  Bull. Chem. Soc. Jpn., 59, 2071—2080 (1986)

Electrochemical Properties of Electropolymerized Poly(1-pyrenamine) Films

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(Received December 25, 1985)

The electropolymerization of 1-pyrenamine (PA) in an acetonitrile solution led to the polymeric film formation on electrode surfaces. The chemical, spectroscopic, electrical and electrochemical characterization of the resulting poly(1-pyrenamine) (PPA) films was carried out. The number-average molecular weight of the PPA film, measured by gel permeation chromatography, was 1.8×10^3, corresponding to the degree of the polymerization of ca. 8. The PPA films were polymer-anion composites which contained ca. 0.3 anions (e.g., BF_4^-) per repeating aromatic unit, which is considered to be composed of three PA molecules. The oxidized form of the PPA film displayed the ESR response. The g factor was 2.0082 and the concentration of radical in the PPA film was determined to be 4.8×10^{19} e^-g^{-1}. The conductivities of the PPA films in the dry state at 300 K were in the range 10^{-11}—10^{-10} S cm^{-1}. The PPA film was electroactive in an aqueous solution as well as in a non-aqueous solution. The cyclic voltammetric responses depended on pH of aqueous solutions and supporting electrolyte in non-aqueous solutions. The thickness(ϕ) of the PPA film and the surface concentration(Γ) of the electroactive site in the PPA film were proportional to the amount (Q) of the charge passed during the electrolysis (when $Q<$ ca. 120 mC cm^{-2}). The volume concentrations of the electroactive site were 9.7×10^{-4} and 1.7×10^{-3} mol cm^{-3} for the PPA films prepared in the $NaClO_4$ and $TBABF_4$ (tetrabutylammonium tetrafluoroborate) electrolytes, respectively. From the normal pulse voltammetric, potential-step chronoamperometric and potential-step chronocoulometric experiments of the PPA films in a 0.2 M $NaClO_4$ aqueous solution (pH 1.0), the effective apparent diffusion coefficient (D_{app}) for the diffusion-like charge transport within the PPA films, and the standard rate constant (k°) and anodic transfer coefficient (α_a) of the heterogeneous electron-transfer reaction between the In_2O_3 electrode and the electroactive site in the PPA film were estimated to be $(1.5\pm0.5)\times10^{-10}$ cm^2 s^{-1}, $(1.9\pm0.4)\times10^{-5}$ cm s^{-1} and 0.67 ± 0.03, respectively.

In a series of recent papers,[1-9] we have reported (i) the preparation of polymeric films by electropolymerization of aniline, phenol and their derivatives, (ii) the electrochemical, spectroscopic, electrical and physicochemical characterization of the prepared polymeric films, and (iii) the applications of the polymer film-coated electrodes as "hybrid electrode materials." It has been demonstrated therein that whether or not the polymer film formation occurs and the structures and properties of the prepared films depend on the kind of the monomer used for polymerization as well as the experimental conditions used in their preparations (e.g., solvent, electrode material, supporting electrolyte, pH of electrolytic solution, current density, temperature, and electrolysis mode (potential sweep electrolysis, potentiostatic electrolysis, galvanostatic electrolysis, etc.)). Also, it has become apparent that one could prepare the polymeric films, chemical preparations of which are not always easy or in some cases very difficult, relatively easily by electropolymerization of commercially available reagents.

Along this line of investigation, the studies on the electropolymerization of polynuclear aromatic hydrocarbons containing hydroxyl or amino groups (e.g., 1-pyrenamine, 1-naphthylamine, and 1-naphtol) have been also started. The film formation during the electro-oxidation of a variety of polynuclear aromatic hydrocarbons has been previously observed by Peover and White,[10,11] and more recently the comprehensive study concerning their electropolymerization has been done by the IBM research group.[12-16] For polynuclear aromatic hydrocarbons containing hydroxyl or amino groups, only a few papers[17,18] concerning the electropolymerization of these compounds have appeared recently. The electrochemical oxidation of polynuclear aromatic amines (e.g., 1-naphthylamine,[19-21] 2-fluorenamine,[22] 10-phenyl-9-anthracenamine[23] and 9-(arylamino)anthracene[24]) has been recently studied by several investigators whose attention has been mainly directed to the mechanism of the formation of the dimeric products soluble in the electrolytic solutions used. Little attention has been paid to the formation of the polymeric films on the electrode surface, although the film formation has been obviously observed in some cases.[19,20] It would be worthwhile to examine the effect of a nucleus other than benzene in the electropolymerization of the aromatic amines and phenols.

In the present paper, we will report the preparation of the polymeric films by electropolymerization of 1-pyrenamine in an acetonitrile solution and the electrochemical, electrical, physicochemical and spectroscopic characterization of the resulting polymer films. It is demonstrated that the prepared polymeric films possess some interesting properties which differ from those obtained for the polymeric films[1-9,25-38] (e.g., polyaniline and polyphenol) prepared from mononuclear aromatic monomers with hydroxyl and/or amino groups.

Experimental

Materials. 1-Pyrenamine (PA)(Aldrich) was purified by

the following way: The commercially available PA reagent was dissolved in acetonitrile and then insoluble materials were filtered out, then the solvent was evaporated off and the resultant PA solids were purified by ordinary recrystallization techniques from hexane. Pyrene of reagent grade (Wako Chemical Co.) was purified by recrystallization from benzene. Acetonitrile (Wako) was distilled by ordinary technique after dehydration on molecular sieves (3A 1/16, Wako). Sodium perchlorate ($NaClO_4$) (Kanto Chemical Co.), tetrabutylammonium tetrafluoroborate ($TBABF_4$), tetrabutylammonium perchlorate(TBAP) (Tokyo Kasei Co.), tetraethylammonium chloride (TEACl) (Wako) which were used as supporting electrolytes were reagent grade. Tetrabutylammonium hexafluorophosphate($TBAPF_6$) (used as supporting electrolyte) was prepared from tetrabutylammonium bromide and potassium hexafluorophosphate and purified by recrystallization from H_2O/C_2H_5OH mixture. The basal-plane pyrolytic graphite(BPG) (Union Carbide Co.) and In_2O_3 were used as working electrodes. All other chemicals were reagent grade and were used without further purification.

Apparatus and Procedures. The electropolymerization and electrochemical measurements were conducted by using a standard three-electrode, two-compartment electrochemical cell. The electrode assembly consists of a BPG (or an In_2O_3) electrode as working electrode, a sodium chloride saturated calomel electrode(SSCE) as reference electrode and a spiral platinum wire as counter electrode. For cyclic voltammetry, potential-step chronoamperometry, potential-step chronocoulometry and normal pulse voltammetry, a home-made instrument was employed along with an X-Y recorder(Watanabe Co.).[39,40] The amounts (Γ) of the electroactive site in the electropolymerized poly(1-pyrenamine) (PPA) films were estimated in units of mol cm^{-2} by measuring the area of cyclic voltammograms(for the redox reaction of PPA film) obtained at slow potential scan rates(1—5 mV s^{-1}) in a 0.2 M (1 M=mol dm^{-3}) $NaClO_4$ aqueous solution (pH 1.0).[39-41] The molar concentration (in units of mol cm^{-3})of the electroactive site was calculated from the Γ thus obtained using the measured thicknesses of the PPA films. The electropolymerization of PA was carried out by a potential-sweep electrolysis and/or a constant potential electrolysis in an acetonitrile solution containing 5 or 10 mM PA+0.2 M supporting electrolyte (mainly $NaClO_4$ or $TBABF_4$). The film thicknesses of the resulting PPA films were measured with a Surfcom 550A (Surface Texture Measuring Instrument, Tokyo Seimitsu). An IR absorption spectroscopy (A-302 Infrared Spectrophotometer, Japan Spectroscopic Co., LTD.) was used to identify the PPA films formed on electrodes. ESR spectra were taken on JES-FEIX ESR Spectrometer for the oxidized forms of the PPA films. The conductivities (σ) of the PPA films in dry state were measured by using two-point probe technique at ambient temperature (300K) by means of d.c. power supply (Metronix Corp., Model 5126) and d.c. microvolt ammeter (Toa Electronic LTD., Model PM-18R). The weight- and number-average molecular weights of the PPA films were estimated by means of gel permeation chromatography by using narrow molecular weight polystyrene standards (Waters Assoc., Inc., Milford, Mass) as probe for measuring resolution and calibration.

Results and Discussion

Cyclic Voltammetric Behavior of PA Monomer. Typical cyclic voltammograms of PA at BPG electrode in an acetonitrile solution containing 0.2 M $TBABF_4$, and 10 mM PA are shown in Fig. 1 where the cyclic voltammograms of pyrene in the same supporting electrolytic solution are given for comparison. PA electro-oxidizes irreversibly and produces complicated cyclic voltammograms. The voltammograms contain multiple peaks which are broad and overlapping. In the first forward scan of the potential, the several anodic peaks were obtained at ca. 0.6, 0.95, 1.2, and 1.4 V vs. SSCE (at 50 mV s^{-1}). During the first reverse scan, the ill-defined cathodic peaks corresponding to the anodic peaks observed during the forward scan and the well-defined one at ca. 0.3 V were observed. In the second forward scan, the anodic peak corresponding to the cathodic one at 0.3 V was obtained at ca. 0.4 V. This paired anodic and cathodic peaks correspond to the redox reaction of the polymeric products being formed on the electrode surface. The oxidation potential (ca. 0.4 V) of the polymeric products is lower than that (ca. 0.6 V) of parent PA. Such a behavior seems to be a general feature of a number of families of homologous oligomers of aromatic compounds.[13,42] According to the fact,[13,42] the dimer or any higher oligomer is more easily oxidized than parent monomer. The

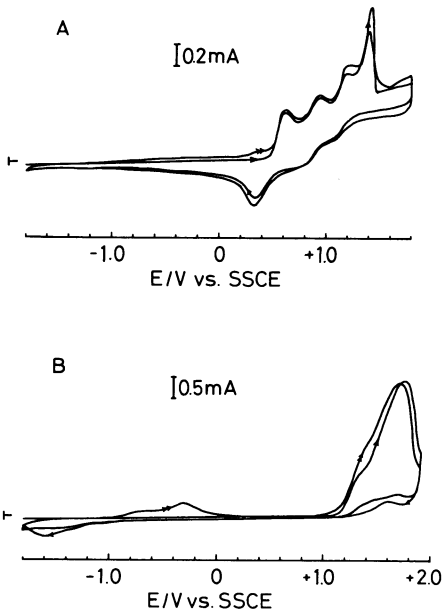


Fig. 1. Typical cyclic voltammograms of (A) PA and (B) pyrene at BPG electrodes in acetonitrile solutions under an atmosphere of nitrogen. Solution composition: (A) 10 mM PA+0.2 M $TBABF_4$, (B) 10 mM pyrene+0.2 M $TBABF_4$. Scan rate: 50 mV s^{-1}. Electrode area: 0.17 cm^2. The arrow indicates the direction of potential scan.

increase in the peak currents with successive potential scans indicates the build-up of the electroactive polymeric products on the electrode.

The cyclic voltammetric response of PA is considerably different from that for pyrene in that (i) the voltammetric responses are more complicated than those for pyrene, (ii) the first oxidation peak (ca. 0.6 V vs. SSCE) is much less positive than that (ca. 1.3 V) for pyrene, and (iii) the redox response of the polymeric product is observed at ca. 0.35 V, which is considerably negative compared with that (ca. 0.9 V) for the polymeric product from pyrene. Of course, PA as well as pyrene electro-oxidize and produce the respective polymeric films on electrode surfaces. The cyclic voltammetric data for pyrene shown in Fig. 1 are in good agreement with those reported previously by Diaz et al.[15]

By holding the electrode potential at the potential which is slightly over the first oxidation peak potential(typically this is 0.75 V vs. SSCE), the formation of the polymeric film on the electrode surface was observed. The electrolyses at more positive potentials (e.g., 1.0 V vs. SSCE) did not give the substantially different results: The cyclic voltammetric responses and IR spectra of the PPA films prepared by the electrolyses at 0.75 and 1.0 V vs. SSCE were the same. However, the electrolyses at much more positive potentials (e.g., 1.8 V vs. SSCE) did not lead a significant film formation on electrode surfaces. Thus, in the experiments mentioned below, the electrolysis was carried out at the potential which is slightly over the first oxidation peak potential. The typical cyclic voltammograms of this case are shown in Fig. 2. As the potential scan was cycled, the anodic peak current at 0.65 V decreased, while the new peaks at 0.35 and 0.45 V increased slowly. As a result, the formation of a purplish black thin film was observed on the electrode surface. The oxidized form of the film was purplish black and the reduced form was yellow. The redox response corresponding to the polymer film produced on the electrode surface was observed at ca. 0.3 V, when after the electrolysis the electrode was washed with benzene and then transferred into the supporting electrolytic solution containing no PA (0.2 M $NaClO_4$ aqueous solution, pH 1.0). The voltammetric response remained substantially unchanged even after the potential scan cycling of several hours.

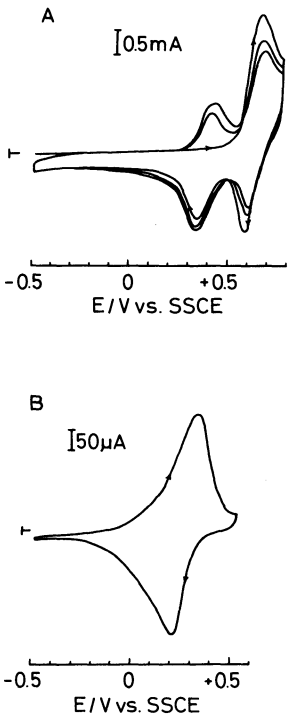


Fig. 2. (A) Typical cyclic voltammograms of PA at a BPG electrode in an acetonitrile solution containing 5 mM PA+0.2 M $TBABF_4$. Scan rate: 5 Vs^{-1}. Electrode area: 0.17 cm^2. (B) Cyclic voltammogram representing the electroactivity of the PPA film deposited on a BPG electrode in a 0.2 M $NaClO_4$ aqueous solution (pH=1.0). Scan rate: 50 mVs^{-1}.

Spectroscopic, Electrical and Chemical Characterization of PPA Film. The IR spectra of the PPA films formed on the In_2O_3 electrodes during the anodic oxidation of PA are shown in Fig. 3 in which the IR spectrum of PA monomer is also shown for comparison. These IR spectral data are summarized in Table 1. In the case of the oxidized form of the PPA film, the observation of the peak at 1660 cm^{-1}

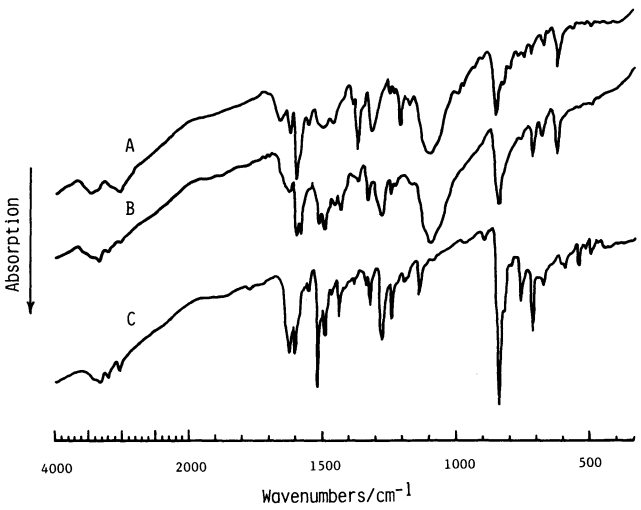


Fig. 3. IR spectra of (A) the oxidized form and (B) the reduced form of the PPA film and (C) PA monomer. The oxidized form of the PPA film was prepared on an In_2O_3 electrode by a constant-potential electrolysis (at 0.75 V vs. SSCE) in a 0.2 M $NaClO_4$ acetonitrile solution containing 10 mM PA and 10 mM pyridine. The reduced form was prepared by reducing electrochemically the oxidized form deposited on electrodes at −0.5 V vs. SSCE in a 0.2 M $NaClO_4$ aqueous solution (pH=1.0).

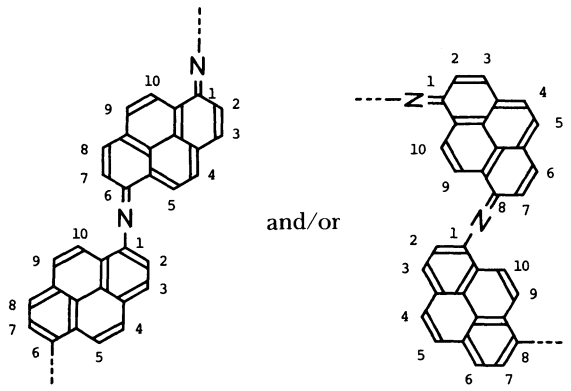
Table 1. IR Spectra of PPA Films and PA Monomer
(Fundamental Vibrations, Frequencies in cm^{-1})

Compound	Vibration mode[c,d,e]						
	ν(C=C)	ν(C-H)	γ(C-H)	ν(C=N)	ν(C-N)	ν(N-H)	ClO_4^-
PA	1600 s	3030 w	840 s	f	1280 s	3330 w	f
	1510 s		820 m				
	1490 m		760 m				
	1440 m		720 s				
			680 m				
Oxidized[a] form of PPA	1600 s	3030 w	850 s	1660 w	g	3350 w	1100 s
	1550 w		820 m				
	1490 w		760 w				
	1450 w		740 w				
			720 w				
			670 w				
Reduced[b] form of PPA	1600 s	3030 w	840 s	f	1280 s	3350 w	1100 s
	1580 s		820 m				
	1510 m		710 m				
	1430 m		680 w				

a) The oxidized form of the PPA film was prepared on an In_2O_3 electrode by a constant-potential electrolysis at 0.75 V vs. SSCE in an acetonitrile solution containing 10 mM PA + 10 mM pyridine + 0.2 M $NaClO_4$. b) The reduced form of the PPA film was prepared by reducing electrochemically the oxidized form deposited on electrodes at −0.5 V vs. SSCE in a 0.2 M $NaClO_4$ aqueous solution(pH 1.0). c) ν=Stretching vibration. d) γ= Out-of-plane bending vibration. e) Absorption intensity (not quantitative); s(strong), m(medium) and w(weak). f) No absorption. g) Absorption was observed as "shoulder".

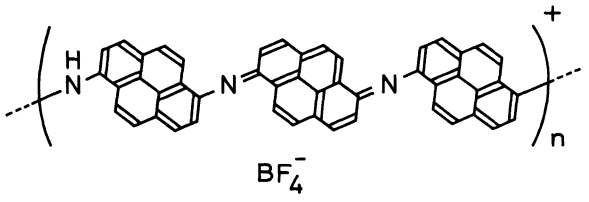
corresponding to the stretching of the C=N bonds seems to point to polymers based on imine links of the type C-N=C.[43,44] This absorption peak was not observed with the reduced form of PPA as well as PA monomen The relatively strong absorption peaks at 1280 cm^{-1} which are ascribable to the stretching of C-N bonds[43,44] were observed with PA monomer and the reduced form of PPA, while in the case of the oxidized form the corresponding absorption peak was observed slightly as a "shoulder". The strong absorption peaks at 1100 cm^{-1} observed in the spectra of the oxidized and reduced forms of the PPA film are assigned to the presence of ClO_4^- ions,[43,44] which were used as an electrolytic anion during the film formation. The absorption peaks due to the N-H stretching at 3330—3350 cm^{-1} were observed for the oxidized and reduced forms of the PPA film and PA monomer. The other absorption peaks shown in Table 1 (i. e., ν(C=C), ν(C-H), and γ(C-H)), which are common to the PPA films and PA monomer, are characteristic of the various vibration modes of the C-H and C-C bonds of the aromatic nuclei.[43,44] From these results, the electropolymerization of PA seems to proceed via the formation of the C-N=C bonds and the C-NH-C bonds. In this point, the electropolymerization reaction of PA may be similar to that proposed recently for aniline and its derivatives.[2-4,6,7,27,30,46]

For the electropolymerized films of aniline and its derivatives,[2-4,6,7,46] an analysis of the absorption peak pattern between ca. 900 and 700 cm^{-1} which arises from the C-H out-of-plane bending modes[43,45] enabled us to assign correctively the substitution pattern of the aromatic ring and to elucidate the structures of the films. A fairly good correlation between the positions of the absorption bands and the substitution pattern in terms of numbers of adjacent hydrogen atoms was found for the condensed aromatic ring series (i.e., benzene, acene and phen series).[43,45,47,48] However, no conclusive results on the basis of the same idea were obtained for pyrene, which is a peri-condensed hydrocarbon. Recently, the empirical rules connecting substitution pattern and bond positions in a broad variety of substituted pyrenes (137 pyrene derivatives) has been suggested by Hansen and Berg.[49] According to their empirical rules, along with the above-mentioned discussions about the linkage between PA units in the PPA film, it can be concluded that the electropolymerization of PA proceeds via the coupling of the aromatic rings at the 1- and 6-positions and/or the 1- and 8-positions as follows:



On the basis of the concept of radical cation dimerization, Bargon et al.[13] have recently suggested that the polypyrene, the polymeric product resulting from the electropolymerization of pyrene, is made up of 1,6-pyrenediyl and/or 1,8-pyrenediyl units. The PPA films were soluble in dimethyl sulfoxide and *N*,*N*-dimethylformamide(DMF). The weight- and number-average molecular weight ($\bar{M}_w$ and $\bar{M}_n$) of the PPA films were estimated by means of gel permeation chromatography (solvent: DMF). The values of $\bar{M}_n$ and $\bar{M}_w$ were 1.8×10^3 and 3.0×10^3, respectively which correspond to the degree of polymerization of 8 and 14, respectively. Note that the true molecular weight of the PPA film may be smaller than that estimated on the basis of polystyrene standards (as mentioned above), because PA is more rigid than styrene.

The elemental analysis of the PPA film (oxidized form) prepared in the $TBABF_4$ acetonitrile solution indicated that the weight percents of C, H, N, and BF_4^- in the PPA film are 78.07, 3.76, 5.72, and 12.45%, respectively which correspond to the molar ratios of 15.9(C), 9.1(H), 1.0(N) and 0.35(BF_4^-) (relative to the molar numer of N). This fact indicates that the PPA films are polymer-anion composites which contain ca. 12% BF_4^- by weight. From these molar ratios of C, H, N, and BF_4^- a possible structure of the repeating aromatic unit of the PPA film may be predicted as follows:



The molar ratios of C, H, N, and BF_4^- for the repeating unit structure predicted above are 16.0, 8.3, 1.0, and 0.33, respectively, which are in fair agreement with the experimental elemental analysis. Thus, the PPA film contains ca. 0.3 BF_4^- anions per repeating aromatic unit which is thought to be composed of three PA molecules. Further, it is worth noting that the elemental composition is somewhat hydrogen-rich. This may suggest that the double bonds of the pyrene rings of the PPA are partially hydrogenated, as previously proposed for the hydrogen-rich elemental compositions of the polymers prepared by the electropolymerization of polycyclic aromatic hydrocarbons such as pyrene and fluorene.[15]

In Fig. 4 is shown the ESR spectrum of the oxidized form of the PPA film. The ESR spectrum consists of a simple, symmetrical, narrow line with Lorentzian shape. The peak-to-peak line width was 0.90 mT at room temperature. The *g* factor measured against a 2,2-diphenyl-1-picrylhydrazyl radical standard was 2.0082. The concentration of radical in the PPA film was determined to be 4.8×10^{19} e^- g^{-1}, which is compared to the value ($(1-7)\times10^{19}$ e^- g^{-1}) for polyaniline[50,53] (oxidized form) and that (1.4×10^{19} e^- g^{-1}) for polyacetylene.[51] Assuming that the elemental composition of the PPA is $C_{48}H_{25}N_3(BF_4)_1$, it is thought that there is one unpaired electron per ca. 17 repeating units. Even after the reduction of the oxidized form of the PPA film by the chemical procedure (using the reductants such as $Na_2S_2O_4$ and C_2H_5SH) or by the electrochemical one (by holding the PPA-coated electrode at the potetial at which the PPA film could be reduced), no NMR spectra of the reduced form (as well as the oxidized form) of the PPA film were obtained.

The conductivities (σ) of the PPA films in the dry state, measured at 300 K by using the two-point probe technique, were in the range 10^{-11}—10^{-10} S cm^{-1} for both oxidized and reduced forms irrespective of the supporting electrolytes used (i.e., $NaClO_4$ and $TBABF_4$). Also, the σ values were nearly independent of the presence or absence of pyridine in the electrolytic solution. Note that the σ values for the PPA films are about 6 to 10 orders of magnitude smaller than those obtained for the other electropolymerized films, for example, the σ values (10^{-4}—10^{-1} S cm^{-1}) for polyaniline, poly(*o*-phenylenediamine) and poly(*N*-methylaniline).[3,5,53] Further, the

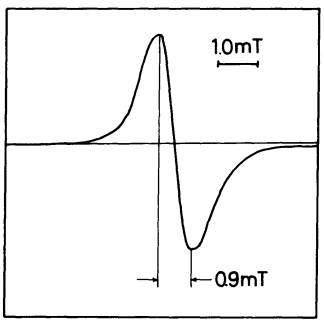


Fig. 4. ESR spectrum of the oxidized form of the PPA film at 298 K. The oxidized form of the PPA film was prepared by the same procedure as shown in Fig. 3.

following fact should be noted: In the case of the polyaniline films which were equilibrated with aqueous solutions of different pH's, washed in acetonitrile, and then dried under vaccum, changing pH from 0 to 6 has been reported to decrease σ by 6 orders of magnitude,[53] whereas in the case of the PPA film the slight dependence of σ on pH was observed, i.e., the σ values of the PPA films treated at pH 1.0 and 12.0 were ca. 10^{-10} and 10^{-12} S cm^{-1}, respectively. Such significant differences in the σ values and their pH dependences are considered to originate from the difference in the basic structures of the PPA and polyaniline, that is, the former contains polynuclear aromatic rings, while the latter contains mononuclear aromatic rings.

Electrochemical Response of PPA Film. Figure 5 shows the correlation between the thickness (ϕ) of the PPA film and the amount (Q) of the charge passed during the anodic oxidation of PA. In this case, the films were prepared by the anodic oxidation of PA at 0.75 V vs. SSCE in an acetonitrile solution containing 0.2 M $NaClO_4$ (or $TBABF_4$), 10 mM PA and 10 mM pyridine. The ϕ's are proportional to Q when $Q<$ca. 120 mC cm^{-2}. The proportionality constant of ϕ to Q is 4.2×10^{-3} cm^3 C^{-1} for the PPA film prepared in the $NaClO_4$ electrolyte and 1.9×10^{-3} cm^3 C^{-1} for that prepared in the $TBABF_4$ electrolyte. Thus, under the conditions of the same amount of the charge passed, the PPA film prepared in the $NaClO_4$ electrolyte is over twice thicker than that in the $TBABF_4$ solution. Such an observed proportionality is surprising in view of the fact that the film-forming reaction was accompanied by the formation of soluble, purplish products as can readily be seen from the colored (purplish) electrolytic solution. The similar proportionality of ϕ to Q has been also obtained in the electropolymerization of the other aromatic monomers (e.g., aniline,[1] *N*-methylaniline,[5] *o*-phenylenediamine[5] and *N*,*N*-dialkylanilines[6,7]), irrespective of the apparent observation of the production of the soluble products. The proportionality constants obtained for the PPA films are 5—10 times larger than that obtained for the electropolymerization of aniline. At any rate, the data shown in Fig. 5 indicate that the PPA film thickness can be arbitrarily controlled by the charge passed during the electrolysis.

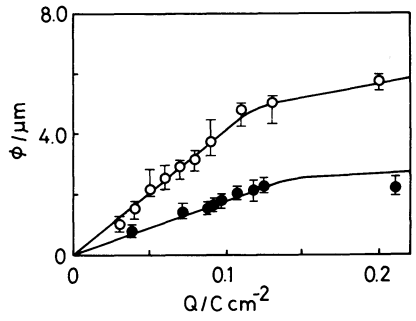


Fig. 5. Correlation between the PPA film thickness (ϕ) and the amount (Q) of the charge passed during the anodic oxidation of PA. The PPA films were prepared on BPG electrodes by a constant-potential electrolysis at 0.75 V vs. SSCE in acetonitrile solutions. Solution composition: (○) 10 mM PA+10 mM pyridine+0.2 M $NaClO_4$; (●) 10 mM PA+10 mM pyridine+0.2 M $TBABF_4$. Widths of error bars indicate uncertainties in thickness measurements.

Figure 6 shows the correlation between the Γ value and Q, where the Γ indicates the surface concentration of electroactive site in PPA films, measured by cyclic voltammetry in an aqueous $NaClO_4$ solution (pH 1.0). The Γ's are proportional to Q when $Q<$ca. 120 mC cm^{-2}. Thus, from the results shown in Figs. 5 and 6, the volume concentrations of electroactive site in the PPA films were estimated to be 9.7×10^{-4} and 1.7×10^{-3} mol cm^{-3} for the PPA films prepared in the $NaClO_4$ and $TBABF_4$ solutions, respectively. In this case, the current efficiency for the preparation of the PPA films was 30—40 per cent. This value is considerably high compared with those (several per cent) for polyaniline,[1] poly(*N*-methylaniline),[5] and poly(*o*-phenylenediamine)[5] films. It is interesting that the correlations between ϕ and Q, and Γ and Q depend on the supporting electrolyte used in the PPA film formation and as a result the volume concentrations of the electroactive site in the PPA films are different. This may probably be due to the different

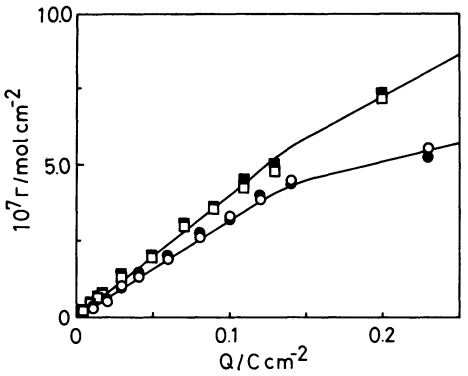


Fig. 6. Correlation between the surface concentration (Γ) of electroactive site in the PPA films and the amount (Q) of the charge passed during the anodic oxidation of PA. The PPA films were prepared by the same procedure as shown in Fig. 5. (□, ■): the PPA films prepared in the $NaClO_4$ electrolyte, (○, ●): the PPA films prepared in the $TBABF_4$ electrolyte. The estimation of the Γ values was conducted by measuring the area of cyclic voltammograms (for the redox reaction of the PPA film) obtained at the potential scan rate of 2 mVs^{-1} in a 0.2 M $NaClO_4$ aqueous solution (pH=1.0). The open and solid symbols indicate the Γ values estimated from the integration of the anodic and cathodic currents, respectively, of the cyclic voltammograms of the PPA films.

morphology of the PPA films formed in the different supporting electrolytes. The PPA films prepared from the $NaClO_4$ electrolyte appeared rough to the naked eye, while those from the $TBABF_4$ electrolyte appeared more lustrous. The latter PPA films were more adhesive to the electrode surface. Thus it may be thought that the PPA film prepared from the $NaClO_4$ electrolyte is more porous than that from the $TBABF_4$ electrolyte, so that the PA monomers can more easily penetrate the PPA film prepared from the $NaClO_4$ electrolyte to reach the electrode surface than that prepared from the $TBABF_4$ electrolyte. This is apparent from the Q vs. t curves obtained during the electrolysis at a constant potential (see Fig. 7).

The PPA films are electroactive in an aqueous solution. The pH-dependences of the cyclic voltammograms of the PPA films are shown in Fig. 8. For the PPA of $\Gamma=2.2\times10^{-9}$ mol cm^{-2}, corresponding to ca. 20 monolayers based on a monolayer coverage of $\sim10^{-10}$ mol cm^{-2}, the cyclic voltammetric response is similar to that obtained for the solution-phase redox species the electrode reaction of which is reversible, that is, the voltammograms are diffusion-like with broad peaks and diffusional tails and the cathodic and anodic peak currents are almost the same (Fig. 8A). The anodic and cathodic peak potentials (E_p^a and E_p^c) shifted to the negative potential with increasing pH (Fig. 9). The dependences of E_p^a and E_p^c on pH are complicated, indicating that proton (H^+) and electron (e^-) take part in the electrode reaction of the PPA film and in this case the numbers of H^+ and e^- involed in the electrode reaction vary with pH of the solution. However, in an acidic solution (pH<4.0) the slopes of E_p^a (and E_p^c) vs. pH plots are about -60 mV/pH. This suggests that the overall electrode reaction of the PPA film is the H^+/e^- reaction in an acidic

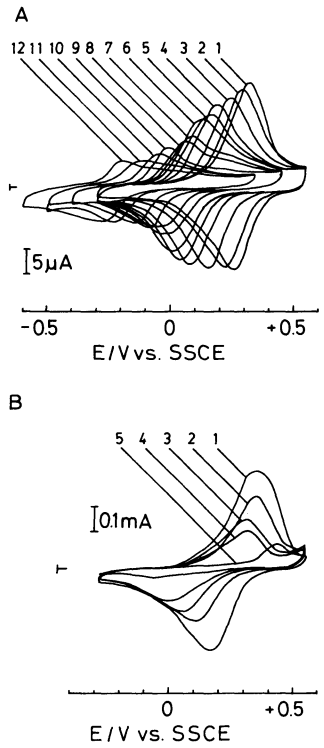


Fig. 8. Cyclic voltammetric responses of the PPA films on BPG electrodes in 0.2 M $NaClO_4$ aqueous solutions of various pH's. The Γ values of the PPA films: (A) 2.2×10^{-9} mol cm^{-2}; (B) 9.7×10^{-8} mol cm^{-2}. Scan rate: 100 mV s^{-1}. Electrode area: 0.19 cm^2. The PPA films were prepared by the same procedure as shown in Fig. 5. The numbers on respective cyclic voltammograms indicate pH values.

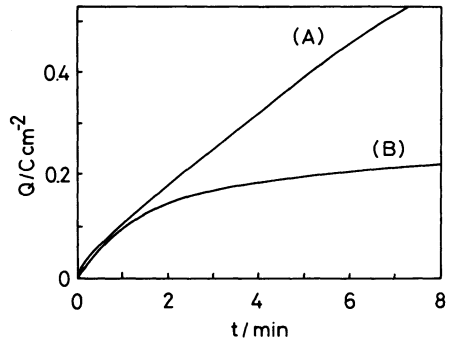


Fig. 7. Potential-step chronocoulometric responses for the anodic oxidation of PA at a BPG electrode in acetonitrile solutions. Solution composition: (A) 10 mM PA+10 mM pyridine+0.2 M $NaClO_4$; (B) 10 mM PA+10 mM pyridine+0.2 M $TBABF_4$. Electrode area: 0.17 cm^2. The electrode potential was stepped from 0.0 to 0.75 V vs. SSCE.

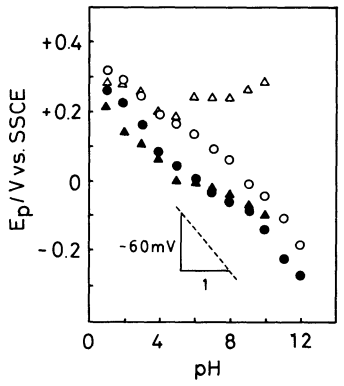


Fig. 9. Typical pH-dependences of the anodic and cathodic peak potentials of the cyclic voltammograms of the PPA films. The Γ values of the PPA films: (○, ●) 2.2×10^{-9} mol cm^{-2}, (△, ▲) 9.7×10^{-8} mol cm^{-2}. The open and solid symbols indicate the anodic and cathodic peak potentials (E_p^a and E_p^c), respectively. Other experimental conditions are the same as in Fig. 8.

aqueous solution. For the thicker film of $\Gamma = 9.7\times10^{-8}$ mol cm^{-2} corresponding to ca. 1000 monolayers, the cyclic voltammetric response is considerably complicated, compared with that for the thin film (Fig. 8B). In this case, the cyclic voltammetric response depended on the scan rate of the potential. The similar behavior has been also observed for the other electroactive electropolymerized films (e.g., polyaniline film[1,25,28]). It seems to be the reason for such a behavior that the PPA film contains the redox sites with slightly different redox potentials and/or its electrode reaction involves any chemical process which actually determines the rate of the overall electrode reaction at the time scale of the measurements. The decreases in the peak currents with increasing pH, shown in Fig. 8, are associated with the fact that a proton addition-elimination reaction is involved in the overall electrode reaction of the PPA film itself, as mentioned above. The magnitude of the peak currents reflects the apparent rate of the overall electrode reactions which decreases with a decrease in the concentration of proton. In this case, these decreases were found to be due to neither the dissolution of the PPA film on electrodes nor its chemical change to any electroinactive compounds (when soaked in alkaline solutions) from the following facts: The Γ values for a given PPA film-coated BPG electrode, measured in the solutions of different pH's, were the same within experimental errors. The coloration of the solution due to the dissolution was not observed. The IR spectra of the PPA films, which were equilibrated with the aqueous solutions of pH1.0 and 12.0 and then dried under vacuum, were essentially the same.

Figure 10 shows the typical normal pulse voltammograms for the oxidation of the PPA film on an In_2O_3 electrode in a 0.2 M $NaClO_4$ solution (pH 1.0). The PPA film was the electropolymerized one in the $NaClO_4$ acetonitrile solution. The plots of the anodic limiting current (i_{lim}) of these normal pulse voltammograms against the inverse square root of the sampling time (τ) were found to be linear (Fig. 11), indicating that the limiting currents were diffusion-controlled.[39,40] Thus the values of the apparent diffusion coefficients, D_{app}, for the charge-transport process within the PPA films were obtained from the slope of the i_{lim} vs. $\tau^{-1/2}$ plot by using the Cottrell equation, as has been done for other surface-confined polymers[39,40]: $D_{app}=1.3\times10^{-10}$ cm^2 s^{-1} (for anodic process). The potential-step chronoamperometric and chronocoulometric experiments (PSCA and PSCC) gave also the D_{app} values: from PSCA, the D_{app} values were determined to be 2.0×10^{-10} and 1.2×10^{-10} cm^2 s^{-1} for anodic and cathodic processes, respectively and from PSCC, the D_{app} values were determined to be 1.9×10^{-10} and 1.0×10^{-10} cm^2 s^{-1} for anodic and cathodic processes, respectively. The D_{app} values estimated by these different procedures are almost the same within experimental errors. These values of D_{app} are about 1—2 orders of magnitude smaller than those previously reported for other electroactive electropolymerized films.[1,8,52] Furthermore, from the analysis[39,40] of the rising part of the normal pulse voltammograms shown in Fig. 10, the standard rate constant (k°) and the anodic transfer coefficient (α) of the heterogeneous electron-transfer reaction were estimated to be $(1.9\pm0.4)\times10^{-5}$ cm s^{-1} and 0.67 ± 0.03, respectively.

The PPA films are also electroactive in a non-

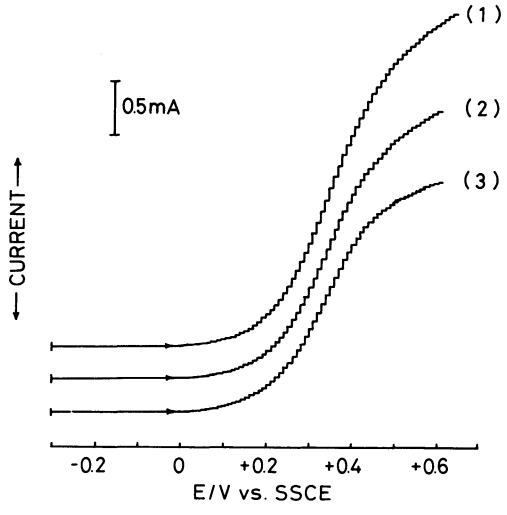


Fig. 10. Typical normal pulse voltammograms for the oxidation of the PPA film on an In_2O_3 electrode in a 0.2 M $NaClO_4$ aqueous solution (pH 1.0). The PPA film was prepared by the same procedure as in Fig. 5. Concentration of the electroactive site in the PPA film: 1.75×10^{-3} mol cm^{-3}. Thickness of the PPA film: 1.1×10^{-4} cm. Sampling time (τ): (1) 5, (2) 8 and (3) 10 ms. Electrode area: 0.16 cm^2.

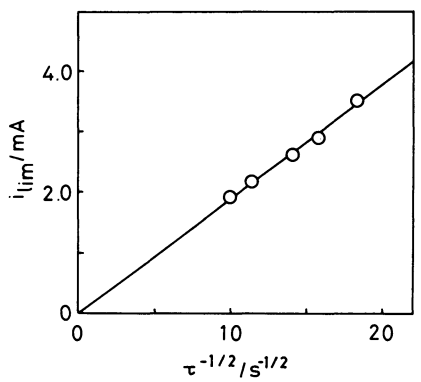


Fig. 11. Normal pulse voltammetric Cottrell plots of limiting current (i_{lim}) vs. (sampling time)$^{-1/2}$ for the oxidation of the PPA film on an In_2O_3 electrode in a 0.2 M $NaClO_4$ aqueous solution (pH 1.0). Other experimental conditions are the same as in Fig. 10.

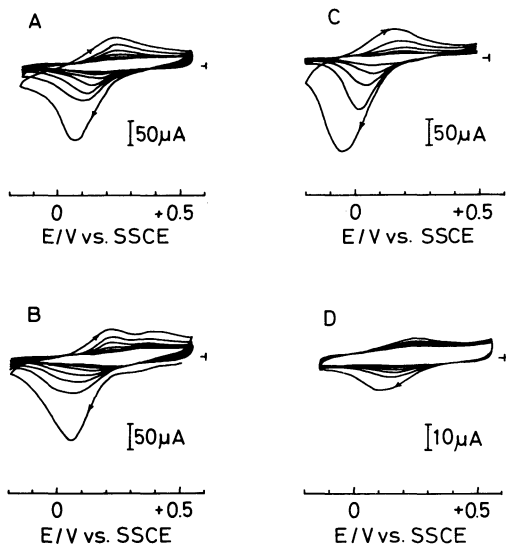


Fig. 12. Cyclic voltammetric responses of the PPA films on BPG electrodes in acetonitrile solutions containing different supporting electrolytes. Supporting electrolyte (0.2 M): (A) $TBABF_4$, (B) TBAP, (C) TEACl, and (D) $TBAPF_6$. Scan rate: 50 mVs^{-1}. Electrode area: 0.17 cm^2. The arrow indicates the direction of potential scan. The PPA films in (A)—(D) were prepared on BPG electrodes by a constant-potential electrolysis at 0.75 V vs. SSCE in acetonitrile solutions containing 10 mM PA+10 mM pyridine+0.2 M supporting electrolyte ((A) $TBABF_4$, (B) TBAP, (C) TEACl, and (D) $TBAPF_6$). In respective electrolysis, the amount of the charge passed was 30 mC cm^{-2}.

aqueous solution. For example, the cyclic voltammetric responses of the PPA film in acetonitrile solutions containing different supporting electrolytes are shown in Fig. 12. The peak current decreased with the cycling of potential scan, probably because of the relatively large solubility of the reduced form of the PPA film in an acetonitrile. The cathodic and anodic peak potentials seem to vary with the supporting electrolyte. The redox response of the PPA film in the acetonitrile solutions may be regarded as the so-called electrochemical doping-undoping process,[54,55] that is, the uptake/exclusion of the supporting electrolytic ions into/out of the film which is coupled to the electrode reaction proper of the PPA film. As mentioned above, the protons take part in the electrode reaction of the PPA in an aqueous solution and the bond formation (during the cathodic process) and cleavage (during the anodic process) of the N-H bonds occurs. Thus, the electrode reactions of the PPA film in aqueous and non-aqueous solutions are considered to be different from each other.

This work was partially supported by Grant-in-Aid for Scientific Research No. 59550510, for Noboru Oyama, from the Ministry of Education, Science, and Culture, Japan and the Nissan Science Foundation.

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