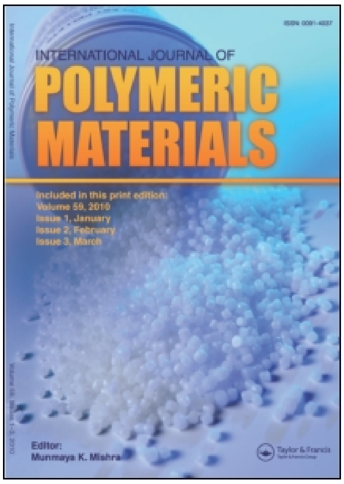

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Electrochemical Polymerization of 3-Methoxyaniline and Characterization of the Obtained Polymer

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Electropolymerization of 3-methoxyaniline on platinum electrode in acid medium was carried out under different reaction conditions such as temperature, current density, hydrochloric acid, and monomer concentrations with duration time. The initial rate of the electropolymerization reaction is small and the orders are found to be 0.99, 0.98, and 0.97 with respect to current density, acid, and monomer concentrations, respectively. The apparent activation energy (E_a) is found to be 59.673 KJ mol^{-1}. The rate law is $RP = K_2[D]^{0.99}[HCl]^{0.98}[M]^{0.97}$. The obtained polymer films were characterized by ^{1}H-NMR, elemental analysis, IR, and cyclic voltammetry. The mechanism of the electropolymerization reaction has also been discussed. The thermogravimetric analysis (TGA) 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 were used to investigate the surface morphology.

Keywords: electropolymerization, 3-methoxyaniline, characterization, cyclic voltammetry

INTRODUCTION

The electropolymerization of conducting polymers on electrode surfaces has been a very active research area in electrochemistry

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because of their outstanding 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 because of its many promising properties at 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 a 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 in 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 has been studied [34–35]. Also, polyaniline and poly-3-methoxyaniline were obtained by electropolymerization in tetra-n-butylammonium salt and 1,2-dichloroethane solution [36–38].

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

The objective of the present work is to investigate the kinetic and optimum conditions for the electrochemical preparation of 3-methoxyaniline in aqueous hydrochloric acid medium and characterization of the obtained polymer film. The surface morphology of the obtained polymer was characterized by scanning electron microscopy and X-ray diffraction.

EXPERIMENTAL

Materials

3-methoxyaniline (vacuum distilled and stored in the absence of light before use), hydrochloric acid solution, and anhydrous sodium sulphate were of analytical pure grade provided by Merk, Germany. All solutions were freshly prepared using doubly distilled water.

Cell and Electrodes

The experimental setup used was described previously [44–47] and consisted of rectangular Perspex cell provided with two platinum foil paralled electrodes. Each electrode had 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 circulate 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 d.c.-power supply (Thurby–Thandar PL 330).

Electrochemical Polymerization of 3-Methoxyaniline

Anodic oxidative electropolymerization of 3-methoxyaniline was carried out in aqueous solutions containing monomer (concentration range between 0.03 and 0.10 M) using 0.1 M Na_2SO_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 between 0.7 and 1.2 M) at different temperatures in the range between 283 and 318°K.

Cyclic Voltammetry Measurements

A standard three-electrode 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 was 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 by computer software from the same company (Model 352 and 270/250).

Infrared, Thermogravimetric Analysis, 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 Shimdazu 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 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	Scan speed: 8 deg · min^{-1}
Current: 30 mA	Voltage: 40 kV
Preset time:	10 s

RESULTS AND DISCUSSION

Anodic Oxidative Electropolymerization

Effect of Duration Time

Anodic oxidative electropolymerization of 3-methoxyaniline 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 values of current densities. The data reveal that the weight of the obtained polymer increases with increasing duration time up to 20 min and then tends to decrease as a result of degradation and the solubility of the polymer film from the platinum surface in case of 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 3-methoxyaniline was studied at constant time intervals (20 min) using 0.03 M monomer concentrations, 0.1 M Na_2SO_4 in dimethyl formamide/water mixture (30:70 v/v), and 1 M HCl at 298°K which were kept constant. The data reveal that, as the applied 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 an oxygen and chlorine evolution takes place as a side

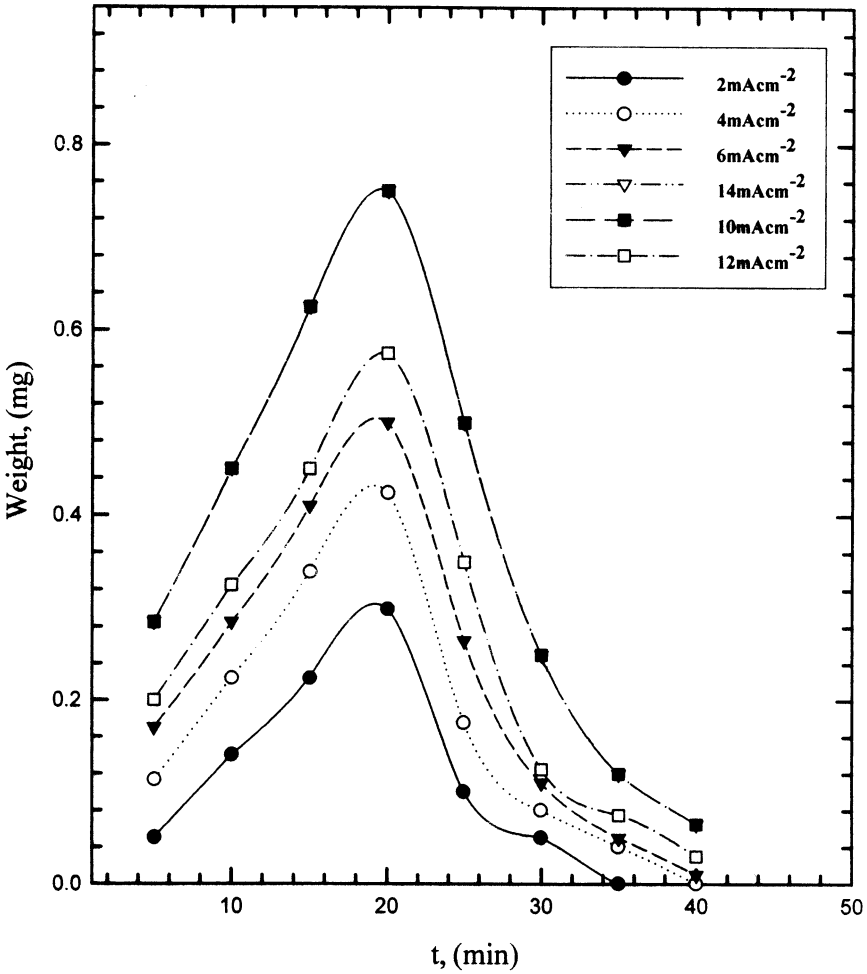


FIGURE 1 Yield-time curve for the effect of duration time on the anodic polymerization of 3-methoxyaniline from solution contaning 0.03 M monomer, 1.0 M HCl, and 0.1 M Na_2SO_4 at 298°K.

reaction especially a high current densities. Each value of the used current density was studied with different time intervals and the yield-time curve was estimated. The data are graphically represented 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 is found to be 0.99.

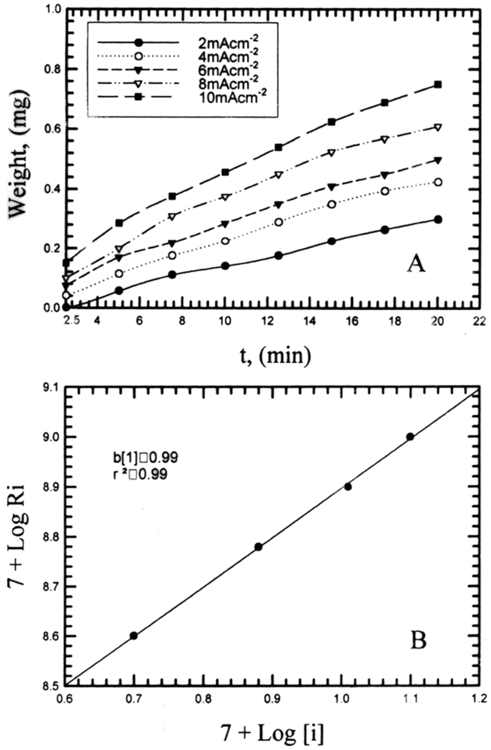


FIGURE 2 (A) Yield-time curve for the effect of current densities; (B) Double logarithmic plot of initial rate of electropolymerization versus different current densities values.

Effect of HCl Concentration

Anodic oxidative electropolymerization of 3-methoxyaniline was carried out using 0.03 M of monomer concentration, 0.1 M Na_2SO_4 in dimethyl formamide/water mixture (30:70 v/v), current density = 10 mA cm^{-2} at 298°K, which were kept constant. But the hydrochloric acid concentration was varied in the range between 0.6 and 1.2 M (above 1.0, 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 show that the maximum weight was obtained when 1 M HCl concentration was used. The effect of HCl concentration in the range between 0.7 and 1 on the electropolymerization rate was studied. The weight of the deposited polymer film on the platinum electrode in each experiment was plotted against the duration time as shown in Figure 3A.

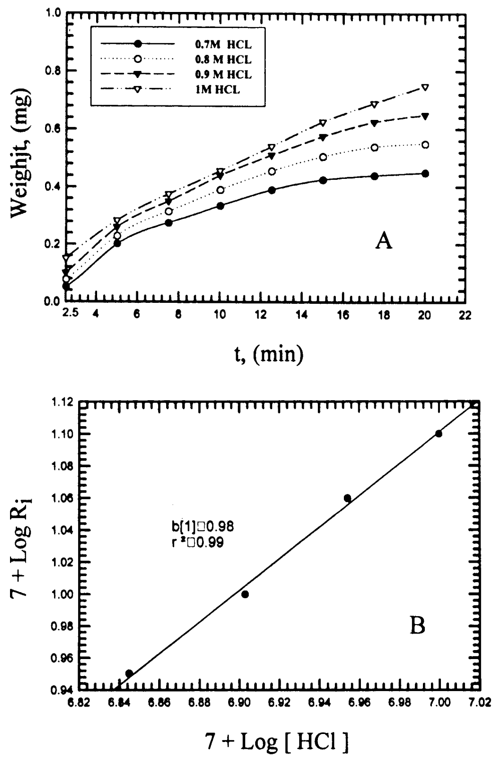


FIGURE 3 (A) Yield-time curve for the effect of HCl concentration; (B) Double logarithmic plot of initial rate of electropolymerization versus HCl concentrations.

The 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 that has a slope equal to 0.98, which means that the order of the reaction with respect to HCl concentration is a first order reaction.

Effect of Monomer Concentration

The electropolymerization reaction was carried out by keeping all the aforementioned conditions constant at 1 M HCl, current density = 10 mA cm^{-2}, Na_2SO_4 (0.1 M) and temperature at 298°K, but the monomer concentration was varied in the range between 0.03 and 0.10 M. Then, the weight of the obtained polymer film in each case was calculated. The obtained data reveal that the maximum weight of the polymer was obtained when 0.07 M of monomer concentration was used. It was also noticed that the weight of the polymer film decreases

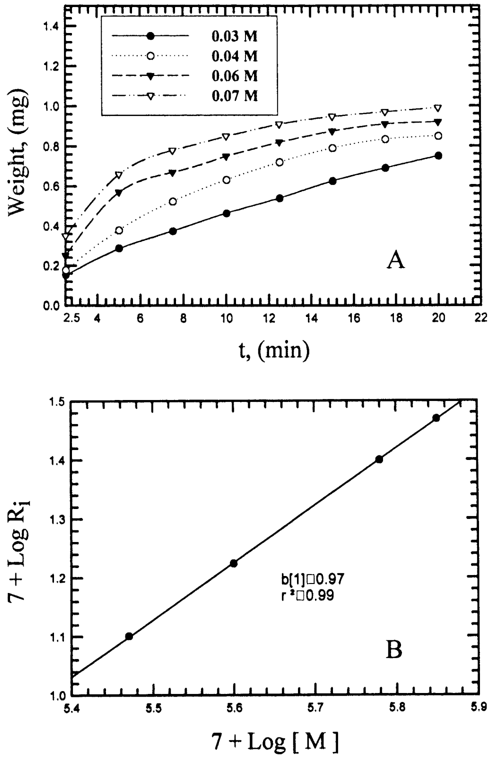


FIGURE 4 (A) Yield-time curve for the effect of monomer concentrations; (B) Double logarithmic plot of initial rate of electropolymerization versus monomer concentrations.

at higher concentrations of the monomer, which means that polymer degradation may be occurring. The electropolymerization of 3-methoxyaniline 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 gives a straight line with a slope equal to 0.97, which means that the order of the electropolymerization reaction of 3-methoxyaniline is a first order reaction with respect to monomer concentration.

Effect of Temperature

Anodic oxidative electropolymerization of 3-methoxyaniline was carried out under the following constant conditions: 1 M HCl, 0.07 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 318°K. The maximum weight of polymer film was recorded at 303°K. It was noticed during the experiments that, at high temperatures (higher than 303°K), some polymer were formed in the solution near the anode and not adhered at the electrode, which means that, at temperature higher than 303°K, the adhesion of the film to the electrode is decreased. The electro-polymerization of 3-methoxyaniline 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 determined and plotted versus the duration time. The yield-time curves are represented in Figure 5A. The initial rate of electropolymerization was calculated at each investigated temperature and the logarithm of the initial rate was plotted versus 1/T (c.f. Figure 5B), which gives a striaght line with a slope equal to –3.122. By applying Arrhenius equation, the apparent activation energy was calculated and was found to be 59.673 kJ mol^{-1}.

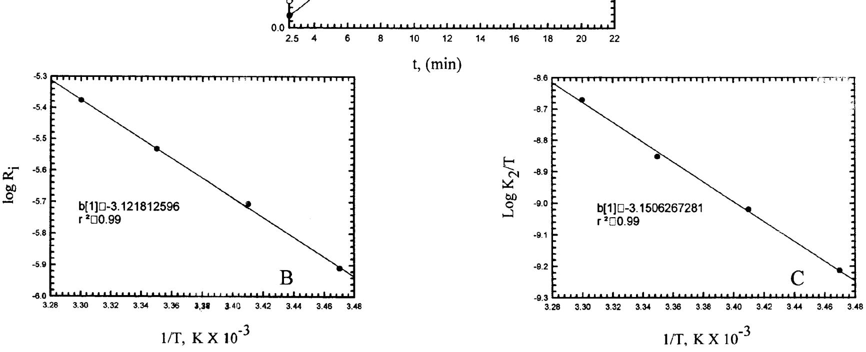


FIGURE 5 (A) Yield-time curve for the effect of temperature; (B) Arrhenius plot for the electropolymerization; (C) Eyring equation plot for the electropolymerization.

Calculations 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:

$$\text{Reaction rate} = K_2[\text{HCl}]^{0.98}[\text{current density}]^{0.99}[\text{monomer}]^{0.97}$$

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) a linear relationship was obtained with a slope of $-\Delta H^*/2.30\,R$ and an intercept, of $\log (R/Nh) + \Delta S^*/2.303\,R$. From the slope and intercept, the values of ΔH^* amd ΔS^* are found to be 60.224 kJ mol^{-1} and –361.62 kJ mol^{-1}, respectively.

Cyclic Voltammetry Characterization

Cyclic voltammograms of polymerization of 3-methoxyaniline on Pt electrode from solution containing 1.0 M HCl and 0.1 M Na_2SO_4 at 303°K without and with 0.07 M monomer in the potential range from –1000 to 2000 mV versus SCE with scan rate of 25 mV s^{-1} are shown in Figure 6A and B, respectively. The voltammogram in the presence of monomer exhibits two oxidation peaks (A and B), which progressively developed at –263 and 1100 mV, respectively. The first oxidation peak A corresponds to removal of electron from nitrogen atom of amine group to give radical cation. The formed radical cation reacts with 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 as shown in Scheme 1.

The presence of methoxy group in the meta position of the amino group facilitates the first oxidation process and formation of the radical cation, which occurs immedially at low potential (–263 mV). This indicates that the aromatic chain is rapidly charged by isolated, delocalized, polarons. This potential is lower than the first oxidation peak potential exhibited by meta chloroaniline [46] due to the presence of methoxy group (as electorn donating group), whereas chlorine atom acts as electron withdrawing group.

On the other hand, the second oxidation process during the electropolymerization appears at high potential (1100 mV versus SCE),

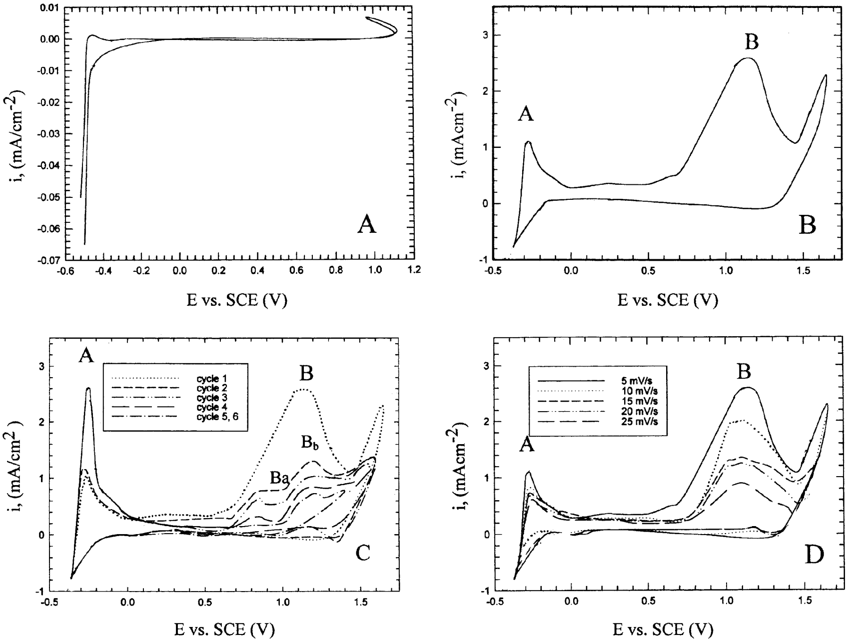
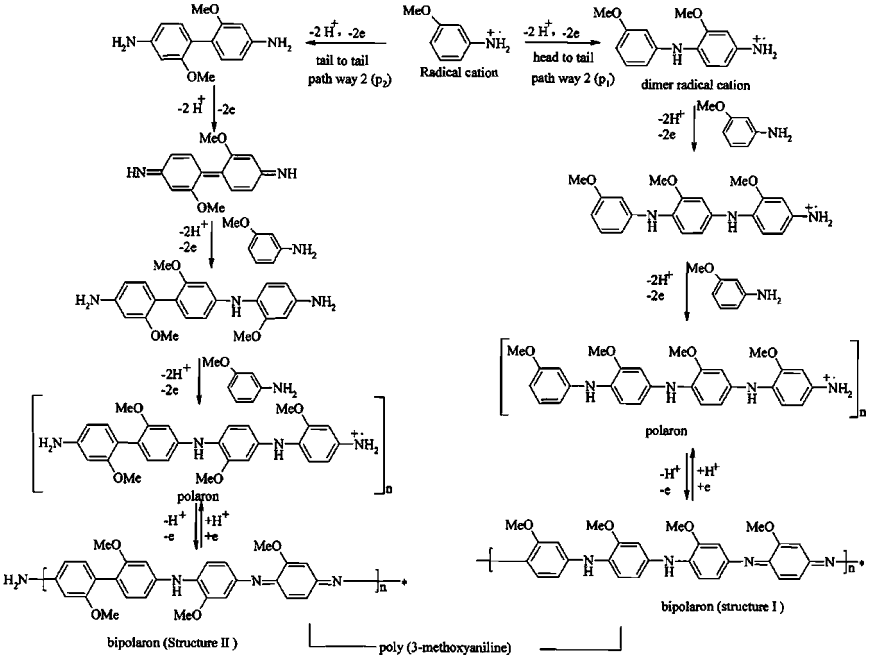


FIGURE 6 (A) Cyclic voltammaogram curve without monomer; (B) Cyclic voltammogram curve with monomer; (C) Repetitive cycling; (D) Effect of scan rate.

which is assigned to the oxidation of the semiquinone radial (polaron state) to quinone imine (bipolaron) as shown in Scheme 1. In other words, the second oxidation process is attributed to the conversion of the radical cations to the fully oxidized form (quinoid structure). The polymer chain consists mainly of para coupling of semiquinone, quinone, and benzene rings in ratio depending on the applied potential as mentioned by Buzarovka et al. [28] in case of o-toluidine. The second oxidation state appears at high potential due to the presence of the substituted methoxy group in the meta position of aniline moiety, which retards the polymerization process. However, as soon as polymerization is initiated, a thick highly adherent and brown polymer film rapidly deposits on the electrode surface. The potential difference between first and second oxidation peaks is 1363 mV.

On the other hand, the second oxidative peak at 3-chloroaniline voltamogram appears at 1000 mV [46], which is lower than the second oxidative peak of 3-methoxyaniline 1100 mV. This is due to the bulky effect of methoxy group being bulkier than chlorine atom.



SCHEME 1 Structures and mechanisms of products.

The data reveal that the two oxidation processes are irreversible, and no cathodic peaks appear upon reversing the potential sweep up to –2000 –mV.

Figure 6C represents the influence of repetitive cycling on the voltammogram of electropolymerization of 3-methoxyaniline. The data show that upon repetitive cycling the height of the anodic peak A (which corresponds to the formation of radical cations) increases whereas the second oxidation peak (B) (which corresponds to the polymer formation) decreases. The increasing of the height of peak A with each cycle reflects the growth of polymer film on the electrode surface and the increase in the anodic surface area as a result of increasing surface roughness. Moreover, repetitive cycling leads to splitting of peak (B) into two peaks (B_a and B_b).

This splitting could be attributed to the possibility of two reaction pathways (P_1 and P_2) as shown in Scheme 1. The first pathway (P_1) leads to structure I formation (head to tail) corresponding to peak B_b, but the second pathway (P_2) leads to structure II formation (tail to tail) corresponding to peak B_a. It seems that the electropolymerization structure I (head to tail) is the dominant pathway (P_1) [48].

Figure 6D illustrates the influence of scan rate (5–25 mV s^{-1}) on the anodic polymerization curves for the electropolymerization of 3-methoxyaniline on Pt electrode. The data reveal that the peak current densities of Ip_A and Ip_B for peaks A and B, respectively, increase with increasing scan rate. These results indicate that the electropolymerization process is at least partially under diffusion control.

Cyclic voltammetric characteristics of the polymer film formation on platinum electrode as a function of the concentrations of HCl, monomer, and temperature were also investigated. Figure 7A represents the influence of HCl concentration (0.7 to 1 M) on the characteristic features of the response. As can be seen, the anodic peak current is enhanced with increasing the acid concentration up to 1 M and then starts to decrease.

Figure 7B shows that, by increasing the concentration of the monomer from 0.33 to 0.07 M, the anodic peak current enhances up to 0.07 M and then starts to decrease.

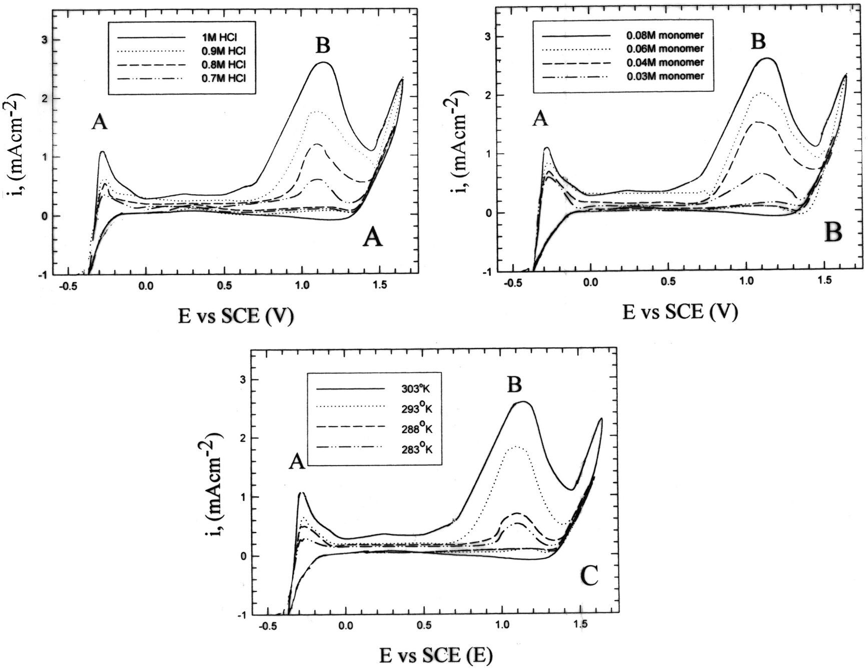


FIGURE 7 Cyclic voltammogram curves for the electropolymerization of methoxy aniline from solution containing 0.1 M Na_2SO_4; (A) Effect of HCl concentration; (B) Effect of monomer concentration; (C) Effect of temperature.

TABLE 1 Elemental Analysis of the Prepared Poly(3-methoxyaniline)

Element (%)	C (%)	H (%)	N (%)	Cl (%)
Calculated	53.2	4.44	8.88	11.26
Found	52.90	4.23	7.65	9.88

Figure 7C illustrates the influence of solution temperature (288 to 308°K) on the cyclic voltammetric response of the polymer formation. It is obvious that a rise of temperature up to 303°K results in a progressive increase of the charge included in the anodic peak. The data of Figure 7A–C confirm the obtained data from the kinetic studies.

Elemental and Spectroscopic Analysis

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

The molecular weight data obtained by GPC analysis was found to be as follows: Mw = 439049, Mn = 178261, Mv = 396873 and the polydispersity = 2.463.

The infrared absorption bands and their assignments for poly(3-methoxyaniline) are summarized in Table 2. The medium band appearing at 600 cm^{-1} may be attributed to the stretching vibration of C–O. The two medium adsorption bands appearing at 691 and 760 cm^{-1} are attributed to out of plane C–H deformation for the

TABLE 2 Infrared Absorption Bands of the IR Spectrum of the Prepared Poly(3-methoxyaniline)

Wave number (cm^{-1})	Assignments[49]
600^m	Rocking vibration of C–H in CH_3-group
691^m, 760^m	Out of plane deformation showing 1,3-disubstituted benzene ring
872^w	Out of plane deformation showing 1,4-disubstituted benzene ring
952^w, 998^m, 1050^m	In plane deformation of C–C aromatic
1186^m	Symmetric stretching vibration of C–N group in Aryl-NH or Aryl-NH_2 and C–O group in Aryl-OCH_3
1411^m, 1461^m	Symmetric stretching vibration of C=N in quinonide structure
1525^s, 1583^s	Symmetric stretching vibration of C=C in benzene
3051^m	Symmetric stretching vibration C–H aromatic moity
3388^m	Symmetric stretching vibration of N–H in Aryl-NH or Aryl-NH_2

w: weak; m: medium; s: sharp.

1,3-disubstituted benzene ring. The absorption band appearing at $872\,cm^{-1}$, is attributed to the 1,4-disubstituted benzene ring. The broad absorption band appearing at $3388\,cm^{-1}$ is attributed to the streching vibration of –NH group solvated by water molecules. Other absorption bands and their assignments are given in Table 2.

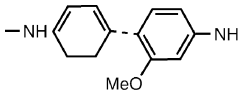
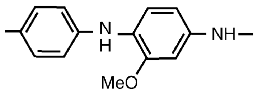
The ^1H-NMR spectrum of the prepared poly(3-methoxyaniline) shows a singlet signal at δ 3.569, which is characteristic for OCH_3 group and a singlet signal at δ 7.166 ppm and broad signal at δ 7.652 ppm, which are characteristic for the two types of benzene ring protons. The singlet signal, which appears at δ 8.428 ppm, may be attributed to the NH group proton.

Thermal Analysis of the Chemically Prepared poly(3-methoxyaniline) and the Electroprepared Sample

Thermogravimetric analysis (TGA) for the electrochemical prepared poly(3-methoxyaniline) sample has been investigated and the thermal degradation steps are shown in Table 3. From the scheme, it is clear that there are five stages:

1. The first stage includes the loss of water hydration (four molecules) in the temperature range between 25–105°C. The estimated weight loss for this step is found to be 10.5% and the calculated one is 11.5%.

TABLE 3 Thermogravimetric Data of the Prepared poly(3-methoxyaniline)

	Weight loss (%)		
Temperature range °C	Calculated	Found	The removed molecule
25–105	11.5	9.06	$4H_2O$
105–208	11.3	11.66	2HCl
208–220	10.22	11.46	$2CH_3O$
220–600	33.22	33.50	 or 
>600	—	44.4	Carbon residual or Na_2SO_4 (supporting electrolyte)

2. The weight loss in the second stage, in the temperature range 105–208°C, is found to be 11.66%, which is attributed to the loss of two molecules of HCl. The calculated weight loss of this stage is equal to 11.3%.
3. In the third stage, in the temperature range between 208–220°C, the weight loss is found to be 11.46%, indicating a loss of two molecules of methoxy groups from the polymeric chain. The calculated weight loss is equal to 10.22%.
4. In the fourth stage, in the temperature range between 220–600°C, one molecule of N-phenyl-4-amino-2-methoxyaniline structure or 4,4-diamino-2-methoxybiphenyl at the polymeric chain have been lost (according to the mentioned possibility of the two pathways in Scheme 1). The estimated weight loss for this step is 33.22%, which is in good agreement with the calculated value of 33.5%.
5. In the last stage, above 600°C, a residual material remains as carbon or supporting electrolyte materials, which is 44.4%.

Surface Morphology

Homogenous, smooth, brown, and well-adhering polymer films were electrodeposited on platinum surface in most conditions. The surface

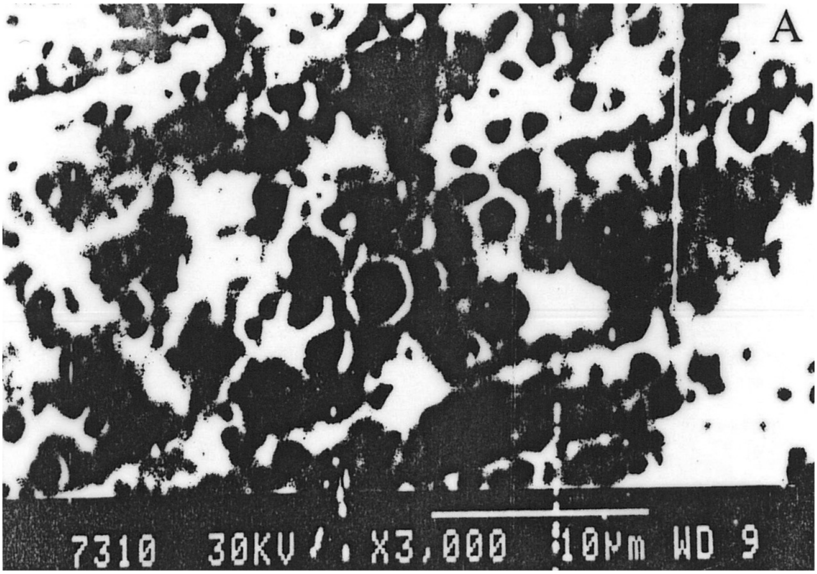


FIGURE 8 The picture of scanning electron microsope of electropolymerized poly(3-methoxyaniline).

morphology of the electrodeposited poly(3-methoxyaniline) film at the optimum condition was examined by scanning electron microscopy and X-ray diffraction analysis. The data show that the film is amorphous in structure and may contain a very small portion of crystallinity (cf. Figure 8), whereas poly(3-methoxyaniline), which was chemically prepared by Sayyah et al. [42], is amorphous.

From the aforementioned data, it can be concluded that the electrochemical preparation deposits the prepared polymeric chains onto the electrode surface.

CONCLUSION

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

1. The initial rate of the electropolymerization reaction of 3-methoxyaniline 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, monomer, and HCl concentrations.
2. The order of the electropolymerization reaction of 3-methoxyaniline is 0.99, 0.98, and 0.97 with respect to current density, hydrochloric acid, and monomer concentrations, respectively. The rate law is

$$\mathrm{Rp} = \mathrm{K}_2[\mathrm{D}]^{0.99}[\mathrm{HCl}]^{0.98}[\mathrm{M}]^{0.97}$$

3. The apparent activation energy (E_a) is $59.673\,\mathrm{KJ\,mol^{-1}}$.
4. Cyclic voltammogram exhibits two oxidation peaks at –263 and 1100 mV (vs SCE), the first oxidation peak corresponds to the formation of semiquinone radical cation (polaron state) whereas the second may be assigned to the oxidation of semiquinone radical cation (polaron state) to quinone imine (bipolaron state).
5. The prepared poly(3-methoxyaniline) film is smooth, brown, and well adhered on platinum electrode surface.
6. X-ray diffraction analysis and scanning electron microscopy picture show that the obtained polymer is amorphous with very small portion of crystallinity.

REFERENCES

[1] Evans, G. P., Gerischer, H., and Tobias, C. H. (Eds.) (1990). *Advances in Electrochemical Science and Engineering*, Vol. 1, VCH, New York.

[2] Salaneck, W., Clark, D., and Samuelsen, E. (Eds.) (1991). *Science and Applications of Conducting Polymers*, Hilger, Bristol.

[3] Tatsuma, T., Sotomura, T., Sato, T., Buttry, D., and Oyama, N., *J. Electrochem. Soc.* **142**, 182 (1995).

[4] Kaneto, K., Knaeko, M., Min, Y., and MacDiarmid, A., *Synth. Met.* **71**, 2211 (1995).

[5] Ye, S., Girard, F., and Belanger, D., *J. Phys. Chem.* **97**, 12373 (1993).

[6] Ye, S. and Belanger, D., *J. Electrochem. Soc.* **141**, 149 (1994).

[7] Morita, M., Miyazaki, S., Ishikawa, M., Matsuda, Y., Tujima, H., Adachi, K., and Anan, F., *J. Power Sources* **54**, 214 (1995).

[8] Kobayashi, T., Yoneama, H., and Tamoura, H., *J. Electro-Anal. Chem.* **161**, 419 (1984).

[9] Genies, E. M., Lipkowski, M., Santier, C., and Viel, E., *Synth. Met. 18*, 631 (1987).

[10] Nguyen, M. T. and Dao, L. H., *J. Electrochem. Soc.* **136**, 2131 (1989).

[11] Paul, E. W., Ricco, A. J., and Wrighton, M. S., *J. Phys. Chem.* **89**, 1441 (1985).

[12] Noufi, R., Nozik, A. J., White, J., and Warren, L. F., *J. Electrochem. Soc.* **129**, 2261 (1982).

[13] Mengoli, G., Musiani, M. M., Pelli, B., and Vecchi, E., *J. Appl. Polym. Sci.* **28**, 1125 (1983).

[14] Ohno, H., Nishihara, A., and Armoki, K., *Corros. Eng.* **36**, 361 (1987).

[15] Lu, W., Elsenbaumer, R., and Wessling, B., *Synth. Met.* **71**, 2163 (1995).

[16] Brusic, V., Angelopoulos, M., and Grahami, T., *J. Electro-Chem. Soc.* **144**, 436 (1997).

[17] Bernard, M. C., Joiret, S., Hugot-Le Goff, A., and Phong, P. V., *J. Electrochem. Soc.* **148**, 12 (2001).

[18] Beek, F. and Hulser, P., *J. Electroanal. Chem.* **280**, 159 (1990).

[19] Kalaji, M., Peter, L. M., Abrantes, L. M., and Mesquita, J. C., *J. Electroanal. Chem.* **274**, 289 (1989).

[20] Lacroix, J. C., Kanazawa, K. K., and Diaz, A., *J. Electro-Chem. Soc.* **130**, 1308 (1989).

[21] MacDiarmid, A. G., Chiang, J. C., Halpem, M., Huang, W. S., Mu, S. L., Somasiri, N. L., Wu, W., and Yaniger, S. I., *Mol. Cryst. Liq. Cryst.* **121**, 173 (1985).

[22] MacDiarmid, A. G., Chiang, J. C., Richter, A. F., and Epstein, A. J., *Synth. Med.* **18**, 285 (1987).

[23] MacDiarmid, A. G. and Epstein, A. J., *Faraday Discuss Chem. Soc.* **88**, 317 (1989).

[24] Travers, J. P., Genoud, F., Menardo, C., and Nechtschein, M., *Synth. Met.* **35**, 159 (1990).

[25] Genies, E. M., Boyle, A., Capkowski, M., Tsinavis, C., *Synth. Met.* **36**, 139 (1990).

[26] Viva, F., Andrade, M., Molina, F., and Florite, M., *J. Electroanal. Chem.* **471**, 180 (1999).

[27] Sazou, D., *Synth. Met.* **118**, 133 (2001).

[28] Buzarovska, A., Arsova, I., and Arsov, L., *J. Serb. Chem. Soc.* **66**, 27 (2001).

[29] Shenglong, W., Fosong, W., and Xiaohui, G., *Synth. Met.* **16**, 99 (1986).

[30] Muller, D. and Jozefowicz, M., *Bull. Soc. Chim. Fr.* **11**, 4083 (1972).

[31] Chiba, K., Ohsaka, T., and Oyama, N., *J. Electroanal. Chem.* **217**, 239 (1987).

[32] Hagiwara, T., Demura, T., and Iwata, K., *Synth. Met.* **18**, 317 (1987).

[33] Huang, W., Humphrey, B. D., and MacDiarmid, A. G., *J. Chem. Soc. Faraday Trans.* **82**, 2385 (1986).

[34] Cui, S. Y. and Park, S. M., *Synth. Met.* **105**, 91 (1999).

[35] Duic, L. and Mandic, Z., *J. Electroanal. Chem.* **335**, 207 (1992).

[36] Kobayashi, N., Yamada, K., and Hirohashi, R., *Chem. Lett.* 1983 (1990).

[37] Kobayashi, N., Yamada, K., and Hirohahi, R., *Electro-Chim. Acta.* **37**, 2101 (1992).

[38] Teshima, K., Yamada, K., Kobayashi, N., and Hirohashi, R., *J. Electroanal. Chem.* **426**, 97 (1997).

[39] Sayyah, S. M., Abd El-Khaek, A. A., Bahgat, A. A., and Abd El-Salam, H. M., *Polym. Int.* **50**, 197 (2001).

[40] Sayyah, S. M., Abd El-Khalek, A. A., Bahgat, A. A., and Abd El-Salam, H. M., *Int. J. Polym. Mater.* **49**, 25 (2001).

[41] Sayyah, S. M., Bahgat, A. A., and Abd El-Salam, H. M., *Int. J. Polym. Mater.* **51**, 291 (2002).

[42] Sayyah, S. M., Bahgat, A. A., and Abd El-Salam, H. M., *Int. J. Polym. Mater.* **51**, 915 (2002).

[43] Bahgat, A. A., Sayyah, S. M., and Abd El-Salam, H. M., *J. Polym. Mater.* **52**, 499 (2003).

[44] Sayyah, S. M., Abd El-Rehim, S. S., and El-Deeb, M. M., *J. Appl. Polym. Sci.* **90**, 1783 (2003).

[45] Sayyah, S. M., Abd El-Rehim, S. S., and El-Deeb, M. M., *Int. J. Polym. Mater*. **53**, 1783 (2003).

[46] Sayyah, S. M., Abd El-Rehim, S. S., and El-Deeb, M. M., *J. Appl. Polym. Sci.* **94**, 941 (2004).

[47] Sayyah, S. M., Abd El-Rehim, S. S., and El-Deeb, M. M., *J. Appl. Polym. Sci.* **97**, 2067 (2005).

[48] Yang, H. and Bard, A. J., *J. Electroanal. Chem.* **339**, 423 (1992).

[49] Silverstein, R. M., Bassler, C. G., and Morill, T. C. (1974). *Spectroscopic Identification of Organic Compounds*, Wiley, New York.