonium persulfate, d) CuCl₂ x 2H₂O

However, poly(2-aminophenol) P2APh and poly(3-aminophenol) P3APh are not similar, as the absorption regions placed at 1600-1400 cm^{-1} and 800-600 cm^{-1} are different. Kunimura [16,17] has reported the formation of C-O-C bonds during the electrochemical synthesis of poly(2-aminophenol) by using phenoxazine as pattern. The FT-IR of the electro-synthesized polymers and that of the present polymer are similar. There are absorption signals attributed to C-O-C. Thus, the absorption bands at 1050-1235 cm^{-1} are characteristics of C-O-C stretching vibration [16,17]. The absorption region between 900 and 700 cm^{-1} corresponds to C-H bending of an aromatic ring substitution. According to the FT-IR spectra (see figure 1) there are 3 to 6 bands which are in agreement with 1,2-; 1,2,3- or 1,2,4- and 1,2,4,5- or 1,2,3,4-tetra-substitution in poly(2-aminophenol). For poly(3-aminophenol) substitution pattern can be : 1,3-; 1,2,4- 1,2,3- or 1,3,5-trisubstitution and 1,2,3,4- ; 1,2,4,5; 1,2,3,5-tetrasubstitution. For Cu-P3APh the substitution is similar to that of P3APh.

On the other hand, only P2APh synthesized with ammonium persulfate is soluble in DMSO and it was possible to be characterized by C^{13}-NMR spectroscopy. There are 18 signals between 100 and 180 ppm which would correspond to three different rings. ^{1}H-NMR spectrum shows several singlets, doublets, and a multiplet, between 6.5 and 7.7 ppm indicating the presence of a branched structure. These rings would be coupled in a way which is very difficult to characterize but it includes the C-O-C bond.

The table 1 summarizes the bond energy values and relative atomic composition in the decomposition peak of the different components of the polymers (see figures 2 and 3) [18].

Table 1: Bonds energy (eV) and relative (%) atomic decomposition values of the peak decomposition.

Polymer	C1s		N1s	O1s	Cu 2p3/2	
	C-C	C-O-C or C-OH	C-N	C-O-C or C-OH	Cu(I)	Cu(II)
P2APh[a]	(285 eV) 83%	(286.7 eV) 17%	(399.6 eV) 3.0%	(553.8 eV) 39%	-----	-----
Cu-P2Aph[b]	(285 eV) 69%	(286.8 eV) 27%	(400 eV) 2.1%	(533.2 eV) 49%	(933.5 eV) 86%	(935.2eV) 14%
P3APh[a]	(285 eV) 83%	(286.0 eV) 13%	(400.1 eV) 3.3%	(533.3 eV) 42%	-----	-----
Cu-P3Aph[b]	(285 eV) 78%	(286.4 eV) 19%	(400.2 eV) 2.6%	(533.8 eV) 50%	(933.2 eV) 1.4%	-----

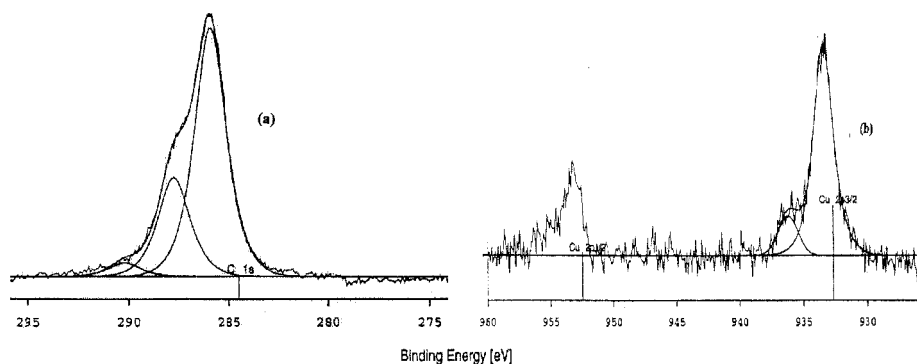[a]Synthesized with ammonium persulfate, [b] Synthesized with CuCl$_2$

Figure 2. XPS spectra of P2APh synthesized with CuCl$_2$ x 2H$_2$O in 1M HCl media a) C1s, b) Cu 2p 3/2

Figure 3. XPS spectra of P3APh synthesized with CuCl$_2$ x 2 H$_2$O in 1M HCl media. a) C1s, b) Cu 2p 3/2

The decomposition of C1s peak gives three peaks (see figures 2a and 3a).The first one, placed at 285 eV has been attributed to C-C bonds. The second one can be assigned to the C-OH and/or C-O-C bonds, while that situated at about 290 eV corresponds to some oxidized carbon, probably C=O, product of the partial decomposition of the sample [13]. The decomposition of the peak Cu2p3/2 gives two peaks (see figure 2b), the one placed at 933 eV has been attributed to Cu(I) and the second one at 935 eV was assigned to Cu(II) [13]. It can be appreciated (see table 1) that CuP3APh has only Cu(I) whose peak is placed at 933 eV (see figure 3b). This Cu(I) corresponds to the reduced form of the oxidizing reagent ($CuCl_2$).

As shown by XPS measurements, after etching (1-6 min) the samples Cu-P2APh and Cu-P3APh by XPS (time: 1 a 6 min) always contain metal ions, indicating that copper is present not only on the surface but also in the polymeric matrix volume probably as donor-acceptor complex (see table 2).

According to the elemental analysis and XPS data it is possible to postulate the following empirical formula for the polymers:

P2APh: $C_{6.00} H_{3.62} N_{0.67} (HCl)_{0.11} O_{1.60}$

Cu-P2APh: $C_{6.00} H_{3.41} N_{0.63} (CuCl)_{0.30} (CuCl_2)_{0.05} O_{1.91}$

P3APh: $C_{6.00} H_{4.54.} N_{0.86} (HCl)_{0.26.} (HSO_4^-)_{0.075} O_{1.83}$

Cu-P3APh: $C_{6.00} H_{4.06} N_{0.78} (HCl)_{0.42} (CuCl)_{0.02} O_{1.92}$

Table 2: Atomic composition (%) of copper vs etching time for Cu-polymer

Polymer sample	Etching time (min)	Atomic composition (%)
Cu-P2Aph	0	3.0
	1	6.6
	3	7.0
	6	7.0
Cu-P3Aph	0	0.3
	1	0.5
	3	0.5
	6	0.5

Only P3APh contains sulfur which can be due to sulfate and bisulfate anions formed during the reduction of the oxidizing reagent.

Figure 4 shows the thermograms of the polymers. The polymers containing copper show a higher thermal stability. Besides, the substituent in position 2 has a higher thermal stability than in position 3. Cu-P2APh shows a weight-loss of only 8% at 330°C, but without copper the same weight-loss occurs at 300°C. Cu-P3APh shows a lower thermal stability with a weight-loss of 8% at 220°C and without copper at 200°C.
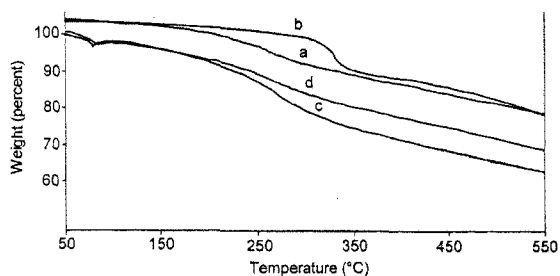
Figure 4. Thermogram of a) P2APh, b) Cu-P2APh, c) P3APh, d) Cu-P3APh

The ESR results obtained on the pure polymers P2APh, P3APh and the copper doped Cu-P2APh and Cu-P3APh are presented in figures 5 and 6.
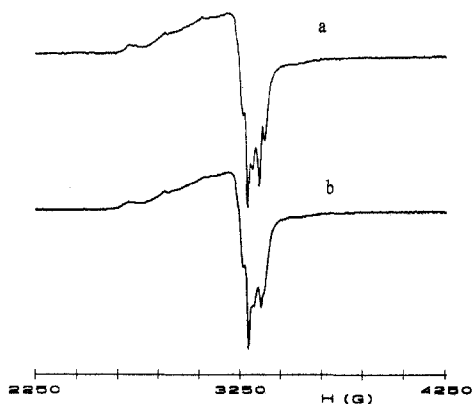

Figure 5. ESR spectra obtained at 300K (a) and 105K (b) for CuP2APh. The temperature does not change the shape of the spectra, we note only an increase of the line width.
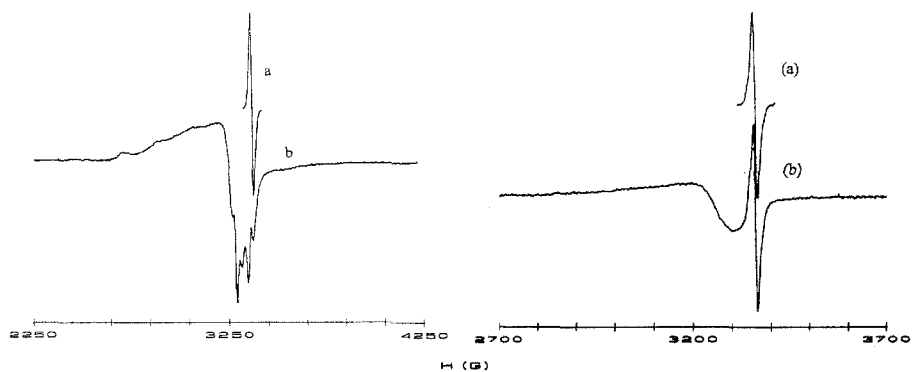

Figure 6. (Left) ESR spectra obtained at 300K for a)P2APh pure and b) Cu-P2APh. We note that the signal observed for the pure material is still present in the doped one. (Right) ESR spectra obtained at 300K for a) P3APh pure and b) Cu-P3APh. We note that the signal observed for the pure material is still present in the doped one.

As indicated in FT-IR study the two polymers are not identical and the ESR observations are different. Firstly, we examine the case of the pure P2APh polymer (figure 6a, left). The spectrum can be fitted by an axial distribution with g// equal to 2.005, g $\perp$ equal to 1.9985 and a width of 14G (see figure 7, left). The calculated <g> is equal to 2.0028 close to the free electron value indicating a carbon radical center. When the copper is introduced in CuCl form, there is an oxidation of some part of the Cu^+ ions in Cu^{+2} giving an ESR signal (see figure 5). The ESR parameters of the axial distribution are: g// = 2.020, A// = 172G, g$\perp$ = 2.268 and A$\perp$ = 35G. The observation of the hyperfine constant indicates that the copper centers are well distributed in the polymer.

Secondly for the pure P3APh the observed spectrum cannot be explained by only one distribution. Two distributions are necessary with the following parameters: D1 (g// = 2.0035, g$\perp$ = 1.9985 and a width of 7G), D2 (g// = 2.006, g $\perp$ = 1.997 and a width of 10G) (see figure 7, right). The relative intensity of the second distribution is 37%. When the polymer is doped by CuCl, there is a very low doping level, one order of magnitude lower than the one observed for the P2APh polymer. The ESR signal intensity of Cu^{+2} observed for Cu-P3APh is also very low and it is not possible to see any hyperfine lines, which may indicate the presence of copper clusters. This result can explain the low copper doping level in the P3APh polymer, in fact the doping process fails in this case and the copper remains at the surface of the powder. Only P2APh is doped with the copper and its distribution is homogeneous.

The electrical conductivity of poly(2-aminophenol), Cu-poly(2-aminophenol), poly(3-aminophenol), and Cu-poly(3-aminophenol) are 3.8 10^{-10}, 3.5 10^{-10}, 5.0 10^{-8} and 2.3 10^{-9} Scm^{-1} respectively. In this type of materials, the content acid (doping) and metal ion incorporated do not produce an increase of the electrical conductivity.
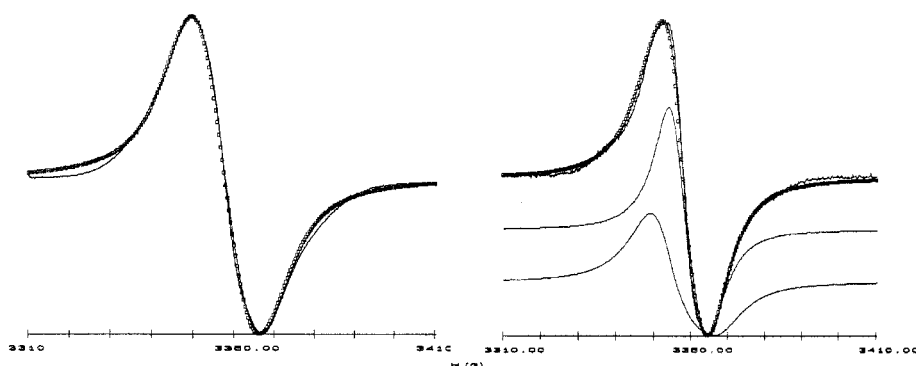

Figure 7. (left) ESR signal decomposition of pure P2APh at 300K, continuous lines: different contributions, 8 8 8 theoretical curve, ^v^v experimental data. (Right) ESR signal decomposition of pure P3APh at 300K. continuous lines: different contributions, 8 8 8 theoretical curve, ^v^v experimental data.

Conclusions

The use of different oxidizing reagents allowed to obtain polymers with very similar spectroscopic (FT-IR, XPS) and electrical conductivity properties. The synthesis of polymers with $CuCl_2$ permitted easily the incorporation of Cu(I) and Cu(II) into the polymer matrix. These metal ion cations increased the thermal stability of the polymeric materials. However, as shown by ESR and XPS measurements, Cu can be distributed homogeneously in the polymer matrix only in the case of P2APh. In the case of PA3Ph the copper introduction is very small and not homogeneous. The new P2APh polymer-copper material may be used as catalysts.

References

1. Kost KM, Bartak DE, Kazee B, Kuwana T (1988) Anal Chem 60: 2379
2. LabordeH, Leger JM, Lamy C(1994) J Appl Electrochem 24: 219
3. Esteban PO, Leger JM, Lamy C, Genies E (1989) J Appl Electrochem 19: 462
4. Bhaskar C. Das, Javed Iqbal (1997) Tetrahedron Letters 38: 1235
5. Asit De, Prakriti Basak, Javed Iqbal (1997) Tetrahedron Letters 38: 8383
6. Cosnier S, Deronzier A, Mout JC (1985) J Electroanal Chem 193: 193
7. Bettelheim A, White BA, Raybuck SA, Murray RW (1987) Inorgan. Chem. 26: 1009
8. Deronzier A, Marques MJ (1992) J Electroanal Chem 334: 247
9. Bartlett PN, Chung LY, Moore P (1990) Electrochim Acta 35: 1051
10. Macdiarmid AG, Chang JC, Richter AF, Somasiri NLD, Epstein A (1987) J. In Conducting Polymers; Alcacer, Reidel Publishing Co. Holland 105
11. Casella IG, Cataldi TRI, Guerrieri A, Desimons E (1996) Analyt. Chim. Acta 335: 217
12. Briggs D, Seach MP (1990) Practical Surface Analysis 2d. Ed., John Wiley & Sons. 2543
13. Ursu F (1968) La résonnace paramagnétique électronique Paris, Ed. Dunod. 142
14. Nguyen TP, Giffard M, Molinié P (1994) J Chem Phys 100: 8340
15. Angot A (1972) Compléments de mathématiques. Paris, Masson. 27
16. Kunimura S, Ohsaka T, Oyama N (1988) Macromolecules 21: 894
17. Oyama N, Ohsaka T, Hirokawa T, Suzuki T (1987) J Am Chem Soc 15: 1133
18. Beamon G, Briggs D (1992) High Resolution XPS of Organic Polymers. The Sciencia ESCA 3000 Database & Sons.