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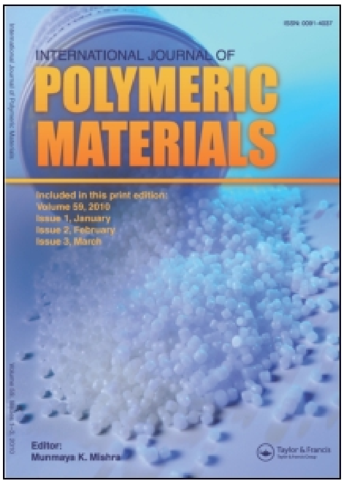

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Electrochemical Polymerization of 2,6-Dichloroaniline and Characterization of the Obtained Polymer

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Electrochemical Polymerization of 2,6-dichloroaniline and Characterization of the Obtained Polymer

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Electropolymerization of 2,6-dichloroaniline on platinum electrode in acid medium was carried out under different reaction conditions as temperature, current density hydrochloric acid, and monomer concentrations with reaction during time. The initial rate of the electro-polymerization reaction is small and the orders are found to be 0.94, 1.13, and 1.26 with respect to current density, acid, and monomer concentrations, respectively. The apparent activation energy (Ea) is found to be 65.1 kJ mol^{-1}*. The rate law is* $Rp = K_2[D]^{0.94}[HCl]^{1.13}[M]^{1.26}$*. The obtained polymer films are characterized by* ^{1}*H-NMR, elemental analysis, IR, and cyclic voltammetry. The mechanism of the electro-polymerization reaction has also been discussed. The thermogravimetric analysis is used to confirm the proposed structure and determination of the number of water molecules associated with each polymeric chain unit. X-ray and scanning electron microscopic analyses are used to investigate the surface morphology.*

Keywords: electropolymerization, 2,6-dichloroaniline, characterization, cyclic voltammetry

INTRODUCTION

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

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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, such as 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 modified by substituents in 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 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].

Sayyah et al. [39] studied the effect of current density, monomer, and acid concentrations on the kinetics of the electropolymerization of 3-chloroaniline on platinum electrode from acidic aqueous (DMF/H2O (30:70 v/v)) solution. From the obtained data, they found that the kinetic rate equation is $Rp = K_2[D]^{0.99}[HCl]^{0.96}[M]^{1.2}$.

The kinetics of the electropolymerization of 2-chloroaniline on platinum electrode in HCl aqueous solution were investigated [40]. The reaction orders with respect to current density, monomer, and acid concentrations were 1.0, 0.96, and 1.06, respectively.

The kinetics of the chemical and electrochemical polymerization and copolymerization of some substituted aniline 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 been investigated by Sayyah et al. [41–47].

The objective of the present work was to investigate the kinetics and optimum conditions for the electrochemical preparation of 2,6-dichloroaniline in aqueous hydrochloric acid medium and characterization of the obtained polymer film. The surface morphology of the obtained polymer is characterized by scanning electro microscopy and X-ray diffraction.

EXPERIMENTAL

Materials

2,6-dichloroaniline, hydrochloric acid solution, and anhydrous sodium sulphate are of analytically pure grade provided by Merk, Germany. All solutions were freshly prepared using double-distilled water.

Cell and Electrodes

The experimental setup used was described previously [39–40,46–47] and consisted of rectangular Perspex cell provided with two platinum foil parallel electrodes. Each electrode had a dimension of 1 cm length 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 each experiment, the anode was withdrawn, washed with distilled water, dried, and weighed. The polymerization current was supplied [by a d.c.-power supply (Thurby ~ Thandar PL 330).

Electropolymerization of 2,6-dichloroaniline

Anodic oxidative electropolymerization of 2,6-dichloroaniline was carried out in aqueous solutions containing monomer (concentration range between 0.02 and 0.09 M) using 0.1 M Na_2SO_4 as the supporting electrolyte and current densities in the range between 2 and 14 $mAcm^{-2}$. Electropolymerization was carried out in hydrochloric acid solution (concentration range between 0.4 and 1.6 M) at different temperatures in the range between 288 and 323°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 dimensions were $1 \times 0.5 \times .05$ cm. Before each run, the platinum electrode was cleaned as mentioned in the section Cell and Electrodes.

The electrochemical experiments were performed with Potentiostat/Galvanostat Wenking PGS 95. The *I-E* curves were recorded by computer software (Model ECT).

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

Infrared measurements were carried out using a Shimadzu FTIR-430 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 obtained from their solutions in dimethyl sulphoxide using tetramethylsilane as internal reference.

Thermogravimetric analyses of the obtained polymers were performed using a Shimadzu DT-30 thermal analyzer. The weight loss in air 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 microanalytical 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, which were kept constant in all runs:

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 Reaction Duration

Anodic oxidative electropolymerization of 2,6-dichloro-aniline 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 increased duration time up to 12 min and then tends to decrease as a result of degradation and solubility of the polymer film off the platinum surface in case of all investigated current densities. The data are graphically represented in Figure 1.

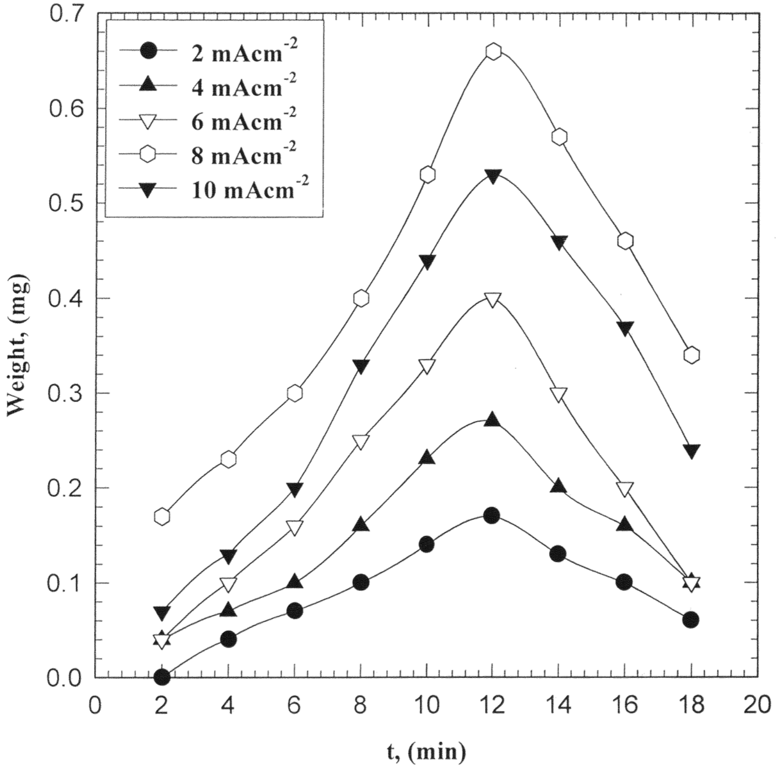


FIGURE 1 Effect of duration time on the electropolymerization of 2,6-dichloroaniline from solution containing 0.05 M monomer, 1.0 M HCl, 0.1 M Na_2SO_4 at 30°C with different current densities.

Effect of Current Density

The effect of applied current density on the anodic oxidative electropolymerization of 2,6-dichloroaniline was studied in the range between 2 and 10 mAcm^{-2} at equal duration times (12 min) using 0.05 M monomer concentration, 0.1 M Na_2SO_4 in dimethyl formamide/ water mixture (30:70 v/v), and 1.0 M HCl at 303°K, which were kept constant. The data reveal that, as the applied current density increases, the weight of the obtained polymer increases up to 8 mAcm^{-2} and then tends to decrease. This finding implies that an oxygen and chlorine evolution takes place as a side reaction, especially at high current densities. Each value of the used current density (2, 4, 6 and 8 mAcm^{-2}) was studied with different time intervals and the yield-time curve was estimated. The data are graphically represented

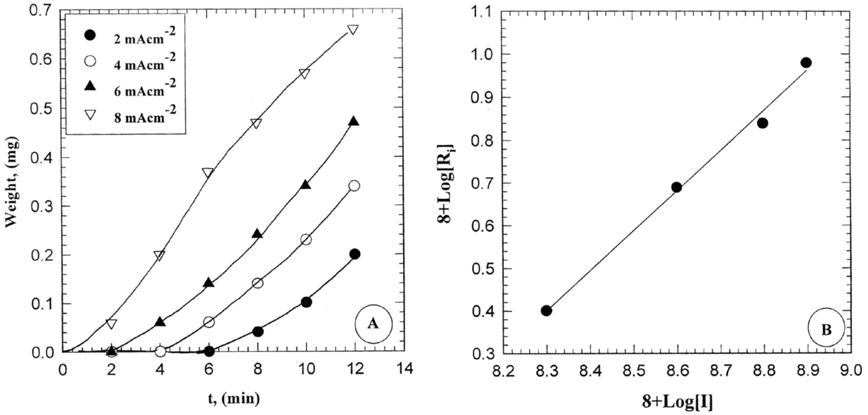


FIGURE 2 (A) Yield-time curve for the effect of current densities; (B) Double-logarithmic plot of the initial rates of electropolymerization versus different current density values.

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 is found to be 0.94.

Effect of HCl Concentration

Anodic oxidative electropolymerization was carried out using 0.05 M monomer concentration, 0.1 M Na_2SO_4 in dimethyl formamide/water mixture (30:70 v/v), current density = 8 mAcm^{-2} at 303°K, which were kept constant. But the hydrochloric acid concentration was varied in the range between 0.4–1.6 M at 0.4 M, the adherence of the polymer film is decreased and the polymer is formed in the solution near the anode). The obtained polymer film in each experiment was weighed. The obtained results show that the maximum weight is obtained when 1.0 M HCl concentration is used. The effect of HCl concentrations in the range between 0.4 and 1.0 M 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 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 that has a slope equal to 1.13. This means that the order of the electropolymerization reaction with respect to HCl is a first-order reaction.

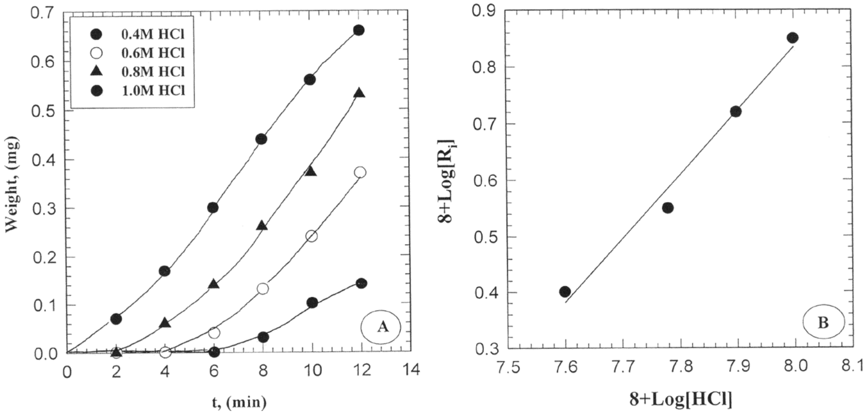


FIGURE 3 (A) Yield-time curve for the effect of HCl concentration; (B) Double-logarithmic plot of the initial rates of electropolymerization versus HCl concentrations.

Effect of Monomer Concentration

The electropolymerization reaction was carried out by keeping all the aforementioned conditions constant at 1.0 M HCl, current density = 8 mAcm^{-2}, Na_2SO_4 (0.1 M), duration time = 12 min and temperature at 303°K, but the monomer concentrations were varied in the range between 0.02 and 0.09 M. The weight of the obtained polymer film in each case was calculated. From the obtained data, it was noticed that the maximum weight of the polymer film is obtained when 0.05 M-monomer concentration is used. It was also noticed that the weight of the polymer film decreases at higher concentrations ($>$0.05 M) of the monomer, which means that polymer degradation may be occurring. The electropolymerization of 2,6-dichloroaniline was studied using different monomer concentrations in the range between 0.02 and 0.05 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 relation gives a straight line with a slope equal to 1.26, which means that the order of the electropolymerization reaction of 2,6-dichloroaniline is a first order reaction with respect to the monomer concentration.

Effect of Temperature

Anodic oxidative electropolymerization of 2,6-dichloroaniline was carried out under the following constant conditions: 1.0 M HCl,

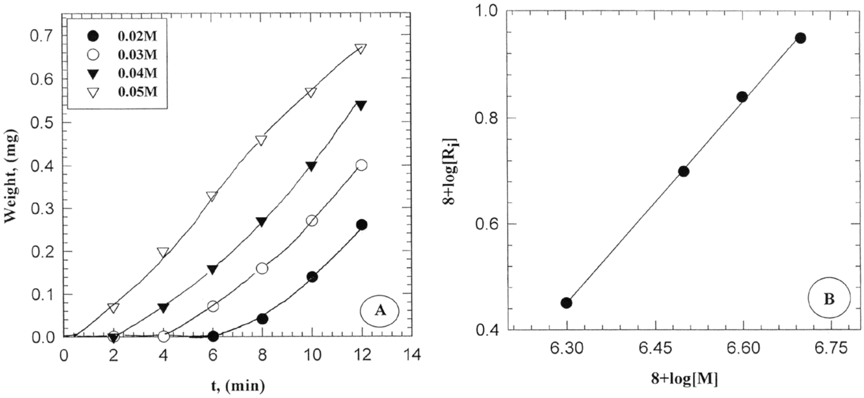


FIGURE 4 (A) Yield-time curve for the effect of monomer concentration; (B) Double-logarithmic plot of the initial rates of electropolymerization versus different monomer concentrations.

0.05 M monomer, 0.1 M Na_2SO_4, 8 mAcm^{-2}, but the reaction was carried out at different temperatures in the range between 288 and 323°K. The maximum weight of the polymer film was recorded at 303°K. It was noticed during the experiments that at higher temperatures than 303°K some polymers are formed in the solution near the anode and do not adhere to the electrode, which means that, at temperatures higher than 303°K, the adhesion of the film to the electrode is decreased. The electropolymerization of 2,6-dichloroaniline was carried out at temperatures of 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 time and the yield–time curve is represented in Figure 5(A). The initial rate of electropolymerization was calculated for each investigated temperature and the logarithm of the initial rate was plotted versus 1/T (cf. Figure 5(B)), which gives a straight line with a slope equal to -3.4. By applying the Arrhenius equation, the apparent activation energy was calculated and found to be 65.1 kJ/mol.

Calculation of Thermodynamic Parameters

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

$$\text{Reaction rate} = k_2[\text{HCl}]^{1.13}[\text{D}]^{0.94}[\text{M}]^{1.26}$$

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

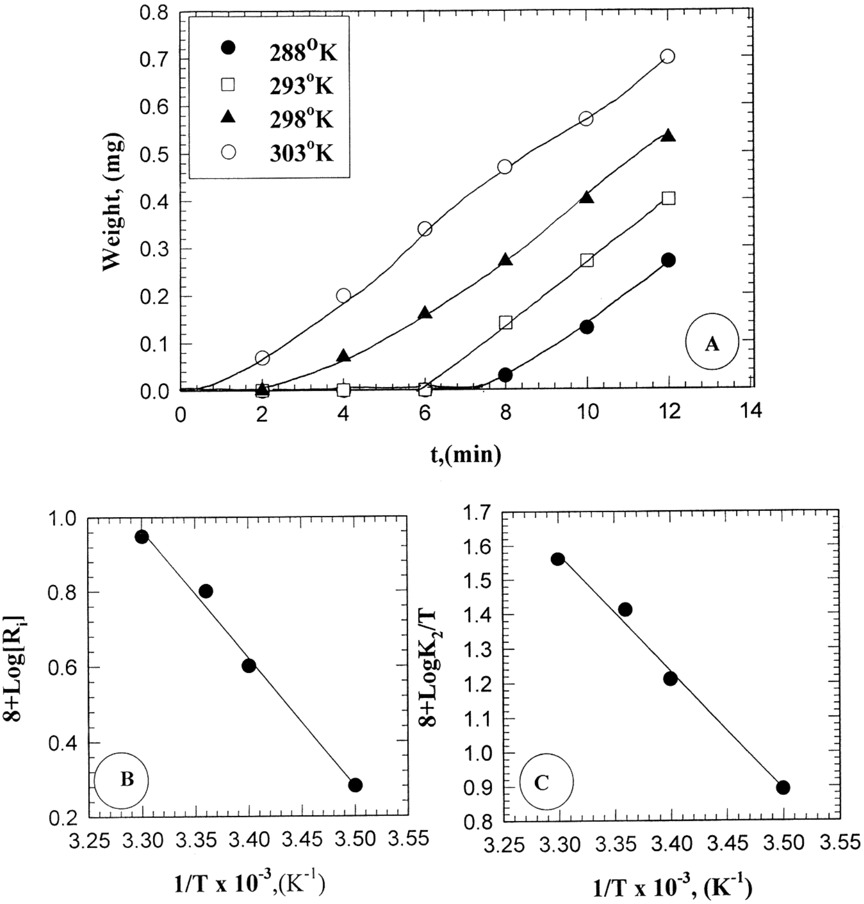


FIGURE 5 (A) Yield-time curve for the effect of temperature; (B) Arrhenius plot for the electropolymerization; (C) Eyring equation plot for the electropolymerization.

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 Plank's constant. By plotting log k_2/T versus 1/T (cf. Figure 5(C)) a linear relationship is obtained 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 63 kJ mol^{-1} and -200 JK^{-1} mol^{-1}, respectively.

Cyclic Voltammetry Characterization

Cyclic voltammograms of 2,6-dichloroaniline on Pt electrode from solution containing 1.0 M HCl and 0.1 M Na_2SO_4 at 303°K with and without 0.05 M monomer in the potential range from −500 to 2000 mV versus SCE with scan rate of 25 mVs^{-1} is shown in Figure 6 (A & B). The voltammogram in the presence of monomer exhibits two oxidation peaks, which progressively developed at −300 and 1000 mV. The first oxidation peak corresponds to the removal of electron from the nitrogen atom of amine to give radical cation. The formed radical cation interacts with another monomer molecule to form dimer radical cation. This is followed by further reaction with monomer molecule

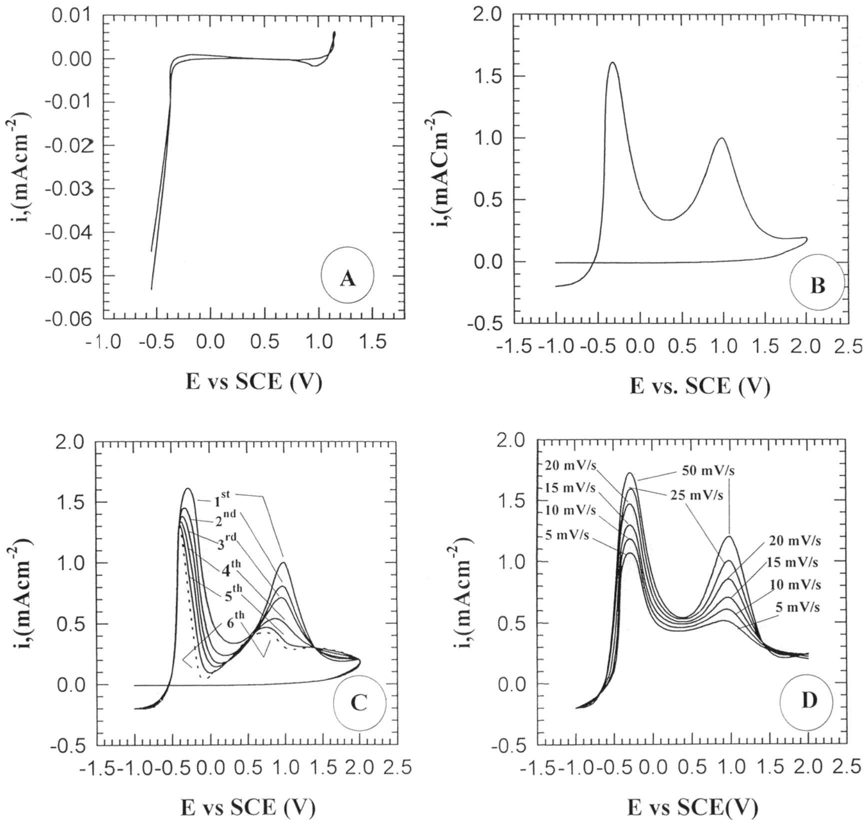
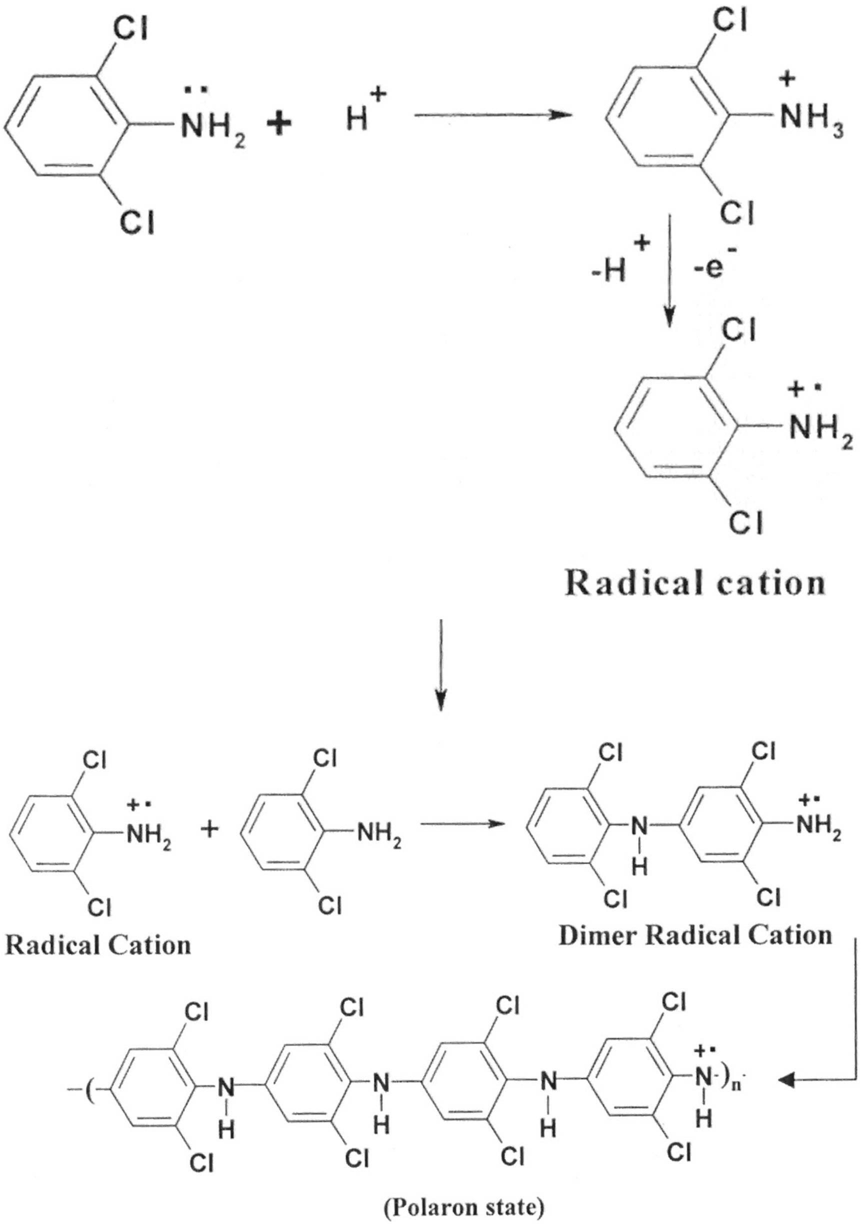


FIGURE 6 (A) Cyclic voltammogram curve without monomer; (B) Cyclic voltammogram curve with monomer; (C) Repetitive cycling of electropolymerization; (D) Effect of scan rate on the electropolymerization.

to give trimer radical cation and so on. Finally, the semiquinone radical cation (polaron state) is formed as shown in Scheme 1.



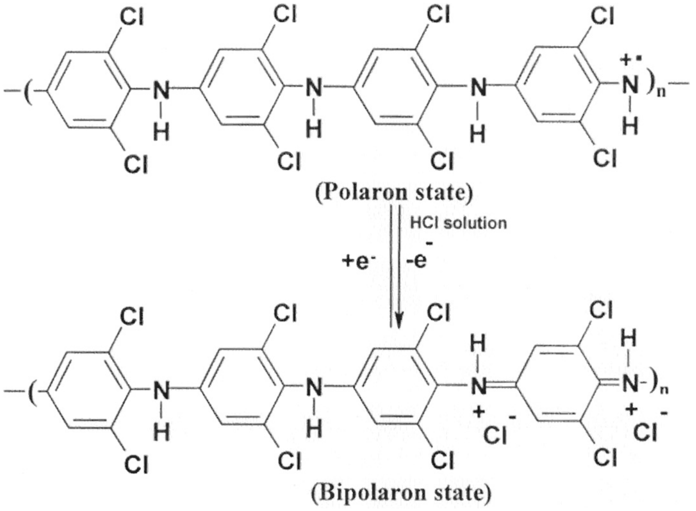
SCHEME 1 Mechanism of the electropolymerization reaction of 2, 6 dichloroaniline.

The presence of two chlorine atoms in the ortho position facilitates the first oxidation process and formation of the radical cation occurs immedially at low potential (−300 mV) in comparison with 2-chloroaniline (−80 mV), previously studied by Sayyah et al. [40]. This indicates that the aromatic chain is rapidly charged by an isolated, delocalized polaron.

On the other hand, the second oxidation process during the electropolymerization appears at high potential (1000 mV versus SCE). The second oxidation peak is assigned to the oxidation of the semiquinone radical (polaron state) to quinone imine (bipolaron) as shown 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 [39–40].

The second oxidation state appears at high potential due to the presence of two substituted chlorine atoms in the ortho positions of the aniline moiety that retards the electropolymerization process. However, as soon as polymerization is nucleated, a thick, highly adherent and brown polymer film is rapidly deposited on the electrode surface. The potential difference between the first and second oxidation peaks is 1300 mV, and no middle peaks were observed,



SCHEME 2 The equilibrium state between polaron and bipolaron structures.

which confirms the non-existence of degradation products, high regularity, homogeneity, and adherence of the deposited film to the electrode surface. The data demonstrate that the two-oxidation processes are irreversible because no cathodic peaks appear upon reversing the potential sweep.

Figure 6(C) shows the effect of repetitive cycling on the electropolymerization of 2,6-dichloroaniline. The data reveal that the anodic peak current (i_P) decreases upon continued cycling as the film become thicker. An increase in the thickness of the deposited film decreases its conductivity and also decreases the rate of the diffusion within the film.

Figure 6(D) illustrates the influence of scan rate ($5-50\,\mathrm{mVs}^{-1}$) on the anodic electropolymerization curves for the formation of poly(2,6-dichloroaniline) on Pt electrode. The data reveal that the peak current densities of i_{P1} and i_{P2} for the first and second anodic peak, respectively, increase with increasing scan rate.

Cyclic voltammetry curves for the effect of HCl concentration, monomer concentration and temperature on the obtained polymer film on platinum electrode are graphically represented in Figure 7(A–C). Figure 7(A) and (B) represent the effect of HCl (0.4 to 1.0 M) and monomer (0.02 to 0.05 M) concentrations on the formation of poly (2,6-dichloroaniline), respectively. As can be seen, the anodic peak current is enhanced with increasing the acid concentration up to 1.0 M and monomer concentration up to 0.05 M.

Figure 7(C) illustrates the influence of solution temperature (288 to 303°K) on electropolymerization reaction. The data reveal 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 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 for the suggested structure given in Scheme 3. The elemental analysis data are given in Table 1 on the basis of the repeated polymeric unit.

The infrared absorption bands and their assignments for poly (2,6-dichloroaniline) are summarized in Table 2. The medium band appearing at $530\,\mathrm{cm}^{-1}$ may be attributed to the stretching vibration of C$-$Cl. The medium absorption band at $651\,\mathrm{cm}^{-1}$ is attributed to the bending deformation of NH group. The absorption bands appearing at 803, 818, and $878\,\mathrm{cm}^{-1}$ are attributed to the 1,2,4-trisubstituted benzene ring. The broad absorption bands at 3344 and $3363\,\mathrm{cm}^{-1}$ are

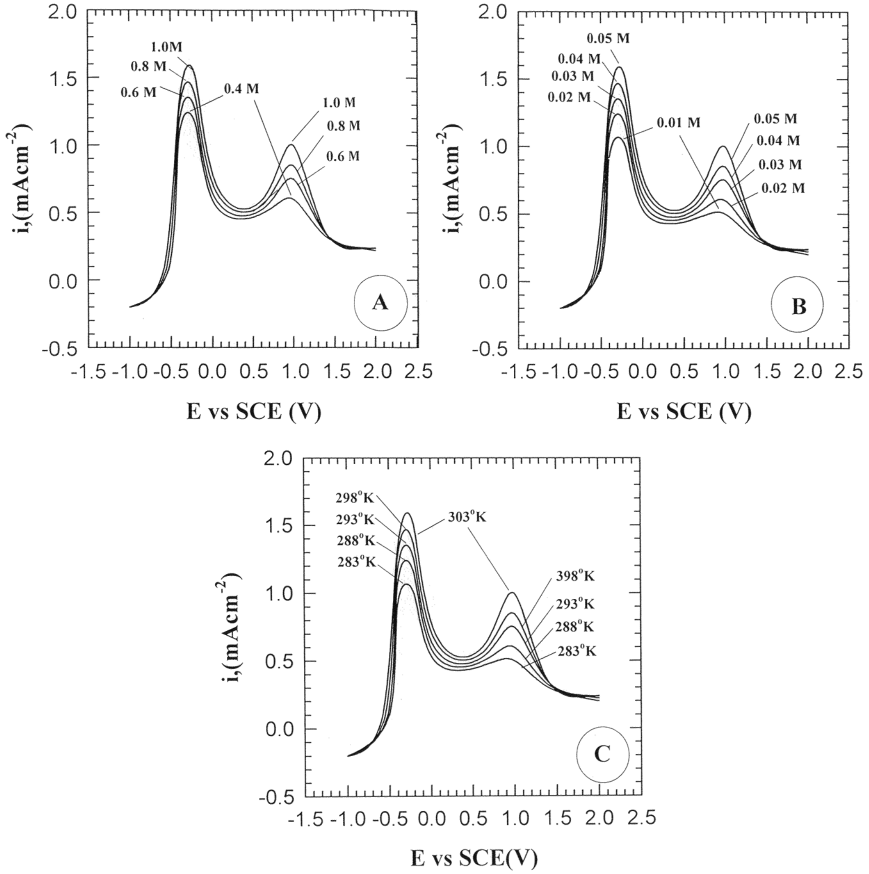
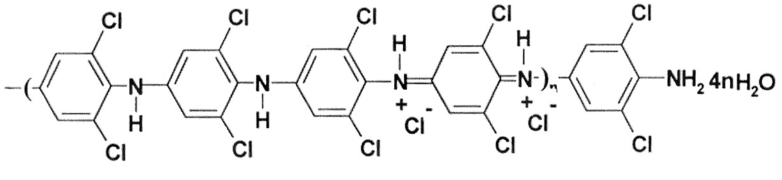


FIGURE 7 Cyclic voltammogram curves for the effect of (A) HCl concentrations; (B) monomer concentrations; and (C) temperature on the formation of poly(2,6-dichloroaniline) from solution containing 0.1 M Na_2SO_4.

attributed to the stretching vibration of –NH group in aryl-NH or aryl-NH_2, whereas that appearing at 3447 cm^{-1} is attributed to asymmetric vibration for terminal NH_2 group solvated by water



SCHEME 3 Overall structure of poly(2,6—dichloroaniline).

TABLE 1 Elemental Analysis of the Prepared Poly(2,6-dichloroaniline)

	C (%)	H (%)	N (%)	Cl (%)
Calculated	38.10	1.70	7.40	45.10
Found	38.90	2.30	7.50	44.70

molecules. Other absorption bands and their assignments are given in Table 2.

The ^{1}H-NMR spectrum of the prepared poly(2,6-dichloroaniline) shows a singlet signal at δ 7.2 ppm and a broad signal at δ 7.6 ppm, which are characteristic for the 2 types of benzene ring protons. The singlet signal, which appears at δ 8.2 ppm, may be attributed to the NH group proton. The singlet signal that appears at δ 8.4 ppm may be attributed to the NH_2 group.

Thermal Analysis of the Prepared Poly(2,6-dichloroaniline)

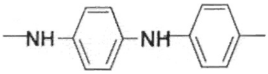
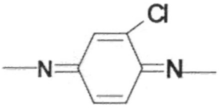
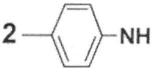
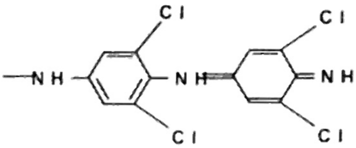
Thermogravimetric analysis (TGA) for the electrochemically prepared poly(2,6-dichloroaniline) sample has been performed and the data are

TABLE 2 Infrared Absorption Bands of the IR Spectrum of the Prepared Poly(2,6-dichloroaniline)

Wavenumber (cm^{-1})	Assignments [46, 48]
530^m	Aryl C–Cl str.
680^m 742^m 783^m	Out of plane deformation showing 1,3-disubstituted benzene ring
818^w 882^w	Out of plane deformation showing 1,4-disubstituted benzene ring
990^w 1034^m 1072^m	In plane deformation of aromatic ring
1230^m 1280^s 1406^m	Stretching vibration of C–N group
1461^m 1508^m	Stretching vibration of C–N in aryl NH or aryl NH_2 group
1589^s	Stretching vibration C=C in benzene or C=N in quinonoid moity
3100^{sh}	CH aromatic
3394^b	Symmetric stretching vibration of NH in NH_2 terminal group solvated by water molecules

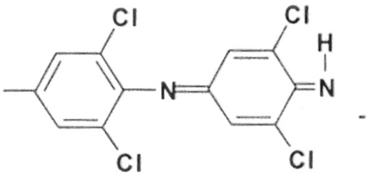
m = medium, w = weak, s = strong, sh = shoulder, b = broad

TABLE 3 Thermogravimetric Data of the Prepared Poly(2,6-dichloroaniline) in Comparison with Poly(2-chloroaniline)

Stage	Temperature range (°C)	Calculated (%)	Found (%)	Removed molecules
Poly(2-chloroaniline) [40]				
I	25–70	—	2.466	Water of humidity
II	70–317	11.16 11.32 16.51 38.99	39.00	4 H_2O 2 HCl 3 Cl
III	317–600	32.86	33.00	
>IV	>600	21.5	22.00	
Poly(2,6-dichloroaniline)				
I	25–200	9.19	9.12	4 H_2O
II	200–281	9.32	9.20	2 HCl
III	281–388	18.14	19.00	$2Cl_2$
IV	388–600	22.7	21.67	
V	>600	40.69	41.4	

summarized in Table 3. From the table, it is clear that there are five stages:

1. The first stage includes the loss of water of hydration (4 molecules) in the temperature range between 25–200°C. The estimated weight loss for this step is found to be 9.12% and the calculated one is 9.19%.
2. The weight loss in the second stage, in the temperature range between 200–281°C is found to be 9.2%, which is attributed to the loss of 2 molecules of HCl. The calculated weight loss of this stage is equal to 9.32%.
3. In the third stage, in the temperature range between 281–388°C, 2 chlorine molecules are lost from the polymeric chain, with an



SCHEME 4 Residue of thermal degradation.

estimated weight loss of 19% whereas the calculated weight loss is 18.13%.

4. In the fourth stage, in the temperature range between 388–600°C, 2 C_6H_5NH are lost. The estimated weight loss for this step is 21.76%, which is in a good agreement with the calculated value of 22.7%.
5. The last stage, above 600°C, a residual material (41.4%) is remained as Scheme 4.

Comparison between the thermal behavior of poly(2 chloroaniline) prepared by Sayyah et al. [40] and poly(2,6-dichloroaniline) is shown in Table 3. From the table, it is clear that the prepared poly (2,6-dichloroaniline) is thermally more stable than poly(2-chloroaniline).

Surface Morphology

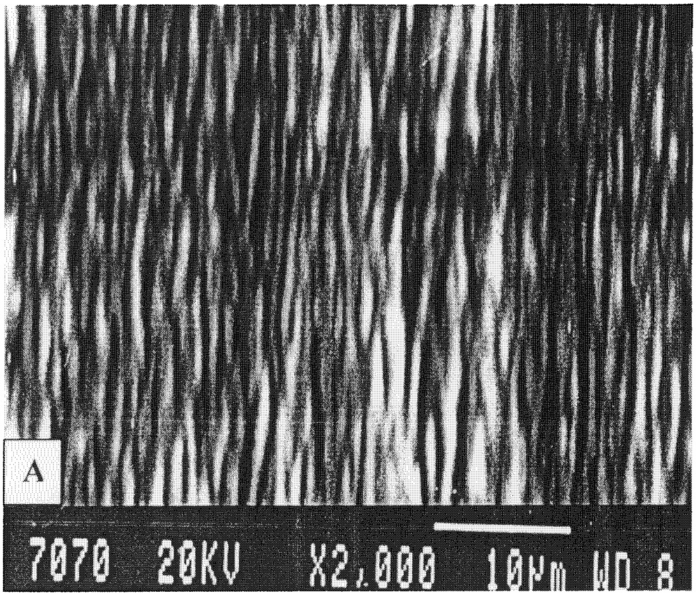
Homogenous, smooth, brown, and well-adhering polymer films were electrodeposited on platinum surface in most conditions. The surface morphology of poly(2,6-dichloroaniline) film electrodeposited at the optimum condition was examined by scanning electron microscopy and X-ray diffraction analysis. The data show that the electropolymerized poly(2,6-dichloroaniline) sample is crystalline with fibrillar elongated structure (cf. Figure 8(A)). From the X-ray pattern represented in Figure 8(B), it is clear that the polymeric sample is crystalline with characteristic peak at $2\theta = 20.7$ and d-value equals to 4.27.

These data are in good agreement with these obtained by Sayyah et al. in case of poly(2-chloroaniline) [40].

CONCLUSION

In conclusion, the data reveal the following:

1. The initial rate of the electropolymerization reaction of 2,6-dichloroaniline on platinum surface is relatively low. The fraction of the



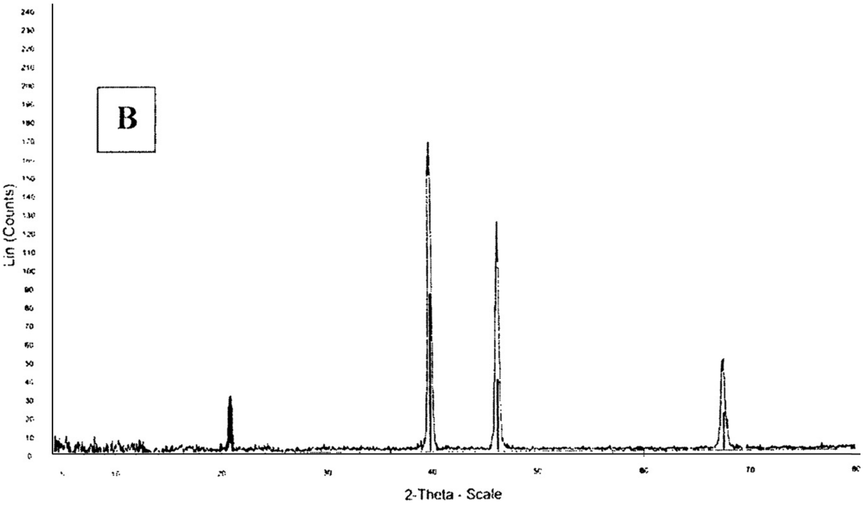


FIGURE 8 (A) Photomicrograph of the electropolymerized poly(2,6-dichloroaniline); (B) X-ray diffraction pattern of the electropolymerized poly(2,6-dichloroaniline).

dissolved product strongly depends on temperature and monomer or HCl concentrations.

2. The orders of the electropolymerization reaction of 2,6-dichloroaniline is 0.94, 1.13, and 1.26 with respect to current density, hydrochloric acid, and monomer concentrations, respectively.
3. The apparent activation energy (E_a) is 65.1 kJ/mol.
4. Cyclic voltammogram exhibits two oxidation peaks at -300 and 1000 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(2,6-dichloroaniline) film is fibrillar crystalline material, smooth, brown, and well adhered on the platinum electrode.
6. The prepared poly(2,6-dichloroaniline) is thermally more stable than poly(2-chloroaniline).

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., Kaneko, 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., Yoneyama, H., and Tamoura, H., *J. Electroanal. 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. Electrochem. 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. Electrochem. 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. Met.* **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., and Tsintavis, 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 Hirohashi, R., *Electrochim. 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-Rehim, S. S., and EL-Deeb, M. M., *J. Appl. Polym. Sci.* **94**, 941 (2004).

[40] Sayyah, S. M., Abd El-Rehim, S. S., Ibrahim, M. A., and Kamal, S. M., *Int. J. Polym. Mater.* **54**, 815 (2005).

[41] Sayyah, S. M., Abd EL-Khalek, A. A., Bahgat, A. A., and Abd EL-Salam, H. M., *Polym. Int.* **50**, 197 (2001).

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

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

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

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

[46] Sayyah, S. M., Abd El-Rehim, S. S., and EL-Deeb, M. M., *J. Appl. Polym. Sci.* **91**, 941, (2004).

[47] Sayyah, S. M., Abd El-Rehim, S. S., EL-Rabiey, M. M., and Azooz, R. E., *Int. J. Polym. Mater.* **55**, 1, (2006).

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