

Synthesis, Characterization, and Electrical Conductivity of Polyaniline Derivatives: Study with the Metal Ions Cu(II), Ni(II), and Co(II)

B. L. RIVAS, C. O. SÁNCHEZ

Department of Polymers, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile

Received 15 August 2000; accepted 2 December 2000

ABSTRACT: Poly(2-aminophenol), poly(3-aminophenol), poly(2-aminobenzyl alcohol), and poly(3-aminobenzyl alcohol) were synthesized by using ammonium persulphate as oxidizing reagent in HCl and HCl/CH₃CN mediums in the presence and absence of Cu(II), Ni(II), and Co(II) ions. The polymers were characterized by Fourier transform infrared spectroscopy, ultraviolet-vis spectroscopy, thermal analysis, and electrical conductivity measurements. The substituent in 2- and 3-positions decreases the yield regarding aniline. Poly(2-,3-aminobenzyl alcohol) are obtained in an intermediate redox state and polymerized as aniline. On the contrary, poly(aminophenols) are obtained as overoxidated structures. The presence of metal ion produces an important increase of the polymerization yield. The metal cations would act as oxidizing agents. The incorporation of these metal ions depends on the reaction medium. The metal ion increases the thermal stability. Poly(2-aminobenzyl alcohol)-copper ions also increases the electrical conductivity. The electrical conductivity is higher by acid doping than by the incorporation of metal ions. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 330–337, 2001

Key words: polyaniline derivatives; metal ions; electrical conductivity

INTRODUCTION

Polyaniline (Pani) is a conducting polymer that presents good stability^{1,2} and can be chemically and electrochemically synthesized by oxidation of aniline following a head-to-tail coupling mechanism^{3–8} (Scheme 1).

This polymer may exist in a variety of oxidation states, according to the value of Y . When $Y = 1$, the polymer is fully reduced (only benzenoid-diamine groups), for $Y = 0$, the form is fully oxidized (only quinoid-diimine groups), and when $Y = 0.5$,

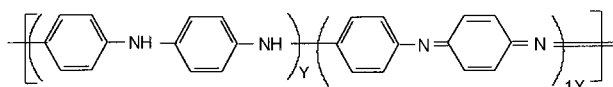
the polymer presents 50% of the benzenoid-diamine groups and 50% of quinoid-diimine groups.^{4,9,10}

This polymer shows very useful redox and electrical properties for wide application fields, particularly when combined and/or associated with metal ions. Pani with Pt particles (introduced as hexaplatinate anion) highly dispersed into the polymer is used as electrocatalyst for methanol oxidation.¹¹ Pani supported with Co(II) acetate is used as catalyst for alkene oxidation, catalyzing the stereoselective conversion of cinnamoyl amide of L-leucine methyl ester.^{12,13} Moreover, redox reagents such as Fe(CN)₆⁻³ and Ru(NH₃)₆⁺³ can be used to modify a polyaniline-based transistor¹⁴ and a system Pani-CuCl₂ has been investigated as dehydrogenation catalyst of cinnamyl alcohol to the corresponding aldehyde.^{15,16}

Correspondence to: B. L. Rivas.

Contract grant sponsor: FONDECYT; contract grant number: 3990011.

Journal of Applied Polymer Science, Vol. 82, 330–337 (2001)
© 2001 John Wiley & Sons, Inc.



Scheme 1

In most of the cases, the metal ion is incorporated as anion complex. The incorporation of metal cations to Pani is important for the potential applications but it is very difficult to achieve it.

The aim of this report is to introduce metal ions Cu(II), Ni(II), and Co(II) to functional polyaniline by using Pani derivatives containing donor groups in 2- and 3-positions which may interact with these metal cations. 2-Aminophenol, 3-aminophenol, 2-aminobenzyl alcohol, and 3-aminobenzyl alcohol are used as monomers. The best polymerization conditions were investigated and subsequently their effect was studied regarding yield, thermal stability, and electrical conductivity in the polymers, with and without metal ions. Moreover, the effect of the substituent on the polymerization was investigated.

EXPERIMENTAL

Reagents

Monomers 2-aminophenol, 3-aminophenol (Merck, Stuttgart, Germany) were purified by recrystallization from ethanol/ CHCl_3 . 2-Amino benzyl alcohol (Merck, Stuttgart, Germany) was recrystallized from ethanol/diethyl ether. 3-Amino benzyl alcohol (Merck) was dissolved in the minimum amount of 1M HCl, filtered, and the solution adjusted at pH = 5–6 with 0.5M NaOH. The monomer was extracted with chloroform and the sol-

vent removed by rotatory evaporator. Finally, the monomer was recrystallized from CHCl_3 /diethyl ether and dried without vacuum. The metal salts $\text{CuCl}_2 \times 2\text{H}_2\text{O}$, $\text{NiCl}_2 \times 6\text{H}_2\text{O}$, and $\text{CoCl}_2 \times 6\text{H}_2\text{O}$ were obtained in analytical grade from Merck.

Polymerization: Synthesis of Polymers in the Presence of Metal Cations

In all polymerizations, a monomer/metal ion mol ratio (1:3) and a monomer/oxidizing reagent mol ratio (1:1) were used. The polymerization conditions are shown in Tables I, II, and IV. All the polymers were synthesized under the same conditions. For example, the synthesis of poly(2-aminophenol) in the presence of Cu(II) (sample No. 14) is described as follows: 2.0 g (18.3 mmol) of monomer was dissolved in 30 mL of 1M HCl. Then, 9.375 g (55.0 mmol) of $\text{CuCl}_2 \times 2\text{H}_2\text{O}$ was added under stirring, 4.187 g (18.3 mmol) of ammonium persulphate was dissolved drop-wise in 20 mL 1M HCl for 20 min at 18°C. The mixture was stirred for 480 min, filtered, washed with 1M HCl up to decoloration of the filtrate, then dried for 2 days at 60°C.

To polymerize at low proton concentration, the monomers were solubilized adding acetonitrile by using 0.852 and 0.564 v/v ratios in a 10^{-4}M HCl/ CH_3CN mixture.

The products synthesized in HCl/ CH_3CN medium were filtered and washed with HCl/ CH_3CN solution (ratio $r = 0.852$ or $r = 1.564$, according to the synthesis medium) then washed with 10^{-4}M HCl, and dried under vacuum for 2 days at 60°C.

The polymers in base form (dedoped) were obtained by treatment with NH_4OH 12.5 wt % for 48 h, filtered, washed with water, and finally

Table I Reaction Conditions^a for Polymerization of Aniline Derivatives in 1M HCl

Sample No.	Monomer	Monomer Concentration (m)	Temperature (°C)	Time (min)	Yield (%)
1	Aniline	0.071	0	120	81.1
2	2-Amino phenol	0.367	18	500	44.7
3	3-Amino phenol	0.367	18	480	<1.0
4	3-Amino phenol	0.734	18	480	30.6
5	2-Amino benzyl alcohol	0.285	0	120	3.1
6	2-Amino benzyl alcohol	0.285	0	300	40.6
7	3-Amino benzyl alcohol	0.285	0	300	0.6
8	3-Amino benzyl alcohol	0.180	18	360	45.7

^a Polyaniline was synthesized according to Focke et al.⁴

Table II Reaction Conditions of Aniline Derivatives in the Presence and Absence of Metal Ions in 1M HCl

Sample No.	Monomer	Monomer Concentration (m)	Metal Ion Concentration (m)			Time (min)	T (°C)	Metal in Polymer (%)	Yield (%)
			Cu(II)	Ni(II)	Co(II)				
9	2-Amino phenol	0.367	—	—	—	500	18	—	44.7
10		0.367	1.10	—	—	500	18	2.80	69.2
11		0.368	—	1.10	—	500	18	0.06	47.6
12		0.367	—	—	1.10	500	18	0.02	48.9
13	3-Amino phenol	0.734	—	—	—	480	18	—	30.6
14		0.735	2.20	—	—	480	18	2.22	33.0
15		0.734	—	2.20	—	480	18	0.03	20.2
16		0.735	—	—	2.20	480	18	0.07	40.6
17	2-Amino benzyl alcohol	0.285	—	—	—	300	0	—	40.6
18		0.284	0.852	—	—	300	0	0	59.3
19		0.284	—	0.852	—	300	0	0	63.1
20		0.284	—	—	0.851	300	0	0	59.2
21	3-Amino benzyl alcohol	0.180	—	—	—	360	18	—	45.7
22		0.180	0.540	—	—	360	18	0	46.6
23		0.181	—	0.540	—	360	18	0	46.0
24		0.180	—	—	0.540	360	18	0	46.9

dried in an oven under vacuum for 48 h. The poly(2-aminophenol) and poly(3-aminophenol) synthesized in 1M HCl were soluble in alkaline aqueous medium, and the insoluble fraction was characterized. These products synthesized in HCl/CH₃CN medium were completely soluble in 12.5 wt % NH₄OH and it was not possible to obtain them in a base form. After pouring the polymers in alkaline medium, they were filtered, washed with water, and dried under vacuum at 60°C.

Characterization

Fourier transform infrared (FTIR) spectra were obtained from KBr pellets on a Magna Nicolet 550 spectrophotometer. The ultraviolet (UV)-vis spectra were recorded on a Lange Model CADAS 100 spectrophotometer, using a 1-cm cell and dimethyl sulfoxide as solvent.

The quantification (wt %) of the metals incorporated into the polymers was performed by calcinating the solid sample, solubilizing it with HNO₃, and determining the metal concentration by AAS using an Atomic Absorption Spectrometer (Perkin Elmer 3100).

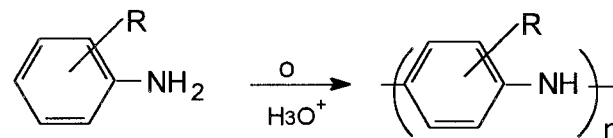
The amount (wt %) of total chloride in the polymers for ASTM standard method¹⁷ was determined. Electrical conductivity was measured on an Elchema Electrometer, by using pellets and

the four probe method. Pellets were obtained by pressing the finely ground polymer at about 24,000 Psi.

RESULTS AND DISCUSSION

In this report, aniline derivatives were synthesized by ammonium persulphate as an oxidizing agent in the presence and absence of Cu(II), Ni(II), and Co(II), according to the general reaction shown in Scheme 2.

The polymerization conditions of aniline derivatives in the absence of metal ions are shown in Table I. Under the same experimental conditions of aniline, only colored solutions but not polymerization products, are obtained with the aniline derivatives. To obtain polymerization products, it is necessary to increase the reaction time.



R = OH and CH₂OH in position 2 or 3

Scheme 2

The substituent in 3-position decreased the polymerization yield (see sample Nos. 2, 3, 6, and 7). It is possible to attribute steric hindrance, which has also been reported,^{4,8} that aniline polymerizes by coupling through the nitrogen atom and the p-position of the aromatic ring. Therefore, the 4-position is more hindered when the substituent is in 3-position than in 2-position. Table II also shows that the yield increases as the monomer concentration, time, and temperature of polymerization are increased.

Figure 1 shows the FTIR spectra of the polymers as a base form obtained in 1M HCl (polymer sample Nos. 2, 4, 6, and 8).

In polyaniline, the absorption signal at 1586 cm^{-1} was assigned to C=N and C=C stretchings of the quinoid-diimine units, and at 1494 cm^{-1} to C=C stretching of the benzenoid-diamine units.^{6,18,19} The intensities of these two bands are a measurement of the polyaniline oxidation degree.^{20,21}

The poly(2-amino benzyl alcohol) and poly(3-amino benzyl alcohol), according to the intensities of the benzenoid and quinoid signals, show an intermediate redox state of polyaniline [see Fig. 1(a), (b), and (e)]. When the substituents are placed in 2-position, a more oxidized structure is obtained [see Fig. 1(c) and (d)]. This is demonstrated by the higher intensity of the quinoid band (C=C and C=N), regarding benzenoid. For poly(2-aminophenol) and poly(3-aminophenol), the intensity of the benzenoid groups is lower than that of the quinoid groups [see Fig. 1(c) and (d)].

Figure 2 shows the UV-vis spectrum of poly(2-aminophenol) as a base form synthesized in 1M HCl (sample No. 2). The signals placed at 414 nm are more intense than those placed at 250 nm indicating a higher oxidation which is in accordance with the FTIR spectra.

Poly(3-aminophenol), poly(2-amino benzyl alcohol), poly(3-amino benzyl alcohol) in base form were completely insoluble in common organic solvents. Hence, it was not possible to record UV-vis spectra. It has been reported^{10,18} that polyaniline in a completely oxidized form (only with quinoid-diimine groups) the FTIR and UV-vis spectra of polyaniline does not correspond to those of poly(2-aminophenol) and poly(3-aminophenol), for which these polymers presented a higher fraction of oxidized units than Pani in their completely oxidized form. Hence, 2- and 3-aminophenol were polymerized in a different way than aniline.

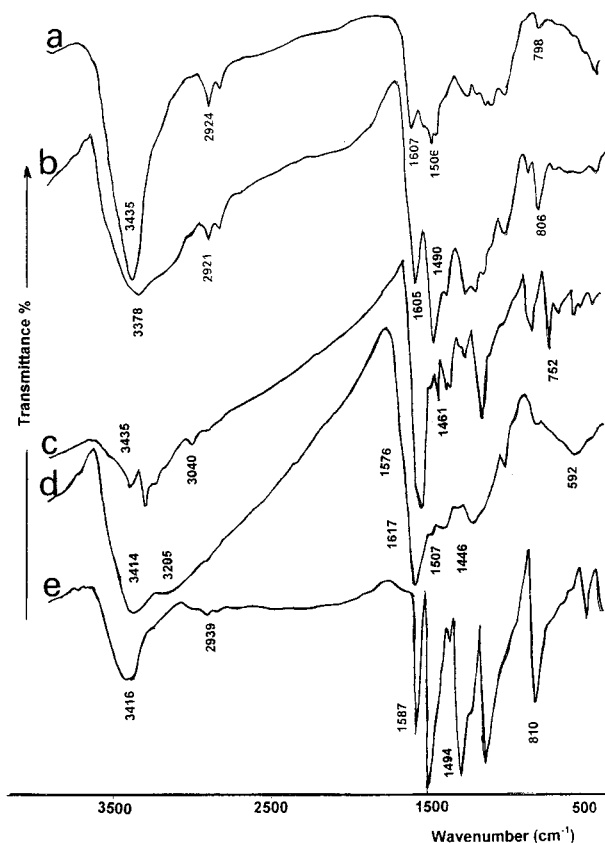


Figure 1 FTIR spectra of (a) poly(2-amino benzyl alcohol); (b) poly(3-amino benzyl alcohol); (c) poly(2-aminophenol); (d) poly(3-aminophenol); and (e) polyaniline. Pellets KBr.

Table II shows the reaction conditions and the results of polymerization in the presence and absence of metal ions. The medium was 1M HCl. There exists a tendency to increase the yield because of a possible oxidizing effect of the metal ion. The same reactions were performed in the absence of ammonium persulfate. The reaction with 2-aminophenol in the presence of $\text{CuCl}_2 \times 2\text{H}_2\text{O}$ produced a polymer with 6.8% yield. With 2-aminobenzyl alcohol and metal ion, no reaction was observed even after 24 h. However, the yield increased (sample Nos. 18, 19, and 20) indicating that the metal ions would act during propagation. Contrariwise, for 3-aminobenzyl alcohol, the yield did not vary in the presence of metal ions (sample Nos. 22, 23, and 24) not interfering with the polymerization.

Table III shows the reaction conditions and results of the polymers synthesized in the presence and absence of metal ions in a HCl/ CH_3CN mixture. A decrease of the yield was observed regarding the polymers obtained in 1M HCl, prob-

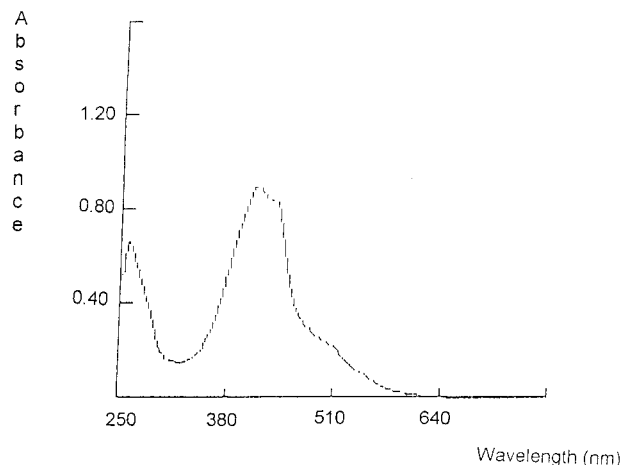


Figure 2 UV-vis spectrum of poly(2-aminophenol) in a base form (sample No. 2). Solvent: dimethyl sulfoxide.

ably because of a decrease of the redox potential of ammonium persulfate related with the decrease of the proton concentration and/or the solvent (CH_3CN) which would inhibit polymerization.

When the polymers were synthesized in a $\text{HCl}/\text{CH}_3\text{CN}$ mixture and in the presence of $\text{Cu}(\text{II})$ ions, an important increase in the yield (sample Nos. 26, 30, 34, and 38) was observed, for which the metal cation was acting as oxidizing reagent. However, the presence of $\text{Ni}(\text{II})$ and $\text{Co}(\text{II})$ did not affect significantly the yield, with the exception of

sample No. 27. The increase of polymerization yield in the absence of metal ions was more important in the presence of $\text{Cu}(\text{II})$ in a $1\text{M HCl}/\text{CH}_3\text{CN}$ mixture. This is because, in this medium, the groups should be protonated and oxidation is more difficult to achieve.

The percentages of the metal ions incorporated into the polymer are summarized in Tables II and III. In 1M HCl medium only, poly(amino phenols) incorporated metal ions, but in $\text{HCl}/\text{CH}_3\text{CN}$ medium, an increase of the metal ion incorporated to poly(amino benzyl alcohol) was also observed. In general, the metal ion incorporation was low, which is attributed to the repulsion interactions between the metal cation and the oxidized species produced according to the oxidative polymerization mechanism. It is possible to suggest that by decreasing the proton concentration, incorporation of the metal ions into the polymers would increase, which is probably attributed to the deprotonation of the donor groups. This behavior favors the polymer-metal ion interaction (the monomers are insoluble in 10^{-4}M HCl).

Figures 3 and 4 show the FTIR spectra of the poly(amino benzyl alcohol) derivatives in base form obtained with metal ions.

Poly(2-aminobenzyl alcohol) with metal ions incorporated at the polymer chain (see Fig. 3) shows a shifting of $\text{C}=\text{C}$, $\text{C}=\text{N}$ stretching absorption signals of quinoid-diimine. The absorption

Table III Reaction Conditions of Polymerization of Aniline Derivatives in the Presence and Absence of Metal Ions in $\text{HCl}/\text{CH}_3\text{CN}$

Sample No.	Monomer	Monomer Concentration (m)	Metal Ion Concentration (m)			Time (min)	T ($^{\circ}\text{C}$)	Metal in Polymer (%)	Yield (%)	$\text{HCl}/\text{CH}_3\text{CN}$ (v/v)
			$\text{Cu}(\text{II})$	$\text{Ni}(\text{II})$	$\text{Co}(\text{II})$					
25	2-Amino phenol	0.171	—	—	—	500	18	—	13.0	0.852
26		0.171	0.511	—	—	500	18	4.02	51.3	0.852
27		0.171	—	0.512	—	500	18	—	0.0	0.852
28		0.171	—	—	0.512	500	18	0.05	11.9	0.852
29	3-Amino phenol	0.399	—	—	—	480	18	—	7.8	1.564
30		0.398	1.200	—	—	480	18	2.88	27.5	1.564
31		0.399	—	1.200	—	480	18	0.96	9.2	1.564
32		0.398	—	—	1.200	480	18	0.26	7.4	1.564
33	2-Amino benzyl alcohol	0.284	—	—	—	300	0	—	4.9	0.852
34		0.284	0.853	—	—	300	0	0.27	57.3	0.852
35		0.285	—	0.853	—	300	0	4.18	8.1	0.852
36		0.285	—	—	0.852	300	0	0.45	11.2	0.852
37	3-Amino benzyl alcohol	0.180	—	—	—	480	18	—	0.0	0.852
38		0.181	0.540	—	—	360	18	0.27	57.7	0.852
39		0.180	—	0.540	—	360	18	0.84	1.0	0.852
40		0.180	—	—	0.539	360	18	0.57	5.2	0.852

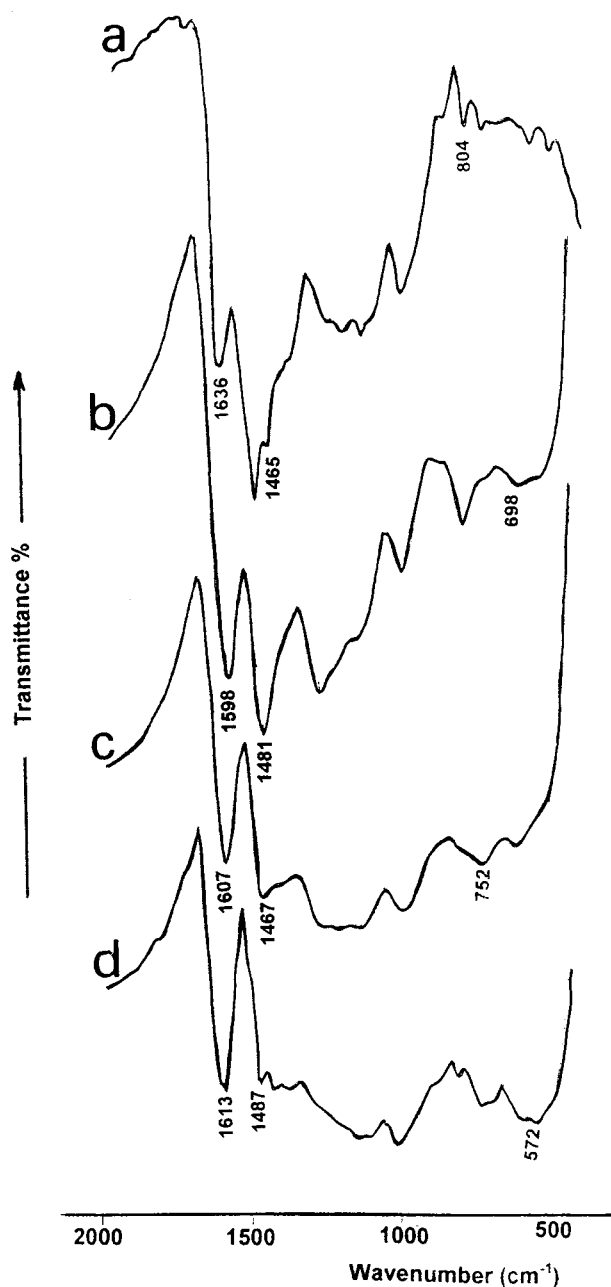


Figure 3 FTIR spectra of poly(2-aminobenzyl alcohol) of: (a) without metal ion (sample No. 33); (b) with Cu(II) (sample No. 34); (c) with Ni(II) (sample No. 35); and (d) with Co(II) (sample No. 36).

signals corresponding to C=C from benzenoid-diamine are shifted to lower frequencies with respect to the polymer without metal ion [see Fig. 3(a)]. The same occurs with poly(3-amino benzyl alcohol) (see Fig. 4), except that C=C absorption signals of benzenoid-diamine are not too different from the analogue synthesized in 1M HCl [see Fig. 1 (b)]. The shifting at lower frequency is

possibly attributed to interactions between the metal ion and the π -conjugated polymer chain.

The weight-loss behavior of the different polymers demonstrated that up to 200°C it was lower than 20%. As the temperature increases, the weight loss also increases. No important effect of the position of the substituent on the thermal stability is observed. In general, the polymers synthesized in HCl/CH₃CN medium show a lower thermal stability than in HCl medium. Materials with lower thermal stability correspond to poly(2-aminophenol), sample No. 25, and poly(3-aminophenol)-Ni(II), sample No. 31, with a weight loss of 63.8 and 72.8%, respectively.

Table IV shows the electrical conductivity values of polymers with and without metal ion.

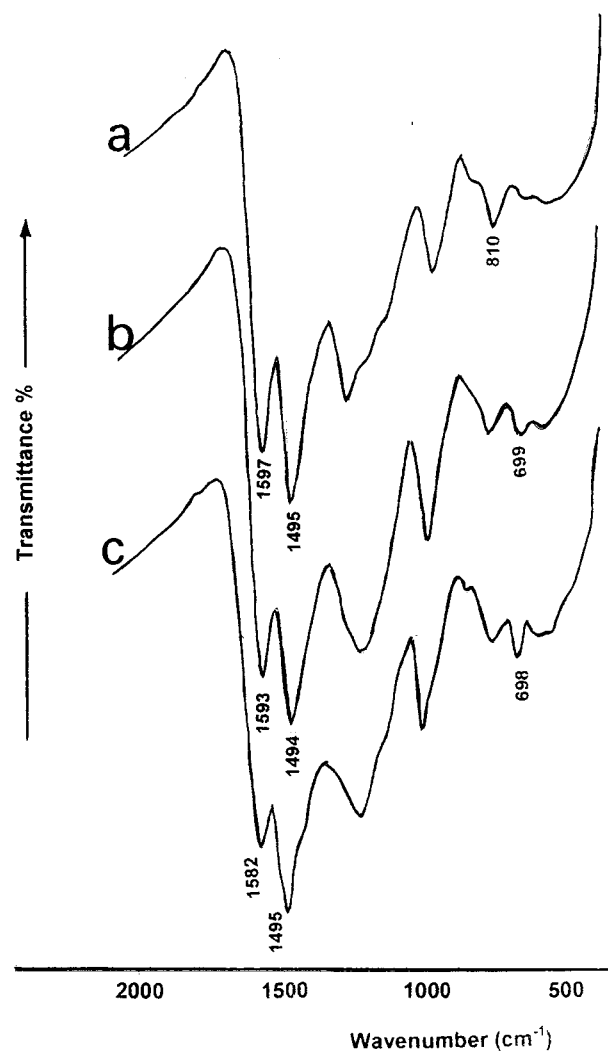


Figure 4 FTIR spectra of poly(3-aminobenzyl alcohol) of (a) with Cu(II) (sample No. 38); (b) with Ni(II) (sample No. 39); and (c) with Co(II) (sample No. 40).

Table IV Values of Electrical Conductivity at Room Temperature of the Polymers with and without Metal Ions

Polymer	Sample No.	Chloride (%)	Metal Ion in Polymer (%)	$\sigma \times 10^9$ (Scm ⁻¹)
Poly(2-amino phenol)	9	2.4	—	3.2
	10	5.6	2.8	3.5
	25	<1.0	—	3.3
	26	<1.0	4.02	3.4
Poly(3-amino phenol)	13	14.2	—	12.9
	14	15.7	2.22	12.9
	29	3.4	—	3.5
	30	6.6	2.88	4.7
Poly(2-amino benzyl alcohol)	17	12.0	—	86,800
	33	2.8	—	69.0
	34	<1.0	0.27	16080
	35	<1.0	4.18	82.9
	36	<1.0	0.45	73.1
Poly(3-amino benzyl alcohol)	21	13.3	—	752.8
	38	2.0	0.27	335
	39	3.1	0.84	2.38
	40	<1.0	0.57	2.24

Poly(2-aminobenzyl alcohol) and poly(3-aminobenzyl alcohol) (sample Nos. 17–40) show a higher electrical conductivity than poly(aminophenols) because they have an intermediate redox state with a high doping level. Poly(aminophenols) show that an increase of the chloride content (%) did not increase the electrical conductivity as expected, which can be attributed to their over-oxidated structures. Moreover, the electrical conductivities practically did not vary with the presence of metal ions. Poly(2-aminobenzyl alcohol) containing metal ions (sample Nos. 34–36) have a higher conductivity than that without metal ions (sample No. 33). This significant increase is possibly attributed not only to acid doping (contains <1.0% of chloride), but also to the active participation of the metal ions in the electrical conductivity.

The electrical conductivity of the poly(3-aminobenzyl alcohol) with Ni(II) and Co(II) (sample Nos. 39 and 40) show that for the polymer-Cu(II) (sample No. 38) there is an important increase of the conductivity that cannot be associated only with the acid doping (>2%).

CONCLUSIONS

The 2- and 3-aniline derivatives are less reactive than aniline. It is necessary to increase the con-

centration, time, and/or temperature of polymerization to yield polymerization products. The substituents in 2-position favor the oxidation degree of the polymers. According to FTIR spectra, both poly(2-amino phenol) and poly(3-amino phenol) did not polymerize similarly to aniline. The presence of metal cations increases the yield because of the oxidation action during polymerization.

It is possible to increase the electrical conductivity of the polymers by incorporating copper ions. However, the effect of the acid doping is more important than the metal ion. Poly(2-amino benzyl alcohol) and derivatives have electrical conductivity values in the semiconducting range. Some of these materials could be investigated to be applied as catalysts and semiconductors.

REFERENCES

- Boyle, A.; Penneau, J. F.; Genies, E.; Riekel, C. *J Polym Sci Part B, Polym Phys* 1992, 30, 265.
- Amano, K.; Ishikawa, H.; Kobayashi, A.; Satoh, M.; Hasegawa, E. *Synt Met* 1994, 62, 229.
- Huang, W.-S.; Humphrey, B. D.; Macdiarmid, A. G. *J Chem Soc, Faraday Trans 1* 1986, 82, 2385.
- Focke, W. W.; Wnek, G. E.; Wei, Y. *J Phys Chem* 1987, 91, 5813.
- Díaz, A. F.; Logan, J. A. *J Electroanal Chem* 1980, 111, 111.

6. Wudl, F.; Angus, R. O.; Lu, F. L.; Allemand, P. M.; Vachon, D. J.; Nowak, M.; Liu, Z. X.; Heeger, A. J. *J Am Chem Soc* 1987, 109, 3677.
7. Wei, Y.; Sun, X.; Jang, G.-W.; Tang, X. *J Polym Sci Part C, Polym Lett* 1990, 28, 81.
8. Wei, Y.; Tang, X.; Sun, Y. *J Polym Sci Part A, Polym Chem* 1989, 27, 2385.
9. Kang, E. T.; Neoh, K. G.; Tan, T. C.; Khor, S.; Tan, K. L. *Macromolecules* 1990, 23, 2918.
10. Sun, Y.; Macdiarmid, A. G.; Epstein, A. *J Chem Soc, Chem Comm* 1990, 529.
11. Kost, K. M.; Bartak, D. E.; Kazee, B.; Kuwana, T. *Anal Chem* 1988, 60, 2379.
12. Das, B. C.; Iqbal, J. *Tetrahedron Lett* 1997, 38(7), 1235.
13. De, A.; Basak, P.; Iqbal, J. *Tetrahedron Lett* 1997, 38(48), 8383.
14. Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J Phys Chem* 1985, 89, 1441.
15. Hirao, T.; Higuchi, M.; Ikeda, I.; Ohshiro, Y. *J Chem Soc Chem Commun* 1993, 194.
16. Higuchi, M.; Ikeda, I.; Hirao, T. *J Org Chem* 1997, 62(4), 1072.
17. ASTM method 1981, 30, 103.
18. Lu, F. L.; Freed, W.; Novak, M.; Heeger, A. J. *J Am Chem Soc* 1986, 108, 8311.
19. Furukawa, Y.; Ueda, F.; Hyodo, Y.; Harada, I.; Nakajima, T.; Kawagoe, T. *Macromolecules* 1988, 21, 1297.
20. Wei, Y.; Kesyyin, F.; Hsueh, Y. G.; Jang, W. *Macromolecules* 1994, 27, 518.
21. Saricifti, N. S.; Kuzmany, H.; Neugebauer, H.; Neckel, A. *J Chem Phys* 1990, 92, 4530.