

Electropolymerization of Pyrrole and Characterization of the Obtained Polymer Films

S. M. Sayyah,¹ S. S. Abd El-Rehim,² M. M. El-Deeb¹

¹Chemistry Department, Faculty of Science (Beni-Suef Branch), Cairo University, 62514 Beni-Suef, Egypt

²Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

Received 6 November 2002; accepted 21 February 2003

ABSTRACT: Electrochemical oxidative polymerization of pyrrole on platinum electrode in acid medium was carried out. Different reaction parameters were investigated such as current density, acid concentration, monomer concentration, and temperature with duration of time. The orders of the electropolymerization reaction were found to be 1.3, 1.26, and 1.2 with respect to current density, acid concentration, and monomer concentration, respectively. The apparent activation energy was found to be 38.3 kJ mol^{-1} . The obtained polymer films were characterized by ¹H-NMR, elemental

analysis, thermogravimetric analysis, and cyclic voltammetry. The mechanism of the electrochemical polymerization reaction was also discussed. The surface morphology of the obtained polymer film was characterized by X-ray diffraction and scanning electron microscopy. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1783–1792, 2003

Key words: electropolymerization; polypyrroles; kinetics (polym.); cyclic voltammetry; thermogravimetric analysis (TGA)

INTRODUCTION

The preparation of conducting polymers is an active area of both academic and industrial research because of their many potential applications in batteries,^{1–6} electrochromic devices,^{7–9} microelectronic devices,¹⁰ electrochemical chromatography,¹¹ and as corrosion inhibitors to protect semiconductors and metals.^{12–18}

After the discovery of polyacetylene,¹⁹ great interest continues to be generated in electrically conducting organic polymers, especially for device applications.²⁰ A considerable amount of work has been devoted to conducting polymers,^{21–24} although control of the growth orientation of the conducting polymers is especially important to obtain a polymer possessing excellent physical and/or chemical properties, such as high electronic conductivity.^{22–24}

In the series of conducting polymers, considerable attention has been drawn to the pyrrole family of polymers prepared by electrochemical oxidation such as polypyrrole, poly(*N*-methyl pyrrole), and their copolymers for their applications in solid-state devices.²⁵ Several investigations have been performed to observe the effects of various parameters such as solvent, electrolyte, and temperature on their mechanical strength, stability, and conductivity.^{26–33}

The kinetics of electrooxidative polymerization of heteroarenes to afford thin films of electronically con-

ductive polymer is strongly dependent on the electrode material.³⁴ The process of polymerization relies on oxidation of the heteroarene to afford radical cations that couple to form oligomers. These oligomers must precipitate to nucleate polymerization on the electrode surface.

Scanning electron microscopy studies on polypyrrole prepared by electrochemical polymerization show that the surface morphology is greatly influenced by several factors like the dopant anion, composition of the electrolytic solution, applied current density, and electrode configuration.^{26,29,31,32}

The kinetics of the chemical polymerization of some substituted polyaniline in aqueous solution and characterization of the obtained polymers by IR, UV-visible, X-ray, electron microscopy, TGA-DTA analysis and ac conductivity were previously investigated by Sayyah et al.^{35–39} To the best of our knowledge, no study reported in the literature has investigated the rate of the electropolymerization reaction, reaction orders with respect to different electropolymerization parameters such as current density, monomer concentration, and acid concentration. Also, thermodynamic activation parameters such as enthalpy (ΔH^*), entropy (ΔS^*), and activation energy (E_a) for the electrochemical polymerization were not reported.

The objective of the present work was to investigate the kinetics and optimum conditions for the electrochemical preparation of pyrrole in aqueous hydrochloric acid medium. The obtained polymer prepared at the investigated optimum conditions was characterized by ¹H-NMR, elemental analysis, and thermogravimetric analysis (TGA). Cyclic voltammetry mea-

Correspondence to: S. M. Sayyah (smsayyah@hotmail.com).

measurements were carried out at different concentrations and parameters. The surface morphology of the obtained polymer was characterized by scanning electron microscopy and X-ray diffraction.

EXPERIMENTAL

Materials

Pyrrole, hydrochloric acid solution, and anhydrous sodium sulfate, all of analytical pure grade, were provided by Merck (Darmstadt, Germany). Dimethyl formamide (DMF) was provided by El-Nasr Pharmaceutical Chemical Co., Egypt. All solutions were freshly prepared using double-distilled water.

Cell and electrodes

The experimental setup used was described previously⁴⁰⁻⁴² and consisted of a rectangular Perspex cell provided with two platinum foil parallel electrodes (dimensions: 1 cm height \times 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 $\pm 1^\circ\text{C}$ using 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 dc power supply (Thurby-Thandar PL 330).

Electropolymerization of pyrrole

Anodic oxidative polymerization of pyrrole was carried out in aqueous solutions containing monomer (concentration range between 0.01 and 0.055M) using 0.1M 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 out in hydrochloric acid solution (concentration range between 0.6 and 1.6M) 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 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 earlier.

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

$^1\text{H-NMR}$ and TGA

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

Scanning electron microscopy and X-ray diffraction

Scanning electron microscopic analysis was carried out using a JSM-T20 scanning electron microscope (JEOL, Tokyo, Japan). The X-ray diffractometer (Philips 1976 Model 1390, The Netherlands) was operated under the following conditions that were kept constant for all the analysis processes: X-ray tube, Cu; scan speed, $8^\circ/\text{min}$; current, 30 mA; voltage, 40 kV; and preset time, 10 s.

RESULTS AND DISCUSSION

Anodic oxidative electropolymerization

Effect of duration time

Anodic oxidative electropolymerization of pyrrole was studied under the influence of different plating and operating parameters. The effect of duration time on the weight of the obtained polymers was studied with different current density values. The data reveal that the weight of the obtained polymer increased with increases of duration time up to 10 min, after which it tended to decrease as a result of degradation and the solubility of the polymer film from the platinum surface in the case of all investigated values of the current densities. The data are graphically represented in Figure 1.

Effect of current density

The effect of applied current density on the anodic oxidative electropolymerization of pyrrole was studied at constant time intervals (10 min) using 0.05M monomer concentration, 0.1M Na_2SO_4 in a dimethyl formamide/water mixture (30 : 70 v/v), and 1M HCl at 303 K, all of which were kept constant. The data reveal that as the applied current density increased, the weight of the obtained polymer increased to 8 mA cm^{-2} after which it tended to decrease. This finding implies that an oxygen and chlorine evolution takes place as a side reaction especially at high current densities. Each value of the used current density was

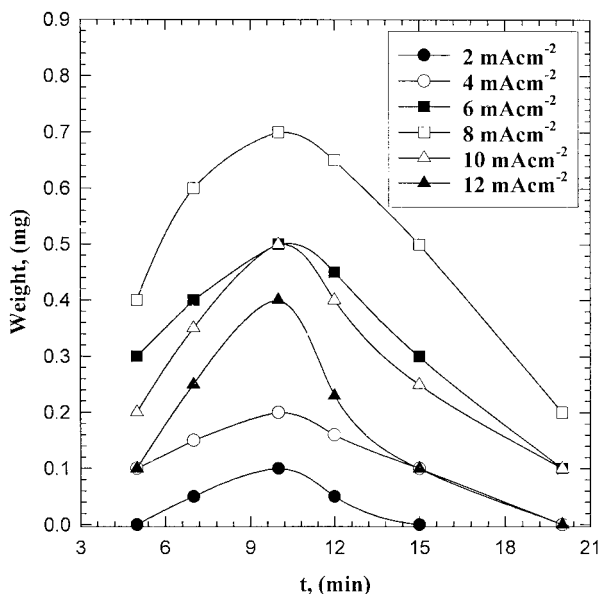


Figure 1 Yield-time curve for the effect of duration time on the anodic polymerization of pyrrole from solution containing 0.05M monomer, 1.0M HCl, and 0.1M Na₂SO₄ at 303 K.

studied with different time intervals and the yield-time curve was plotted. 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), and was found to be 1.3.

Effect of HCl concentration

Anodic oxidative electropolymerization was carried out using 0.05M monomer concentration, 0.1M Na₂SO₄ in a dimethyl formamide/water mixture (30 :

70 v/v), and a current density of 8 mA cm⁻² at 303 K, all of which were kept constant. However, the hydrochloric acid concentration was varied in the range between 0.6 and 1.6M (<0.6M, 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 data show that the maximum weight is obtained when 1.2M HCl concentration was used. The effect of HCl concentrations in the range between 0.6 and 1.2M on the electropolymerization rate was investigated. The weight of the deposited polymer film on the platinum electrode in each experiment is plotted against the duration time as shown in Figure 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 of 1.26. This means that the order of the reaction with respect to HCl is a first-order reaction.

Effect of monomer concentration

The electropolymerization reaction was carried out by keeping all the above-mentioned conditions constant at 1.2M HCl, a current density of 8 mA cm⁻², Na₂SO₄ (0.1M), and temperature at 303 K, although the monomer concentrations were varied in the range between 0.01 and 0.055M. The weight of the obtained polymer film in each case was calculated. From the obtained data, one may observe that the maximum weight of the polymer film is obtained when 0.05M monomer concentration was used. It may also be observed that the weight of the polymer film decreases at higher concentrations of monomer, which means that polymer degradation may have occurred. The electropoly-

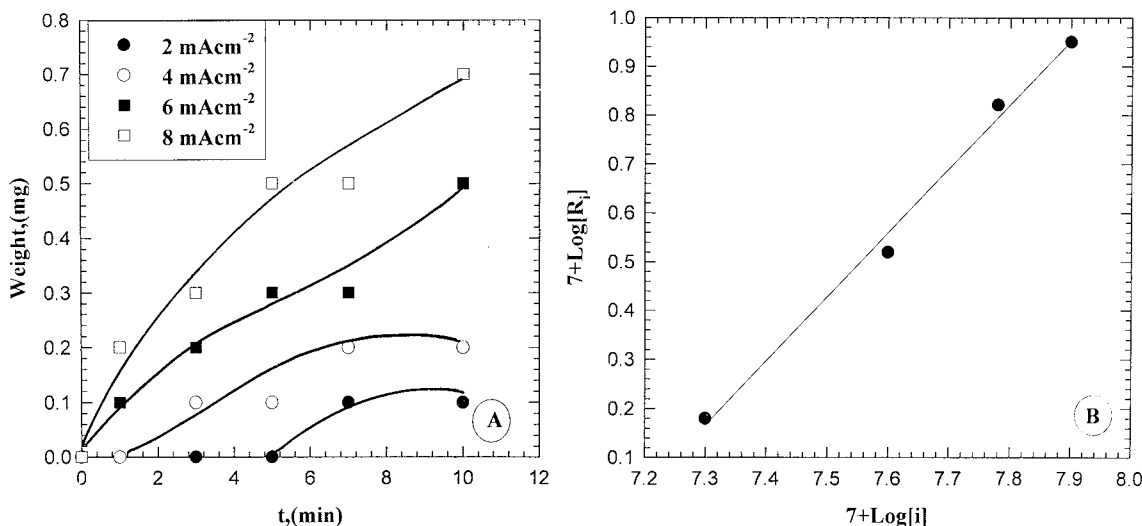


Figure 2 (A) Yield-time curve for the effect of current density. (B) Double-logarithmic plot of initial rate of electropolymerization versus different current density values.

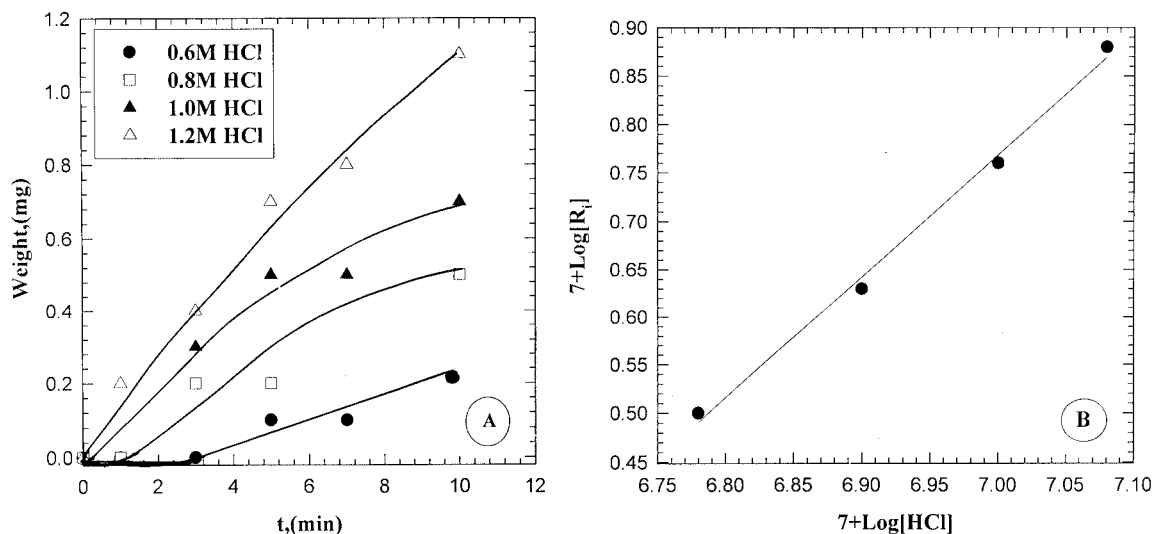


Figure 3 (A) Yield-time curve for the effect of HCl concentration. (B) Double-logarithmic plot of initial rate of electropolymerization versus different HCl concentrations.

merization of pyrrole was performed using different monomer concentrations in the range between 0.01 and 0.05M 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 gave a straight line with a slope of 1.2, which means that the order of the electropolymerization reaction of pyrrole is a first-order reaction with respect to the monomer concentration.

Effect of temperature

Anodic oxidative electropolymerization of pyrrole was carried out under the following constant condi-

tions: 1.2M HCl, 0.05M monomer, 0.1M Na_2SO_4 , and 8 mA cm^{-2} , although 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 may be observed during the experiments that, at temperatures higher than 303 K, some polymers are formed in the solution near the anode that 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 pyrrole 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 time and the yield-time curve is represented in Figure 5(A). The initial rate of electropolymerization was calculated at each investigated

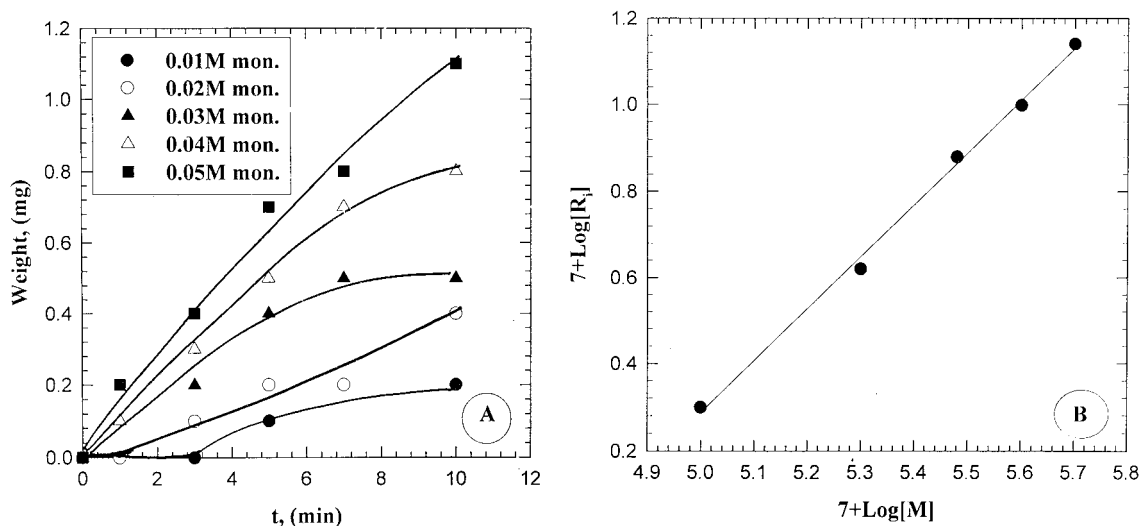


Figure 4 (A) Yield-time curve for the effect of monomer concentration. (B) Double-logarithmic plot of initial rate of electropolymerization versus different monomer concentrations.

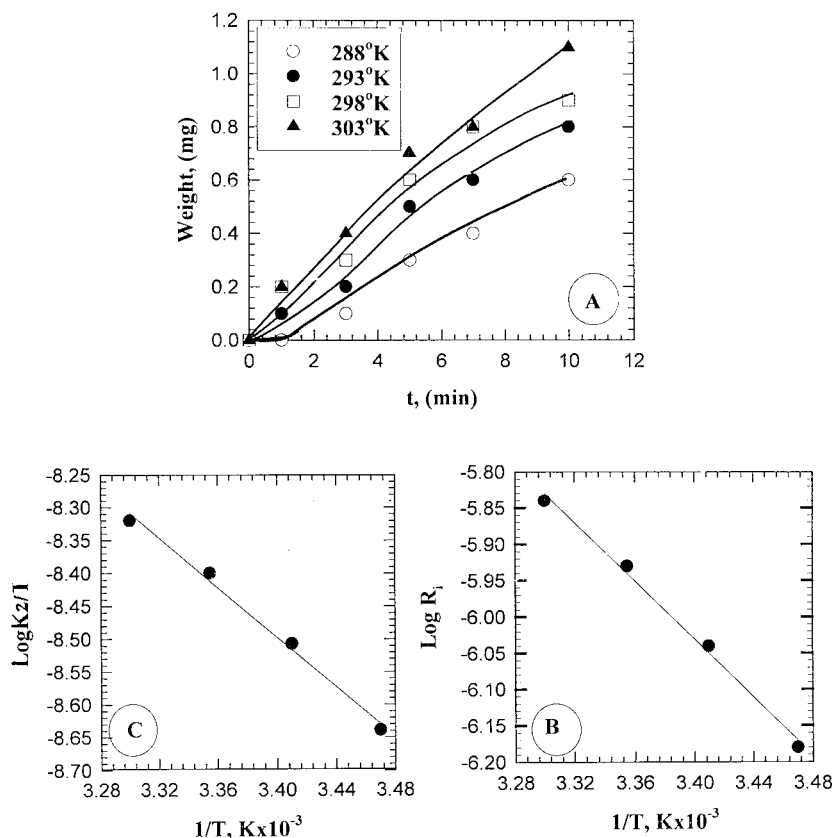


Figure 5 (A) Yield–time curve for the effect of temperature. (B) Arrhenius plot for the electropolymerization. (C) Eyring equation plot for the electropolymerization.

temperature and the logarithm of the initial rate was plotted versus $1/T$ [c.f. Fig. 5(B)], which gave a straight line with a slope of -2.00 . By applying the Arrhenius equation, the apparent E_a was calculated and was found to be 38.3 kJ/mol.

Calculation of thermodynamic parameters

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

Reaction rate

$$= k_2[\text{HCl}]^{1.26}[\text{current density}]^{1.3}[\text{monomer}]^{1.2}$$

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:

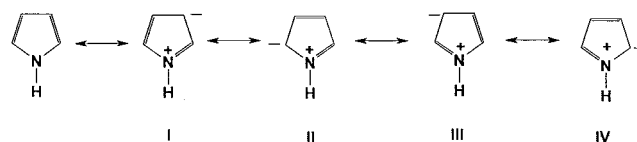
$$k_2 = \frac{RT}{Nh} e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$

where k_2 is the rate constant, R is the universal gas constant, N is Avogadro's number, and h is Plank's constant. By plotting $\log k_2/T$ versus $1/T$ [c.f. Fig. 5(C)] we obtained a linear relationship with a slope of

$-\Delta H^*/2.303R$ and an intercept of $\log\{(R/Nh) + \Delta S^*\}/2.303R$. From the slope and intercept, the values of ΔH^* and ΔS^* were found to be 36.19 and -237.4 kJ mol⁻¹, respectively.

Mechanism of the electropolymerization

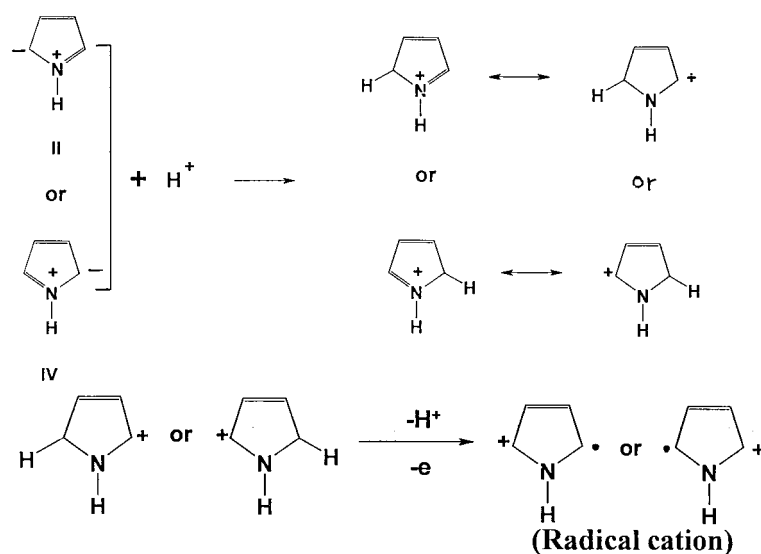
Pyrrroles present as resonating structures⁴³ as follows:



Structures II and IV are more stable resonating structures in the above scheme because of the presence of positive and negative charges near each other. The negative charge is predominant at C2 or C5 in the two resonating structures II and IV. The anodic oxidative electropolymerization proceeds in two steps, initiation and propagation, as follows.

Initiation step

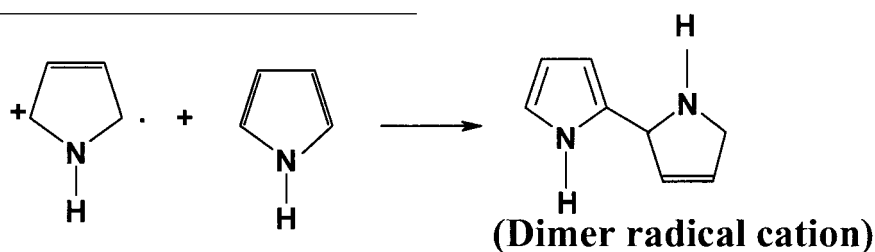
In this step, the pyrrole monomer is oxidized by loss of electrons and formation of the radical cations as shown in the following equation of **Scheme 1**:



Scheme 1

Propagation step

This step involves the interaction between the formed radical cation and the monomer to form a dimer radical cation as follows (**Scheme 2**):

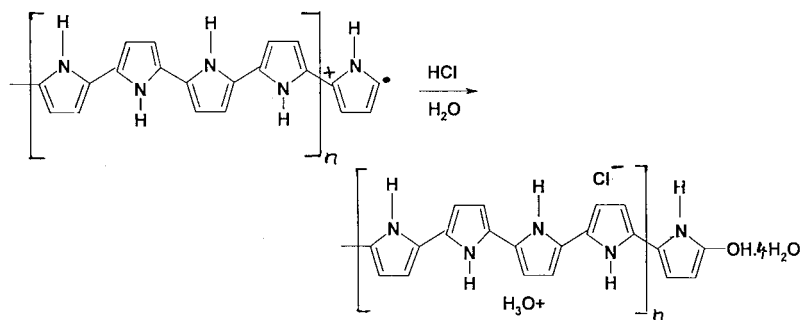


Scheme 2

This reaction is followed by further reaction of the formed dimer radical cations with monomer molecules to give trimer radical cations, and so on. The degree of electropolymerization depends on different factors such as current density, HCl concentration, monomer concentration, and temperature. From the

elemental analytical data given in Table I, it is clear that the repeating unit of the polymeric chain contains four pyrrole units, one chloride ion, one proton present as hydronium ion, and four water molecules.

At the end of the experiment and cessation of the flow current, the termination step occurs as follows:



Scheme 3

TABLE I
Elemental Analysis of Polypyrrole

	%C	%H	%N	%Cl
Calcd	49.60	5.90	14.48	9.18
Found	48.70	5.60	13.90	8.70

As shown in **Scheme 3**, the presence of five water molecules for each repeated unit is confirmed by thermogravimetric analysis. The TGA data of the prepared polypyrrole are represented in Table II. From the table, it is clear that there are five stages.

First stage. Includes the loss of one molecule of water. In the temperature range between 25 and 100°C, the weight of loss of this step was found to be 4.60%, which is in good agreement with the calculated value (4.66%).

Second stage. In the temperature range between 100 and 200°C, the weight loss was found to be 8.7%, which could be attributed to the loss of two molecules of water. The calculated weight loss in this case was 9.3%.

Third stage. In the temperature range between 200 and 250°C, the weight loss was found to be 8.0%, which may be attributed to the loss of two molecules of water. The calculated weight loss of this stage was 9.3%.

Fourth stage. In the temperature range between 250 and 320°C, one molecule of hydrochloric acid was lost; the weight loss of this stage was found to be 10.7%, although the calculated value was 9.4%.

Fifth stage. Above 500°C, a residual material (8%) remained.

Also, from ¹H-NMR studies, it is clear that the OH proton, which appeared as a broad singlet at 8.8 ppm, disappeared after addition of deuterated water. This confirms the presence of the terminal OH group in the polymeric units.

Cyclic voltammetric characterization

Cyclic voltammograms of the polypyrrole film deposited on platinum electrodes in 1.0M HCl, 0.1M Na₂SO₄ at 303 K, without and with monomer at potential between -400 and 1600 mV versus SCE, are shown in Figure 6(A) and (B), respectively. A well-adhering, homogeneous polypyrrole black film is electrodeposited on the electrode surface. The voltammogram shows a distinct anodic peak in the anodic excursion and a very small plateau in the cathodic cycle. The onset oxidation potential of pyrrole shown as a rise in the anodic current is 300 mV. The oxidation of the monomers to radical cations or dimer species is considered to be the first step in the polymerization of the conducting polymers.

Figure 6(C) shows the repetitive cycling of pyrrole electropolymerization. The data reveal that the peak current i_p of the anodic peak decreases significantly 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 diffusion within the film.

Figure 6(D) illustrates the influence of scan rate ν (5–25 mVs⁻¹) on the anodic polarization curve for electropolymerization of pyrrole on platinum electrode. It is obvious that the peak current i_p of the anodic peak increases with increasing scan rate. Figure 7 shows the linear dependency of i_p versus $\nu^{1/2}$. This linear relation suggests that the electroformation of polypyrrole film on the electrode surface may be described partially by a diffusion-controlled process (diffusion of reacting species to the polymer film/solution interface). Moreover, the permeation of the reacting species from this interface into the polymer film or the charge transport within the film itself limits the overall current. Under such conditions, the peak current i_p is given by the Randles⁴⁴ and Sevcik⁴⁵ equation:

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

where A is constant, n is the number of exchanged electrons, C is the bulk concentration, D is the diffusion coefficient of diffusing species, and ν is the scan rate.

Cyclic voltammetric characteristics of the polymer film formation on platinum electrode as a function of the concentrations of HCl and monomer and temperature were investigated. Figure 8(A) represents the influence of HCl concentration (0.6 to 1.4M) on the characteristic features of the response. As can be seen, the anodic peak current is enhanced with increasing the acid concentration up to 1.2M after which it starts to decrease.

Figure 8(B) shows that, by increasing the concentration of the monomer from 0.01 to 0.055M, the anodic peak current is enhanced by increasing the monomer concentration to 0.05M after which it starts to decrease.

TABLE II
Thermogravimetric Data of the Prepared Polypyrrole

Temperature range (°C)	Weight loss (%)		Removed molecule
	Calcd	Found	
25–100	4.66	4.60	H ₂ O
100–200	9.30	8.70	2H ₂ O
200–250	9.30	8.00	2H ₂ O
250–320	9.40	10.70	HCl
Remaining weight (%) above 500°C		8.00	

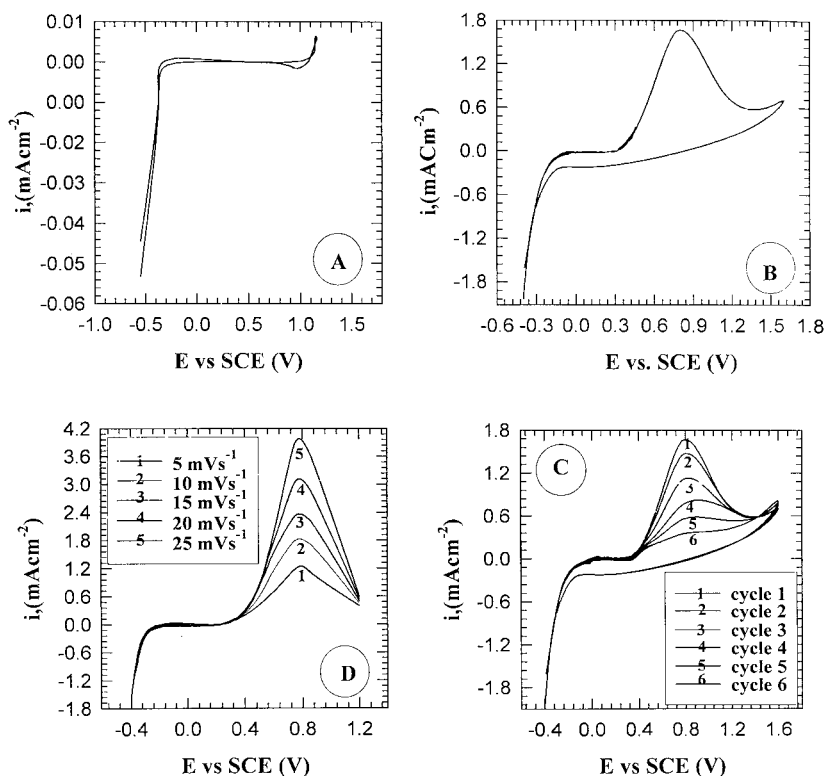


Figure 6 (A) Cyclic voltammogram curve without monomer. (B) Cyclic voltammogram curve with monomer. (C) Repetitive cycling of electropolymerization. (D) Effect of scan rate on the electropolymerization.

Figure 8(C) illustrates the influence of solution temperature (288 to 308 K) on the cyclic voltammetric response of the polymer formation. The data reveal that an increase of temperature to 303 K results in a progressive increase of the charge included in the anodic peak. The data of Figure 8(A)–(C) are in good agreement with the kinetic data.

Surface morphology

Homogeneous, smooth, black, and well-adhering polymer films were electrodeposited on a platinum surface in most conditions. The surface morphology of polypyrrole film electrodeposited at optimum conditions was examined by scanning electron microscopy. The SEM micrograph shows tubular or fibrillar elongated crystals [c.f. Fig. 9(A)]. The X-ray diffraction pattern shows that the prepared polypyrrole sample is a crystalline material, as shown in Figure 9(B), from which it is clear that there are three strong peaks at 2θ angle of 39, 46.5, and 67.

CONCLUSIONS

In conclusion, the above data revealed the following:

1. The initial rate of the electropolymerization reaction of pyrrole on a platinum surface is relatively

low, given that calculation of the initial rate was taken on the basis of the adhered polymer film on the platinum electrode. The fraction of the dissolved product may be strongly dependent on temperature and monomer or HCl concentration.

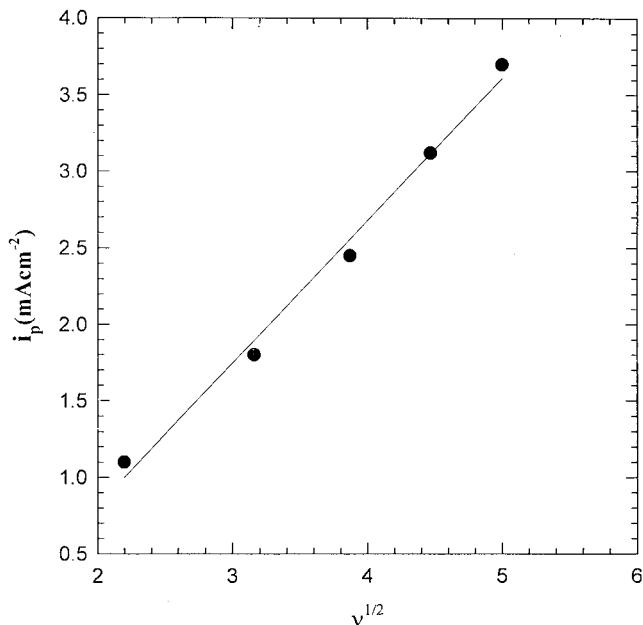


Figure 7 Relation between $v^{1/2}$ and i_p .

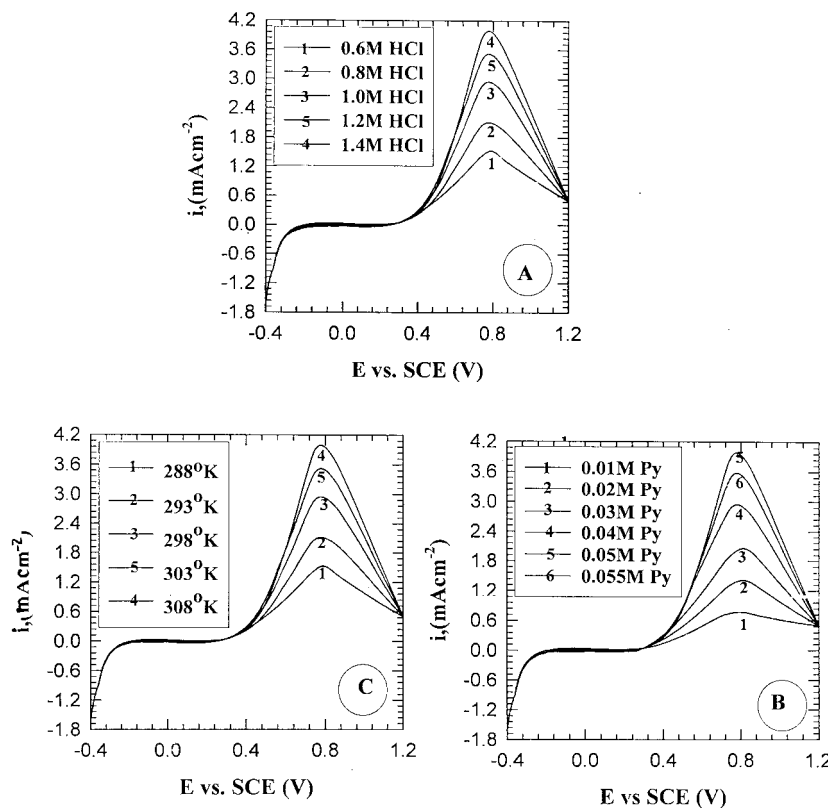


Figure 8 Cyclic voltammogram curves for the electropolymerization of pyrrole from solution containing 0.1M Na₂SO₄: (A) effect of HCl concentration; (b) effect of monomer concentration; (C) effect of temperature.

- The order of the electropolymerization reaction of pyrrole is 1.3, 1.26, and 1.2 with respect to current density, acid concentration, and monomer concentration, respectively.

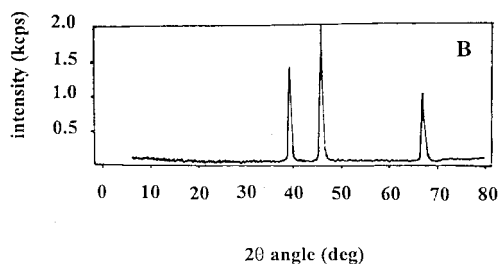


Figure 9 (A) SEM micrograph of electropolymerized polypyrrole. (B) X-ray diffraction pattern of electropolymerized polypyrrole.

- The apparent activation energy is 38.3 kJ/mol.
- The prepared polypyrrole film is tubular or fibrillar nanocrystalline material, smooth, black, and well adhered on the platinum electrode.
- From cyclic voltammetry studies, it is clear that the onset oxidation potential of pyrrole is 300 mV and the electroformation of polypyrrole film on the electrode surface may be described partially by a diffusion-controlled process.
- Further investigations on the effect of different electrolytes and the presence of organic solvent on the physical properties of the prepared film are necessary. Also, use of this material as a corrosion-inhibiting coating for steel in different media should be carried out.

References

- Kitani, A.; Kaya, M.; Sasaki, K. *J Electrochem Soc* 1986, 133, 1069.
- Mac Diarmid, A. G.; Yang, L. S.; Huang, W. S.; Humphrey, B. D. *Synth Met* 1987, 18, 393.
- Girard, F.; Ye, S.; Laperriere, G.; Belanger, D. *J Electroanal Chem* 1992, 334, 35.
- Ye, S.; Girard, F.; Belanger, D. *J Phys Chem* 1993, 97, 12373.
- Ye, S.; Belanger, D. *J Electrochem Soc* 1994, 141, 149.
- Morita, M.; Miyazaki, S.; Ishikawa, M.; Matsuda, Y.; Tujima, H.; Adachi, K.; Anan, F. *J Power Sources* 1995, 54, 214.
- Kobayashi, T.; Yoneyama, H.; Tamoura, H. *J Electroanal Chem* 1984, 161, 419.

8. Genies, E. M.; Lipkowski, M.; Santier, C.; Viel, E. *Synth Met* 1987, 18, 631.
9. Nguyen, M. T.; Dao, L. H. *J Electrochem Soc* 1989, 136, 2131.
10. Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J Phys Chem* 1985, 89, 1441.
11. Nagaoka, T.; Kakuno, K.; Fujimoto, M.; Nakao, H.; Yano, J.; Ogura, K. *J Electroanal Chem* 1994, 369, 315.
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. Brusica, V.; Angelopoulos, M.; Grahmi, 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. Shirakawa, H.; Louis, E. J.; Mac Diarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J Chem Soc Chem Commun* 1977, 578.
20. Roth, S. *Ind J Chem* 1994, 33A, 543.
21. Skotheim, T. A., Ed. *Handbook of Conducting Polymers*, Vols. 1, 1a, 2; Marcel Dekker: New York, 1986.
22. Cai, Z.; Martin, C. R. *J Am Chem Soc* 1989, 111, 4138.
23. Tierney, M. J.; Martin, C. R. *J Phys Chem* 1989, 93, 2878.
24. Cai, Z.; Lie, J.; Liang, W.; Menon, V.; Martin, C. R. *Chem Mater* 1991, 3, 960.
25. Schneider, O.; Schwitzgebel, G. *Synth Met* 1993, 55, 1046.
26. Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W. Y. *J Electroanal Chem* 1981, 129, 115.
27. Kanazawa, K. K.; Diaz, A. F.; Krounbi, M. T.; Street, G. B. *Synth Met* 1981, 4, 119.
28. Street, G. B.; Lindsey, S. E.; Nazzari, A. I.; Wynne, K. J. *Mol Cryst Liq Cryst* 1985, 118, 137.
29. Diaz, A. F.; Hall, B. *IBM J Res Dev* 1983, 27, 342.
30. Munstedt, H.; Naarman, H.; Kohler, G. *Mol Cryst Liq Cryst* 1985, 118, 129.
31. Cvetko, B. F.; Brungs, M. P.; Burford, R. P.; Skyllas-Kazacos, M. *J Mater Sci* 1988, 23, 2102.
32. Sun, B.; Jones, J. J.; Burfoed, R. P.; Skyllas-Kazacos, M. *J Mater Sci* 1989, 24, 4024.
33. Rhee, H. W.; Jeon, E. J.; Kim, J. S.; Kim, C. Y. *Synth Met* 1989, 28, 605.
34. Witkowski, A.; Freund, M. S.; Brajter-Toth, A. *Anal Chem* 1991, 63, 622.
35. Sayyah, S. M.; Abd El-Khalek, A. A.; Bahgat, A. A.; Abd El-Salam, H. M. *Polym Int* 2001, 50, 197.
36. Sayyah, S. M.; Abd El-Khalek, A. A.; Bahgat, A. A.; Abd El-Salam, H. M. *Int J Polym Mater* 2001, 49, 25.
37. Sayyah, S. M.; Bahgat, A. A.; Abd El-Salam, H. M. *Int J Polym Mater* 2002, 51, 291.
38. Sayyah, S. M.; Bahgat, A. A.; Abd El-Salam, H. M. *Int J Polym Mater* 2002, 51, 915.
39. Sayyah, S. M.; Bahgat, A. A.; Abd El-Salam, H. M. *Int J Polym Mater* 2003, 52, 499.
40. Abd El-Rehim, S. S.; Sayyah, S. M.; El-Deeb, M. M. *Appl Surf Sci* 2000, 165, 249.
41. Abd El-Rehim, S. S.; Sayyah, S. M.; El-Deeb, M. M. *Plating Surf Finish* 2000, 87, 93.
42. Abd El-Rehim, S. S.; Sayyah, S. M.; El-Deeb, M. M. *Trans IMF* 2000, 78, 74.
43. Joule, J. A.; Smith, G. F. *Heterocyclic Chemistry*, 2nd ed.; Cambridge University Press: Cambridge, UK, 1984; pp. 8-9.
44. Randless, J. P. *Trans Faraday Soc* 1948, 44, 327.
45. Sevcik, A. *Collect Czech Chem Commun* 1948, 13, 349.