Poly(2-) and (3-aminobenzoic acids) and Their Copolymers with Aniline: Synthesis, Characterization, and Properties

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ABSTRACT: Poly(2-aminobenzoic acid) and poly(3-aminobenzoic acid) were synthesized by chemical polymerization of the respective monomers with aqueous $1M$ hydrochloric acid and $0.49M$ sodium hydroxide, using ammonium persulfate as an oxidizing agent. In addition, polymerization in an acid medium was carried out in the presence of metal ions, such as Cu(II), Ni(II), and Co(II). Poly(2-aminobenzoic acid-*co*-aniline) and poly(3-aminobenzoic acid-*co*-aniline) were synthesized by chemical copolymerization of aniline with 2- and 3-aminobenzoic acids, respectively, in aqueous $1M$ hydrochloric acid. The copolymers were synthesized at several mole fractions of aniline in the feed and characterized by UV–visible and FTIR spectroscopy, the thermal stability, and the electrical conductivity. Metal ions, such as Cu(II), Ni(II), and Co(II), were incorporated into homo- and copolymers by the batch method. The percentage of metal ions in the polymers was higher in the copolymers than in the homopolymers. The thermal stability of the copolymers increased as the feed mole fraction of aniline decreased and varied with the incorporation of metal ions in the polymers. The electrical conductivity of the homo- and copolymers was measured, which ranged between 10^{-3} and 10^{-10} S cm^{-1}. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2641–2648, 2003

INTRODUCTION

Transition metals dispersed in modified polymer electrodes have been recognized recently as having potential applications in electrocatalysis. Mikhaylova et al. have reported platinum microparticles incorporated into polyaniline (PANI) films with electrocatalytic applications in the oxidation of methanol.[1] Moreover, metal microparticles dispersed in 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] On the other hand, it is known that PANI is an insulator in alkaline media.[6,7] Casella et al.[8] reported that PANI-Cu(II) films in alkaline media show electrocatalytic oxidative properties toward several organic molecules, such as amino acids and carbohydrates. Kimisha et al.[9] investigated a porphyrin-*co*-PANI complex that shows a stable redox activity over a wide pH range that is due to the self-doping carboxy substituents in the polymer chain. PANI and transition metal salts, such as Cu(II) and Fe(II) chloride, formed complexes, which were effective in the dehydrogenative oxidation of cinnamyl alcohol and mandelic acid. In those complex systems, transition metals are considered to electronically interact through π-conjugate polymer chains.[10] If the monomers are functionalized by small donor groups, the resulting polymer would be able to interact with the metal ions.

We report the synthesis of copolymers of 2-aminobenzoic acid, 3-aminobenzoic acid, and aniline and the synthesis of poly(amino acids) by chemical oxidation in order to incorporate metal ions in the polymers. The incorporation of the ions, the thermal stability, and the electrical conductivity of the resulting materials is studied.

EXPERIMENTAL

Reagents

The monomers 2- and 3-aminobenzoic acid (Merck, Stuttgart, Germany) were purified by recrystallization from ethyl alcohol and water. The metal salts CuCl$_2$ × 2H$_2$O, NiCl$_2$ × 6 H$_2$O, and CoCl$_2$ × 6H$_2$O were analytical grade (Merck).

Characterization

FTIR spectra were obtained from KBr pellets with a Magna Nicolet 550 spectrophotometer, and UV–visible (UV–vis) spectra were recorded in a Perkin–Elmer Lambda 11 spectrophotometer with a 1-cm cell and using dimethylsulfoxide as a solvent.

The quantification (wt %) of the metals incorporated into the polymers was done by calcinating the solid sample, solubilizing it with aqueous HNO$_3$, and de-

termining the metal concentration by atomic absorption spectrometry using an atomic absorption spectrometer (Unicam Solaar 5M).

The electrical conductivity was measured on an Elchema Electrometer using pellets and the four probe method. The pellets were obtained by pressing the finely ground polymer at about 24,000 psi.

Thermograms were recorded under nitrogen with a Polymer Laboratories STA 625 thermal analyzer.

Synthesis of polymers

Synthesis in alkaline media

Six grams of 2- or 3-aminobenzoic acid (43.8 mmol) in 89.3 mL of NaOH ($0.488M$) were dissolved and maintained at 15–18°C in a water bath. Then 9.98 g (43.7 mmol) of ammonium persulfate dissolved in 30.0 mL of water under stirring was added dropwise to the amino acid solution. The solution was maintained at 15–18°C for 19 h and then filtered through a Büchner funnel, washed with abundant water, and dried under a vacuum at 60°C. A 49% yield was obtained for poly(2-aminobenzoic acid) and a 68.1% yield for poly(3-aminobenzoic acid).

Synthesis in acid medium

Three grams (21.9 mmol) of 2- or 3-aminobenzoic acid were dissolved in 95 mL of $1M$ HCl and heated to 50°C in an oil bath. Then 4.996 g (21.9 mmol) of ammonium persulfate dissolved in 14.4 mL of $1M$ HCl were added dropwise to the amino acid solution with constant stirring. The solution was maintained under stirring at 50°C for 8 h and then filtered and washed with hot water. The polymers were dried under a vacuum at 60°C for 2 days. In addition, the polymers were synthesized in a way similar to the above but in the presence of metal ions ($CuCl_2 \times 2H_2O$, $NiCl_2 \times 6H_2O$, or $CoCl_2 \times 6H_2O$). The corresponding monomer/metal ion ratio (1 + 2, mol/mol) was added after the solubilization of the momomer in $1M$ HCl.

Synthesis of copolymers

The copolymers of aniline with 2-aminobenzoic acid and 3-aminobenzoic acid were prepared by chemical oxidation of aniline and aminobenzoic acids at several mole fractions of aniline in the feed (f_1) using ammonium persulfate as the oxidizing agent in $1M$ HCl. The procedure was as follows: a 2- or 3-aminobenzoic acid/aniline solution ($f_1 = 4$) was prepared by dissolving 4.51 g (32.9 mmol) of 2- or 3-aminobenzoic acid and 0.76 g of aniline (8.16 mmol) in 143 mL of $1M$ HCl and heating it to 50°C in an oil bath. Then 7.49 g (32.8 mmol) of ammonium persulfate dissolved in 22 mL of $1M$ HCl was added dropwise to the comonomer so-

lution with constant stirring. The solution was maintained at 50°C for 8 h and then filtered and washed with hot $1M$ HCl. [In the case of the synthesis of poly(3-aminobenzoic acid-co-aniline), it was washed with hot $1M$ HCl and abundant water.] All the copolymers were dried under a vacuum at 60°C for 2 days.

The homopolymer of aniline was also synthesized under experimental conditions identical to the copolymers.

Incorporation of metal ions during polymerization and by batch procedure

The metal ions Cu(II), Ni(II), and Co(II) were incorporated into the polymers synthesized in an acid medium during polymerization and those synthesized in an alkaline medium by the batch method. The base form of copolymers was obtained at room temperature (ca. 20°C), suspended in an aqueous NH_4OH (1 + 1, v/v) solution, and stirred for 24 h. The products were filtered, washed with water, and dried under a vacuum at 60°C until constant weight.

Polymer or copolymer (0.18 g) in 5 mL of HCl (concentrations from 10^{-1} at $10^{-6}\,M$) and 1.31 mmol of metal salt were added into a heterogeneous medium under stirring for 24 h. The products were filtered, washed with HCl of the same concentration, and dried under a vacuum at 60°C for 2 days.

RESULTS AND DISCUSSION

Poly(2-aminobenzoic acid), poly(3-aminobenzoic acid), and copolymers of aniline and 2- and 3-aminobenzoic acid were synthesized according to the following general reactions:
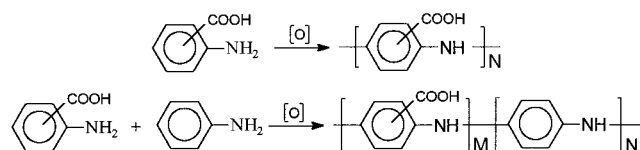
The FTIR spectra of poly(2-aminobenzoic acid) and poly(3-aminobenzoic acid) synthesized in the absence of metal ions in acid and alkaline media are shown in Figure 1.

The FTIR spectra are very similar. The most important absorption bands are 1693 and 1686 (C=O stretching), 1575–1567 (C=C stretching), 1511–1508 (benzenoid ring C=C stretching), and 838–685 cm^{-1} (C—H out of plane bending modes).[11] These results suggest the presence of an emeraldine structure for both homopolymers. Yan et al.[12] had similar observations from X-ray photon spectroscopy for poly(2-aminobenzoic acid).

For the copolymers, the FTIR spectrum for $f_1 = 3$ is shown in Figure 2. The absorption bands vary as 1693
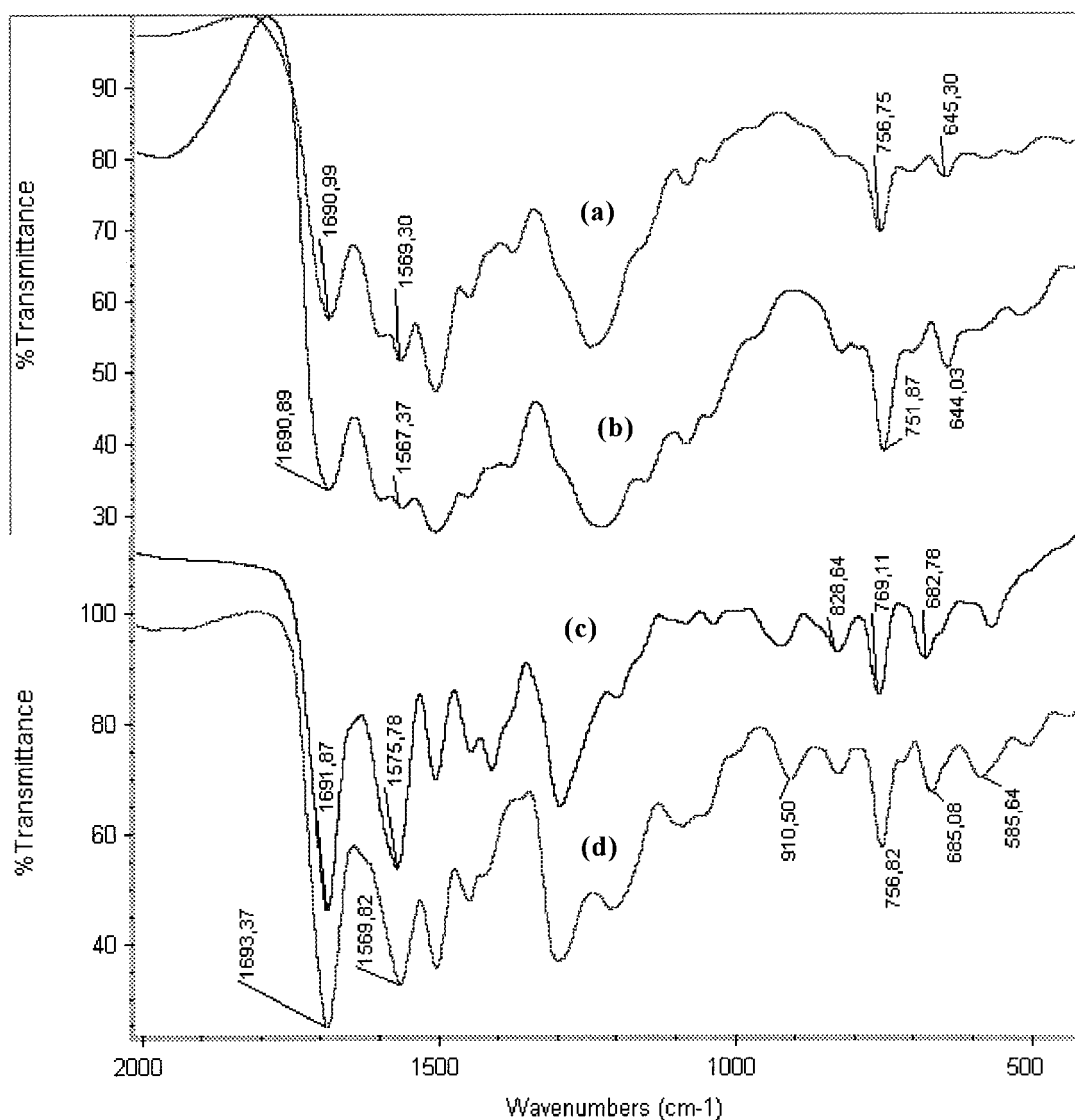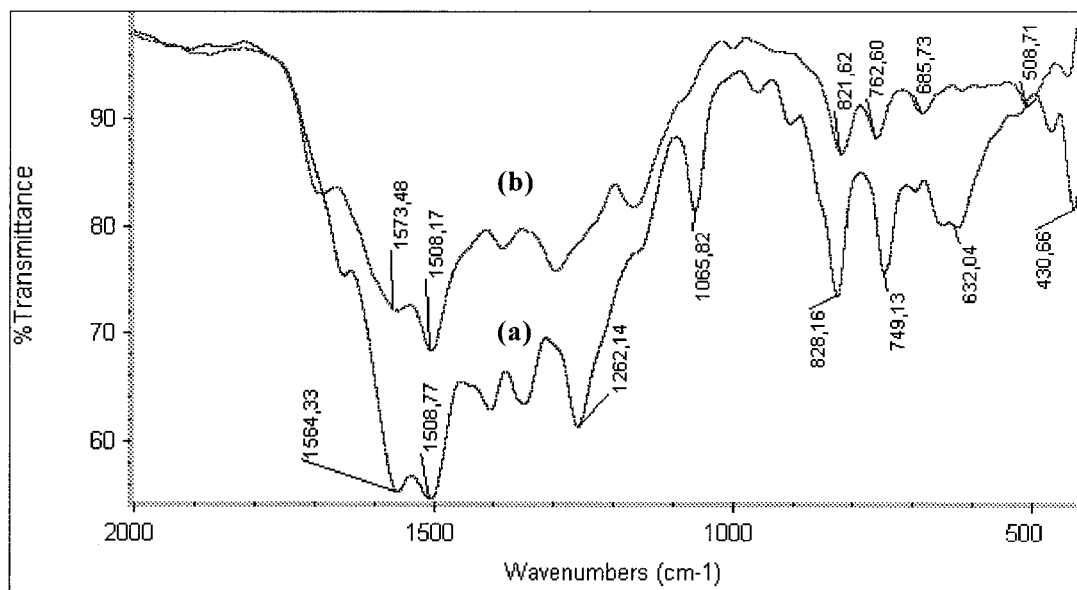
Figure 1 FTIR spectra of poly(2-aminobenzoic acid) synthesized in acid media (spectrum a) and alkaline media (spectrum b) and poly(3-aminobenzoic acid) synthesized in acid media (spectrum c) and alkaline media (spectrum d).

and 1686 (C=O stretching), 1592–1564 (C=C stretching), 1518–1503 (benzenoid ring C=C stretching), and 828–650 cm^{-1} (aromatic ring C—H out of plane bending modes); they are similar to those of the homopolymers of 2- and 3-aminobenzoic acid. The bands at 1693–1686 cm^{-1} that are attributed to the C=O bonds of the copolymer are of lower intensity than those of the homopolymers. All FTIR spectra are similar for both series of copolymers of different f_1 values. The FTIR spectra of the copolymers show an absorption band at 822–828 cm^{-1}, the intensity of which increases as the molal fraction of aniline (f_1) in the feed decreases. This band has been reported[11] as due to the C—H bending modes of the pattern disubstitution of 1,4 aromatic rings in PANI. Hence, this result corroborates the presence of the aniline in the copolymers. The copolymer composition is richest in aniline as the value of f_1 is decreased. This is corroborated by the

color of the copolymers that varies from brown to green (Table I) when f_1 is decreased.

Table II shows the wavelength of maximum absorption (λ_{max}) values of the UV–vis spectra for all the copolymers. Undoped PANI shows two absorption bands at 330 and 635 nm that are attributed to benzenoid (π–π^* transition) and quinoid rings, respectively.[13,14]

The π–π^* transitions are related to the extension of the conjugation along the polymer backbone.[15,16] These bands show a hypsochromic shift from 330 nm for PANI to 267 nm for the copolymers, indicating a decrease in the extension of the conjugation with respect to PANI.[15,16] The UV–vis spectra of both copolymer series are similar. The lower extension of the conjugation is the result of the carboxylic acid groups effect with the increase of the torsion angle between close phenyl rings[15,16] with respect to PANI. This in-

Figure 2 FTIR spectra of poly(2-aminobenzoic acid-*co*-aniline) at $f_1 = 3$ (spectrum a) and poly(3-aminobenzoic acid-*co*-aniline) at $f_1 = 3$ (spectrum b).

crease would produce a different copolymer conformation.

The polymerization of 2-aminobenzoic acid in $1M$ HCl media using ammonium persulfate as an oxidizing agent gave a yield of 15.0% polymer. However, in the presence of metal ions, the yields increased to 31.0, 17.8, and 22.8% for Cu(II), Ni(II), and Co(II), respectively. For the polymerization of 3-aminobenzoic acid in $1M$ HCl, the yield increased only in the presence of Cu(II) ions; the yields were 8.7% in the absence and 15.3% in the presence of Cu(II).

The amount of metal ions incorporated into the polymer during the polymerization varied between 0.01 and 0.4%. The metal ions react as oxidizers and/or catalysts. We reported[17–19] analogous results

for the polymerization of other derivatives such as poly(aminoalcohol), poly(aminophenol)s, and poly-(diaminobenzene) in the presence of metal ions.

To prepare the polymers with a higher content of free functional groups (carboxylate salt) in the absence of metal ions, poly(2-aminobenzoic acid) and poly(3-aminobenzoic acid) were synthesized in an alkaline medium. Then 0.18 g of these powdered polymers was added to 5 mL of HCl of different concentrations that contained 1.31 mmol of metallic salt (batch). The percentages of metal ions in the polymers are shown in Figures 3 and 4.

TABLE I
Yield and Electrical Conductivity of Doped Copolymers of Different Acid/Anitine Mole Ratios (f_1)

| Polymers	(f_1)	Yield (%)	σ (S cm^{-1})	Color of Copolymer
Poly(2-amino benzoic acid-*co*-aniline)	4:1	28.1	$\times 10^{-10}$	Brown
	3:1	42.1	$\times 10^{-8}$	Brown
	2:1	40.1	4×10^{-5}	Brown
	1:1	32.3	7×10^{-3}	Green
	1:3	20.2	3×10^{-3}	Green
Polyaniline	—	75	1×10^{-2}	Green
Poly(3-amino benzoic acid-*co*-aniline)	4:1	40.2	5×10^{-10}	Brown
	3:1	42.0	4×10^{-7}	Brown
	2:1	40.7	7×10^{-4}	Brown
	1:1	35.4	6×10^{-4}	Green
	1:3	20.4	4×10^{-3}	Green

TABLE II
Values of UV–Vis Peaks of Copolymer in Base Form with Dimethylsulfoxide Solvent

Polymer	f_1	Benzenoid	λ_{max} (nm) Quinoid
Poly(2-amino benzoic-*co*-aniline)	4:1[a,b]	286	—
	2:1	326	596
	1:1	317	607
	1:3	331	619
Poly(3-amino benzoic acid-*co*-aniline)	4:1[c]	267	—
	2:1	325	607
	1:1	321	627
	1:3	327	639
Polyaniline	—	330	635

[a] There is a small band at 391 nm.
[b] This polymer is soluble in an alkaline medium, but a small amount of polymer in its base form by undoping was obtained.
[c] There is a small band at 373 nm.
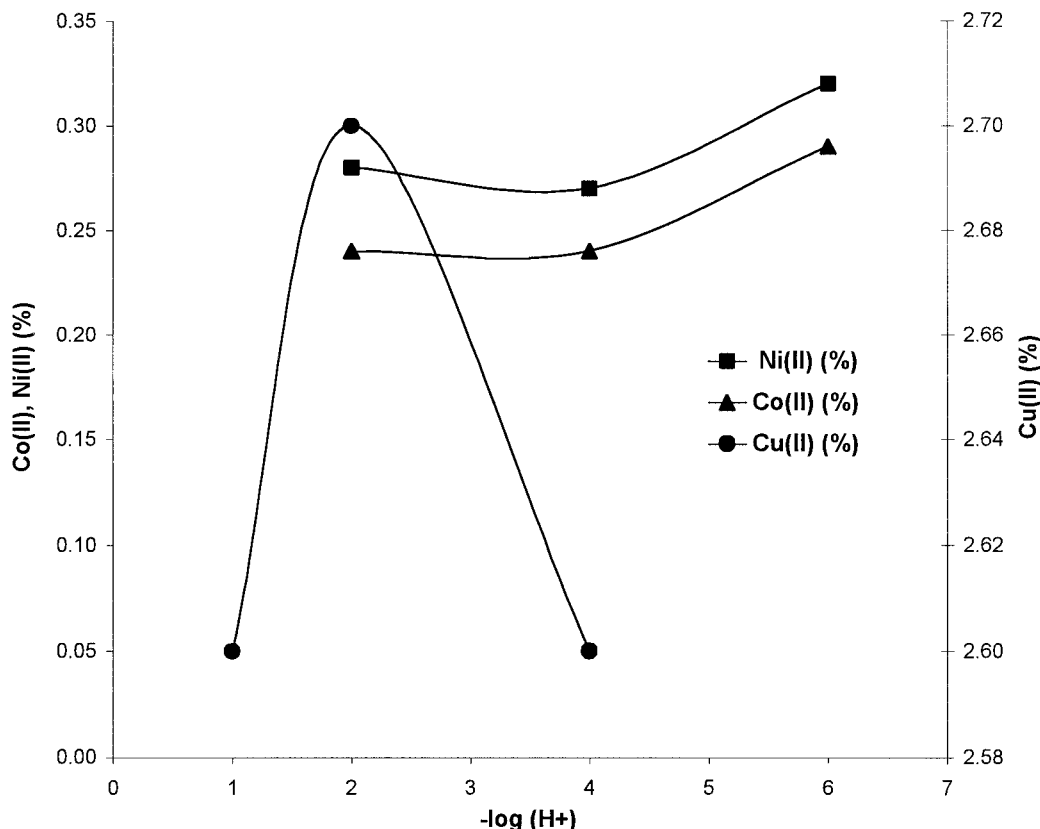
Figure 3 The percentage of metal ions in the poly(2-aminobenzoic acid) synthesized in alkaline media at different concentrations of HCl.

By changing the concentration of HCl used in the batch method from 10^{-6} to 10^{-2} M, the amount of Ni(II) and Co(II) ions in both polymer series was made approximately constant. The Cu(II) ions in poly(2-aminobenzoic acid) are also constant from 10^{-4} to 10^{-1} M of HCl, but for poly(3-aminobenzoic acid) they increased approximately twofold. In general, the incorporation of those metal ions in the homopolymers does not depend on the acid conditions in the batch procedure

The polymerization yield and the electrical conductivity are summarized in Table I. By decreasing the acid/aniline ratio (f_1), the electrical conductivity increases because of the presence of an aniline moiety.

When the f_1 value is higher than 2, the copolymer series are soluble in 12.5% NH_4OH. This could be attributed to the higher content of carboxylic groups. Because of the total solubility of these copolymers, it was possible to obtain their base form (undoped) only for an f_1 value lower that 3. Hence, 0.18 g of copolymers (and PANI) in base form were suspended (by the batch method) in a solution of 10^{-4} M HCl, which contained 1.31 mmol $CuCl_2$ (aqueous 10^{-6} M HCl for $NiCl_2$ and $CoCl_2$), stirred for 24 h; filtered; washed with 10^{-4} or 10^{-6} M HCl (according to the metal ion); and dried until constant weight.

The percentages of metal ions in PANI, the copolymers with different f_1 values, and their electrical conductivities are given in Table III.

The amount of Cu(II), Ni(II), and Co(II) in the copolymers of different f_1 is higher than that of poly(2-aminobenzoic acids) and poly(3-aminobenzoic acids) synthesized in acid and alkaline media. When the f_1 increases, the percentage of Ni(II) and Co(II) increases (Table III). This could be attributed to a higher content of the carboxylic acid groups at the backbone as the f_1 rises. However, for the poly(amino acids), the percentage of these ions is very low (Figs. 3 and 4), which was not expected, indicating that it is difficult to achieve a higher affinity for the metal ions. The amount of Cu(II) ions increases at $f_1 = 2–1$ and then decreases at $f_1 = 1–0.33$. The lowest value corresponds to PANI (2.6%). Moreover, there is a relationship between the torsion angle of adjacent units ($\pi–\pi^*$ transition, Table II) and the amount of Cu(II) ions in the copolymers. When the peak of λ_{max} of the benzenoid ring is shifted to a lower wavelength, the percentage of Cu(II) in the copolymers increases (Tables II and III).

It is possible to attribute the higher polymer metal ion interactions to the carboxylic acid groups. By increasing the presence of aniline, these interactions would be not favored.
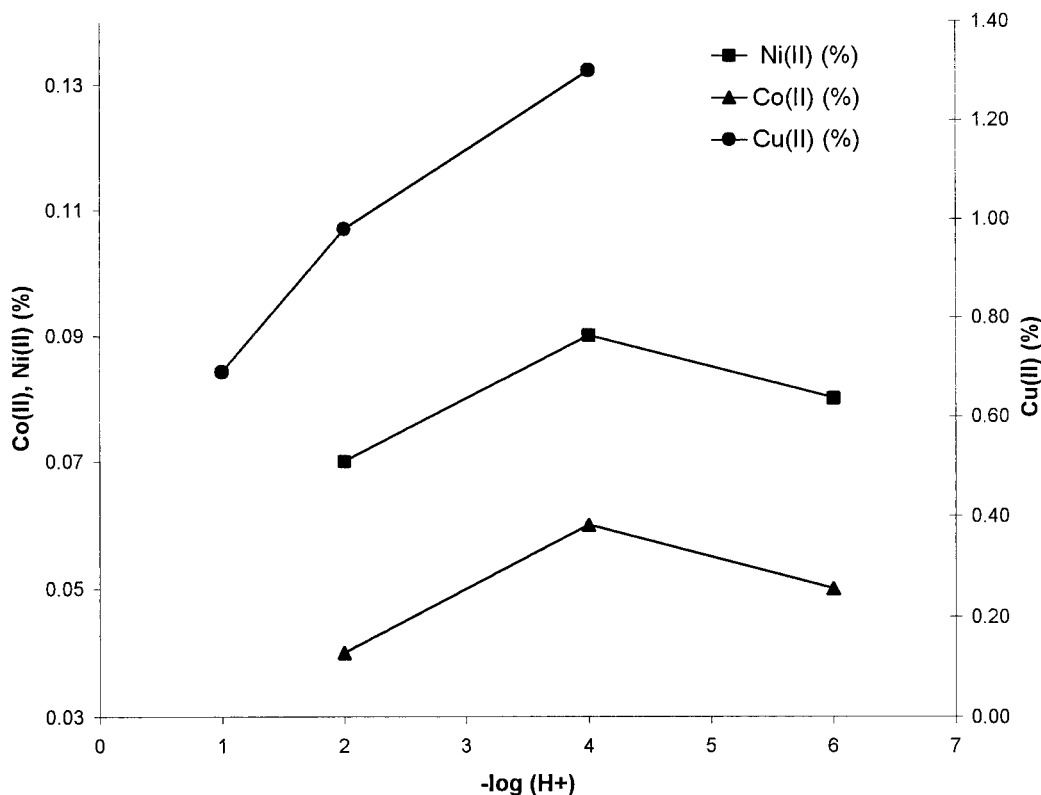
Figure 4 The percentage of metal ions in the poly(3-aminobenzoic acid) synthesized in alkaline media at different concentrations of HCl.

TABLE III
Effect of Concentration of HCl in Batch Procedure on Amount of Metal Ion Retained by Copolymers

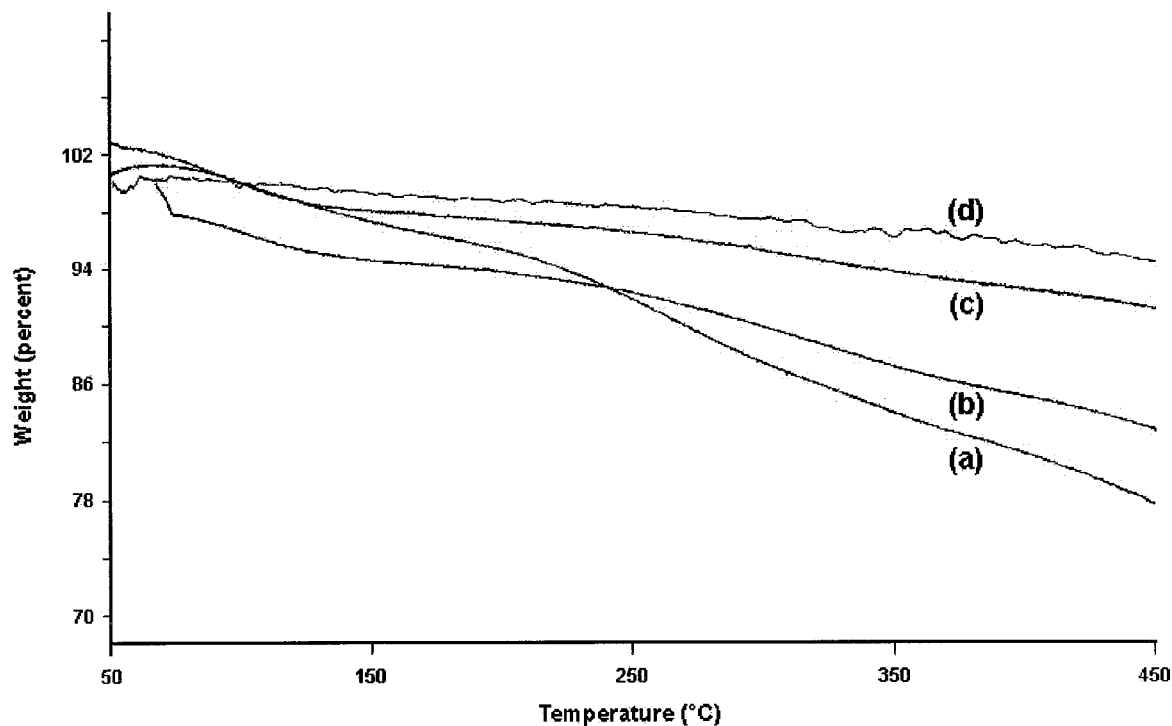| Polymer	f_1	Cu(II) (%)	Ni(II) (%)	Co(II) (%)	Concn of HCl Used $-\log_{10}$	(Sσ cm^{-1})
Poly(2-amino benzoic acid-*co*-aniline)	2:1	6.3	—	—	4	2.5×10^{-8}
		—	1.6	—	6	1.0×10^{-8}
		—	—	2.8	6	2.8×10^{-9}
	1:1	6.9	—	—	4	1.1×10^{-7}
		—	1.3	—	6	7.6×10^{-8}
		—	—	1.5	6	5.6×10^{-9}
	1:3	5.9	—	—	4	9.0×10^{-9}
		—	0.7	—	6	5.8×10^{-9}
		—	—	0.7	6	5.5×10^{-10}
Poly(3-amino benzoic acid-*co*-aniline)	2:1	5.8	—	—	4	9.2×10^{-9}
		—	0.8	—	6	9.9×10^{-9}
		—	—	1.0	6	3.3×10^{-9}
	1:1	6.8	—	—	4	8.0×10^{-10}
		—	0.6	—	6	9.2×10^{-10}
		—	—	0.8	6	5.0×10^{-10}
	1:3	4.8	—	—	4	6.4×10^{-9}
		—	0.5	—	6	5.3×10^{-10}
		—	—	0.5	6	5.1×10^{-10}
Polyaniline	—	2.6	—	—	4	11.3×10^{-9}
		—	0.6	—	6	5.6×10^{-10}
		—	—	0.5	6	4.2×10^{-10}

Figure 5 The thermal stability of the base form of poly(2-aminobenzoic acid-*co*-aniline) with feed molal ratios (f_1) of aniline of 2 (spectrum a), 1 (spectrum b), and 0.33 (spectrum c); and polyaniline (spectrum d).

Regarding the electrical conductivity, no important changes are observed with the incorporation of the metal ion. The electrical conductivity values are close to 10^{-8} –10^{-10} S cm^{-1}, which is similar to the base form of the copolymer (10^{-10} S cm^{-1}).

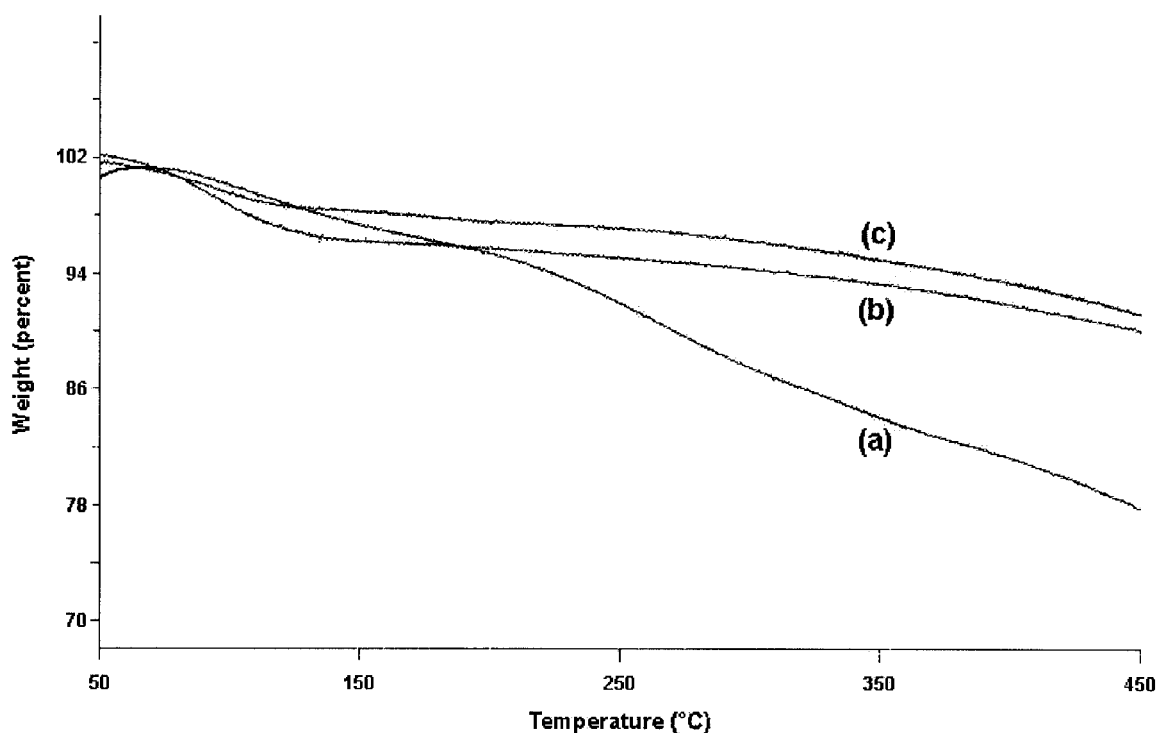Figures 5 and 6 show the thermal stability of the

Figure 6 The thermal stability of the base form of poly(3-aminobenzoic acid-*co*-aniline) with feed molal ratios (f_1) of 2 (spectrum a), 1 (spectrum b), and 0.33 (spectrum c).

copolymers with different f_1 values. Decreasing f_1 causes a tendency to increase the thermal stability in both copolymer series. This is attributed to the higher content in the aniline units (Fig. 5, spectrum d). In both copolymer series with $f_1 = 2$, there is a decrease of the thermal stability at approximately 200–250°C. Moreover, for the same f_1 value, poly(3-aminobenzoic acid-*co*-aniline) has higher stability than poly(2-aminobenzoic acid-*co*-aniline), except for $f_1 = 2$.

CONCLUSIONS

2-Aminobenzoic and 3-aminobenzoic acids can be homo- and copolymerized with aniline by chemical oxidation using ammoniun persulfate as the oxidizing reagent. The copolymers incorporated a higher amount of metal ions than the homopolymers. By varying the comonomer fraction in the feed, it was possible to obtain soluble products in alkaline media with a wide range of electrical conductivities (10^{-3}– 10^{-10} S cm^{-1}), and higher thermal stability.

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