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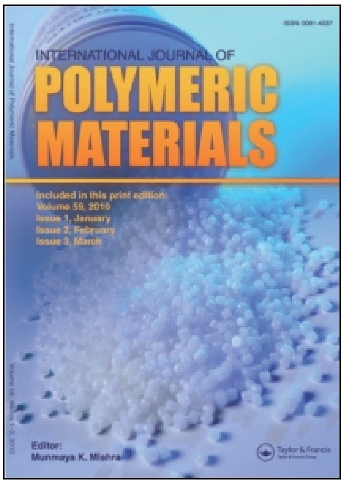

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Electrocopolymerization of a Binary Mixture of 2-chloroaniline and 2-amino-4-(4-methoxyphenyl) thiazole

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Electrocopolymerization of a Binary Mixture of 2-chloroaniline and 2-amino-4-(4-methoxyphenyl) thiazole

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Electropolymerization of a binary mixture of 2-chloroaniline and 2-amino-4-(4-methoxyphenyl) thiazole on platinum electrode in acid medium was carried out under varying reaction conditions as temperature, current density, hydrochloric acid, and monomer concentrations with duration time. The initial rate of the electrocopolymerization reaction was small and the rate law was $R_P = K_2[D]^{0.92}[HCl]^{0.98}[M]^{1.93}$. *The apparent activation energy* (E_a) *was found to be* 57.34 kJ mol^{-1}. *The obtained copolymer films were characterized by* ^{1}*HNMR, elemental analysis, GPC, IR, UV-visible, and cyclic voltammetry compared with those of the two homopolymers. The mechanism of the electrocopolymerization reaction had been also discussed. The monomer reactivity ratio* (r_1 *and* r_2) *was calculated. The thermogravimetric analysis (TGA) was used to confirm the proposed structure and determination of the number of water molecules in the copolymeric chain unit. X-ray and scanning electron microscopic analysis were used to investigate the surface morphology.*

Keywords: 2-amino-4-(4-methoxyphenyl)thiozole, characterization, electrocopolymerization, ^{1}H-NMR, IR, kinetics 2-chloroaniline

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INTRODUCTION

Preparations of conducting polymers are being extensively researched for their applications in 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 semiconductors and metals [18–23].

Conducting polymers containing two compounds can be prepared as copolymers, composite, bilayers, or blend. This is done for the improvement of the physical, chemical, mechanical, and electrical properties beyond those of the homopolymers. In a research 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 Pernaut [33] studied the kinetic of the electrochemical charge transfer in polypyrrole by the determination of the apparent diffusion coefficient (Dapp) of the transferred species by a chronoabsorptometric method. The data show that the Dapp is a function of the eletrolyte concentration in the solution in contact with the polymer film. The kinetic parameters of the electrogenerated polypyrrole film doped with $LiClO_4$ on graphite electrode were calculated [34].

The kinetic of electrooxidative polymerization of heteroarenes to give thin films of electronically conductive polymer is strongly dependent on the electrode materials [35].

The kinetics of the chemical and electrochemical polymerization of some N-substituted aniline and its meta-, ortho-derivatives, pyrrole and other substituted 2-amino-4-phenylthiazole in hydrochloric acid solution were investigated by Sayyah et al. [36–46]. The order of electropolymerization reaction with respect to some reaction parameters as current density, monomer, and acid concentration were calculated. The rate laws and the apparent activation energies (E_a) of the electropolymerization process were determined. The characterization of the obtained polymers were carried out by ^{1}HNMR, IR, UV-visible, X-ray, scanning electron microscopy, thermal gravimetric analysis, and cyclic voltammetry.

The objective of the present work is to investigate the kinetic and optimum conditions for the electropolymerization of a binary mixture od 2-chloroaniline and 2-amino-4-(4-methoxyphenyl)thiazole in aqueous hydrochloric acid solution and characterization of the obtained copolymer film by ^{1}H-NMR, IR, UV-visible, elemental analysis, GPC, TGA, and

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cyclic voltammetry. The surface morphology of the obtained copolymer was characterized by scanning electron microscopy and X-ray diffraction.

EXPERIMENTAL

Materials

2-chloroaniline (vacuum distilled and stored in the absence of light before use), hydrochloric acid solution, and anhydrous sodium sulphate were of analytical pure grade provided by Merk, Germany. 2-amino-4-(4-methoxyphenyl)thiazole was synthesized in the laboratory by the method reported in the literature [47] and its purity was obtained by recrystallization and by TLC. All solutions were freshly prepared using doubly distilled water.

Cell and Electrodes

The experimental setup used was described previously [42–46] and consisted of rectangular Perspex cell provided with two platinum foil parallel electrodes. Each electrode has a dimension of 1 cm height and 0.5 cm width. Before each run, the platinum anode was cleaned and washed with distilled water, rinsed with ethanol, dried, and weighed. The experiments were conducted at the required temperature ±1°C with the help of circular water thermostat. At the end of the experiment, the anode was withdrawn, washed with distilled water, dired, and weighed using a 4504 MP8 Santorius ultramicrobalance (10^{-} gm precision). The polymerization current was supplied by constant potential d.c.-power supply (Thurby-Thandar PL 330).

Electrocopolymerization Reaction

Anodic oxidative electrocopolymerization of a binary mixture of 2-chloroaniline and 2-amino-4-(4-methoxyphenyl) thiazole was carried out in aqueous solution containing monomer (concentration range between 0.01 and 0.04 M) (1:1 molar ratio) using 0.1 M Na_2SO_4 as the supporting electrolyte and the current density values were investigated in the range between 4 and 14 mA cm^{-2}. Electrocopolymerization was carried in hydrochloric acid solution (concentration range between 0.7 and 1.7 M) at different temperatures in the range between 283 and 318°K.

Cyclic Voltammetry Measurements

A standard three-electrode cell was used in the cyclic voltammetry measurements with saturated calomel electrode (SCE) as the reference electrode. The auxiliary electrode was a platinum wire; the platinum working electrode was $1 \times 0.5 \times 0.05$ cm. Before each run, the platinum electrode was cleaned as mentioned in the section Cell and Electrodes.

The electrochemical experiments were performed with a EG&G potentiostat/Gavanostat Model 273 supplied by EG&G Princeton Applied Research. The *I-E* curves were recorded by computer software from the same company, Model 352 and 270/250.

Infrared Thermogravimetric Analysis and ^{1}HNMR Spectroscopy

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°C min^{-1} to determine 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).

^{1}H-NMR measurements were carried out using a Varian EM 360 L, 60 MHz NMR spectrometer. NMR signals of the electrocopolymerized samples were recorded in dimethylsulphoxide using tetramethylsilane as internal reference.

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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, kept constant for all the analysis processes:

X-ray tube: Cu Scan speed: 8 deg · min^{-1}
Current: 30 mA Voltage: 40 κV
Preset time: 10 s

RESULTS AND DISCUSSION

Anodic Oxidative Electrocopolymerization

Effect of Duration Time

Anodic oxidative electrocopolymerization of a binary mixture of 2-chloroaniline and 2-amino-4-(4-methoxyphenyl)thiazole was studied

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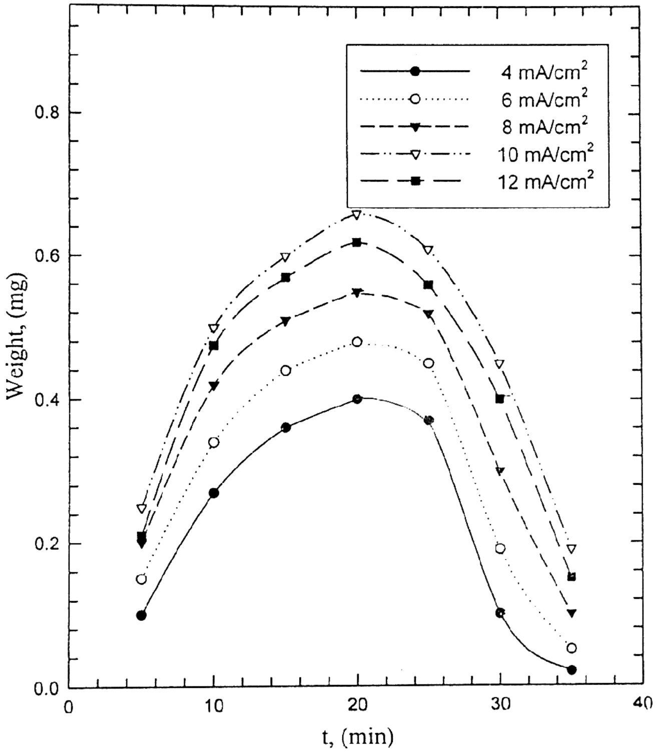

FIGURE 1 Effect of duration time on the anodic oxidative electrocopolymerization of a binary mixture of AMPTh and 2-CAn from solution contaning 0.03 M monomer (1:1 molar ratio), 1.0 M HCl and 0.1 M Na_2SO_4 at 298°K at different current density values.

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 data reveal that the a weight of the obtained copolymer increases with increasing time duration up to 20 min and then tends to decrease as a result of degradation and solubility of the copolymer film from the platinum surface in case of all the investigated values of the current densities. The data are graphically represented in Figure 1.

Effect of Current Density

The effect of applied current density on the anodic oxidative electrocopolymerization of a binary mixture of 2-chloroaniline and 2-amino-4-(4-methoxyphenyl)thiazole was studied at 20 min using 0.025 M monomer concentration (1:1 molar ratio), 0.1 M Na_2SO_4 in dimethylformamide/water mixture (30:70 v/v), and 1.0 M HCl at 298°K. All the aforementioned 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 mA cm^{-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 density values. Each value of the used current density was studied with different time intervals and yield-time curve, was estimated. The data are graphically represented in Figure 2a, 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 presented in Figure 2b. The exponent was found to be 0.92, which means that the reaction order is first with respect to the current density.

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Effect of HCl Concentration

Anodic oxidative electrocopolymerization was carried out using 0.025 M monomer concentration (1:1 molar ratio), 0.1 M Na_2SO_4 in dimethylformamide/water mixture (30:70 v/v), current density 10 mA cm^{-2} at 298°K for 20 min. All these parameters were kept constant except hydrochloric acid concentration, which was studied in the range 0.7–1.7 M. The weight of the obtained copolymer film in each experiment was determined. The obtained data reveal that the maximum weight is obtained when 1.5 M HCl concentration was used. Figure 2c illustrates the variation of the weight of deposited film as a function of time using different acid concentrations in the range between 1.0 and 1.5 M. The initial rate of the electrocopolymerization reaction was calculated and the double logarithmic plot of the initial rate versus HCl concentration is presented in Figure 2d. A straight line is obtained, which has a slope equal to 0.98. This means that the order of the reaction with respect to HCl is a first-order reaction.

Effect of Monomer Concentration

The electrocopolymerization reaction was carried out by keeping the following conditions constant at 1.5 M HCl, current density = 10 mA cm^{-2}, Na_2SO_4 (0.1 M), reaction time (20 min) and temperature at 298°K, but the monomer concentration (1:1 molar ratio) was varied in the range between 0.01 and 0.04 M. 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 polymer film is obtained when 0.03 M monomer mixture concentration was used. It is also noticed that the weight of the copolymer film decreases at higher

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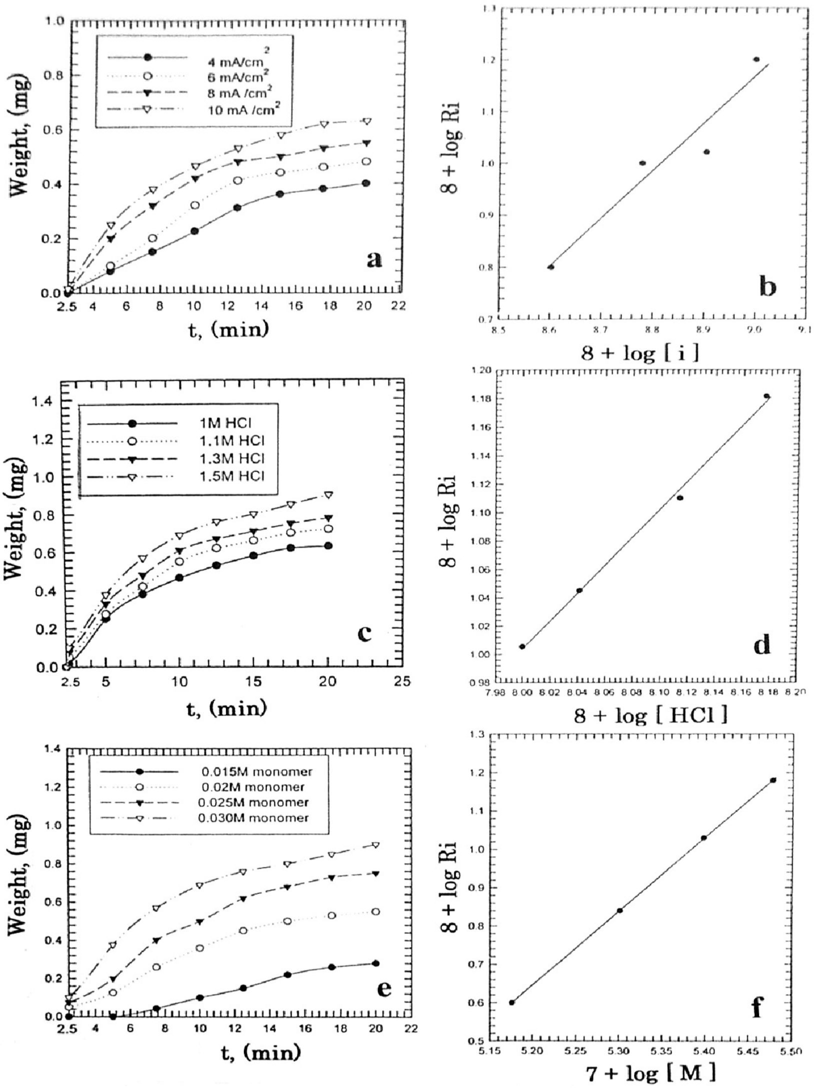

FIGURE 2 (a) Yield-time curves for the effects of current density values; (b) Double logarithmic plot of initial rate of electrocopolymerization versus different current density values; (c) Yield-time curves for the effects of different HCl concentrations; (d) Double logarithmic plot of initial rate of electrocopolymerization versus different HCl concentrations; (e) Yield-time curves for the effects fo different monomers concentrations (1:1 molar ratio); (f) Double logarithmic plot of initial rate of electrocopolymerization versus different monomers concentrations (1:1 molar ratio).

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concentrations of the monomer mixture, which means that copolymer degradation may have occurred. The electrocopolymerization of a mixture of 2-chloroaniline and 2-amino-4-(4-methoxyphenyl)thiazole is performed using different monomer concentrations in the range between 0.015 and 0.03 M (1:1 molar ratio) at different time intervals. The data are graphically presented in Figure 2e. The initial rate of electrocopolymerization was calculated and the double logarithmic plot of the initial rate versus the monomer concentration is represented in Figure 4f. This relation gives a straight line with a slope equal to 1.93, which means that the order of the electrocopolymerization reaction is a second order reaction with respect to monomer concentration.

Effect of Temperature

Anodic oxidative electrocopolymerization of a mixture of 2-chloroaniline and 2-amino-4-(4-methoxyphenyl) thiazole was carried out under the following constant conditions: 1.5 M HCl, 0.03 M monomer (1:1 molar ratio), 0.1 M Na_2SO_4, 10 mA cm^{-2} and the duration time was 20 min but the reaction was carried out at different temperatures in the range between 283 and 318°K. The maximum weight of the copolymer film was recorded at 303°K. It was noticed during the experiments that, at higher temperatures than 303°K, some copolymer is formed in the solution near the anode and does not adheres to the electrode. This means that, at temperatures higher than 303°K, the adhesion of the film to the electrode surface decreased. The electrocopolymerization of a mixture of 2-chloroaniline and 2-amino-4-(4-methoxyphenyl)thiazole was carried out at different temperatures 288, 293, 298, and 303°K for different time intervals. At each temperature the weight of the formed copolymer at the anode was determined at different duration times. The yield-time curves are represented in Figure 3a. The initial rate of electrocopolymerization was calculated at each investigated temperature and the logarithm of the initial rate was plotted versus 1/T (cf. Figure 3b), which gives a straight line with a slope of -3.0. By applying the Arrhenius equation, the apparent activation energy was calculated and found to be 57.34 kJ mol^{-1}.

Calculations 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:

$$\text{Reaction rate} = k_2[\text{HCl}]^{0.98}[\text{current density}]^{0.97}[\text{monomer}]^{1.93}$$

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

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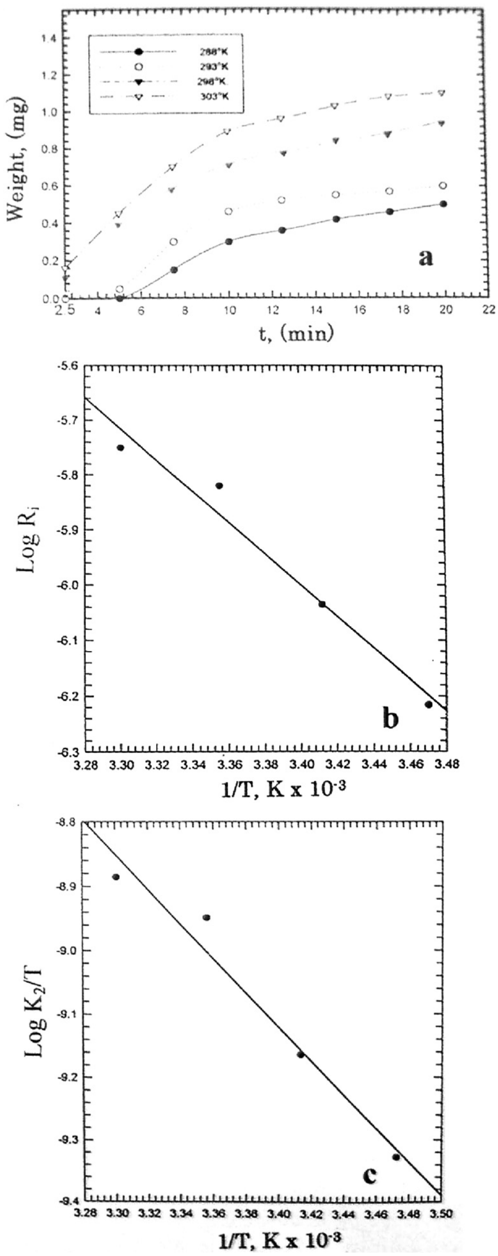

FIGURE 3 (a) Yield-time curves for the effects of different temperatures; (b) Arrhenius plot for the electrocoplymerization; (c) Eyring equation plot for the electrocoplymerization.

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 3c) a linear relationship was obtained with a slope of $\Delta H^*/2.303\,R$ and intercept = log R/Nh) + $\Delta S^*/2.303\,R$. From the slope and intercept, the values of ΔH^* and ΔS^* are found to be 56.22 kJ mol^{-1} and -224.32 Jk^{-1} mol^{-1}, respectively.

Spectroscopic Analysis

Infrared Spectroscopic Analysis

The infrared spectrum of the prepared copolymer in comparison with those of the two homopolymers, poly[2-amino-4-(4-methoxyphenyl]thiazole P(AMPTh) and poly (2-chloroaniline) P(2-CAn) are presented in Figure 4. From the Figure, it seems that the weak band at 549 cm^{-1}, which may be attributed to the stretching vibration of C−Cl in case of P(2-CAn), appears as a medium absorption band at 569 cm^{-1}. The weak absorption band appearing at 640 cm^{-1} in the case of P(2-CAn) and the sharp absorption band appearing at 660 cm^{-1} in the case of P(AMPTh) appears as a medium absorption band in the case of P(AMPTh-co-2-CAn) at 670 cm^{-1}, all of which are attributed to the wagging vibration of NH_2 group. The medium absorption band at 744 cm^{-1} in the case of P (2-CAn) appears also in the case of P(AMPTh) and the copolymer at 746 and 753 cm^{-1} and could be attributed to 1.2 disubstitued benzene ring or out of plane deformation of NH group. The two medium absorption bands appearing in the case of P(2-CAn) and P(AMPTh) at 800 and 820 cm^{-1}, respectively, appear in the case of the copolymer at 810^{-1}, and may be attributed to the 1,4-disubstituted benzene ring. The medium absorption bands appearing at 1539 and 1568 cm^{-1}, which may be assigned to the stretching vibration of C=C in benzene ring or symmetric stretching vibration of C=N group in quinoid structure, in the case of P(2-CAn) and P(AMPTh), respectively, appears at 1565 cm^{-1} as a strong absorption band in case of the copolymer. The broad absorption bands appearing at 3400 cm^{-1} case of P(AMPTh) and at 3350 cm^{-1} in the case of P(2-CAn) are attributed to the NH terminal NH_2 group solvated by water molecules, appears at 3421 cm^{-1} in case of the copolymer. The other infrared absorption bands and their assignments are summarized in Table 1.

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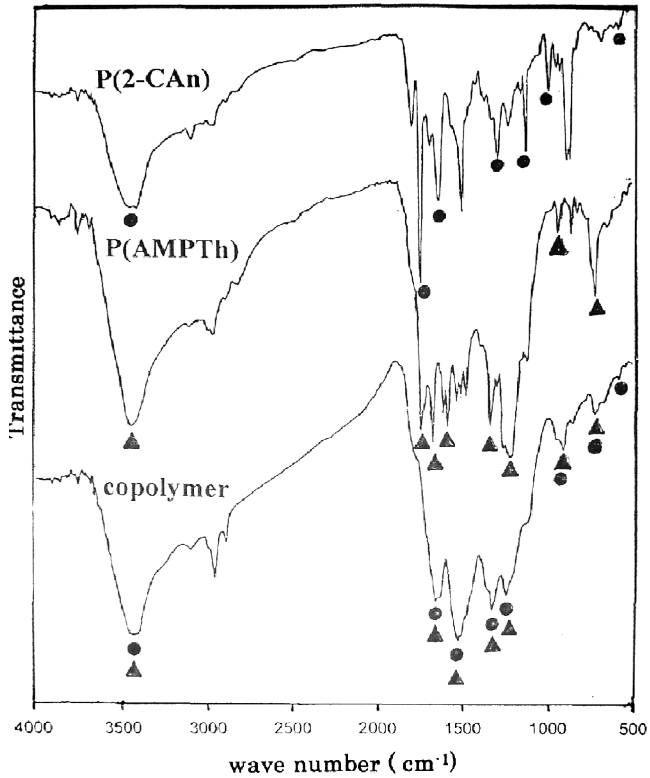

FIGURE 4 IR-spectra showing the different absorption bands of the two homopolymers and copolymer.

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^{1}H NMR Spectroscopic Analysis

The ^{1}H NMR spectrum of the prepared copolymer in comparison with those of the two homopolymers P(AMPTh) and P(2-CAn) gives the following characteristic signals:

1. The phenyl ring protons appear as a multiplet signal at $\delta = 6.9$–7.0 ppm in the case of P(AMPTh), at $\delta = 7.2$–7.9 ppm in the case of P(2-CAn), and at $\delta = 6.9$–7.4 ppm in the case of the copolymer.
2. The singlet signal appearing at $\delta = 7.2$–7.4 ppm in the case of P(AMPTh) and at $\delta = 7.6$–7.9 ppm in the case of the copolymer could be attributed to thiazole five in membered ring protons that disappear in case of P(2-CAn).
3. The singlet signal appearing at $\delta = 8.0$–8.1 bpm in case of P(AMPTh), at $\delta 8.3$ ppm in the case of P(2-CAn) and doublet signal

TABLE 1 Infrared Absorption Bands of P(AMPTh), P(2-CAn), and Their Prepared Copolymer

P(2-CAn) Wave number (cm^{-1})	P(AMPTh) Wave number (cm^{-1})	Copolymer Wave number (cm^{-1})	Assignments
549^{m}	—	569^{m}	Stretching vibration of C–Cl
640^{m}	660^{m}	670^{m}	NH_2 wagging
744^{m}	746^{m}	753^{m}	Out of plane deformation of N–H
800^{m}	820^{w}	810^{m}	Out of plane deformation showing 1, 4-disubstituted benzene ring
980^{w}	906^{w}	925^{m}	In plane deformation of C–C in aromatic ring or stretching vibration for S–C=N or C–S stretching in thiazole
1026^{w}	1010^{w}	1028^{m}	
1084^{w}	1073^{m}		
1150^{m}	1090^{m}	1168^{sp}	Stretching vibration of C–N group or C–O group in case of P(AMPTh) and copolymer
1180^{sp}	1187^{s}	1198^{sp}	
1250^{m}	—	1249^{m}	
1307^{w}	—	—	
	1399^{m}	1385^{m}	Out of plane deformation of $-O-CH_3$ group
—	1494^{m}	1445^{m}	Stretching vibration of C–N in aryl NH or NH_2 group
—	—	1460^{m}	
1539^{m}	1568^{sp}	1565^{sp}	Stretching vibration of C=C in benzene or C=N in conjugation moiety
1627^{sp}	1628^{sp}	1598^{sp}	
—	—	1610^{sp}	
—	2847^{m}	—	C–H aliphatic
—	2952^{m}	2924^{m}	
3066^{m}	3118^{m}	3071^{m}	C–H aromatic
$3236^{b,sp}$	3261^{m}	3250^{m}	Symmetric and asymmetric stretching vibration of N–H in terminal NH_2
3350^{b}	3400^{b}	3421^{m}	Symmetric and asymmetric stretching vibration of NH in terminal solvated NH_2 by H_2O

sp = sharp; m = medium; w = weak; b = broad.

TABLE 2 ^{1}HNMR Spectroscopic Analysis for the Two Homopolymers P(AMPTh) and P(2-CAn) and the Obtained Copolymer

PAMPTh δ(ppm)	2-CAn δ(ppm)	Copolymer δ(ppm)	Assignment
2.5 (s)	2.5 (s)	2.5 (s)	Solvent protons
3.5 (s)	3.5 (s)	3.5 (s)	
6.9–7.3 (m)	6.5–7.4 (m)	6.9–7.5 (m)	Phenyl ring protons
7.4–7.8 (s)	—	7.6–7.9	Thiazole five-membered ring protons
8.3–8.8 (s)	8.6 (s)	8.04–8.13 (m)	NH and NH_2 protons

s (singlet); m (multiplet).

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at $\delta = 8.05$–8.13 ppm in the case of the copolymer are due to the NH and NH_2 end group protons. The data of ^1H NMR spectrum are given in Table 2.

Elemental and Molecular Weight Analysis

The percentage 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 3.

The molecular weight data obtained by GPC analysis was found to be as follows:

$$M_w = 338000,\ M_n = 185000,\ \text{and the polydispersity} = 1.83$$

Thermogravimetric Analysis (TGA)

Thermogravimeteric data of the prepared copolymer are summarized in Table 4, from which it is clear that there are four degradation stages:

1. The first stage: includes the loss of one water molecule in the temperature range between 25 and 161.29°C. The weight loss for this step is found to be 0.903%, which is in good agreement with the calculated value of 1.01%.
2. The second stage: in the temperature range 161.29–369.35°C, the weight loss of this step is found to be 12.35%, which is attributed to the loss of four water molecules and four molecules of HC1. The calculated weight loss of this stage is equal to 13.14%.
3. The third stage: in the temperature range between 369.35 and 512.9°C, the weight loss is found to be 21.67%, which may be due to the loss of three chlorine atoms and then three benzenoid moieties. The calculated weight loss is 21.51%.
4. The fourth stage: in the temperature range between 512.9 and 600°C, the weight loss is found to be 11.98%, which may be due to the loss of one NH_3 molecule, one OCH_3 molecule, and the last thiazole moiety. The calculated weight loss is equal to 13.30%.
5. In the last stage: above 600°C a residual material (53.40%) remained (as carbon and supporting electrolyte materials); the calculated weight loss is 51.04%.

Comparison between the thermal behavior of poly(2-chloroaniline) [45], poly 2-amino-4-(4-methoxyphenyl)thiazole [46], and the obtained copolymer in the present study, shows that 2-amino-4-(4-methoxyphenyl) thiazole-2-chloroaniline copolymer is thermally more stable than the two homopolymers.

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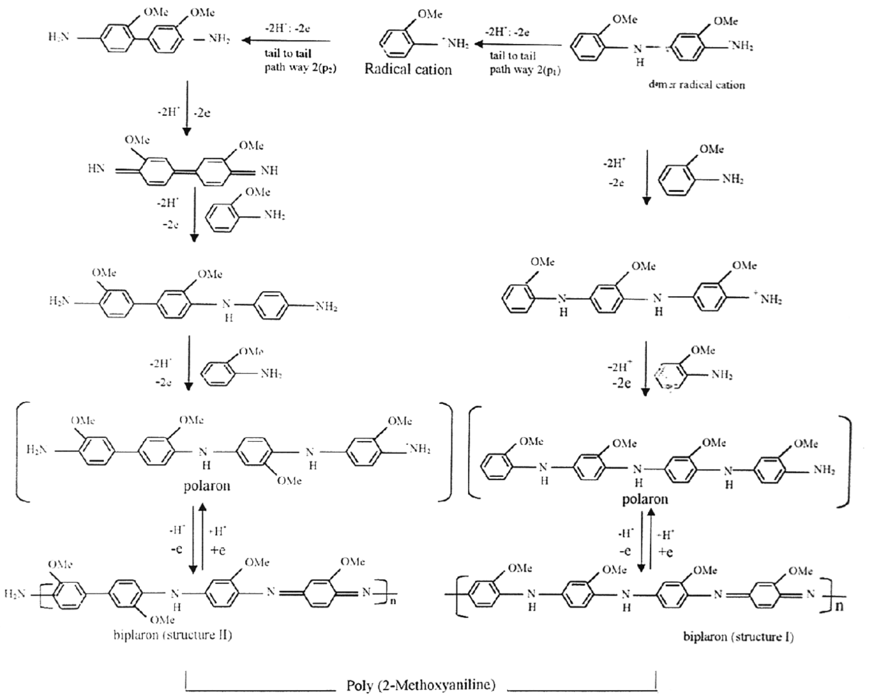

SCHEME 1 Mechanism of the electropolymerization reaction of 2-chloroaniline and 2-amino-4-(4-methoxyphenyl) thiazole.

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Copolymer Structure and the Mechanism

The monomer reactivity ratios of the copolymerization system (r_1 and r_2) involving 2-chloroaniline and the sulphur containing monomer were determined on the basis of the co-monomer composition–copolymer composition relationship. The monomer reactivity ratios were calculated according to the Fineman-Ross method [48] as follows.

The copolymerization reaction, between, 2-CAn and AMPTh was carried out as mentioned in the section Cell and Electrodes. The two monomers are incorporated into the copolymer chain depending on their relative concentration and reactivities. The composition of the copolymer was quantitatively determined by sulphur 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 (cf. Figure 5a).

Where $F = M_1/M_2$ (molar ratio for monomer composition) and $f = M_1/m_2$ (molar ratio for copolymer composition).

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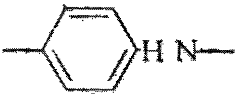
TABLE 3 Elemental Analysis of the Obtained Copolymer

Elements	C (%)	H (%)	N (%)	Cl (%)
Calculated	48.9	2.77	10.38	21.9
Found	48.4	2.45	9.91	20.61

The slope and the intercept equal $r_1 = 2.66$ and $r_2 = 0.169$, respectively. From the data, the value of r_1 is more than one and r_2 is less than one. In this case the propagation reaction type 11 and 21 will be preferred over types 12 and 22, hence the probability of M_1 (2-CAn) entering into the copolymer chain is higher compared to M_2 (AMPTh). Therefore, the formed copolymer will be richer in M_1.

The copolymer composition data for the investigated system were calculated and the relation between 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 5b. The diagonal line represents the case in which both monomers have identical reactivity. All the values of n_1 for the copolymers are above the diagonal line, indicating that the copolymers have a higher fraction of 2-CAn units than AMPTh units and that the 2-CAn is much more reactive than AMPTh. From these data, it is clear that the copolymer structure is a block structure, therefore the copolymerization mechanism can be represented as shown in Scheme 1.

TABLE 4 Thermogravimetric Data of the Obtained Copolymer

	Weight loss (%)		
Temperature range °C	Calculated	Found	The removed molecule
25–161.29	1.01	0.903	$1H_2O$
161.29–369.35	13.14	12.35	$4H_2O$ 4HCl 3Cl
369.35–512.9	21.51	21.67	3 Benzenoid 
512.9–600	13.30	11.98	one NH_3, one OCH_3, one thiazole moiety
>600	51.04	53.40	residual of the copolymer chain and Na_2SO_4 (supporting electrolyte)

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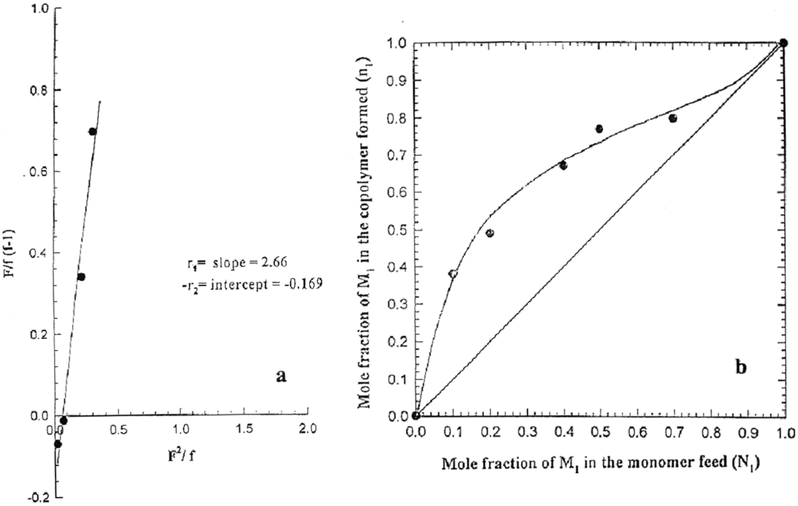

FIGURE 5 (a) Fineman-Ross plot for the determination of monomer reactivity ratios of AMPTh-Co-2-CAn in aqueous HCl solution copolymerized by electrochemical method on pt electrode; (b) Composition curve for the electropolymerized between 2-CAn (M_1) and AMPTh (M_2) in aqueous HCl solution on pt electrode.

Cyclic Voltammetry Characterization

Cyclic Voltammograms of the electropolymerization of the two separate monomers (2-chloroaniline) (2-CAn) and (2-amino-4-(4-methoxy phenyl) thiazole (AMPTh) 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 HC1 (1 M) are shown in Figures 6a–c. The voltamogram in Figure 6a shows that the cyclic voltammogram of 2-CAn (vs. SCE) involves two oxidation peaks (A_1 and A_2). The first oxidation peak (A_1) at -80 mV is related to the formation of dimer radical cation via removal of electron from nitrogen atom in 2-CAn molecule, which reacts with another molecule and so on to form semiquinone radical cation (polaron state). The second oxidation peak (A_2) at 1120 mV involves the oxidation of the semiquinone radical cation to quinone imine (bipolaron) and a reactive peak appear on reversing the scan A_3 could be attributed to partial removal of the deposited film from the electrode surface as a result of polymer degradation [45]. The cyclic voltammogram of AMPTh (versus SCE) exhibits a couple of redox peaks, an anodic peak (A) at 1040 mV (within which oxidation of the monomer and formation of the polymer occurs), and cathodic peak (C) at 480 mV

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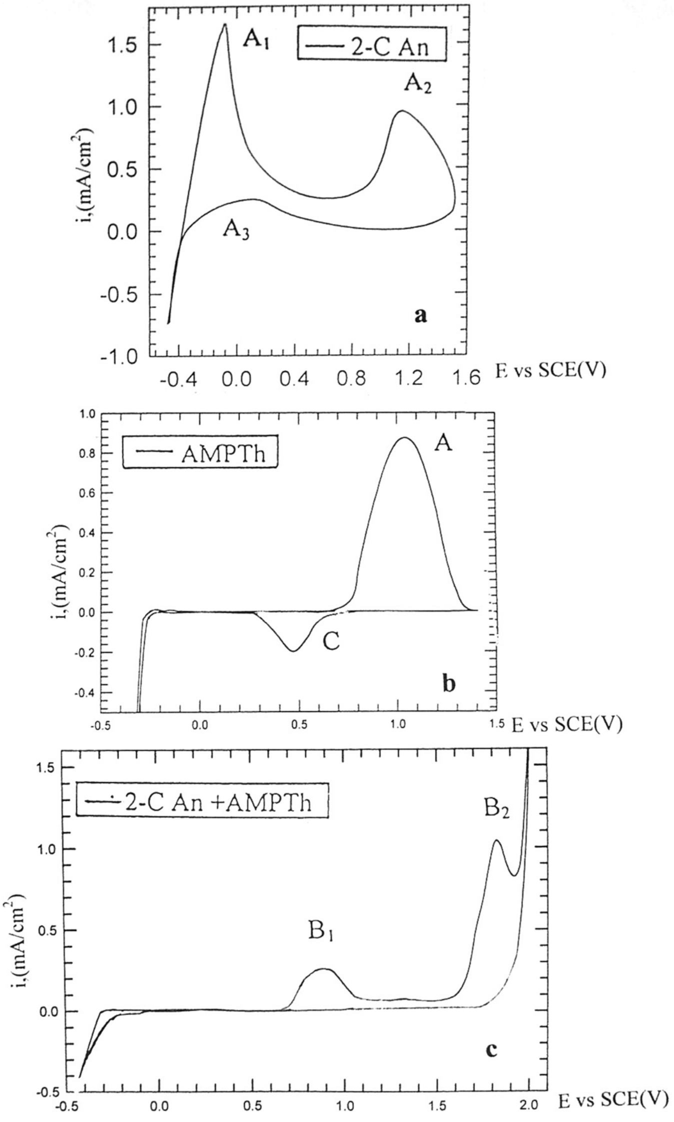

FIGURE 6 (a) Cyclic voltammogram of 2-CAn Polymerization with 25 $\mathrm{mVs^{-1}}$ scan rate; (b) Cyclic voltammogram of AMPTh polymerization with 25 $\mathrm{mVs^{-1}}$ scan rate; (c) Cyclic voltammogram of a binary mixture of AMPTh and 2-CAn (1:1 molar ratio) copolymerization with 25 $\mathrm{mVs^{-1}}$ scan rate.

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corresponding to the reduction of the formed polymer [46]. However, the cyclic voltammogram of the binary monomer mixture (versus SCE) exhibits two oxidation peaks (B_1) at 910 and (B_2) at 1860 mV, respectively. The first anodic peak (B_1) could be assigned to the first oxidation step of 2-CAn and formation of its radical cations (Scheme 1). The second anodic peak (B_2) of the mixture could be attributed to the simultaneous formation of the copolymer. In order to confirm these results, two series of cyclic experiments were performed; the first series was carried out by using mixtures containing constant AMPTh monomer concentration and different 2-CAn monomer concentrations. The second series was carried out by using mixtures containing constant 2-CAn monomer concentration and different AMPTh mpnomer concentrations. The voltammograms are represented in Figure 7a and b, respectively, from which it is clear that the quantity of electricity consumed within these two anodic peaks (B_1 and B_2) increase with increasing 2-CAn concentration. Moreover, in mixtures containing variable concentrations of AMPTh and constant 2-CAn, only the second oxidation peak (B_2) increases with increasing AMPTh concentration (with low rate). These results confirm the earlier suggestion.

The oxidation peaks of the binary mixture are shifted to more positive potential than the corresponding anodic peaks of the homopolymer indicating the retardation of the electrocopolymerization. These results are in a good agreement with the calculated activation energy.

$$\underset{44.75\,\text{kJ/mol}}{E_{a(2-CAn)}} < \underset{57.34\,\text{kJ/mol}}{E_{a(AMPTh-co-2-CAn)}} < \underset{67.29\,\text{kJ/mol}}{E_{a(AMPTh)}}$$

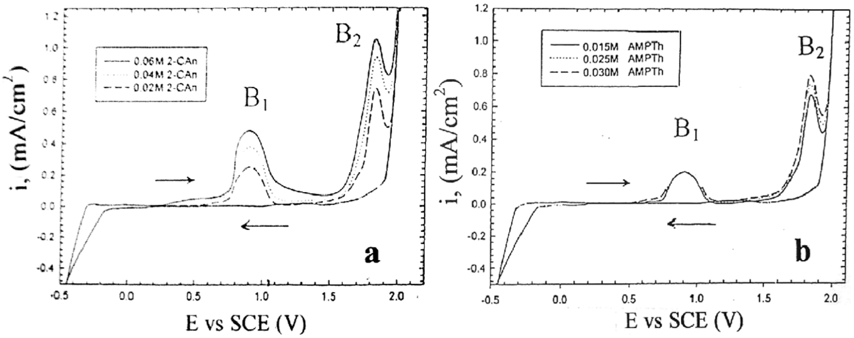

FIGURE 7 (a) Cyclic voltammogram of a binary mixture of 0.03 M AMPTh at three different concentrations of 2-CAn (0.02, 0.04 and 0.06 M); (b) Cyclic voltammogram of a binary mixture of 0.02 M 2-CAn at three different concentrations of AMPTh (0.015, 0.025 and 0.03 M).

Moreover, the reverse scan of a binary monomer mixture (1:1 molar ratio) does not involve any cathodic peak as in the case of AMPTh cyclic voltammograms, indicating that the copolymer is more rich in 2-CAn units, which is confirmed by the relation between monomer feed, ratio of 2-CAn (N_1) and copolymer composition (n_1) as shown in Figure 5b.

Figure 8a shows repetitive cycling of the electrocopolymerization of a binary mixture of AMPTh and 2-CAn (1:1 molar ratio). The data reveal that the two anodic current peaks, ip_{a1} and ip_{a2}, decease significantly on continued cycling as the film becomes thicker. An increase in the thickness of the deposited film decreases its conductivity and also decreases the rate of diffusion within the film.

Figure 8b illustrates the influence of scan rate, υ, (5–100 mV s^{-1}) on the anodic electrocopolymerization of a binary mixture of AMPTh and 2-CAn (1:1 molar ratio) on platinum electrode. Inspection of the data demonstrates that the peak current densities of ip_{a1} and ip_{a2} for the first and second anodic peak, respectively, increase with increasing scan rate.

Figure 8c shows the linear dependence of ip_{a1} versus $\upsilon^{1/2}$. This linear relation suggests that the electroformation of copolymer (AMPTh-co-2-CAn) film on the electrode surface may be described as a partially 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 copolymer film or the charge transport within the film itself limits the overall current as mentioned earlier.

Cyclic voltammograms of the copolymer film formation on platinum electrode as a function of HC1 concentration, monomer concentration and temperature changes were created. Figure 8d represents the influence of HCl concentration variations in the range between (1 and 1.5 M). The two anodic current peaks ip_{a1} and ip_{a2} are enhanced with increasing HCl concentration up to 1.5 M. Figure 8e illustrates the influence of monomer concentration changes on cyclic voltammetric of copolymer formation (AMPTh-co-2-CAn) (molar ratio 1:1), which shows that by increasing the concentration of the monomer from 0.015 to 0.031 M, the two anodic current peaks increase up to 0.03 M.

Figure 8f points out the influence of solution temperature changes from (283 to 303°K) on the anodic polarization response of the copolymer formation. The data reveal that the rise of the reaction temperature results in a progressive increase of the charge included in the anodic peaks. These data are in good agreement with the Kinetic data.

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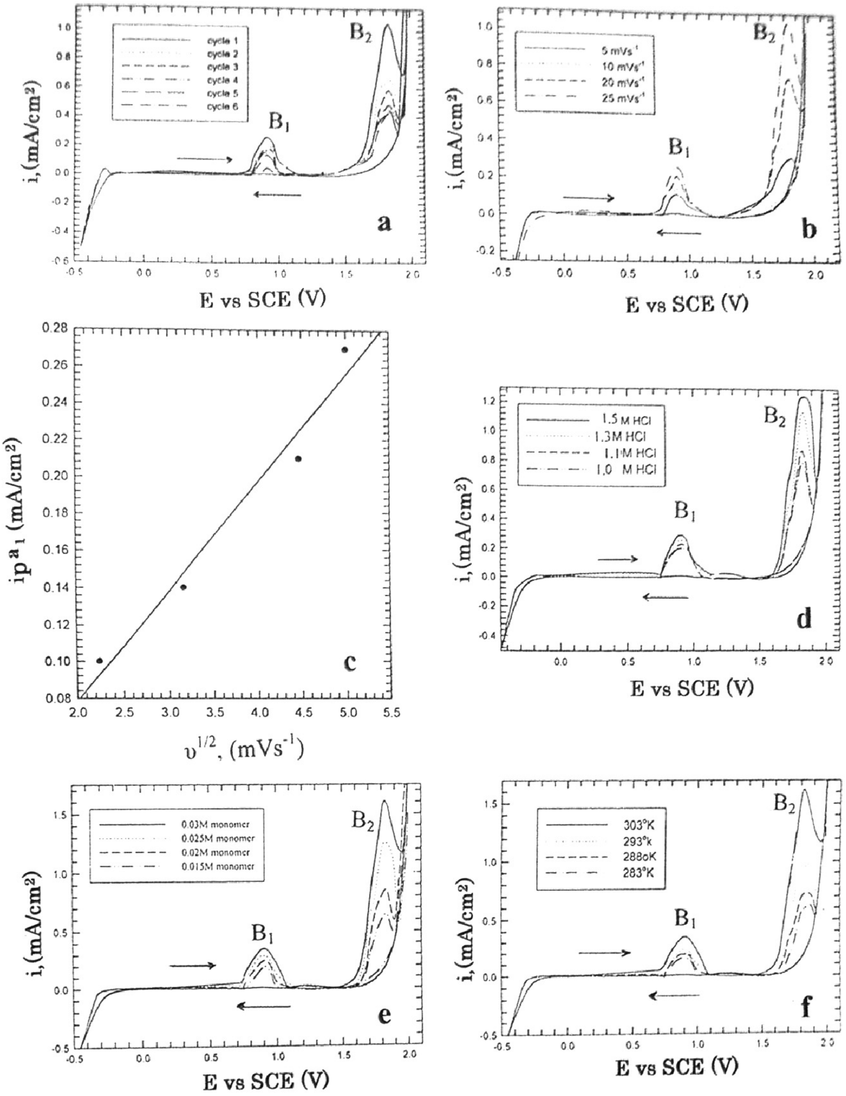

FIGURE 8 (a) Cyclic voltammogram of repetitive cycling; (b) Cyclic voltammogram of effect of scan rate; (c) The relation between $\nu_{1/2}$ and ipa$_1$ of a binary mixture of AMPTh and 2-CAn (1:1 molar ratio); (d) Cyclic voltamogram curves for the effects of different HCl concentrations of copolymerization of the binary mixture (1:1 molar ratio); (e) Cyclic voltamogram curves for the effects of different monomers concentrations of copolymerization of the binary mixture (1:1 molar ratio); (f) Cyclic voltamogram curves for the effects of different temperatures of copolymerization of the binary mixture (1:1 molar ratio).

Surface Morphology

Homogenous, smooth, dark brown, and well-adhering copolymer films were electrodeposited on platinum surface in most conditions. The surface morphology of the obtained copolymer and the two homopolymers (P(AMPTh) and P(2-CAn) were examined by scanning electron microscopy and X-ray diffraction analysis. The data show that the electropolymerized P(2-CAn) is crystalline with tubular or fibrillar elongated structure (cf. Figure 9a), while P(AMPTh) is amorphous

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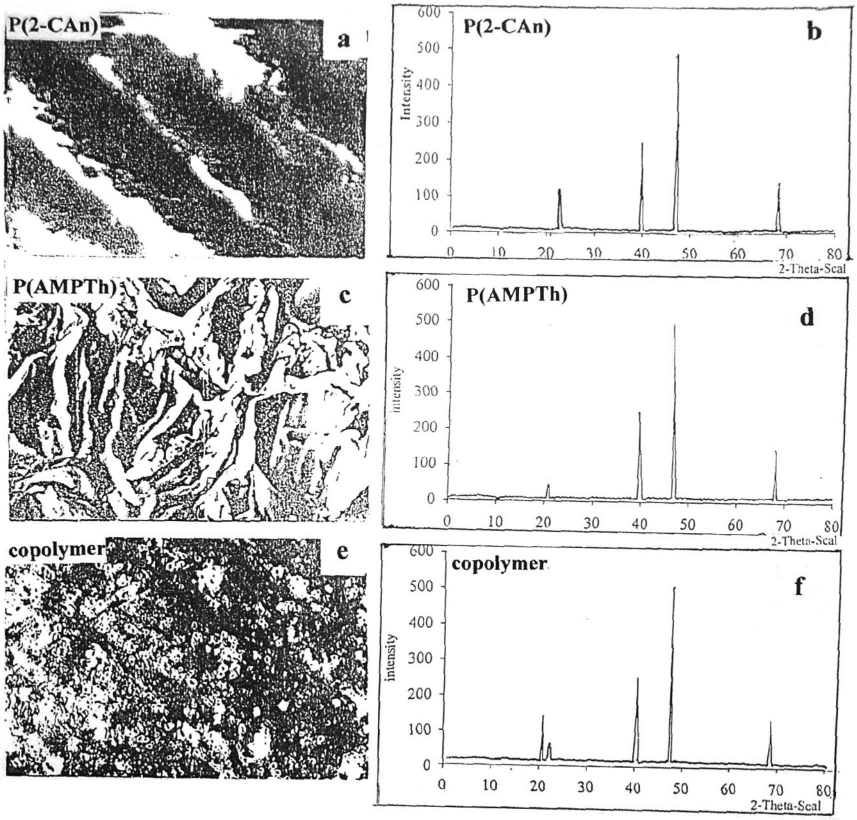

FIGURE 9 (a) Picture of scanning electron microscope of P(2-CAn); (b) X-ray diffraction patterns of P(2-CAn), major peaks may be those of platinum electrode; (c) Picture of scanning electron microscope of P(AMPTh); (d) X-ray diffraction patterns of P(AMPTh), ditto; (e) Picture of scanning electron microscope of copolymer P(AMPTh-co-2-CAn), (f) X-ray diffraction patterns of copolymer P(AMPTh-co-2-CAn), ditto.

(cf. Figure 9c). The copolymer is crystalline with tubular or fibrillar structure with a small portion of amorphous particles (cf. Figure 9e). Similarly, the X-ray diffraction analysis shows that the electropolymerized P(2-CAn) is crystalline (cf. Figure 9b), while P(AMPTh) is amorphous (cf. Figure 9d). The copolymer is crystalline with amorphous particles (cf. Figure 9f) confirming the scanning electron microscopy data.

CONCLUSION

In conclusion, the data in this article reveal the following:

1. The initial rate of the electrocopolymerization reaction of a binary mixture of 2-chloroaniline and 2-amino-4-(4-methoxyphenyl) thiazole (1:1 molar ratio) on platinum surface is relatively low based on the amount 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 0.92, 0.98, and 1.93 with respect to current density, hydrochloric acid, and monomer concentrations, respectively. The rate law is

$$R_p = k_2[D]^{0.92}[HCl]^{0.98}[M]^{1.93}$$

3. The apparent activation energy (E_a) is 57.43 kJ/mol, which is intermediate between E_a of P(2-CAn) and P(AMPTh).
4. The monomer reactivity ratio r_1 is 2.66 where as r_2 is 0.169 and the copolymer structure is block and rich with 2-chloroaniline units.
5. The oxidation potentials of the binary mixture are shifted to lower values than those of the 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 structures and a small portion of amorphous particles.

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