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Autoacceleration/degradation of electrochemical polymerization of substituted anilines

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Abstract

A comparative study was conducted on the kinetic of electropolymerization of *ortho*, *meta* and *N*-alkyl and alkoxy substituted anilines in 1.0 M HCl using cyclic voltammetry. The results show that the net rate of polymer formation was strongly dependent upon the steric hindrance, stability of the radical cations, reactivity of the monomers as well as switch potential. Substituents determine the relative importance of the pathways that lead to formation of polymer or soluble products. The results also indicate that the mutual effect of switch potential on the growth of polymer and its degradation is closely related to the electronic effect of substituent groups. A kinetic expression for the autoacceleration process in the electrochemical polymerization of these aniline derivatives is expressed as $\nu = k[p]^n[M]^{n'} + k'[M]^{n'} - k''[p]^{n''}$ in which k, k', $[M]$, $[p]$, and k'' are the initiation (nucleation process) rate constant, the rate constant when the polymer is deposited on the electrode, monomer concentration, the total amount of polymer, and the rate constant of degradation process, respectively.

Keywords: Polyaniline; Degradation; Kinetics

1. Introduction

The electrogeneration of conducting polymers via electrochemical oxidative polymerization of aromatic compounds has been widely utilized to obtian these materials [1–3]. A great deal of research effort has been devoted to the preparation and investigation of structure–property relationship of these polymers [4–6]. Polyaniline (PAN) and its substituted derivatives because of their moderately high conductivity upon doping, their possible processibility and good environmental stability are more interesting material among the other conductive polymers [7,8]. There have been several reports on the syntheses and properties of alkyl [9,10] or alkoxyl [11,12] ring-substituted polyanilines. These PAN derivatives have improved solubilities and different electronic and electrochemical properties in comparison with PAN. The availability of various conducting polymers presents a unique opportunity to investigate the effect of substituents on the overall properties of these materials. In particular, simple substituents placed strategically on the monomer moiety have allowed variations in the properties of various polymer films. For example 1-alkyl-substituted polypyrrole films are more oxygen stable and less electrically conducting than the parent polypyrrole [13,14]. Poly (*o*-ethoxy aniline) was reported to be water soluble [9] and both poly (*o*-toluidine) (POT) and poly(*m*-toluidine) (PMT) showed interesting electrochemical properties caused by steric effects of the substituent groups [15]. Several reports have been introduced on the study of polymers by kinetic methods [16–20].

Wie et al. [16,17] studied PAN and some alkyl substituted derivatives films grown on Pt electrode for cyclic voltammetric scans of −0.2 to 0.8 V (vs. SCE) and reported that the polymerization rate of aniline is an intrinsically pseudo-first order reaction in aniline concentration. In this case, as temperature increases, the rate of reaction increases according to the Arrhenius equation. The apparent activation energy was determined to be 15.6 kJ/mol which was concluded to correspond to an increase in the rate of reaction by 10.9% per degree increase in temperature. Also it was stated that the polymerization process could not been mainly controlled by diffusion process because the rate of polymerization was not affected by stirring the solution. On the other hand, the growth rate of PAN and poly toluidines film grown by cyclic voltammetry scans of −0.2 to 0.8 V (vs. SCE) was examined

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by Yang [21] under various agitation conditions and it concluded that the polymerization rate is first order in monomer concentration and affected with agitation of the solution.

Effect of upper potential limit on the rate of polymer formation of PAN and poly toluidines was investigated by Wei et al. [16]. Wei believed that usage of high upper switch potentials above 0.7 V vs. SCE could cause degradation and/or crosslinking reactions during the polymerization. On the other hand, high applied potentials are required to achieve a fast rate of polymerization.

Formation of PAN and poly toluidins was examined in the range of −0.2 to 1.2 V by Yang [21]. Yang revealed that the polymerization rate of PAN for the upper potential limit of 1.2 V is significantly promoted in comparison with the case of 0.8 V upper potential limit. However, in contrast, the polymerization of OT is completely inhibited at the upper potential limit of 1.2 V. This result was attributed to the formation of a ‘barrier band’ of oriented $–CH_3$ groups on the OTs, that can prevent the attachment of new OT molecules (in the solution phase) to active sites on the electrode surface, and then it was concluded that suppression of polymer formation is not related to the degradation of polymer in high switch potentials.

In the present work, effects of substituent groups on the rate of polymerization of aniline monomers in relation with steric hindrance and electronic effects induced by substituents on the reactivity of the monomers and stability of their radical cations are discussed. A new kinetic expression is presented for the polymerization of the monomers. Effect of temperature, on the rate of polymer formation and degradation are studied and activation energies for the polymerization of monomers are also evaluated. It is shown that the reported activation energy and the conclusion adapted based on it by Wei et al. has been in error [17]. Suppression of rate of polymer formation in high switch potentials is explained truly based on effect of degradation of polymer and side reactions which occur during polymer formation in high potentials.

2. Experimental

Reagent grade *o*-toluidine (OT), *o*-ethyl aniline (OEA), *m*-ethyl aniline (MEA), *ortho*-anisidine (OAN), *meta*-anisidine (MAN) and *N*-methyl aniline (NMA) (Merck) were doubly distilled and the resulting colorless liquids were kept in darkness. Electrochemical synthesis and cyclic voltammetry were performed on a Behpajooh BHP 2063-B++ voltammetric analyzer. A three-electrode one compartment cell was used with a saturated calomel (SCE) electrode acting as the reference, platinum foil ($3.0\ cm^2$) and carbon rods ($6.0\ cm^2$) were used as working and counter electrodes respectively. The syntheses and measurements were all performed under a nitrogen atmosphere. A 1.0 M HCl solution was prepared from concentrated HCl (Merck).

The polymer was electrochemically deposited by cyclic voltammetry on Pt electrode in 1.0 M HCl aqueous solutions containing various concentration of monomers. All the electrochemical reactions were carried out at 25 °C unless otherwise specified in the text. The potential sweep, operating at a scan rate of $100\ mV\ s^{-1}$, covered the −200 to 1000 mV potential range. From the cyclic voltammograms of the polymerization process recorded simultaneously with the synthesis of the polymer (Fig. 1), the anodic faradic current of the first oxidation peak was measured by subtracting the small background current from the total anodic current. This net current was then plotted against the cycle number (the reaction time). Kinetic parameters have also been obtained from the evaluation of the electrical charges stored in polymer films, which were previously generated at different polymerization times and under different concentration of monomers. Data treatment was performed using Excel (version ’97) and Statistica softwares.

3. Results and discussion

The cyclic voltammograms (CVs) for the polymerization of OT, OEA, MEA, OAN, MAN, and NMA are demonstrated in Fig. 1. In the first potential scan starting from −0.2 V one anodic peak appears at ca. 0.92–0.95 V. This peak is attributed to the oxidation of the monomers and is irreversible because of lack of the corresponding cathodic currents in the reduction process. In the subsequent scans, for OT (and OAN), two new anodic peaks at ca. 0.22 and 0.38 V (0.2 and 0.4 V) appear whereas, for OEA only one broad peak at ca. O.45 V appear and the onset anodic current for the polymer formations shifts to a lower potentials. After a thick film of POT has been deposited on the electrode, the anodic peak originally observed at ca. 0.25 V (0.2 V for POAN) shifts gradually to higher potentials as the number of scans increases. The corresponding cathodic peak also shifts slightly to lower potentials. Similar effect was observed for other monomers. These shifts could be attributed to an IR drop and, therefore, the more shift in potentials.

The electrochemical behavior of the resulting polymers was examined by cyclic voltammetry in an aqueous 1.0 M HCl solution free of monomers. Fig. 2a shows a representative cyclic voltammogram of the POT film, which consists of two redox pairs with the E_p values of ca. 0.22 and 0.47 V vs. SCE. These two redox processes are attributed to two quasi-reversible redox reactions of POT, interconversions between fully reduced and fully oxidized forms of POT, respectively [21].

In comparison with aniline, the first redox couple appears at higher potential, and the second redox couple shifts to lower potential. These potential shifts should be attributed to the effects of the alkyl group on the aromatic polymer chains. The first positive peak shifts to higher potential due possibly to the dominance of steric hindrance, The second positive peak shifts to a lower potential due possibly to the dominance of electron-donating effects for alkyl groups. These effects are more observable for OEA and OAN polymerization, so two peaks are joined and forms a broad peak. Table 1 compares the E_p values for all used monomers and their corresponding polymers. From Table 1 it is obvious that if the substituent is

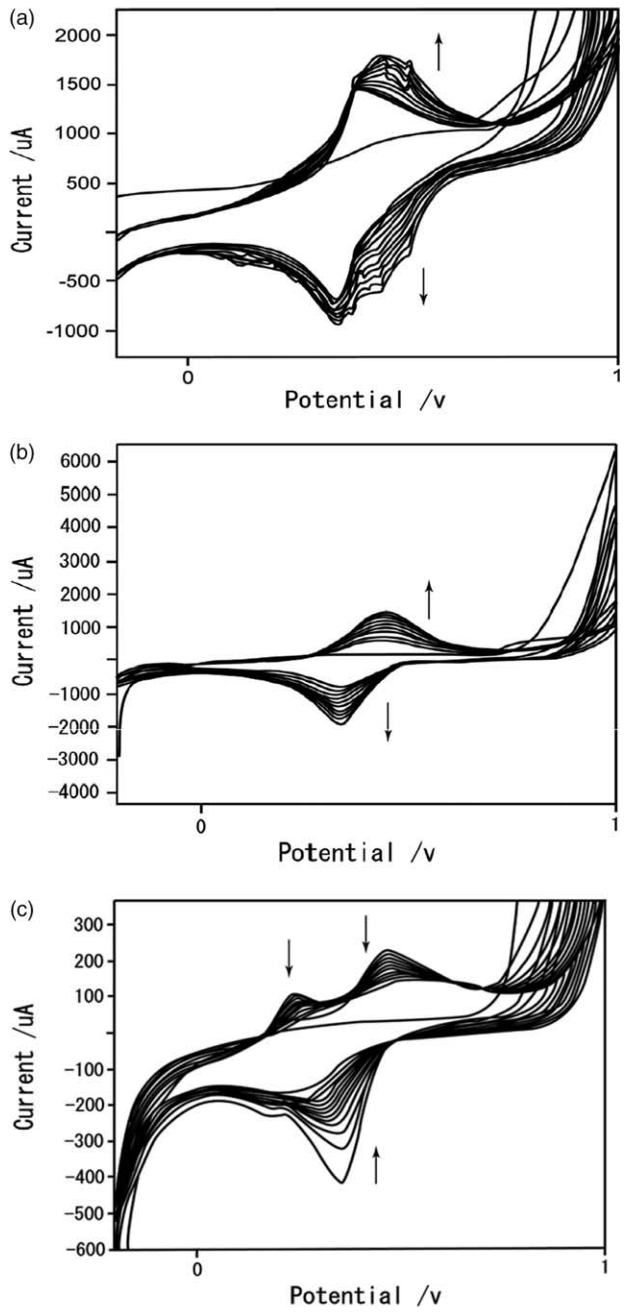

Fig. 1. Cyclic voltammograms of polymerization of 0.15 M (a) OT (b) OEA (c) MEA (d) OAN (e) MAN (f) NMA in 1 M HCl solution on a Pt electrode.

more electron donating in ortho position the oxidation peak potential of the monomer is lower and the monomer is more reactive.

3.1. Effect of monomer concentration on polymerization rate

It is well known that the reaction order of monomer and electrolyte in the electropolymerization kinetics provides information about the nature of the reaction and the chemical structure of polymer. From the influence of the monomer and the electrolyte concentration empirical kinetics can be obtained:

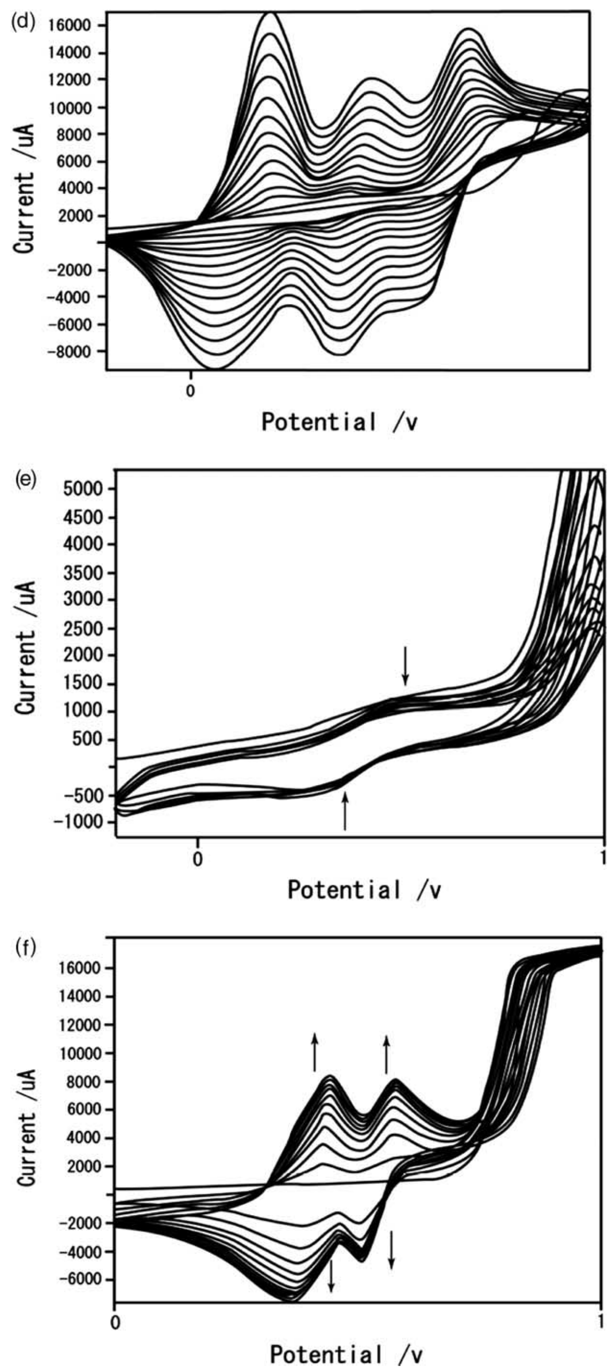

Fig. 1 (*continued*)

$$\nu = k[\text{Monomer}]^a[\text{Electrolyte}]^b$$

Effect of electrolyte concentration (HCl) on the growth rate of polyaniline has been studied by M.M. Ayad [22,23], and it was concluded that the growth rate of polymer increases as the acid concentration increases up to ∼0.1 M. However, as the concentration of HCl increases from 0.1 M, the rate decreases. Therefore, it is concluded that the most suitable HCl concentration for PAN film deposition is ∼0.1 M. Then, by keeping the HCl concentration constant in higher level (4–5

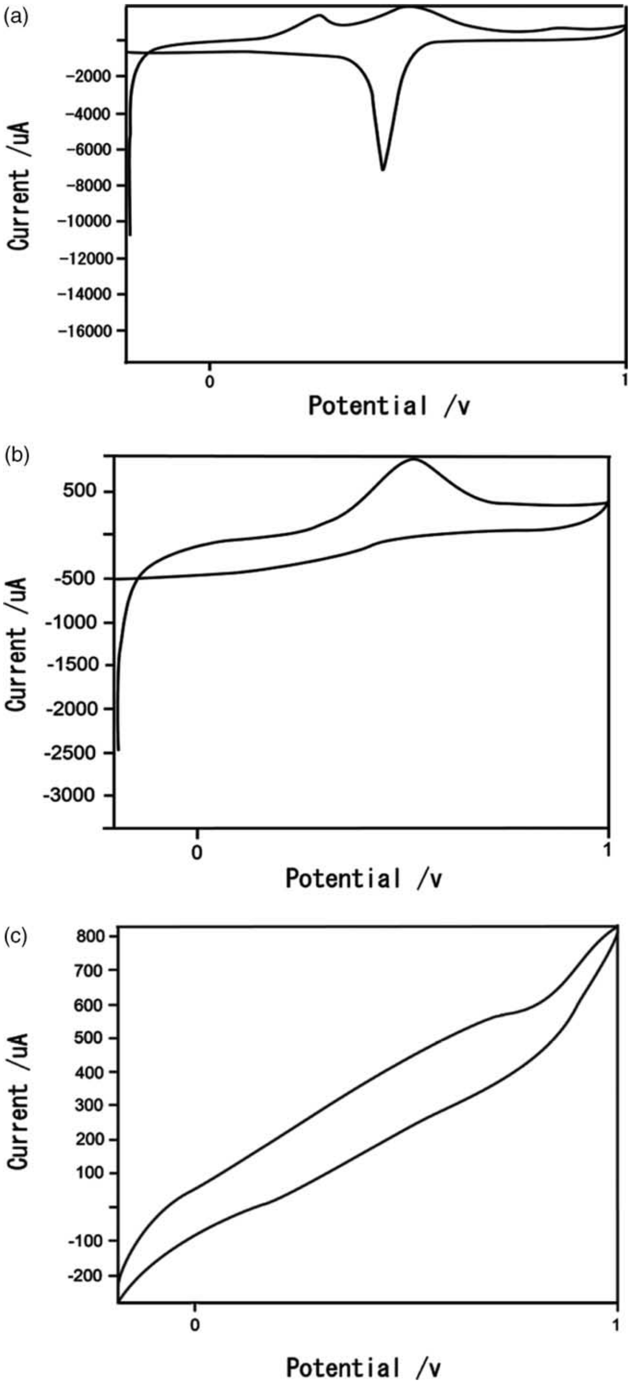

Fig. 2. Cyclic Voltammogram of poly (a) OT (b) OEA (c) MEA (d) OAN (e) MAN (f) NMA in 1 M HCl solution on a Pt electrode. Scan rate, 40 mV/s.

times more than monomer concentration) such as 1.0 M and varying the monomer concentration, the kinetic equation could be expressed by the following exponential equation:

$$\nu = k^{\mathrm{app}}[\mathrm{Monomer}]^{a}$$

The electrochemical polymerization kinetics can be explored through Tafel slopes [24], microgravimetric studies [25], electrical studies [7], and charge storage kinetics [24]. In charge storage kinetic method, charge passed during the

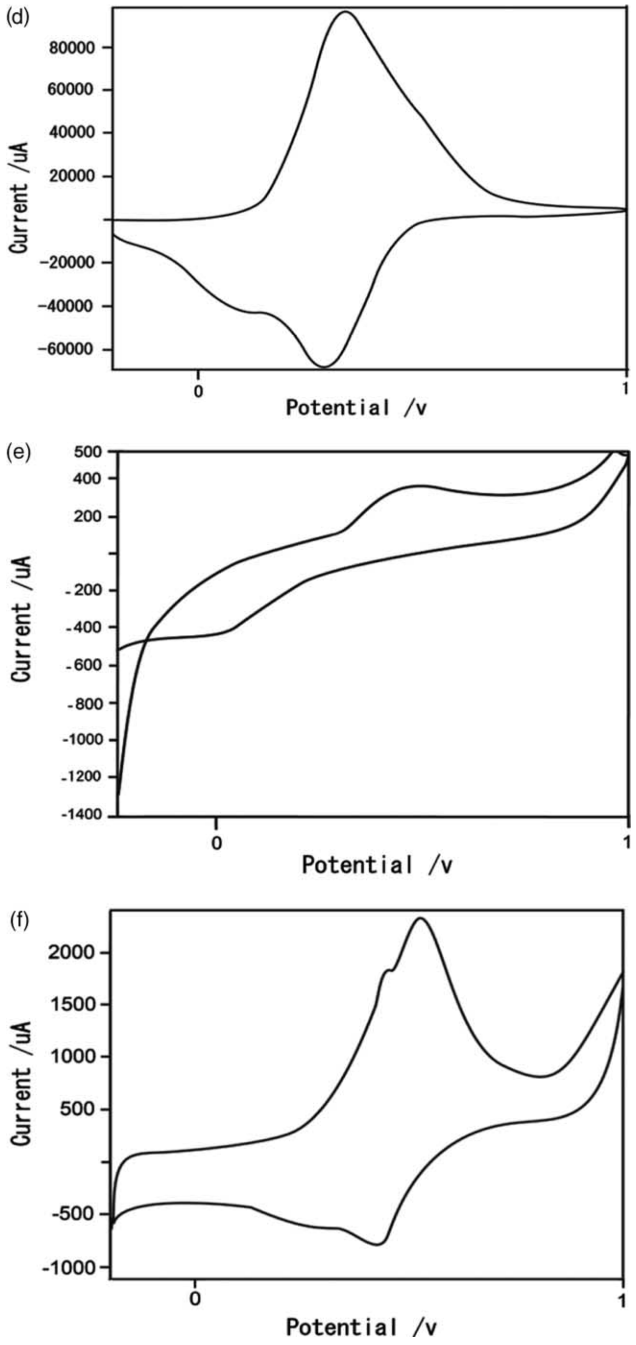

Fig. 2 (*continued*)

electrooxidation of polymeric film in blank solution is used as measure for the amount of polymer deposited on the electrode. Kinetic parameters can be obtained from evolution of the electrical charges stored in polymer films, which were previously generated at different polymerization times and under different concentrations of monomers. The kinetics were followed at different concentration of OT: 0.05, 0.075, 0.1, 0.15, and 0.2 M in HCl solutions. A linear increase of anodic storage charge obtained vs. time of polymerization at each concentration of OT was observed. Increasing slopes were obtained for increasing concentration. Each slope represents a

Table 1
E_p values for OT, OEA, and MEA monomers and their corresponding polymers

	$E_p\text{ox}^1$(V vs. SCE)	$E_p\text{ox}^2$(V vs. SCE)
OT	0.950	–
OEA	0.920	–
MEA	0.950	–
OAN	0.900	–
MAN	0.950	–
NMA	0.950	–
POT	0.220	0.380
POEA	0.440	–
PMEA	0.24	0.470
POAN	0.200	0.400
PMAN	0.450	–
PNMA	0.430	0.620

polymerization rate, the empirical kinetics is as follows:

$$v = k^{\text{app}}[\text{Monomer}]$$

where k^{app} is a set of apparent-first-order reaction rate constants.

It was reported that the total mass of polymer deposited on the electrode is proportional to the anodic peak current (I_p) in the electrochemical polymerization of aniline and its derivatives [17]. Anodic peak currents measured from CVs at various monomer concentration as a function of cycle number (i.e. reaction time), have been plotted in Fig. 3

It is apparent that the amount of polymer formation depends on the monomer concentration. The amount of polymer formation increases with increasing monomer concentration due to monomer increase, which facilitates formation of nucleation sites on the electrode surface. The slope at any point on these curves gives the rate of polymer deposition at the corresponding reaction time. In Fig. 4, these slopes are plotted against the concentration of OT monomer at various anodic current values.

An examination of Fig. 4, reveals that all of the plots are linear, implying that the rate of polymer formation (v) is first order in monomer concentration $[M]$ as expressed in Eq. (1) [17].

$$v = k^{\text{app}}[M] \tag{1}$$

This conclusion is the same as result obtained by charge storage kinetic method.

From an examination of Eq. (1) and Fig. 4, it is noted that the k^{app} values of OT depend on the extent of polymer formation. The values of k^{app} increase with increasing amount of polymer deposited on the electrode. This situation is similar to those observed and proposed as self-catalysis or auto-acceleration of PAN [16]. Among used monomers, OT shows the effect of autoacceleration throughout the polymerization in which the more polymer deposited on the electrode, the higher is the rate of polymer formation. It is worthwhile noting that polymerization of MEA and MAN monomers on the Pt surface electrode in the range of −0.2 to 1.0 V is completely inhibited. This effect is attributed to the steric hindrance of ethyl or ethoxy groups that prevent formation of 2,2′-diethyl benzidine and 2,2′-diethoxy benzidine which is the well known structure produced in dimerization step, the slowest step in the polymer formation process [16]. Since the polymer chain could grow on both the p-amino diphenyl amine type and benzidine type of dimmers, prohibited formation of the benzidine type dimmers should lead to a very lower rate of polymerization. In particular, it should be noted that there are two possible growing centers in the benzidine type of dimmers, but, only one in the *p*-amino diphenyl amine type of dimmers. Thus, 2,2′-diethyl phenyl hydrazine and 2,2′-diethoxy phenyl hydrazine dimmers preferably are generated during oxidation of MEA and MAN on the surface of the Pt electrode without

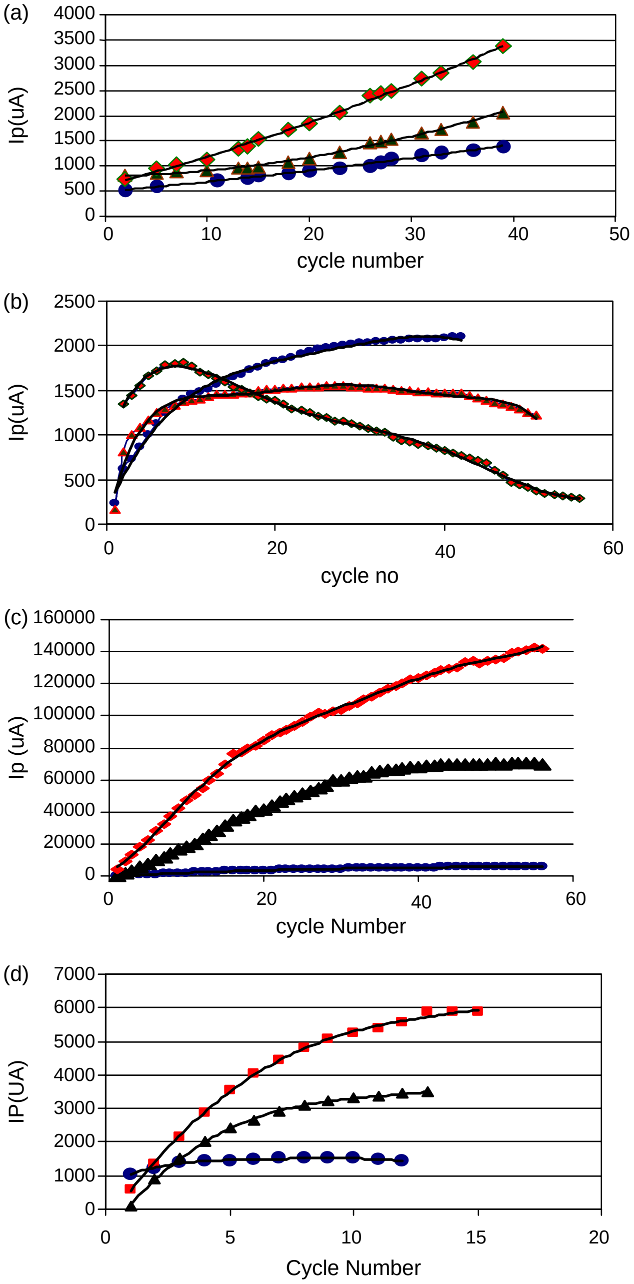

Fig. 3. Dependence of the positive peak current on cycle number (i.e. reaction time) for monomers (a) OT; (b) OEA; (c) OAN; (d) NMA. The reaction conditions were the same as in Fig. 1, except that the concentrations of monomers were (◆) 0.15; (▲) 0.1; and (●) 0.05 M.

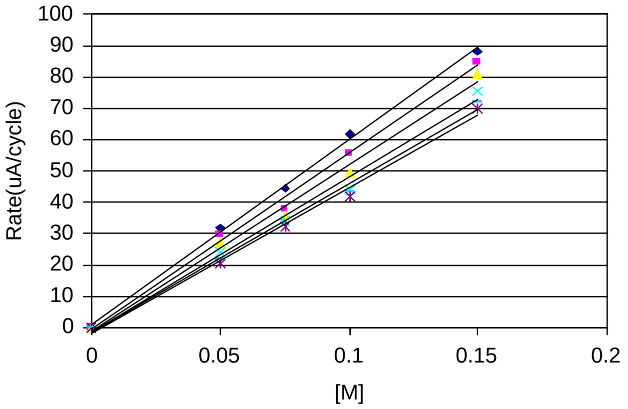

Fig. 4. Plots of the rates of POT formation at various positive peak currents against the concentration of OT monomer.

benzidine rearrangement. Therefore, formation and growth of polymer molecules are stopped.

3.2. Effect of temperature on the rate of polymer formation

In general, the rate of polymerization increases as the temperature is increased. This increase in the rate of reaction is expected to be about 10% per degree increase in temperature according to the Arrhenius equation if the polymer growth itself is first order in POT concentration. The electrochemical polymerization of 0.15 M OT was carried out in 1.0 M HCl aqueous solution at different temperature ranging from 5.0 to 30.0 °C. Fig. 5 presents the Arrhenius plot of logarithmic rate constant of polymer formation reaction (k_{app}) versus $1/T$ which yields a straight line, indicating that the polymerization also obeys the Arrhenius equation. At the reaction temperatures higher than 30 °C, the ln k_{app} deviates slightly from the straight line owing probably to excessive diffusion of the radical cations away from the vicinity of the electrode. The apparent activation energy and preexponential factor are determined to be 28.75 kJ mol^{-1}, and 6.5×10^7, respectively, which corresponds to an increase in the rate of reaction by 4.2% per degree increase in temperature. If the reaction rate is controlled by the diffusion of OT onto the electrode surface, according to Fik's law, the diffusion rate is first order in terms of concentration and the increasing rate is generally in the range of 1.0–1.5% per degree increase in temperature. Increasing the temperature would lead to diffusion of cation radicals away from the surface of electrode and also polymer chains with less favorable structures by α or β-linkages and degradation because higher reactivity of radical cations in higher temperatures. Therefore, by increasing the temperature, rate of mislinkages and diffusion of cation radicals away from the electrode surface increases concurrently with increase of rate of polymer formation. As a result, increase in the rate of polymerization is expected generally to be lower than 10% per degree increase in temperature. The activation energies and preexponential factors are listed in Table 2 for OT, OEA, OAN, and NMA monomers.

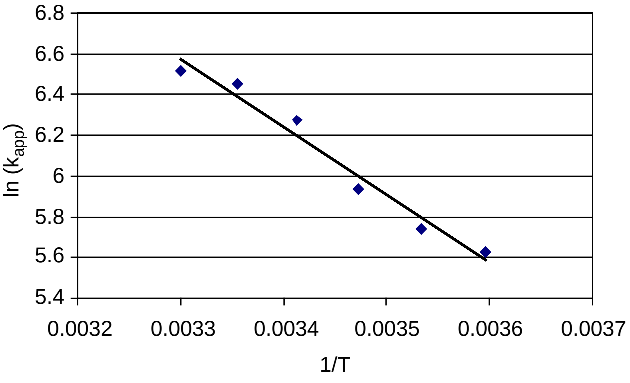

Fig. 5. Plot of ln kapp against $1/T$ for the electrochemical polymerization of OT.

Table 2
Representative activation parameters for the polymerization of aniline derivatives

Monomer	OT	OEA	OAN	NMA
E_a (kJ/mol)	28.75	44.42	17.66	40.30
A	6.5×10^7	5.3×10^9	2.7×10^9	2.11×10^6

It seems there is a disagreement between E_p values and activation energy of OT and NMA. However, it should be noticed that E_p values are related to only the charge transfer process on the surface of the electrode, while, activation energies here reported are related to reaction between radical cations as well as radical cations formation on the surface of the electrode. Then, steric effects can influence the activation energies for the total process of polymer chain growth. In the case of NMA and OEA steric hindrance of substituted alkyl group is higher than the case of OT.

Substituting Eqs. (3) into (1), the overall rate of polymer formation can be expressed as

$$R_p = kI_p^{0.5}[M] + k'[M] \tag{2}$$

In order to evaluate the autoacceleration quantitatively, the k^{app} values were plotted against the $I_p^{0.5}$ (therefore, amount of polymer deposited on the electrode), $[P]$, as shown in Fig. 6. A linear relationship is obtained in the experimental case of OT; k^{app} is proportional to the total amount of POT, $[P]^{0.5}$, while the intercept represents the rate constant, k', for the initiation or nucleation process [17].

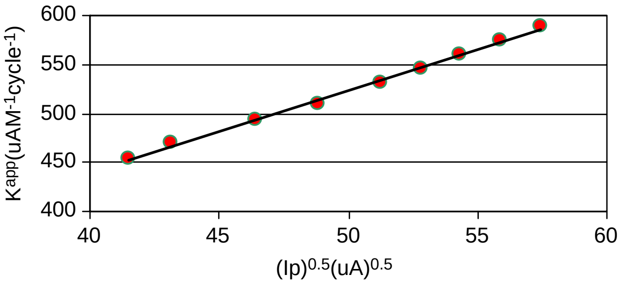

Fig. 6. Relationship of the k^{app} values with $I_p^{0.5}$.

Table 3
Rate constants of electrochemical polymerization of OEA and OAN monomers

	k	k'	k''	n	n'	n''
OEA	0.101067	13062	0.001185	2	2	2
OAN	0.008285	23295	0.000166	2	2	1.92

$$K^{\mathrm{app}} = kI\mathrm{p}^{0.5} + k' \tag{3}$$

where k is the reaction rate constant when the polymer has been deposited on the electrode and k' is the reaction rate constant before polymer is formed on the electrode

In this experiment, k and k' are 105.16 $(\mu\mathrm{A})^{0.5}\mathrm{M}^{-1}\mathrm{cycle}^{-1}$ and 8.38 $\mu\mathrm{AM}^{-1}\mathrm{cycle}^{-1}$, respectively, and the ratio of the two rate constants (k'/k) for POT is $\approx 3.6\times 10^{-3}\mathrm{g}^{0.5}$. Thus, when the amount of polymer on the electrode is grater than $\approx 1.3\times 10^{-5}$ g, the rate of polymer formation mainly dominated by first term in Eq. (2). The values of k and k' we found for POT, in comparison with those resulted by Wei et al. [16] are much smaller and larger, respectively. Both k and k' are functions of switching potential, scan rate, reaction temperature, size of the electrode, pH of the solution and the type and concentration of anions etc. The upper switching potential applied for oxidation of OT by Wei is 0.7 V vs. SCE, whereas, we prepared the polymer by 1.0 V upper limit potential. When the switch potential is increased, amount of the dimeric species generated from the oxidation of monomer is significantly promoted in comparison with the 0.7 V upper potential limit which leads to the acceleration of nucleation rate. Conversely, at the applied potentials grater than 0.7 V vs. SCE polymer could undergo degradation and cross-linking reactions and then the rate of polymer growth decreases. In the case of OEA, OAN, as it can be seen from plots in Fig. 3, in the initial stages of polymerization, rate of polymer growth increases and then with increasing the amount of polymer on the electrode, degradation rate increases and in final stages of potential cycling will prevail over polymer formation and, therefore, the net rate of polymerization decreases. According to this argument the overall rate of polymerization can be expressed as

$$\nu = k[p]^n[M]^{n'} + k'[M]^{n'} - k''[p]^{n''} \tag{4}$$

where k'' is the degradation rate constant. In the initial stages of polymerization the third term in Eq. 4 is negligible because small amount of polymer on the Pt electrode. However, in subsequent potential cycling amount of polymer increases while amount of monomer near to surface of electrode decreases and then the third term can prevail and causes the rate of polymer formation decreases.

In the initial stages of reaction by ignoring the third term Eq. 5 is resulted:

$$\nu = k[p]^n[M]^{n'} + k'[M]^{n'} \approx k_{\mathrm{app}}[M]^{n'} \tag{5}$$

A linear relationship between ν and $[M]^2$ for OEA and OAN was found. Incorporating these account into Eq. 4, k', k'', n, and n'' also can be resulted. These values are tabulated in Table 3.

4. Conclusion

Alkyl and Alkoxy substituted anilines polymerization in 1.0 M HCl solutions by cycling potential between −0.2 to 1.0 V shows that although, presence of electron donating substituent could enhance the rate of polymerization but for getting the higher rate of reaction the anodic cutoff potential should be reduced when the reactivity of the monomer is higher due to the presence of an electron-donating group. A kinetic equation $\nu = k[p]^n[M]^{n'} + k'[M]^{n'} - k''[p]^{n''}$ was employed for the prediction of autoacceleration and degradation processes in the electrochemical polymerization of these aniline derivatives. For all used monomers the third term is negligible when the switch potential is lower than 0.8 V. In the case of OT in which the steric hindrance and electron-donating effect is moderate (relative to OEA, OAN, and NMA) the third term can be neglected even at 1.0 V switch potential. On the other hand, in the case of MEA and MAN, high steric hindrance of alkyl or alkoxy group prevents formation of benzidine or diphenyl amine types of dimmers. Therefore, preferably the hydrazine type dimmer is formed without benzidine rearrangement (due to steric hindrance), then the rate of polymer formation is very slow, so the rate of degradation of polymer in potentials as large as 1.0 V is higher than polymer formation. In the case of OEA, OAN and NMA, in the initial stages of polymerization, rate of polymer growth increases. Then, with increasing the amount of polymer on the electrode, degradation rate increases and in final stages of potential cycling, it will prevails over polymer formation and, therefore, the net rate of polymerization decreases.

Increase in the rate of polymer formation is lower than 10% per degree increase in temperature because of mislinkage, degradation and diffusion of cation radicals away from surface of the electrode.

Finally, by combining the electropolymerization results for the substituted anilines we see that the switch potential has a dramatic effect on the polymerization rate.

The radical cation intermediate generated at the surface of electrode can undergo the reaction with each other to form polymer chain (k_{p}), can form soluble product and diffuse away from the electrode (k_{d}), or can react with solvent (S) or anions (X^-) in the vicinity of the electrode surface (k_{s}). Therefore, the fraction of the radical cation that leads to polymer chains is given by

$$F_{\mathrm{p}} = k_{\mathrm{p}}/k_{\mathrm{p}} + k_{\mathrm{d}} + k_{\mathrm{s}}([S] + [X^-]) \tag{6}$$

Then the electropolymerization will occur when the stability of the radical cation intermediate is such that $k_{\mathrm{p}} \gg k_{\mathrm{d}} + k_{\mathrm{s}}([\mathrm{S}] + [\mathrm{X}^-])$. If the radical cation becomes sufficiently unstable either intrinsically or via a substituent such that k_{s}

becomes grater than $k_p + k_d$, under this condition it reacts indiscriminately with either the solvent or anions at the electrode surface. Thus, the upper cutoff potential for these monomers occur at lower potentials.

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