Kinetic Study of the Electropolymerization of Aniline Using Chronoamperometric Techniques

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Aniline was electropolymerized using constant-potential electrolysis. The chronoamperograms during the electropolymerization definitely had two different time dependences on the electrolytic current. During the initial stage, the current increased with the square root of the electrolysis time, and then increased linearly with the time. Those results were intrinsically the same as those of the electrodeposition of metal ions. To determine the kinetic parameters, the electrolytic current during the polymerization was analyzed on the basis of metal electrodeposition models developed by Fleischmann and Thirsk. The rate constant of the polymerization reaction was found to be directly proportional to the concentration of protons, to the concentration of anions and to the square of the concentration of aniline; also, the rate constant was formulated using the concentrations as well as the electrolysis potential and temperature. The concentration dependence of the rate constant led to the belief that the rate-determining reaction in the polymerization was the electro-oxidation of the dimer of aniline, *p*-aminodiphenylamine.

Keywords Polyaniline, aniline, electropolymerization, chronoamperometry, kinetics

Electropolymerization is now a popular method for synthesizing organic conducting polymers such as polyanilines, polypyrroles and polythiophenes. The polymerization usually proceeds according to Faraday's law as if metal deposition were taking place. During the initial stage of such polymerization, the polymer growth on the electrode surface is also very similar to the nucleation process of metal deposition. The nucleation processes of the conducting polymers have been reported for polyaniline¹, polypyrrole² and polythiophene.³ However, kinetic studies of the nucleation processes have been very limited. If the kinetics of an electropolymerization reaction could be elucidated, not only the nature of the reaction, but also the chemical structure of the obtained polymer would be revealed. Besides, both the nature and structure are significant information for controlling the physical properties, such as the electrical conductivity, which are practically important properties. An attempt to formulate the rate constant of the electropolymerization of aniline is made in this paper.

If the electrical conductivity of polyanilines could be enhanced, their useful functions would be effectively expanded. In contrast to polypyrroles and polythiophenes, polyaniline is electrically conducting only when it is prepared in acidic solutions.⁴ There is no doubt that protons as well as dopant anions participate in the electropolymerization reactions. In other words, the

electrical conductivity depends greatly on both the degree of protonation and the amount of the dopant anions. The kinetic parameters of the polymerization reaction therefore provide helpful information for enhancing the conductivity, though this seems to perhaps be a circuitous route.

The morphologies of polyanilines influence the mechanical properties and the conductivity of the obtained polyanilines. It has been reported that an electropolymerized polyaniline film consists of two different layers: a compact layer formed on the electrode surface during the initial stage of electropolymerization, and a less dense layer grown on a compact layer.⁵ Each layer governs the conductivity of the whole film. The two nucleation processes are probably different. We will examine whether or not the two nucleation processes have different kinetics.

The rate-determining reaction is also suggested in this paper based on the rate constant formulated from the kinetic parameters of the electropolymerization reaction of aniline. The rate-determining reaction is a key factor in the effective preparation of new polyanilines. Although we electro-oxidized several aniline derivatives in acidic solutions to prepare new polyanilines other than polyaniline, only a few new polyanilines were obtained.⁶ There is a possibility of preparing new functional polyanilines by electro-oxidation of aniline derivatives under appropriate electrolysis conditions based on the rate-determining reaction.

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Experimental

The aniline (Katayama Kagaku Kogyo Co.) was reagent grade and was used after distilling under reduced pressure. Other chemicals were of reagent grade and were used as received without further purification. Water was purified with an Auto-Still WG-22 system (Yamato Co.) and used within a few hours. Aqueous electrolyte solutions were prepared from the distilled water. Twenty test solutions to be electropolymerized were prepared: (a) eight solutions with different aniline concentration, $[\text{aniline}] = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7,$ and 0.8 M ; (b) six solutions with different Cl^- concentration, $[\text{Cl}^-] = 0.57, 0.87, 1.07, 1.37, 1.57,$ and 2.57 M ; (c) six solution with different pH, $\text{pH} = 0, 0.5, 1.0, 1.5, 2.0,$ and 2.5 . The (a) solutions were pH 1 Walpole buffer solutions ($1 \text{ M CH}_3\text{COONa} : 1 \text{ M HCl} : \text{H}_2\text{O} = 5 : 7 : 13$) and $[\text{Cl}^-]$ was kept at 1.76 M by the addition of KCl . The (b) solutions were buffer solutions containing 0.2 M aniline and different amounts of KCl . The (c) solutions were buffer solutions containing 0.2 M aniline and 1.76 M Cl^- ; the pH value was adjusted by regulating the composition of each component of the buffer solution.

A conventional three-electrode system was employed for the oxidative electropolymerization of aniline and electrochemical measurements. All electrolyses were performed in an H-shaped two-compartment cell. A Pt wire electrode was used as the test electrode throughout. The electrode was a 1 mm Pt wire, sealed in a glass tube, with a small glass globe at the lower end (total electrode area $= 0.510 \text{ cm}^2$). A saturated calomel electrode (SCE) was used as the reference electrode and a Pt plate having an electrode area of about 8 cm^2 as the counter electrode. Prior to use, the Pt wire electrode was treated with aqua regia for 30 s and then polarized by repeated potential cycling between -0.2 and 1.25 V vs. SCE in $0.1 \text{ M H}_2\text{SO}_4$ until it gave a voltammogram showing the features associated with hydrogen adsorption/desorption and oxide formation/removal.⁷ The SCE was connected to the cell by means of a salt bridge filled with saturated KCl solution. The solution level in the calomel compartment was lower than the level in the working cell, so that contamination by chloride ions was prevented.

Electrolyses were carried out using a potentiostat/galvanostat (Model HA-301, Hokuto Denko Co.) with a potential scanner (Model HB-104, Hokuto Denko Co.). The chronoamperograms during the electropolymerization were monitored and recorded by an $x-t$ recorder (Model R-61K, Rikadenki Co.). During the electrolysis, a nitrogen environment was maintained above the electrolyte solution. The temperature of the electrolysis cell was maintained at the desired temperature with a Yamato BL-22 water bath.

In various stages of the electropolymerization, the microstructures of the polyaniline electrodeposited on the electrode surface were observed using a Hitachi S-800 scanning electron microscope (SEM).

Results and Discussion

For the electropolymerization of pyrrole, thiophene and aniline, the polymer growth on the electrode surface is reported to be very similar to the nucleation process of metal electrodeposition. The polymer growth processes of polypyrrole² and polythiophene³ in acetonitrile were examined on the basis of the metal electrodeposition theory. The electropolymerization of aniline also includes a nucleation process similar to the nucleation process in metal electrodeposition.⁸ Although the nucleation processes are described in several papers, their kinetic studies have been very limited. The rate constant has not yet been formulated using the electrolysis potential, the electrolysis temperature and the concentrations of monomer, dopant anions and protons. A formulation is the aim of this paper.

We have succeeded in preparing several conducting polyanilines by the electro-oxidation of aniline derivatives in acidic solutions.⁶ Among the polyanilines, polyaniline and poly(*N*-methylaniline) have a much higher electrical conductivity than that of other polyanilines.^{6,9} The high conductivity is strongly related to the electropolymerization mechanism. We have revealed that the electropolymerization of both polyaniline¹⁰ and poly(*N*-methylaniline)¹¹ is not a radical-coupling polymerization, but an incorporation-oxidation polymerization, shown schematically in Fig. 1. The incorporation-oxidation polymerization proceeds as follows. During the initial stage, a seed polymer of low molecular weight is electrodeposited on the electrode surface. The seed polymer is electro-oxidized and cation radicals are generated in the seed polymer.

(a) Very initial stage

(b) Deposition of P_{low}

(c) Incorporation-oxidation polymer growth

Fig. 1 Schematic depiction of incorporation-oxidation polymer growth. P_{low} : electrodeposited seed polymer of low molecular weight. M : monomer.

Fig. 2 Chronoamperogram during the electropolymerization of aniline in a Wolpole buffer solution containing 0.5 M aniline, 1.76 M Cl^- . Electrolysis potential: 0.8 V vs. SCE. Electrolysis temperature: 30°C. Solution pH: 1.0.

The cation radicals oxidize dissolved monomers and incorporate the oxidized monomers.

Very recently, we found that in the incorporation-oxidation polymerization the electrodeposited amount of polymer is found to obey Faraday's law.¹² This fact enables us to determine the kinetic parameters by analyzing the chronoamperograms during electropolymerization. Figure 2 shows a typical chronoamperogram during electropolymerization. During the initial stage, the anodic current slightly decreases and then increases with the square of the electrolysis time. This behavior is also seen for the electropolymerization of pyrrole² and thiophene.³ The slight decrease in the current is attributed to the formation of a uniform polyaniline film through the radical-coupling polymerization shown in Fig. 1. In radical-coupling polymerization, the current is controlled by the diffusion of aniline, and a slight current decrease is observed. In addition, the charging current of the electric double layer was subtracted from the current for the polymerization. In contrast to the chronoamperograms for polypyrrole and polythiophene, it is interesting to find that even after the initial stage the anodic current continues to increase with the electrolysis time. The nucleation processes in the initial stage (first stage) and after the initial stage (second stage) correspond to two-dimensional growth of progressive nucleation and one-dimensional growth of progressive nucleation in metal electrodeposition.¹³ For those two cases, the overall rate constant for the growth process (defined in $\text{mol cm}^{-2} \text{s}^{-1}$) (k) is dependent of the electrolytic time (t), and the electrolytic current (i) is given by

$$i = zF\pi MhAN_0k^2t^2/\rho, \quad (1)$$

Fig. 3 Scanning electron microscope pictures of polyaniline electrodeposited on a Pt plate electrode: (a) at the first stage (deposited amount=80 mC cm^{-2}) and (b) at the second stage (deposited amount=170 mC cm^{-2}).

$$i = zFAN_0Sk t, \quad (2)$$

respectively, where z is the electron-transfer number per activated complex, F the Faraday's constant, M the atomic weight, h the height of the cylindrical center, A the nucleation rate constant, N_0 the total number of nucleation sites, ρ the density and S the surface area.

Figure 3 shows the morphologies of the polyaniline surfaces of the first and second stages. In the first stage, polyaniline fibrils grow two-dimensionally on the electrode surface (a). After the entire electrode surface is covered with a network of the polyaniline fibrils, the network grows one-dimensionally toward the bulk solution (b). Although neither Eq. (1) nor (2) can be directly applied to an analysis of the chronoamperograms during electropolymerization, the dependence of k on the current is intrinsically the same as in the case of metal electrodeposition; additionally, both k and k' depend on five parameters: [aniline], $[\text{Cl}^-]$, $[\text{H}^+]$, the electrolysis potential (E) and the electrolysis temperature (T).

$$i \propto k^2t^2 \quad (\text{first stage}), \quad (3)$$

$$i \propto k't \quad (\text{second stage}), \quad (4)$$

To examine the dependences of [aniline], $[\text{Cl}^-]$, $[\text{H}^+]$ and E for k , the chronoamperograms were analyzed using the normalized current (i_N) and time (t_N) as shown in Fig. 4. A slight decrease during the very initial stage

Fig. 4 Normalized electrolysis time (t_N) and anodic current (i_N). $t = t - t_0$, $i_N = i - i_0$

of the chronoamperograms in Fig. 2 is probably due to the formation of a seed polymer by the radical coupling of a monomer. Nucleation starts at t_0 and the current for the analysis should be taken from the minima (i_0).

$$t_N = t - t_0 \quad (5)$$

$$i_N = i - i_0 \quad (6)$$

To analyze the kinetics of the first stage, we introduce an apparent rate constant, k_{app} . It is possible to evaluate k_{app} ,

$$k_{app} = i_N t_N^{-2}, \quad (7)$$

from the slope of the i_N vs. t_N^2 plots. For example, Fig. 5 shows the i_N vs. t_N^2 plots from Fig. 2, and k_{app} is found to be $1.41 \times 10^{-3} \text{ mA cm}^{-2} \text{ s}^{-2}$. Similarly, for the twenty test solutions described in the Experimental section, k_{app} was evaluated from each chronoamperogram. Figure 6 shows $\log k_{app}$ vs. $\log[\text{aniline}]$ plots. They show a straight line and the slope is 3.5. In addition, the slope value was almost the same when $E=0.75, 0.70, 0.65$ and 0.6 V . A linear relationship was also obtained for the $\log k_{app}$ vs. $[\text{Cl}^-]$ plots, for the $\log k_{app}$ vs. $[\text{H}^+]$ plots and for the $\log k_{app}$ vs. E plots. The slope values are summarized in Table 1. From each slope value, k_{app} can be expressed by

$$k_{app} \propto [\text{aniline}]^{3.5} [\text{Cl}^-]^{2.4} [\text{H}^+]^{1.6} \exp(2.303 \times 15.82E). \quad (8)$$

Because k_{app} is intrinsically proportional to k^2 (Eq. (3)), k is formulated for the first stage by the following equation,

Fig. 5 i_N vs. t_N^2 plots obtained from the chronoamperogram shown in Fig. 2.

Fig. 6 Logarithmic relationship between the apparent rate constant (k_{app}) and the concentration of aniline, $[\text{aniline}]$, for the first stage.

Table 1 Slope values of the $\log k_{app}$ vs. $[\text{aniline}]$, $[\text{Cl}^-]$, $[\text{H}^+]$ and E plots in the first stage

Relationship	Slope	Correlation coefficient
$\log k_{app}$ - $[\text{aniline}]$	3.5	0.9946
$\log k_{app}$ - $[\text{H}^+]$	1.6	0.99995
$\log k_{app}$ - $[\text{Cl}^-]$	2.4	0.98537
$\log k_{app}$ - E	15.82	0.99517

where A_0 is a constant and R is the gas constant:

$$k = A_0 [\text{aniline}]^{1.8} [\text{Cl}^-]^{1.2} [\text{H}^+]^{0.8} \exp(0.48FE/RT). \quad (9)$$

Table 2 Slope values of the $\log k'_{\text{app}}$ vs. [aniline], $[\text{Cl}^-]$, $[\text{H}^+]$ and E plots in the second stage

Relationship	Slope	Correlation coefficient
$\log k'_{\text{app}}\text{--}[\text{aniline}]$	2.1	0.99361
$\log k'_{\text{app}}\text{--}[\text{H}^+]$	1.1	0.99605
$\log k'_{\text{app}}\text{--}[\text{Cl}^-]$	1.4	0.99653
$\log k'_{\text{app}}\text{--}E$	8.70	0.97639

A kinetic analysis of the second stage was carried out in a similar manner. Another apparent rate constant (k'_{app}) was introduced for the analysis. Each k'_{app} value was determined by

$$k'_{\text{app}} = i_N t_N^{-1} \quad (10)$$

the slope of the i_N vs. t_N plots from the corresponding chronoamperogram. The logarithmic relationships between k'_{app} and [aniline], $[\text{Cl}^-]$, $[\text{H}^+]$ and E were examined. The respective slope values are given in Table 2. The slope values lead to Eq. (11). Because k'_{app} is directly proportional to k'

$$k'_{\text{app}} \propto [\text{aniline}]^{2.1} [\text{Cl}^-]^{1.4} [\text{H}^+]^{1.1} \exp(2.303 \times 8.659 E) \quad (11)$$

(Eq. (4)), k' is derived from Eq. (11), where A_0' is a constant.

$$k' = A_0' [\text{aniline}]^{2.1} [\text{Cl}^-]^{1.4} [\text{H}^+]^{1.1} \exp(0.53 FE/RT) \quad (12)$$

Although the concentration dependences are apparently non-stoichiometric in Eqs. (9) and (12), they are probably regarded as stoichiometric because of the following reason. We have assumed that the nucleation processes of the first and second stages obey Eqs. (1) and (2). In fact, however, higher-dimensional growth of progressive nucleation must take place, though slightly; three-dimensional growth in the first stage and two-dimensional growth in the second stage. According to the theory about metal deposition described previously¹³, k_{app} is proportional to k^3 in the first stage and to k^2 in the second stage. Therefore, the dimensions of the concentrations are estimated highly, and the stoichiometric relations are given by

$$k = A_0 [\text{aniline}]^2 [\text{Cl}^-] [\text{H}^+] \exp(0.48 FE/RT), \quad (13)$$

$$k' = A_0' [\text{aniline}]^2 [\text{Cl}^-] [\text{H}^+] \exp(0.53 FE/RT). \quad (14)$$

It is noteworthy that k and k' have almost the same concentration dependence for aniline, Cl^- and H^+ . This implies that the rate-determining reaction is the same during the electropolymerization. In other word, the electropolymerization reaction is the same in the first and second stages. Therefore, the different nucleation processes in the first and second stages are probably due to a physical properties of the growing polyaniline film,

electric conductivity. During the very initial stage of polymerization, a compact layer is formed on the entire electrode surface. Although the electric field is applied from the electrode to the bulk in the polymerizing solution, the nucleation occurs two-dimensionally because of the high electric conductivity of the compact layer. In the second stage, the thickness of the film is higher, and the conductivity becomes lower. The low conductivity prefers one-dimensional nucleation to two-dimensional nucleation. From the concentration dependence of the rate constant, we speculate about the reaction mechanism in the rate-determining step (Eq. (15)), which is the same in the first and second stages. Although the activated complex is a matter of dispute (Eq. (15)) it is consistent with the concentration

dependence. Monomeric aniline is converted into hydrazobenzene through the activated complex, and the rearrangement of hydrazobenzene yields *o*- and/or *p*-aminodiphenylamine. Although the rearrangement of hydrazobenzene is well-known as the benzidine rearrangement, *o*- and/or *p*-aminodiphenylamines are formed instead of benzidine when hydrazobenzene is substituted with electron-withdrawing groups. The activated complex is the dication of hydrazobenzene, and it is readily subject to the electronic environment.¹⁴ An electron-withdrawing environment results in the formation of *o*- and/or *p*-aminodiphenylamines. Polyaniline polymeric chains have amine and/or imine nitrogens, and the nitrogens are protonated in an acidic solution.¹⁵ The positively charged nitrogens act as an electron-withdrawing environment, and the rearrangement of hydrazobenzene at the active sites of polyaniline mainly yields *o*- and/or *p*-aminodiphenylamines. In addition, the formation of *p*-aminodiphenylamine is presumably dominant because of the electrostatic repulsion of the activated complex, the dication of hydrazobenzene. The fact that the main product in the polymerizing solution is found to be *p*-aminodiphenylamine¹² is evidence, though indirect.

The mechanism (Eqs. (15) to (18)) is energetically favorable for electropolymerization. Figure 7 shows the cyclic voltammograms of aniline, *p*-aminodiphenylamine and polyaniline. It should be noted that, in general, the oxidation potential of polymer-forming materials decreases in the order monomer > dimer > trimer > ... > polymer.^{16,17} It is thermodynamically

Fig. 7 Cyclic voltammograms of 0.5 mol dm^{-3} aniline (----), 0.1 mol dm^{-3} *p*-aminodiphenylamine (.....) and electrodeposited polyaniline (—) in $0.1 \text{ M H}_2\text{SO}_4$ at 100 mV s^{-1} .

unfavorable for monomeric aniline to be directly oxidized by the cation radical generated in the electrodeposited polyaniline, because the oxidation potential of aniline is much higher than that of polyaniline. In contrast to aniline, the oxidation potential of the dimer (*p*-aminodiphenylamine) is lower than the second oxidation potential of polyaniline. As a result, the cation radicals generated in the deposited polyaniline oxidize the dimer, and polymerization proceeds. The activated complex for electropolymerization determines the chemical and physical properties of the obtained polyaniline, and the detailed nature of the complex needs to be elucidated.

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