Synthesis, Characterization, and Properties of Poly-(*m*-aminophenyl propionic acid) and Its Copolymers with Aniline

B. L. Rivas,[1] C. O. Sánchez,[1] J.-C. Bernede,[2] L. Basaez[3]

[1]*Department of Polymers, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile*
[2]*Equipe Couches Minces et Materiaux Nouveaux, FSTN, Faculté des Sciences et des Techniques de Nantes, 2 rue de la Houssiniere, BP 92208, F-44322 Nantes Cedex 3, France*
[3]*Department of Analytical and Inorganic Chemistry, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile*

ABSTRACT: The synthesis of poly(*m*-aminophenyl propionic acid) (PAPPA) was carried out by polymerization in different aqueous media, from the respective monomer, using ammonium persulfate as oxidizing agent. The copolymer of aniline and *m*-aminophenyl propionic acid was also synthesized. The polymers were characterized by FTIR, UV-vis, X-ray electron spectroscopy, nuclear magnetic resonance spectroscopy, elemental analysis, thermal stability analysis (TGA), and electrical conductivity. PAPPA showed a high doping by HCl and H_2SO_4. If the composition of the comonomer acid decreases, the incorporation of copper ion and the electrical conductivity are increased. Thermal stability is favored by an increase of the content of aniline and copper ions. The polymeric structures have amine and imine groups. The last units are preferentially doped. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 706–715, 2003

Key words: poly(*m*-aminophenyl propionic acid) (PAPPA); copolymer; copper; conducting polymers; thermal properties

INTRODUCTION

Conductive materials containing conjugated π bonds have attracted a great deal of interest in scientific and technological areas in the past 20 years. Conducting polymers such as polytiophene, poly(*p*-phenylene), polypyrrole, and polyaniline have commonly been used in scientific and industrial studies, for example, as rechargeable batteries, sensors, diodes, in transistor and microelectronic devices, and as modified electrodes.[1–6]

Among conducting polymers, polyaniline holds a unique position because of its simple synthesis, environmental stability, and ability to dope with protonic acid.[7–9] Therefore, attempts have been made to overcome the unsolved problems such as solubility in common organic solvents, processability at higher temperature, and poor mechanical properties.[10,11] The last two properties are the major disadvantages of polyaniline. This was overcome by the formation of polyaniline blends and composites. The mechanical properties of polyaniline can be improved by forming a blend or a copolymer with an unsaturated hydrocarbon such as polyisoprene.

In 1862, polyaniline was the first conducting polymer to be synthesized.[12] and also the first conducting polymer to be commercialized. Polyaniline can exist in three different oxidation states: leucoemeraldine base (fully reduced state), emeraldine base (partially oxidized state), and pernigraniline (fully oxidized state).

Polyaniline and its derivatives can be synthesized both chemically and electrochemically by using suitable protonation media.[13–15] The electrochemical synthesis of polyaniline on carbon fibers was also reported.[16,17] It is difficult to coat polyaniline on nonnoble working electrodes because of preferential dissolution of the substrates attributed to the formation of poorly conducting salt or oxide films during the anodic polymerization.

Polyaniline protonated with inorganic acid such as HCl or H_2SO_4, unstable above 150°C, cannot be used for thermal processing with most of the commercial plastics such as acrylonitryle–butadiene–styrene (ABS), or polyethylene terephthalate (PET). Although efforts were made to increase processability and stability of polyaniline by using phosphoric acid diesters as a dopant, the time required and the cost involved to prepare these dopants make this process unsuitable at a commercial level.[18,19]

We previously reported that small amounts of metal ion on functionalized polyaniline increased the thermal stability.[20–22]

R= CH$_2$CH$_2$COOH   X = Cl$^-$, and HSO$_4^-$
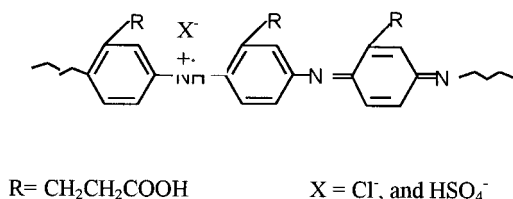
Scheme 1

Accordingly, the aim of this work was the synthesis in different media of poly(*m*-aminophenyl propionic acid) (PAPPA) and its copolymers with aniline. The effect of the propionic acid group on the properties of the new polymer was also investigated. These polymers were characterized by FTIR spectroscopy, elemental analysis, and thermal stability. The effect of the incorporation of copper on the thermal stability of these polymers was also studied.

EXPERIMENTAL

Reagents

Diethyl malonate (98%) and 3-nitrobenzyl chloride were obtained from Aldrich (Milwaukee, WI) and

used without further purification. The CuCl$_2$·2H$_2$O was obtained in analytical grade from Merck (Darmstadt, Germany). The aniline (Aldrich) was purified by distillation under vacuum. The catalyst (Fluka AG, Buchs, Switzerland) was platinum on activated carbon (10% Pt).

Measurements

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 Analytical Instruments, Madison, WI). UV-vis spectra were recorded in a Perkin–Elmer UV/Vis spectrophotometer Lambda 11 (Perkin Elmer Cetus Instruments, Norwalk, CT), in 1-cm cells using dimethyl sulfoxide (DMSO) as solvent. X-ray electron spectroscopy (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. High-resolution scans with a good signal-to-noise ratio were obtained in the C$_{1s}$, N$_{1s}$, O$_{1s}$, S$_{2p3/2}$, and Cl$_{2p3/2}$ regions of the spectrum. The decomposition of the XPS peaks into
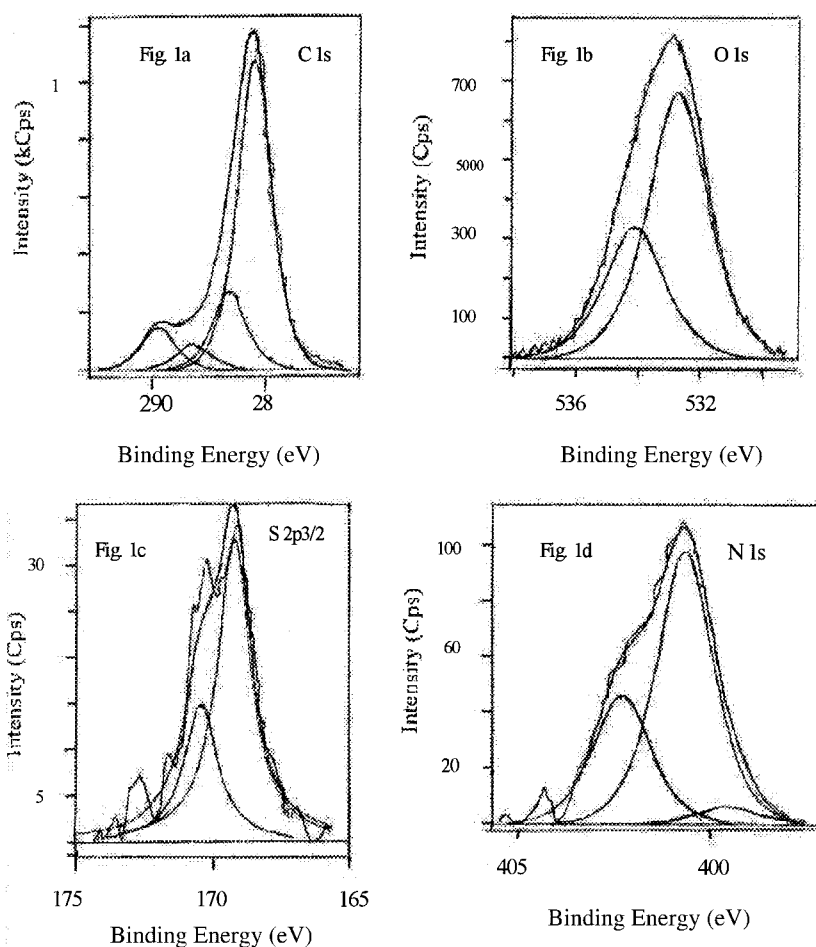
Figure 1 XPS spectra of PAPPA synthesized in 1*M* HCl: (a) C$_{1s}$, (b) O$_{1s}$, (c) S$_{2p3/2}$, (d) N$_{1s}$.
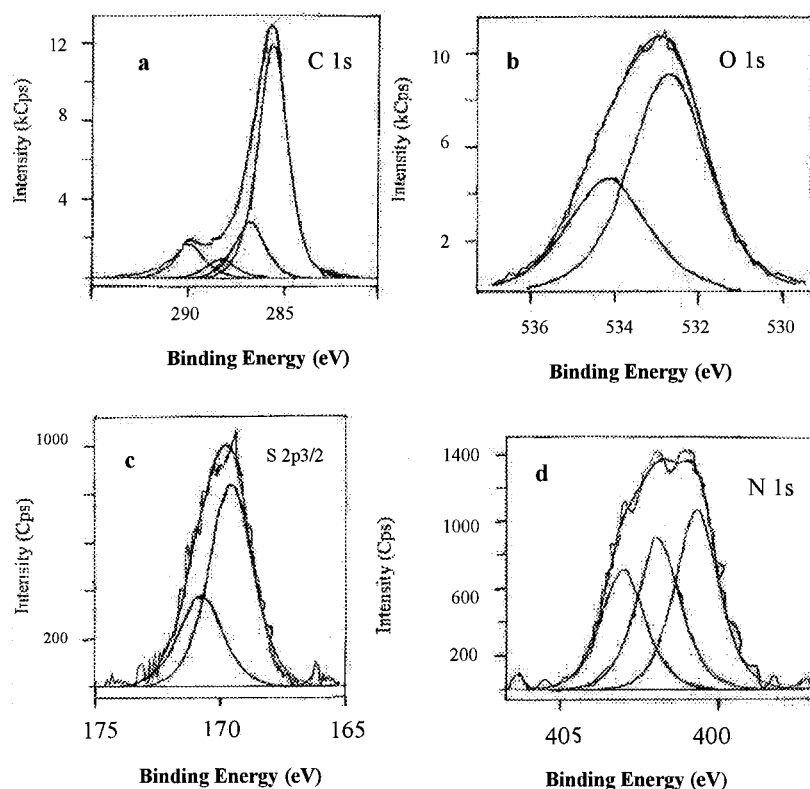
Figure 2   XPS spectra of PAPPA synthesized in 0.98M NaOH: (a) C_{1s}, (b) O_{1s}, (c) $S_{2p3/2}$, (d) N_{1s}.

different components was made after subtraction of the background using Shirley's method.[23] The polymer powder was pressed onto a sheet and the binding energy of the carbon–carbon bond (285 eV) was taken as reference[23] and the nitrogen atom signals were assigned according to Kang and coworkers.[24]

The ^{1}H-NMR spectra were recorded in DMSO-d_6 as solvent using a Bruker Multinucleus AM 200 spectrophotometer (Bruker Instruments, Billerica, MA).

The electrochemical characterization was performed in a Voltammetric Analyzer CV 50 W (Bioanalytical Systems, Inc., USA) and carried out by cyclic voltammetry using 1M HCl aqueous solution as support electrolyte. A Pt disc (0.5 mm diameter) was used as the working electrode, which was previously immersed in the respective polymer in DMF solution, and subsequently the solvent was evaporated. This operation was repeated several times for a reliable electrode coating. The electrode potential was scanned between 0.0 and 0.8 V versus Ag/AgCl at 25 mV s^{-1}. Ag/AgCl and a Pt coil were used as reference and auxiliary electrodes, respectively. The electrolytic solutions were kept under nitrogen atmosphere before and during the measurements.

The quantification (wt %) of copper incorporated into the polymers was done by calcinating the solid

TABLE I
Bond Energy (eV) for the Most Important Bonds and Contribution of Each Atom (%)

	Bond energy (eV)		Atom contribution (%)	
Bond	PAPPA–HCl[a]	PAPPA–NaOH[b]	PAPPA–HCl[a]	PAPPA–NaOH[b]
C=O	532.2	532.0	67.2	66.2
C—OH	533.6	533.5	32.8	33.8
N=	399.1	400.0	4.1	40.0
$N^{+\delta}$	401.8	402.3	30.8	26.6
NH	400.2	401.2	65.1	33.4
C—C	285.0	285.0	68.2	68.5
C—N	286.1	286.2	17.0	16.3
C—OH	289.1	289.2	9.2	9.6
C=O	287.7	287.6	5.6	5.6

[a] PAPPA synthesized in 1M HCl.
[b] PAPPA synthesized in 0.98M NaOH.
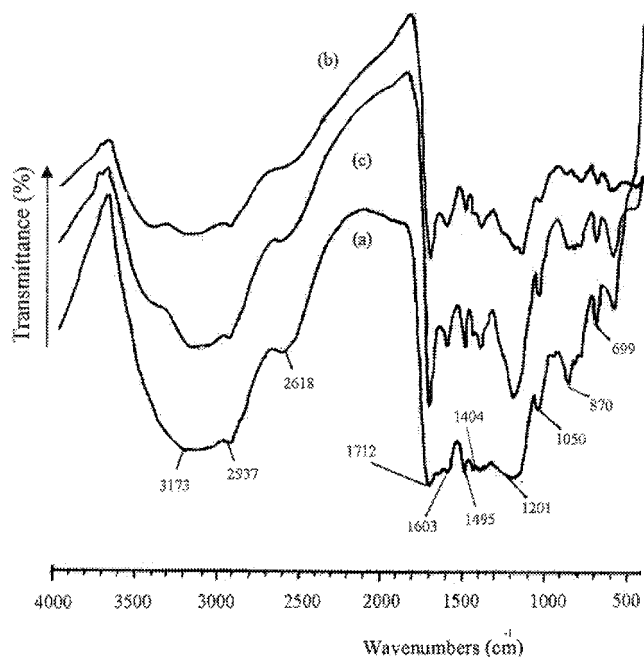
Figure 3 FTIR spectra of PAPPA synthesized in (a) $1M$ HCl, (b) 10^{-4} M HCl, (c) 0.98M NaOH.

sample, solubilizing with HNO_3, and determining the metal concentration by atomic absorption spectrometry using an atomic absorption spectrometer (AAS) Unicam Solaar 5M Series (UK). The amount (wt %) of total chloride in the polymers without copper was determined by standard methods by combustion of the polymer in a closed flask in the presence of oxygen and a solution of H_2O_2 with aqueous NaOH, after which the total chloride was determined by volumet-

ric 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 the Polymer Laboratories (Amherst, MA) STA 625 thermal analyzer. The copolymers were undoped by suspension dusted polymer and added to an aqueous solution of NH_4OH (2 + 1, v/v, NH_4OH/H_2O), then stirred for 48 h, filtered, and washed with water. The polymers were dried under vacuum for 2 days at 60°C. The incorporation of copper to the undoped polymer was determined by the batch method: 0.10 g of powder polymer was suspended in 0.10 g $CuCl_2\cdot2H_2O$ dissolved in 5 mL 10^{-4} M HCl. The mixture was kept under stirring for 3 days at room temperature, filtered through a Büchner funnel, and the polymer washed with abundant amounts of 10^{-4} M HCl. These samples were dried under vacuum at 60°C for 2 days.

Synthesis of monomer

The synthesis of *m*-aminophenyl propionic acid was carried in three steps according to Gulland and coworkers[25] modified, as shown in Scheme 1.

3-Nitrobenzyl malonic acid

Diethyl malonate [46.7 g (290 mmol), 98%] was added rapidly to a hot solution of sodium ethoxide prepared with 6.60 g (290 mmol) of $Na_{(s)}$ in 140 mL dried ethyl
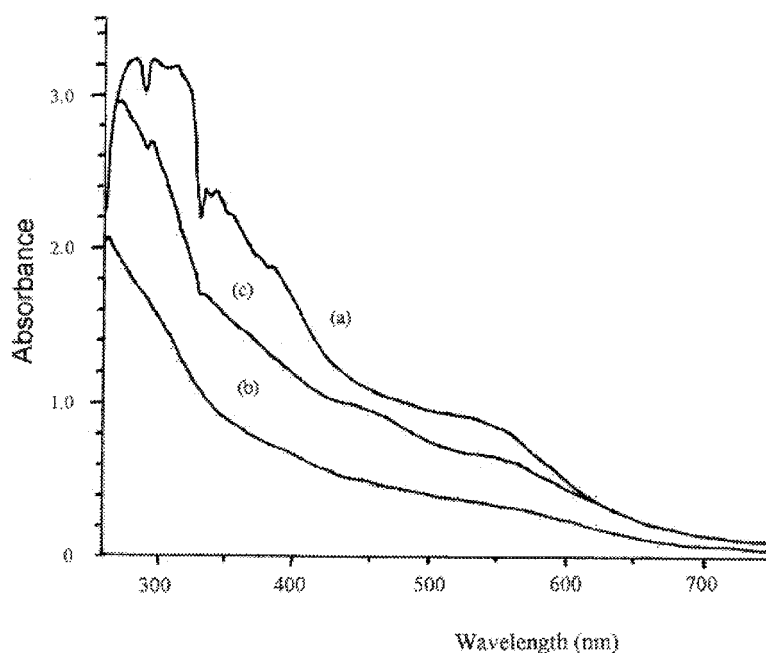
Figure 4 UV-vis spectra of PAPPA synthesized in (a) $1M$ HCl, (b) 10^{-4} M HCl, (c) 0.98M NaOH.

TABLE II
Empirical Formula of PAPPA Synthesized in Three Different Media

Medium	Empirical formula[a]
$1M$ HCl	$C_9H_{8.2}N_{0.85}O_{3.3}(HSO_4^-)_{0.06}(HCl)_{0.39}$
$10^{-4} M$ HCl	$C_9H_{7.8}N_{0.80}O_{3.0}(HSO_4^-)_{0.07}(HCl)_{0.17}$
$0.98M$ NaOH	$C_9H_{9.1}N_{0.90}O_{3.9}(HSO_4^-)_{0.12}$

[a] HSO_4^- was determined by elemental analysis of sulfur and HCl by elemental analysis of total Cl^-.

alcohol. The mixture reaction was heated and then added rapidly to the hot solution ($>65°C$) of 25.3 g (143 mmol) of 3-nitrobenzyl chloride (97%) dissolved in 200 mL of dried ethyl alcohol. The mixture of the reaction was kept under reflux for 2.5 h and the alcohol removed by distillation under vacuum (temperature of bath: 55–60°C). The residue was kept steady for 1 day and then acidified (pH = 1–2) with 45 mL HCl 1 : 2 (1 HCl 37% + 2H$_2$O, v/v) and extracted twice with 100 mL of CHCl$_3$. The CHCl$_3$ was dried with Na$_2$SO$_4$ and removed by distillation. The residue was shaken for 1 h with 110 mL KOH (30%, pH = 12), and added to 120 mL of water and stirred for 30 min. The mixture was placed in a freezer for 40 min, after which it was filtered; the liquid was acidified with 50 mL HCl (37%) and extracted twice with 200 mL of ethyl ether. The extract was dried with Na$_2$SO$_4$ and the ether was removed by distillation. The yellow product was recrystallized with 250 mL of water at 90–95°C, cooled in freezer, and then filtered. The com-

pound was dried at 60–70°C under vacuum for 3 days. Yield: 14.81 g (42.1%), mp = 163–164°C (dec.)

β-3-Nitrophenyl propionic acid

3-Nitrobenzyl malonic acid [14.74 g (61.6 mmol)] was heated in an oil bath at 180–190°C for 3 h until the evolution of carbon dioxide ceased. Hot water (50 mL) was added at room temperature and when the mixture came to a boil, the supernatant liquid was poured into a 500-mL vessel. This operation was repeated several times occupying a total volume of 400 mL of water. The aqueous solution was kept steady for 1 day and then filtered; the white solid was dried under vacuum at 60–80°C for 1 day. Yield: 10.8 g (89.6%), mp = 111–112°C.
^{1}H-NMR (250 MHz, DMSO-d_6): 8.16 ppm (1H, 1s); 8.11 ppm (1H, 1d); 7.79 ppm (1H, 1d); 7.64 ppm (1H, 1t); 3.03 ppm (2H, 1t, methylene); 2.70 ppm (2H, 1t, methylene).

β-3-Aminophenyl propionic acid hydrochloride

3-Nitrophenyl propionic acid [1 g (5.12 mmol)] was added to 11 mL absolute ethyl alcohol, and the mixture was hydrogenated at 3 atm under strong stirring for about 12 h with a catalyst of 10% Pt/carbon. The mixture was filtered and the alcohol removed by distillation under vacuum in rotating vapor. The colorless oil product was added to 50 mL of ethyl ether and 1 mL HCl (37%) under stirring. The mixture was kept
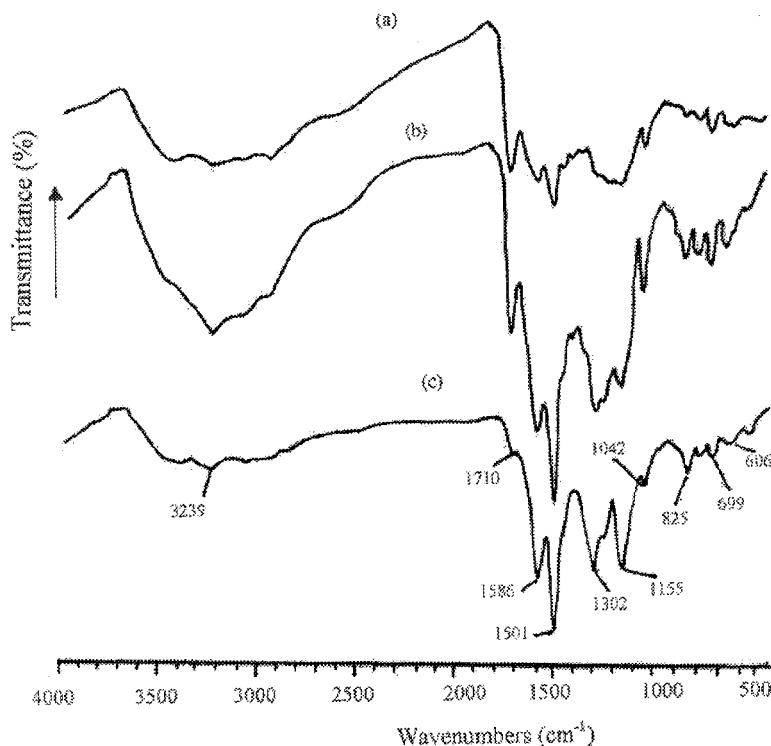
Figure 5 FTIR spectra of copolymers synthesized in $10^{-4} M$ HCl of composition (a) $F_1 = 5.94$, (b) $F_1 = 4.64$, (c) $F_1 = 3.75$.
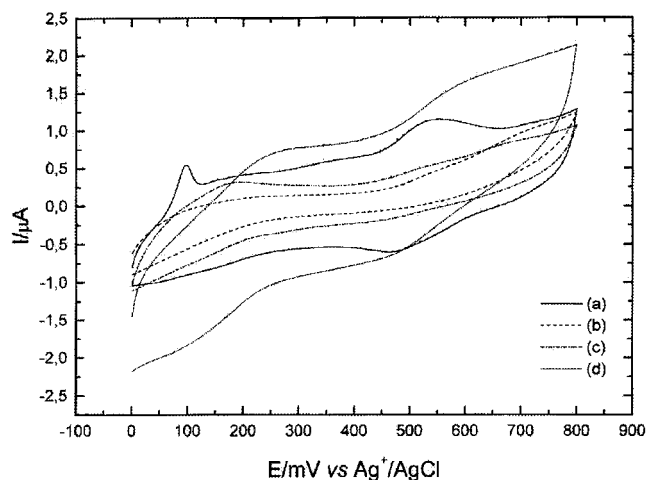
Figure 6 Cyclic voltammograms in $1M$ HCl medium, between 0.0 and 0.8 V versus Ag/AgCl at a scan rate of 25 MV/s, and Pt electrodes coated with chemically prepared polymer: (a) polyaniline synthesized in $0.25M$ HCl; (b) PAPPA synthesized in $0.98M$ NaOH; (c) poly(*m*-aminophenyl propionic acid-*co*-aniline), $F_1 = 4.64$; (d) poly(*m*-aminophenyl propionic acid-*co*-aniline), $F_1 = 3.75$.

for 1 day and then filtered. The white product was dried under vacuum at 50°C. Yield: 0.59 g (57%), mp = 158–159°C.
^{1}H-NMR (250 MHz, DMSO-d_6): 8.5 ppm (1H, 1s, acid); 7.78 ppm (1H, 1d); 7.63 ppm (3H, m); 4.7 ppm (NH, broad); 3.23 ppm (2H, 1t, methylene); 2.94 ppm (2H, 1t, methylene).

Synthesis of polymer in acid medium

3-Aminophenyl propionic acid hydrochloride [1.01 g (5.0 mmol)] was dissolved in 2.5 mL $1M$ HCl aqueous, then in a thermostatic bath at 60°C; 2.25 g (9.86 mmol) of ammonium persulfate dissolved in 3.8 mL $1M$ HCl was added to the monomer solution. The mixture was stirred for 90 h, then the hot mixture was filtered, and the polymer washed with $1M$ HCl until obtaining a colorless product. The polymer was dried at 60°C under vacuum until a constant weight was obtained. Yield: 0.408 g (40.4%).

TABLE IV
Amount of Cu(II) in Homo- and Copolymers Undoped

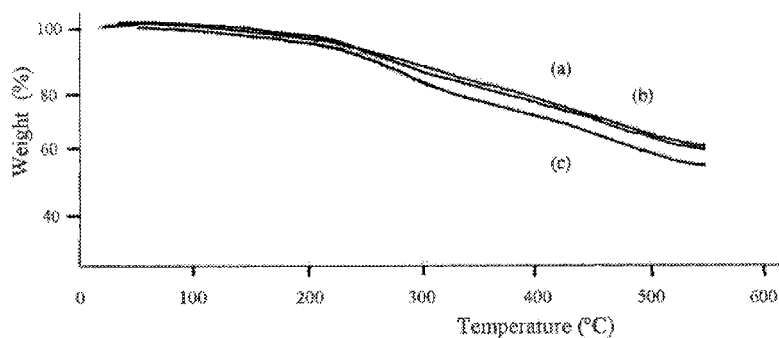| Polymer	Weight of Cu(II) (%)
PAPPA synthesized in acid media	0.57
PAPPA synthesized in 10^{-4} M HCl	0.54
PAPPA synthesized in alkaline medium	0.55
Copolymer composition	
$F_1 = 5.94$	0.42
$F_1 = 4.64$	0.86
$F_1 = 1.06$	1.06

Synthesis of polymer in alkaline medium

3-Aminophenyl propionic acid hydrochloride [1.0 g (4.96 mmol)] was added in 2.5 mL $0.98M$ NaOH. The solution was heated in a thermostatic bath at 60°C and 2.25 g (9.86 mmol) ammonium persulfate dissolved in 3.8 mL $0.95M$ and NaOH was added. The mixture was stirred for 19 h, after which the hot mixture was filtered and then washed with water. The polymer was dried under vacuum at 60°C for 2 days. Yield: 0.48 g (47.1%).

Synthesis of polymer in 10^{-4} M HCl medium

3-Aminophenyl propionic acid hydrochloride [0.503 g (2.49 mmol)] was added to 5 mL 10^{-4} M HCl. The solution was heated in a thermostatic bath at 60°C and 0.57 g (2.50 mmol) ammonium persulfate dissolved in 2.3 mL 10^{-4} M HCl was added. The mixture was stirred for 90 h, after which the hot mixture was filtered and then washed with 10^{-4} M HCl. The polymer was dried under vacuum at 60°C for 2 days. Yield: 0.055 g (11.0%).

Synthesis of copolymers in 10^{-4} M HCl medium

The copolymers of aniline with *m*-amino phenyl propionic acid were prepared by chemical oxidation at several feed mol ratios of aniline (f_1) using ammonium persulfate as oxidizing agent in $1M$ HCl. The amount (in mol) of oxidizing agent added was similar to the

TABLE III
Copolymer Composition (F_1), Electrical Conductivity, and Empirical Formula of the Copolymeres

f_1	F_1^a	Electrical conductivity σ (S cm^{-1})	Empirical formula[b]
2.00	5.94	3.0×10^{-10}	$C_9H_{7.90}N_{0.88}O_{2.39}(HSO_4^-)_{0.12}(HCl)_{0.11}$
0.67	4.64	4.8×10^{-9}	$C_9H_{7.41}N_{1.10}O_{1.71}(HSO_4^-)_{0.15}(HCl)_{0.08}$
0.25	3.75	5.0×10^{-7}	$C_9H_{7.12}N_{1.26}O_{1.08}(HSO_4^-)_{0.15}(HCl)_{0.08}$

[a] Determined by ^{1}H-NMR, in DMSO-d_6.
[b] HSO_4^- was determined by elemental analysis of sulfur, HCl by total analysis of chloride. Oxygen was determined by the difference in total % of elemental analysis.

Figure 7 Thermograms of PAPPA, synthesized in (a) $1M$ HCl, (b) 10^{-4} M HCl, (c) $0.98M$ NaOH.

sum (in mol) of both comonomers. As an example, the procedure was as follows: for f_1 = 2. 0.131 g (1.41 mmol) of aniline was dissolved in 10 mL 10^{-4} M HCl. The solution was heated in a thermostatic bath at 60°C and 0.57 g (2.83 mmol) of 3-aminophenyl propionic acid was added, after which 0.964 g (4.22 mmol) ammonium persulfate dissolved in 5 mL 10^{-4} M HCl was added. The mixture was stirred for 19 h at 60°C, after which the hot mixture was filtered and then washed with 10^{-4} M HCl. The copolymers were dried under vacuum at 60°C for 2 days.

RESULTS AND DISCUSSION

The XPS spectra show the different bonds for the polymers synthesized in acid and alkaline media (see Figs. 1 and 2).

The spectra of C_{1s} show that the different peaks correspond to the contribution of C—C, C—N, C=O, and C—OH bonds [see Figs. 1(a) and 2(a)], and in the spectra of O_{1s}, these contributions are assigned to C=O and C—OH bonds [see Figs. 1(b) and 2(b)]. In both spectra the polymers were synthesized in alkaline medium. In acid medium a doublet centered at about 170 eV appears [see Figs. 1(c) and 2(c)]. This bond energy was attributed to the oxidized sulfur. It is possible that this signal corresponds to sulfate or bisulfate ions, which constitute the reduced form of the oxidizing reagent ($S_2O_8^= \rightarrow 2SO_4^- - 2e$), and this ion should act as a dopant of the polymer in both

media. Moreover, in the XPS spectrum of the polymer synthesized in $1M$ HCl, two doublets at about 201 eV are present. This signal corresponds to chlorine. The atomic percentage of each contribution was assigned to ionic and covalent chloride. The ion chloride corresponds to an acid doped by HCl and the covalent should be given by a side reaction of Cl_2 to the ring. The amount of the covalent chloride was 5.1%.

The spectra of N_{1s} and PAPPA synthesized in acid and alkaline media are different [see Figs. 1(d) and 2(d)]. For chemically synthesized Pani it has been demonstrated that the ratios of quinoid diimine (–N= structure), benzenoide amine (–NH– structure), and positively charged nitrogens correspond to a particular oxidation state and protonation level of polyaniline. Kang and coworkers[24] assigned those structures at 398.2, 399.4, and >400 eV to imine, amine, and charged nitrogen, respectively. We have assigned the bonding energy of the different nitrogen components by consideration of previous results from copolymers derived from aniline. These results show a shift at higher bond energy of 1–2 eV. For PAPPA synthesized in alkaline media, the proportion of groups imine : amine is 40 : 33.4. Thus the polymer is obtained in an intermedial redox state. The high atomic percentage of charged nitrogen (26.6%) shows that this polymer is obtained as doped material. The elemental analysis (see Table II) and the XPS spectra [see Fig. 2(c)] show that the doping is attributed to HSO_4^- or $SO_4^=$ ions. This polymer treated in suspension with $1M$ HCl was
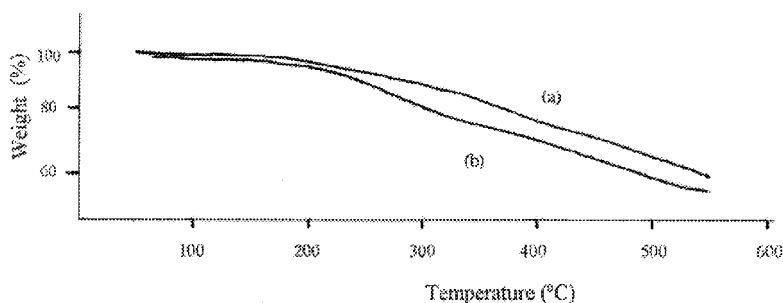
Figure 8 Thermograms of PAPPA, synthesized in $0.98M$ NaOH, (a) with Cu(II), (b) without Cu(II).
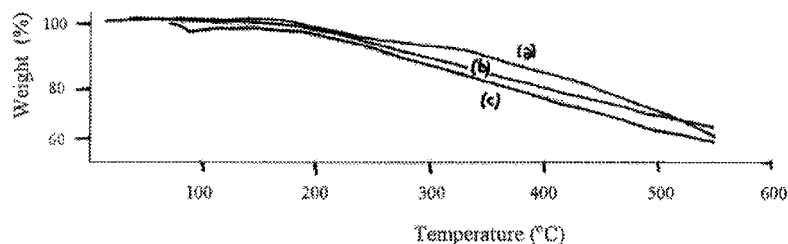
Figure 9 Thermograms of polymers (a) $F_1 = 3.75$, (b) $F_1 = 5.94$, (c) $F_1 = 0$ (homopolymer synthesized in $1M$ HCl).

not doped. On the contrary, PAPPA synthesized in $1M$ HCl medium is obtained as doped by Cl^- and HSO_4^- (or $SO_4^=$) ions [see Table II and Fig. 1(c)]. The low proportion of imine structure (4.1%; see Table I) shows that the doping is produced on the nitrogen atoms of the quinoid diimine groups.

The O_{1s} spectra [see Figs. 1(b) and 2(b)] are asymmetric. The atomic percentage of the C=O contribution is higher than that of the C—OH bonds (see Table I). According to the atomic percentage of each contribution, about 67.2% of the substituents in the polymer synthesized in acid media and about 66.2% of substituents in the polymer synthesized in alkaline media are as COOH group.

Figure 3 shows the FTIR spectra of PAPPA synthesized in different media. The most important absorption bands associated with the polymers are: 3386–3178 cm^{-1} (N—H stretching); 2931 cm^{-1} (C—H aromatic stretching); 1712 cm^{-1} (C=O stretching); 1609 cm^{-1} (C—C quinoid ring, C=N and C=C stretching); 1201 cm^{-1} (C—O stretching). The FTIR spectra of PAPPA are basically similar when the polymer was prepared in different media. However, the XPS spectra show that they are structurally somewhat different.

For the polymers synthesized in three different media the absorption bands are similar, which at 300 nm are associated with π–π^* transitions of benzenoid rings and the absorption bands of the visible region (550 nm) associated with transference of charge transitions[26] of quinoid rings (see Fig. 4). As PAPPA synthesized in $1M$ HCl is doped, one can expect a conduction band at a wavelength of 600 nm.[27,28] There-

fore, a high doping (0.53) in PAPPA is not enough to increase the electrical conductivity. The electrical conductivity of doped PAPPA synthesized in different media is low ($\sim 10^{-10}$ S cm^{-1}).

The empirical formulas, determined by elemental analysis, of the polymers synthesized in three different media show that they present an excess of oxygen atoms, corresponding to water molecules, which are very difficult to discard. Moreover, the elemental analysis shows a doping by Cl^- and HSO_4^- (or $SO_4^=$), where the nitrogen atoms of the amine and/or imine groups are protonated (see Table II).

According to the preceding results, it is possible to suggest the following structure for PAPPA, which contains amine and imine groups.

On the other hand, copolymers at several ratios (in mol) of aniline in the feed were synthesized. Figure 5 shows the FTIR spectra. The absorption band associated with the carbonyl group (1711 cm^{-1}) increases the intensity as the propionic acid/aniline ratio F_1 increases.

The FTIR bands of the copolymers ranged between the following values: 3380 cm^{-1} (N—H stretching); 2950–2927 cm^{-1} (aromatic C—H stretching); 1717–1711 cm^{-1} (C=O stretching); 1587–1572 cm^{-1} (quinoid ring C=N and C=C stretching); 1501–1498 cm^{-1} (benzenoid ring C=C stretching); 1245–1200 cm^{-1} (C—O stretching); 831–693 cm^{-1} (C—H aromatic bending).

The cyclic voltammograms of polyaniline in acid media consist of two redox processes, corresponding to the oxidation/reduction of benzenoid diamine
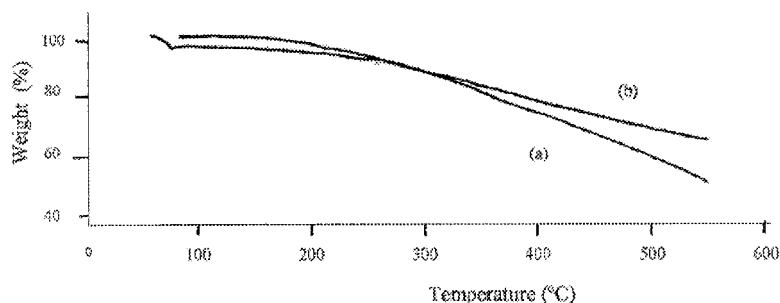

Figure 10 Thermograms of copolymers of (a) $F_1 = 5.94$, (b) $F_1 = 5.94$ with Cu(II).
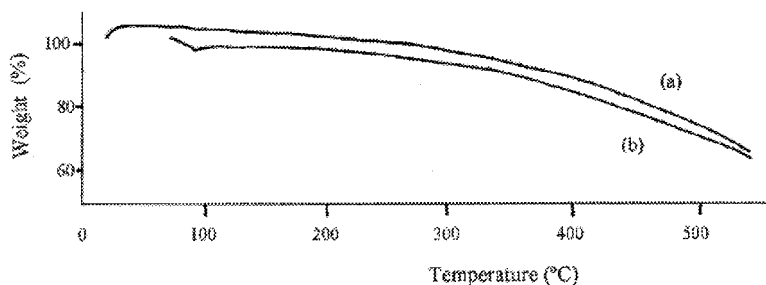
Figure 11 Thermograms of copolymers of (a) $F_1 = 4.64$ with Cu(II), (b) $F_1 = 4.64$.

units (lower potential) and quinoid diimine units (higher potential), respectively.[29]

Figure 6 shows four cyclic voltammograms obtained in a potential window of 0.0 at 0.8 V versus Ag/AgCl. The voltammogram [see Fig. 6(a)] corresponding to polyaniline shows the classical oxidation-reduction process. Nevertheless, the copolymers [see Fig. 6(c), (d)] show an evident shift of the potentials, obtaining completely different voltammetric profiles. A comparison of the voltammograms of polyaniline and such polymers establishes that these products are true copolymers between aniline and comonomer acid and they are not a mixture of the respective homopolymers.

Table III shows the ratios (in mol) of comonomer acid/aniline (f_1) in the feed and the copolymer composition (F_1).

The reactivity of the monomer depends on the electronic steric effects of the substituents.[30] In this case, the electron-donor effect of the methylene groups linked to the aromatic ring increases the speed of copolymerization, which predominates, on the steric hindrance. According to the reaction conditions, the reactivity of the acid comonomer is higher than that of aniline.

The electrical conductivity is also favored by the incorporation of aniline in the copolymer structure (see Table III).

To incorporate Cu(II) into the polymers, these were undoped with NH_4OH_{aq} previously dried under vacuum and treated by the batch method, a heterogeneous suspension of the polymer with $CuCl_2$ in HCl 10^{-4} M. Table IV shows the contents of Cu(II) in these materials.

For the homopolymers, the percentage of Cu(II) is approximately constant. If the aniline unit content is increased, it is possible to suggest that the nitrogen atoms and/or the donor-electron π effect of aniline units in the copolymer have a higher affinity with the copper ions.

The thermograms of PAPPA synthesized in three different media show that the one obtained in alkaline media is slightly less stable than that obtained in acid media. The former shows a weight loss of about 10% at 250°C (see Fig. 7).

Figure 8 shows the thermogram of PAPPA synthesized in alkaline medium with 0.55% of Cu(II). It shows a higher thermal stability at a temperature higher than 200°C. A weight loss of 10% is achieved at 300°C. The thermograms of PAPPA synthesized in acid medium, with and without Cu(II), are overlapped and no important effect of Cu(II) on the thermal stability was observed.

For the copolymers, the thermograms of those with a copolymer composition $F_1 = 5.94$ and $F_1 = 3.75$ show that they are more stable than those of the homopolymer. Therefore it is possible to suggest that the aniline units stabilize the copolymer (see Fig. 9).

The copolymers that contain copper (II) showed a higher thermal stability with respect to those without copper ions (see Figs. 10–12).
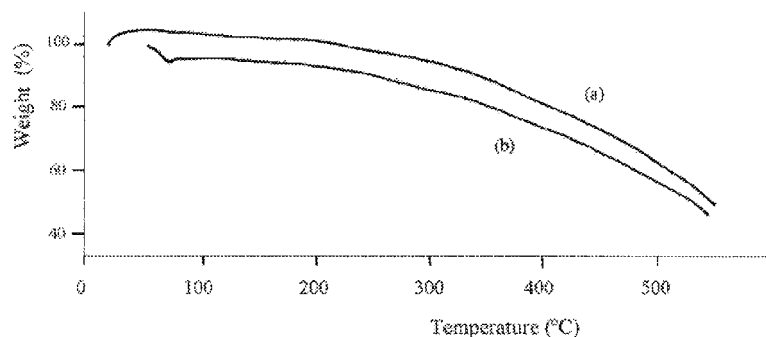

Figure 12 Thermograms of copolymers of (a) $F_1 = 3.75$ with Cu(II), (b) $F_1 = 3.75$.

CONCLUSIONS

Poly(*m*-aminophenyl propionic acid) and the copolymers with aniline were synthesized by chemical oxidation in different media. The synthesis in acid media favored doping. This polymer with high-level doping did not show an increase of electrical conductivity. The units of aniline in the copolymers increased the incorporation of copper ions, increasing the thermal stability. The effect of an active ring substituent of aniline favored the composition of propionic acid monomeric units in the copolymers.

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