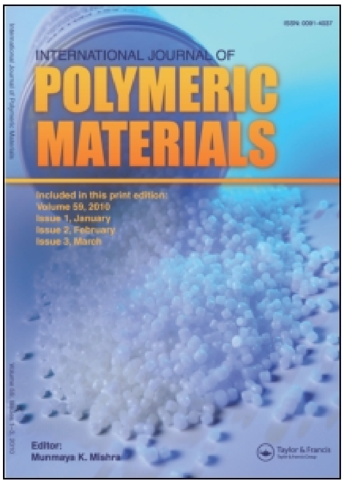

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Electrochemical Polymerization of 2-Chloroaniline and Characterization of the Obtained Polymer Films

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Electrochemical Polymerization of 2-Chloroaniline and Characterization of the Obtained Polymer Films

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Electrochemical polymerization of 2-chloroaniline on platinum electrode in acid medium was carried out under various reaction conditions, altering temperature, current density, hydrochloric acid, and monomer concentrations and time duration. The initial rate of the electropolymerization reaction is small and the orders are found to be 1.00, 1.06, and 0.96 with respect to current density, acid, and monomer concentrations, respectively. The apparent activation energy (E_a) is found to be 44.336 kJ mol^{-1}. The rate law is $R_P = K_2[D]^{1.00}[HCl]^{1.06}[M]^{0.96}$. The obtained polymer films are characterized by ^{1}H-NMR, elemental analysis, IR, and cyclic voltammetry. The mechanism of the electropolymerization reaction is also discussed. The thermogravimetric analysis (TGA) is used to confirm the proposed structure and determination of the number of water molecules in the polymeric chain unit. X-ray and scanning electron microscopic analysis are used to investigate the surface morphology.

Keywords: electropolymerization, 2-chloroaniline, characterization, cyclic voltammetry

INTRODUCTION

The electropolymerization of conducting polymer on electrodes' surfaces has been a very active research area in electrochemistry because

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of their properties, which allow polymer modified electrodes to be used as sensors, catalysts, electrochromic materials, batteries, and microelectronic devices [1–11] and also as corrosion inhibitors to protect semiconductors and metals [12–18].

From an application point of view, polyaniline is considered as one of the best organic conducting materials. Its synthesis is performed generally either chemically or electrochemically. One of its many promising properties is a fast switching rate (the ability to switch reversibly from the insulating to the conducting state either by electrochemical or chemical doping) [19–22]. In recent years, several reviews on polyaniline have been published [23–25].

In the search for new conducting polymers of the aniline type, investigations have been directed toward aniline modification by substituents on the ring [26–29] or at the nitrogen atom [30–32]. Electropolymerization of aniline and its derivatives has usually been carried out at low pH acidic aqueous solutions (e.g., HCl or H_2SO_4 aqueous solution) [33].

Electropolymerization of aniline in 0.5 M H_2SO_4, neutral aqueous perchlorate and nitrate solutions have been studied [34–35]. Also, polyaniline and poly 2-chloroaniline were obtained by electropolymerization in tetra-n-butylammonium salt and 1,2-dichloroethane solution [36–38].

The kinetics of the chemical and electrochemical polymerization of some substituted aniline, pyrrole, and thiazole in aqueous acidic solutions and characterization of the obtained polymers by IR, U.V.-visible, X-ray, scanning electron microscopy, thermal gravimetric analysis and, cyclic voltammetry have all been investigated by Sayyah et al. [39–47].

The objective of the present work is to investigate the kinetics and optimum conditions for the electrochemical polymerization of 2-chloroaniline in aqueous hydrochloric acid medium and characterization of the obtained polymer film. The surface morphology of the obtained polymer will be characterized by scanning electron microscopy and X-ray diffraction.

EXPERIMENTAL

Materials

2-chloroaniline (vacuum distilled and stored in the absence of light before use), hydrochloric acid solution, and anhydrous sodium sulphate are of analytical pure grade, obtained from Merck, Germany. All solutions are freshly prepared using double distilled water.

Cell and Electrodes

The experimental setup used was described previously [44–47] and consists of a rectangular Perspex cell provided with two parallel platinum foil electrodes. Each electrode has a dimension of 1 cm height and 0.5 cm width. Before each run, the platinum anode was cleaned and washed with distilled water, rinsed with ethanol, dried and weighed. The experiments were conducted at the required temperature ±1°C with the help of circular water thermostat. At the end of the experiment, the anode was withdrawn, washed with distilled water, dried and weighed. The polymerization current was supplied by constant potential dc-power supply (Thuby ~ Thandar PL 330).

Electrochemical Polymerization of 2-Chloroaniline

Anodic oxidative electropolymerization of 2-chloroaniline was carried out in aqueous solution containing monomer (concentration range between 0.05 and 0.10 M) using 0.1 M Na_2SO_4 as the supporting electrolyte and the current densities were varied within the range of 2 to 12 $mA\,cm^{-2}$. Electropolymerization was carried in hydrochloric acid solution (concentration range between 1.0 and 1.9 M) at different temperatures in the range between 283 and 313 K.

Cyclic Voltammetry Measurements

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

The electrochemical experiments were performed with EG&G potentiostat/Galvanostat model 273 supplied by EG&G Princeton Applied Research. The I–E curves were recorded using computer software from the same company (Model 352 and 270/250).

Infrared, Thermogravimetric, Elemental Analysis, and ^{1}H-NMR Spectroscopy

Infrared measurements were carried out using a Shimadzu FTIR-430 Jasco spectrophotometer. ^{1}H-NMR measurements were carried out using a Varian EM 360 L, 60 MHz NMR spectrometer. NMR signals of the electropolymerized samples were recorded in dimethylsulphoxide using tetramethylsilane as internal reference.

Thermogravimetric analyses of the obtained polymers were performed using a Shimadzu DT-30 thermal analyzer. The weight loss was measured from ambient temperature up to 600°C, at the rate of 10°C min^{-1} to determine the degradation rate of the polymer.

Elemental analysis was carried out in the micro-analytical center at Cairo University by oxygen flask combustion and dosimat E415 titrator (Switzerland).

Scanning Electron Microscopy and X-Ray Diffraction

Scanning electron microscopic analysis was carried out using a JSM-T20 scanning electron microscope (JEOL, Japan). The X-ray diffractometer (Philips 1976 model 1390) was operated for the polymer film adhered on the platinum electrode 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 deg min^{-1}
Voltage: 40 kV

RESULTS AND DISCUSSION

Anodic Oxidative Electropolymerization

Effect of Time Duration

Anodic oxidative electropolymerization of 2-chloroaniline was studied under the influence of different plating and operating parameters. The effect of time duration on the weight of the obtained polymers was studied with different values of current densities. The data reveal that the weight of the obtained polymer increases with increasing time duration up to 20 min and then tend to decrease as a result of degradation and the solubility of the polymer film from the platinum surface. This holds for all the investigated values of the current densities. The data are graphically represented in Figure 1.

Effect of Current Density

The effect of applied current density on the anodic oxidative electropolymerization of 2-chloroaniline was studied at constant time intervals (20 min) using 0.08 M monomer concentration, 0.1 M Na_2SO_4 in dimethyl formamide/water mixture (30:70 v/v), and 1 M HCl at 298°K which is kept constant. The data reveal that, as the applied

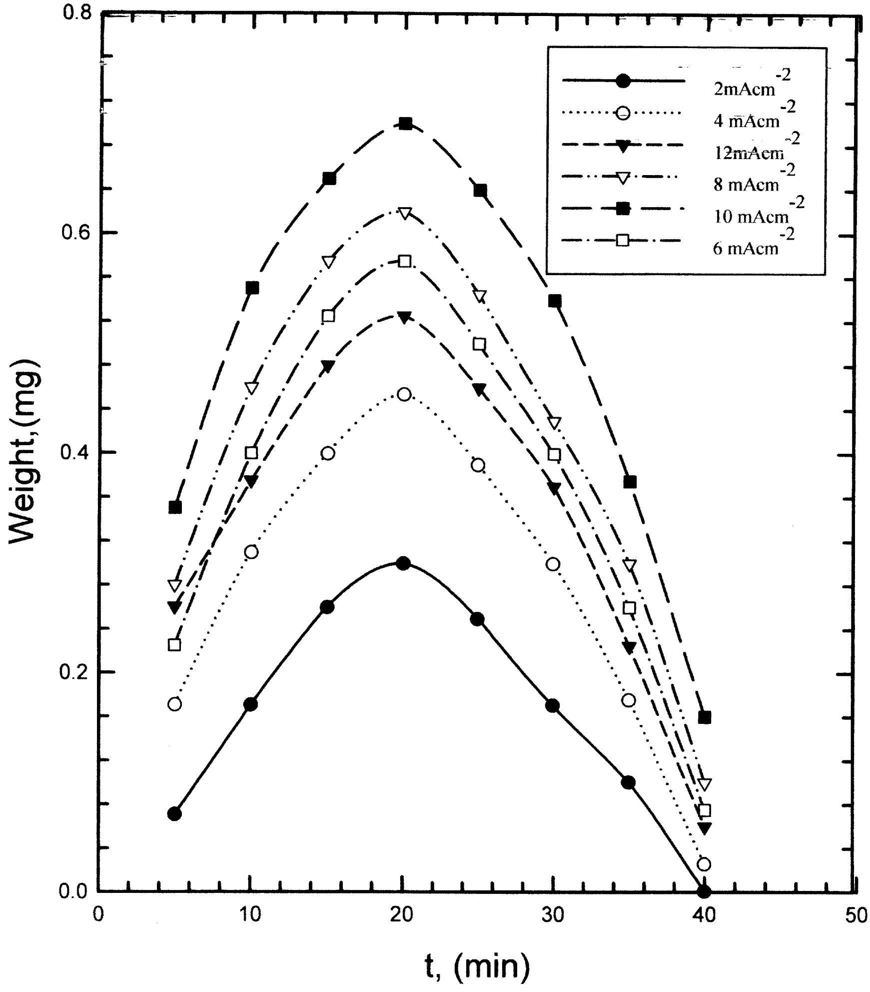


FIGURE 1 Yield-time curve for the effect of time duration on the anodic polymerization of 2-chloroaniline from solution containing 0.08 M monomer, 1 M HCl, and 0.1 M Na_2SO_4 at 298°K.

current density increases, the weight of the obtained polymer increases up to $10\,mA\,cm^{-2}$ and then tends to decrease. This finding implies that 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 a yield-time curve was estimated. The data are graphically represented

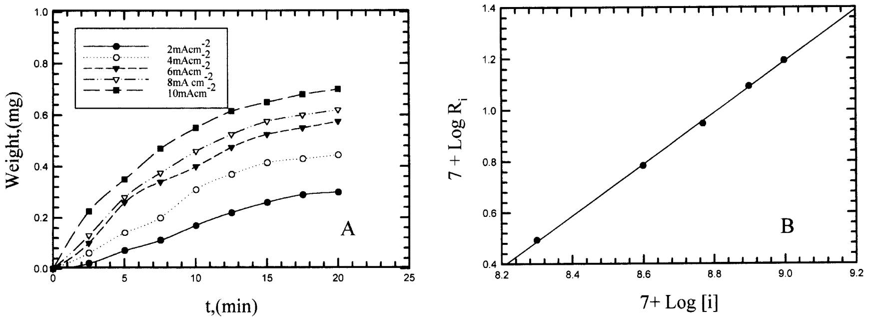


FIGURE 2 (**A**) Yield-time curve for the effect of current densities; (**B**) Double logarithmic plot of initial rate of electropolymerization versus different current densities values.

in Figure 2A, from which the initial rate of the electropolymerization was determined. The reaction exponent with respect to the current density was determined from the slope of the straight line presented in Figure 2B. The exponent was found to be 1.0.

Effect of HCl Concentration

Anodic oxidative electropolymerization of 2-chloroaniline was carried out using 0.08 M of monomer concentration, 0.1 M Na_2SO_4 in dimethyl formamide/water mixture (30:70), current density = 10 mA cm^{-2} at 298°K, which were kept constant. But the hydrochloric acid was varied in the range between 1.0–1.9 M (below 1.0 M, the adherence of the polymer film decreases and the polymer is formed in the solution near the anode). The obtained polymer film in each experiment was weighed. The obtained data shows that the maximum weight is obtained when 1.6 M HCl concentration is used. The weight of the deposited polymer film on the platinum electrode in each experiment was plotted against the time duration 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, which has a slope equal to 1.06. This means that the order of the reaction 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 1.6 M HCl, current density = 10 mA cm^{-2}, Na_2SO_4 (0.1 M) and temperature at 298°K, but

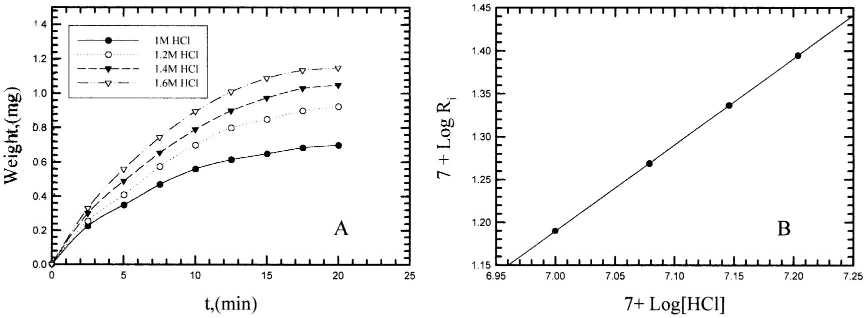


FIGURE 3 (**A**) Yield-time curve for the effect of HCl concentration; (**B**) Double logarithmic plot of initial rate of electropolymerization versus HCl concentrations.

the monomer concentrations were varied in the range between 0.05 and 0.10 M. Then, the weight of the obtained polymer film in each case was determined. From the obtained data, it was noticed that the maximum weight of the polymer film was obtained when 0.08 M monomer concentration was used. It was also noticed that the weight of the polymer film decreased at higher concentration of the monomer, which meant that polymer degradation may have occurred. The electropolymerization of 2-chloroaniline was performed using 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

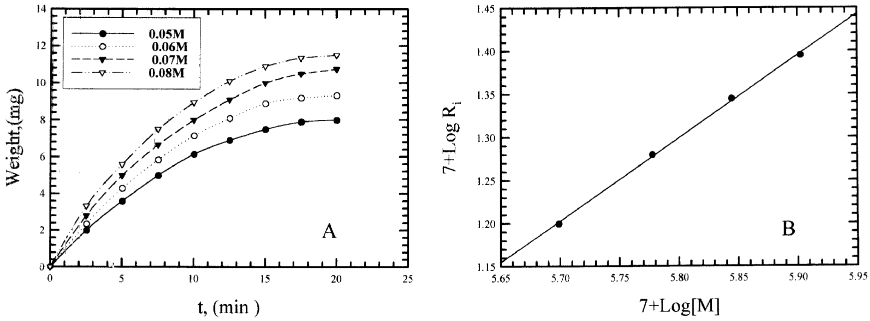


FIGURE 4 (**A**) Yield-time curve for the effect monomer concentrations; (**B**) Double logarithmic plot of initial rate of electropolymerization versus monomer concentrations.

gives a straight line with a slope equal to 0.96, which means that the order of the electropolymerization reaction of 2-chloroaniline is a first-order reaction with respect to monomer concentration.

Effect of Temperature

Anodic oxidative electropolymerization of 2-chloroaniline was carried out under the following constant conditions: 1.6 M HCl, 0.08 M monomer, 0.1 M Na_2SO_4, 10 mA cm^{-2}, but the reaction was carried out at different temperatures in the range between 283 and 313°K. The maximum weight of polymer film was recorded at 303°K. It was noticed during the experiments that, at temperatures higher than 303°K, some polymer was formed in the solution near the anode and did not adhere to the electrode, indicating that, at temperatures higher than 303°K, the adhesion of the film to the electrode is decreased. The electropolymerization of 2-chloroaniline was carried out at the temperatures of 288, 293, 298, and 303°K for different time intervals. At each temperature the weight of the formed polymer at

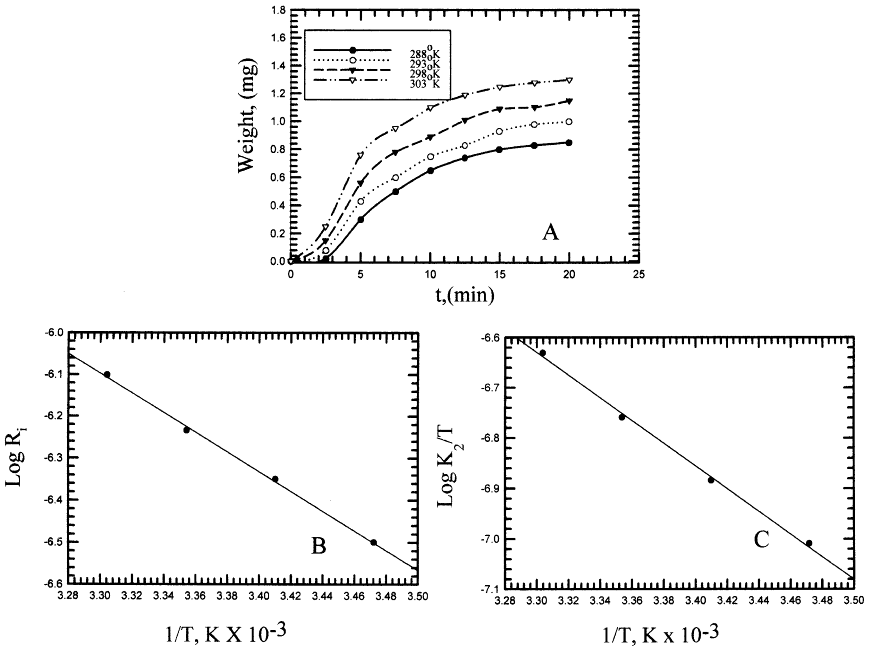


FIGURE 5 (**A**) Yield-time curve for the effect of temperature; (**B**) Arrhenius plot for the electropolymerization; (**C**) Eyring equation plot for the electropolymerization.

the anode was plotted versus the duration time and the yield–time curve is represented in Figure 5A. The initial rate of the electropolymerization reaction was calculated at each investigated temperature and the logarithm of the initial rate was plotted versus 1/T (cf. Figure 5B), which gives a straight line with a slope equal to −2.3194. By applying Arrhenius equation, the apparent activation energy was calculated and was found to be 44.336 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:

$$\text{Reaction rate} = K_2[\text{HCl}]^{1.006}[\text{current density}]^{1.00}[\text{monomer}]^{0.96}$$

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 the Avogadro's number, and h is the Planck's constant. By plotting log K_2/T versus 1/T (cf. Figure 5C) the authors obtained a linear relationship with a slope of $-\Delta H^*/2.303R$ and an intercept of $\log(R/Nh) + \Delta S^*/2.303R$. From the slope and intercept, the values of ΔH^* and ΔS^* were found to be 43.06 kJ mol^{-1} and –197.28 Jkmol^{-1}, respectively.

Cyclic Voltammetry Characterization

Cyclic voltammograms of poly(2-chloroaniline) on Pt electrode from solution containing 1.0 M HCl and 0.1 M Na_2SO_4 at 298°K with and without 0.08 M monomer in the potential range from –500 to 1500 mV versus SCE with scan rate of 25 mV s^{-1} are shown in Figure 6 (A & B). The voltammogram in the presence of monomer exhibits two oxidation peaks that progressively developed at −80 and 1120 mV. The first oxidation peak corresponds to the removal of an electron from the nitrogen atom of amine group to give radical cation. The formed radical cation interacts with another monomer molecule to form dimmer radical cation, followed by further reaction with a monomer molecule to give trimer radical cation and so on. Finally, the semiquinone radical cation (polaron state) is formed as is shown in Scheme 1.

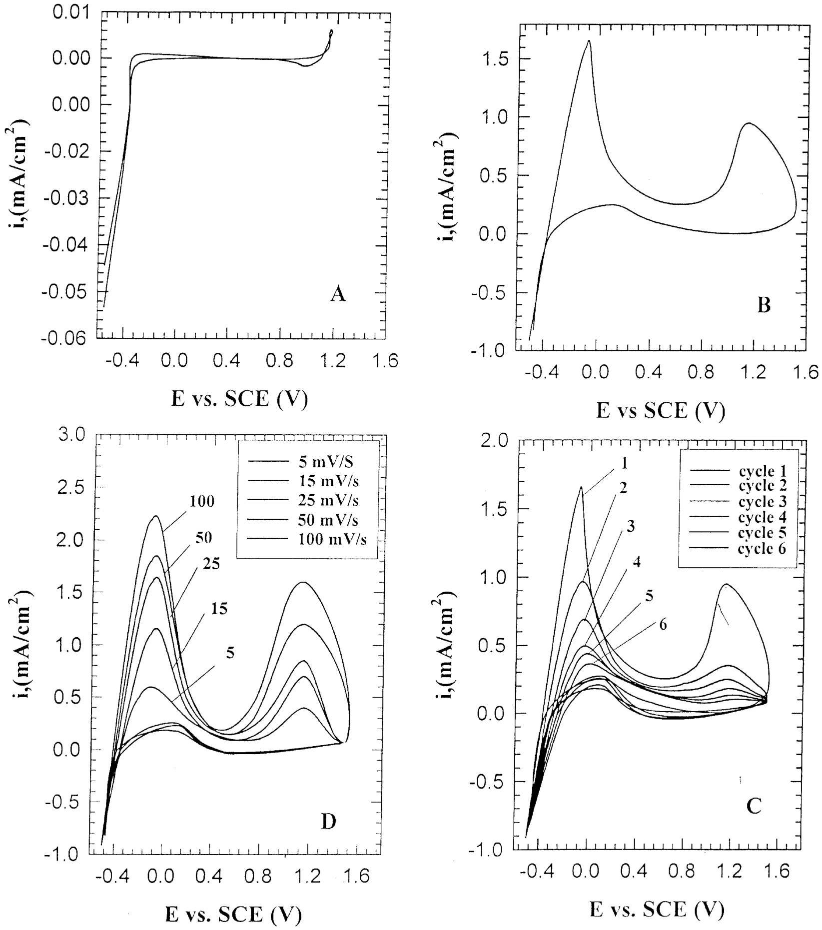
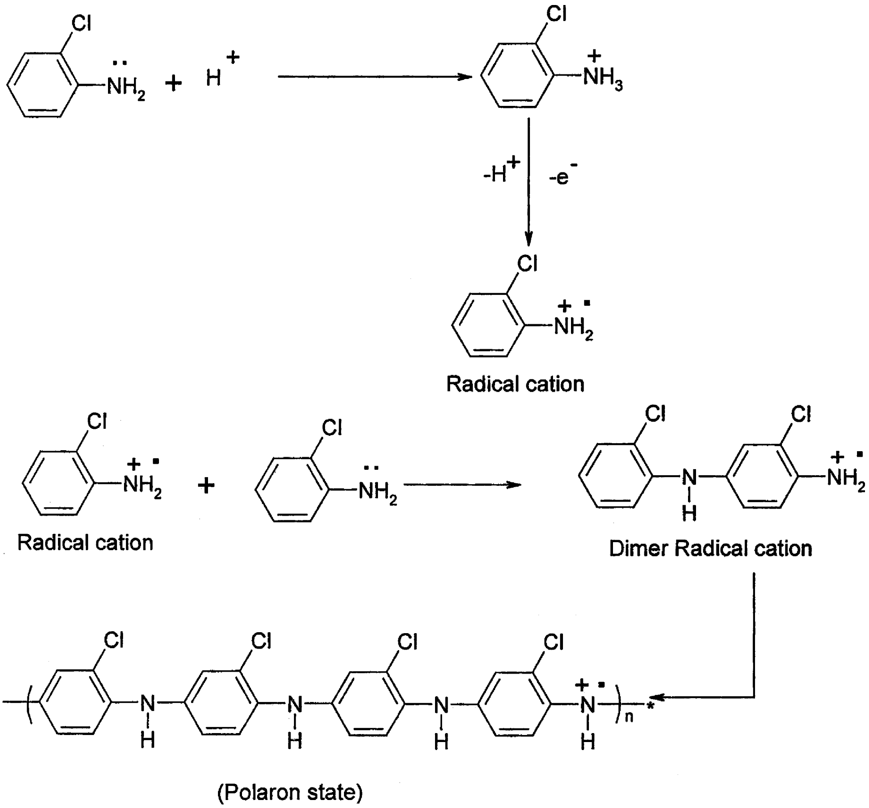


FIGURE 6 (**A**) Cyclic voltammogram curve without monomer; (**B**) Cyclic voltammogram curve with monomer; (**C**) Repetitive cycling; (**D**) Effect of scan rate.

The presence of chlorine atom in the ortho position shifts the first oxidation process to a more positive value (−80 mV versus SCE) than in the case of meta position (–150 mV versus SCE) [46] and formation of the radical cation occurs at higher potential than with the meta position.

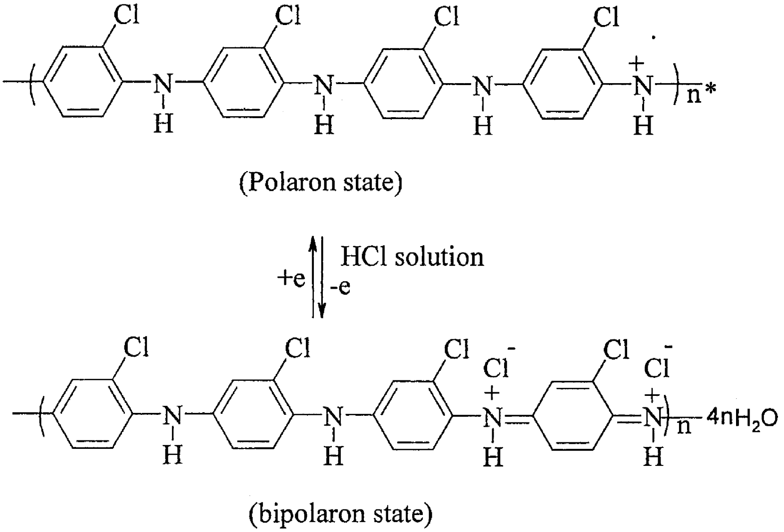
On the other hand, the second oxidation process during the electropolymerization appears at high potential (1120 mV versus SCE) comparing with that in the case of the meta position (1000 mV versus SCE) [46]. The second oxidation peak was assigned to the oxidation of



SCHEME 1 Process associated with the first oxidation peak.

the semiquinone radical (polaron state) to quinone imine (bipolaron) as follows in Scheme 2.

In other words, the second oxidation process is attributed to the conversion of the radical cations to the fully oxidized form (quinoidal structure). The polymer chain consists mainly of para coupling of semiquinone, quinone, and benzene rings in a ratio depending on the applied potential [28,46]. The second oxidation state appears at high potential due to the presence of the substituent chlorine atom in the ortho position of aniline moiety, which retards the polymerization process. However, as soon as the polymerization is nucleated, a brown polymer film is rapidly deposited on the electrode surface. The potential difference between the first and second oxidation peaks is 1200 mV, and no middle peaks were observed, which confirms the high regularity, homogeneity, and adherence of the deposited film to



SCHEME 2 Process associated with the second oxidation peak.

the electrode surface. The data demonstrate that the two-oxidation processes are irreversible; no cathodic peaks appear upon reversing the potential sweep.

On reversing the potential scan from 1500 mV up to about 0.4 mV, the reversing current is very small, indicating the presence of an adhered layer of the polymer on the electrode surface. Beyond 0.4 mV, the reversing current starts to increase, forming a reactive anodic peak. The appearance of this reactive peak indicates the partial removal of the deposited polymer film from the surface due to the degradation and consequently radical cation formation at this potential.

Figure 6C shows repetitive cycling on the formation of poly (2-chloroaniline). The data reveal that the peak currents, Ip, of the two anodic peaks decrease as well as the peak current of the reactive peak. The decrease in the anodic currents could be attributed to the presence of a part of the polymer film on the electrode surface; therefore, the current of the following anodic half cycle decreases. It is possible that the stability of the deposited film is enhanced with successive cycling, and therefore the peak currents decrease with repetitive cycling.

Figure 6D illustrates the influence of scan rate (5–100 mV s^{-1}) on the anodic electropolymerization curves for the formation of poly (2-chloroaniline) on Pt electrode. The data reveal that the peak current densities of Ip_1 and Ip_2 for the first and second anodic peak, respectively, increase with increasing scan rate.

Cyclic voltammetry characteristics of the formation of poly(2-chloroaniline) on platinum electrode as a function of the concentrations of HCl, monomer, and temperature, were investigated. Figure 7A represents the influence of HCl concentration (1.0 to 1.6 M) on the electropolymerization process. As can be seen, the anodic peak current is enhanced with increasing acid concentration up to 1.6 M.

Figure 7B shows that, by increasing the concentration of the monomer from 0.05 to 0.08 M, the anodic current is enhanced with increasing the monomer concentration up to 0.08 M.

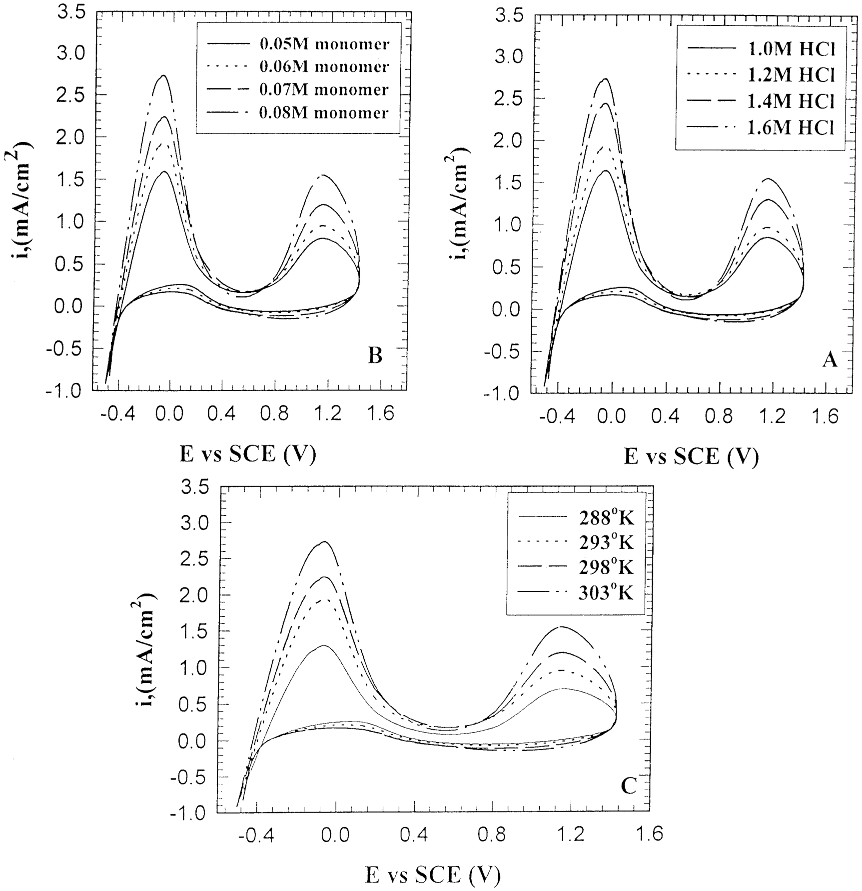


FIGURE 7 Cyclic voltammogram curves for the electropolymerization of 2-chloroaniline from solution containing 0.1 M Na_2SO_4. (**A**) Effect of HCl concentrations; (**B**) Effect of monomer concentrations; (**C**) effect of temperature.

TABLE 1 Elemental Analysis of the Prepared Poly(2-chloroaniline)

	C (%)	H (%)	N (%)	Cl (%)
Calculated	44.65	2.48	8.68	33.02
Found	44.20	2.9	9.1	32.61

Figure 7C illustrates the influence of solution temperature (288 to 308°K) on the cyclic voltammetry response of the formation of poly (2-chloroaniline). The data reveal that a rise of the temperature up to 303°K results in a progressive increase of the charge included in the anodic peak. The data of Figures 7 A–C are in good agreement with those of the kinetic data.

Elemental and Spectroscopic Analysis

The percentages of C, H, N, and Cl are in good agreement with those calculated from the suggested structure given in Scheme 2. The elemental analysis data are given in Table 1.

The infrared absorption bands and their assignments for poly (2-chloroaniline) are summarized in Table 2. The medium band appearing at 583 cm^{-1} may be attributed to the stretching vibration of C—Cl. The two medium adsorption bands appearing at 658 and 740 cm^{-1}, are attributed to the bending deformation of NH group. The absorption bands appearing at 777, 796, 834, and 859 cm^{-1} are attributed to the 1,2,4-trisubstituted benzene ring. The broad absorption band appearing at 3394 cm^{-1} is attributed to the stretching vibration of –NH group in Aryl-NH or Aryl-NH_2 whereas that appearing at 3410 cm^{-1} is attributed to asymmetric vibration for solvated terminal NH_2 group. Other absorption bands and their assignments are given in Table 2.

The ^{1}H-NMR spectrum of the prepared poly(2-chloroaniline) shows a singlet signal at δ 6.54 ppm and a broad signal at δ 7.94 7.94 pm, which are characteristic for the two types of benzene ring protons. The singlet signal, which appears at δ 8.61 ppm, may be attributed to the NH group proton.

Thermal Analysis of the Prepared Poly(2-Chloroaniline)

Thermogravimetric analysis (TGA) of the prepared poly(2-chloroaniline) sample has been performed and the data are summarized in Table 3. From the table, it is clear that there are four stages:

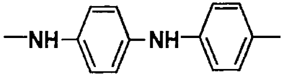
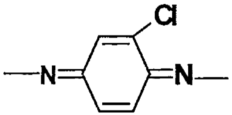
TABLE 2 Infrared Absorption Bands of the IR Spectrum of the Prepared Poly(2-chloroaniline)

Wave number (cm^{-1})	Assignments[48]
583^{m}	Symmetric stretching for C–Cl group
658^{w}	Bending deformation of NH group
740^{w}	
777^{s}	Out of plane deformation showing 1,2,4-trisubstituted benzene ring
796^{s}	
834^{m}	
859^{m}	
903^{m}	In plane deformation of C–C aromatic
1043^{m}	
1072^{m}	
1148^{m}	Symmetric stretching vibration of C–N group in Aryl-NH or Aryl NH_2
1214^{m}	
1249^{m}	
1289^{w}	
1431^{m}	Symmetric stretching vibration of C=N in quinonide structure
1510^{w}	
1573^{m}	
1620^{m}	Symmetric stretching vibration of C=C in benzene ring
1681^{s}	
3066^{m}	Symmetric stretching for C–H in aromatic moiety
$3394^{b,sp}$	Symmetric stretching vibration of N–H in Aryl-NH or Aryl-NH_2
$3410^{b,sp}$	Asymmetric stretching for solvated terminal NH_2 group

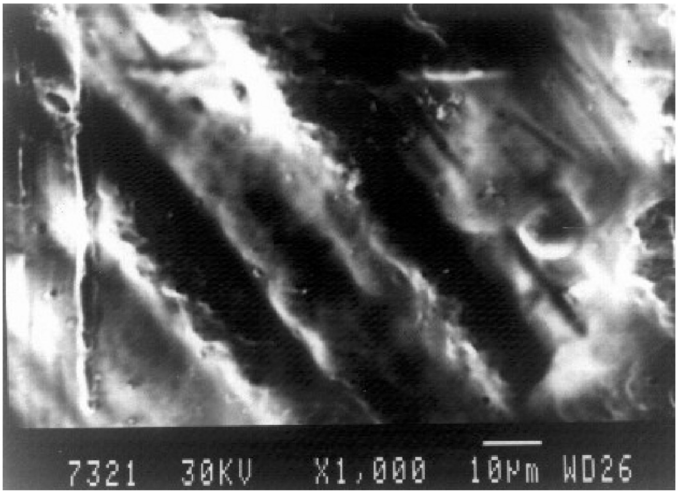
s = strong
m = medium
w = weak
b = broad
sp = solvated terminal

1. The first stage includes the loss of humidity in the temperature range between 25–70°C. The estimated weight loss for this step was found to be about 2.47%.
2. The weight loss in the second stage, in the temperature range between 70–317°C was found to be 39%, which is attributed to the loss of four molecules of H_2O, two molecules of HCl, and three chlorine atoms attached to a benzene ring. The calculated weight loss of this stage is about 38.99%.
3. The third stage, in the temperature range between 317–600°C was found to be 33%, which is attributed to the loss of two benzenoid moities. The calculated weight loss is equal to 32.86%.
4. The last stage, above 600°C, a residual material (22%) remained as one quinonide moiety containing one chlorine atom and supporting electrolyte materials.

TABLE 3 Thermogravimetric Data of the Prepared Poly(2-chloroaniline) in Comparison with Poly(3-chloroaniline)

	Poly(2-chloroaniline)					Poly(3-chloroaniline)[46]			
Stage	Temperature range (°C)	Calculated (%)	Found (%)	Removed molecules	Stage	Temperature range (°C)	Calc. (%)	Found (%)	Removed molecules
I	25–70	—	2.466	Water of humidity	I	25–269	11.16	10.10	4 H_2O
II	70–317	11.16 11.32] 38.99 16.51	39.00	4 H_2O 2 HCl 3 Cl	II	269–378	11.30	11.00	2 HCl
III	317–600	32.86	33.00		III	378–430	22.00	23.00	4 Cl
IV	>600	21.5	22.00		IV	430–500	56.00	54.00	All polymer segments are destroy
					V	>500	—	4%	Carbon residual or Na_2SO_4 (supporting electrolyte)

(A)



(B)

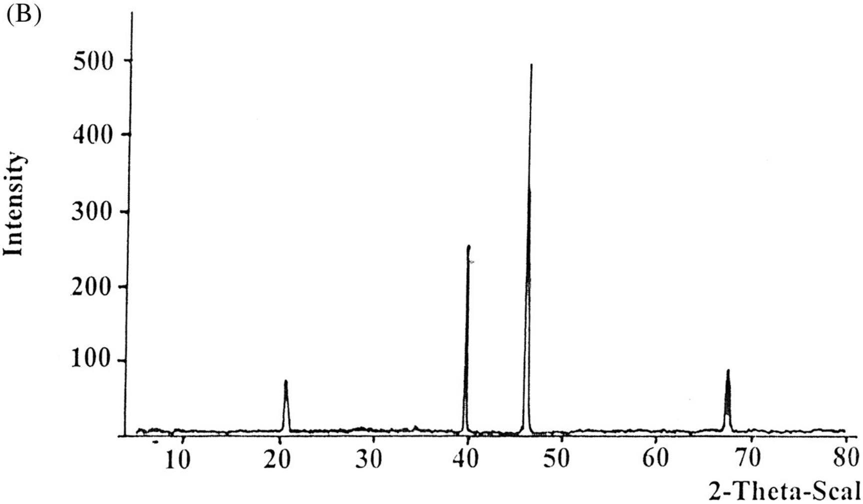


FIGURE 8 (**A**) The picture of scanning electron microscopy of electropolymerized poly(2-chloroaniline); (**B**) X-ray diffraction pattern of poly(2-chloroaniline).

Comparison between the thermal behavior of poly(3-chloroaniline) prepared by Sayyah et al. [46] and poly(2-chloroaniline) is shown in Table 3. From the table, the data show that the poly(2-chloroaniline) is thermally more stable than poly(3-chloroaniline).

Surface Morphology

Homogeneous, smooth, brown, and well-adhering polymer films were electrodeposited on platinum surface in most conditions. The surface morphology of poly(2-chloroaniline) film electrodeposited at the optimum condition was examined by scanning electron microscopy and X-ray diffraction analysis. The data show that the electropolymerized poly(2-chloroaniline) sample is crystalline with tubular or fibrillar elongated structure (cf. Figure 8A & B). These data are in good agreement with that obtained by Sayyah et al. in case of 3-chloroaniline [46].

CONCLUSIONS

In conclusion, the article's data reveal the following:

1. The initial rate of the electropolymerization reaction of 2-chloroaniline on platinum surface is relatively low, because the calculation of the initial rate is taken on the basis of the adhered polymer film on the platinum electrode. The fraction of the dissolved product may strongly depend on temperature and monomer or HCl concentrations.
2. The order of the electropolymerization reaction of 2-chloroaniline is 1.00, 1.06, and 0.96 with respect to current density, hydrochloric acid, and monomer concentrations, respectively. The rate law is

$$R_P = K_2[D]^{1.00}[HCl]^{1.06}[M]^{0.96}$$

3. The apparent activation energy (E_a) is 44.336 kJ/mol.
4. Cyclic voltammogram exhibits two oxidation peaks at −80 and 1120 mV (vs. SCE). The first oxidation peak corresponds to the formation of semiquinone radical cation (polaron state) whereas the second can be assigned to the oxidation of semiquinone radical cation (polaron state) to quinone imine (bipolaron).
5. The prepared poly(2-chloroaniline) film is smooth, brown, and well adhered on platinum electrode. X-ray diffraction analysis shows that the obtained polymer is crystalline.
6. Scanning electron microscopy shows that the polymer has tubular or fibrillar structure.

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