

Electrical Conductivity and Thermal Properties of Poly(*m*-aminophenyl acetic acid) and Its Copolymers with Aniline

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ABSTRACT: Poly(*m*-aminophenyl acetic acid) was synthesized under different conditions from the respective monomer, using ammonium persulfate as oxidizing agent in both the presence and the absence of CuCl₂ in HCl(aq). Moreover, the copolymers between aniline and *m*-aminophenyl acetic acid were prepared at several feed mol ratios (f_1) of aniline. Copper was introduced by the Batch method in the homo- and copolymers of different compositions. The polymers were characterized by FTIR and UV-vis spectroscopy, elemental analysis, thermal analysis, and electrical conductivity. The thermal stability and the content of copper

increased as the content of aniline was increased in the copolymers. Moreover, the copolymers showed a high thermal stability; at 400°C a weight loss < 10% was observed. The electrical conductivity was increased with a higher content of aniline in the copolymers, achieving semiconduction values. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1484–1492, 2003

Key words: thermal properties; conducting polymers; UV-vis spectroscopy

INTRODUCTION

Conducting polymers are very interesting materials because of their wide variety of potential applications. However, an understanding of the factors that control the electrochemical charging and discharging processes is really necessary for this purpose.

Among the family of electrically conductive conjugated materials, polyaniline (Pani) has always been at the forefront of interdisciplinary research because of its unique reversible protonic dopability, excellent redox recyclability, chemical and environmental stability, low cost, and easy preparation.¹ These properties have made Pani attractive for applications in electronic display devices, microelectronics, batteries, and electrode materials.^{2–5}

Transition metal dispersed into modified polymer electrodes recently has been recognized to possess potential applications in electrocatalysis. Electrodeposition of platinum into Pani films with electrocatalytic applications in the oxidation of methanol has been reported.⁶ Pani–Co(II) acetate catalyzes the oxidation of different alkenes in the presence of molecular oxygen.^{7,8} Moreover, metal microparticles dispersed in the polymer on glassy carbon electrodes were previ-

ously described as amperometric sensors in acidic and neutral media.^{9–12}

The incorporation of transition-metal cations into conducting organic polymers is difficult because of the repulsive nature of the positive-cation radicals of the polymers. One way to incorporate the metal cations into polymers has been the functionalization by metallic complexes of the bipyridyl type,^{13–15} porphyrins,^{16,17} tetraazaannulene,^{18,19} metallated cyclam,^{20,21} phthalocyanine,^{22,23} and phenanthroline.²⁴ These ligands are difficult to synthesize and require multistep synthesis. If the monomers are functionalized by small-size donor groups, the resultant polymer would be able to interact with the metal ions.

The aim of this paper was to synthesize, characterize, and study the preliminary properties of poly(*m*-aminophenyl acetic acid) and its copolymers with aniline. It would be expected that the copolymers would improve the properties of the polymeric materials with respect to both homopolymers. These materials can entrap different amounts of Cu(II) ions. The effect of the polymer composition on the incorporation of Cu(II), electrical conductivity, and thermal behavior were also investigated.

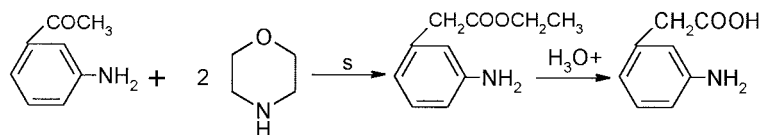
EXPERIMENTAL

Reagents

The metal salt CuCl₂·2H₂O, analytical grade, was obtained from Merck (Darmstadt, Germany). The aniline (Aldrich, Milwaukee, WI) was purified by distillation under vacuum. *m*-Aminoacetophenone (90%) and

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Scheme 1

morpholine (99%) were obtained from Merck and used without further purification.

Elemental analysis of C, H, N, and S was performed in a Fisons elemental analyzer EA-1108 (USA). FTIR spectra were obtained from KBr pellets on a Magna Nicolet 550 spectrophotometer (Nicolet Instruments, Madison, WI). UV-vis spectra were recorded in a Perkin-Elmer UV/Vis spectrometer Lambda 11 (Perkin Elmer Cetus Instruments, Norwalk, CT), in 1-cm cells using DMSO as solvent.

The quantification (wt %) of copper incorporated into the polymers was done by calcinating the solid sample, solubilizing with HNO_3 , and determining the metal concentration using a Unicam Solar M series atomic absorption spectrometer (UK). The amount (wt %) of total chloride in the polymers was determined by the standard method by combustion of the polymer in a closed flask in the presence of oxygen and a solution of H_2O_2 with 0.1M NaOH. Then, the total chloride was determined by volumetric analysis using HgCl_2 as titration agent and diphenylcarbazone as indicator. Electrical conductivity was measured on an Elchema electrometer (USA), using pellets and the four-probe method. Pellets were obtained by pressing the finely ground polymer at about 24,000 psi.

Thermograms were recorded under nitrogen with an STA 625 thermal analyzer (Polymer Laboratories, Poole, UK). The incorporation of copper to the undoped polymer was determined by the Batch method: 0.18 g of polymer powder was suspended in 0.12 g $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ dissolved in 5 mL of 10^{-4} M HCl. The mixture of the reaction was maintained under stirring for 3 days at room temperature, filtered through a Büchner funnel, and washed with 10^{-4} M HCl. These samples were dried under vacuum at 60°C for 2 days.

The copolymers were undoped by suspension of dusted polymer and added to an aqueous solution of NH_4OH (2 + 1, v/v, $\text{NH}_4\text{OH}/\text{H}_2\text{O}$), then stirred for 48 h, filtered, and washed with abundant water. The polymers were dried under vacuum for 2 days at 60°C .

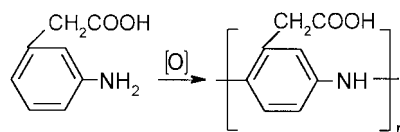
Synthesis of *m*-aminophenyl acetic acid

This monomer was synthesized according to King et al.²⁵, with some modifications. This reaction is shown in Scheme 1.

A mixture of *m*-aminoacetophenone (20.25 g, 0.150 mol), sulfur in powder (12.0 g, 0.374 mol), and mor-

pholine (26.1 g, 0.300 mol) were refluxed for 2 h. The mixture was cooled at room temperature and CHCl_3 was added to attain a volume of 300 mL. Each 100 mL of CHCl_3 was washed twice with 25 mL of water. The portions of CHCl_3 were collected and then removed under vacuum by rotatory vapor. The residue was refluxed for 4 h with a mixture of 100 mL HCl (fuming) and 20 mL HCl (37%). The mixture was cooled at room temperature and then filtered. The filtrate was completely dried under high vacuum (temperature bath: 85°C). The residue was kept for 1 day, then 80–90 mL KOH (35%) was slowly added (pH = 13–14). The solution was filtered and the liquid was again completely dried at high vacuum (temperature of bath: $85\text{--}95^\circ\text{C}$). An excess (pH = 1–2) of HCl (37%) was added and the mixture was completely dried for a third time under high vacuum (temperature of bath: $75\text{--}80^\circ\text{C}$), then the residue (*m*-aminophenyl acetate hydrochloride) was added to boiling ethanol in small portions to attain a total volume of 150 mL. The alcoholic extract was kept for 3 days, then heated at reflux for 30 min, and the alcohol was removed at high vacuum (temperature of bath $\leq 70^\circ\text{C}$) to complete dryness, yielding a residue of 20.7 g of semisolid mass. This residue was refluxed for 0.5 h with 41 mL 37% HCl and the liquid removed at high vacuum (temperature of bath $\leq 85^\circ\text{C}$), yielding 25.6 g (91.3%) of impure *m*-aminophenyl acetic acid hydrochloride [mp = 165°C (dec)]. A 25.6-g sample of this compound was added to 4.91 g NaOH (0.9 eq) dissolved in 138 mL water, then heated with active carbon at $75\text{--}80^\circ\text{C}$, and then hot-filtered. The mixture was kept 1 day and the supernatant liquid was concentrated at high vacuum (temperature of bath $\leq 80^\circ\text{C}$) up to half of the volume, then cooled at room temperature and filtered. The solid was dried under vacuum for 1 day at 50°C . *m*-Aminophenyl acetic acid [yield: 6.5 g (29%), brown color, mp = $142\text{--}143^\circ\text{C}$] was obtained.

$^1\text{H-NMR}$ (250 MHz, $\text{DMSO-}d_6$): 7.05 ppm (1H, t); 6.59 ppm (1H, s); 6.57 ppm (2H, 2d); 4.31 ppm (NH, broad); 3.47 ppm (2H, 1s, methylene).



Scheme 2

TABLE I
Poly(*m*-aminophenyl acetic acid) Synthesized under Different Conditions

Sample	Oxidizing agent ^a	Concentration of monomer (m)	[HCl] (M)	Time of reaction (h)	Temperature (°C)	Cu(II) in the polymer (%)	Yield (%)
1	P	0.37	1	18.5	16	—	10.2
2	P + Cu(II)	0.37	1	18.5	16	0.18	32.7
3	Cu(II)	0.74	1	96.0	50	—	3.0
4	P	0.37	1	18.5	50	—	23.2
5	P	0.37	1	18.5	70	—	21.1
6	P + Cu(II)	0.37	1	18.5	50	0.51	33.0
7	P + Cu(II)	0.37	1	18.5	70	0.42	31.9
8	P	0.15	1	18.5	50	—	5.1
9	P	0.08	1	18.5	50	—	<1
10	P	0.15	10 ⁻³	18.5	50	—	22.0
11	P + Cu(II)	0.15	10 ⁻³	18.5	50	1.9	20.9

^a P, Synthesized in the presence of ammonium persulfate; P + Cu(II), synthesized in the presence of ammonium persulfate and CuCl₂.

Synthesis of poly(*m*-aminophenyl acetic acid) with ammonium persulfate

m-Aminophenyl acetic acid (1.0 g, 6.62 mmol) was dissolved in 13.3 mL 1M HCl; then 1.51 g (6.62 mmol) ammonium persulfate, dissolved in 4.7 mL 1M HCl, was added to the monomer solution. The mixture was then stirred for 18.5 h at 15–16°C, filtered, and washed with 1M HCl. The polymer was dried at 60°C under vacuum.

Synthesis of poly(*m*-aminophenyl acetic acid) with ammonium persulfate in the presence of CuCl₂

m-Aminophenyl acetic acid (0.30 g, 2.0 mmol) was dissolved in 4.0 mL 1M HCl, after which 0.677 g (4.0 mmol) CuCl₂·2H₂O was added and 0.459 g (2.0 mmol) of ammonium persulfate was dissolved in 1.4 mL 1M HCl. The reaction mixture was stirred at 15–16°C for 18.5 h, after which it was filtered and washed with 1M HCl. The polymer was dried at 60°C for 2 days under vacuum.

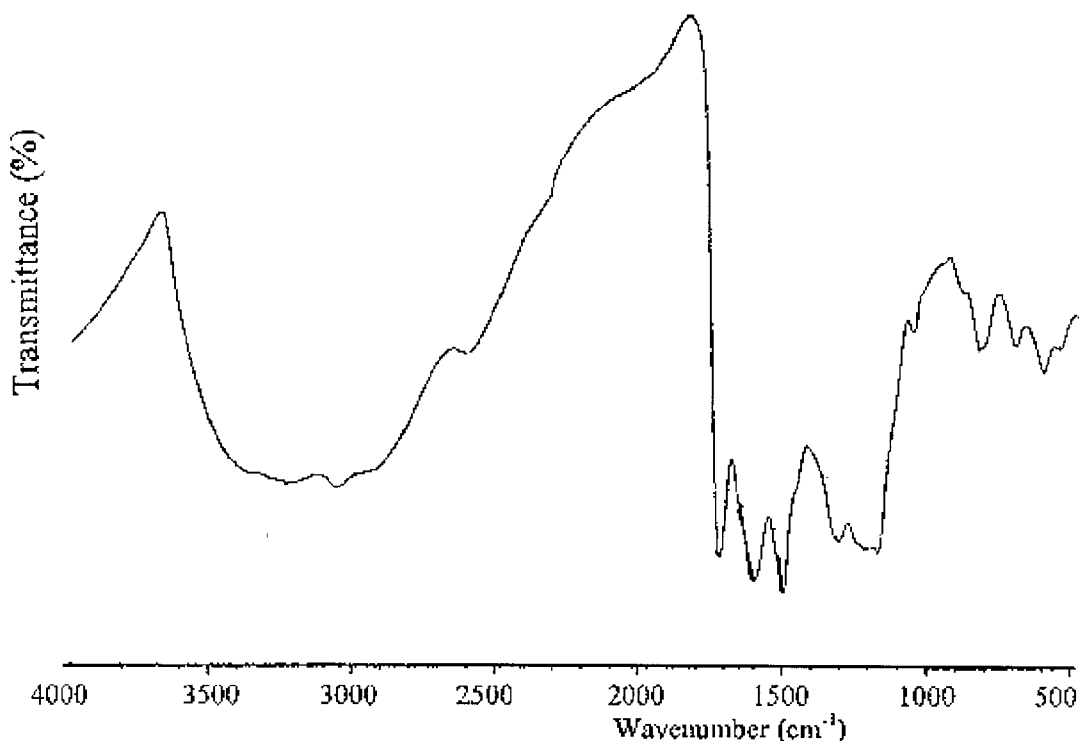
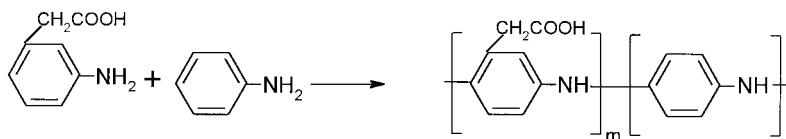


Figure 1 FTIR spectrum of poly(*m*-aminophenyl acetic acid) synthesized in 1M HCl (sample 1).



Scheme 3

Synthesis of poly(*m*-aminophenyl acetic acid) with CuCl_2

m-Aminophenyl acetic acid (0.40 g, 2.6 mmol) was dissolved in 2.3 mL 1M HCl and heated at 50°C; then 1.35 g (7.9 mmol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in hot 1 mL 1M HCl. The mixture reaction was maintained under stirring for 96 h at 50°C, then hot-filtered through a Büchner funnel and washed with 1M HCl. The polymer was dried under vacuum at 60°C for 2 days.

Synthesis of copolymers with ammonium persulfate

The copolymers of aniline with *m*-aminophenyl acetic acid were prepared by chemical oxidation of aniline and *m*-aminophenyl acetic acid at several feed mol ratios of aniline (f_1) using ammonium persulfate as oxidizing agent in 1M HCl. The procedure was as follows: an equimolar *m*-aminophenyl acetic acid/aniline mixture ($f_1 = 0.5$) was prepared by dissolving 0.7 g (4.6 mmol) of *m*-aminophenyl acetic acid and 0.86 g (9.2 mmol) of aniline in 9.3 mL of 1M HCl and maintained at 15–16°C in a water bath. Ammonium persulfate (1.06 g, 4.6 mmol) was dissolved in 3.3 mL of 1M HCl, then added to the comonomer solution. The mixture reaction was maintained under stirring at 15–16°C for 18.5 h and then filtered through a Büchner funnel, washed with 1M HCl, and dried under vacuum at 60°C for 2 days.

In all the reactions of copolymerization, an equimolar ratio of *m*-aminophenyl acetic acid/ammonium persulfate was used.

RESULTS AND DISCUSSION

Polymers were prepared with ammonium persulfate in both the presence and the absence of CuCl_2 , according to Scheme 2.

Table I shows the experimental conditions of the synthesis of poly(*m*-aminophenyl acetic acid).

The yield of poly(*m*-aminophenyl acetic acid) synthesized with ammonium persulfate in 1M HCl (sample 1) was 10.2%. However, in the presence of Cu(II), there was an important increase of the yield (32.7%, sample 2). When the polymer was synthesized with only Cu(II), in the absence of ammonium persulfate but increasing the concentration of monomer, temperature, and time of reaction, a low yield (3%) was observed (sample 3). Therefore, this ion acts as a catalyst, but not as an oxidizing agent. When the polymer was synthesized with ammonium persulfate in the presence of Cu(II), this catalytic effect was not detected because of the decrease of the concentration of the acid (samples 10 and 11). If polymerization was carried out with ammonium persulfate, the temperature was increased from 16 to 70°C (samples 1, 4, and 5) and an increase of the yield (10.2–23.2%) was observed. If the reaction was carried out under more dilute conditions (samples 4, 8, and 9), the yield sharply decreased. We previously reported^{26,27} this phenomena of catalysis with copper, nickel, and cobalt for other derivatives of polyaniline, such as poly(aminophenols), poly(diamines), and poly(amino acids).

Figure 1 shows the FTIR spectrum of sample 1. The spectra of samples 2–11 are very similar. The most important bands (in cm^{-1}) attributed to the polymers were placed as follows: 3216 (N—H stretching); 3056 (aromatic C—H stretching); 1715 (C=O stretching); 1596 (quinoid ring C=N and C=C stretching); 1494 (benzenoid ring C=C stretching); 1204 (C—O stretching); 816–693 (aromatic C—H bending).

The copolymers were prepared according to Scheme 3 in 1M HCl using ammonium persulfate as oxidizing agent.

Table II shows the *m*-aminophenyl acetic acid/aniline ratios in the feed (f_1), the copolymer composition

TABLE II
Electrical Conductivity of Doped Polymers and Their Copolymer Compositions (F_1)

Polymer sample	Feed mol ratio of aniline (f_1)	F_1	Electrical conductivity, σ (S cm^{-1})
Homopolymer (sample 1)	—	—	8.5×10^{-10}
Copolymer	2 : 1	1.41	2.6×10^{-8}
Copolymer	1 : 1	0.78	1.0×10^{-8}
Copolymer	1 : 2	0.37	9.2×10^{-5}
Copolymer	1 : 4	0.20	3.3×10^{-3}

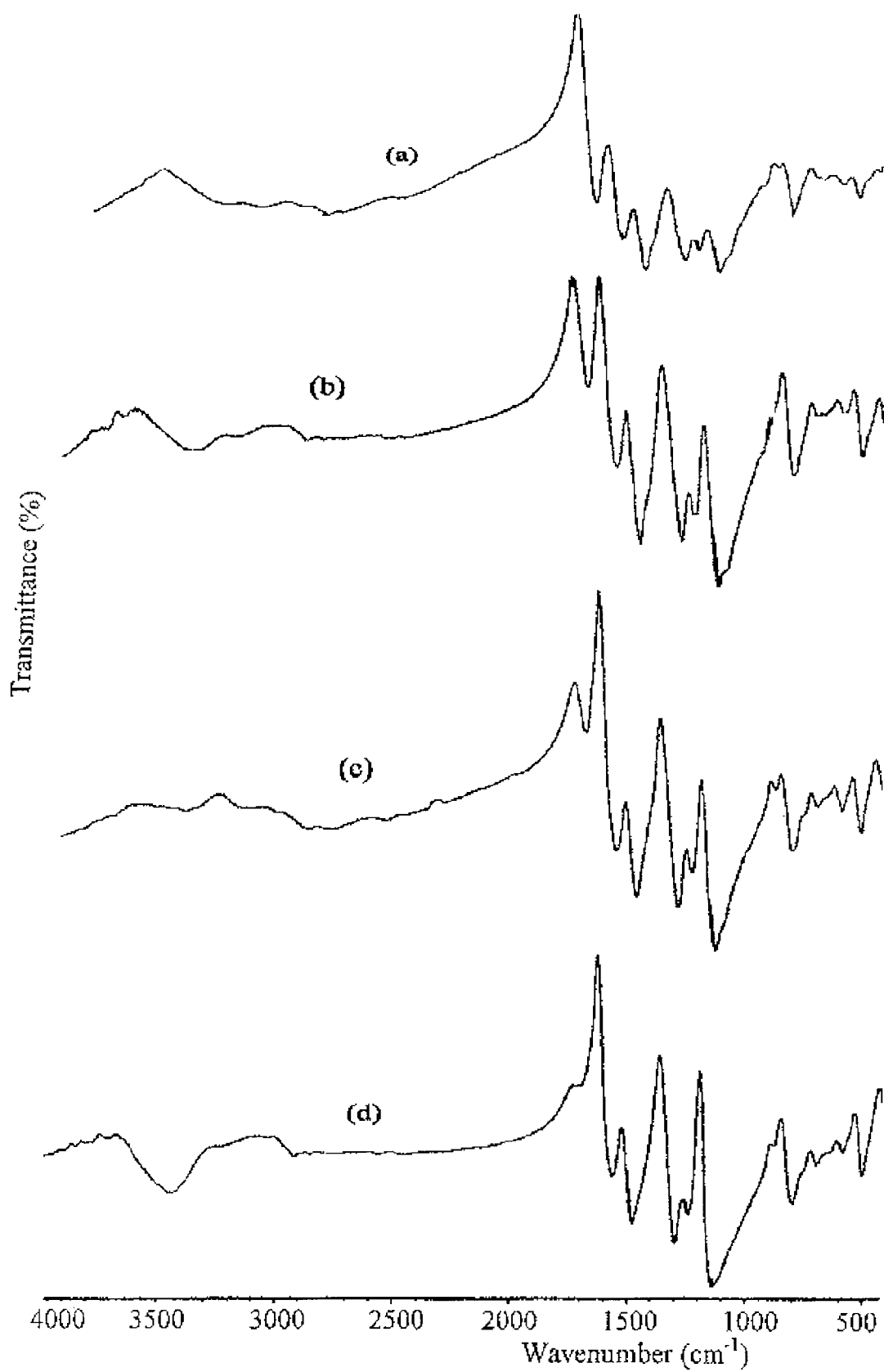


Figure 2 FTIR spectra of copolymers of different compositions: (a) $F_1 = 1.41$, (b) $F_1 = 0.78$, (c) $F_1 = 0.37$, (d) $F_1 = 0.20$.

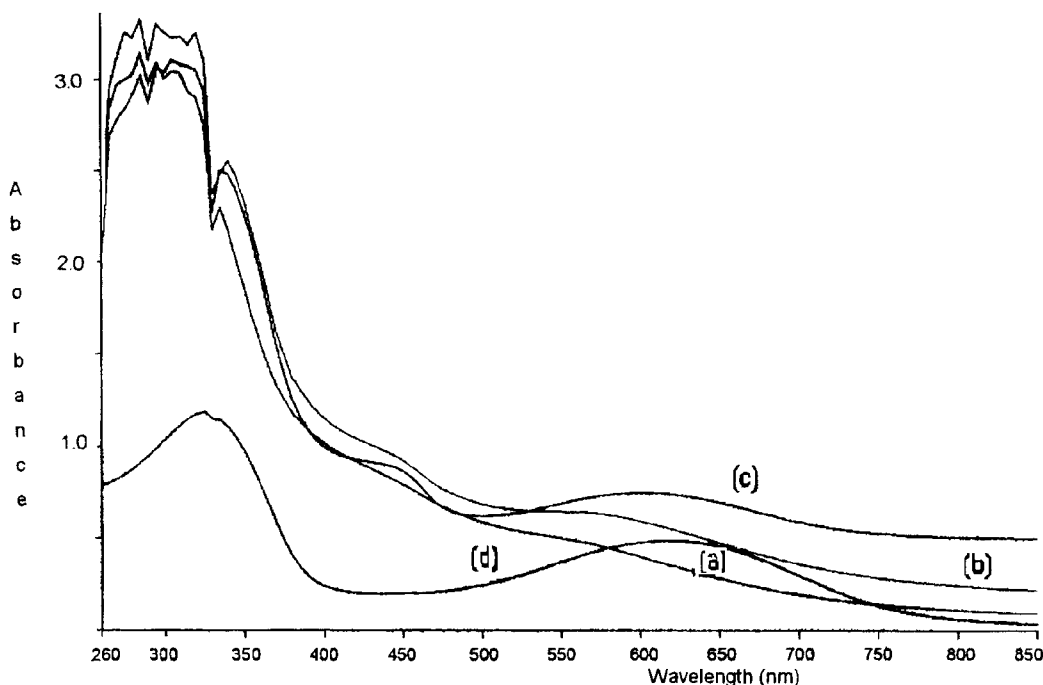


Figure 3 UV-vis spectra of undoped copolymers of different copolymer compositions: (a) $F_1 = 1.41$; (b) $F_1 = 0.78$; (c) $F_1 = 0.37$; (d) $F_1 = 0.20$.

(F_1), and the electrical conductivity of polymers. The composition of copolymers was determined by elemental analysis. F_1 values are lower than those of f_1 .

By increasing the content of aniline in the copolymer, the electrical conductivity increases. This could be attributed to a block of aniline units, which contributes to an increase in electrical conductivity. The effect of *m*-aminophenyl acetic acid units should be lower in the copolymers. The homopolymer (sample 1) has a low electrical conductivity value.

The FTIR spectra of copolymers between *m*-aminophenyl acetic acid and aniline are shown in Figure 2, where one notes a similarity in the spectra. As the composition with aniline in the copolymers increased, the band attributed to C=O decreased. The structures were corroborated by UV-vis spectroscopy. The lower bands at 350 nm are attributed to $\pi-\pi^*$ transitions, and the visible region is attributed to the quinoid

groups. The intensity of the band increases by decreasing f_1 or F_1 (see Fig. 3). The spectrum of Figure 3(d) is typical of polyaniline.

According to the doping level (see Table III), the homopolymer (sample 1) and the copolymers with F_1 values of 1.41 and 0.78 have the same doping value. Therefore, the low conductivity value is attributed to the small units of quinoid groups, which was corroborated by the low intensity of the bands in the visible region (see Fig. 3). On the contrary, the higher intensity of the quinoid groups, attributed to the higher content of the aniline moiety, was observed for the copolymers with F_1 values of 0.37 and 0.20, showing a higher level of doping and conductivity.

Poly(*m*-aminophenyl acetic acid) (sample 1) and its undoped copolymers were treated with Cu(II) by the Batch method, using a suspension of the dusted polymer with an aqueous solution of CuCl_2 in 10^{-4} M HCl.

TABLE III
Doping Level and Empirical Formula of Polymers

F_1	Empirical formula ^{a,b}	Level of doping Cl^-/N	Level of doping HSO_4^-/N
1.00 (homopolymer sample 1)	$\text{C}_{8.00}\text{H}_{5.76}\text{N}_{1.05}\text{O}_{2.93}(\text{HSO}_4^-)_{0.25}(\text{HCl})_{0.34}$	0.32	0.24
1.41	$\text{C}_{20}\text{H}_{9.63}\text{N}_{2.79}\text{O}_{3.26}(\text{HCl})_{0.91}$	0.33	0
0.78	$\text{C}_{20}\text{H}_{10.87}\text{N}_{2.91}\text{O}_{2.55}(\text{HCl})_{0.93}$	0.32	0
0.37	$\text{C}_{20}\text{H}_{12.92}\text{N}_{3.06}\text{O}_{1.66}(\text{HSO}_4^-)_{0.21}(\text{HCl})_{1.13}$	0.37	0.07
0.20	$\text{C}_{20}\text{H}_{14.0}\text{N}_{3.16}\text{O}_{1.04}(\text{HSO}_4^-)_{0.06}(\text{HCl})_{1.20}$	0.38	0.02

^a HSO_4^- was determined by elemental analysis of sulfur, and HCl by total analysis of chloride.

^b Oxygen was determined by the difference in total % of elemental analysis.

TABLE IV
Content (%) of Cu(II) in the Polymer

Polymer	F_1	Cu(II) in the polymer (%)
Homopolymer (sample 1)	—	1.91
Copolymer	1.41	2.86
Copolymer	0.78	3.74
Copolymer	0.37	4.66
Copolymer	0.20	5.38

As the content of aniline increased, the incorporation of Cu(II) in the copolymers (see Table IV) also increased; aniline units in the copolymer would then favor the interactions with this metal ion.

According to Tables I and IV, it is possible to incorporate a higher content of copper ions by the Batch method than by polymerization in the presence of this ion, given that the oxidative mechanism hinders the affinity by this ion. However, it is possible to increase

the yield if the polymer is synthesized in the presence of such a metal ion.

The thermal stability for the undoped copolymers is shown in Figure 4. The thermograms of copolymers with F_1 values of 1.41 and 0.78 overlap and show a weight loss of 10% at 300°C. For the copolymers with a composition of $F_1 \leq 0.37$, the thermal stability increased and both undoped copolymers show a weight loss of 10% at 380°C (see Fig. 4). For the copolymer with $F_1 = 0.20$, the thermal stability has a sharp decrease at about 400°C. The undoped copolymer with $F_1 = 0.37$ shows the highest thermal stability.

If these same undoped copolymers contain Cu(II), the thermal stability changes slightly at higher temperature. The copolymers with F_1 values of 0.78 and 0.37 show a weight loss of 10% at 350 and 450°C, respectively. Meanwhile, copolymers with F_1 values of 1.41 and 0.33 show a thermal behavior similar to that of copolymers with copper. The copolymer with $F_1 = 0.20$, with Cu(II), is more stable above 340°C (see Fig. 5).

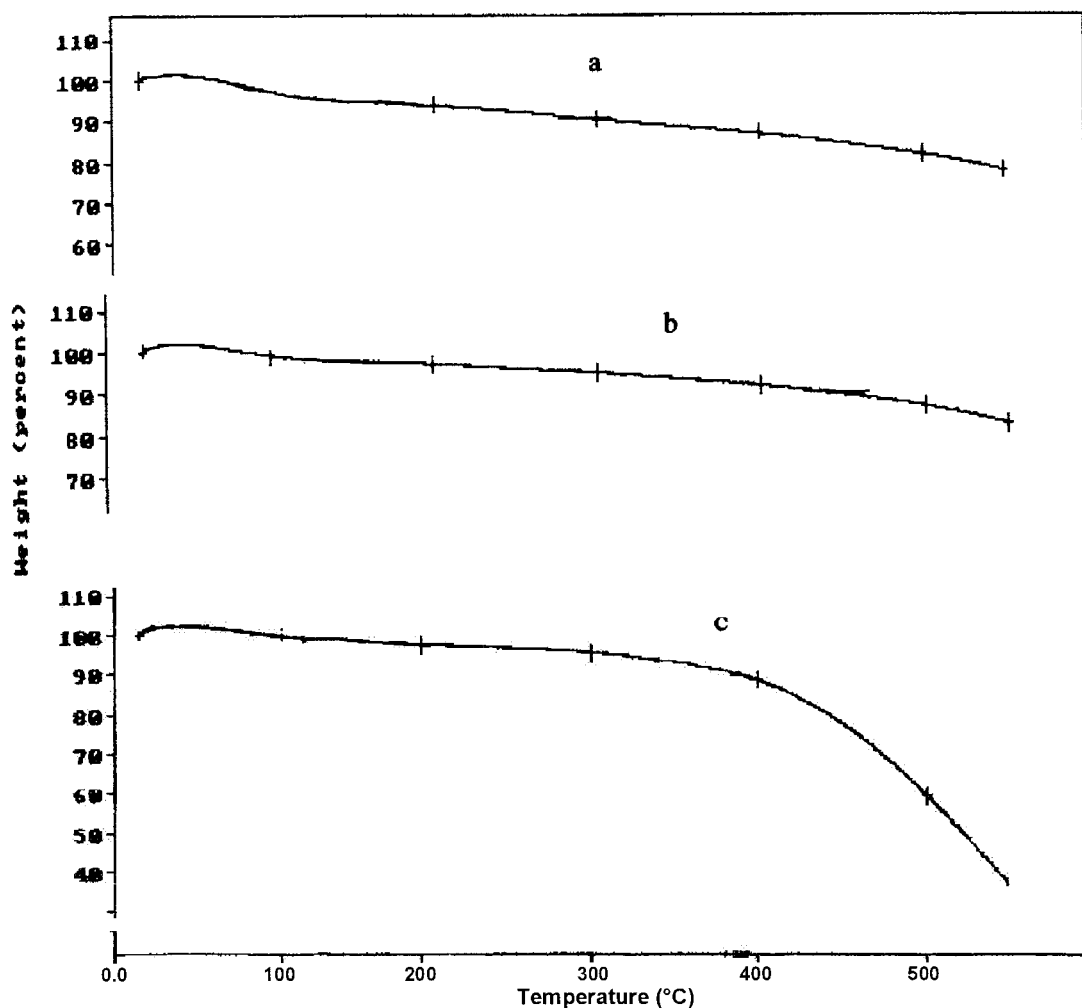


Figure 4 Thermal behavior of undoped copolymers: (a) $F_1 = 1.41$; (b) $F_1 = 0.37$; (c) $F_1 = 0.20$.

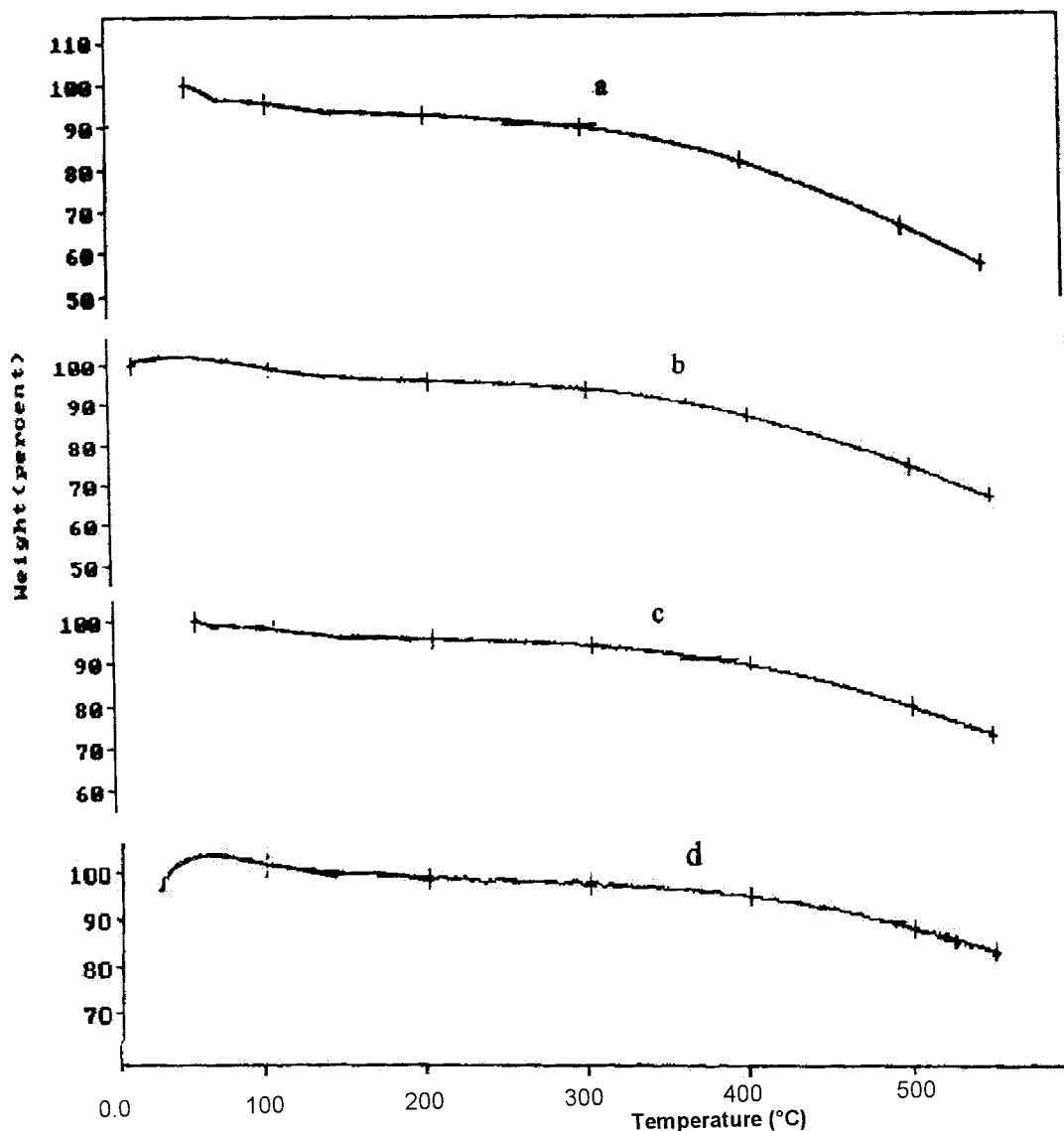


Figure 5 Thermal behavior of copolymers with Cu(II): (a) $F_1 = 1.41$, (b) $F_1 = 0.78$, (c) $F_1 = 0.37$; (d) $F_1 = 0.20$.

The doped copolymers with F_1 values of 1.41 and 0.37 show a thermal stability similar to that of the copolymer with $F_1 = 0.78$, but the doped copolymer of composition $F_1 = 0.20$ shows a higher stability at about 300°C compared to that of copolymers with a lower composition of acid comonomer (see Fig. 6).

Homopolymer (sample 1) is the least stable doped polymer and has a weight loss of 10% at about 180°C, which may be attributed to the undoping of acid or to the aniline chains that stabilize the structures of the copolymers.

CONCLUSIONS

Poly(*m*-aminophenyl acetic acid) and its copolymers with aniline were synthesized in 1M HCl, using am-

monium persulfate as oxidizing agent. The amount of copper, electrical conductivity, and thermal stability increased by increasing the content of aniline in the copolymer. The amount of copper in the copolymer was higher than that in the homopolymer. The incorporation of copper ion by the Batch method in the polymer was higher than its incorporation by the polymerization method, thus obtaining new hybrid materials. The copolymer with a copolymer composition of $F_1 = 0.20$ shows the highest electrical conductivity value, $\sigma = 3.3 \times 10^{-3}$ (S cm⁻¹), which corresponds to a semiconduction range.

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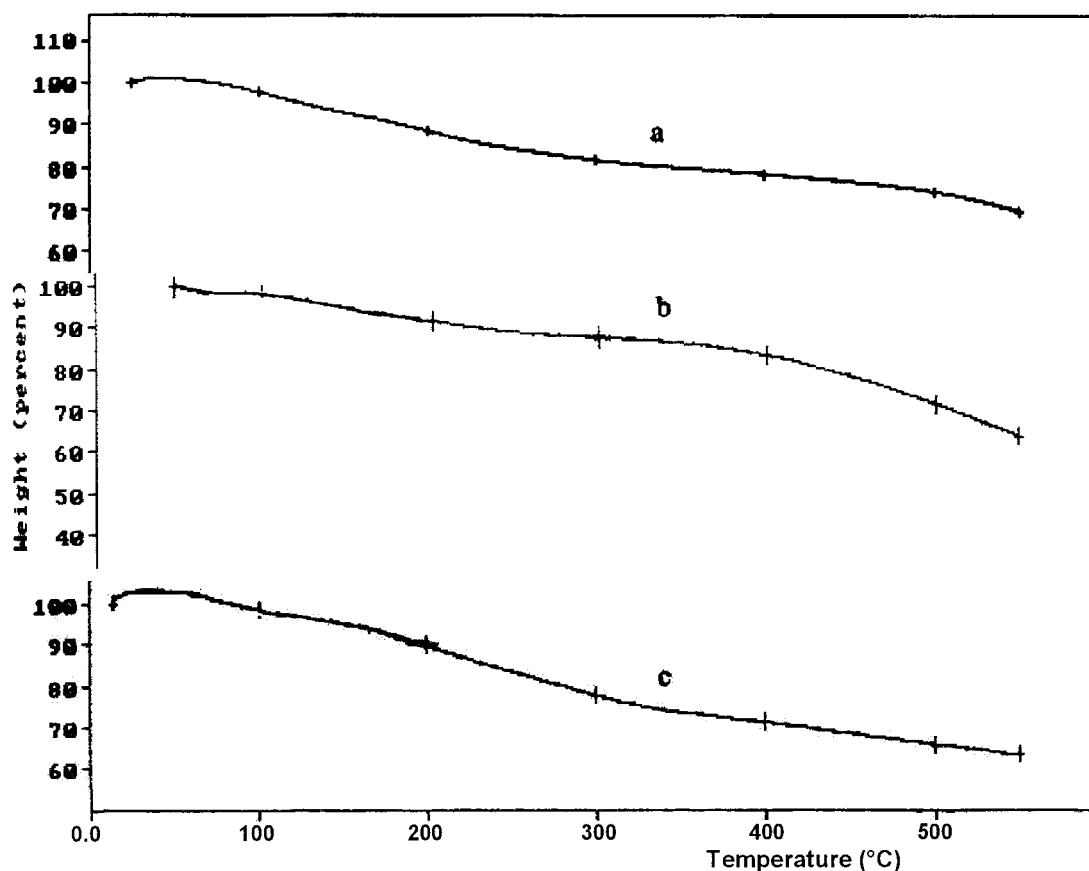


Figure 6 Thermal stability of homopolymers and doped copolymers: (a) $F_1 = 0.78$; (b) $F_1 = 0.20$; (c) homopolymer (sample 1).

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