

Poly(1,2-diaminobenzene) and Poly(1,3-diaminobenzene): Synthesis, Characterization, and Properties

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ABSTRACT: Poly(1,2-diaminobenzene) (1,2-DAB) and poly(1,3-diaminobenzene) (1,3-DAB) have been synthesized by using ammonium persulfate as oxidizing agent in the presence and in the absence of the following metal ion salts: CuCl_2 , NiCl_2 , and CoCl_2 with different HCl concentrations. The products showed a different content of the metal ion depending on the HCl concentration. The polymers were characterized by Fourier transform infrared (FTIR), ultraviolet-visible (UV-Vis) spectroscopy, thermal analysis, and electrical conductivity. The polymerization yield depended on the presence of metal ions that can react as oxidizing reagents and/or catalysts. The polymerization mechanism depended on the position of the substituent. For poly(1,2-DAB) a ladder-type structure was obtained, and for poly(1,3-DAB) one similar to that of polyaniline. The thermal stability increased as the metal ion content in the polymer matrix increased. The electrical conductivity of the polymer did not depend on the metal ion content in the polymer. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2564–2572, 2002

Key words: polyaniline derivatives; metal ions; electrical conductivity

INTRODUCTION

Conductive polymers and particularly those with metal ions show very useful redox and electrical properties for a wide application fields.^{1–6}

The functionalization by metallic complexes of bipyridyl type,^{7–9} porphyrins,^{10,11} tetraazaanulene,^{12,13} metallated cyclam,^{14,15} phthalocyanine,^{16,17} and phenanthroline¹⁸ has been investigated as a way to incorporate the metal cations into the polymers. Usually the ligands are difficult to synthesize as they need multistep synthesis and also very expensive.

The electrosynthesis of poly(1,2-DAB) films with various functions depending on the electrol-

ysis conditions has been reported. These functions include electrochemical diode properties,¹⁹ electron transfer mediation catalysis,¹⁹ and protection metal corrosion (anthiphoto corrosion).^{20,21} The incorporation of metal cations into polymers is important for the potential applications, but it is very difficult due to the repulsion interactions between the metal and the radical cations of the polymer.

In an attempt to improve the conductivity, stability, and other properties of the polymers, we have been investigating and found that poly(aminophenols) and poly(amino benzyl alcohol)s have incorporated metal ion into the polymer matrix, changing significantly some properties of these polymers.²²

The aim of this paper deals with the synthesis of poly(1,2-diaminobenzene) and poly(1,3-diaminobenzene) under different experimental conditions, and to investigate their ability trapping

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metal ions such as copper, nickel, and cobalt during the synthesis. Thus, the metal ions may interact with donor amino groups of polymers. The effect of metal ions on thermal stability, concentration of HCl, and electrical conductivity of the polymer with and without metal ion was investigated. Moreover, the effect of the substituent on polymerization was also investigated.

EXPERIMENTAL

Reagents

The monomers (Merck, Stuttgart, Germany) were purified by recrystallization. 1,3-Diaminobenzene (1,3-DAB) was from ether/ethanol (10:1, v:v), and 1,2-diaminobenzene (1,2-DAB) from CH_2Cl_2 with charcoal. 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.

Synthesis of Polymers

Synthesis of the Polymers with Ammonium Persulfate

The amount of 2.0 g (18.5 mmol) of 1,3-DAB was dissolved in 42 mL of 1M HCl. The amount of 4.22 g (18.5 mmol) of ammonium persulfate dissolved in 8.4 mL 1M HCl drop to drop under stirring was added. The mixture reaction was stirred for 4 h at 18°C. It was filtered and washed with 1M HCl. The polymer was dried for 2 days at 50°C. 1,3-DAB was also polymerized as described above, but at different concentrations of HCl and in the presence of CuCl_2 (37.0 mmol) (NiCl_2 or CoCl_2). The metal salt was added in solid state after the addition of the monomer. All the polymers were washed with HCl at the same concentration used for polymerization. Poly(1,2-diaminobenzene)s were synthesized as above, but in the presence and absence of metal ion, at different concentrations of HCl, but at higher temperature (40°C).

Synthesis of the Polymers with Copper(II) Chloride

The amount of 2.0 g (18.5 mmol) of monomer 1,3-DAB was dissolved in 40 mL 10^{-4}M of HCl. The amount of 6.31 g (37.0 mmol) of $\text{CuCl}_2 \times 2\text{H}_2\text{O}$ dissolved in 10.4 mL 10^{-4}M of HCl were added under stirring at 18°C. The mixture of reaction was stirred for 4 h at 18°C. It was filtered and washed with hot 10^{-4}M HCl. The polymer

was dried at 50°C until constant weight. P1,2-diamino benzene was also polymerized as above but using $\text{CuCl}_2 \times 2\text{H}_2\text{O}$ as oxidizing agent, but with 1M HCl and 10^{-4}M HCl at 40°C.

Characterization

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

The quantification (weight %) of the metal ions incorporated into the polymers was done by treatment with HNO_3 ($D = 1.5$ g/mL), calcinating the solid sample, solubilizing with dilute HNO_3 , and determining the metal concentration by atomic absorption spectrometry (AAS) using an Atomic Absorption Spectrometer, Perkin Elmer 3100.

The amount (weight %) of total chloride in the polymers for the ASTM standard method²³ was determined. Electrical conductivity was measured on an Elchema Electrometer using pellets and the four-probe method. Pellets were obtained by pressing at about 24,000 psi the finely ground polymer.

Thermograms were recorded under nitrogen with the Polymer Laboratories STA 625 Thermal Analyzer.

The yield (weight %) of the polymers were calculated considering the mass of monomer used.

RESULTS AND DISCUSSION

Table I shows the yield of the polymers synthesized in the presence and in the absence of metal ions with ammonium persulfate as oxidizing agent at different concentrations of HCl. In the absence of metal ions, by decreasing the concentration of HCl used during polymerization, the yield increased only for poly(1,3-DAB). It is possible to attribute to this to effect of position (2 or 3) of amino substituent.

When poly(1,3-DAB) was synthesized with ammonium persulfate in the presence of metal ions, the polymerization yield increased (see Table I). The effect of the HCl concentration (without metal ions) is very strong for polymerization of 1,3-DAB but not for that of 1,2-DAB. By the presence of metal ions, there is no important effect of the HCl concentration (from 10^{-1} to 10^{-6}M) on the polymerization yield. These monomers were

Table I Polymerization Yield (%) of Polyaniline Derivatives

HCl [M]	Yield (%)							
	Poly(1,2-DAB)				Poly(1,3-DAB)			
	Absence of ions	Presence of CuCl ₂	Presence of NiCl ₂	Presence of CoCl ₂	Absence of ions	Presence of CuCl ₂	Presence of NiCl ₂	Presence of CoCl ₂
1	55	44	41	34	27	39	36	37
10 ⁻¹	—	48	26	19	—	83	50	54
10 ⁻²	—	38	11	30	—	81	50	52
10 ⁻⁴	56	56	18	37	62	79	54	50
10 ⁻⁶	—	—	17	31	—	—	56	58

only treated (in absence of persulfate) with NiCl₂, CoCl₂, and CuCl₂ in acid medium. After one week of reaction, only polymerization products with CuCl₂ were observed. However, these ions can also act as catalysts and/or oxidizing reagents during the polymerization with ammonium persulfate. In the case of poly(1,2-DAB), the polymer-

ization yield decreased when it is synthesized in the presence of metal ions. Treating of 1,2-DAB only with CuCl₂ and aqueous HCl (<10⁻¹M), a green product was easily decanted. This product showed an absorption at 430 nm (in DMSO), which means a strong monomer-Cu(II) interaction. This green complex is less stable when the

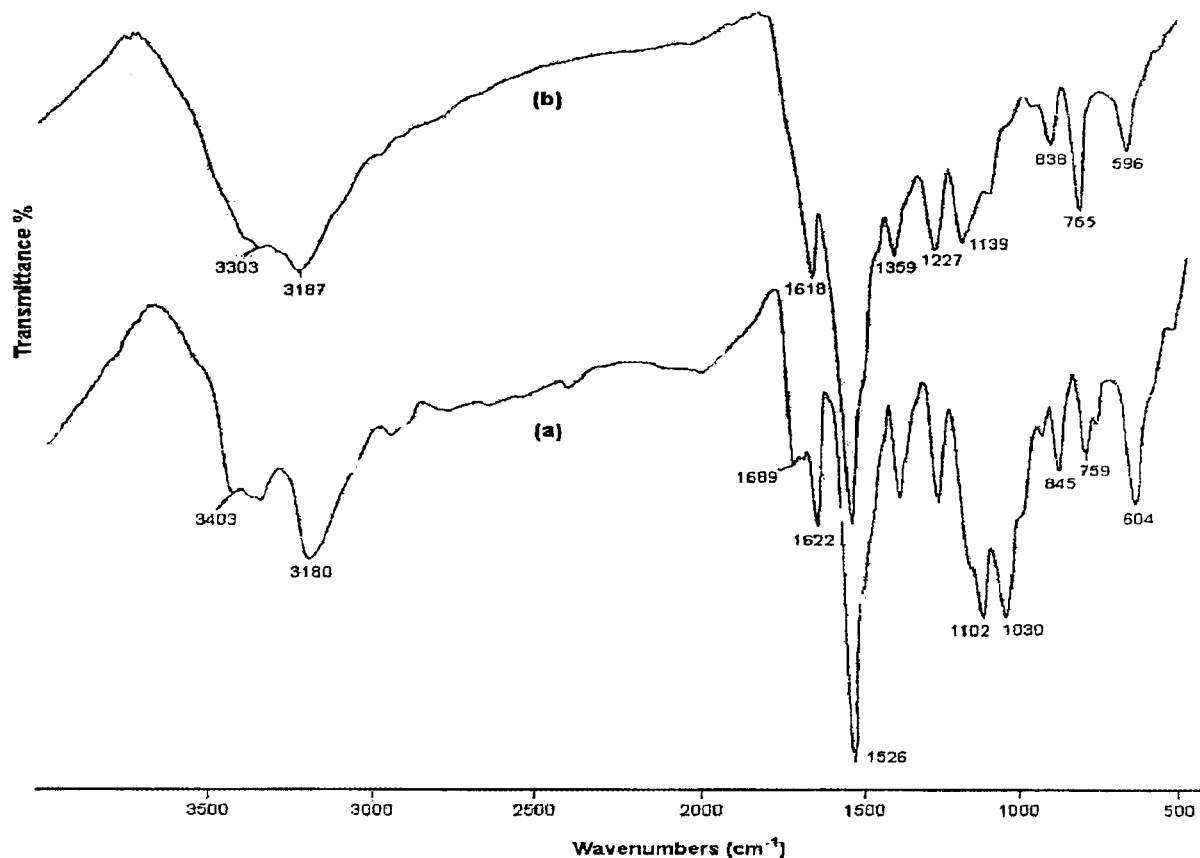


Figure 1 FTIR spectra of poly(1,2-DAB) synthesized with (a) ammonium persulfate in 10⁻⁴M HCl and (b) ammonium persulfate in the presence of CuCl₂ in 10⁻⁴M HCl.

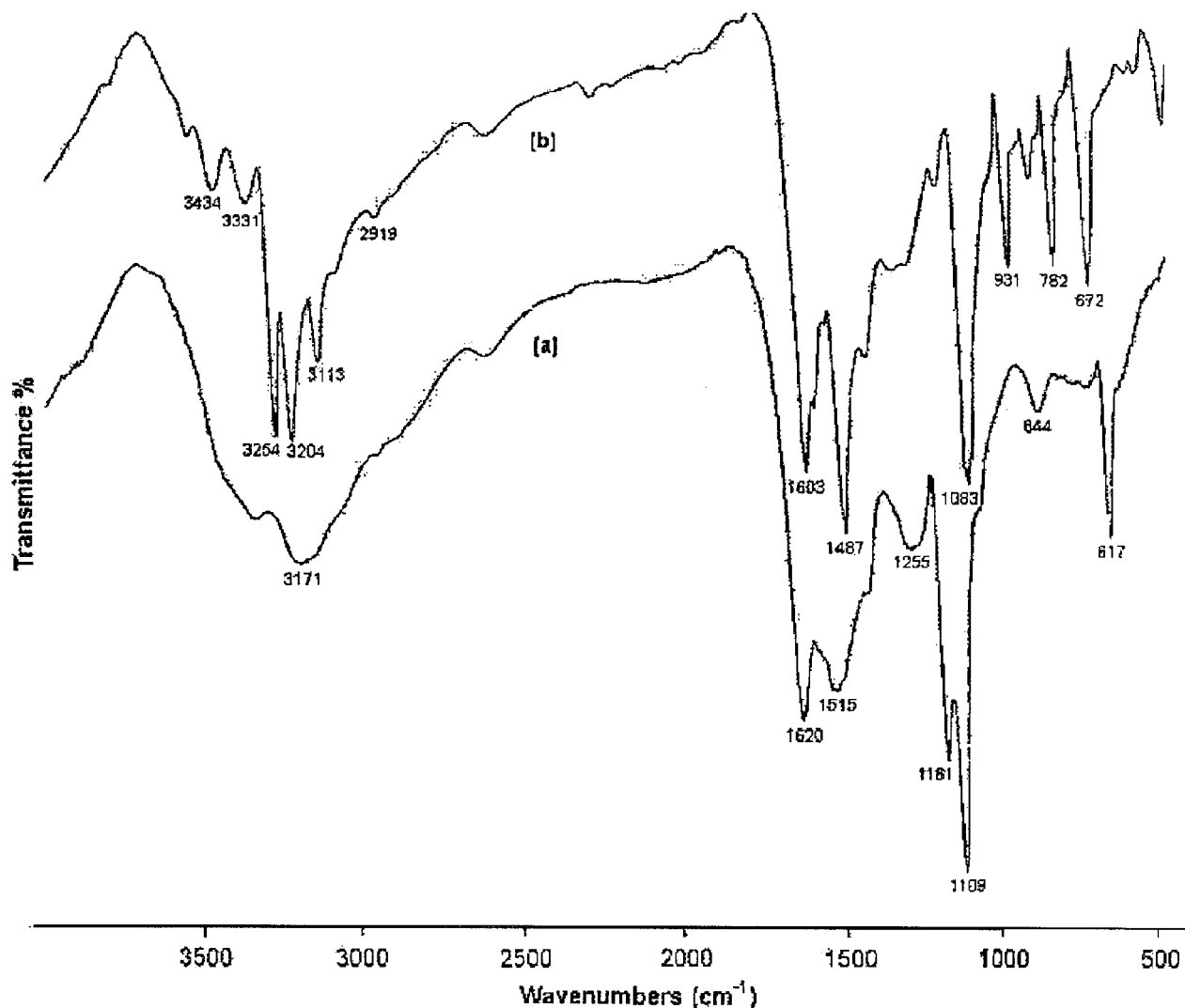


Figure 2 FTIR spectra of poly(1,3-DAB) synthesized with (a) ammonium persulfate in $10^{-4}M$ HCl and (b) $CuCl_2$ in $10^{-4}M$ HCl.

concentration decreases and time and temperature are increased, yielding a product after 4 h of reaction. The diminution of yield of poly(1,2-DAB) was observed when it is synthesized with ammonium persulfate in the presence of metal ion. This is attributed to the interactions between the amino groups in positions 1 and 2 with the metal ions which delay the polymerization.

Figure 1 shows the FTIR spectra of poly(1,2-DAB) synthesized with ammonium persulfate in $10^{-4}M$ HCl in the presence and in the absence of $CuCl_2$.

The absorption signals between 900 and 700 cm^{-1} are attributed to C—H out-of-plane bending modes. These bands correspond to the substitution pattern of the di-, tri-, or tetrasubstitution

aromatic ring. The absorption bands at 1526 and 1622 cm^{-1} are characteristics of the stretching vibration modes of C—C bonds of the aromatic ring. Moreover, the absorption band at 1622 cm^{-1} corresponding to stretching C=N^{24–26} was observed. This signal has also been observed with polyaniline.^{24–26} The absorption signal at 1689 cm^{-1} may be ascribable to the stretching C=O of quinone.^{27,28}

All FTIR spectra of poly(1,2-DAB) synthesized in the presence of nickel(II) and cobalt(II) are similar to those of Figure 1(a), except those polymers synthesized with ammonium persulfate in presence of copper ions and concentration of HCl lower than 1M [see Fig. 1(b)]. In this case, the absorption band attributed to C=O was not ob-

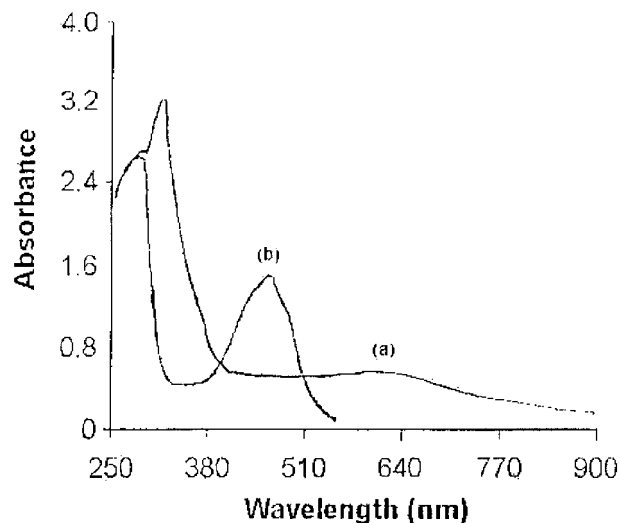


Figure 3 UV-Vis Spectra of (a) poly(1,3-DAB) synthesized with CuCl_2 in $10^{-4}M$ HCl and (b) poly(1,2-DAB) synthesized with ammonium persulfate in $10^{-4}M$ HCl—both in DMSO.

served. Moreover, when the content of copper(II) in the polymer was increased (see Fig. 8) there was a tendency to shift at lower frequency the associated bands of $\text{C}=\text{N}$ and $\text{C}-\text{C}$ of the aromatic rings (1622 cm^{-1}).

Figure 2 shows the FTIR spectrum of poly(1,3-DAB). The stretching band of $\text{C}=\text{N}$ bonds (and $\text{C}-\text{C}$ aromatic rings) at 1620 cm^{-1} is more intense than that of poly(1,2-DAB) [see Fig.1(a)]. All the FTIR spectra of poly(1,3-DAB) synthesized with ammonium persulfate in the presence and in the absence of metal ions are similar to that of Figure 2(a). The absorption band of $\text{C}=\text{O}$ was not observed as occurred for poly(1,2-DAB). However, the $\text{C}=\text{O}$ formation can be avoided by the presence of metal ions during polymerization.

Figure 2(b) shows the FTIR spectrum of poly(1,3-DAB) synthesized only with CuCl_2 . Here, the substitution pattern corresponds to di-, tri-, and/or tetrasubstitution, and it is different (particularly in the zone of $\text{C}-\text{H}$ out-of-plane bending modes) to series of polymers synthesized with ammonium persulfate [see Fig. 2(a)]. This could corroborate that the polymers are structurally different when they are synthesized with different oxidizing agents. Moreover, FTIR spectrum [see Figs. 2(a) and 1(a)] shows that 1,3-diaminobenzene is polymerized in a different way than that of 1,2-diaminobenzene.

Poly(1,3-DAB) compounds synthesized with ammonium persulfate in the presence and in the absence of metal ions were insoluble in organic solvents. The UV-Vis spectrum of poly(1,3-DAB)

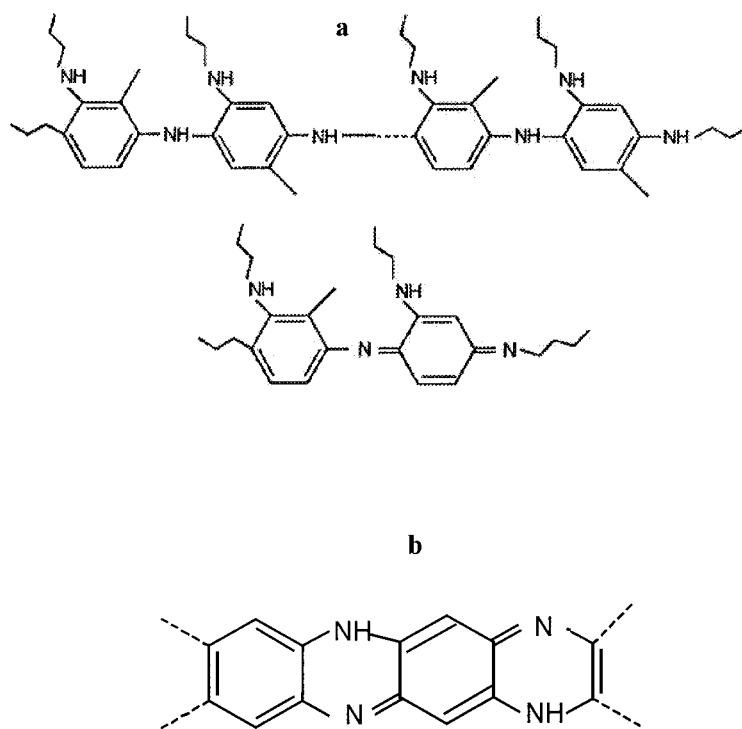


Figure 4 (a) Ladder structure type of poly(1,2-DAB) (ref. 32); (b) lineal structure type of poly(1,3-DAB).

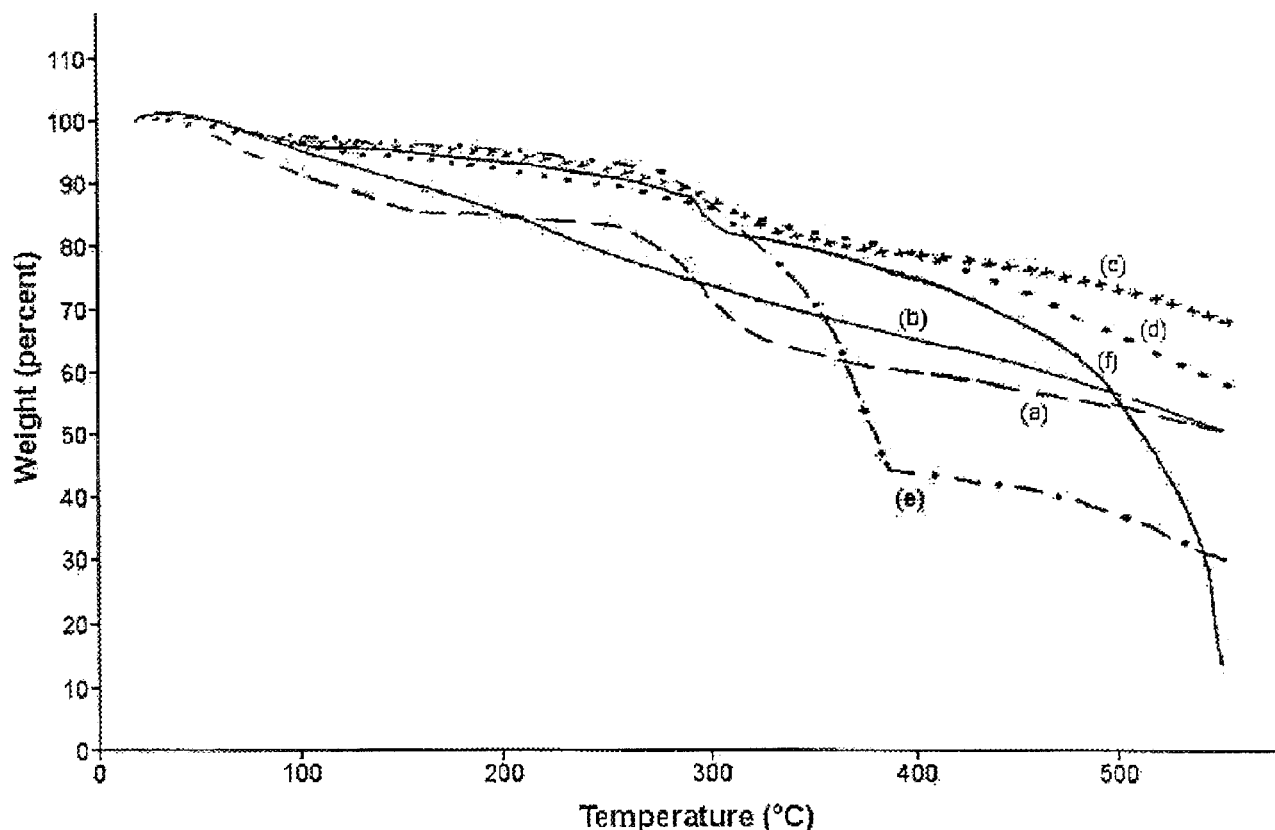


Figure 5 Thermogram of poly(1,2-DAB) synthesized with (a) ammonium persulfate in $10^{-4}M$ HCl (0% ion); (b) ammonium persulfate in the presence of $CuCl_2$ in $1M$ HCl (0.07% copper); (c) ammonium persulfate in the presence of $CuCl_2$ in $10^{-4}M$ HCl (7.64% copper); (d) $CuCl_2$ in $10^{-4}M$ HCl (15.7% copper); (e) ammonium persulfate in the presence of $NiCl_2$ in $10^{-6}M$ HCl (0.30% nickel); (f) ammonium persulfate in the presence of $CoCl_2$ in $10^{-6}M$ HCl (3.03% cobalt).

is shown in Figure 3(a), showing two absorption signals at 320 and other broad band at 600 nm. Poly(1,2-DAB) shows absorption bands at 274 and 450 nm [see Fig. 3(b)]. The solution of poly(1,3-DAB) is blue. UV-Vis and FTIR spectra are characteristics of polyaniline.²⁹⁻³¹

Chiba et al.^{32,33} reported the electrochemical synthesis of poly(1,2-DAB) and postulated a ladder structure type [see Fig. 4(a)]. The FTIR spectrum obtained by them is similar to those obtained chemically by us.

On the other hand, 1,3-diaminobenzene was polymerized chemically as Pani yielding a lineal structure, with some branches [see Fig. 4(b)]. These results demonstrate that the position of the substituent influences the polymerization mechanism.

Figures 5 and 6 show the thermograms of poly(1,2-DAB) and poly(1,3-DAB) respectively. As the copper(II) ions content increases in the polymer, the thermal stability also increases

[see Fig. 5(a-d)]. A similar effect was observed with Ni(II) and Co(II) [see Figs. 5(e) and 6(f)]. With cobalt(II) the weight loss is close to 11% at 300°C and without metal ion the same weight loss occurred at 120°C. In general, the thermal stability did not depend on the HCl content into the polymer. Poly(1,3-DAB) has a slightly higher thermal stability than that of poly(1,2-DAB) [see Figs. 5(a) and 6(a)]. On the contrary, for the poly(1,3-DAB), as the metal ion content increases in the polymer, no significant change in the thermal stability was observed (see Fig. 6). Only when the polymer has a high copper ion content (23.0%), is the thermal stability increased. This was only observed when the polymer was synthesized with $CuCl_2$ [see Fig. 6(d)].

The thermograms of poly(1,3-DAB) containing nickel(II) or cobalt(II) are similar to those of Figure 6(a). The thermal stability did not vary due to the low metal ion content.

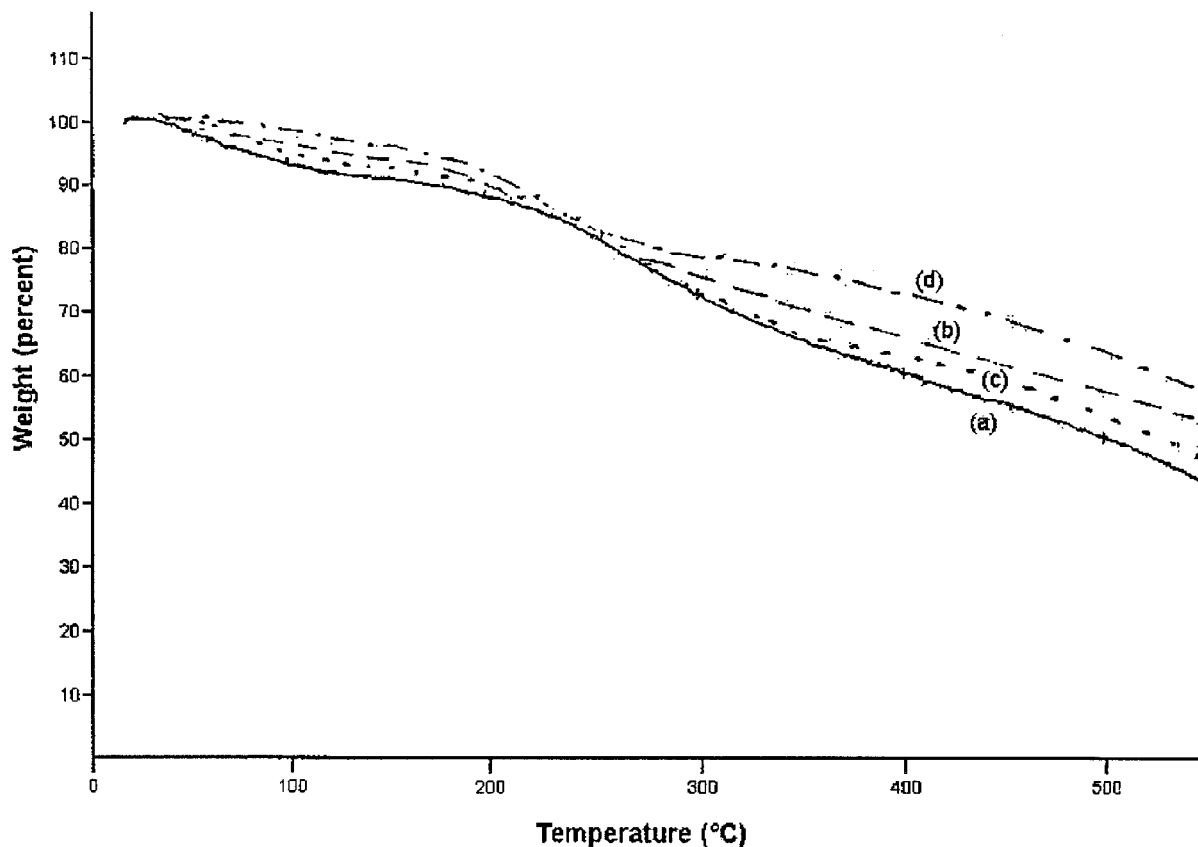


Figure 6 Thermogram of poly(1,3-DAB) synthesized with (a) ammonium persulfate in $10^{-4}M$ HCl (0% metal); (b) ammonium persulfate in the presence of $CuCl_2$ in $1M$ HCl (0.13% copper); (c) ammonium persulfate in the presence of $CuCl_2$ in $10^{-4}M$ HCl (3.1% copper); (d) $CuCl_2$ in $10^{-4}M$ HCl (23.0% copper).

Figure 7 shows the metal ion incorporated (%) into the polymers at different HCl concentrations. Poly(1,2-DAB) is able to trap a higher percentage of metal ion in all HCl concentration ranges used. Moreover, the metal ion content is higher as the HCl concentration is decreased. When both polymers (1,2-DAB and 1,3-DAB) are synthesized only with $CuCl_2$ as oxidizing agent, polymers with a high content in copper ions are obtained, 15.7% with poly(1,2-DAB) and 23.0% with poly(1,3-DAB) respectively.

Table II shows the electrical conductivity values at room temperature of poly(1,2-DAB) and poly(1,3-DAB). In Pani, the percentage of Cl^- is a measure of the acid doping whose content increases significantly the electrical conductivity.³⁴⁻³⁶ On the contrary, basic poly(1,2-DAB) shows an electrical conductivity of $0.43 \times 10^{-9} S cm^{-1}$ and by acid doping (15.2% of Cl^-), the electrical conductivity did not vary. This polymer synthesized in $10^{-4}M$ HCl has a chloride content

lower than 1% and the value of the electrical conductivity is very small. On the contrary, in poly(1,3-DAB) in their base form, the electrical conductivity increased from 0.64 up to 410 (640 times). This is due basically to the similar behavior of Pani. When poly(1,3-DAB) was synthesized at low HCl concentrations ($10^{-4}M$), its electrical conductivity value ($0.48 \times 10^{-9} S cm^{-1}$) is similar to that of the polymer in the base form synthesized in $1M$ HCl.

For poly(1,2-DAB) and poly(1,3-DAB) synthesized in presence of $CuCl_2$, the percentage of chloride is high but no important changes in their electrical conductivity with respect to the basic polymers were observed.

Due to fact that the poly(1,2-DAB) synthesized with $CuCl_2$ as oxidizing agent has a molar ratio $Cu/Cl^- = 0.57$, the chloride percentage corresponds to electroneutrality of Cu(II) ions but not to the acid doping. The same occurs for poly(1,3-DAB) synthesized with $CuCl_2$ as oxidizing agent

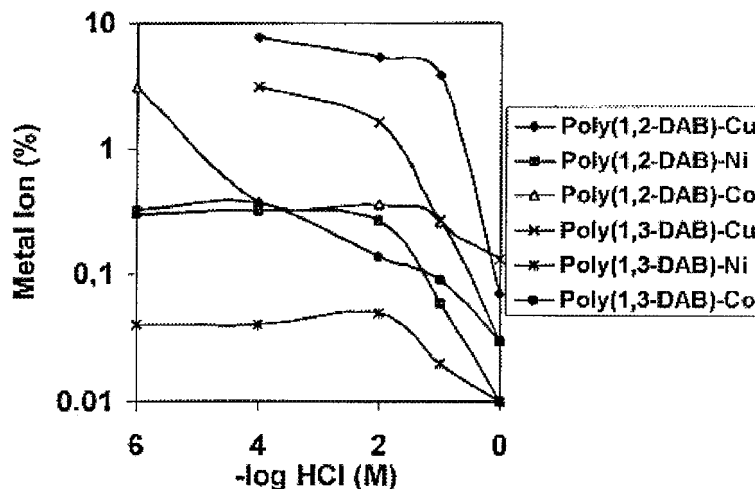


Figure 7 Metal ion incorporated (%) vs concentration of HCl used in the synthesis of poly(1,2-DAB) and poly(1,3-DAB).

in $10^{-4}M$ HCl, whose molar ratio is $Cu/Cl^- = 0.55$.

The polymers containing Ni(II) and Co(II) ions did not increase significantly their electrical conductivity.

CONCLUSIONS

Polyaniline derivatives have been synthesized with a higher yield by the presence of metal ions in their synthesis. The polymerization mecha-

nism depended on the substituent position. For poly(1,2-DAB) and poly(1,3-DAB), a ladder structure and one similar to that of polyaniline were obtained, respectively. Thermal stability of these materials can be increased according to metal ion content.

The electrical conductivity behavior did not depend strongly on the metal ion content.

To elucidate the true structure of these polymers and the action of the metal ions during the reaction, it is necessary to carry out other studies.

Table II Electrical Conductivity of Poly(1,2-DAB) and Poly(1,3-DAB)

Polymer	HCl [M]	Oxidizing Agent ^a	Cl ⁻ (%) ^b	σ (Scm ⁻¹) $\times 10^9$
Poly(1,2-DAB)	1	P	15.2	0.46
				0.43 (basic)
	10^{-4}	P	<1.0	1.20
	10^{-4}	Cu(II)	15.4	0.48
				0.49 (basic)
	1	P + Cu(II)	6.15	0.34
	1	P + Ni(II)	15.9	0.62
Poly(1,3-DAB)	1	P + Co(II)	15.9	0.65
	1	P	12.1	410
				0.64 (basic)
	10^{-4}	P	< 1.1	0.48
	10^{-4}	Cu(II)	23.2	0.45
	1	P + Cu(II)	17.6	15.0
	1	P + Ni(II)	15.0	86.0
1	P + Co(II)	14.3	40.0	

^a The total chloride was measured by method Volhard, using ASTM standard method.

^b P = ammonium persulfate.

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REFERENCES

- Kost, K. M.; Bartak, D. E.; Kazee, B.; Kuwana, T. *Anal Chem* 1988, 60, 2379.
- Das, B. C.; Iqbal, J. *Tetrahedron Lett* 1997, 38, 1235.
- De P. Basak, A.; Iqbal, J. *Tetrahedron Lett* 1997, 38, 8383.
- Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J Phys Chem* 1985, 89, 1441.
- Hirao, T.; Higuchi, M.; Ikeda, I.; Ohshiro, Y. *J Chem Soc Chem Commun* 1993, 194.
- Higuchi, M.; Ikeda, I.; Hirao, T. *J Org Chem* 1997, 62, 1072.
- Cosnier, S.; Deronzier, A.; Moutet, J. C. *J Electroanal Chem* 1985, 193, 193.
- De Giovanni, W. F.; Deronzier, A. *J Electroanal Chem* 1992, 337, 285.
- Cosnier, S.; Deronzier, A.; Roland, J. F. *J Electroanal Chem* 1991, 310, 71.
- Bettelheim, A.; White, B. A.; Raybuck, S. A.; Murray, R. W. *Inorg Chem* 1987, 26, 1009.
- Deronzier, A.; Devaux, R.; Limosin, D.; Latour, J. M. *J Electroanal Chem* 1992, 324, 325.
- A.; Deronzier, Marques, M. J. *J Electroanal Chem* 1992, 334, 247.
- Ricciardi, G.; Lelj, I. *Polyhedron* 1992, 11, 2089.
- Bartlett, P. N.; Chung, L. Y.; Moore, P. *Electrochim Acta* 1990, 35, 1051.
- Sable, E.; Handel, M.; Her, M. L. *Electrochim Acta* 1991, 36, 15.
- Choi, C. S.; Tachikawa, H. *J Am Chem Soc* 1990, 112, 1757.
- Saunders, B. R.; Murray, K. S.; Fleming, R. J. *Synth Met* 1992, 47, 167.
- Bidan, G.; Billon, M.; Divisia-Blohorn, B.; Kern, J. M.; Sauvage, J. P. *J Electroanal Chem* 1993, 360, 189.
- Oyama, N.; Chiba, K.; Ohnuki, Y.; Ohsaka, T. *Nippon Kagaku Kaishi* 1985, 1172.
- Volkov, A.; Tourillon, G.; Lacaze, P. C.; Dubois, J. E. *J Electroanal Chem* 1980, 116, 279.
- White, H. S.; Abruna, H. D.; Bard, A. J. *J Electrochem Soc* 1982, 129, 265.
- Rivas, B. L.; Sánchez, C. O. *J Appl Polym Sci* 2001, 82, 330.
- ASTM Method 1981, 30, 103.
- 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.
- Lu, F. L.; Freed, W.; Novak, M.; Heeger, A. J. *J Am Chem Soc* 1986, 108, 8311.
- Furukawa, Y.; Ueda, F.; Hyodo, Y.; Harada, I.; Nakajima, T.; Kawagoe, T. *Macromolecules* 1988, 21, 1297.
- Diaz, F. R.; Sánchez, C. O.; del Valle, M. A.; Tagle, L. H.; Bernede, J. C.; Tregouet, Y. *Synth Met* 1998, 92, 99.
- Leclerc, M.; Guay, J.; Dao, L. H. *Macromolecules* 1989, 22, 649.
- Wei, Y.; Kesyin, F.; Hsueh, Y. G.; Jang, W. *Macromolecules* 1994, 27, 518.
- Troise, F. M. H.; Denvault, G. *J Electroanal Chem* 1993, 354, 331.
- Meixiang, W. *J Polym Sci Part A: Polym Chem* 1992, 30, 543.
- Chiba, K.; Ohsaka, T.; Ohnuki, Y. *J Electroanal Chem* 1987, 219, 117.
- Ohsaka, T.; Watanabe, T.; Kitamura, F.; Oyama, N.; Tokuda, K. *J Chem Soc, Chem Commun* 1991, 1072.
- Huang, W. S.; Humphrey, B. D.; Macdiarmid, A. G. *J Chem Soc, Faraday Trans I* 1986, 82, 2385.
- Park, Y. W.; Moon, J. S.; Bak, M. K. Jin, J. I. *Synth Met* 1989, 29, E389.
- Dao, L. H.; Leclerc, M.; Guay, J.; Chevalier, J. W. *Synth Met* 1989, 29, E377.