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Electrochemical Study on the Initial Stages of the Electropolymerization of 1-Pyrenamine in Acetonitrile

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The kinetic study of the mechanism for the reaction of the initial stages of the electropolymerization of 1-pyrenamine (PA) in an acetonitrile solution was carried out by cyclic voltammetry (CV) and double potential-step chronoamperometry (DPSCA). The experiments were conducted at various time windows (i.e., at various scan rates of CV and various potential-step widths of DPSCA) and under the conditions of the presence or absence of the basic or acidic additives (pyridine, 2,6-lutidine, trifluoroacetic acid). As a result, it was found that the mechanism of the reaction of the initial stages of the electropolymerization of PA is an "ECE" mechanism, and that the chemical reaction interposed between successive electron transfers is considered as the radical–radical coupling reaction rather than the radical–parent monomer coupling reaction. The second-order rate constant for the radical–radical coupling reaction was estimated to be $(1.0\pm0.8)\times10^5\ M^{-1}\,s^{-1}$ ($1\ M=1\ mol\ dm^{-3}$). The cyclic voltammetric responses for the oxidation of PA were varied by the presence or absence of the basic or acidic additives. This can be explained considering the basicity of the additives and their influences in the deprotonation reactions following the heterogeneous electron-transfer step.

One of the most active areas in a recent electrochemical research deals with "electropolymerization."[1–60] The attractiveness of electropolymerization stems not only from its potentiality in the synthesis[27–44] of new organic conducting, semiconducting or nonconducting polymers, but also from the point of the modification of electrode surfaces.[1–26] A number of recent papers[1–60] on electropolymerization are concerned with the preparation of polymeric compounds, the characterization of their electrochemical, electrical, physicochemical, spectroscopic and other kinds of properties, and the applications of "composite electrode materials" produced by the modification of electrode surfaces by electropolymerization. In contrast, there have been only a few papers[38,45,46,55,61–63] concerning the studies of the mechanism of electropolymerization.

It seems to be quite difficult (or impossible) to elucidate quantitatively the whole mechanism of the electropolymerization of a given monomer, since in general many reaction steps are involved in the chemical polymerization reaction, as being apparent from the fact that it can be regarded as "chain reactions." However, the electropolymerization occurs at and/or in the vicinity of electrode surface and at least the first step of the polymerization (i.e., dimerization) can be considered as "follow-up chemical reaction" from a viewpoint of the mechanism of electrode reaction.[65] In other words, in the initial step of electropolymerization the initiators for polymerization (they are usually radical ions) are first produced at electrode surface by the heterogeneous electron-transfer reaction of parent monomers and then dimerization and any higher polymerization proceed at and/or in the vicinity of electrode surface. Many electrochemical methods which are suitable for the study of such chemical reactions coupled to the heterogeneous electron-transfer have been ever developed.[66]

In this paper, we report the kinetic study of the mechanism of the reaction of the initial stages in the electropolymerization of 1-pyrenamine (PA, Fig. 1) in an acetonitrile solution by means of cyclic voltammetry (CV) and double potential-step chronoamperometry (DPSCA) which have proved to be useful for the study of the chemical reactions which are associated with heterogeneous electron-transfer reaction proper.[66–69] Recently, we[36] have reported the preparation of poly(1-pyrenamine) (PPA) film by the electropolymerization of PA, the characterization of its electrochemical, physicochemical and electrical properties,and the spectroscopic identification of the structure of the PPA film. The electrochemical responses obtained for the initial step of the electropolymerization of PA seem to be simple compared with other monomers (e.g., aniline and pyrrole). This is the first reason why we chose PA as the first candidate for the examination of the mechanism of electropolymerization. The second reason is that the first dimerization reaction, regarded as a follow-up chemical reaction, is not so fast and thus DPSCA can be applied to the determination of the rate constant of the dimerization reaction. In addition, the third reason is that no study has been reported on the mechanism of the initial-step

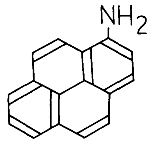

Fig. 1. Structure of 1-pyrenamine.

reactions in the electropolymerization of PA. It will be shown that the mechanism of the reaction of the initial stages in the electropolymerization of PA is an "ECE" mechanism, and that the chemical reaction interposed between successive electron transfers is considered as the radical-radical coupling reaction rather than the radical-parent monomer coupling reaction.

Experimental

Materials. 1-Pyrenamine (PA) (Aldrich Chemical Co.) was purified by the procedure described previously.[36] Acetonitrile (Wako Pure Chemical Industries, LTD) was distilled by ordinary technique after dehydration on molecular sieves (5A 1/16, Wako). Pyridine (Wako) of reagent grade was twice distilled under reduced pressure. Tetrabutylammonium tetrafluoroborate ($(n\text{-}C_4H_9)_4NBF_4$, $TBABF_4$) (Tokyo Kasei Co.) was of reagent grade. The basal-plane pyrolytic graphites (BPG) (Union Carbide Co.) were used as electrodes.[36] All other chemicals were of reagent grade and were used as received without further purification.

Apparatus and Procedures. A standard three-electrode electrochemical cell was used for all electrochemical experiments. The electrode assembly consists of a BPG disk electrode (area; 0.20 cm^2) as working electrode, a sodium chloride saturated calomel electrode (SSCE) as reference electrode and a spiral platinum wire as counter electrode. The compositions of the electrolytic solutions were 0.2 M $TBABF_4$+1—10 mM PA+0—25 mM pyridine (or CF_3COOH or 2,6-lutidine) in acetonitrile.

For cyclic voltammetry and double potential-step chronoamperometry (DPSCA), a home-made instrument was employed. The experiments of DPSCA were conducted according to the previously described procedure.[69] The width (τ) of the applied potential pulse was varied from 0.5 to 100 ms. An IR compensation was employed. The current-time responses of DPSCA were monitored and stored on a Nicolet 3091 oscilloscope and then the enlarged current-time curves were displayed on an X-Y recorder (Graphtec Co. WX 4403). The analysis of DPSCA's data was carried out according to the procedure originally suggested by Schwarz and Shain[70].

All experiments were run under nitrogen atmosphere at laboratory temperature (25±1°C). Potentials were measured and are quoted with respect to SSCE.

Results

Cyclic Voltammetry. The typical cyclic voltammograms obtained at a BPG disk electrode in an acetonitrile solution containing 0.2 M $TBABF_4$+5 mM PA are shown in Fig. 2, where to prepare a fresh electrode surface the BPG electrode was cut parallel to the eletrode surface with a scalpel each measurement. In the first forward potential scan at 10 V s^{-1} the anodic peak can be observed at ca. 0.65 V vs. SSCE. This peak is considered to correspond to the oxidation of PA to the corresponding cation radical ($PA^{\dagger}$).[84] When the electrode potential was scanned to more positive potentials than 0.65 V vs. SSCE, additional anodic peaks were obtained.[36] From the viewpoint of polymer formation, the potential application of about 0.8 V vs. SSCE to the working electrode is enough to lead to the electropolymerization of PA at electrode surface. When the electrode potential was turned to negative, the cathodic peak corresponding to the anodic peak at 0.65 V vs. SSCE was observed at 0.55 V vs. SSCE, though the peak current is much smaller than the anodic one due to the consumption of the electrogenerated $PA^{\dagger}$ by the follow-up chemical reaction. Furthermore, the cathodic peak at ca. 0.3 V corresponds to the reduction of the oxidized forms of the dimeric, oligomeric, and/or polymeric products which can be considered to be formed from the electrogenerated $PA^{\dagger}$'s and/or PA's during the period (ca. several tens ms) of the potential scan from ca. 0.5 V to 0.8 V and then to ca. 0.5 V at 10 V s^{-1}. During the second forward scan, the new anodic peak is observed at ca. 0.4 V and corresponds to the cathodic peak at 0.3 V. In the further potential cycling between −0.5 and 0.8 V, two anodic peaks and two cathodic ones are obtained as shown in Fig. 2A. The peak currents at 0.55 and 0.65 V tend to decrease with the potential cycling, while the peak currents at 0.3 and 0.4 V tend to increase with the cycling of electrode potential. This suggests that the electroactive products deposite onto the electrode surface and at the same time the diffusion of PA monomers to the electrode surface through the deposited product layer becomes more difficult.[36]

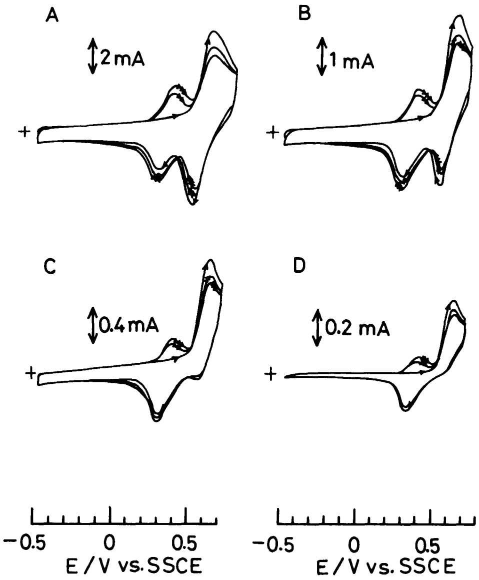

Fig. 2. Scan rate dependence of cyclic voltammograms obtained at a BPG disk electrode in an acetonitrile solution containing 0.2 M $TBABF_4$ and 5.0 mM PA. Scan rate: (A): 10, (B): 5.0, (C): 1.0, and (D): 0.2 Vs^{-1}. Electrode area: 0.20 cm^2.

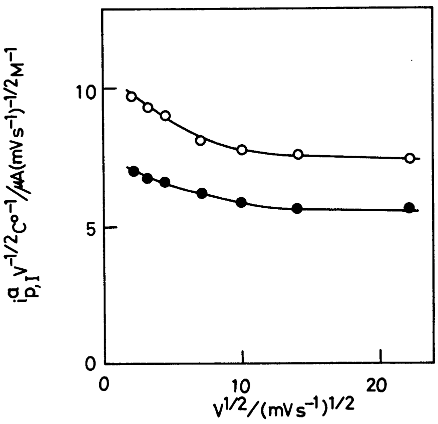

Fig. 3. Dependence of $i^a_{p,I}/v^{1/2}C^{\circ}$ on potential scan rate ($v^{1/2}$) at different concentrations of PA. Concentration of PA (C°): (○): 1.0 mM, (●): 5.0 mM. Other experimental conditions are the same as in Fig. 2.

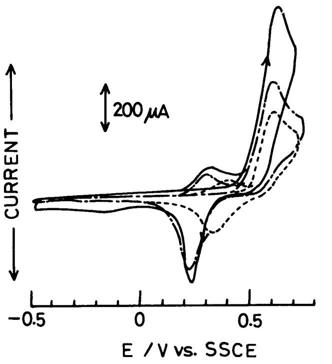

Fig. 4. Cyclic voltammograms of PA and PA–pyridine mixtures. Concentration of PA: 5.0 mM. Concentration of pyridine: (——): 25.0, (– – –): 2.5, and (----): 0 mM. Scan rate: 100 mV s^{-1}. Other experimental conditions are the same as in Fig. 2.

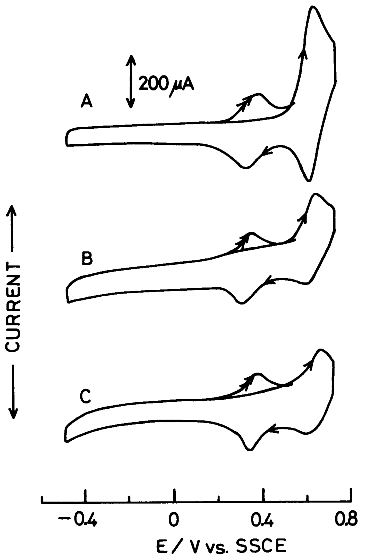

Fig. 5. Cyclic voltammograms of PA in the presence and absence of CF_3COOH. Concentration of PA: 1.0 mM. Concentration of CF_3COOH: (A): 0, (B): 1.0, and (C): 10.0 mM. Scan rate: 1 V s^{-1}. Other experimental conditions are the same as in Fig. 2.

Furthermore, it is apparent from Fig. 2 that the peak current ratio of the cathodic peak current ($i^c_{p,I}$) corresponding to the reduction of $PA^{+\cdot}$ to the anodic peak current ($i^a_{p,I}$) corresponding to the oxidation of PA decreased with decreasing the potential scan rate (v) and at v=0.2 V s^{-1} the $i^c_{p,I}$ was not substantially observed. Also, the values of $i^a_{p,I}/C^{\circ}v^{1/2}$ (C°: concentration of PA) decreased with $v^{1/2}$ in a way which is dependent on C° (Fig. 3). This behavior is taken as an indication that the chemical complication that follows the electron transfer may have a higher than first-order kinetics. These results suggest that the follow-up chemical reactions which consume the electrogenerated $PA^{+\cdot}$'s occur at and/or in the vicinity of the electrode surface on the time scale of this experiment.

Figure 4 shows the effect of the addition of various amounts of pyridine into the electrolytic solution upon the cyclic voltammetric response of PA. An increase of pyridine concentration produces an increase in $i^a_{p,I}$ towards a value corresponding to a two-electron electrode reaction. A similar result was obtained when 2,6-lutidine was used instead of pyridine. The effect of an acidic medium was also studied by addition of anhydrous CF_3COOH to the electrolytic solutions. The results are shown in Fig. 5. Increasing amounts of CF_3COOH produced a decrease in $i^a_{p,I}$, while the peak potential ($E^a_{p,I}$) shifted to more positive values. This was expected, since in an acidic medium the free amine forms a protonated species which is electrochemically inactive.

Double Potential-Step Chronoamperometry (DPSCA). Figure 6 shows the typical current-time curve obtained in the DPSCA's experiment of the PA system. In this case, the electrode potential (E_1) was first set at the potential region where no oxidation of PA occurs substantially and then the potential was stepped to the potential (E_2) at which the oxidation of PA is diffusion-controlled and for a given period (τ) the electrode potential was held at this potential, and after that the electrode potential was re-stepped to the potential (E_3) at which the reduction of the electrogenerated $PA^{+\cdot}$ is diffusion-controlled. Typically, E_1=−0.2 V, E_2=0.7 V, and E_3=0.4 V vs. SSCE. However, it is not easy to choose appropriately the potentials E_2 and E_3, as can be seen from the cyclic voltammograms shown in Fig. 2. The reasons are as follows: (i) the potential regions corresponding to E_2 and E_3 are narrow due to the occurrence of the succeeding oxidation or reduction process and (ii) the peak potentials ($E^c_{p,I}$ and $E^a_{p,I}$) corresponding to $i^c_{p,I}$ and $i^a_{p,I}$ shift to more cathodic and anodic potentials, respectively, with shortening the time window of the

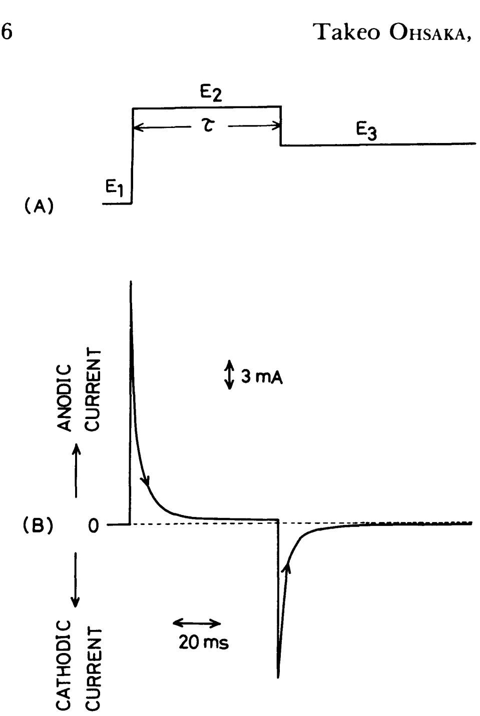

Fig. 6. (A) Typical potential-step mode used in the DPSCA measurement of the PA system. $E_1=-0.2$, $E_2=0.7$, and $E_3=0.4$ V vs. SSCE. Potential-step width (τ): 60 ms. (B) The current-time curve obtained for the potential-step application shown in A. Solution composition: 0.2 M $TBABF_4$+1.0 mM PA in acetonitrile. Electrode area: 0.20 cm^2.

measurement (i.e., τ). The latter phenomenon is apparent from Fig. 2 and is due to the fact that the electrode reaction of the $PA/PA^{\dagger}$ redox couple is not completely reversible on the time scale of the measurement. To overcome these problems, the cyclic voltammogram of PA was observed at the scan rate which corresponds to the time scale of each DPSCA's experiment and then on the basis of the obtained cyclic voltammogram the most reasonable E_2 and E_3 potentials were chosen. Furthermore, by changing slightly the E_2 and E_3 potentials, the DPSCA's measurement was repeated. The current-time response obtained for the forward potential step, during which the oxidation of PA to $PA^{\dagger}$ occurs, was found to nearly obey the chronoamperometric Cottrell equation, that is, a plot of i vs. $t^{-1/2}$ was almost linear and passed the origin.[66]

From the cyclic voltammetric behavior shown in Fig. 2, we assumed that the mechanism of the reaction of the initial stages of the electropolymerization of PA is apparently the "ECE" mechanism, that is, the oxidation reaction of PA to $PA^{\dagger}$ (E), the follow-up chemical reaction consuming $PA^{\dagger}$ (C) and the reduction (and oxidation) of the product (i.e., dimer) produced by the follow-up chemical reaction (E) occur continuously. We can assume various mechanisms for such chemical reactions interposed between successive electron transfers.[66,67] In this study, the mechanisms of the most popular two types were suggested for the follow-up chemical reaction; "radical-radical coupling" reaction and "radical-parent monomer coupling" reaction. Thus, the following two ECE mechanisms were assumed for the initial stages of the electropolymerization of PA.

Mechanism I:

$$A \overset{E_1^{0\prime}}{\rightleftarrows} B \tag{1}$$

$$2B \xrightarrow{k} C \tag{2}$$

$$C \overset{E_2^{0\prime}}{\rightleftarrows} D \tag{3}$$

Mechanism II:

$$A \overset{E_1^{0\prime}}{\rightleftarrows} B \tag{1}$$

$$A + B \xrightarrow{k} C \tag{2'}$$

$$C \overset{E_2^{0\prime}}{\rightleftarrows} D \tag{3}$$

where Eqs. 1 and 3 show the heterogeneous electron-transfer reactions of the A/B couple and the C/D couple, respectively, the formal oxidation-reduction potentials of which are $E_1^{0\prime}$ and $E_2^{0\prime}$, respectively and $E_2^{0\prime}<E_1^{0\prime}$, and Eqs. 2 and 2′ indicate the chemical reactions which proceed at and/or in the vicinity of electrode surface. In the present case, A, B, C, and D correspond to PA, $PA^{\dagger}$, $(PA)_2$ and $(PA)_2^{\dagger}$, respectively, where $(PA)_2$ and $(PA)_2^{\dagger}$ are the dimer of PA and its cation radical, respectively.

The distinction between Mechanism I and Mechanism II is possible by analyzing the dependence of the current ratio $i^c(t=2\tau)/i^a(t=\tau)$ on $\log(kC^{\circ}\tau)$,[67] where $i^c(t=2\tau)$ and $i^a(t=\tau)$ show the cathodic current (at $t=2\tau$) for the reduction of $PA^{\dagger}$ to PA and the anodic current (at $t=\tau$) for the oxidation of PA to $PA^{\dagger}$, respectively, in the DPSCA's current-time curves, τ is the potential-step width, and k is the apparent rate constant of the reactions expressed by Eqs. 2 and 2′. The theoretical curves[67] representing the relations between $i^c(t=2\tau)/i^a(t=\tau)$ and $\log(kC^{\circ}\tau)$ for Mechanisms I and II are shown in Fig. 7 together with the experimental plots. As can be expected from these theoretical curves,[67] the examination of the dependences of $i^c(t=2\tau)/i^a(t=\tau)$ on $\log(kC^{\circ}\tau)$ at larger values of $\log(kC^{\circ}\tau)$ allowed us to determine which of the two mechanisms more suitably applies to the initial stages of the follow-up chemical reaction. The experimentally available quantity $i^c(t=2\tau)/i^a(t=\tau)$ is plotted vs. $\log(C^{\circ}\tau)$. By overlaying the experimental and theoretical plots and by appropriately shifting the experimental plot along the abscissa and ordinate of the theoretical plot, the two can be superimposed. The relative location of the experimental and theoretical axes permits the evaluation of the rate constant, k.

The resulting plots of $i^c(t=2\tau)/i^a(t=\tau)$ vs. $\log(C^{\circ}\tau)$ seem to fall on a continuous curve which represents

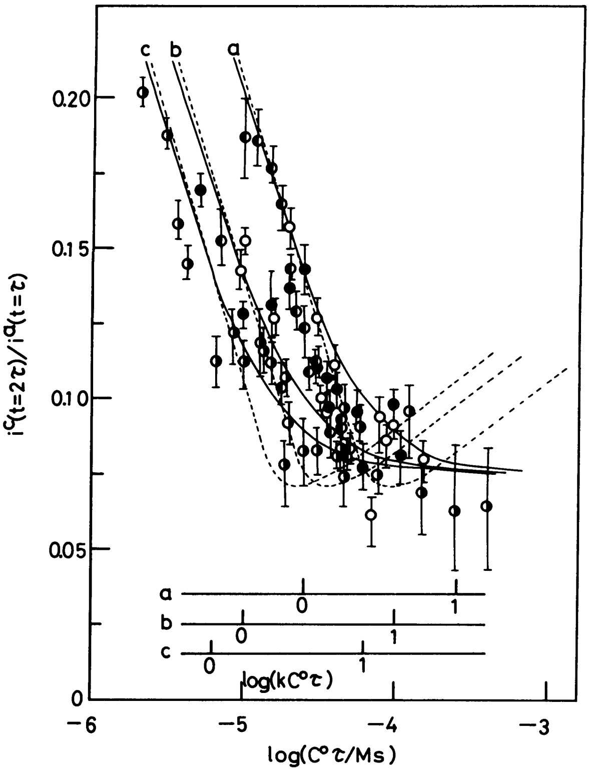

Fig. 7. Polts of $i^c(t=2\tau)/i^a(t=\tau)$ vs. $\log(C^\circ\tau)$. Solid and dashed curves indicate the theoretical $i^c(t=2\tau)/i^a(t=\tau)-\log(kC^\circ\tau)$ curves for Mechanism I and Mechanism II, respectively. The curves a, b, and c correspond to $k=0.4\times10^5$, 1.0×10^5, and 1.6×10^5 $M^{-1}\,s^{-1}$, respectively. Closed circles indicate the experimental data. Supporting electrolyte: 0.2 M $TBABF_4$. Concentration of PA: (●): 0.5, (○): 1.0, (◑): 5.0, and (◐): 10.0 mM. Widths of error bars indicate uncertainties in the measurements of $i^c(t=2\tau)/i^a(t=\tau)$.

the $i^c(t=2\tau)/i^a(t=\tau)-\log(kC^\circ\tau)$ relation for Mechanism I rather than that for Mechanism II, irrespective of the used values of C° and τ. In this case, the C°'s used were 0.50, 1.0, 5.0, and 10.0 mM, and the τ's were arbitrarily changed in the range of ca. 0.5 to 100 ms. Using the overlay matching technique just described the experimental points were matched with the theoretical curve. From the comparison of these experimental and theoretical curves, the value of k was estimated to be $(1.0\pm0.8)\times10^5$ $M^{-1}s^{-1}$.

Discussion

From the data obtained above, one can see that the initial-stage process of the electropolymerization of PA is symbolized as an ECE type of mechanism, and that the chemical reaction interposed betweeen successive electron transfers is the radical-radical coupling (PA^{+}-PA^{+} coupling) reaction rather than the radical-parent monomer coupling (PA^{+}-PA coupling) reaction. Further, from the previous paper,[36] the coupling of PA^{+}'s is considered to occur at the 1- and 6- positions and/or the 1- and 8- positions. The mechanistic scheme for an electropolymerization via such a radical-radical coupling seems to be familiar in the electropolymerization of many aromatic compounds.[41,45,46,55,61,64,72,73] In the case of these electropolymerization, when the electrode oxidation reaction occurs, the radical cation concentration at the anode surface is high, whereas the concentration of parent monomer is low, rendering reactions between radical cations more probable than their reactions with parent monomers. This may be due to the fact that the radical–radical coupling reaction is likely to be faster than the diffusion of the parent monomer into the vicinity of the electrode. Therefore, the situation under consideration is very different from typical polymerization reactions occurring in the bulk of a solution, where the concentration of parent monomer is always much higher than those of the reactive intermediates (such as radical ions).

Two types of electrochemical polymerizations have seemed to be recently accepted;[55,74–77] one is the electrochemically initiated polymerization[75–77] and the other is the stoichiometric electrochemical polymerization.[55,74] In the former case, the initiators of polymerization are formed by the heterogeneous electron-transfer reaction of parent monomers and then the propagation reaction, chain-transfer reaction, termination reaction, etc. are thought to occur as in usual chemical polymerization reactions. In the latter case, on the other hand, the reactive intermediates are formed by the heterogeneous electron-transfer reactions of parent monomers as well as the products (the aromatic dimer, the higher molecular weight oligomers, etc.) and the electropolymerization via the reactions between them proceeds. The stoichiometric electrochemical polymerization was first described with polypyrrole by the IBM research group[55,74] and since then, it has been reported that it is applicable to the heterocyclic compounds such as pyrrole, thiophene, indole and benzo[*b*]thiophene,[38,55,72–74] the nonbenzenoid aromatic hydrocarbons such as azulene,[55,78] and the polycyclic aromatic hydrocabons such as pyrene and fluorene.[37–39,55] The electrochemical polymerization of PA is also regarded as a stoichiometric electrochemical polymerization. In general, such a stoichiometric electrochemical polymerization is symbolized as $E(CE)_n$ on the basis of an extension of customary electrochemical abbreviation.[55,65] In the present study, the initial stages of the electropolymerization of PA were elucidated as an ECE mechanism. Of course, note that further reactions proceed actually as can be seen from the fact that the degree of the polymerization of PA is ca. 8.[36]

Further, it is remarkable that the cyclic voltammetric responses for the oxidation of PA were varied by the presence or absence of the basic or acidic additives. An increase of pyridine (or 2,6-lutidine) concentration produces an increase in $i^{a}_{p,I}$ towards about twice the $i^{a}_{p,I}$ value in the absence of pyridine (or 2,6-lutidine). These additives are stronger bases than PA in acetonitrile and would replace it as proton acceptor. Then, the overall reaction corresponding to the first anodic peak may be considered as a two-electron process, as being previously suggested for the anodic oxidation of 1-naphthylamine in acetonitrile[80,81] and would thus be represented by the following equation:

$$2PA + B \rightleftarrows D^{2+} + 2BH^{+} + 4e^{-} \qquad (4)$$

where B is the basic additives, BH^{+} is the protonated form of B and D^{2+} is the dicationic dimer of PA. In contrary, the addition of the acidic additives such as CF_3COOH to the electrolytic solution of PA caused a decrease in $i^{a}_{p,I}$ and a shift of $E^{a}_{p,I}$ to more anodic values. This may be understood considering that if PA is protonated in an acidic medium, it becomes electroinactive. The similar behaviors have been reported for the anodic oxidation of the other aromatic compounds (e.g., 2-fluorenamine,[79] 1-naphthylamine,[80,81] *o*- and *p*-phenylenediamine,[64,82] and aniline[83]) in nonaqueous solutions. From a viewpoint of the preparation of the poly(1-pyrenamine) film on electrode surfaces, it is preferable to electrolyze PA in the presence of basic additives, as reported previously.[36]

Finally, we demonstrate that the DPSCA technique used in this study would be successfully applicable to the kinetic study (e.g., the determination of mechanistic pathways and associated chemical rate) of the initial stages of the electropolymerization of many aromatic compounds other than PA.

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