

Electrocopolymerization Kinetics of a Binary Mixture of 3-Chloroaniline 2-Amino-4-phenylthiazole and Characterization of the Obtained Block Copolymer Films

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ABSTRACT: Electrocopolymerization of a binary mixture of 3-chloroaniline and 2-amino-4-phenylthiazole 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 electrocopolymerization reaction on platinum electrode is small and the rate law is $R_p = K_2 [D]^{1.29} [HCl]^{0.97} [M]^{1.94}$. The apparent activation energy is found to be 38.87 kJ/mol. The obtained copolymer film is characterized by ¹H-NMR, elemental analysis, GPC IR, UV-visible, and cyclic voltammetry and compared with those of the two homopolymers. The mechanism of the electrocopo-

lymerization reaction is also discussed and the monomer reactivity ratio (r_1 and r_2) is calculated. The thermogravimetric analysis (TGA) is used to confirm the proposed structure and determination of the number of water molecules in the polymeric chain unit. X-ray and scanning electron microscopic analysis are used to investigate the surface morphology. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2076–2087, 2005

Key words: electrocopolymerization; characterization; kinetics; cyclic voltammetry; TGA

INTRODUCTION

Preparation of conducting polymers has been being extensively researched for a wide range of new technologies. A few popular examples of conducting polymers are polyacetylene, polyaniline, polypyrrole, and polythiophene, which have potential applications in electric display,¹ as electrode materials in batteries,^{2–7} as molecular electronic circuit elements,⁸ in restoration of data,⁹ as gas sensors,^{10–12} in biochemical analysis^{13–17} and as corrosion inhibitors to protect semiconductor and metals.^{18–23}

Conducting polymers containing two compounds can be prepared as copolymers, composites, bilayers, or blends to improve the physical, chemical, mechanical, and electrical properties. In a search of new conducting polymers of the aniline type, investigations have been directed toward aniline modified by substituents in the ring,^{24–27} at the nitrogen atom^{28–30} or formation of copolymers.^{31,32}

Genies and Pernaut³³ studied the kinetics of the electrochemical charge transfer in polypyrrole by determination of the apparent diffusion coefficient

(D_{app}) of the transferred species by a chronoabsorptometric method. The data show that the D_{app} is a function of the electrolyte concentration in the solution in contact with the polymer film.

The kinetic parameters of the electrogenerated polypyrrole film doped with LiClO₄ on a graphite electrode have been calculated.³⁴

The kinetics of electrooxidative polymerization of heteroarenes to give thin films of electronically conductive polymer are strongly dependent on the electrode materials.³⁵

The kinetics of the chemical and electrochemical polymerization of some *meta*, *ortho*, and *N*-substituted aniline, pyrrole, and 2-amino-4-phenylthiazole in hydrochloric acid solution were investigated by Sayyah et al.^{36–45} The orders of the electropolymerization reaction with respect to some reaction parameters as current density, monomer, and acid concentrations were calculated. The rate laws and the apparent activation energies (E_a) of the electropolymerization process were determined. Characterization of the obtained polymers was carried out by ¹H-NMR, IR, UV-visible, X-ray, scanning electron microscopy, thermal gravimetric analysis, and cyclic voltammetry.

The objective of the present work was to investigate the kinetics and optimum conditions for the electrocopolymerization of a binary mixture of 3-chloroaniline and 2-amino-4-phenylthiazole in aqueous hydro-

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chloric acid medium and characterization of the obtained copolymer film by $^1\text{H-NMR}$, IR, UV-visible, elemental analysis, GPC, TGA, and cyclic voltammetry. The surface morphology of the obtained copolymer was characterized by scanning electron microscopy and X-ray diffraction.

EXPERIMENTAL

Materials

3-Chloroaniline (vacuum distilled and stored in the absence of light before use), hydrochloric acid solution, and anhydrous sodium sulfate were of analytical pure grade provided by Merck, Germany. 2-Amino-4-phenylthiazole was synthesized in our laboratory by the method reported in the literature⁴⁶ and its purity established by recrystallization and by TLC. All solutions were freshly prepared using double distilled water.

Cell and electrodes

The experimental set up used was described previously⁴²⁻⁴⁵ and consisted of a rectangular Perspex cell provided with two platinum foil parallel electrodes. Each electrode had dimensions 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 $\pm 1^\circ\text{C}$ with the help of a circulating water thermostat. At the end of the experiment, the anode was withdrawn, washed with distilled water, dried, and weighed using a 4504 MP8 Sartorius ultramicrobalance (10^{-7} g precision). The polymerization current was supplied by constant potential dc-power supply (Thurby-Thandar PL 330).

Electrocopolymerization reaction

Anodic oxidative electrocopolymerization of a binary mixture of 3-chloroaniline and 2-amino-4-phenylthiazole was carried out in aqueous solutions containing monomer [concentration range between 0.01 and 0.08M (1 : 1M ratio)] using 0.1M Na_2SO_4 as the supporting electrolyte and the current densities were investigated in the range between 2 and 16 mAcm^{-2} . Electrocopolymerization was carried in hydrochloric acid solution (concentration range between 0.2 and 1.4M) at different temperatures in the range between 288 and 323K.

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 $1 \times 0.5 \times 0.05$ cm. Before each run, the platinum electrode was cleaned as mentioned above.

The electrochemical experiments were performed with 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 (Models 352 and 270/250).

Ultraviolet, infrared, thermogravimetric, elemental analysis, and $^1\text{H-NMR}$ spectroscopy

Ultraviolet-visible adsorption spectra of the homo- and copolymer samples were measured using a Shimadzu UV spectrophotometer (M160 PC) at room temperature in the 200 –to 400-nm region using dimethyl formamide as a solvent and reference.

$^1\text{H-NMR}$ measurements were carried out using a Varian EM 360L, 60 MHz NMR spectrometer. NMR signals of the electropolymerized samples were recorded in dimethyl sulfoxide using tetramethyl silane as the internal reference.

Infrared measurements were carried out using a Shimadzu FTIR-430 Jasco spectrophotometer.

Thermogravimetric analyses of the obtained copolymers were performed using a Shimadzu DT-30 thermal analyzer. The weight loss was measured from ambient temperature up to 600°C , at the rate of $10^\circ\text{C min}^{-1}$, 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 a 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°min^{-1} ; current: 30 mA; voltage, 40 kV; preset time: 10 s.

RESULTS AND DISCUSSION

Anodic oxidative electrocopolymerization

Effect of duration time

Anodic oxidative electrocopolymerization of a binary mixture of 3-chloroaniline and 2-amino-4-phenylthiazole was studied under the influence of different plating and operating parameters. The effect of duration time on the weight of the obtained copolymers was studied with different values of current densities. The

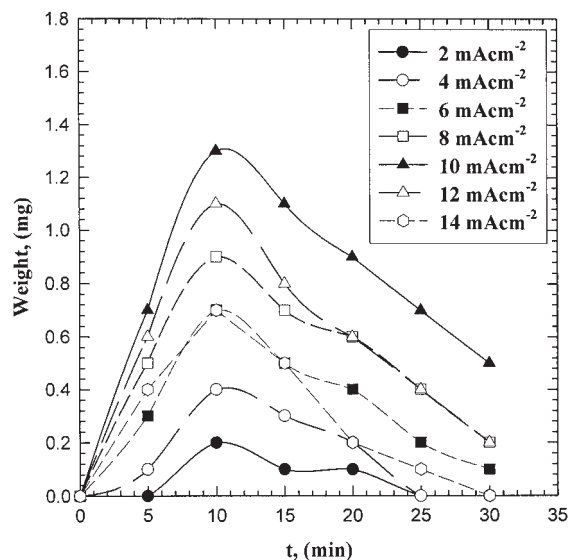


Figure 1 Yield-time curve for the effect of duration time on the anodic copolymerization of 3-chloroaniline and 2-amino-4-phenylthiazole from solution containing 0.05M monomer, 1.0M HCl, and 0.1M Na_2SO_4 at 303K.

data reveal that the weight of the obtained copolymer increases with the increase of duration time up to 10 min and then tends to decrease as a result of degradation and the solubility of the copolymer film from the platinum surface for all of the investigated values of the current densities. The data are graphically represented in Figure 1.

Effect of current density

The effect of the applied current density on the anodic oxidative electrocopolymerization of a binary mixture of 3-chloroaniline and 2-amino-4-phenylthiazole was studied at 10 min using 0.05M monomer concentration

(1 : 1M ratio), 0.1M Na_2SO_4 in dimethyl formamide/water mixture (30 : 70 v/v), and 1.0M HCl at 303K. All of the above-mentioned parameters were kept constant except current density. The data reveal that, as the applied current density increases, the weight of the obtained copolymer increases up to 10 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 current density used was studied with different time intervals and the yield-time curve was estimated. The data are graphically represented in Figure 2(a), from which the initial rate of the electrocopolymerization was determined. The exponent of the electrocopolymerization reaction with respect to the current density was determined from the slope of the straight line of the double logarithmic relation between current density and initial rate and is presented in Figure 2(b). The exponent is found to be 1.29, which means that the reaction order is first order with respect to current density.

Effect of HCl concentration

Anodic oxidative electrocopolymerization was carried out using a 0.05M monomer concentration (1 : 1M ratio), 0.1M Na_2SO_4 in dimethyl formamide/water mixture (30 : 70 v/v), and current density at 10 mAcm^{-2} at 303K, which were kept constant, but the hydrochloric acid concentration was varied in the range between 0.2 and 1.4M. The weight of the obtained copolymer film in each experiment was determined. The obtained data show that the maximum weight is obtained when a 0.8M HCl concentration is used. The effect of HCl concentration on the electrocopolymerization rate was carried out in the concentration range between 0.2 and 0.8M. The weight of the

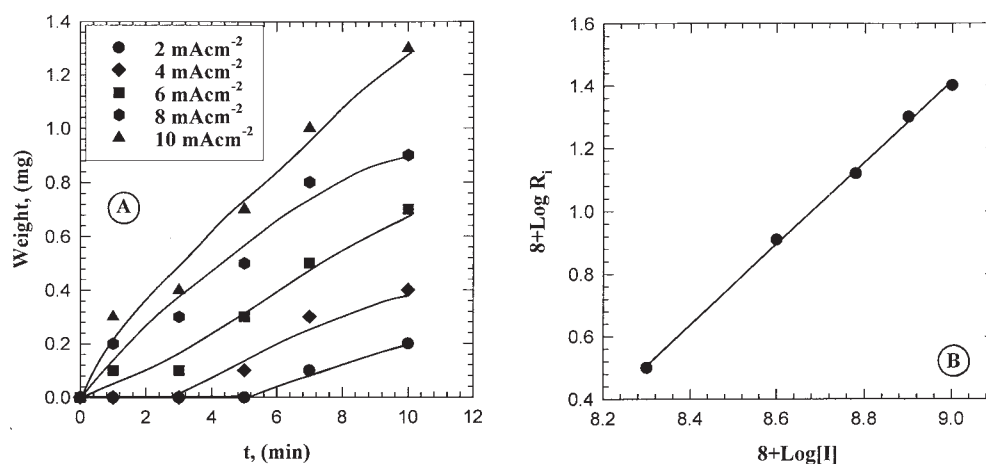


Figure 2 (a) Yield-time curve for the effect of current densities. (b) Double logarithmic plot of initial rate of the electrocopolymerization versus different current density values.

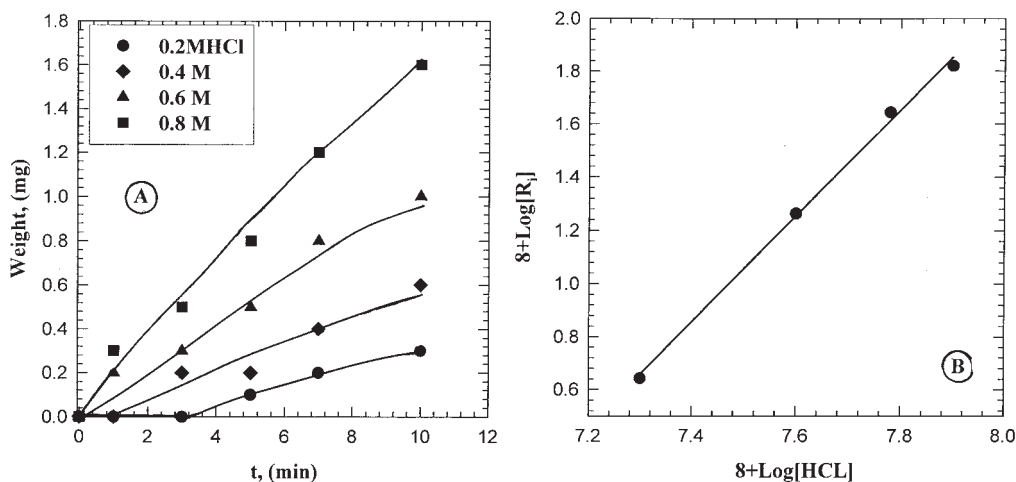


Figure 3 (a) Yield–time curve for the effect of HCl concentrations. (b) Double logarithmic plot of initial rate of the electrocopolymerization versus different HCl concentrations.

deposited copolymer 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 electrocopolymerization reaction is calculated and the double logarithmic plot of the initial rate versus HCl concentration is represented in Figure 3(b). A straight line is obtained which has a slope equal to 0.97. This means that the order of the reaction with respect to HCl is first order.

Effect of monomer concentration

The electrocopolymerization reaction was carried out by keeping the following conditions constant at 0.8M HCl: current density at 10 mAcm^{-2} , Na_2SO_4 (0.1M), reaction time (10 min), and temperature at 303K, but the monomer concentrations were varied in the range between 0.01 and 0.08M (1 : 1M ratio). The weight of

the obtained copolymer film in each case was calculated. From the obtained data, it is noticed that the maximum weight of the copolymer film is obtained when a 0.05M monomer mixture concentration (1 : 1M ratio) is used. It is also noticed that the weight of the copolymer film decreases at higher concentrations of the monomer mixture, which means that copolymer degradation may be occurring. The electrocopolymerization of a mixture of 3-chloroaniline and 2-amino-4-phenylthiazole was performed using different monomer concentrations in the range between 0.01 and 0.05M (1 : 1M ratio) at different time intervals. The data are graphically represented in Figure 4(a). The initial rate of the electrocopolymerization was calculated and the double logarithmic plot of the initial rate of the electrocopolymerization versus the monomer concentration is represented in Figure 4(b). This rela-

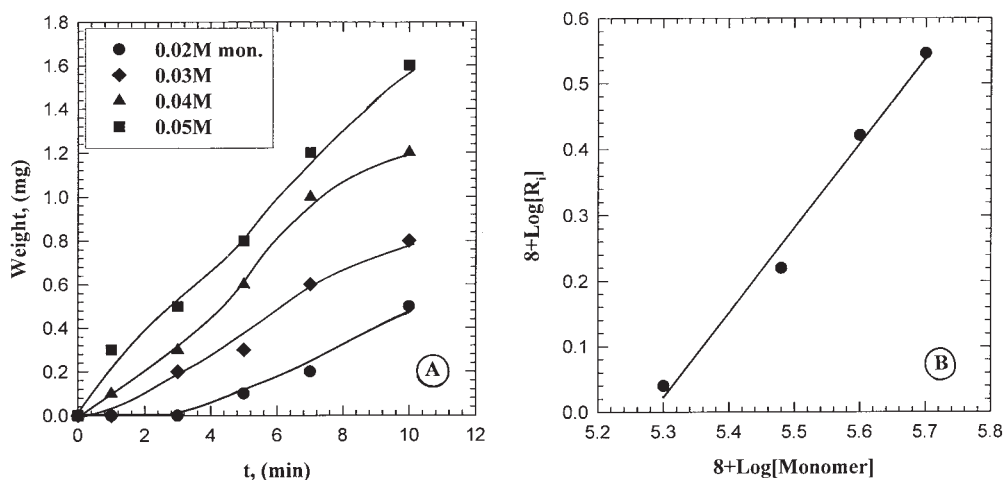


Figure 4 (a) Yield–time curve for the effect of monomer concentrations. (b) Double logarithmic plot of initial rate of the electrocopolymerization versus different monomer concentrations.

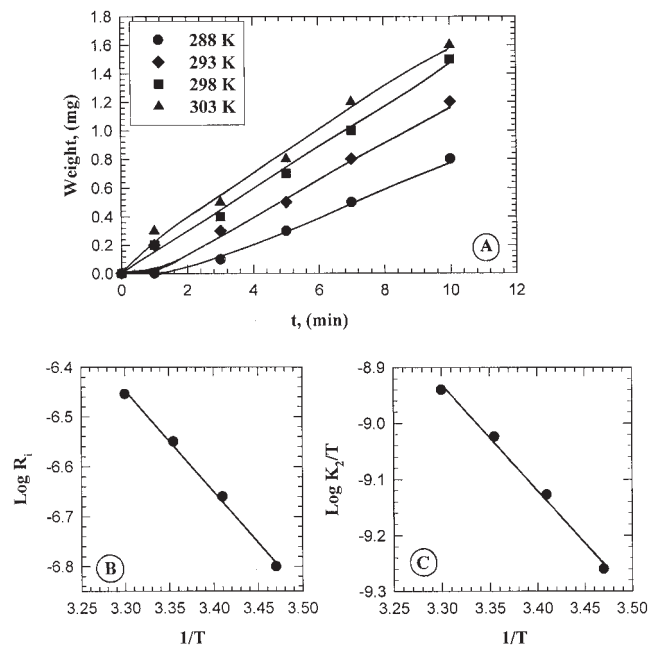


Figure 5 (a) Yield–time curve for the effect of temperature. (b) Arrhenius plot for the electrocopolymerization. (c) Eyring equation plot for the electrocopolymerization.

tion gives a straight line with a slope equal to 1.94, which means that the order of the electrocopolymerization reaction is second order with respect to the monomer concentration.

Effect of temperature

Anodic oxidative electrocopolymerization of a mixture of 3-chloroaniline and 2-amino-4-phenylthiazole was carried out under the following constant conditions: 0.8M HCl, 0.05M monomer (1 : 1M ratio), 0.1M Na₂SO₄, and 10 mAcm⁻², with a duration time of 10 min, but the reaction was carried out at different temperatures ranging between 288 and 323K. The maximum weight of the copolymer film was recorded at 303K. It was noticed during the experiments that, at temperatures higher than 303K, some copolymers were formed in the solution near the anode and did not adhere to the electrode, which means that, at temperatures higher than 303K, the adhesion of the film to the electrode is decreased. The electrocopolymerization of a mixture of 3-chloroaniline and 2-amino-4-phenylthiazole was carried out at different temperatures, 288, 293, 298 and 303K, for different time intervals. At each temperature the weight of the formed copolymer at the anode was plotted versus the duration time and the yield–time curve is represented in Figure 5(a). The initial rate of the electrocopolymerization was calculated at each investigated temperature and the logarithm of the initial rate was plotted versus 1/T [c.f. Figure 5(b)], which gives a straight line

with a slope equal to -2.03 . By applying the Arrhenius equation, the apparent activation energy was calculated and found to be 38.87 kJ/mol.

Calculation of thermodynamic parameters

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

$$\text{reaction rate} = k_2[\text{HCl}]^{0.97} [\text{current density}]^{1.29} \times [\text{monomer}]^{1.94}$$

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 Avogadro's number, and h is Planck's constant. By plotting $\log k_2/T$ versus $1/T$ [c.f. Figure 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 37.20 and -230.21 kJ mol⁻¹, respectively.

Spectroscopic analysis

Infrared spectroscopic analysis

The IR spectrum of the prepared copolymer in comparison with those of the two homopolymers, poly(2-amino-4-phenylthiazole) (PAPTh) and poly(3-chloro-aniline) (PCAn), are presented in Figure 6.

The IR spectrum of the copolymer exhibits the characteristic bands of each of the homopolymers. The weak band appearing at 469 cm⁻¹ in PAPTh appears as a medium band at 466 cm⁻¹ in the copolymer, which is attributed to the out-of-plane deformation of C–C–N in the thiazole moiety. The medium band appearing at 532 cm⁻¹ in PCAn and appearing as a medium band at 528 cm⁻¹ in the copolymer could be attributed to the symmetric stretching vibration of Ar–Cl.

The medium bands appearing at 692, 741, and 767 cm⁻¹ in PAPTh and those appearing at 680, 742, 783, 818 and 882 cm⁻¹ in the PCAn appear also with a slight shift in the copolymer as a sharp band at 637 cm⁻¹; weak bands at 743, 781, and 816 cm⁻¹; and a medium band at 872 cm⁻¹ and are attributed to the out-of-plane deformation showing a monosubstituted or 1,3- or 1,4-disubstituted benzene ring.

The three medium absorption bands appearing in the region 1124. . . 1034 cm⁻¹ in the two homopoly-

mers appear as one broad band at 1125 cm^{-1} in the copolymer, which is attributed to the stretching vibration of S-C=N or the in-plane deformation of C-C in the phenyl ring moiety.

Ultraviolet spectroscopic analysis

The UV-visible spectra of the prepared copolymer in comparison with those of the two homopolymers (PAPTh) and (PCAn) show the following absorption bands:

1. The two bands at $\lambda_{\text{max}} = 238$ and 264 nm in PAPTh and at $\lambda_{\text{max}} = 240$ and 270 nm in PCAn appear as one absorption band at $\lambda_{\text{max}} = 270\text{ nm}$ in the copolymer, which are attributed to $\pi-\pi^*$ transition (E_2 band) of the benzene ring and the B band of the $\pi-\pi^*$ transition ($A_{1g}-B_{2u}$).
2. The shoulder absorption band appearing at $\lambda_{\text{max}} = 360\text{ nm}$ in case of PAPTh appears as a broad band for PCAn at $\lambda_{\text{max}} = 380\text{ nm}$, but, in the copolymer, two absorption bands appear at $\lambda_{\text{max}} = 320$ and 380 nm , which could be attributed to the high conjugation of the polymeric chains.

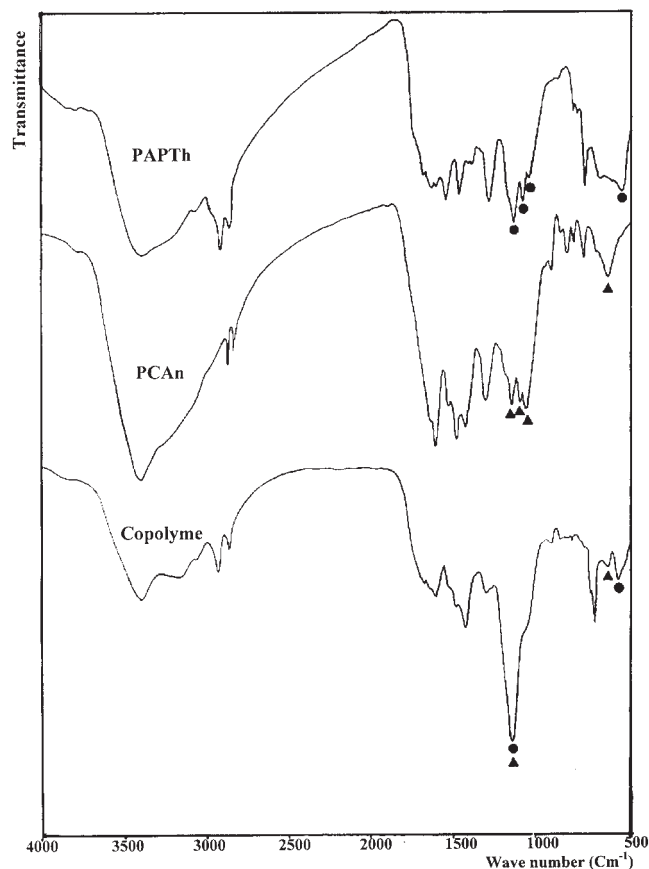


Figure 6 IR spectra showing the different absorption bands of the two homopolymers and copolymer.

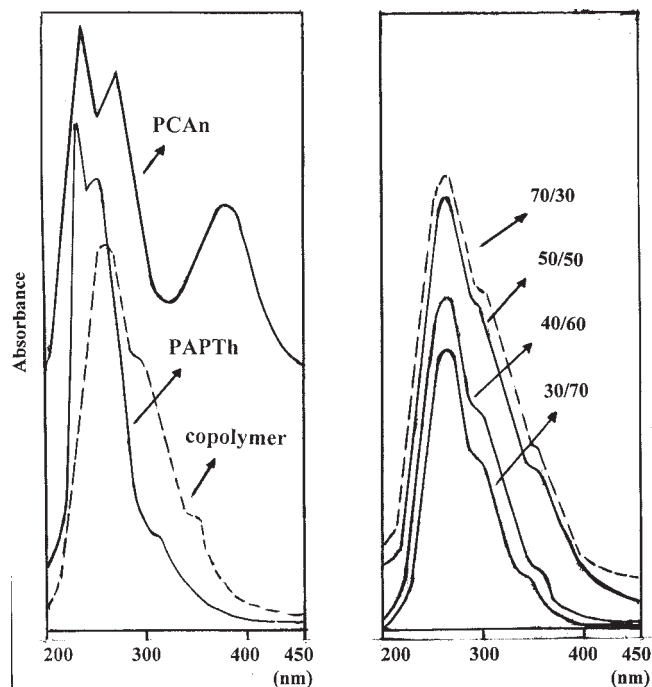


Figure 7 (a) UV-visible spectra of P(APTh), P(CAn), and their copolymer P(APTh-co-3-CAn). (b) UV-visible spectra of P(APTh-co-3-CAn) copolymer prepared from solution containing 0.8M HCl , 0.05M monomer (1 : 1 molar ratio), $0.1\text{M Na}_2\text{SO}_4$, 10 mAcm^{-2} , and 10 min duration time at 303K with different $\text{DMF/H}_2\text{O}$ (v/v) ratios: 30/70, 40/60, 50/50, and 70/30.

Effect of solvent composition on the UV-visible

Different water/DMF ratios were used as a medium during the electropolymerization of the comonomer at a constant monomer feed ratio (1 : 1M ratio). The obtained polymer films prepared in different water/DMF ratios on a platinum electrode at the optimum reaction conditions are dissolved in chloroform and the UV-visible spectra were measured and shown in Figure 7(b); it is clear that there are no drastic changes in the UV-visible spectra of the different copolymer samples. This means that the solvent ratio has no effect on the copolymer structure, which is in a good agreement with Mickley et al.⁴⁷

$^1\text{H-NMR}$ spectroscopic analysis⁴⁸

The $^1\text{H-NMR}$ spectra of the prepared copolymer in comparison with those of the two homopolymers PAPTh and PCAn give the following characteristic signals:

1. The singlet signal appearing at $\delta = 5.6-6.5\text{ ppm}$ PAPTh appears at $\delta = 5.8-6.1\text{ ppm}$ in PCAn and at $\delta = 6.0-6.4$ in the copolymer, which could be attributed to NH protons.

TABLE I
¹H-NMR Spectroscopic Analysis for the Two Homopolymers (PAPTh and PCAn) and the Obtained Copolymer

PAPTh δ (ppm)	PCAn δ (ppm)	Copolymer δ (ppm)	Assignment ⁽⁴⁸⁾
2.5 (s) ^a	2.5 (s)	2.5 (s)	Solvent protons
3.5 (s)	3.5 (s)	3.5 (s)	
5.6–6.5 (s)	5.8–6.1 (s)	6.0–6.4 (s)	NH proton
6.8–7.3 (m)	6.9–7.4 (m)	7.2–7.5 (m)	Phenyl ring protons
7.4–7.9 (s)	—	7.6–7.9 (s)	Thiazole five-membered ring proton
8.6 (s)	7.9 (s)	8.0–8.09 (d)	NH ₂ protons

^a s, singlet; m, multiplet; d, doublet.

- The phenyl ring protons appear as a multiplet signal at $\delta = 6.8\text{--}7.3$ ppm in PAPTh, at $\delta = 6.9\text{--}7.4$ ppm in PCAn, and at $\delta = 7.2\text{--}7.5$ ppm in the copolymer.
- The singlet signal appearing at $\delta = 7.4\text{--}7.6$ ppm in PAPTh and at $\delta = 7.6\text{--}7.9$ ppm in the copolymer could be attributed to a thiazole five-membered ring proton, which disappears in PCAn.
- The singlet signal appearing at $\delta = 8.6$ ppm in PAPTh, at $\delta = 7.9$ ppm in PCAn, and the doublet signal at $\delta = 8.0\text{--}8.09$ ppm in the copolymer are due to the NH₂ end group protons. The data of ¹H-NMR spectra are summarized in Table I.
- For the third stage, in the temperature range between 306 and 600°C, the weight loss is found to be 26.8%, which may be due to the lost of four thiazole moieties and one chloroaniline moiety. The calculated weight loss of this stage is equal to 26.73%.
- In the last stage, above 600°C, residual material (31%) remained (1 thiazole moiety, 3 chloroaniline moieties, and supporting electrolyte).

Comparison between the thermal behavior of poly(3-chloroaniline), poly(2-amino-4-phenyl thiazole),^{43,44} and the obtained copolymer shows that poly(2-amino-4-phenyl thiazole) is thermally more stable than the copolymer and poly(3-chloroaniline).

Elemental and molecular weight analysis

The percentages of C, H, N, S, 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 II.

The molecular weight data obtained by GPC analysis were found to be as follows: $M_w = 115,679$; $M_n = 63,600$; and $M_v = 106,257$ and the polydispersity was 1.819.

Thermogravimetric analysis (TGA)

The thermogravimetric data of the prepared copolymer are represented in Table III. From the table, it is clear that there are four stages:

- The first stage includes the loss of five molecules of water. In the temperature range between 25 and 180°C, the weight loss of this step is found to be 6%, which is in a good agreement with that calculated (5.4%).
- For the second stage, in the temperature range between 180 and 306°C, the weight loss is found to be 36%, which could be attributed to the loss of five phenyl moieties, two chlorine atoms, and four molecules of HCl. The calculated weight loss in this case is equal to 36.36%.

Copolymer structure and the mechanism

The monomer reactivity ratios of the copolymerization system (r_1 and r_2) involving 3-chloroaniline and the sulfur-containing monomer were determined on the basis of the comonomer composition–copolymer composition relationship. The monomer reactivity ratios were calculated according to the Fineman–Ross method as follows.⁴⁹

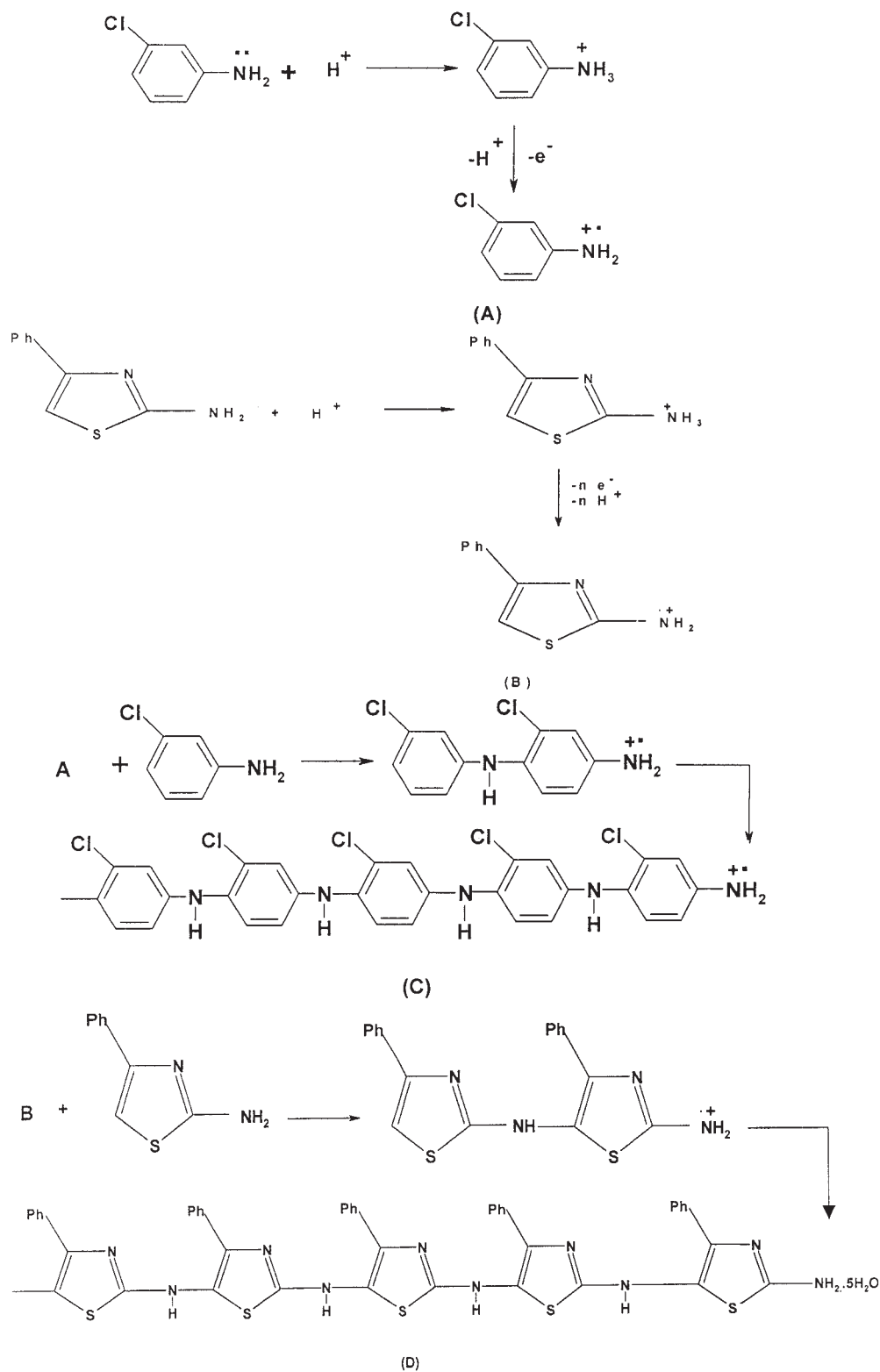
The copolymerization reaction between CAN and APTh was carried out as mentioned under Cell and Electrodes. The two monomers are incorporated into the copolymer chain depending on their relative concentrations and reactivities. The composition of the copolymer was quantitatively determined by sulfur analysis of the copolymer samples. The monomer reactivity ratios r_1 and r_2 of this copolymer were calculated from the Fineman–Ross relationship between F/f ($f-1$) and F^2/f (c.f. Figure 8).

where

$$F = M_1/M_2(\text{molar ratio for monomer composition})$$

$$f = m_1/m_2(\text{molar ratio for copolymer composition})$$

The slope and the intercept are equal to $r_1 = 3.5$ and $r_2 = 0.26$, respectively. From the data, the value of r_1 is



Scheme 1

more than one and r_2 is less than one. In this case the propagation reactions type 11 and 21 will be preferred over types 12 and 22, hence the probability of M_1 (CAn) entering into the copolymer chain is higher

compared to M_2 (APTh); therefore, the formed copolymer will be richer in M_1 .

The copolymer composition data for the investigated system were calculated and the relation between

TABLE II
Elemental Analysis of the Obtained Copolymer

Elements	C(%)	H(%)	N(%)	S(%)	Cl(%)
Calculated	55.00	3.79	11.90	9.70	19.50
Found	55.30	4.20	11.20	9.20	19.40

the mole fraction of M_1 in the formed copolymer (n_1) and the mole fraction of M_1 in the monomer feed (N_1) is represented in Figure 9. The diagonal line represents the case in which both monomers have identical reactivity. All of the values of n_1 for the copolymers are above the diagonal line, indicating that the copolymers have a higher fraction of CAN units than APTh units and that the CAN is much more reactive than APTh. From the above data, it is clear that the copolymer structure is a block structure; therefore, the copolymerization mechanism can be represented as shown in Scheme 1.

Cyclic voltammetry characterization

Cyclic voltammograms of the two separate monomers, 3-chloroaniline (CAN) and 2-amino-4-phenylthiazole (APTh), and the binary mixture of two monomers with molar ratio 1 : 1 in aqueous acid medium (H_2O/DMF 70 : 30 v/v) in the presence of HCl (1M) are represented in Figure 9 and the data are summarized in Table IV. The data reveal that the first oxidation peaks at -150 and -200 mV (versus SCE) for CAN and its binary mixture with APTh, respectively, are attributed to the removal of an electron from the nitrogen atom in the CAN monomer to form a radical cation in both cases (i.e., CAN homo- and comonomer with APTh), which reacts with one molecule of the CAN monomer to form a dimer radical cation and so on to form a semiquinone radical cation (polaron state).^{44,45} The presence of one process at this potential

TABLE III
Thermogravimetric Data of the Obtained Copolymer

Temperature range (°C)	Weight loss (%)		The removed molecule
	Calculated	Found	
25–180	5.4	6.0	5H ₂ O
180–306	36.4	36.0	5 Phenyl moiety 2 Chlorine atom 4 HCl
306–600	26.7	26.8	4 Thiazole moiety 1 Chloroaniline moiety
Above 600	—	31	1 Thiazole moiety 3 Chloroaniline moieties Supporting electrolyte

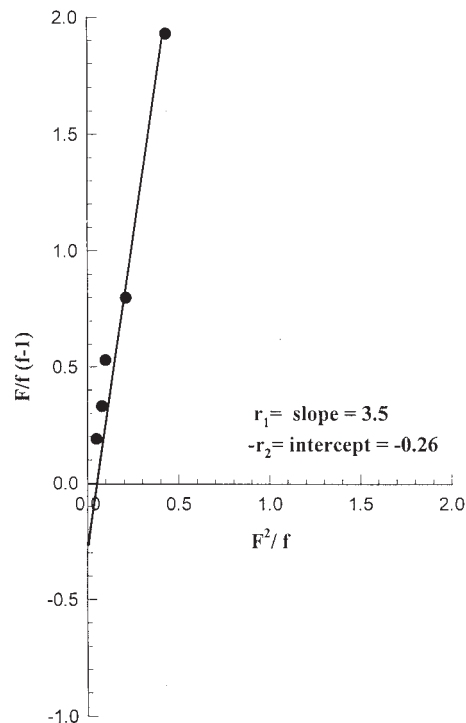


Figure 8 Fineman–Ross plot for the determination of monomer reactivity ratios of P(3-CAN-co-APTh) in aqueous HCl solution copolymerized by electrochemical method on Pt electrode.

is determined from the calculation of the ratio between the anodic charge for first oxidation peak for the binary mixture and the CAN monomer, which is equal to 0.8 (i.e., about 1).

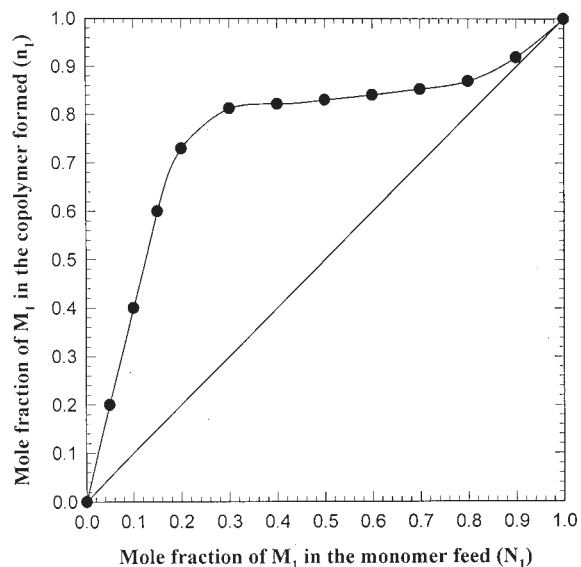


Figure 9 Composition curve for the electrocopolymerization between 3-CAN (M_1) and APTh (M_2) in aqueous HCl solution on Pt electrode.

TABLE IV
Cyclic Voltammometry Data for the Electropolymerization of 3-CAn, APTh, and a Binary Mixture of Both

Monomer name	Anodic oxidation peak potential (mV vs. SCE)		Anodic charge ratio for first and second peak in case of binary mixture and <i>m</i> -CAn
	First peak	Second peak	
3-CAn	-150	1,000	First peak $Q_{\text{binary}}/Q_{\text{CAn}} = 0.8$
Binary mixture 3-CAn + APTh	-200	960	
APTh	Only one peak appears at 1,200		Second peak $Q_{\text{binary}}/Q_{\text{CAn}} = 1.8$

The secondary oxidation peaks at 1,000 and 960 mV (versus SCE) in CAn and the binary mixture, respectively, and only one oxidation peak at 1,200 mV (versus SCE) in APTh are assigned to the oxidation of a semiquinone radical cation (polaron state) in CAn homo- and comonomer with APTh to quinone imine (bipolaron),^{44,45} also, oxidation of APTh monomer to form a radical cation in APTh homo- and comonomer with CAn, which reacts with the other monomer to form a dimer radical cation and so on.⁴³ On the one hand, the presence of the above two processes (radical formation in APTh and structure change in CAn) can

be inferred from the calculation of the anodic charge ratio between the second peak for the comonomer and *m*-CAn, which is approximately more than unity ($1.8 \cong 2$).

The reverse scan of the binary monomer mixture does not include any cathodic peak such as that appearing in APTh (c.f. Figure 10). This indicates that the number of APTh segments in the copolymer chains is small in comparison with CAn, which is confirmed by the relation between the monomer feed ratio of CAn (N_1) and the copolymer composition (n_1) as shown in Figure 9.

On the other hand, the oxidation potentials of the binary mixture are shifted to lower values than that of the two single monomers, indicating that a mixture of both monomers is oxidized more easily than that for the two separate monomers.

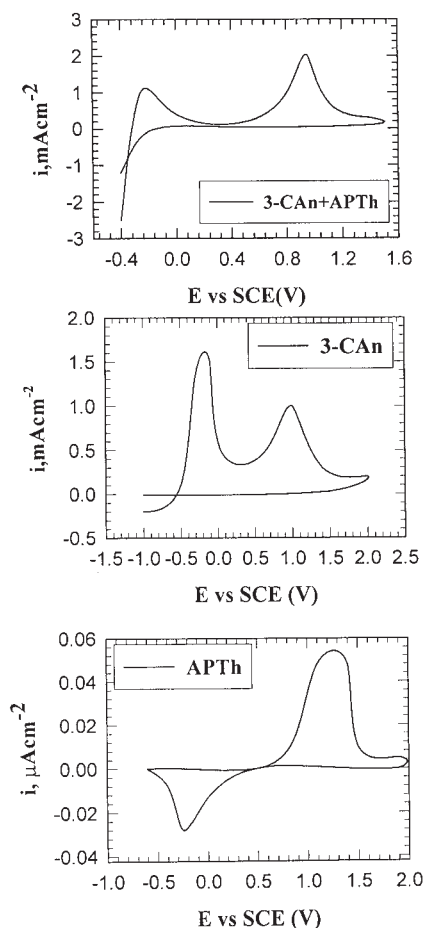


Figure 10 Cyclic voltammogram curves of Pt in 1M HCl aqueous solution in the presence of 3-CAn, APTh, and comonomer with scan rate 20 mVs^{-1} .

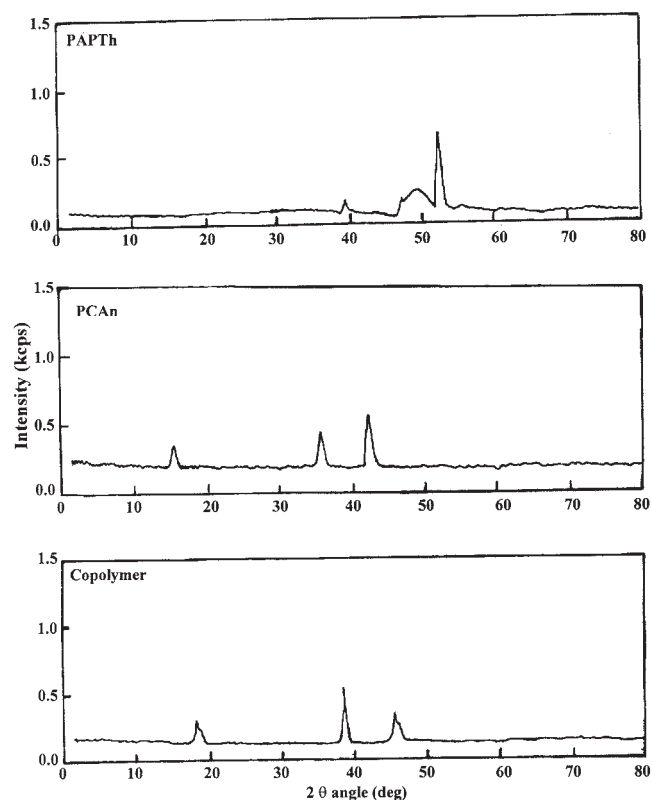


Figure 11 X-ray diffraction pattern of the two homopolymers and copolymer.

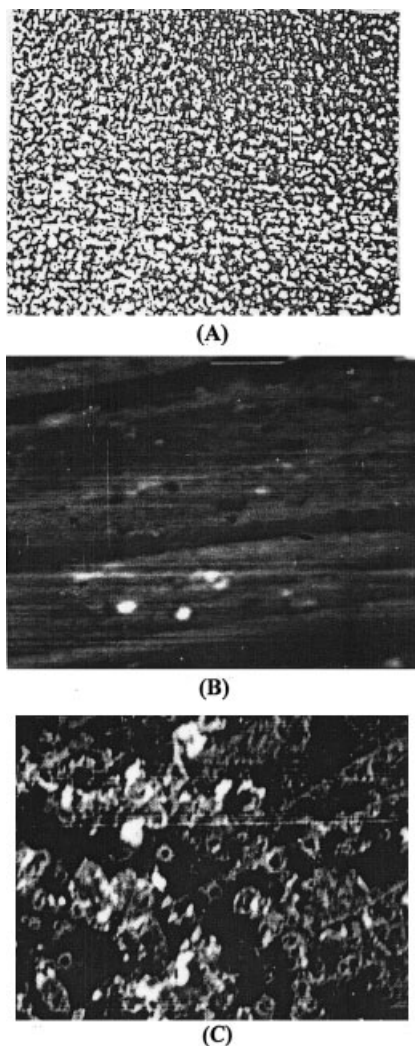


Figure 12 Scanning electron microscope results: (a) PAPTh; (b) PCAn; (c) copolymer.

Surface morphology

Homogeneous, smooth, dark brown, and well-adhering copolymer films were electrodeposited on the platinum surface in most conditions. The surface morphology of the obtained copolymer and the two homopolymers (PAPTh and PCAn) was examined by scanning electron microscopy and X-ray diffraction analysis. The data show that the electropolymerized PAPTh is amorphous [c.f. Figures 11(a) and 12(a)], while PCAn is crystalline with a tubular or fibrillar elongated structure as shown in Figures 11(b) and 12(b). The copolymer is crystalline with a tubular or fibrillar elongated structure with small portion of amorphous particles [c.f. Figures 10(c) and 11(c)].

CONCLUSIONS

1. The initial rate of the electrocopolymerization reaction of a binary mixture of 3-chloroaniline

and 2-amino-4-phenylthiazole (1 : 1M ratio) on a platinum surface is relatively low due to the calculation of the initial rate being taken on the basis of the adhered copolymer film on the platinum electrode. The fraction of the dissolved product may be strongly dependent on temperature and monomer or acid concentrations.

2. The order of the electrocopolymerization reaction is 1.29, 0.97, and 1.94 with respect to current density, hydrochloric acid, and monomer concentration, respectively. The rate law is

$$R_p = K_2[D]^{1.29} [HCl]^{0.97} [M]^{1.94}$$

3. The apparent activation energy (E_a) is 38.87 kJ/mol.
4. The monomer reactivity ratios show r_1 is 3.5 while r_2 is 0.26 and the copolymer structure is blocky and rich with 3-chloroaniline unit
5. The oxidation potentials of the binary mixture are shifted to lower values than that of two separate monomers.
6. The surface morphology of the obtained copolymer is intermediate between the morphology of the two homopolymers, crystalline with tubular or fibrillar elongated structures, and a small portion of amorphous particles.

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