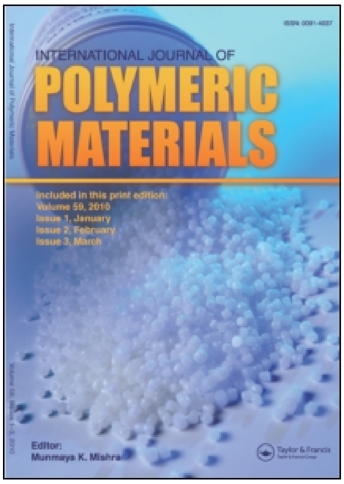

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Electropolymerization of *o*-Aminobenzoic Acid and Characterization of the Obtained Polymer Films

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Poly(ortho-aminobenzoic acid), as a ring substituted derivative of aniline, has been synthesized electrochemically from acid medium on platinum electrode. The reaction parameters such as current density, hydrochloric acid concentration, monomer concentration, temperature, and reaction duration time were investigated. The kinetic study shows that the orders of polymerization reaction are 1.01, 1.33, and 0.41 with respect to hydrochloric acid concentration, monomer concentration, and current density, respectively. The apparent activation energy (E_a) is found to be 134.8 kJ mol^{-1}. The polymer films obtained have been characterized by cyclic voltammetry, X-ray diffraction, elemental analysis, thermogravimetric analysis, scanning electron microscopy, ^{1}H-NMR, and IR spectroscopy. The mechanism of the electrochemical polymerization reaction has been discussed.

Keywords: electropolymerization, ortho-aminobenzoic acid, kinetic study, cyclic voltammetry, characterization

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INTRODUCTION

After the discovery of polyacetylene [1], the electrodeposition of conducting polymers on electrode surfaces has become one of the targets of research in electrochemistry. The great deal of attention in this area is due to the large number of potential applications of conducting polymers alone as well as the modified electrode surfaces; in batteries [2–8], electrochromic devices [2,9–11], microelectronic devices [12], optoelectronic [13], display devices [14], chemically modified electrodes [15], sensors [16], electrochemical chromatography [17], metallization [18], and as corrosion inhibitors to protect semiconductors and metals [18–28].

Polymers such as polythiophenes, polypyrroles, polyanilines, and so on were prepared. Among these polymers, particular interest has been paid to polyaniline (PAni) due to its high conductivity in the oxidized state, easy preparation, and excellent environmental stability in the doped (conducting) form. The monomer is inexpensive, the conversion of monomer to polymer is straightforward, and the polymerization reaction proceeds with a high yield, and PAni shows excellent chemical stability [29–30].

Polyaniline has been extensively studied, but the large-scale application is limited by the insolubility of its protonated state due to the stiffness of its backbone, and difficulty of processing by conventional methods. This shortcoming has been overcome by preparing polyaniline films in acids, synthesis of PAni copolymers [31], as well as the polymerization of different substituted aniline derivatives [19,25,32].

Polyanilines can be prepared chemically or electrochemically: The chemical method of synthesis involves monomer oxidation using an oxidizing agent in an acid medium such as HCl, HF, H_2SO_4, $HCLO_4$, CH_3COOH, $CL_3C-COOH$, and so on. Oxidizing agents such as potassium dichromate, ammonium persulphate, hydrogen peroxide, ceric nitrate, and so on were studied [33–35]. The electrochemical method of synthesis involves the anodic oxidation of the monomer at inert electrodes such as platinum [36–37], different type of carbon (vitreous, pyrolytic, or graphite) [37], stainless steel [21,24,27–28], iron [19–20, 22,25], glass [37], and so on. The preparation can be done by potentiostatic or galvanostatic technique [30]. The polymerization could be performed at room temperature in the presence of various acids, which also act as doping agents for the resulting polymer. Polymerization can also proceed in neutral and alkaline media. Na_2SO_4, $NaCLO_4$, K_2SO_4, and so on work as supporting electrolytes with different concentrations [37–38]. The anodic electrodeposition of polyanilines on oxidizable electrode must be run in suitable electrochemical conditions to prevent the oxidation of the electrode [26].

Ortho-aminobenzoic acid is considered an acidic substituted aniline. It was polymerized chemically [39–40] with low yield $\leq 8.1\%$, and with high yield [33]. It was also polymerized electrochemically by potential sweep in H_2SO_4 solution on glassy carbon electrode [41]. The obtained polymer is of interest as a soluble derivative of polyaniline, soluble in polar solvent like N-methylpyrrolidone in a neutral state, and soluble even in alcohols and water in the carboxylic ion state [40]. Furthermore, poly(*o*-aminobenzoic acid) can have a ring structure due to intermolecular hydrogen bonds, which is similar to the structure of self-doped sulfonated polyaniline [42]. The introduction of acidic group influences the acidity constant of the amine group and appears to offer advantages at less acidic pH values, since conductivity does not fall dramatically with increase pH as happens with PAni [39–40].

The present study intends to investigate the kinetics, optimum conditions, and mechanism of the electrochemical polymerization of *o*-aminobenzoic acid from aqueous HCl solution on platinum electrode. Also, characterization of the obtained polymer film by ^{1}H-NMR, IR, elemental analysis, GPC, TGA, and cyclic voltammetry was performed.

EXPERIMENTAL

Materials

o-Aminobenzoic acid (Fluka, Switzerland), hydrochloric acid solution (Riedel-de Haën, Germany), and Dimethylformamide were provided by El-Naser pharmaceutical Chemical Company (Egypt), anhydrous sodium sulfate was provided by Merck (Darmstadt, Germany). All solutions were freshly prepared using double-distilled water.

Cell and Electrodes

The experimental setup used consisted of a rectangular Prespex cell provided with two platinum foil parallel electrodes [dimensions: 1 cm height × 0.5 cm width] as described previously [43–46]. The polymerization current was supplied by a dc power supply (Thurby ~ Thandar PL 330). Before each run, the platinum anode was cleaned, washed with distilled water, rinsed with ethanol, dried, and weighed. The experiments were run at the required temperature ±1°C using a circular water thermostat. At the end of the experiment, the anode was withdrawn, washed with distilled water, dried, and weighed.

Electropolymerization of *o*-Aminobenzoic Acid

Anodic oxidative polymerization of *o*-aminobenzoic acid was carried out in aqueous solutions containing monomer (concentration range between 0.01 and 0.09 M) using 0.1 M Na_2SO_4 as the supporting electrolyte and the current densities were investigated in the range between 2 and 12 mA cm^{-2}. Electropolymerization was carried out in hydrochloric acid solution (concentration range between 0.2 and 1.2 M) at different temperatures in the range between 293 and 313°K.

Cyclic Voltammetry Measurements

A standard three-electrode cell was used in the cyclic voltammetry measurements with a saturated calomel electrode (SCE) as the standard reference electrode. The auxiliary electrode was a platinum wire. The platinum working electrode was $1 \times 0.5 \times 0.05$ cm. Before each run, the working electrode was cleaned as mentioned earlier.

Electrochemical experiments were performed using an EG&G Potentiostat/Galvanostat Model 273 supplied by EG&G Princeton Applied Research. The *I-E* curves were recorded by computer software from the same company (Model 352 and 270/250).

^{1}H-NMR and TGA

^{1}H-NMR measurements were carried out using a Varian EM 360 L, 60-MHz NMR spectrometer (Varian Associates, Palo Alto, CA, USA). NMR signals of the electropolymerized samples were recorded in dimethylsulphoxide using tetramethylsilane as internal reference. TGA of the obtained polymers was performed using a Shimadzu DT-30 thermal analyzer (Shimadzu, Kyoto, Japan). The weight loss was measured from ambient temperature up to 500°C, at the rate of 20°C min^{-1} to determine the degradation rate of the polymer.

Scanning Electron Microscopy and X-Ray Diffraction

Scanning electron microscopic analysis was carried out using a JSM-T20 scanning electron microscope (JEOL, Tokyo, Japan). The X-ray diffractometer (Philips 1976 Model 1390, Netherlands) was operated under the following conditions that were kept constant for all the analysis processes:

X-ray tube: Cu
Current: 30 mA

Preset time: 10 s
Scan speed: 8°/min
Voltage: 40 kV

RESULTS AND DISCUSSION

Anodic Oxidative Electropolymerization of *o*-Aminobenzoic Acid

Effect of Duration Time

Anodic oxidative electropolymerization of *o*-aminobenzoic acid was studied under the influence of different plating and operating parameters. The effect of duration time on the weight of the obtained polymers was studied with different current density values. The data reveal that the weight of the obtained polymer increased with increases of duration time up to 7.5 min, after which it began to decrease as a result of degradation and the dissolution of the polymer film from the platinum surface in the case of all investigated values of the current densities. The data are graphically represented in Figure 1.

Effect of Current Density

The effect of the applied current density on the anodic oxidative electropolymerization of *o*-aminobenzoic acid was studied at a duration time of 7.5 min using 0.05 M monomer concentration, 0.1 M Na_2SO_4, and 0.8 M HCl at 303°K, all of which were kept constant. The data reveal that as the applied current density increased, the weight of the obtained polymer film increases up to 6 $mAcm^{-2}$ and then tends to decrease. This finding implies that an oxygen and chlorine evolution takes place as a side reaction, especially at high current densities. Each value of the used current density was studied with different time intervals and the yield-time curve was plotted. The data are graphically represented in Figure 2A, from which the initial rate of the electropolymerization reaction was determined. The reaction exponent with respect to the current density was determined from the slope of the straight line presented in Figure 2B, and was found to be 0.41. This means that the order of the electropolymerization reaction with respect to the current density is a half-order reaction.

Effect of HCl Concentration

Anodic oxidative electropolymerization was carried out using 0.05 M monomer concentration, 0.1 M Na_2SO_4, and a current density

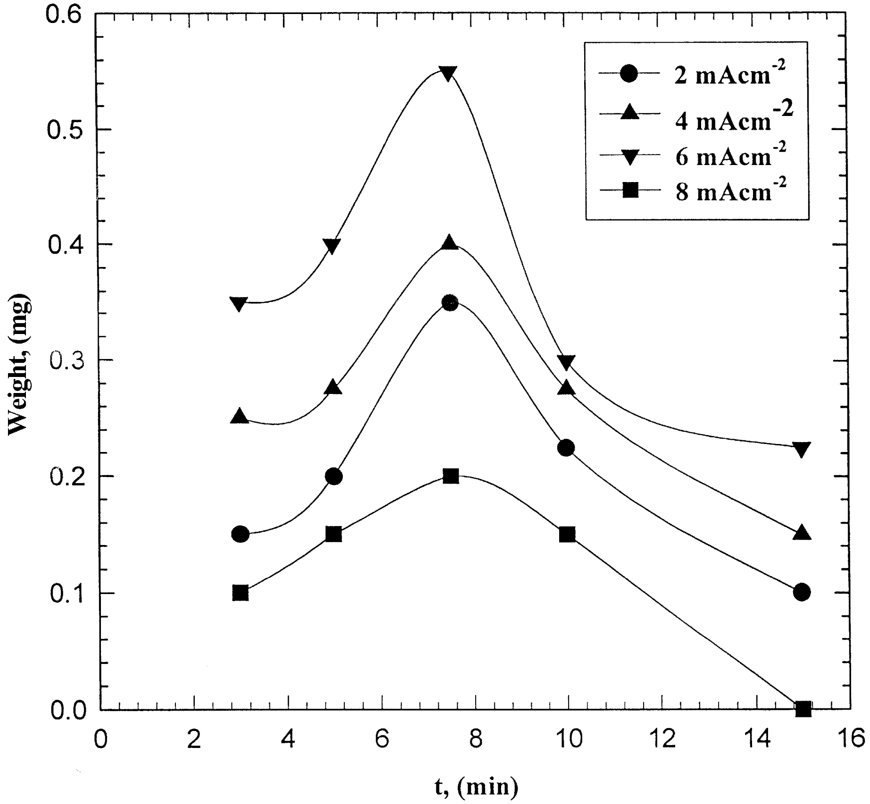


FIGURE 1 Yield-time curve for the effect of duration time on the anodic polymerization of *o*-aminobenzoic acid from solution containing 0.05 M monomer, 1.0 M HCl, and 0.1 M Na_2SO_4 at 302°K.

of 6 mAcm^{-2} at 303°K, for 7.5 min, all of which were kept constant. However, the hydrochloric acid concentration was varied in the range between 0.2 M and 1.2 M. The obtained polymer film in each experiment was weighed. The obtained data reveal that the maximum weight is obtained when 0.8 M HCl concentration was used. The effect of HCl concentration in the range between 0.2 and 0.8 M on the electropolymerization rate was investigated. The weight of the deposited polymer film on the platinum electrode in each experiment is plotted against the duration time as shown in Figure 3A. The initial rate of the electropolymerization reaction was calculated and the double-logarithmic plot of the initial rate versus HCl concentration is represented in Figure 3B. A straight line was obtained with a slop of

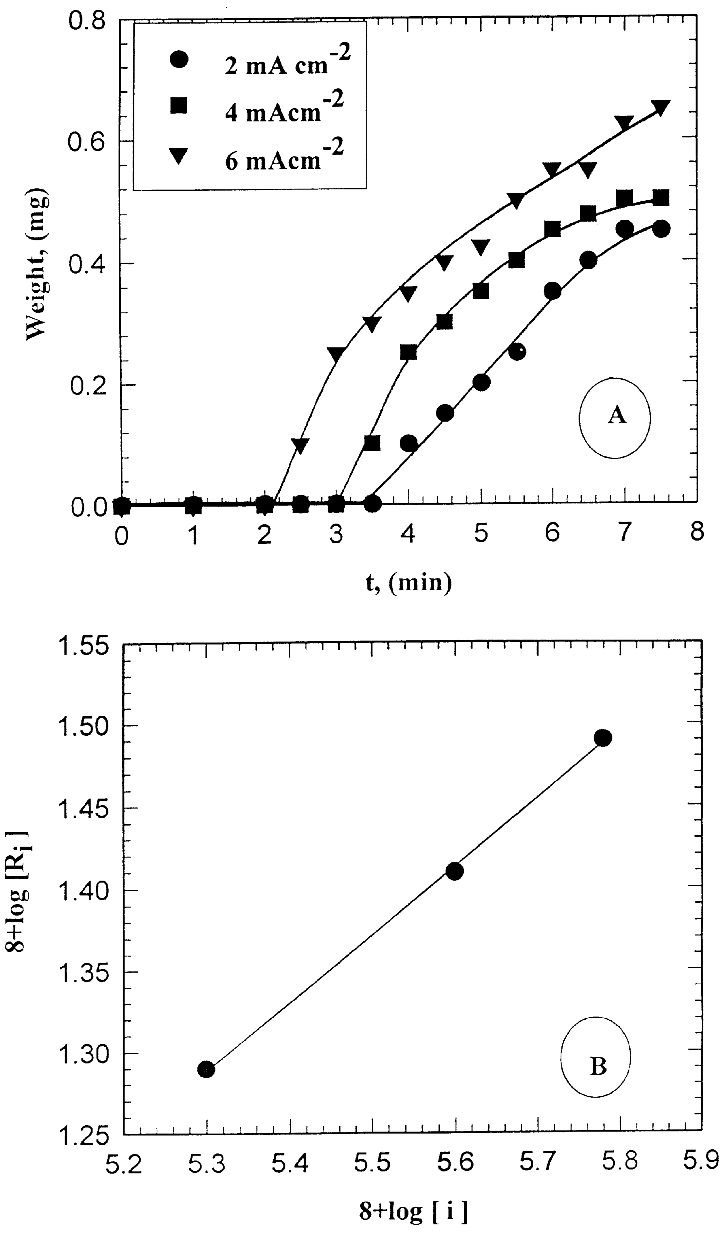


FIGURE 2 (A) Yield-time curve for the effect of current densities; (B) Double-logarithmic plot of initial rate of electropolymerization versus different current densities values.

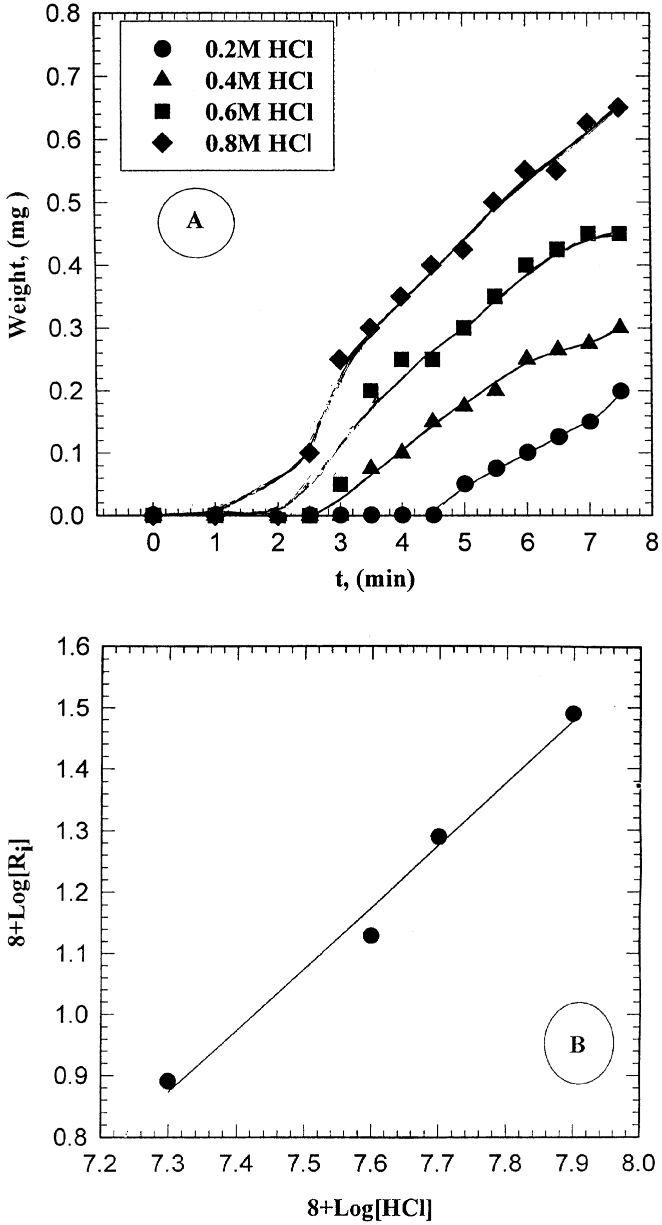


FIGURE 3 (A) Yield-time curve for the effect of HCl concentration; (B) Double-logarithmic plot of initial rate of electropolymerization versus different HCl concentration.

1.01. This means that the electropolymerization with respect to HCl is a first-order reaction.

Effect of Monomer Concentration

The electropolymerization reaction was carried out by keeping all the aforementioned conditions constant at 0.8 M HCl, a current density 6 mAcm^{-2}, Na_2SO_4 (0.1 M), reaction time (7.5 min), and temperature of 303°K, but the monomer concentrations were varied in the range between 0.01 and 0.11 M. The weight of the obtained polymer film in each case was calculated. From the obtained data, it can be deduce that the maximum weight of the polymer film is obtained when 0.05 M monomer concentration was used. It is also noticed that the weight of the polymer film decreases at higher concentration of monomer, which means that polymer degradation may occur. The electropolymerization of *o*-aminobenzoic acid was performed using different monomer concentrations in the range between 0.01 and 0.05 M at different time intervals. The data are graphically represented in Figure 4A. The initial rate of electropolymerization was calculated and the double-logarithmic plot of the initial rate of electropolymerization versus the monomer concentration is represented in Figure 4B. This relation gave a straight line was a slop of 1.33, which means that the order of the electropolymerization of *o*-aminobenzoic acid is a first-order reaction with respect to the monomer concentration.

Effect of Temperature

Anodic oxidative electropolymerization of *o*-aminobenzoic acid was carried out under the following constant conditions: 0.8 M HCl, 0.05 M monomer, 0.1 M Na_2SO_4, and current density = 6 mAcm^{-2}, and the duration time is 7.5 min. But the reaction was carried out at different temperatures in the range between 293° and 313°K. The maximum weight of the polymer film was recorded at 303°K. It is noticed during the experiments that at higher temperatures than 303°K, some polymer is formed in solution near the anode and does not adhere at the electrode surface, which means that the adhesion of the film to the platinum electrodes decreases above 303°K. The electropolymerization of *o*-aminobenzoic acid was carried out at different temperatures (293, 298, 303°K) for different time intervals. At each temperature the weight of the formed polymer was plotted versus the duration time and the yield-time curve is represented in Figure 5A. The initial rate of electropolymerization was calculated at each investigated temperature and the logarithm of the initial rate of polymerization was plotted versus 1/T (c.f. Figure 5B), which gave a

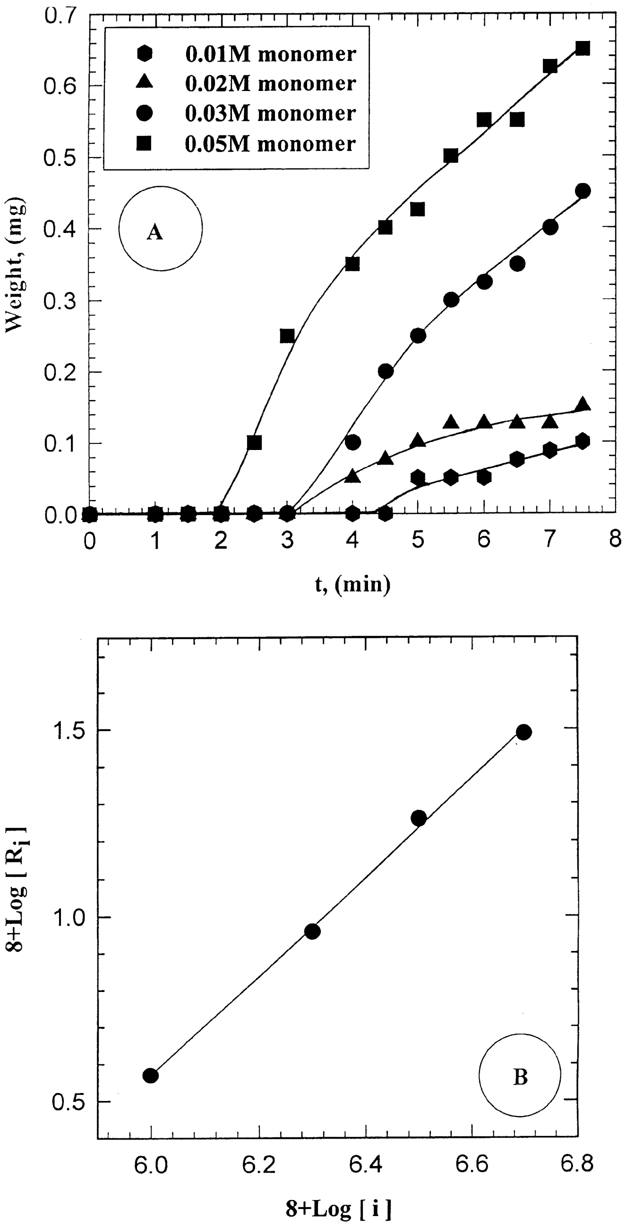


FIGURE 4 (A) Yield-time curve for the effect of monomer concentration; (B) Double-logarithmic plot of initial rate of electropolymerization versus different monomer concentrations.

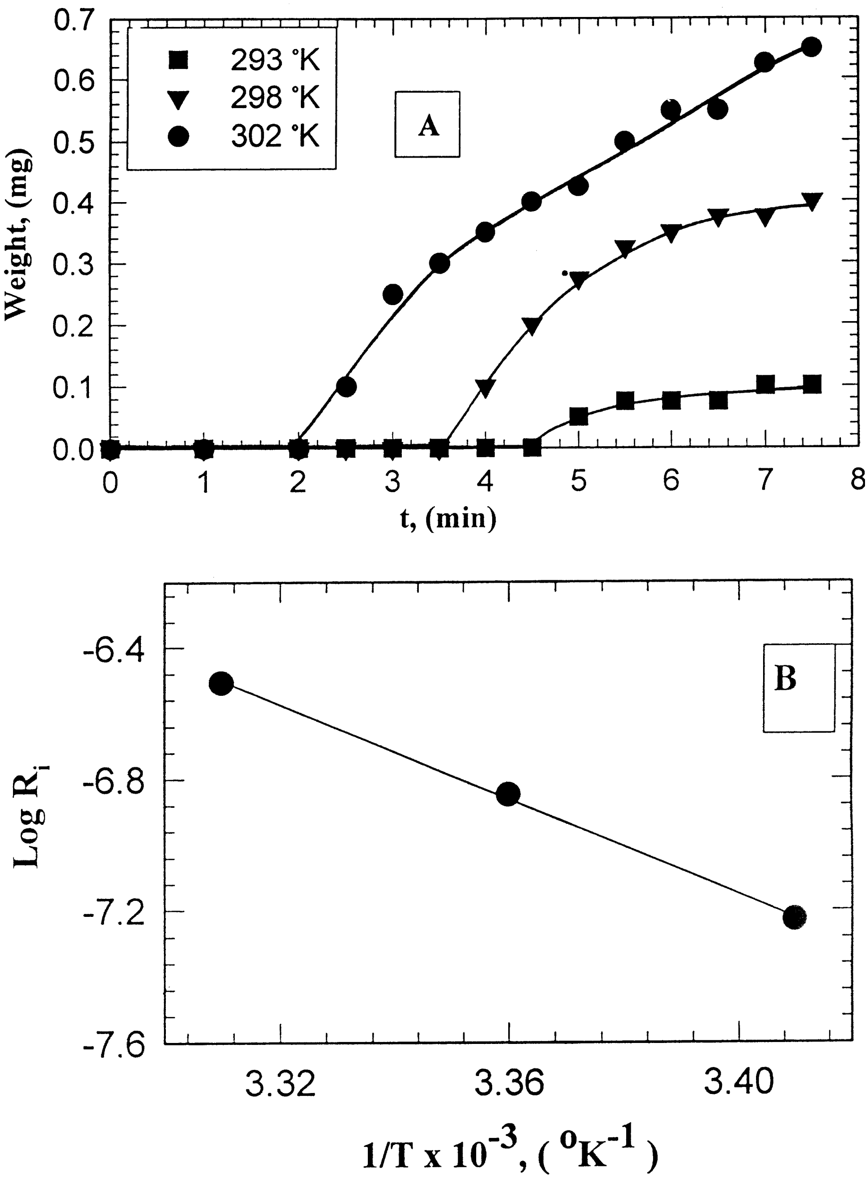


FIGURE 5 (A) Yield-time curve for the effect of temperature; (B) Arrhenius plot for the electropolymerization; (C) Eyring equation plot for the electropolymerization.

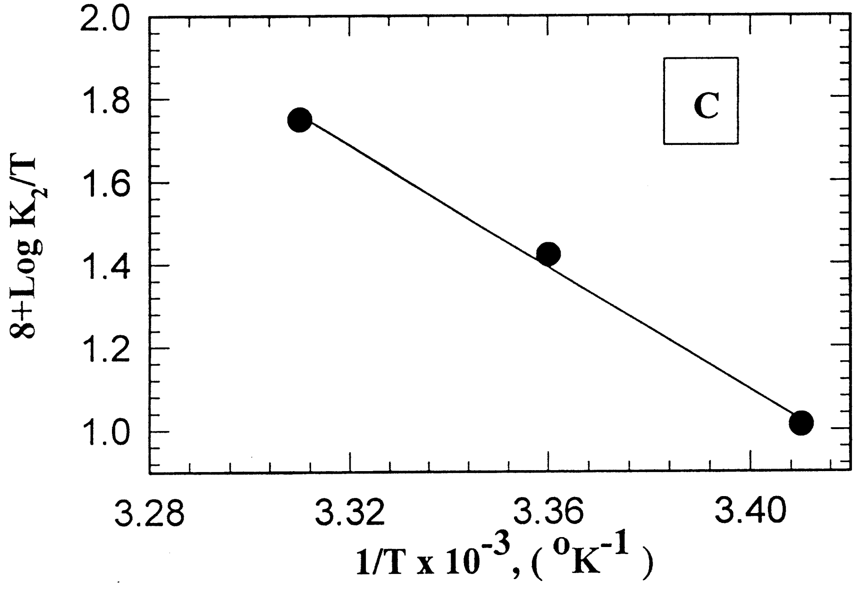


FIGURE 5 Continued.

straight line with a slope of –7200. By applying the Arrhenius equation, the apparent E_a was calculated and was found to be 134.8 kJ/mol.

Calculation of Thermodynamic Parameters

The enthalpy and entropy of activation for the electropolymerization reaction can be calculated from the k_2 values of the following equation:

$$\text{Reaction rate} = k_2[\text{HCl}]^{1.01}[\text{current density}]^{0.41}[\text{monomer}]^{1.33}$$

The values of k_2 at different temperatures were calculated and the enthalpy (ΔH^*) and entropy (ΔS^*) of the activation associated with k_2 were calculated using the Eyring equation:

$$K_2 = RT/Nh\ e^{\Delta S^*/R}\ e^{-\Delta H^*/RT}$$

where k_2 is the rate constant, R is the universal gas constant, N is Avogadro's number, and h is Plank's constant. By plotting log k_2/T versus 1/T (c.f. Figure 5C) a linear relationship was obtained with a slop of $-\Delta H^*/2.303\,R$ and intercept of log $\{(R/Nh) + \Delta S^*/2.303\,R\}$. From the slop and intercept, the values of ΔH^* and ΔS^* were found to be 134.8 kJ mol^{-1} and –149.9 $J^{\circ}K^{-1}$ mol^{-1}, respectively.

Molecular Weight, Spectroscopic Analysis, and Elemental Analysis

The molecular weight, obtained by gel-permeation chromatography (GPC) analysis was found to be as follows:

$$M_w = 10.1 \times 10^4,\ M_n = 6.2 \times 10^4,\ \text{and the polydispersity (Pd)} = 1.634.$$

The infrared absorption bands and their assignments for *o*-aminobenzoic acid and the prepared polymer are summarized in Table 1. The strong absorption band appearing at 692 cm^{-1} in case of monomer, appears as medium band at 700 cm^{-1} in case of polymer, which could be attributed to NH wagging deformation in aromatic amine. Two strong absorption bands appearing at 836 cm^{-1} and 931 cm^{-1} in case of monomer, appear as group of absorption bands in the region 879 cm^{-1}↔1078 cm^{-1} in case of polymer, which could be attributed to C–C stretching vibration in benzene ring. Three medium absorption bands appearing at 1139, 1233, and 1277 cm^{-1} in case of monomer, appears as one broad band at 1251 cm^{-1} in case of polymer, which may be due to C–O stretching vibration in carboxyl group. The strong absorption band appearing at 1369 cm^{-1} in case of monomer, appears at 1402 cm^{-1} in case of polymer, which could be attributed to C–N stretching vibrations. The strong absorption band appearing at 1581 cm^{-1} in case of monomer could be attributed to NH_2 deformation for primary aromatic amine, whereas, a medium absorption band appearing at 1609 cm^{-1} in case of polymer, could be attributed to C–N stretching vibration for quinoide structure. Other infrared absorption bands and their assignments are summarized in Table 1.

The proton NMR spectrum of the prepared poly(*o*-aminobenzoic acid) shows two singlet signals at $\delta = 2.5$ ppm and $\delta = 3.5$ ppm, which are attributed to solvent protons. The singlet signal appears at $\delta = 6.3$ ppm could be attributed to NH proton. The multiple signals appearing in the region from $\delta = 7 \leftrightarrow 8$ ppm could be attributed to benzene ring protons in the polymeric structure. The singlet signal that appears at $\delta = 8.1$ ppm, may be attributed to NH_2 group protons. The singlet signal at $\delta = 11.2$ ppm is attributed to the OH proton in carboxylic group. This signal disappears when deuterated water is added, which confirms the presence of carboxylic (OH) group in the polymeric structure.

Elemental analytical data are given in Table 2, which are in good agreement with those calculated for the suggested structure represented in Scheme 1.

The presence of four water molecules for each repeat unit is confirmed by thermogravimetric analysis. The TGA data of the prepared

TABLE 1 IR-Absorption Bands and Their Assignments of Both *o*-Aminobenzoic Acid and poly(*o*-Aminobenzoic Acid)

Wave number (cm^{-1})		
Names		
Monomer	Polymer	Assignments [47]
418^{w}	—	CH wagging deformation of 1,2-disubstituted benzene ring
450^{w}	—	
470^{w}	470^{w}	
505^{s}	—	
540^{s}	527^{w}	
617^{w}	—	NH wagging deformation in aromatic amine
659^{s}	—	
692^{s}	700^{m}	
757^{s}	757^{m}	CH deformation of 1,2-disubstituted benzene ring
—	799^{m}	CH deformation of 1,4-disubstituted benzene ring
803^{w}	—	C–C stretching vibrations in benzene ring
836^{s}	—	
931^{s}	879^{m}	
—	1022^{w}	
—	1044^{m}	
1070^{w}	1078^{w}	
1139^{m}	—	C–O stretching vibrations
1233^{m}	—	
1277^{m}	1251^{b}	
1319^{m}	—	C–N stretching vibrations
1369^{s}	1402^{s}	
1459^{sp}	1464^{s}	NH scissoring vibrations
1484^{sp}	1506^{w}	
1541^{s}	—	NH_2 deformation for primary aromatic amine
—	1609^{m}	C–N stretching vibrations for quinoid structure or combination band for protonated aromatic amine
1661^{s}	1652^{b}	Stretching vibrations of C=C in benzene ring
1730^{sh}	1702^{b}	Stretching vibrations of C=O in carboxylic group
2544^{b}	—	Stretching vibrations of OH in carboxylic group
—	2925^{s}	Stretching vibrations of secondary aromatic amine
3239^{s}	3250^{sh}	Symmetric stretching of NH group
3324^{s}	—	Asymmetric stretching of NH in aromatic amine
—	3425^{b}	Symmetric stretching of OH (hydrogen bonded) in carboxylic acid

s: strong; w: weak; b: broad; sh: shoulder; m: medium; sp: splitting.

poly(*o*-aminobenzoic acid) are summarized in Table 3. From the table, it is clear that there are four stages during the thermolysis of the polymer sample.

TABLE 2 Elemental Analysis of Poly(*o*-Aminobenzoic Acid)

	%C	%H	%N	%Cl
Calcd.	49.195	4.100	8.199	10.395
Found	48.850	4.640	7.540	9.870

First Stage

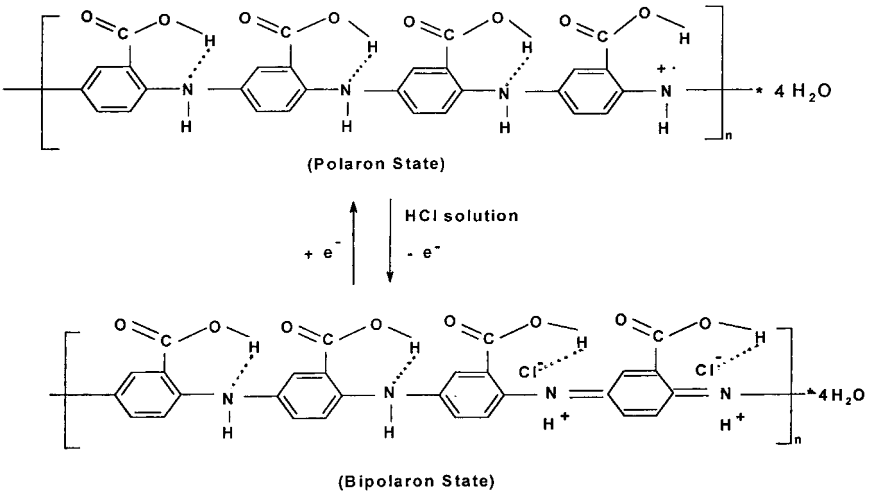
Includes the loss of four water molecules in the temperature range between 25° and 190°C, the weight loss of this step was found to be 11.00%, which is in good agreement with the calculated value of 10.54%.

Second Stage

In the temperature range between 190° and 305°C, the weight loss was found to be 36.20%, which may be attributed to the loss of two molecules of hydrochloric acid and four carboxylic acid groups. The calculated weight loss of this stage was found to be 37.04%.

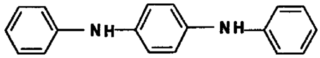
Third Stage

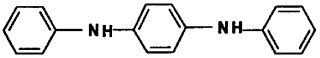
In the temperature range between 305° and 600°C, the weight loss was found to be 37.00%, which may be attributed to the loss of the



SCHEME 1 Polaron and bipolaron states of poly(*o*-Aminobenzoic acid).

TABLE 3 Thermogravimetric Data of the Prepared Poly(*o*-Aminobenzoic Acid)

Temperature range (°C)	Weight loss (%) Calcd	Weight loss (%) Found	Removed molecule
025–190	10.54	11.00	4 H_2O
190–305	37.04	36.20	2 HCl + 4 COOH
305–600	37.33	37.00	
>600	15.09	15.80	Residual (C, Na_2SO_4)

 unit. The calculated weight loss was found to be 37.33%.

Fourth Stage

Above 600°C, a residual material of 15.80% was found, which contains residual carbon and supporting electrolyte materials.

Cyclic Voltammetric Characterization

Cyclic voltammograms of the *o*-aminobenzoic acid on platinum electrodes in 0.2 M HCl, 0.1 M Na_2SO_4, at 298°K without and with 0.02 M monomer at potential between −400 and 1600 mV versus SCE with scan rate 25 mVs^{-1}, are shown in Figure 6A and B, respectively. The voltammograms in the presence of monomer exhibit two oxidation peaks (I and II) that progressively developed at –280 and +970 mV, respectively. On one hand, the first oxidation peak (I) corresponds to the removing of one electron from nitrogen atom of the amino group to give radical cation. The presence of carboxylic group in the ortho position facilitates the oxidation process, –280 mV versus SCE, and the formation of radical cation at low potential. The formed radical cation interacts within other monomer molecule to form dimer radical cation, which followed by further reaction with monomer molecule to give trimer radical cation and so on. Finally, the semiquinone radical cation (polaron state) is formed, which is adsorbed on the electrode surface, as shown in Scheme 2.

On the other hand, the second oxidation peak (II), which is assigned to the oxidation of the formed semiquinone radical cation

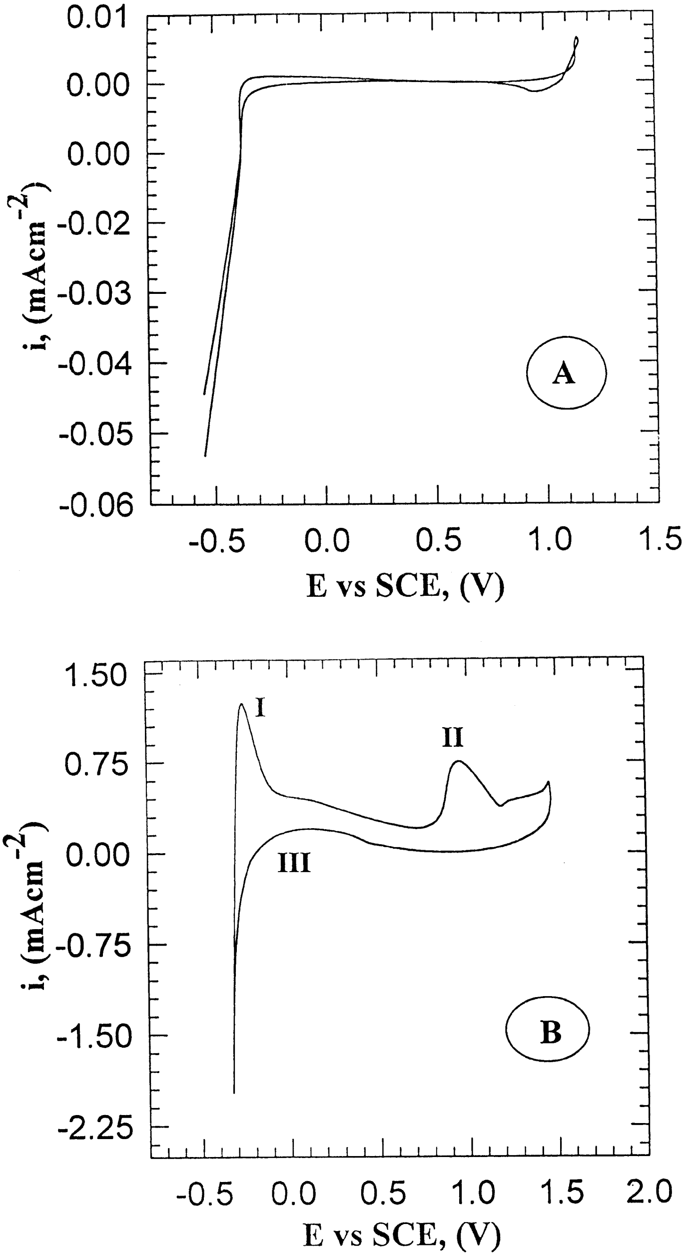


FIGURE 6 (A) Cyclic voltammogram curve without monomer; (B) Cyclic voltammogram curve with monomer; (C) Repetitive cycling of electropolymerization; (D) Effect of scan rate on the electropolymerization.

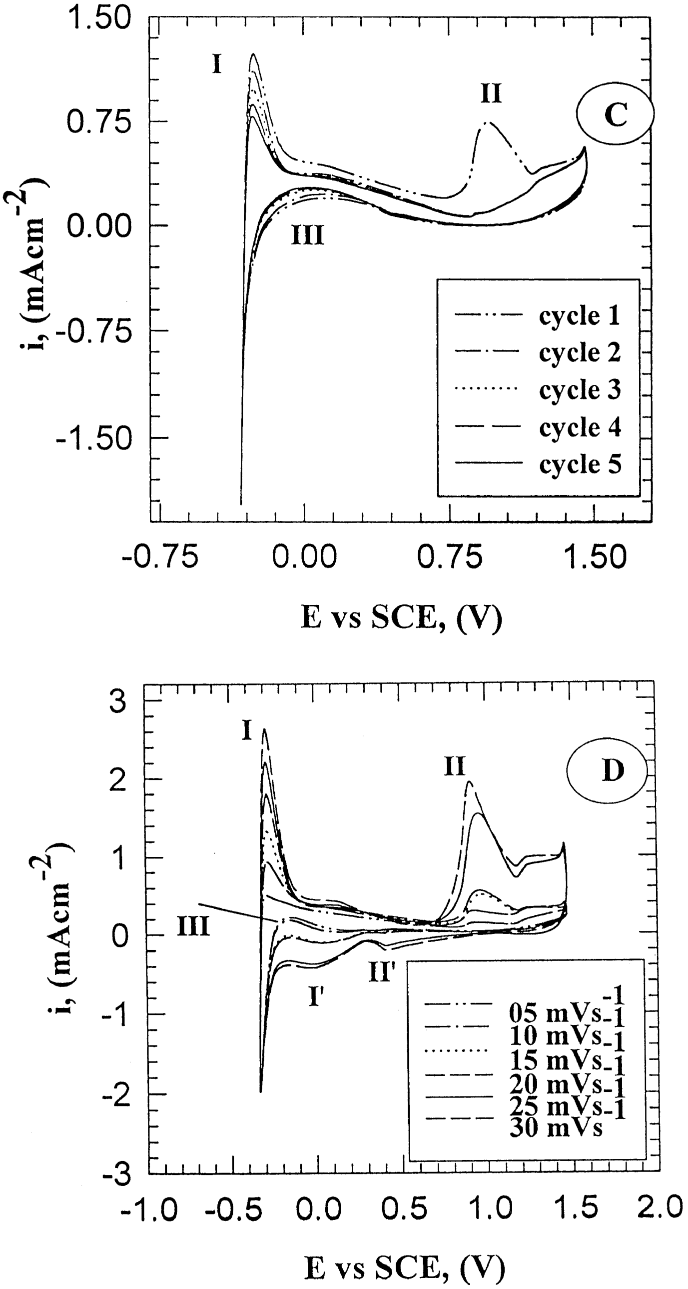
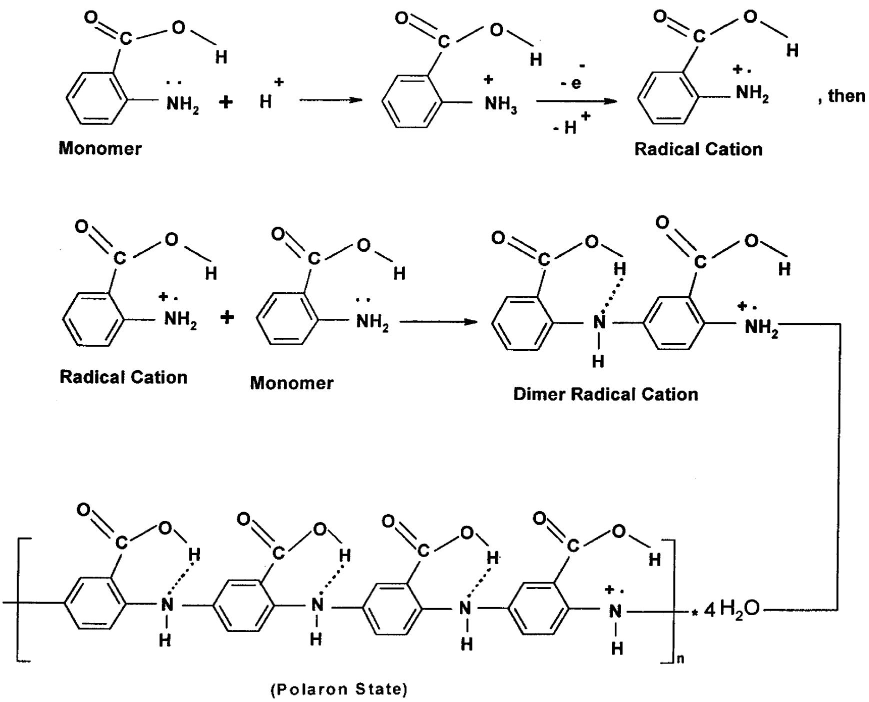


FIGURE 6 Continued.



SCHEME 2 Synthetic steps during polymerization.

(polaron state) to the quinone imine (bipolaron state) [32,45,46], occurs at +970 mV versus SCE, and represented in Scheme (1). Therefore, the second redox process is attributed to the conversion of radical cations to the fully oxidized form (quinoidal structure). However, as soon as polymerization is nucleated, a brown polymer film is rapidly deposited on the electrode surface. The charge of the first peak (I) is higher than that of the second one (II), meaning that not all the formed radical cations interact to give polaron and then bipolaron. The potential difference between the first and the second oxidation peak (I and II) is ≈1220 mV, and no middle peaks were observed between them, which confirms the non-existence of degradation products, higher regularity, homogeneity and adherence of the deposited film on the electrode surface. On reversing the potential scan from +1600 up to −400 mV, the reversing anodic current is very small, indicating the presence of in adhered layer of the polymer on the electrode surface. Beyond +500 mV, the reversing current starts to increase, forming a reactive anodic peak (III), indicating the partial removal of the deposited polymer film from the surface as a result of degradation process and consequently radical cation formation at this potential.

Figure 6C shows the repetitive cycling of the formation of poly (*o*-aminobenzoic acid) from solution containing (0.02 M monomer, 0.2 M, 0.2 M HCl, 0.1 M Na_2SO_4 at 298°K). The data reveal that the peak currents (i_{pI}, i_{pII}) of the two anodic peaks (I and II) decreases as well as the current of the reactive anodic speak (III). The decrease of the anodic currents could be attributed to the presence of a part of the polymer film on the electrode surface, therefore, the currents of the following anodic half cycle decrease. It is possible that the stability of the deposited film enhances with successive cycling and therefore, the peak currents decrease with repetitive cycling. The potential position of the redox peaks does not shift with increasing number of cycles, indicating that the reversibility of the redox reactions is independent of the polymer thickness.

Figure 6D shows the influence of scan rate (5–30 mVs^{-1}) on the anodic polarization curve the electropolymerization of *o*-aminobenzoic acid from solution containing (0.05 M monomer, 0.2 M HCl, 0.1 M Na_2SO_4) at 298°K on platinum electrode. The data reveal that the peak current densities (i_{pI} and i_{pII}) of the first and second anodic peak, respectively, increase with increased scan rate. Figure 7 shows the linear dependence of the first current peak i_{pI}, versus $v^{1/2}$. This linear relation suggests that the electroformation of radical cation may be described partially by a diffusion-controlled process (diffusion of reacting species to the polymer film/solution interface). Under such conditions, the first oxidation peak current i_{pI} is given by Randless [48] and Sevick [49] in the equation:

$$i_p = (2.69 \times 10^5)\ An^{3/2}\ CD^{1/2}\ v^{1/2}$$

where A is constant, n is the number of exchanged electron, C is the bulk concentration, D is the diffusing species, and v is the scan rate. It is seen that the charge of the reactive peak (III) decreases with increasing scan rate up to 20 $mV\,s^{-1}$. This may be a result of increasing thickness and consequently the stability of the polymer film deposited on the electrode surface. Further increase in the scan rate resulted in the disappearance of this peak and at the same time two cathodic peaks start to appear. The first cathodic peak (II′) could be ascribed to the reduction of the bipolaron state to polaron state (conjugated to the second oxidation peak II) whereas the second cathodic peak (I′) could be assigned to the reduction of the formed radical cation to the monomer (conjugated to the first anodic peak [I]).

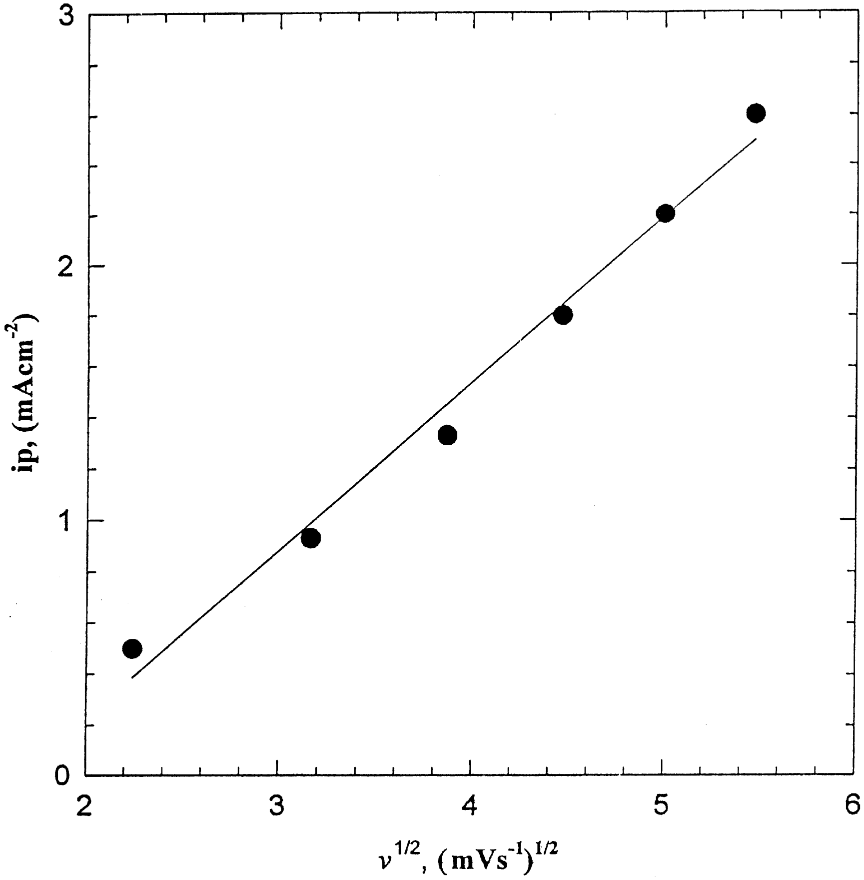


FIGURE 7 Relation between $v^{1/2}$ and ip for the first anodic peak.

The effect of HCl concentration, monomer concentration, and temperature on the cyclic voltammetric characteristics of the polymer film formation on platinum surface was investigated. Figure 8A represents the influence of HCl concentration in the range between (0.2 to 1.0 M) on the electropolymerization process at 25 mVs^{-1}. The plot shows that the peak current densities (i_{pI} and i_{pII}) increase with increasing HCl concentration up to 0.8 M. However, the reverse scan exhibits only the reactive peak (III) as a result of the degradation of the thin film of the polymer formed on the electrode surface when 0.2 M HCl was used. At higher HCl concentrations, the reactive peak (III) disappears as a result of increasing thickness

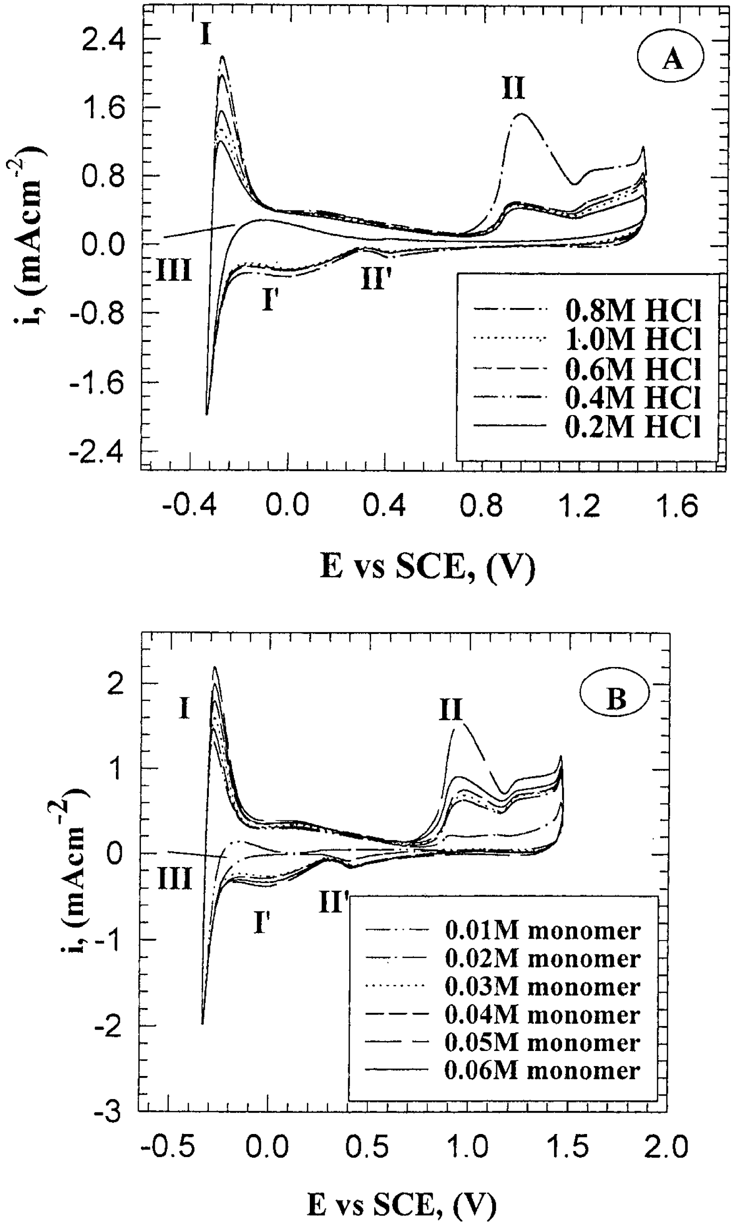


FIGURE 8 Cyclic voltammogram curves for the electropolymerization of *o*-aminobenzoic acid from solution containing 0.1 M Na_2SO_4 (A) effect of HCl concentration; (B) effect of monomer concentration; (C) effect of temperature.

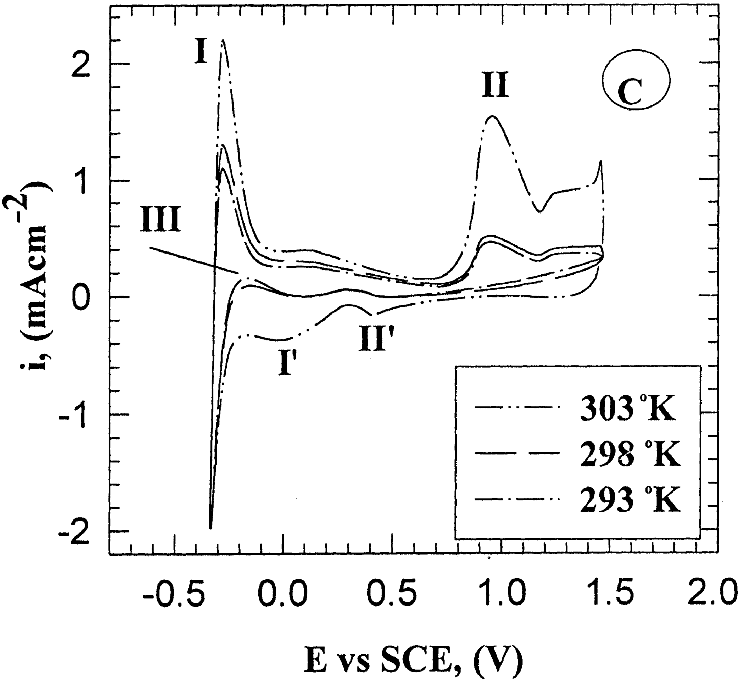


FIGURE 8 Continued.

of the polymer film formed on the electrode surface and the reverse cathodic span exhibits the two cathodic peaks (II′ and I′). The size of these two cathodic peaks increases with increasing HCl concentration.

Figure 8B illustrates the influence of solution temperature from 293° to 303°K on the cycling voltammetric response of the polymer formation. The data reveal that an increase of temperature up to 303°K results in a progressive increase of the charge included in the anodic peaks (I and II). Moreover, an increase in the temperature up to 298°K causes a progressive decreases in the charge included in reactive peak (III). Further increase of temperature resulted in the disappearance of the reactive peak and starting of the appearance of the two cathodic peaks (II′ and I′).

Figure 8C shows that by increasing the concentration of the monomer from 0.01 to 0.05 M, the anodic peak current densities (i_{pI} and i_{pII}) first enhance and then start to decrease. Two reduction peaks (II′ and I′) are formed at higher concentrations.

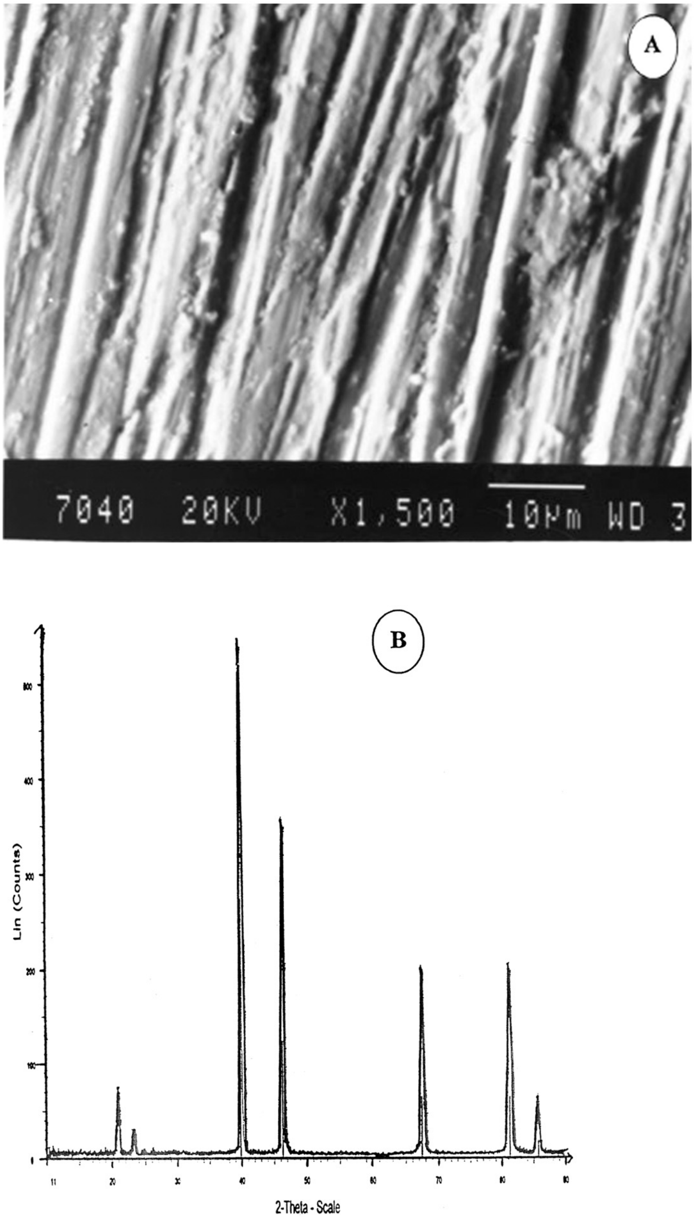


FIGURE 9 (A) The picture of scanning electron microscope of electropolymerized poly(*o*-aminobenzoic acid); (B) X-ray diffraction pattern of electropolymerized poly(*o*-aminobenzoic acid).

Surface Morphology

In most conditions, a homogeneous, smooth, brown and well-adhering poly(*o*-aminobenzoic acid) film was electrodeposited on platinum surface. The surface morphology of the polymer obtained at the optimum conditions was examined by scanning electron microscopy. The SEM micrograph shows tubular or fibrillar elongated entities (c.f. Figure 9A). The X-ray diffraction pattern shows that the prepared polymer is crystalline material as shown in Figure 9B, from which it is clear that there are two peaks at 2θ angles of 20.841 and 23.007.

CONCLUSIONS

In conclusion, the data reveal the following:

1. The initial rate of electropolymerization reaction of *o*-aminobenzoic acid on platinum electrode is relatively low. The fraction of the dissolved product may be strongly dependent on temperature and monomer or HCl concentration.
2. The order of electropolymerization reaction of *o*-aminobenzoic acid on platinum electrode is 1.01, 1.33, and 0.41 with respect to HCl concentration, monomer concentration, and current density, respectively.
3. The apparent activation energy is $134.8\,\text{kJ mol}^{-1}$.
4. The prepared poly(*o*-aminobenzoic acid) is smooth, brown, tubular or fibrillar, crystalline, and well adhered to platinum substrate.
5. From cyclic voltammetry studies, it is clear that the cyclic voltammogram consists of two pairs of resolved peaks at –280 and +970 mV versus SCE, the first corresponding to the conversion of amine nitrogens to radical cations, and the second to the conversion of the radical cations to imine nitrogens. The electroformation of the polymer film on platinum electrode may be described partially by diffusion-controlled process.

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