

Electrochemical Synthesis of Poly(2-iodoaniline) and Poly(aniline-co-2-iodoaniline) in Acetonitrile

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ABSTRACT: Poly(2-iodoaniline) (PIANI) and poly(aniline-co-2-iodoaniline) [P(An-co-2-IAn)] were synthesized by electrochemical methods in acetonitrile solution containing tetrabutylammonium perchlorate (TBAP) and perchloric acid (HClO₄). The voltametry of the copolymer shows characteristics similar to those of conventional polyaniline (PANI), and it exhibits higher dry electrical conductivity than PIANI and lower than PANI. The observed decrease in the conductivity of the copolymer relative to PANI is attributed to the incorporation of the iodine moieties into the PANI chain. The structure and properties of these conduct-

ing films were characterized by FTIR and UV-Vis spectroscopy and by an electrochemical method (cyclic voltametry). Conductivity values, FTIR and UV-Vis spectra of the PIANI and copolymer were compared with those of PANI and the relative solubility of the PIANI and the copolymer powders was determined in various organic solvents. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1652–1658, 2003

Key words: conducting polymers; electrochemistry; copolymerization

INTRODUCTION

Polyaniline (PANI) is the first conducting polymer whose electronic properties can be reversibly controlled by protonation.¹ PANI and some of its derivatives have been extensively studied because of their ease of preparation by chemical and electrochemical methods, their good environmental stability, and the ability of their electrical properties to be modified by both the oxidation state of the main chain and by protonation.^{2–4} Specifically, PANI has been used in organic batteries,^{5,6} electrochromic displays,^{7,8} microelectronic devices,⁹ electrode devices,¹⁰ biosensors,¹¹ and as a corrosion inhibitor.¹²

PANI can be produced by electrochemical oxidation of aniline either potentiostatically^{13,14} or through cyclic voltametry.^{15–17} The structure and properties of the resultant polymer film depend on the kind of electrolytes in solution¹⁸ and the type of substrates employed.¹⁹ Electropolymerization of aniline is usually carried out in aqueous acid solutions. PANI decomposes to form quinone and hydroquinone type products,²⁰ and these products are also electroactive in water.

The commercial exploitation of most applications of PANI is closely linked with its ease of processibility.

Substituted polyanilines are used to increase the processibility of the polymer.^{21,22} The processibility can be enhanced either by substitution into the aromatic nucleus or by copolymerization in such a way that there is variation in the torsion angles between adjacent phenyl rings of the polymer. Several substituted polyanilines with electron-donating groups (alkoxy, alkyl, etc.) have been reported.^{23–27} These polymers are soluble in common solvents but exhibit lower electrical conductivity value (10^{-3} – 10^{-1} S/cm) than the unsubstituted PANI. These results indicate that the side-groups may markedly affect the polymerizability of anilines.²³ The synthesis of different homopolymers and copolymers derived from anilines with electron-withdrawing groups has been reported. Ranger et al. synthesized poly(cyanoanilines) and poly(cyanoaniline-co-aniline) by chemical methods.²⁸ They found that the oxidation of 3-substituted anilines leads to more regular polymers than those obtained from 2-isomers. Neoh et al. reported the chemical copolymerizations of aniline with mono-ortho-halogenated anilines (2-chloroaniline and 2-iodoaniline), and they have shown that the presence of the Cl or I substituted group in the ortho position does not adversely affect the polymerization.²⁹ The measured electrical conductivity of the homopolymers, poly(2-chloroaniline) and poly(2-iodoaniline), is $<10^{-6}$ S/cm, and the electrical conductivity of the copolymers is strongly dependent on the amount of substituted aniline incorporated.²⁹ Palaniappan reported the synthesis of poly(aniline-co-2-chloroaniline)-*p*-toluene-sulfonate and poly(aniline-

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co-2-chloroaniline) formate salts by chemical polymerization.³⁰ He found that the conductivity and yield of poly(aniline-*co*-2-chloroaniline)-*p*-toluene-sulfonate are less than those of poly(aniline-*co*-2-chloroaniline) formate. Diaz et al. synthesized poly(dichloroanilines-*co*-aniline) by chemical copolymerization of aniline with dichloroanilines in aqueous 1M hydrochloric acid using potassium dichromate as an oxidizing agent.³¹ Electrochemical polymerization of *m*-chloroaniline was reported by Anjoli et al.³² Sharma et al. reported the chemical synthesis and characterization of poly(aniline-*co*-fluoroaniline).³³ Kang et al.³⁴ carried out a polymerization study on 2-fluoro and 2-chloroaniline by chromic acid at various pH values. Their results indicated that substitution by an electronegative group lowers the conductivity of a polymer. Iodine was used only as a doping reagent of PANI or polyacetylene. Zeng et al. synthesized PANI by using potassium dichromate as the oxidant, and the PANI was doped with iodine.³⁵ They reported that the iodine-doped polyanilines attained a conductivity of 1.83×10^{-3} S/cm, which was about eight orders of magnitude greater than that of intrinsic PANI. However, electrochemical polymerization of 2-iodoaniline and copolymerization of it with aniline in acetonitrile solution containing HClO₄ were not found in the literature.

In this work, we studied the electrochemical polymerization of 2-iodoaniline and its copolymerization with aniline in acetonitrile solution containing tetrabutylammonium perchlorate (TBAP) and HClO₄. The dry electrical conductivity value of the copolymer [poly(aniline-*co*-2-iodoaniline)] was found to be higher than that of the homopolymer [poly(2-iodoaniline)] and lower than of PANI. The presence of an electron-withdrawing group decreases the electronic conductivity. The structure and properties of these conducting polymers and copolymer were elucidated using cyclic voltametry (CV), FTIR and UV-Vis spectroscopy.

EXPERIMENTAL

Aniline (Aldrich, Milwaukee, WI) was vacuum-distilled (67°C) and maintained under a nitrogen atmosphere. 2-Iodoaniline (Aldrich) was used without further purification. Acetonitrile (Merck, Darmstadt, Germany, LiChrosolv) was used as a solvent. Perchloric acid (70%, Aldrich, Steinheim, Germany) was used as an acid, and TBAP was used as a supporting electrolyte. The preparation of TBAP was described by Pekmez et al.³⁶ All electrochemical experiments were carried out under nitrogen atmosphere. The electrochemical cell used was of the three-electrode type with separate compartments for the reference electrode (Ag/AgCl, sat.) and the counter electrode (Pt spiral).

The acetonitrile containing 0.1M TBAP in the reference electrode compartment was saturated with AgCl. The working electrode for the cyclic voltametric studies was a Pt disc (area, 0.0132 cm²). The working electrode was cleaned by polishing with Al₂O₃ slurry. The macro samples of the polymer and copolymer films were prepared on a Pt foil (area: 1.0 cm²) cleaned by holding in a flame for a few minutes. The electrodes were rinsed with acetonitrile and dried before use.

Electrodeposition was performed by cyclic potential sweeping in the potential range between -0.30 and +1.90 V (vs. Ag/AgCl, sat.) at a sweep rate of 100 mV/s. The films prepared electrochemically were immersed in acetonitrile to remove TBAP and soluble oligomers and dried under vacuum at room temperature. Because of their porosity the films were pressed under a pressure of 5 tons/cm² before use.

The dry electrical conductivity values, which depend on the film thickness, were measured using a four-probe technique at room temperature. Gold plated probes were used to avoid any errors that might arise from the ohmic contacts. At least ten different current values were used in the measurement of the potential drops.

The electrochemical instrumentation consisted of a Bank Wenking POS 88 model potentiostat and a Bank 175 model integrator. The current-voltage curves were recorded with a DAS software program.

UV-Vis spectra of the polymer and copolymer solutions in dimethyl sulfoxide (DMSO) were recorded on a Perkin Elmer spectrophotometer. The polymer and copolymer structures were determined by FTIR spectrophotometry using a Perkin Elmer and KBr pellets of solid samples.

RESULTS AND DISCUSSION

The oxidation of aniline and 2-iodoaniline were recorded at the peak potential of +0.90 V and +1.10 V (vs. Ag/AgCl), respectively, in a TBAP/acetonitrile medium. When the potential scan was reversed toward the cathodic direction, no reduction peak was observed.

Figure 1(a) shows the initial five cyclic voltametric sweeps taken during the oxidation of 75 mM aniline with 30 mM HClO₄ in a 0.1M TBAP/acetonitrile solution. The potential was scanned from -0.30 to +1.90 V (vs. Ag/AgCl) at a scan rate of 100 mV/s. The oxidation peak of the aniline shifts to higher potentials and gradually disappears. The peak shows the formation of a film on the electrode surface and behaves differently from that of the bare Pt working electrode. Figure 1(b) demonstrates the subsequent sweeps obtained in the same solution. The formation and growth of the polymer film can easily be seen in this figure. The oxidation and reduction peaks of the film increase

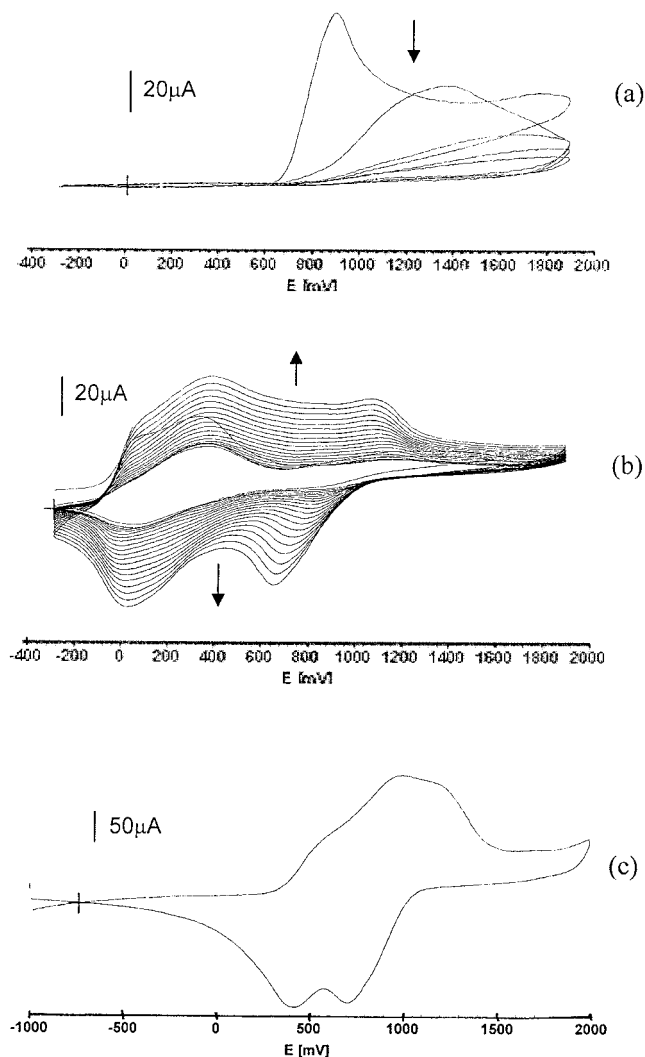


Figure 1 Cyclic voltammograms of the acetonitrile solution containing 75 mM aniline with 30 mM HClO₄/0.1M TBAP. (a) Initial five cyclic voltammograms. (b) Subsequent multi-sweep cyclic voltammograms. (c) Electrochemical behavior of the polymer film in neutral blank solution (0.1M TBAP). Scan rate: 100 mV/s.

in intensity as the film grows. There are two broad oxidation and two reduction peaks observed during the growth of the film. The first oxidation peak at the potential of +0.40 V belongs to the formation of the leucoemeraldine cation radical from leucoemeraldine. The reverse reduction process occurs with a peak potential of +0.025 V. The leucoemeraldine cation radical is further oxidized to emeraldine at the peak potential of +1.10 V with a corresponding cathodic peak at +0.70 V belonging to the reverse process. The cyclic voltammogram of the film in acetonitrile solution containing 0.1M TBAP (neutral blank solution) is shown in Figure 1(c). The film exhibits two broad oxidation and two reduction peaks is related to the blank solution.

Figure 2 illustrates the cyclic voltammograms of acetonitrile solution containing 75 mM 2-iodoaniline and 30 mM HClO₄/0.1M TBAP. A polymeric film was deposited onto the electrode surface during electrooxidation. The electrochemistry of the monomers (aniline and 2-iodoaniline) was quite similar.

Figure 3 shows the cyclic voltametric sweeps taken during the oxidation of 75 mM 2-iodoaniline with 150 mM aniline in acetonitrile solution containing 0.1M TBAP and 30 mM HClO₄. The films were grown in aniline solutions of concentration 25–200 mM by the cycling of the potential between –0.30 and +1.90 V (vs. Ag/AgCl) for the same period of time (30 min) at a scan rate of 100 mV/s. The optimum aniline concentration was found to be 150 mM. There was a considerable decrease in the yield of polymer formation below and above this aniline concentration.

Figures 4 and 5 show the electrochemical behavior of the films in basic and acidic solutions, respectively. PANI itself loses its electroactivity completely even after a few cycles by the addition of small amounts of pyridine (5 mM) into the TBAP/acetonitrile solution.¹⁷ In the cyclic voltammogram of the poly(2-iodoaniline) (PIANI) film in basic blank solution (Fig. 4), containing 0.1M TBAP and 5 mM pyridine, the oxidation and reduction peaks of the film disappeared after a few potential scans, whereas they remained almost unchanged in neutral blank solution. Pyridine causes a rapid loss of electroactivity. Figure 5 shows the electrochemical behavior of the film in acidic blank solution, containing excess HClO₄. The film did not lose its electroactivity in acidic blank solution.

To determine the effect of acid (HClO₄) concentration on the growth of the polymer film, the films were grown in the range of 5–75 mM acid concentration by cycling the potential between –0.30 and +1.90 V over the same time interval (30 min). The charge passed during the electrooxidation of the films in blank solution was measured (Fig. 6). Then charge during the first oxidative cycle of the cyclic voltammogram of the film in blank solution was measured. The anodic charge, which should be proportional to the thickness of the deposit, was found to increase with increasing acid concentration up to 30 mM. It can be concluded that the optimum acid concentration under these conditions is about 30 mM. There was a considerable decrease in the yield of the polymer formation below and above this acid concentration.

The measured dry conductivity values of PANI, PIANI and poly(aniline-co-2-iodoaniline) P(An-co-2-IA) were found to be 2.1, 1.8×10^{-2} and 1.2×10^{-1} S/cm, respectively. The electron-withdrawing effect of iodine was seen on the conductivity of the PIANI and the P(An-co-2-IA) films. As the iodine content increased, the conductivity of the film decreased.

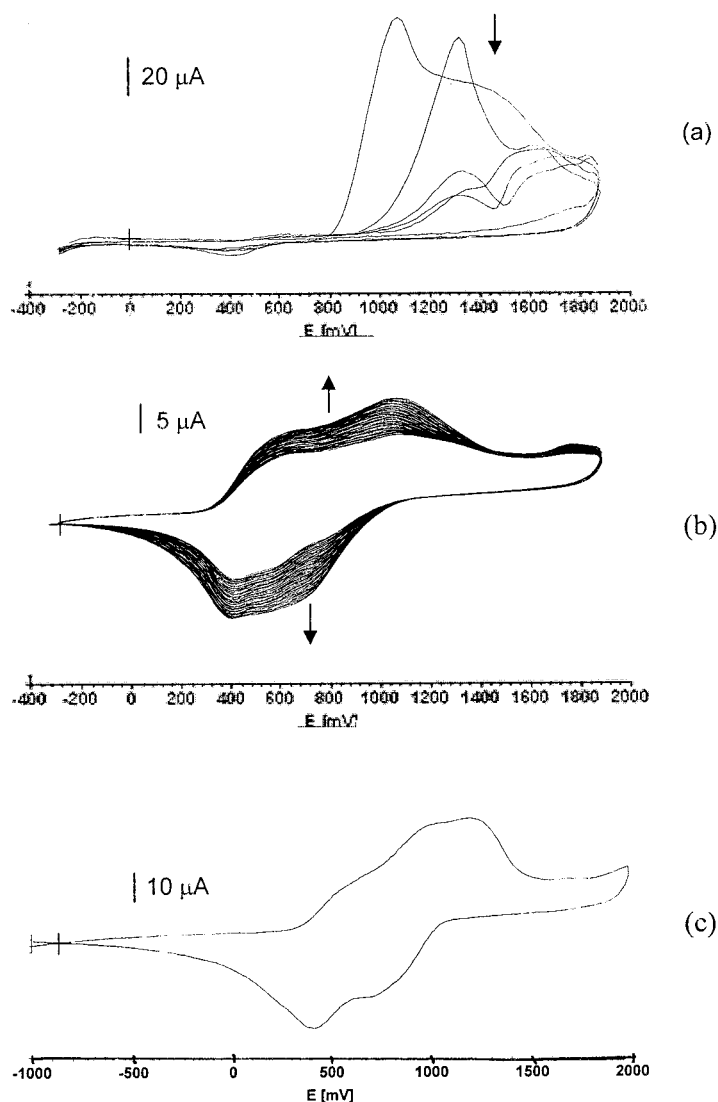


Figure 2 Cyclic voltammograms of the acetonitrile solution containing 75 mM 2-iodoaniline with 30 mM $\text{HClO}_4/0.1\text{M}$ TBAP. (a) Initial five cyclic voltammograms. (b) Subsequent multisweep cyclic voltammograms. (c) Electrochemical behavior of the polymer film in neutral blank solution (0.1M TBAP). Scan rate: 100mV/s.

However, it was found that the measured dry conductivity value of the iodine-doped PANI increased with increasing iodine content.³⁷ The observed decrease in the conductivity of the copolymer relative to PANI is attributed to the incorporation of the iodine moieties into the PANI chain.

The FTIR spectra of the electrochemically prepared samples recorded in the range 2000–400 cm^{-1} is shown in Figure 7. The peak at about 1580 cm^{-1} is due to the C=C double bond of the quinoid rings, whereas the peak at 1460–1500 cm^{-1} arises due to vibration of the C=C bond associated with the benzenoid ring. Aromatic C—N stretching is responsible for the clustering of peaks between 1400 and 1200 cm^{-1} .³⁷ The band at about 1070–1170 cm^{-1} , primarily due to C—H in-plane deformation, has been used by Chiang and

MacDiarmid³⁸ to measure the extent of electron delocalization in the polymer. The peak at 804–831 cm^{-1} is due to aromatic C—H bending.³⁹ The peak observed at 625 cm^{-1} has been attributed to the ClO_4^- ion.¹⁷ The absorption peak of the quinoid units shifted to higher wavelengths in PIANI. On the other hand, there was almost no change the characteristic absorption peak of benzenoid units (1460 cm^{-1}). Two new peaks at about 1400 cm^{-1} and 1025 cm^{-1} were observed in both PIANI and poly(aniline-co-2-iodoaniline) spectra. These peaks were associated with the presence of iodine groups in the polymer and copolymer structure. The synthesized polymer was a homopolymer of 2-iodoaniline (Fig. 7b) and the other one was a copolymer of aniline with 2-iodoaniline and not a mixture of homopolymers (Fig. 7c).

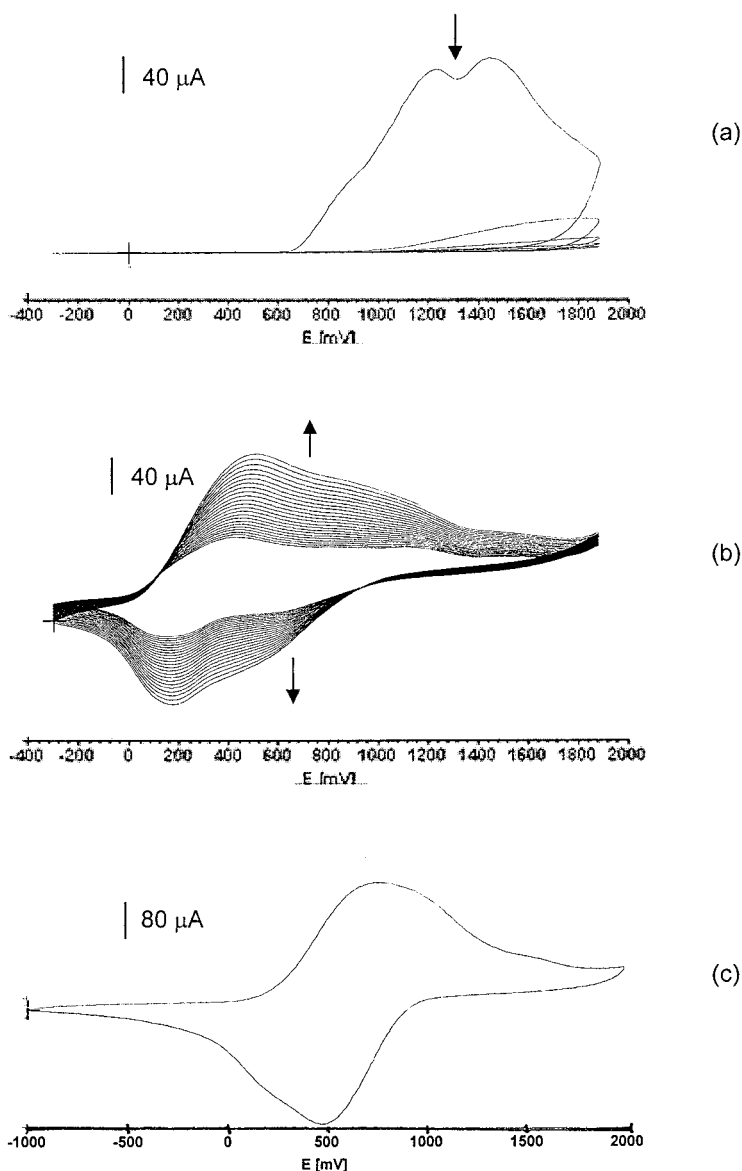


Figure 3 Cyclic voltammograms of the acetonitrile solution containing 75 mM 2-iodoaniline with 150 mM aniline and 30 mM $\text{HClO}_4/0.1\text{M}$ TBAP. (a) Initial five cyclic voltammograms. (b) Subsequent multisweep cyclic voltammograms. (c) Electrochemical behavior of the polymer film in neutral blank solution (0.1M TBAP). Scan rate: 100mV/s.

The UV-Vis spectra of the PANI, PBrANI and P(An-co-2-BrAn) solutions in DMSO recorded at room temperature are shown in Figures 8a, b and c, respectively. The spectra are dominated by two broad absorption bands at 275–300 nm (peak 1) and 525–625 nm (peak 2). According to the general practice of peak assignment, peak 1 is attributed to the π - π^* transition of the benzenoid moieties in the PANI linear structure or simply to the band gap of the polymer.⁴⁰ Peak 2 closely resembles the benzenoid-quinoid transition in the emeraldine form (middle oxidation state) of PANI.^{40,41} However, the actual band positions are blue-shifted with respect to PANI. The blue shift was induced by the presence of iodine units in the polymer

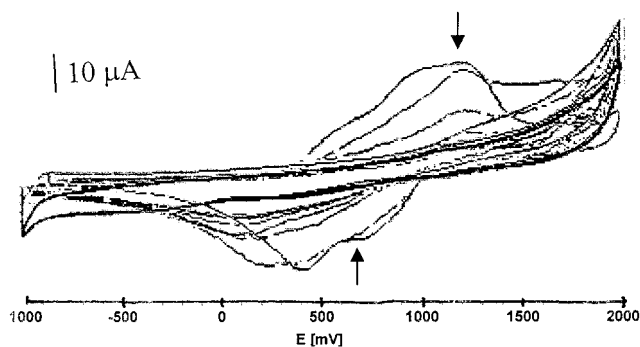


Figure 4 Electrochemical behavior of the film, obtained from 75 mM 2-iodoaniline with 30 mM $\text{HClO}_4/0.1\text{M}$ TBAP in basic blank (pyridine/TBAP) solution. Scan rate: 100 mV/s.

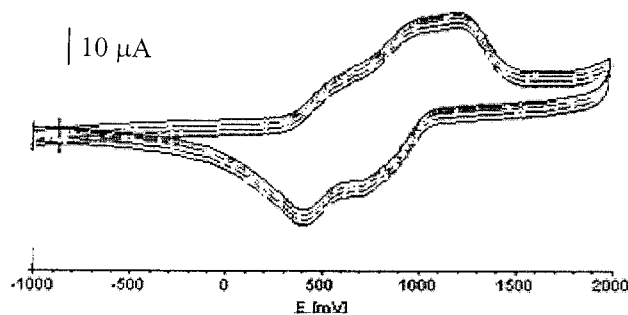


Figure 5 Electrochemical behavior of the film, obtained from 75 mM 2-iodoaniline with 30 mM HClO_4 /0.1M TBAP in acidic blank (HClO_4 /TBAP) solution. Scan rate: 100 mV/s.

and copolymer. The electron-withdrawing character of iodine units restricts the effective dispersion of electrical charge in the conjugated polymeric system, resulting in more locally oxidized polymeric units. The same effects were seen in sulfonated polyanilines^{42–44} because of the electron-withdrawing effect of the sulfonate group. These spectra also suggest that the synthesized materials are poly(2-iodoaniline) and poly(aniline-co-2-iodoaniline).

The solubility of the PANI, PIANI and P(An-co-2-IAn) was tested in DMSO, 1-methyl-2-pyrrolidone (NMP), dimethyl formamide (DMF) and tetrahydrofuran (THF) at room temperature. PANI was soluble in DMSO. However, it was not soluble in NMP, THF or DMF. Unlike PANI, PIANI and P(An-co-2-IAn) were soluble in NMP, THF, DMF and DMSO. Thus, it is possible to cast films of the desired size of the PIANI and P(An-co-2-IAn). The polymers of substituted derivatives of aniline exhibit better solubility than aniline itself, and hence incorporation of these in the copolymer can have the additional effect of enhancing solubility. It is noticed that the presence of a halogen atom in the ring of aniline units can produce polymers and copolymers with better solubility in NMP, THF, DMF and DMSO solvents.

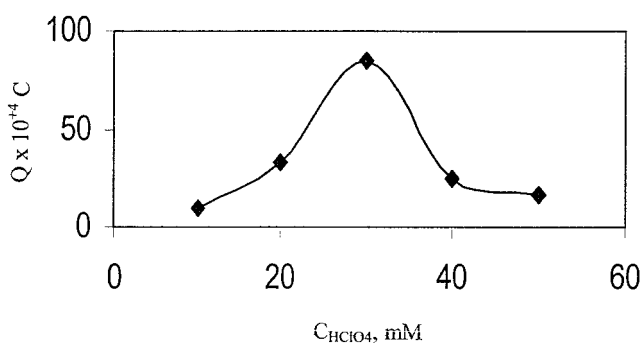


Figure 6 Plot of the charge passed during the electrooxidation of the polymer films in 0.1M TBAP.

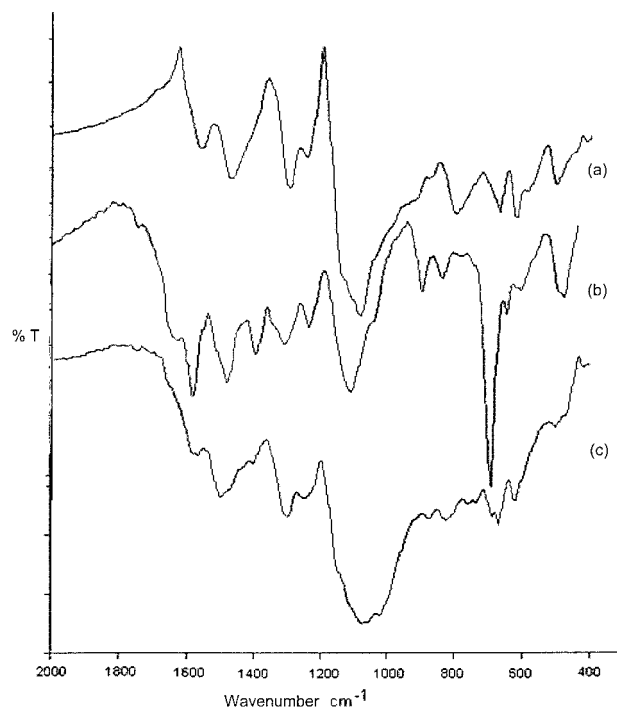


Figure 7 Baseline-corrected FTIR spectra, showing 2000–400 cm^{-1} region, of (a) polyaniline, (b) poly(2-iodoaniline) and (c) poly(aniline-co-2-iodoaniline).

CONCLUSIONS

The synthesis of PIANI and P(An-co-2-IAn) were accomplished using an electrochemical method. The voltammetry of the copolymer shows characteristics similar to those of conventional PANI. The dry electrical conductivity value of the copolymer was found to be lower than that of PANI and higher than that of PIANI. Spectroscopic results (FTIR and UV-Vis)

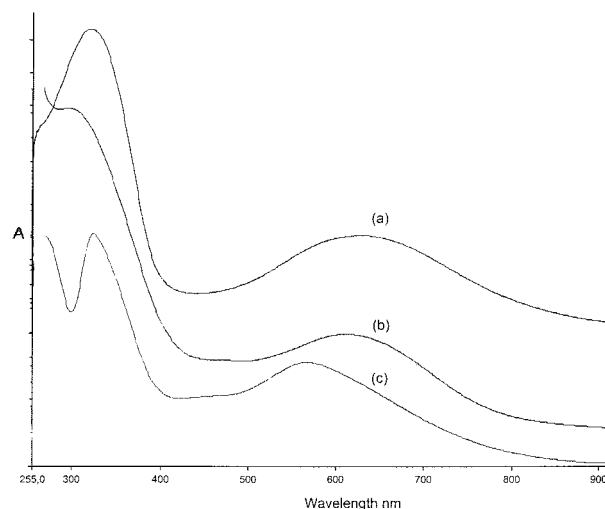


Figure 8 UV-Vis absorption spectra of (a) polyaniline, (b) poly(2-iodoaniline) and (c) poly(aniline-co-2-iodoaniline) in DMSO.

showed that the polymer and copolymer were different from PANI.

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