# Kinetic Studies on the Electrochemical Polymerization of 3-Chloroaniline and Characterization of the Obtained Polymer Films

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**ABSTRACT:** Electropolymerization of 3-chloroaniline on a platinum electrode in an acid medium was carried out under different reaction conditions of temperature, current density and hydrochloric acid and monomer concentrations with duration time. The initial rate of the electropolymerization reaction was small, and the orders were 0.99, 0.96 and 1.2 with respect to current density and acid and monomer concentrations, respectively. The apparent activation energy was 41.6 kJ/mol. The rate law was $R_p = k_2(\text{Current density})^{0.99}[\text{HCl}]^{0.96}[\text{Monomer}]^{1.2}$. The obtained polymer films were characterized by $^1$H-NMR, elemental analysis, IR spectroscopy, and cyclic voltammetry. The mechanism of the electropolymerization reaction is also discussed. Thermogravimetric analysis was 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. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 941–953, 2004

**Key words:** conducting polymers; kinetic (polym.); polyamines; thermogravimetric analysis (TGA); X-ray

## INTRODUCTION

The electropolymerization of conducting polymers on the electrode surface has been a very active research area in electrochemistry because of the outstanding properties of these materials, which allow the polymer-modified electrodes to be used as sensors, catalysts, electrochromic materials, batteries, 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 generally performed either chemically or electrochemically because of its many promising properties, such as a fast *switching rate* (the ability to switch reversibly from the insulating to the conducting state by either electrochemical or chemical doping).[19–22] In recent years, several reviews on polyaniline have been published.[23–25]

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

The 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 kinetic of the chemical and electrochemical polymerizations of some substituted aniline, pyrrole, and thiazole in aqueous acidic solutions and the characterization of the obtained polymers by IR, ultraviolet–visible, X-ray, and scanning electron microscopy; thermal gravimetric analysis; and cyclic voltammetry were investigated by Sayyah and coworkers.[39–45]

The objective of this study was to investigate the kinetic and optimum conditions for the electrochemical preparation of 3-chloroaniline in aqueous hydrochloric acid medium and to characterize the obtained polymer film. The surface morphology of the obtained polymer was characterized by scanning electron microscopy and X-ray diffraction.

## EXPERIMENTAL

### Materials

3-Chloroaniline (vacuum-distilled and stored in the absence of light before use), hydrochloric acid solution, and

anhydrous sodium sulfate were analytically pure and were provided from Merck (Darmstadt, Germany). All solutions were freshly prepared with double-distilled water.

## Cell and electrodes

The experimental set up used was described previously[44-45] and consisted of a rectangular Perspex cell provided with two platinum-foil parallel electrodes. Each electrode was 1 cm high and 0.5 cm wide. 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 $\pm$ 1°C with the help of a 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 a direct-current power supply (Thurby–Thandar PL 330).

## Electropolymerization of 3-chloroaniline

The anodic oxidative polymerization of 3-chloroaniline was carried out in aqueous solutions containing monomer (concentration range = 0.01–0.07$M$) with 0.1$M$ Na$_2$SO$_4$ as the supporting electrolyte, and the current densities were investigated in the range between 2 and 14 mA/cm$^2$. Electropolymerization was carried in hydrochloric acid solution (concentration range = 0.6–2.0$M$) at different temperatures in between 288 and 323 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 platinum electrode was cleaned as mentioned in the Cell and Electrodes section.

The electrochemical experiments were performed with an EG&G potentiostat/galvanostat (model 273, supplied by EG&G Princeton Applied Research, USA). The $I$–$E$ curves ($I$ is the current density and $E$ is the potential) were recorded by computer software from the same company (models 352 and 270/250).

## IR spectroscopy, thermogravimetric analysis (TGA), elemental analysis, and $^1$H-NMR spectroscopy

IR measurements were carried out with a Shimadzu FTIR-430 Jasco spectrophotometer. $^1$H-NMR measurements were carried out with a Varian EM 360L 60-MHz NMR spectrometer, Palo Alto, CA. NMR signals of the
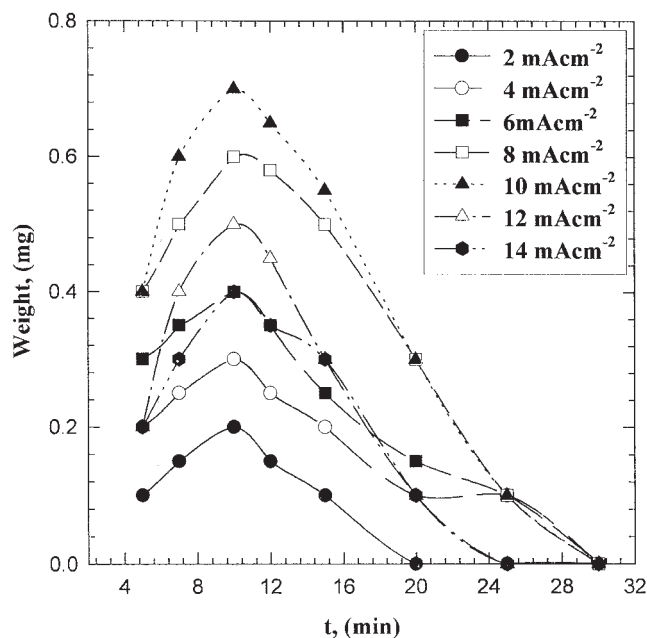


**Figure 1**  Yield–time ($t$) curve for the effect of duration on the anodic polymerization of 3-chloroaniline from a solution containing 0.05$M$ monomer, 0.6$M$ HCl, and 0.1$M$ Na$_2$SO$_4$ at 303 K.

electropolymerized samples were recorded in dimethyl sulfoxide with tetramethylsilane as an internal reference.

TGA of the obtained polymers were performed with a Shimadzu DT-30 thermal analyzer. The weight loss was measured from ambient temperature up to 600°C at a rate of 10°C/min to determine the degradation rate of the polymer.

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

## Scanning electron microscopy and X-ray diffraction

Scanning electron microscopic analysis was carried out with 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, which were kept constant for all of the analysis processes: Cu X-ray tube, scan speed = 8°/min, current = 30 mA, voltage = 40 kV, and preset time = 10 s.

## RESULTS AND DISCUSSION

### Anodic oxidative electropolymerization

Effect of duration

The anodic oxidative electropolymerization of 3-chloroaniline was studied under the influence of different plating and operating parameters. The effect of duration on the weight of the obtained polymers was stud-
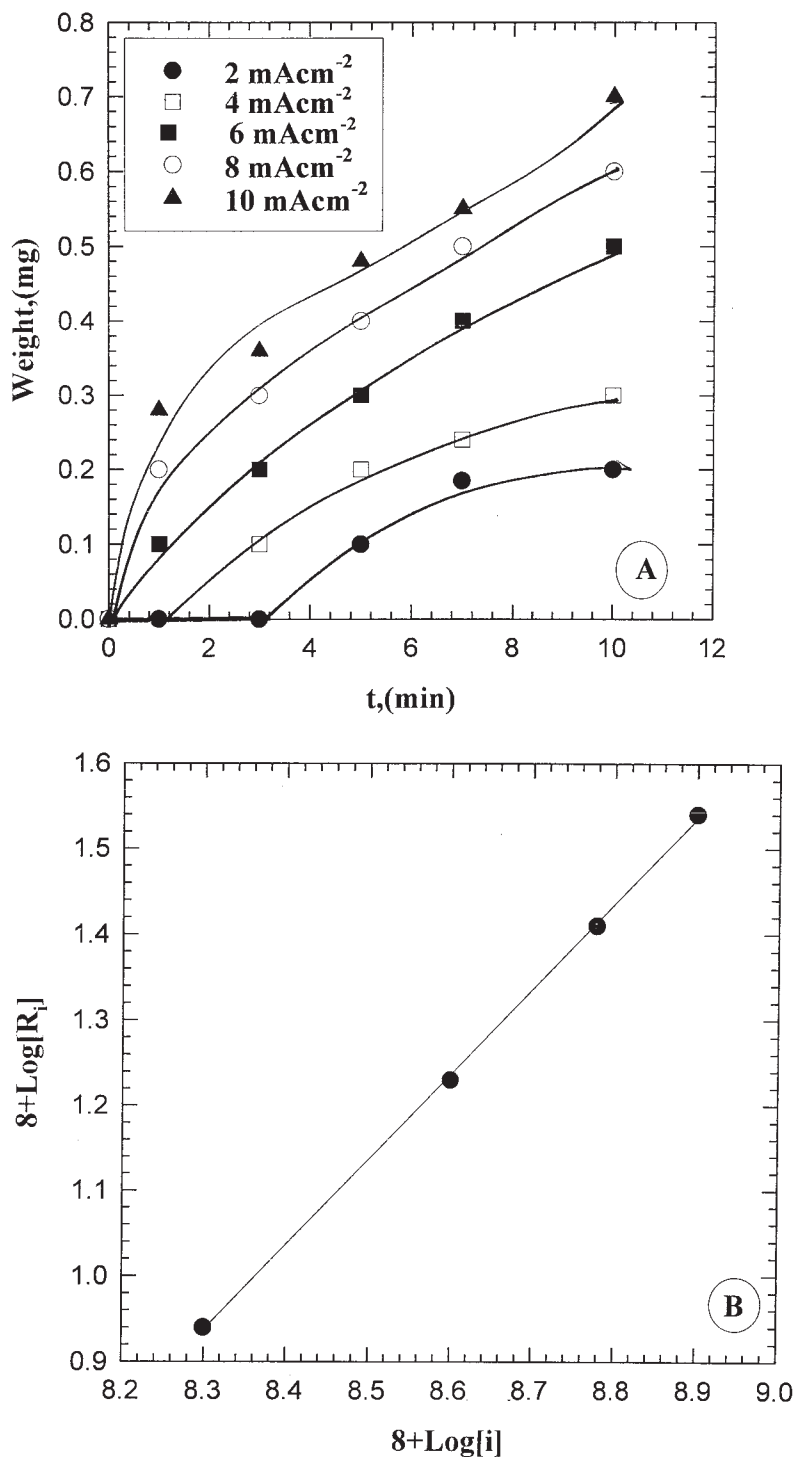
**Figure 2** (A) Yield–time (*t*) curve for the effect of current density and (B) double logarithmic plot of the initial rate of electropolymerization versus current density. $R_i$ = initial rate; $i$ = current density.

ied with different current densities. The data revealed that the weight of the obtained polymer increased with increasing duration up to 10 min and then tended to decrease as a result of degradation and the solubility of the polymer film from the platinum surface for all of the investigated values of current density. The data are graphically represented in Figure 1.

**Effect of current density**

The effect of applied current density on the anodic oxidative electropolymerization of 3-chloroaniline was studied at constant time intervals (10 min) with $0.05M$ monomer, $0.1M$ $Na_2SO_4$ in a dimethyl formamide/water mixture (30:70 v/v), and $0.6M$ HCl at
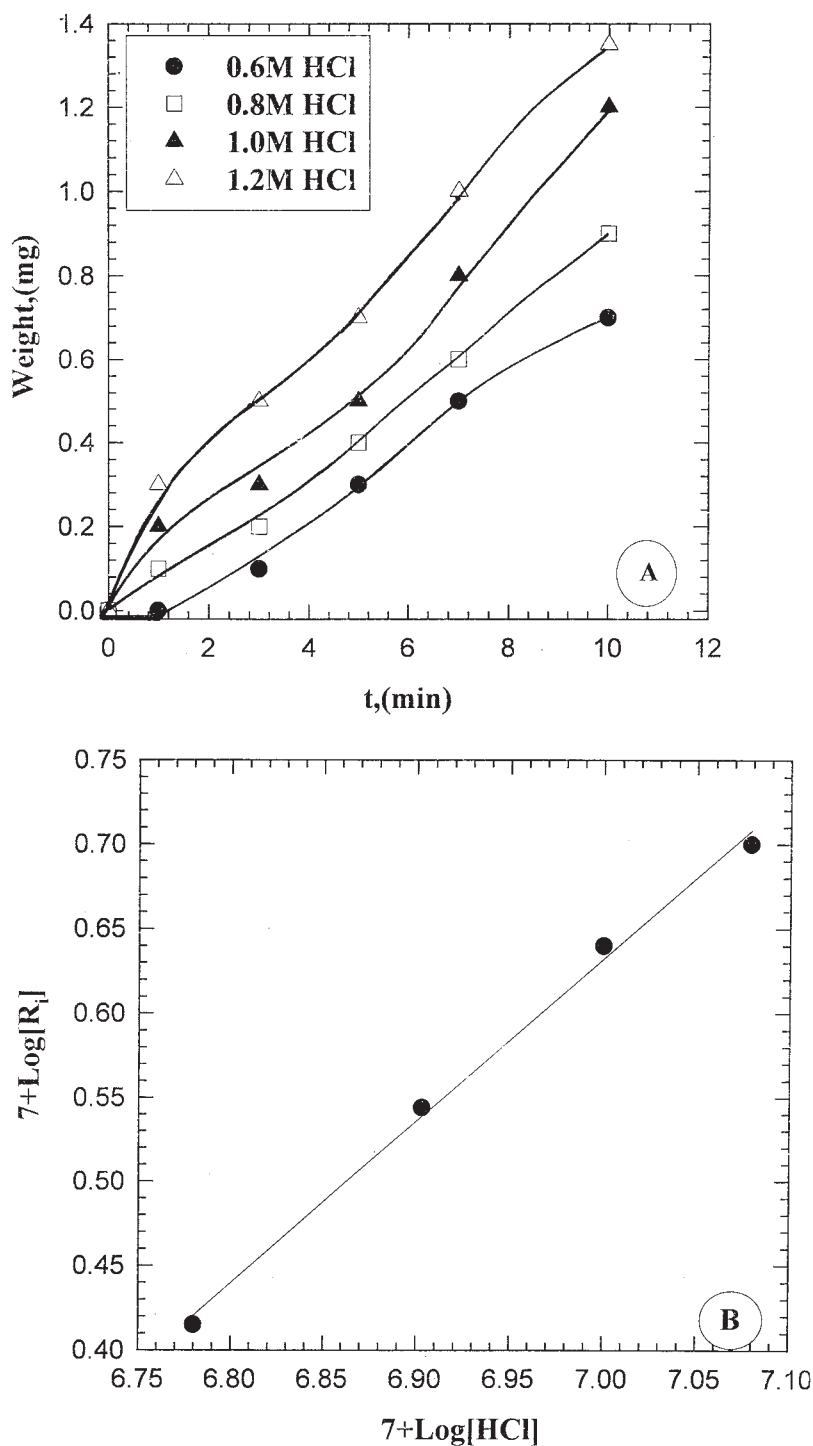
**Figure 3**   (A) Yield–time ($t$) curve for the effect of HCl concentration and (B) double logarithmic plot of the initial rate of electropolymerization versus HCl concentration. $R_i$ = initial rate.

303 K; these values were kept constant. The data revealed that as the applied current density increased, the weight of the obtained polymer increased up to 10 mA/cm$^2$ and then tended to decrease. This finding implied that an oxygen and chlorine evolution took place as a side reaction, especially at high current densities. Each value of the current density was stud-

ied with different time intervals, and the yield–time curve was estimated. The data are graphically represented in Figure 2(A), 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 2(B). The exponent was found to be 0.99.
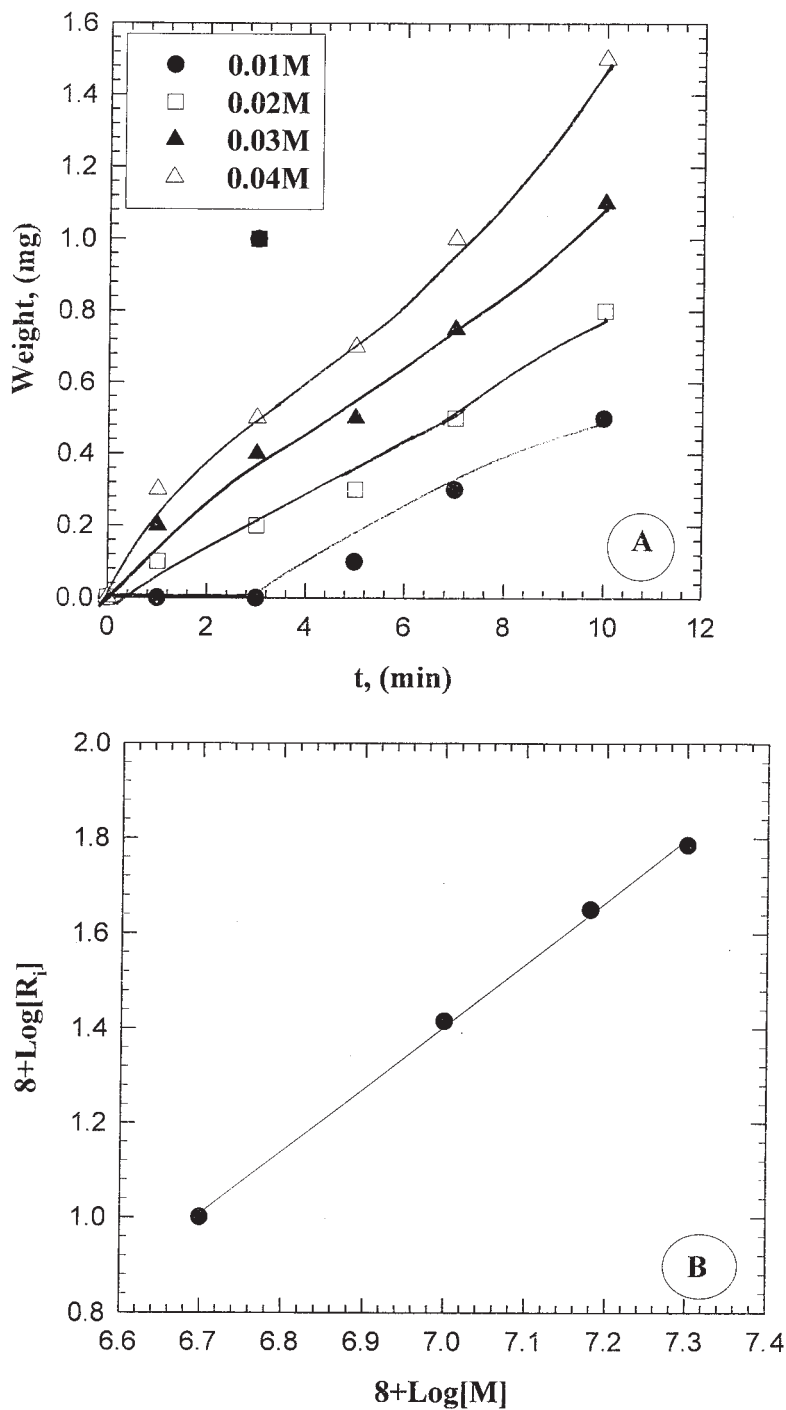
**Figure 4** (A) Yield–time (*t*) curve for the effect of monomer concentration and (B) double logarithmic plot of the initial rate of electropolymerization versus monomer concentration. $R_i$ = initial rate.

Effect of HCl concentration

Anodic oxidative electropolymerization was carried out with 0.05*M* monomer and 0.1*M* Na$_2$SO$_4$ in a dimethyl formamide/water mixture (30:70 v/v) and with a current density of 10 mA/cm$^2$ and at 303 K, both of which were kept constant. However, the hydrochloric acid concentration was varied in the range

0.6–2.0*M* (at <0.6*M*, the adherence of the polymer film decreased, and the polymer was formed in the solution near the anode). The obtained polymer film in each experiment was weighed. The obtained data showed that the maximum weight was obtained when a HCl concentration of 1.2*M* was used. The effect of HCl concentrations in the range 0.6–1.2*M* on the electropolymerization rate was examined. The weight of
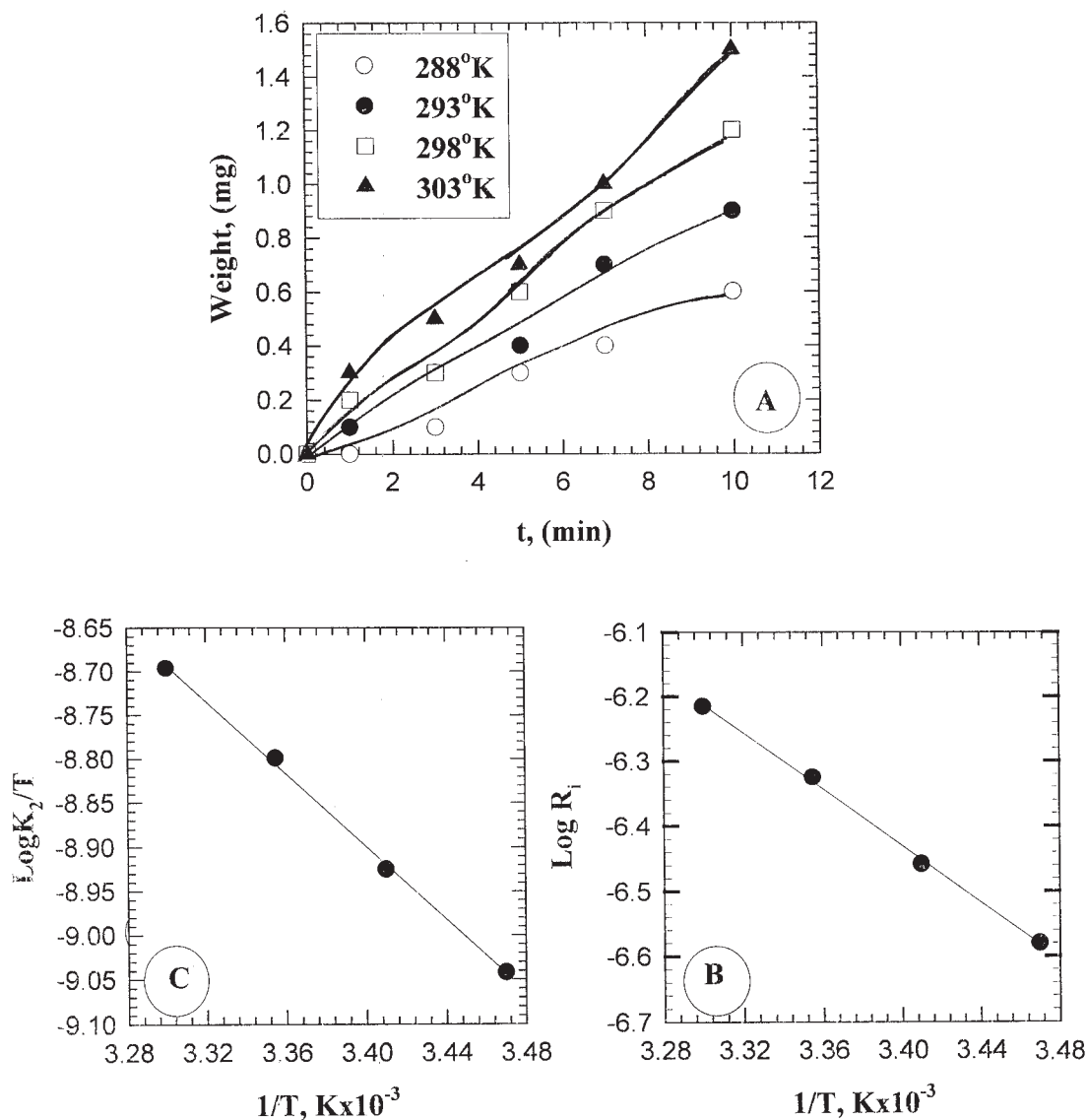
**Figure 5** (A) Yield–time ($t$) curve for the effect of temperature, (B) Arrhenius plot for the electropolymerization, and (C) Eyring equation plot for the electropolymerization. $R_i$ = initial rate.

the deposited polymer film on the platinum electrode in each experiment was plotted against the duration, as shown in Figure 3(A). 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 3(B). A straight line was obtained, which had a slope of 0.96. This means that the order of the reaction with respect to HCl was a first-order reaction.

Effect of monomer concentration

We carried out the electropolymerization reaction by keeping all of the aforementioned conditions constant at $1.2M$ HCl, current density = 10 mA/cm$^2$, $0.1M$ Na$_2$SO$_4$, and temperature = 303 K, but the monomer

concentrations were varied in the range 0.01–0.07$M$. The weight of the obtained polymer film in each case was calculated. From the obtained data, we noticed that the maximum weight of the polymer film was obtained when a monomer concentration of 0.04$M$ was used. Also, the weight of the polymer film decreased at higher concentrations of the monomer, which meant that polymer degradation may have been occurring. The electropolymerization of 3-chloroaniline was performed with different monomer concentrations in the range 0.01–0.07$M$ at different time intervals. The data are graphically represented in Figure 4(A). 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 4(B). This rela-
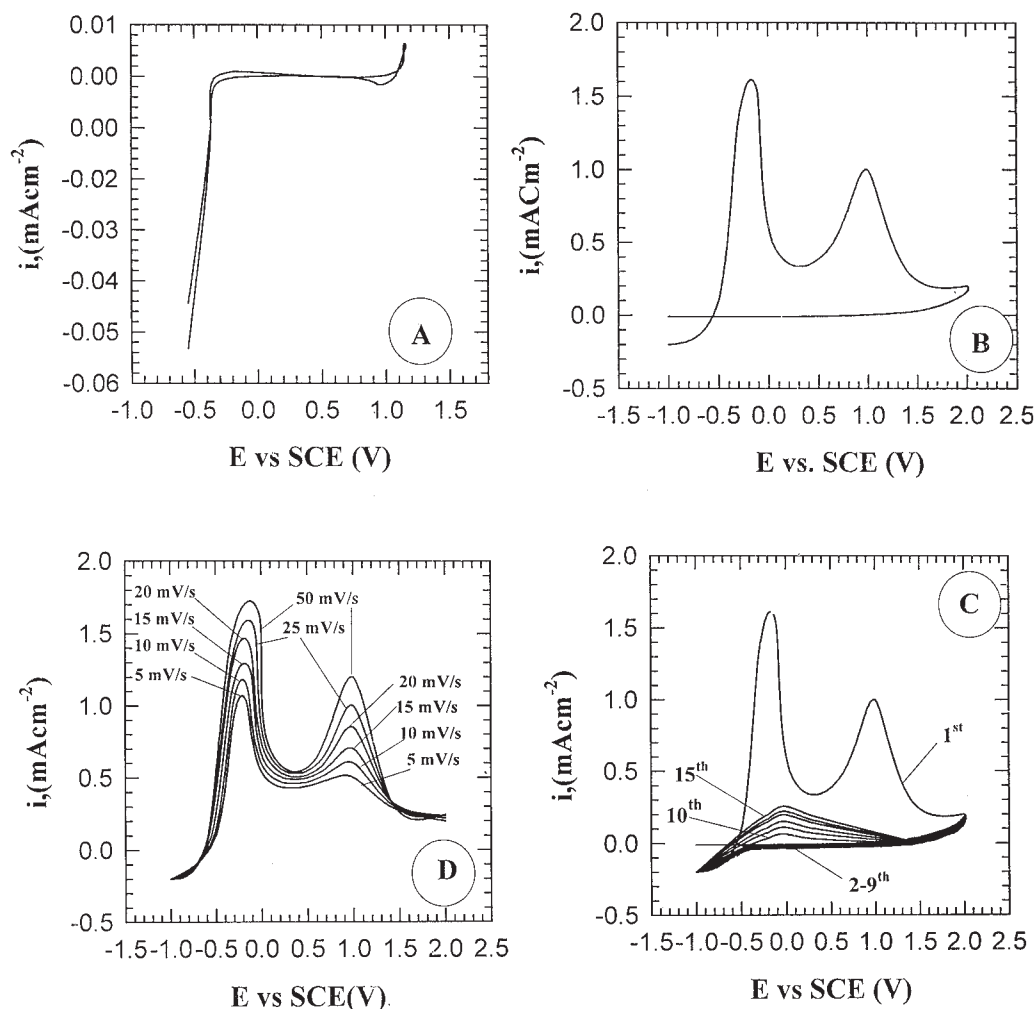
**Figure 6** (A) Cyclic voltammogram curve without monomer, (B) cyclic voltammogram curve with monomer, (C) repetitive cycling of the electropolymerization, and (D) effect of scanning rate on the electropolymerization. $i$ = current density.

tion gave a straight line with a slope equal to 1.3, which means that the order of the electropolymerization reaction of 3-chloroaniline was a first-order reaction with respect to the monomer concentration.

### Effect of temperature

The anodic oxidative electropolymerization of 3-chloroaniline was carried out under the following constant conditions: $1.2M$ HCl, $0.04M$ monomer, $0.1M$ $Na_2SO_4$, and current density = 10 mA/cm$^2$, but the reaction was carried out at different temperatures in the range 288–323 K. The maximum weight of the polymer film was recorded at 303 K. We noticed during the experiments that at temperatures higher than 303 K, some polymers were formed in the solution near the anode and did not adhere at the electrode, which means that at temperatures higher than 303 K, the adhesion of the film to the electrode decreased. The electropolymeriza-

tion of 3-chloroaniline was carried out at different temperatures, 288, 293, 298, and 303 K, for different time intervals. At each temperature, the weight of the formed polymer at the anode was plotted versus the duration, and the yield–time curve is represented in Figure 5(A). The initial rate of electropolymerization was calculated at each investigated temperature ($T$), and the logarithm of the initial rate was plotted versus $1/T$ [cf. Fig. 5(B)], which gave a straight line with a slope equal to $-2.17$. By applying the Arrhenius equation, we calculated the apparent activation energy and found it to be 41.6 kJ/mol.

### Calculation of thermodynamic parameters

The enthalpy of activation ($\Delta H^*$) and entropy of activation ($\Delta S^*$) for the electropolymerization reaction could be calculated from the $k_2$ (rate constant) values of the following equation:
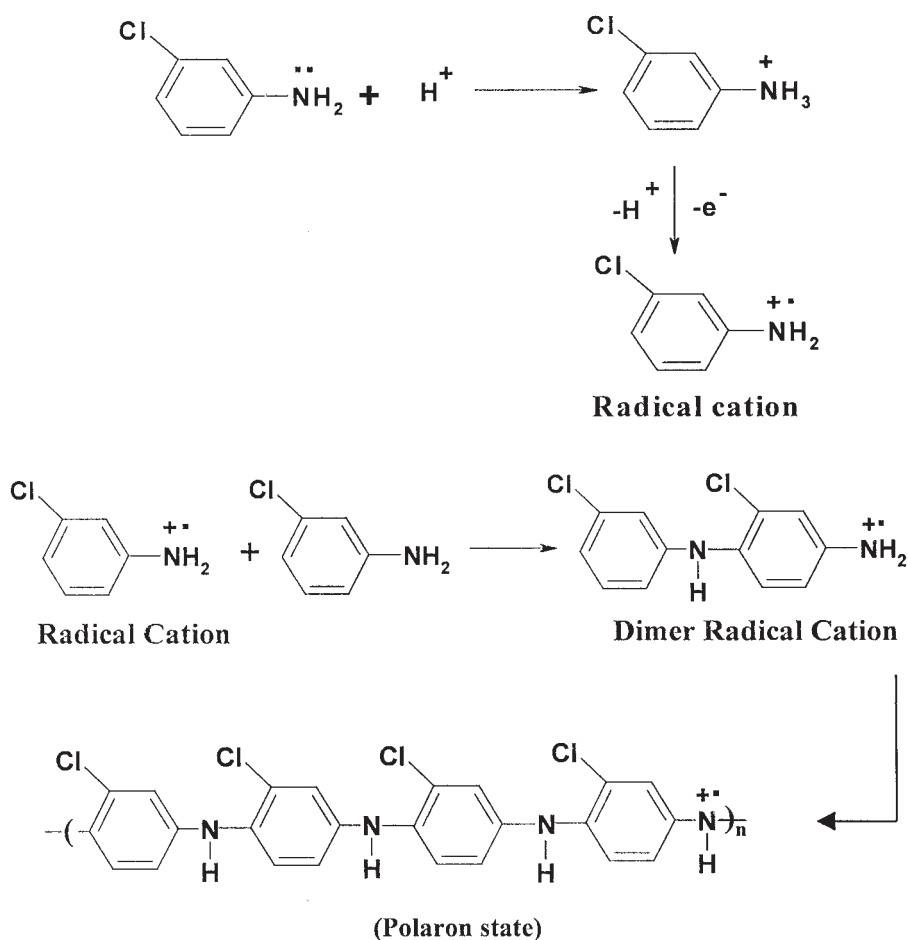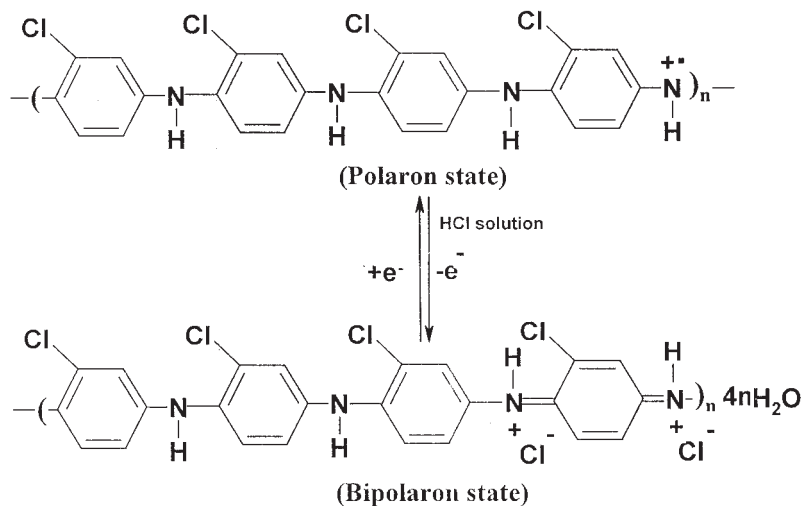
**Scheme 1**

Reaction rate

$$= k_2[HCl]^{0.96}[\text{Current density}]^{0.99}[\text{Monomer}]^{1.3}$$

The values of $k_2$ at different temperature were calculated, and the $\Delta H^*$ and $\Delta S^*$ values associated with $k_2$ were calculated with the Eyring equation:

$$k_2 = RT/Nhe^{\Delta S^*/R}e^{-\Delta H^*/RT}$$

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 $1/T$ [cf. Fig. 5(C)], we obtained a linear relationship with a slop of $-\Delta H^*/2.303R$ and an intercept of $\log(R/Nh) + \Delta S^*/$
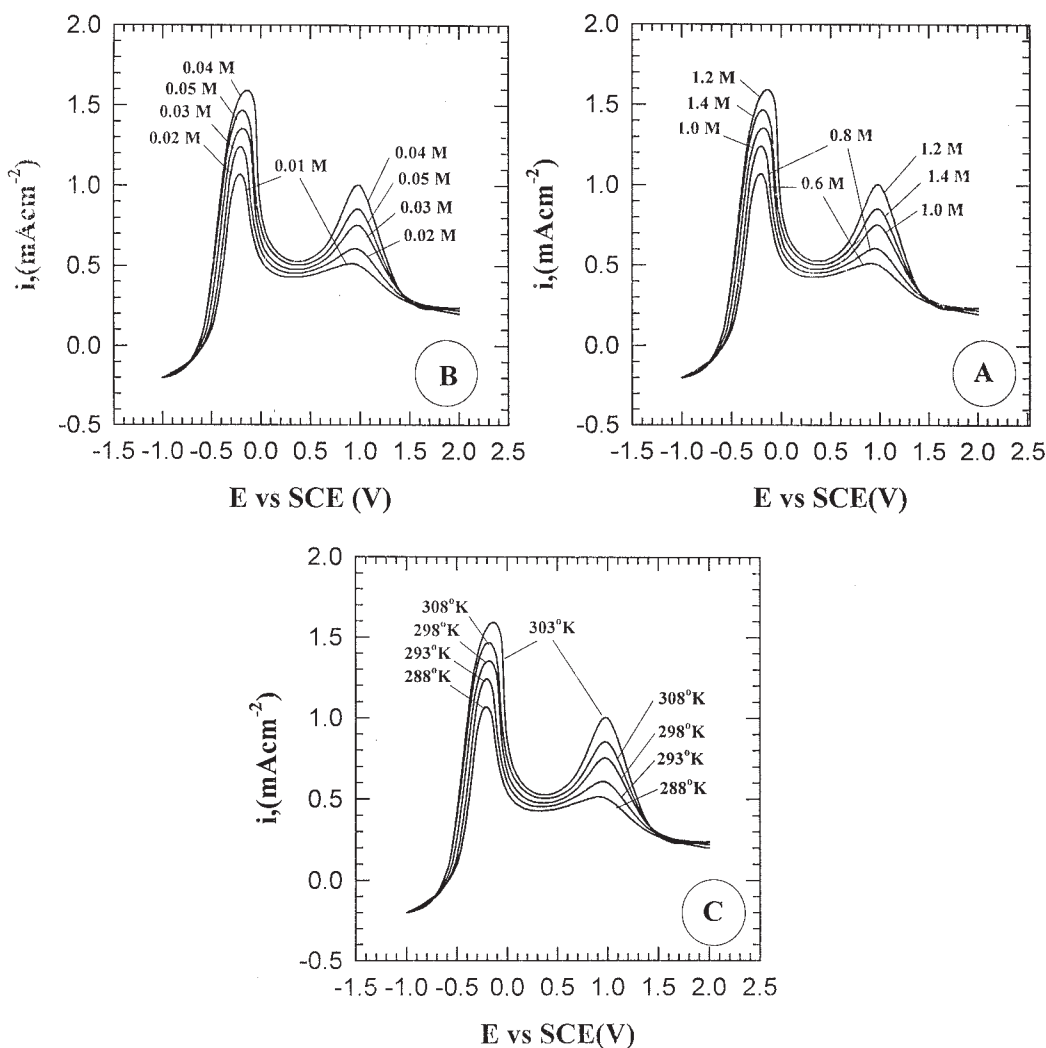


**Scheme 2**

**Figure 7** Cyclic voltammogram curves for the effects of (A) HCl concentration, (B) monomer concentration, and (C) temperature on the formation of poly(3-chloroaniline) from a solution containing $0.1M$ $Na_2SO_4$. $i$ = current density.

2.303$R$. From the slope and intercept, we found the values of $\Delta H^*$ and $\Delta S^*$ to be 39.5 and $-234$ kJ/mol, respectively.

## Cyclic voltammetry characterization

The cyclic voltammograms of poly(3-chloroaniline) formation on Pt electrode from a solution containing $1.0M$ HCl and $0.1M$ $Na_2SO_4$ at 303 K with and without $0.04M$ monomer in the potential range $-1000$ to 2000 mV versus SCE with a scanning rate of 25 mV/s are shown in

**TABLE I**
**Elemental Analysis of the Prepared Poly(3-chloroaniline)**

|       | C (%) | H (%) | N (%) | Cl (%) |
|-------|-------|-------|-------|--------|
| Calcd | 44.65 | 2.48  | 8.68  | 33.02  |
| Found | 45.18 | 3.20  | 9.20  | 32.50  |

Figure 6(A,B). The voltammogram in the presence of monomer exhibited two oxidation peaks, which progressively developed at $-150$ and 1000 mV. The first oxidation peak corresponded to the removal of an electron from the nitrogen atom amine to give a radical cation. The formed radical cation interacted with another monomer molecule to form a dimer radical cation, which was followed by a further reaction with a monomer molecule to give a trimer radical cation and so on. Finally, the semiquinone radical cation (polaron state) was formed, as shown in Scheme 1.

The presence of a chlorine atom in the meta position facilitated the first oxidation process, and the formation of the radical cation occurred immediately at low potential ($-150$ mV). This indicated that the aromatic chain was rapidly charged by an isolated, delocalized polaron.

However, the second oxidation process during the electropolymerization appeared at high potential

(1000 mV vs SCE). The second oxidation peak was assigned to the oxidation of the semiquinone radical (polaron state) to the quinone imine (bipolaron), as shown in Scheme 2.

In other words, the second oxidation process was attributed to the conversion of the radical cations to the fully oxidized form (quinoidal structure). The polymer chain consisted mainly of the para coupling of semiquinone, quinone, and benzene rings in ratios depending on the applied potential, as mentioned by Buzarovska et al.[28] for o-toluidine. The second oxidation state appeared at high potential because of the presence of the substituted chlorine atom in the meta position of the aniline moiety, which retarded the polymerization process. However, as soon as polymerization was nucleated, a thick, highly adherent, brown polymer film was rapidly deposited on the electrode surface. The potential difference between the first and second oxidation peak was 1150 mV, and no middle peaks were observed, which confirmed the nonexistence of degradation products, high regularity, homogeneity, and adherence of the deposited film to the electrode surface. The data demonstrated that the two oxidation processes were irreversible; no cathodic peaks appeared on the reversal of the potential sweep.

Figure 6(C) shows the effect of repetitive cycling on the formation of the polymer film. The data revealed that the two anodic peaks associated with the electropolymerization of 3-chloroaniline that were observed in the first cycle disappeared on repetitive cycling up to the ninth cycle. This behavior could be assigned to the deposition of a thick, nonporous, highly adherent, and poorly conductive polymer film on the electrode surface. However, the first peak appeared after the ninth cycle, and its current increased with the increasing number of cycles.

Figure 6(D) illustrates the influence of the scanning rate (5–50 mV/s) on the anodic polymerization curves for the formation of poly(3-chloroaniline) on a Pt electrode. The data revealed that the peak current densities of $i_{P1}$ and $i_{P2}$ for the first and second anodic peak, respectively, increased with increasing scanning rate.

The cyclic voltammetry curves for the effect of HCl concentration, monomer concentration, and temperature on the obtained polymer film on a platinum electrode are graphically represented in Figure 7(A–C). Figure 7(A,B) shows the effect of the HCl (0.6–1.4M) and monomer (0.01–0.05M) concentrations on the formation of poly(3-chloroaniline); as shown, the anodic peak current was enhanced with increasing acid concentration up to 1.2M and monomer concentration up to 0.04M and then started to decrease.

Figure 7(C) illustrates the influence of the solution temperature (288–308 K) on the electropolymerization reaction. The data revealed that a rise in temperature

### TABLE II
### Absorption Bands of the IR Spectrum of the Prepared Poly(3-chloroaniline)

| Wave number $(cm^{-1})$ | Assignment[46] |
|---|---|
| 532[m] | Aryl C—Cl stretching |
| 680[m] | |
| 742[m] | Out-of-plane deformation showing a 1,3- |
| 783[m] | disubstituted benzene ring |
| 818[w] | Out-of-plane deformation showing a 1,4- |
| 882[w] | disubstituted benzene ring |
| 990[w] | |
| 1034[m] | |
| 1072[m] | In-plane deformation of an aromatic ring |
| 1230[m] | |
| 1280[s] | |
| 1406[m] | Stretching vibration of C—N group |
| 1461[m] | Stretching vibration of C—N in aryl NH |
| 1508[m] | or an aryl $NH_2$ group |
| | Stretching vibration of C=C in benzene |
| 1589[s] | or C=N in a quinonoid moiety |
| 3100[sh] | CH aromatic |
| | Symmetric stretching vibration of NH in |
| | an $NH_2$ terminal group solvated by |
| 3394[b] | water molecules |

s = sharp; m = medium; w = weak; sh = shoulder.

up to 303 K resulted in a progressive increase in the charge included in the anodic peak.

The data of Figure 7(A–C) were in good agreement with the kinetic data.

### Elemental and spectroscopic analyses

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

The IR absorption bands and their assignments for poly(3-chloroaniline) are summarized in Table II. The medium band appearing at 532 $cm^{-1}$ may have been due to the stretching vibration of C—Cl. The three medium absorption bands appearing at 680, 742, and 783 $cm^{-1}$ were attributed to out-of-plane C—H deformation for the 1,3-disubstituted benzene ring. The absorption bands appearing at 818 and 882 $cm^{-1}$ were attributed to the 1,4-disubstituted benzene ring. The broad absorption band appearing at 3394 $cm^{-1}$ was attributed to the stretching vibration of the —NH group solvated by water molecules. Other absorption bands and their assignments are given in Table II.

The $^1$H-NMR spectrum of the prepared poly(3-chloroaniline) showed a singlet signal at δ 7.0 ppm and a broad signal at δ 7.5 ppm, which are characteristic for the two types of benzene ring protons. The singlet signal, which appeared at δ 8.1 ppm, was attributed to the NH group proton.
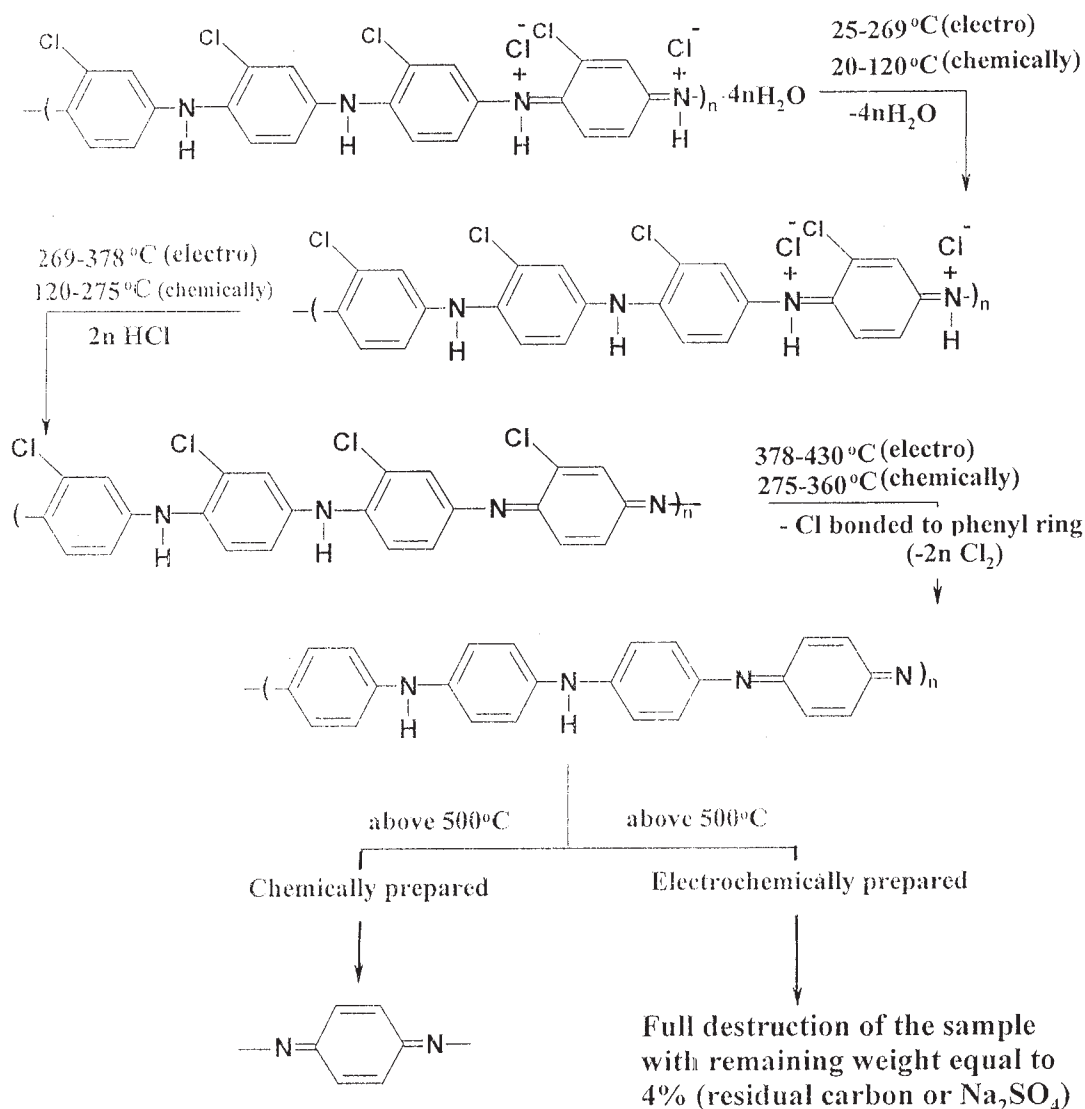
**Scheme 3** Comparison between the thermal behavior for chemically prepared[39] and electrochemically prepared polymer samples.

**Thermal analysis of the chemically prepared poly(3-chloroaniline)[39] and the electroprepared sample**

We performed TGA for the electrochemically prepared poly(3-chloroaniline) sample, and the thermal degradation steps are shown in Scheme 3. As shown in Scheme 3, it was clear that there were five stages:

1. The first stage included the loss of water of hydration (four molecules) in the temperature range 25–269°C. The estimated weight loss for this step was 10.10%, and the calculated loss was 11.16%.
2. The weight loss in the second stage, in the temperature range 269–378°C, was 11%, which was attributed to the loss of two molecules of HCl. The calculated weight loss of this stage was 11.3%.

3. The third stage, in the temperature range 378–430°C, at which all of the chlorine atoms bonded to the aromatic ring were lost from the polymeric chain, had an estimated weight loss of 23% and a calculated weight loss of 22%.
4. In the fourth stage, in the temperature range 430–500°C, all of the polymeric segments were destroyed. The estimated weight loss for this step was 54%, which was in a good agreement with the calculated value of 56%.
5. In the last stage, above 500°C, residual material (4%) remained as carbon or supporting electrolyte materials.

**Surface morphology**

Homogeneous, smooth, brown, well-adhering polymer films were electrodeposited on the platinum
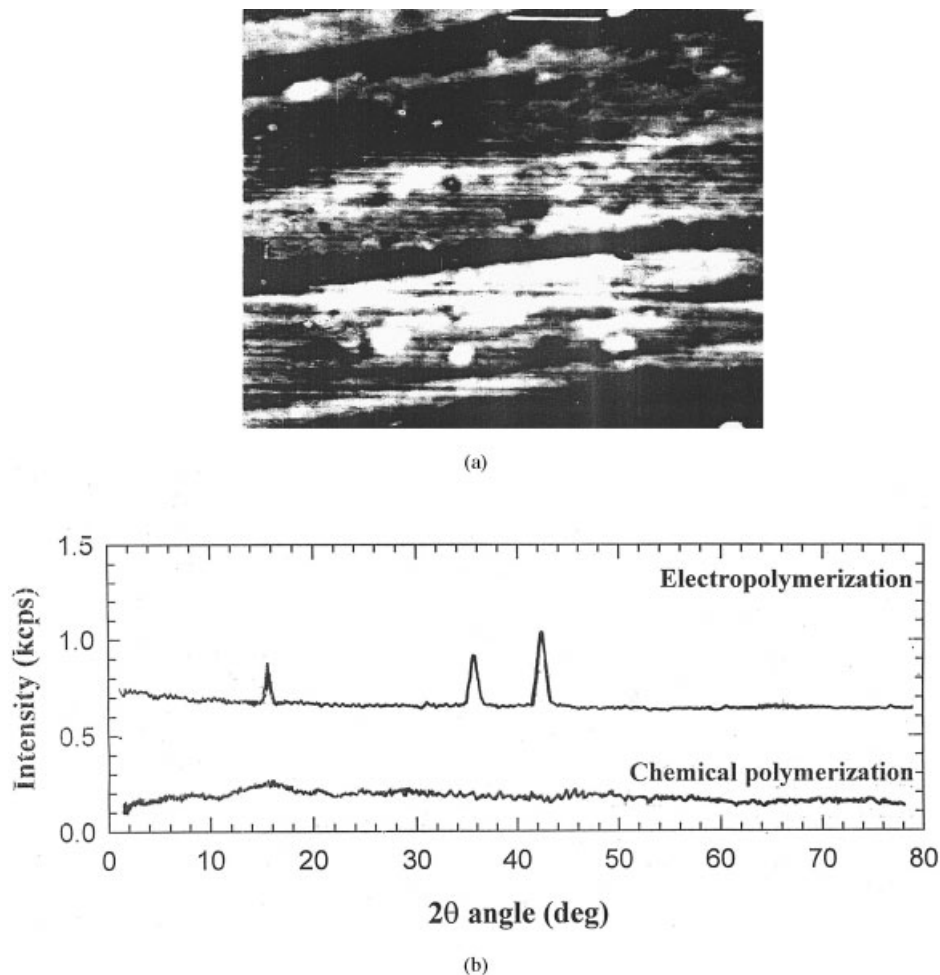
(a)



(b)

**Figure 8**  (A) Scanning electron microscope picture of the electropolymerized poly(3-chloroaniline) and (B) X-ray diffraction patterns of poly(3-chloroaniline).

surface in most conditions. The surface morphology of the poly(3-chloroaniline) film electrodeposited at the optimum conditions was examined by scanning electron microscopy and X-ray diffraction analysis. The data showed that the electropolymerized poly(3-chloroaniline) sample was crystalline with a tubular or fibrillar elongated structure [cf. Fig. 8(A,B)], whereas the poly(3-chloroaniline) chemically prepared by Sayyah et al.[39] was amorphous.

From the previous data, we concluded that electrochemical preparation oriented the prepared polymeric chains onto the electrode surface.

## CONCLUSIONS

In conclusion, the data revealed the following:

1. The initial rate of the electropolymerization reaction of 3-chloroaniline on platinum surface was relatively low because the calculation of the initial rate was taken on the basis of the adhered polymer film on the platinum electrode. The frac-

tion of the dissolved product may have strongly depended on the temperature and monomer or HCl concentrations.
2. The orders of the electropolymerization reaction of 3-chloroaniline were 0.99, 0.96, and 1.2 with respect to current density, hydrochloric acid, and monomer concentrations, respectively. The rate law was $R_p$ (rate of electropolymerization) $= k_2$(Current density)$^{0.99}$[HCl]$^{0.96}$[Monomer]$^{1.2}$.
3. The apparent activation energy was 41.6 kJ/mol.
4. The cyclic voltammogram exhibited two oxidation peaks at $-150$ and 1000 mV (vs SCE), and the first oxidation peak corresponded to the formation of a semiquinone radical cation (polaron state), whereas the second was assigned to the oxidation of a semiquinone radical cation (polaron state) to a quinone imine (bipolaron).
5. The prepared poly(3-chloroaniline) film was a tubular or fibrillar crystalline material, smooth, brown, and well adhered on the platinum electrode.

6. X-ray diffraction analysis showed that the electrochemical preparation oriented the prepared polymer onto the electrode surface, whereas poly(3-chloroaniline) that was chemically prepared was amorphous.

## References

1. Advances in Electrochemical Science and Engineering; Evans, G. P.; Gerischer, H.; Tobias, C. H., Eds.; VCH: New York, 1990; Vol. 1.
2. Handbook of Conducting Polymers; Skotheim, T. A., Ed.; Mercel Dekker: New York, 1986.
3. Tatsuma, T.; Sotomura, T.; Sato, T.; Buttry, D.; Oyama, N. J Electrochem Soc 1995, 142, 182.
4. Kaneto, K.; Kaneko, M.; Min, Y.; MacDiarmid, A. Synth Met 1995, 71, 2211.
5. Ye, S.; Girard, F.; Belanger, D. J Phys Chem 1993, 97, 12373.
6. Ye, S.; Belanger, D. J Electrochem Soc 1994, 141, 149.
7. Morita, M.; Miyazaki, S.; Ishikawa, M.; Matsuda, Y.; Tujima, H.; Adachi, K.; Anan, F. J Power Sources 1995, 54, 214.
8. Kobayashi, T.; Yoneyama, H.; Tamoura, H. J Electroanal Chem 1984, 161, 419.
9. Genies, E. M.; Lipkowski, M.; Santier, C.; Viel, E. Synth Met 1987, 18, 631.
10. Nguyen, M. T.; Dao, L. H. J Electrochem Soc 1989, 136, 2131.
11. Paul, E. W.; Ricco, A. J.; Wrighton, M. S. J Phys Chem 1985, 89, 1441.
12. Noufi, R.; Nozik, A. J.; White, J.; Warren, L. F. J Electrochem Soc 1982, 129, 2261.
13. Mengoli, G.; Musiani, M. M.; Pelli, B.; Vecchi, E.; J. Appl Polym Sci 1983, 28, 1125.
14. Ohno, H.; Nishihara, A.; Armoki, K. Corros Eng 1987, 36, 361.
15. Lu, W.; Elsenbaumer, R.; Wessling, B. Synth Met 1995, 71, 2163.
16. Brusic, V.; Angelopoulos, M.; Grahami, T. J Electrochem Soc 1997, 144, 436.
17. Bernard, M. C.; Joiret, S.; Hugot-Le Goff, A.; Phong, P. V. J Electrochem Soc 2001, 148, 12.
18. Beek, F.; Hulser, P. J Electroanal Chem 1990, 280, 159.
19. Kalaji, M.; Peter, L. M.; Abrantes, L. M.; Mesquita, J. C. J Electroanal Chem 1989, 274, 289.
20. Lacroix, J. C.; Kanazawa, K. K.; Diaz, A. J Electrochem Soc 1989, 130, 1308.
21. MacDiarmid, A. G.; Chiang, J. C.; Halpem, M.; Huang, W. S.; Mu, S. L.; Somasiri, N. L.; Wu, W.; Yaniger, S. I. Mol Cryst Liq Cryst 1985, 121, 173.
22. MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Epstein, A. J. Synth Met 1987, 18, 285.
23. MacDiarmid, A. G.; Epstein, A. J. Faraday Discuss Chem Soc 1989, 88, 317.
24. Travers, J. P.; Genoud, F.; Menardo, C.; Nechtschein, M. Synth Met 1990, 35, 159.
25. Genies, E. M.; Boyle, A.; Capkowski, M.; Tsintavis, C. Synth Met 1990, 36, 139
26. Viva, F.; Andrade, M.; Molina, F.; Florite, M. J Electroanal Chem 1999, 471, 180.
27. Sazou, D. Synth Met 2001, 118, 133.
28. Buzarovska, A.; Arsova, I.; Arsov, L.; Serb, J. Chem Soc 2001, 66, 27.
29. Shenglong, W.; Fosong, W.; Xiaohui, G. Synth Met 1986, 16, 99.
30. Muller, D.; Jozefowicz, M. Bull Soc Chim Fr 1972, 11, 4083.
31. Chiba, K.; Ohsaka, T.; Oyama, N. J Electroanal Chem 1987, 217, 239.
32. Hagiwara, T.; Demura, T.; Iwata, K. Synth Met 1987, 18, 317.
33. Huang, W.; Humphrey, B. D.; MacDiarmid, A. G. J Chem Soc Faraday Trans 1986, 82, 2385.
34. Cui, S. Y.; Park, S. M. Synth Met 1999, 105, 91.
35. Duic, L.; Mandic, Z. J Electroanal Chem 1992, 335, 207.
36. Kobayashi, N.; Yamada, K.; Hirohashi, R. Chem Lett 1990, 1983.
37. Kobayashi, N.; Yamada, K.; Hirohashi, R. Electrochim Acta 1992, 37, 2101.
38. Teshima, K.; Yamada, K.; Kobayashi, N.; Hirohashi, R. J Electroanal Chem 1997, 426, 97.
39. Sayyah, S. M.; Abd El-Khalek, A. A.; Bahgat, A. A.; Abd El-Salam, H. M. Polym Int 2001, 50, 197.
40. Sayyah, S. M.; Abd El-Khalek, A. A.; Bahgat, A. A.; Abd El-Salam, H. M. Int J Polym Mater 2001, 49, 25
41. Sayyah, S. M.; Bahgat, A. A.; Abd El-Salam, H. M. Int J Polym Mater 2002, 51, 291.
42. Sayyah, S. M.; Bahgat, A. A.; Abd El-Salam, H. M. Int J Polym Mater 2002, 51, 915.
43. Bahgat, A. A.; Sayyah, S. M.; Abd El-Salam, H. M. Int J Polym Mater 2003, 52, 499.
44. Sayyah, S. M.; Abd El-Rehim, S. S.; El-Deeb, M. M. J Appl Polym Sci 2003, 90, 1783.
45. Sayyah, S. M.; Abd El-Rehim, S. S.; El-Deeb, M. M. Int J Polym Mater 2004, 53, 1.
46. Silverstein, R. M.; Bassler, C. G.; Morill, T. C. Spectroscopic Identification of Organic Compounds; Wiley: New York, 1974.