

Electrochemical Polymerization of Aniline on Carbon Fibers in Aqueous Toluene Sulfonate Solution

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ABSTRACT: Polyaniline has been successfully formed by aqueous electrochemical polymerization on carbon fibers. The coatings were formed under potentiostatic conditions with toluene-4-sulphonic acid sodium salt as the electrolyte. The effect of monomer concentration, electrolyte concentration, and the applied potential on the rate of polymerization were studied. The amount of polyaniline coatings formed on carbon fibers increased with increased aniline and electrolyte concentration. Increasing the applied potential also increased the weight of coatings formed on the fibers. The presence of positive y-intercept in the weight gain plots are attributed to the adsorption of the electrolyte on the fibers before electropolymerization. The effect of the electrochemical parameters on the degradation of the polymer has been analyzed using infrared spectroscopy. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1503–1509, 2000

Key words: polyaniline, carbon fibers, electropolymerization, rate of reaction, order of reaction

INTRODUCTION

In recent years, electroactive organic polymers have been widely used in industries because of their desirable properties. Polyaniline has excellent environmental and chemical stability and possesses useful chemical properties. It has also been reported to possess moderately high electrical conductivity. Polyaniline is used in making batteries, ion exchangers, and as a corrosion inhibitor. It is also used in microelectronic devices, electrochromic displays, gas separating membranes, and in electrocatalytic oxidation and reduction.¹

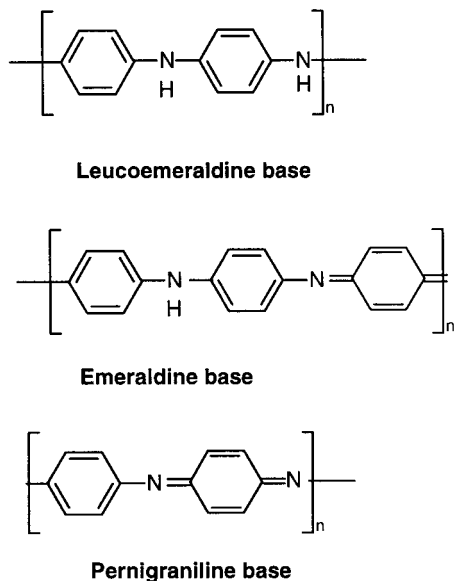
As with other conducting polymers, polyaniline has conjugated double bonds, which promotes delocalization of electrons. Polyaniline can exist in three different oxidation states, such as leucoemeraldine (fully reduced form), pernigraniline (fully oxidized form), and emeraldine form (interme-

diolate form) as shown in Scheme 1. The structure of polyaniline has been fully determined only recently.^{2–5} It has been reported that the conductivity of polyaniline is maximum in the emeraldine form. The conductivity of polyaniline is increased by doping. Sulphonated polyanilines show self-doping characteristics and are readily processible. They also retain high levels of conductivity, even in neutral pH.⁶ Polyaniline can also be doped by perchloric acid, sulfuric acid, and hydrochloric acid.⁷ In fact, hydrochloric acid doped polyaniline can achieve conductivity as high as 100 S cm^{-1} .^{8,9} The conductivity of polyaniline is also affected by chain orientation. Increased chain orientation results in increased conductivity.¹⁰ This behavior is attributable to an increase in the crystallinity of polyaniline. Thus, polyaniline oligomers are more conductive than high molecular weight polyaniline.¹¹

Carbon fibers have good mechanical properties and electronic conductivity. They remain inert over a large potential range. Therefore, they are excellent materials for use as electrodes in electro-oxidation and electroreduction. This property

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Scheme 1 Different oxidation states of polyaniline.

makes it interesting to study the formation of polyaniline on the carbon fiber electrodes. Electrochemical polymerization of aniline has been conventionally performed by using platinum as the working electrode.^{12–22} However, few investigations of the electropolymerization of aniline have been performed on carbon fibers. Zinger and Shkolnik reported the formation of thick polyaniline coatings on carbon fibers by direct anodic oxidation of aniline.²³ The formation of polyaniline on carbon fibers in aqueous methanolic solution using cyclic voltammetry techniques has been reported.^{24,25} Formation of highly conducting polyaniline film on carbon fibers is a positive step in formation of conducting composites with good electrical, electronic, and mechanical properties.

In this article, we report the electrochemical polymerization of aniline in an aqueous toluene-4-sulphonic acid sodium salt solution under potentiostatic conditions. We also report our preliminary investigation of the effect of electrochemical process variables on the electropolymerization of aniline.

EXPERIMENTAL

The electrochemical polymerization of aniline was carried out by using an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 363. A one-compartment electrochemical

cell was used. The carbon fiber working electrode (the anode) is surrounded by two stainless steel counter electrodes (cathode). The unsized 12K T-300 carbon fibers used as the working electrode were donated by AMOCO Performance Products Company. A saturated calomel electrode purchased from Fisher Scientific Company was used as the reference electrode.

Aqueous solution of aniline (99.5% pure) purchased from Aldrich Chemical Company and toluene-4-sulphonic acid sodium salt from Fluka were prepared in deionized water. About 100 mL of solution was used for every reaction. The reactions were carried out by changing such parameters as electrolyte concentration and initial monomer concentration and also by varying the electrode potential. The coated fibers were dried at room temperature for 24 hours followed by additional drying in a vacuum oven at 100°C for 1 h. The weight gain of fibers was determined as the ratio of the weight of the coatings to the weight of the fibers.

The Fourier transform infrared (FTIR) spectra were obtained by using a Perkin–Elmer 1800 FTIR spectrometer. The spectra were taken at a resolution of 4 cm⁻¹ from 4000 to 400 cm⁻¹. The infrared (IR) specimens were prepared by mixing a small quantity of the coatings with IR grade potassium bromide (KBr) powders and subsequent pressing of the mixture into a clear pellet. The I-t curves for the reactions carried out by varying the reaction parameters were plotted out using a model 273A Potentiostat/Galvanostat.

RESULTS AND DISCUSSION

Effect of Reaction Parameters

Effect of Monomer Concentration

Figure 1 shows the plot of percentage weight gain of fibers attributable to formation of polyaniline coatings with respect to time for different concentrations of aniline. The figure shows a linear relationship between the weight gain and the reaction time. The weight gain of fibers increases with increasing aniline concentration. From the slope of a log–log plot of the rate of polymerization against the initial monomer concentration an exponent of 0.73 was obtained; $R_p \propto [M]^{0.73}$. The polymerization of aniline is believed to be initiated by oxidation of aniline and low molecular weight oligomers followed by subsequent coupling of the oxidized species.²⁶ Subsequent (oxidation)

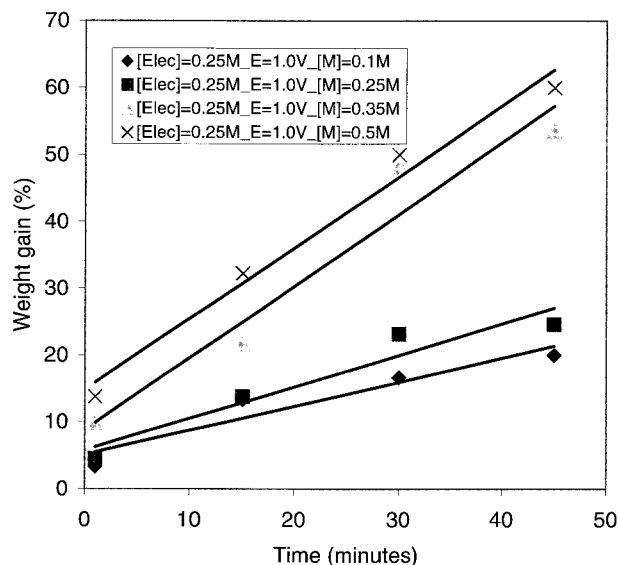


Figure 1 Effect of change of concentration of monomer.

nucleation and coupling (growth) of the oligomers lead to the formation of high molecular weight polyaniline.²⁶

Effect of Electrolyte Concentration

Figure 2 shows the relationship between the percentage weight gain of the fibers with respect to time for different concentrations of electrolytes. It can be seen that the weight gain increases with increasing electrolyte concentration. A plot of the log of rate of polymerization against log of elec-

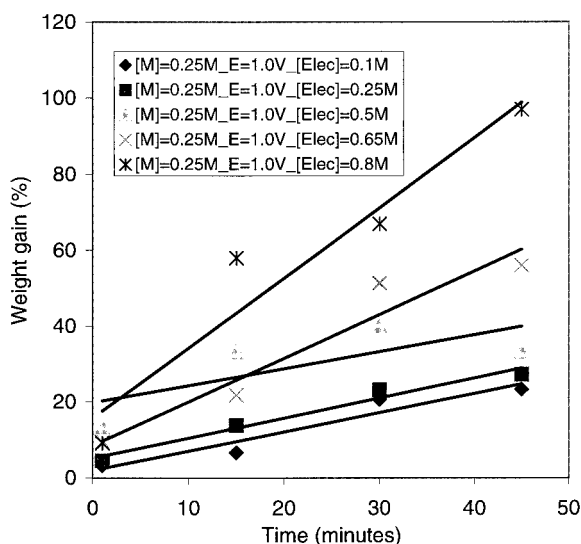


Figure 2 Effect of change in the concentration of electrolyte.

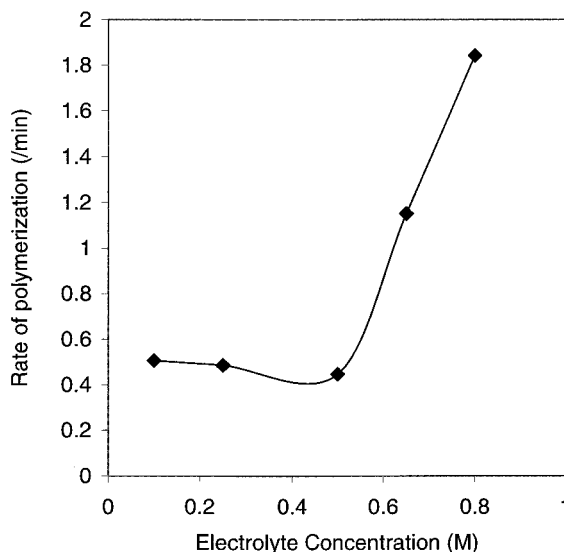


Figure 3 Rate of polymerization versus concentration of electrolyte.

trolyte concentration is shown on Figures 3 and 4. Figures 3 and 4 show that as long as the electrolyte concentration is less than 0.5 M, there is no significant increase in the rate of polymerization. However, as the electrolyte concentration is raised above 0.5 M, the rate of polymerization increases linearly with electrolyte concentration. In this regime, $R_p \propto [\text{Elec}]^{3.04}$ (Fig. 4).

Effect of Applied Potential

Figure 5 shows the variation of percentage weight gain with time for electropolymerization of ani-

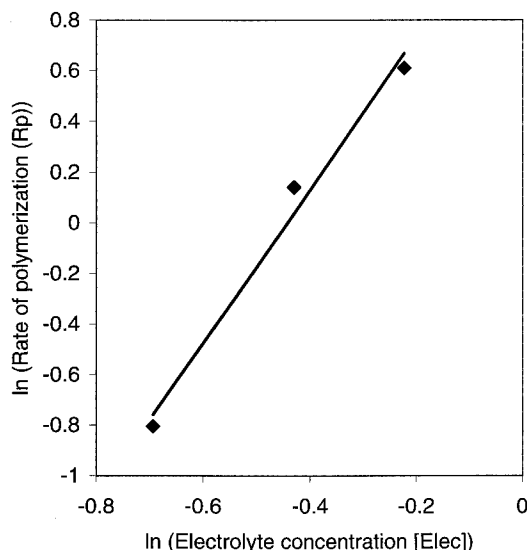


Figure 4 $\ln R_p$ versus $\ln[\text{Elec}]$.

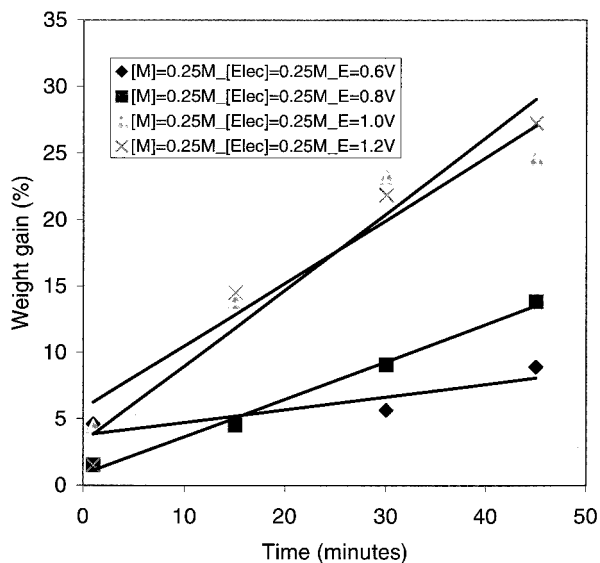


Figure 5 Effect of applied potential.

line. The applied potential was varied between 0.65 to 1.2 V versus SCE. There was a significant increase in the weight gain only for potentials above 0.8 V. This is consistent with literature reports that state that polyaniline starts to form at only about 0.7 V. There seems to be degradation of polyaniline formed at an applied potential of 1.2 V. This inference was made from the weight gain plot and the I - t curves obtained at an applied potential of 1.2 V. A plot of rate of polymerization with applied potential shows a linear relationship (Fig. 6) and an exponent of 2.57 is obtained from the log-log plot, $R_p \propto [E]^{2.57}$.

The I - t curves for the electropolymerization of aniline on carbon fibers are shown in Figures 7–9. It can be seen that current decreases sharply at the onset of electropolymerization followed by a gradual decrease after about 3 min of electropolymerization. The knee of the curve can be attributed to the oxidation of aniline and the formation of polaron and bipolaron.²² From this point, current either remains steady, decreases gradually, or slightly increases with time. This is possibly the phase at which chain propagation occurs. The decrease in the current with increased aniline concentration suggests an increase in the resistance of the working electrode.

Increasing the initial aniline concentration increases the resulting current (Figure 7). This may be attributable to improved conductivity at the electrode–electrolyte interface and deposition of higher levels of doped polyaniline on the working electrode.

The effect of varying electrolyte concentration on the cell current is shown in Figure 8. The cell

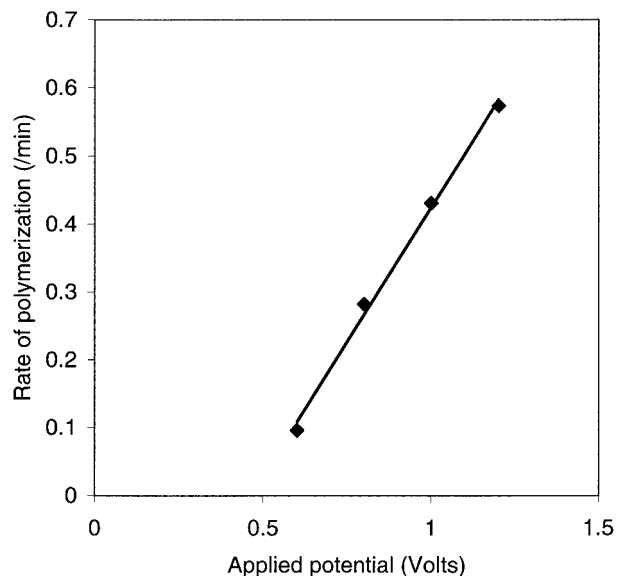


Figure 6 Rate of polymerization versus applied potential.

current decreases sharply at the onset of electropolymerization followed by gradual decrease in the steady-state region. Increasing the electrolyte concentration increases the steady-state current. The increase in the steady-state current is in agreement with the suggested increased conductivity at the electrode–electrolyte interface. Note that the slope of the initial section of the current–time, i - t curves is varying with the electrolyte concentration, indicating varying nucleation rate. The i - t curve for the electropolymerization performed by using 0.8 M of T4SNa showed a sharp

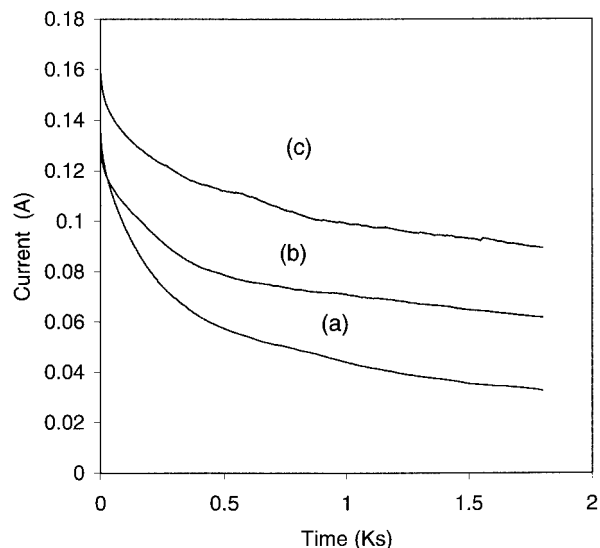


Figure 7 Different mon. con. I - t curves.

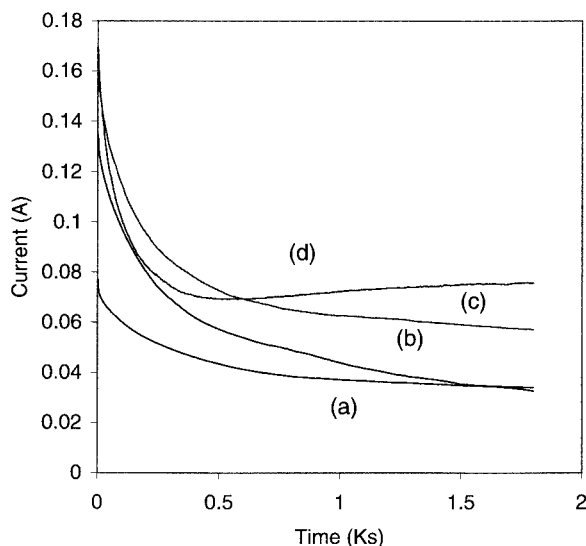


Figure 8 Different elec conc. I-t curves.

decrease in the onset (nucleation) current and an increase in the steady-state current. This increase in the steady-state current is attributable to sharply increased weight gain of fibers at 0.8 M. Figure 8 suggests a transition in the steady-state current obtained at electrolyte concentration ≤ 0.5 M and 0.8 M. This transition is also shown by the weight gain plot in Figure 2. Figure 2 shows a significant increase in the weight gain of fibers at 0.8 M electrolyte concentration. After 3 min of electropolymerization, the slope of the i-t curve (Figure 8, 0.8 M) became positive, indicating increased conductivity of the working electrode because of increased weight gain and doping. The sharp decrease in initial slope of the i-t curve obtained at 0.8 M T4SNa indicates a faster nucleation process.

The effect of applied potential on the i-t curve for the electropolymerization of aniline is shown on Figure 9. Generally, the current shows an initial sharp decrease (at the onset of electropolymerization) followed by a gradual decrease after about 3 minutes of electropolymerization (steady-state region). Increasing the applied potential from 0.8 to 1.0 V, resulted in increased onset current and steady-state current. The difference in the steady-state current, however, decreases with time and approaches $\leq 2\%$ after 30 min of reaction. Further increase in the applied potential to 1.2 V, resulted in a steady-state current lower than that obtained at 1.0 V. Note that the peak oxidation potential for aniline lies between 0.8 and 1.0 V ($0.80 < E_p < 1.0$ V). This phenomenon may be attributable to simultaneous de-

crease in the rate of nucleation and growth and possible degradation of polyaniline at ≥ 1.2 V. Comparison of Figure 9 with Figure 5, indicates that initially ($t \leq 25$ min), the weight gain at 1.2 V was higher than that obtained at 1.0 V. However, at $t > 25$ min, the weight gain at 1.2 V fell below that obtained at 1.0 V. However, the weight gain at 1.2 V remained significantly higher than that obtained at 0.8 V. It is suggested that the decrease in the weight gain at 1.2 V ($t > 25$ min) and the decrease in current at 1.2 V at $t \geq 6.7$ min (Fig. 9), are attributable to the degradation of polyaniline at 1.2 V.

Figures 1, 2, and 5 show positive intercepts, because of the weight gain of fibers caused by the adsorption of electrolytes on the fibers. It was determined that there was zero weight gain of fibers with time when no potential was applied, as shown in Table I, indicating that the electrolyte was not adsorbed on the working electrode. When electrochemical reaction was performed by using varying electrolyte concentration in the absence of aniline, there was a significant increase in the weight gain of the fibers (Fig. 10) because of the adsorption and deposition of the electrolyte on the fibers.

Infrared Spectroscopy

The coatings were characterized using transmission infrared spectroscopy. Figures 11–13 show the IR spectra of polyaniline coatings formed at varying initial aniline concentration, electrolyte concentration, and applied potential, respectively. Polyaniline was found to be in emeraldine

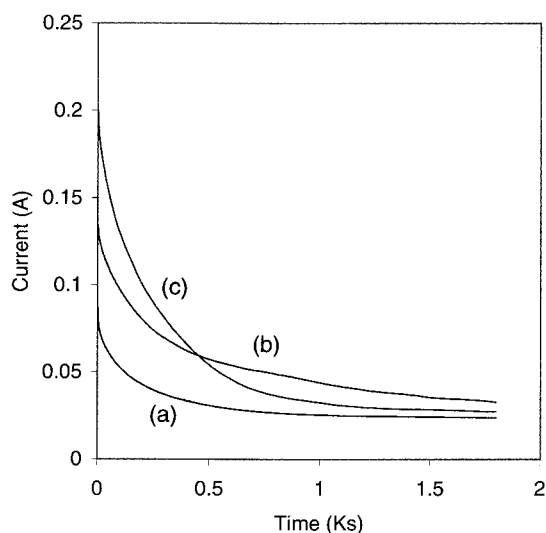


Figure 9 Different pot. I-t curves.

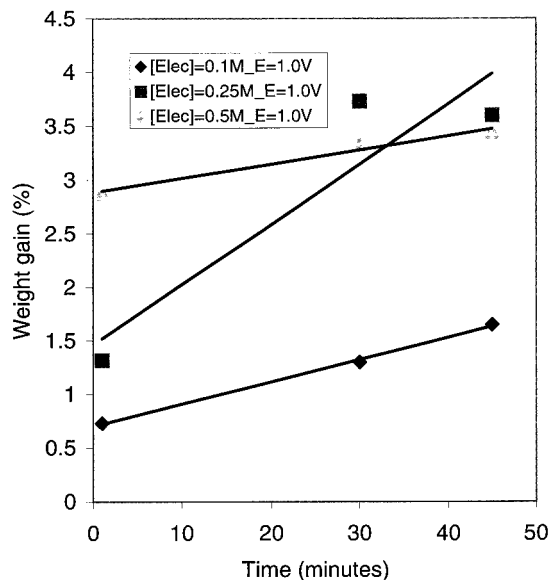
Table Ia Weight Gain of Fibers at Zero Applied Potential

Time (min)	Weight of (fiber + frame) Before Reaction (gm)	Weight of (fiber + frame) After Reaction (gm)
1	7.04	7.04
15	7.31	7.31
30	7.33	7.33
45	7.48	7.48

salt form. The presence of broad peak at 3220–3290 corresponding to hydrogen bonded NH stretch and also the peak at 3450 corresponding to free nonhydrogen bonded NH stretch agree with that reported in literature²⁴ and confirm the presence of emeraldine form. The other prominent IR peaks found at 1590, 1492, 1310, 1150, and 830 cm^{-1} also confirm that polyaniline is in the emeraldine form. The presence of electrolyte ions is seen from the peaks at 1010, 1030, and 2960 cm^{-1} corresponding to sulphonates and aliphatic CH stretch, respectively. There are other significant peaks at 1720 and 1780 cm^{-1} , which are attributable to the presence of quinone. Quinone may be produced by the hydrolysis of polyaniline. It has been reported in the literature that there is competitive reaction between aniline and water with the intermediate bipolaron. In the beginning, water predominates over aniline, but as polyaniline starts forming because of the autocatalytic property of polyaniline, the reaction between aniline and bipolaron starts to predominate over water.²⁵ Our investigation shows similar behavior with increase in the concentration of electrolyte and monomer concentration. We see a gradual decrease in the intensity of the carbonyl peaks with the increase in the concentration of electrolyte and monomer concentrations. This is also confirmed from the corresponding increase in the weight gain of the coatings.

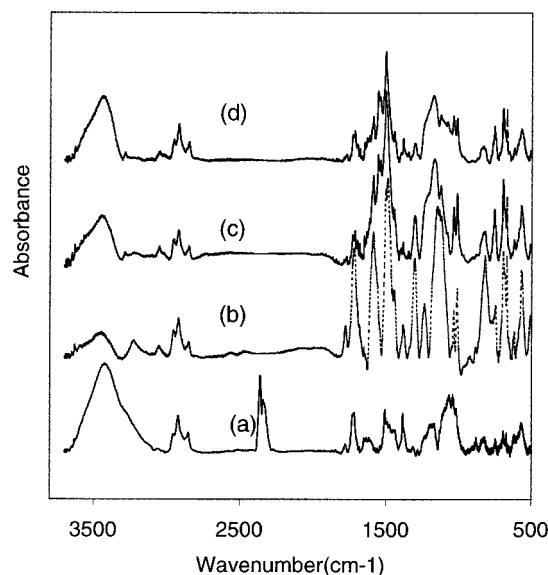
Table Ib Weight Gain of Fibers in the Absence of Aniline (Applied Potential = 1.0 V)

Time (min)	% Weight Gain		
	0.1 M	0.25 M	0.5 M
1	0.73	1.32	2.88
30	1.30	3.73	3.33
45	1.65	3.60	3.44

**Figure 10** Reactions without monomer.

CONCLUSIONS

The effect of reaction parameters on the electrochemical synthesis of polyaniline coatings on carbon fibers were studied. The rate of formation of polyaniline increased with increased initial aniline concentration and increased applied potential. At low electrolyte concentration < 0.5 M, the electrolyte concentration did not significantly affect the rate; however, at higher electrolyte concentration ≥ 0.5 M, a sharp increase in the rate is

**Figure 11** Infrared spectra as a function of monomer concentration, (a) 0.1M, (b) 0.25M, (c) 0.35M and (d) 0.5M.

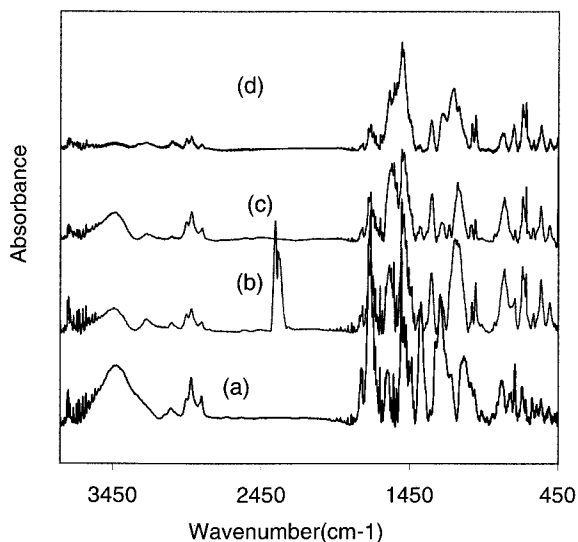


Figure 12 Infrared spectra as a function of electrolyte concentration, (a) 0.1M, (b) 0.25M, (c) 0.5M and (d) 0.8M.

obtained. The *i-t* curves for the electropolymerization of aniline show decreased current with reaction time; however, a significant increase in the steady-state current was obtained at high electrolyte concentration (0.8 M). The presence of emeraldine form of polyaniline is confirmed using IR. The IR spectra also show the presence of dopant electrolyte ions. The presence of quinone and its subsequent decrease with increased electrolyte and the monomer concentrations suggest that, at higher concentrations, the formation of polymer predominates over the hydrolysis of polyaniline.

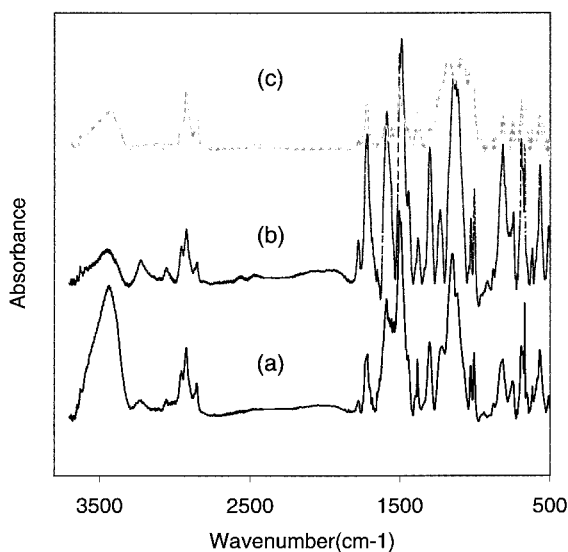


Figure 13 Infrared spectra as a function of applied potential, (a) 0.8V, (b) 1.0V and (c) 1.2V.

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