Synthesis and Characterization of Poly(*o-* and *m-*Amino Benzyl Amine) and the Copolymers with Aniline. Study with Cu(II)

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ABSTRACT: Poly(*o*-amino benzyl amine), poly(*m*-amino benzyl amine), and the copolymers with aniline were synthesized in $10^{-4}M$ HCl by using ammonium persulfate as oxidizing agent. The copolymers were synthesized at various feed mole fractions of comonomer diamine and characterized by elemental analysis, FTIR, ^{1}H-NMR spectroscopy, and electrical conductivity. The polymerization yield depended on the substituent position in the aromatic ring. Copper ion was incorporated in the polymers and the amount depended on the side groups position in the aromatic ring. The thermal stability increased when copper ions and aniline units were incorporated in the polymers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 31–36, 2004

Key words: copolymerization; supports; infrared spectroscopy; thermal properties

INTRODUCTION

Polyaniline has received considerable attention because of its unique polymer conduction mechanism by doping acid,[1,2] good stability,[3] and electrochemistry redox properties,[4–6] utilized in chemically modified electrodes, sensors,[7] biosensors,[8] transistors,[9] and batteries.[10] This polymer is obtained doped when it is treated with acid mineral and is insoluble in organic solvent. However, if polyaniline is treated in alkaline medium, it is obtained undoped and is soluble in *N*-methylpyrrolidone (NMP), dimethylsulfoxide (DMSO), and dimethylformamide (DMF).[11,12] Various derivatives of functionalized polymer have been reported with substituents such as dihalo,[13] *o-* and *m*-amino benzyl alcohol,[14] *o-* and *m*-aminobenzoic acid, *m*-amino phenyl acetic acid, *m*-amino phenyl propionic acid,[15,16] as well as its copolymers with aniline. The copolymers have a lower doping level and/or electrical conductivity.

The incorporation of metal cations into polymers is important for the potential applications; transition-metal dispersed into modified polymer electrodes have applications in electrocatalysis.[17] Pani-Cu(II) films show electrocatalytic oxidative properties of the molecules such as amino acids and carbohydrates.[18] The incorporation of metal ions is very difficult because of the repulsion interactions between the metal and the radical cations of the polymer.

The aim of this article was to blend functionalized polyaniline with methyl amine groups, to investigate the effect of the side substituents on the electrical conductivity, and to incorporate copper ions in these polymers. The effect of copper ion on the thermal stability and the electrical conductivity of the polymer were investigated.

EXPERIMENTAL

Reagents

3-Nitro benzyl alcohol, potassium phthalimide, platinum oxide (catalyst Adams), and hydrate hydracine (80%) were purchased from Aldrich Co. and used without further purification. The 2-amino benzyl amine (Aldrich Co.) was purified by recrystallization from petroleum ether [boiling point (bp) = 40–60°C]. The $CuCl_2 \cdot 2H_2O$ was obtained from Merck (Germany). The aniline (Aldrich Co.) was purified by distillation under vacuum.
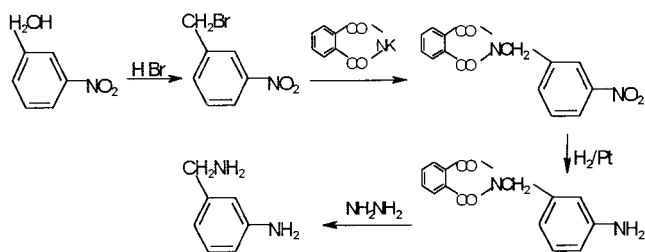
Synthesis of *m*-amino benzyl amine

The monomer *m*-amino benzyl amine was synthesized in various steps and modified according to references (19–21 see Scheme 1).

3-Nitro benzyl bromide

3-Nitro benzyl alcohol (55.0 g, 0.359 mol) was heated at 70–75°C and under stirring 254 mL HBr (*D* = 1.488,

Scheme 1

48%) was added; then the temperature of the mixture reaction was increased at 90–95°C and kept constant for 130 min, poured in a beaker, cooled at room temperature, and left to stand for 4 days. Then it was filtered, dusted, filtered again, and washed with water. This white solid was solubilized in 80 mL ethyl ether; then 32 mL benzyne (bp = 40–60°C) was added. The mixture was cooled, filtered, and dried at room temperature. Yield: 72.6 g, 94%, melting point (mp) = 57–58°C.

N-(3-Nitro benzyl)-phthalimide

3-Nitro benzyl bromide dusted (17.8 g, 82.4 mmol) and potassium phthalimide (98%) (17.8 g, 94.2 mmol) were mixed and heated at 180–200°C for 5 h, and then cooled at room temperature and poured in a beaker; water was added and the mixture was heated at 80–90°C, rapidly filtered by a Büchner funnel, and washed with hot water. The compound was recrystallized with hot glacial acetic acid and dried under vacuum at 60°C for 6 h. Yield: 18.2 g, 78.5%, mp = 163–164°C.

N-(3-Amino benzyl)-phthalimide

A suspension of *N*-(3-nitro benzyl)-phthalimide (13.10 g, 46.4 mmol) and platinum oxide (catalyst Adams) (0.11 g) in 79 mL glacial acetic acid was stirred and hydrogenated at 3 atm for 4–5 h. The reduction product was diluted with 79 mL water and filtered. Under stirring, 20 mL solution 12.5M NaOH was added and filtered. The yellow compound was recrystallized from 82 mL ethyl alcohol/water (2 + 1), cooled, filtered, and dried at 65–70°C under vacuum. Yield: 7.6 g, 65%, mp = 127–128°C.

m-Amino benzyl amine

To a stirred mixture of *N*-(3-amino benzyl)-phthalimide (7.7 g, 30.5 mmol) in ethyl alcohol (44 mL) at 75–80°C, hydrate hydracine (80%) (1.4 mL) was added. At 95°C, it was all dissolved and when a yellow precipitate appeared (∼ 15 min), 5.5M HCl (11 mL) was added. After 15 min, a white solid precipitated, then cooled at room temperature, and was filtered under vacuum to eliminate the acid. The filtered fraction was alkalinized with 10M NaOH (5 mL) (pH = 9–10) and 2 × 50 mL ethyl ether was extracted and dried with KOH pellets. The ether was removed and oil orange was analyzed by chromatography with silica gel by using acetone/CH_2Cl_2 1 + 1, and acetone as eluant. A viscous oil was obtained (1.9 g; 49%).
^{1}H-NMR: 6.93 ppm (1H, t); 6.55 ppm (1H, s); 6.45 ppm (2H, m); 4.91 ppm (2H, s, NH); 4.28 ppm (2H, s, methylene); 3.16 ppm (2H, s, NH).

Synthesis of polymers

o- or *m*-amino benzyl amine (0.58 g, 4.8 mmol) was added to 13 mL $10^{-4}M$ HCl and then heated at 60°C, and, under stirring, ammonium persulfate (1.09 g, 4.8 mmol) was dissolved in 5.8 mL $10^{-4}M$ HCl. The mixture was stirred for 19 h, filtered, and washed with $10^{-4}M$ HCl and acetone. The polymers were dried under vacuum at 50°C for 2 days.

Synthesis of copolymers

The copolymers were prepared in an aqueous acid medium ($10^{-4}M$ HCl) by polymerization of *o*- or *m*-amino benzyl amine and aniline in various feed mole fractions. In all cases, the mole ratio of the oxidant to the total monomer was 0.5M. As an example, the procedure for comonomer diamine feed mole fraction for f1 = 0.50 was as follows: aniline (0.39 g, 4.2 mmol) was added to 11.5 mL $10^{-4}M$ HCl and heated at 60°C. *m*-Amino benzyl amine (0.52 g, 4.3 mmol) was added and, under stirring, a solution of ammonium persulfate (0.94 g, 4.1 mmol) dissolved in 5 mL $10^{-4}M$ HCl was then added to the reaction mixture. It was stirred for 19 h, and the hot mixture was filtered through a Büchner funnel and washed with hot $10^{-4}M$ HCl, and acetone. The polymers were dried under vacuum at

TABLE I
Yield Polymerization of Poly(*o*- and *m*-Amino Benzyl Amine) and Its Copolymers

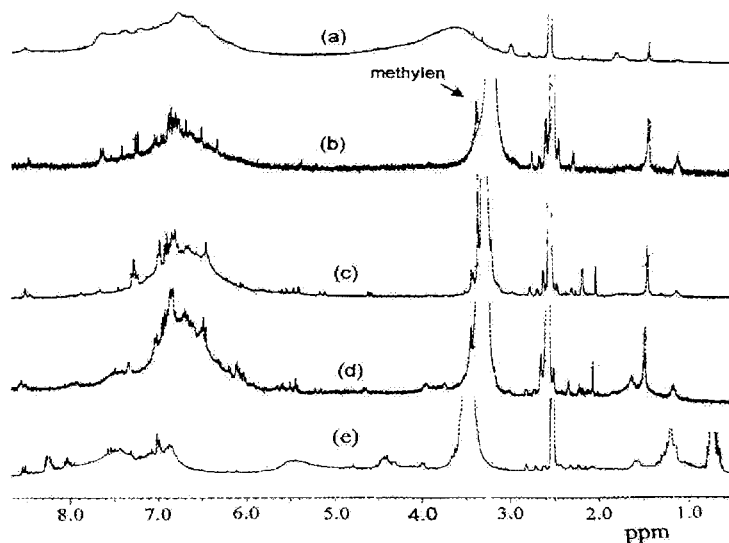| Monomer diamine feed mol fraction		Polymer yield (%)	
o-Amino derivative (f1)	*m*-Amino derivative (f1)	*o*-Amino derivative (%)	*m*-Amino derivative (%)
1.00	1.00	19.8	5.5
0.67	0.50	27.5	8.2
0.20	0.20	45.6	10.0

Figure 1 ^{1}H-NMR spectra of the polymers: (a) poly(*o*-amino benzyl amine); (b) poly(aniline-*co-o*-amino benzyl amine) (f1 = 0.67); (c) poly(aniline-*co-o*-amino benzyl amine) (f1 = 0.20); (d) poly(aniline-*co-m*-amino benzyl amine) (f1 = 0.50); (e) poly(*m*-amino benzyl amine).

50°C for 2 days and were prepared by various copolymers of different compositions.

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 with a Magna Nicolet 550 spectrophotometer (USA). ^{1}H-NMR spectra were recorded by using a Bruker Multinucleous AM 200 (Germany). The samples were solubilized in DMSO-d$_6$ (Merck) containing tetramethyl silane as the internal reference and further dried with molecular sieves. The incorporation of copper ions to the polymer was determined by Batch method: 30 mg of powder polymer was suspended in 89 mg CuCl$_2$·2H$_2$O dissolved in 5.0 mL $10^{-4}M$ HCl. The mixture was maintained under stirring for 2 days at room temperature, filtered, and washed with $10^{-4}M$ HCl. The sam-

ples were dried under vacuum at 60°C for 2 days. The quantification (wt %) of the metal ions incorporated into the polymers was done by calcinating the solid sample, solubilizing with aqueous HNO$_3$, and determining the metal concentration by atomic absorption spectrometry (AAS) by using an atomic absorption spectrometer Unicam Solaar 5M (UK). Thermograms were recorded under nitrogen with the Polymer Laboratories STA 625 thermal analyzer (UK).

RESULTS AND DISCUSSION

When f1 was increased, the polymerization yield decreased. This behavior can be attributed to the steric hindrance of the side groups. The *m*-amino derivative has lower yield than that of *o*-amino derivative (see Table I).

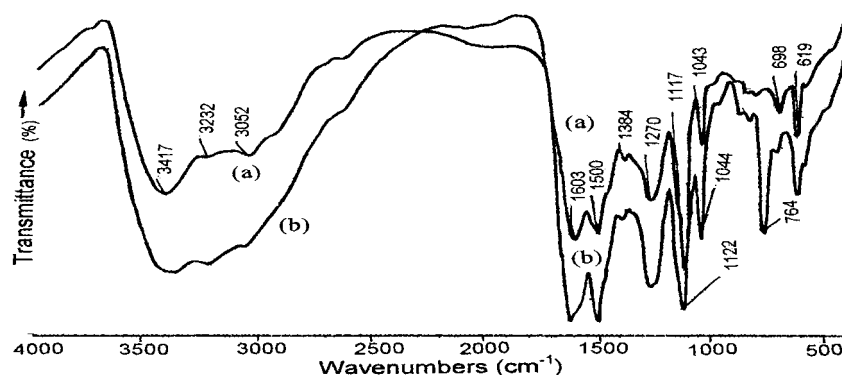The ^{1}H-NMR spectra show that the methylene protons and aromatic ring protons are present in the

Figure 2 FTIR spectra of (a) poly(*m*-amino benzyl amine) and (b) poly(*o*-amino benzyl amine).
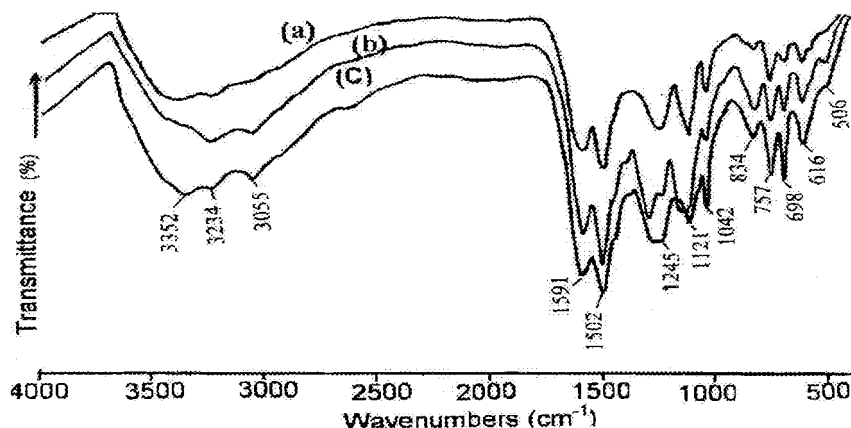
Figure 3 FTIR spectra of (a) poly(aniline-*co*-*o*-amino benzyl amine) (f1 = 0.67); (b) poly(aniline-*co*-*o*-amino benzyl amine) (f1 = 0.20); (c) poly(aniline-*co*-*m*-amino benzyl amine) (f1 = 0.50).

polymers (see Fig. 1). The signals at 3.5 ppm are assigned to the methylene protons and those at 6.5–8.0 ppm are assigned to the aromatic ring protons. The signals at 2.0 ppm are assigned to methyl groups, products of the substituents oxidation by ammonium persulfate during the polymerization.

The composition of the copolymers cannot be determined from the integrals of the chemical shifts. It is due to the overlapping of the signal of the methylene protons with the signal of the water protons (signal at 3.4 ppm).

Figure 2 shows the FTIR spectra of the homopolymers which are very similar. The bands associated to C—H out-of-plane bending vibration of 1,2,4-trisubstituted aromatic ring are at 1044 and 764 cm^{-1}. FTIR spectrum of poly(*m*-amino benzyl amine) shows that there is only the absorption band at 1043 cm^{-1}, indicating that the polymerization of both monomers is different. Moreover, it is possible that its aromatic ring has a tetrasubstituted pattern in poly(*m*-amino benzyl amine) [see Fig. 2(a)].

The FTIR spectra of copolymers between *o*-amino benzyl amine and aniline shown in Figure 3(a, b) are

similar. The absorption bands associated with C—H out-of-plane bending vibrations at 1044 and 758 cm^{-1} correspond to 1,2,4-trisubstitution of *o*-amino benzyl amine units, and at 834 cm^{-1}, C—H out-of-plane bending was attributed to disubstitution of aniline units.[22]
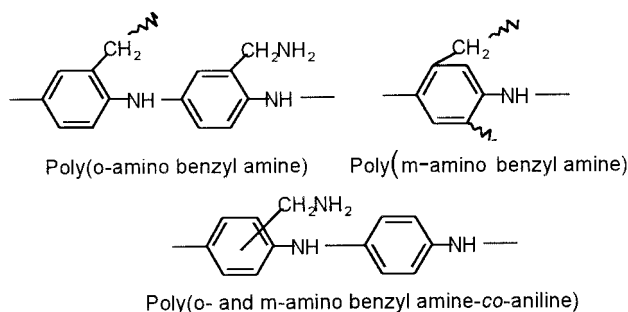
Contrary to FTIR spectrum of poly(*m*-amino benzyl amine) [see Fig. 2(a)], the FTIR spectrum of poly(aniline-*co*-*m*-amino benzyl amine) of f1 = 0.50 [see Fig. 3(c)] shows two bands at 1042 and 757 cm^{-1} associated with 1,2,4-trisubstitution. Therefore, the copolymerization of aniline with *m*-amino benzyl amine occurred by a mechanism that involves the trisubstitution in the diamine comonomer, avoiding tetrasubstitution.

According to the elemental analysis of poly(*o*- and *m*-amino benzyl amine), there is a deamination reaction (see Table II), and moreover, according to the spectroscopic results, it is possible to suggest the following repeat units in the polymers (see Scheme 2).

Cu(II) ions were incorporated by Batch method to the polymers (see Table II). In homopolymers, if the substituent is placed in position 2, the amount of copper ion incorporated is higher than if the substituent is in position 3 in the aromatic ring. In the case of the derivative copolymers substituted in position 2,

TABLE II
Elemental Analysis of Polymers and Copper Incorporated by Batch Method

	Empirical formula	Copper incorporated (%)
o-Amino derivative (f1)		
1.00	$C_{14.0} H_{6.28} N_{2.94} (HSO_4^-)_{0.52}$	3.22
0.67	$C_{14.0} H_{11.52} N_{2.60} (HSO_4^-)_{0.44}$	2.70
0.20	$C_{14.0} H_{13.44} N_{2.41} (HSO_4^-)_{0.33}$	1.82
m-Amino derivative (f1)		
1.00	$C_{14.0} H_{10.74} N_{2.50} (HSO_4^-)_{0.54}$	1.57
0.50	$C_{14.0} H_{12.60} N_{4.02} (HSO_4^-)_{0.38}$	2.56

Poly(o-amino benzyl amine)   Poly(m-amino benzyl amine)

Poly(o- and m-amino benzyl amine-*co*-aniline)

Scheme 2

Figure 4 Thermogram of (a) poly(*o*-amino benzyl amine); (b) poly(*m*-amine benzyl amine).
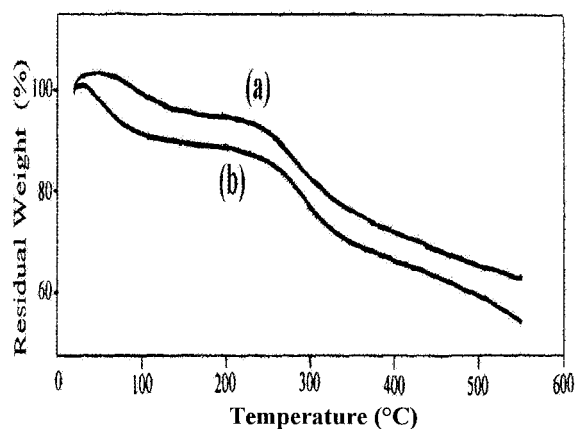

Figure 6 Thermogram of (a) poly(aniline-*co-m*-amino benzyl amine) f1 = 0.50; (b) poly(*m*-amino benzyl amine).

the amount of copper decreased when the aniline units in the copolymer increased. However, if the substituent is placed in position 3, the amount of copper ion incorporated is higher than that of the homopolymer, so when the percentage of nitrogen atom in the polymer is higher, the amount of copper ion is increased.

On the other hand, the side substituent in position 2 of the aromatic ring favored the thermal stability, with respect to position 3 in all temperature ranges (see Fig. 4). The aniline units in the copolymers of both types of derivatives increased the thermal stability. If the polymer has an f1 = 0.20, then there is a weight loss of 10% at 360°C, and the same weight loss in poly(aniline-*co-o*-amino benzyl amine) of f1 = 0.67 is at 250°C (see Fig. 5). In poly(aniline-*co-m*-amino benzyl amine), a weight loss of 10% at 250°C, and in poly(*m*-amino benzyl amine) the same weight loss at 150°C, was observed (see Fig. 6).

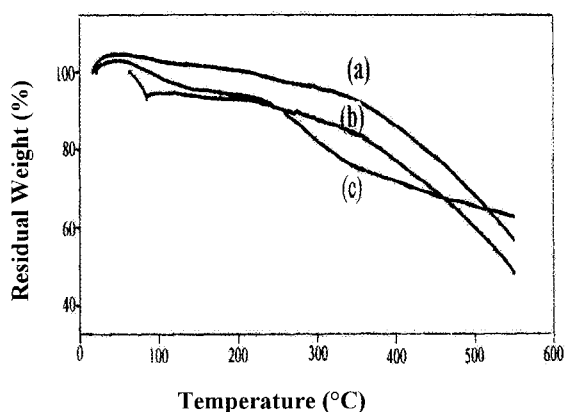The thermogram shows a slight increase at the beginning of heating up to 35°C. It can be attributed to the calibration pattern of the equipment but not to the sample. Subsequently, it was observed that the polymers with copper ions increased the thermal stability at higher temperatures. Poly(*o*-amino benzyl amine) increased the thermal stability after 250°C, and in poly(*m*-amino benzyl amine), the thermal stability increased in all the temperature range (see Figs. 7 and 8). It could be attributed to the modification of the polymer chain by increasing of the crosslinking points.

The electrical conductivity of those polymers with and without copper ion varied from 3×10^{-9} at 6×10^{-9} Scm^{-1}, and no changes associated with the copper ion of the polymers were observed.

In addition, poly(*o*- and *m*-amino benzyl amine) have been synthesized in aqueous media $10^{-4}M$ HCl. The homopolymers presented partial deamination. The incorporation of copper ions increased the thermal stability but it was not observed as an important effect on the electrical conductivity. Moreover, the aniline units increased the thermal stability of the copolymers.

Figure 5 Thermogram of (a) poly(aniline-*co-o*-amino benzyl amine) f1 = 0.20; (b) poly(aniline-*co-o*-amino benzyl amine) f1 = 0.67; (c) poly(*o*-amino benzyl amine).
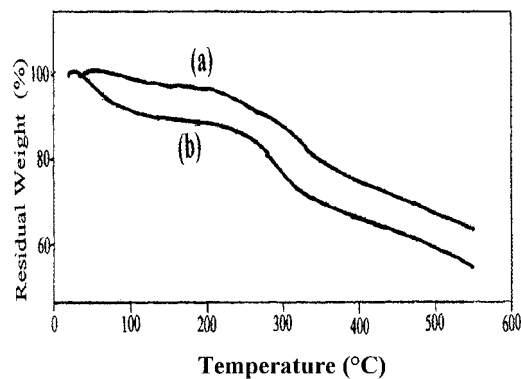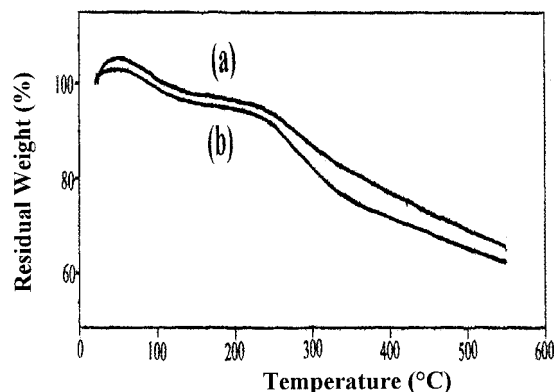

Figure 7 Thermogram of poly(*o*-amino benzyl amine): (a) with Cu(II); (b) without Cu(II).
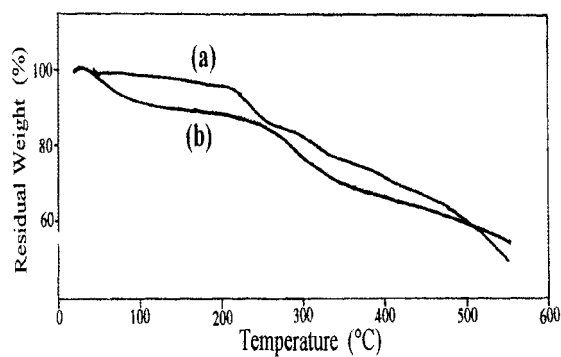
Figure 8 Thermogram of poly(*m*-amino benzyl amine): (a) with Cu(II); (b) without Cu(II).

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