Electropolymerization of *N,N'*-Dimethyl-1,4-dihydropyrrolo[3,2-*b*]pyrrole: a New Heteroaromatic Polymer

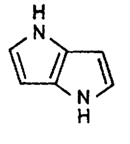
Noboru Oyama,* Takeo Ohsaka, Hirohisa Miyamoto, and Kazuyuki Chiba
Department of Applied Chemistry for Resources, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan
Toshio Mukai,* Shoji Tanaka, and Tsutomu Kumagai
Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980, Japan
Tadashi Aratani and Hiroshi Yoshihara
Takatsuki Research Laboratory, Sumitomo Chemical Corporation, Takatsuki, Osaka 569, Japan

The electro-oxidative polymerization of *N,N'*-dimethyl-1,4-dihydropyrrolo[3,2-*b*]pyrrole (DMPP) in acetonitrile solution led to the formation of a polymeric film on the electrode surfaces. This poly-DMPP film underwent reversible oxidation and reduction processes in both acetonitrile and aqueous solution. The formal redox potential ($E^{\circ\prime}$) was *ca.* 0.10 V *vs.* a sodium chloride/saturated calomel electrode in 0.1M-$NaClO_4$ in acetonitrile solution. The electrical conductivity was 1.1×10^{-5} S cm^{-1} at 298 K. Further physical, electrochemical, electrical, and spectroscopic characterization of poly-DMPP was carried out, and the results were compared with those obtained previously for poly-(1,4-dihydropyrrolo[3,2-*b*]pyrrole) film.

In a previous paper[1] we have demonstrated that the electrochemical oxidation of 1,4-dihydropyrrolo[3,2-*b*]pyrrole (PP) in acetonitrile solution leads to electroactive polymeric films on the electrode surfaces. The present investigation of the electropolymerization of *N,N'*-dimethyl-1,4-dihydropyrrolo-[3,2-*b*]pyrrole (DMPP) was carried out in order to study (*a*) the influence of the methyl groups the electropolymerization; and (*b*) the electrochemical and physical behaviour of the polymeric film prepared (poly-DMPP). Cyclic voltammetry, Fourier transform i.r. spectroscopy, and scanning electron microscopy were employed, together with conductivity and film thickness measurements, to characterize the poly-DMPP films.

Experimental

N,N'-Dimethyl-1,4-dihydropyrrolo[3,2-*b*]pyrrole (DMPP) was prepared as described previously.[2] The electropolymerization and electrochemical measurements were conducted by using a standard three-electrode, two-compartment electrochemical cell. The electrode assembly consisted of a Pt,Au basal-plane pyrolytic graphite (BPG) or In–Sn oxide conducting glass (ITO) as the working electrode, a sodium chloride/saturated calomel electrode (SSCE) as the reference electrode, and a spiral platinum electrode as the counter electrode. The electropolymerization of DMPP was carried out by potential-sweep electrolysis and/or constant-potential electrolysis in 10mM-DMPP and 0.1M-$NaClO_4$ (as supporting electrolyte) in acetonitrile as solvent. Cyclic voltammetry, Fourier-transform i.r. spectroscopy, scanning electron microscopy, and film thickness and conductivity measurements of the films prepared were carried out by the same procedures as described previously.[1] All electrochemical measurements were performed at laboratory temperature (25 ± 1 °C) in a nitrogen- (or argon-) filled glove box. Measured potentials are quoted with respect to the SSCE.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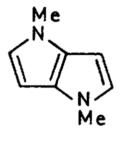
DMPP

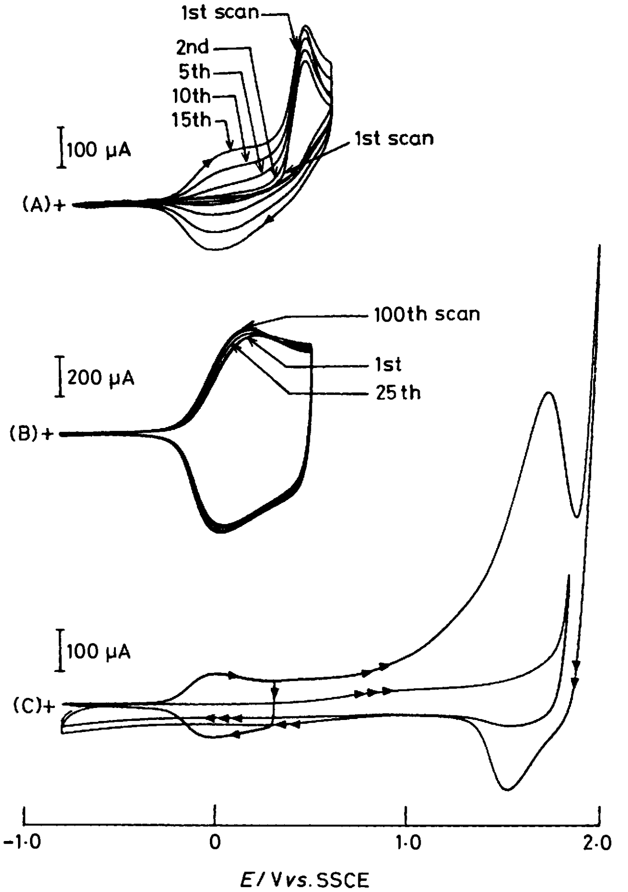

Figure 1. (A) Typical cyclic voltammograms of DMPP at a BPG electrode in 10mM-DMPP and 0.1M-$NaClO_4$ in acetonitrile; electrode area 0.20 cm^2; scan rate 50 mV s^{-1}. (B) Cyclic voltammograms obtained when the electrode used in (A) was washed and transferred to 0.1M-$NaClO_4$ in acetonitrile; scan rate 200 mV s^{-1}; thickness of poly-DMPP film 0.8 μm. (C) Cyclic voltammograms of poly-DMPP film prepared on a BPG electrode in the same solution as used in (B); scan rate 200 mV s^{-1}. The poly-DMPP film-coated electrode was prepared by constant-potential electrolysis at 0.9 V *vs.* SSCE in the same solution as used in (A); film thickness 0.08 μm

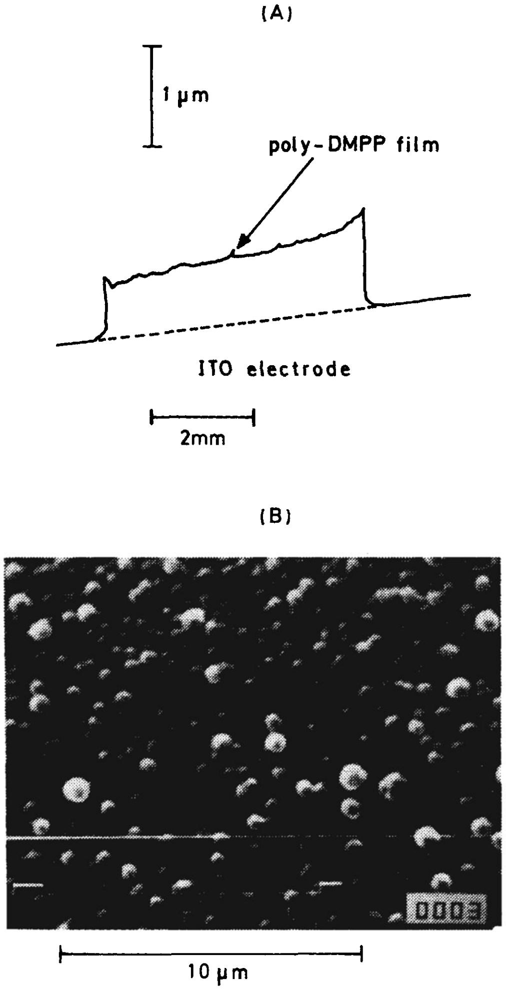

Figure 2. (A) Typical sectional profile of poly-DMPP film. (B) Scanning electron micrograph of poly-DMPP film. The poly-DMPP film (thickness 0.65 μm) was prepared on an ITO electrode by constant-potential electrolysis at 0.9 V *vs.* SSCE in the same solution as used for Figure 1(A)

Table 1. Electrochemical data for DMPP, poly-DMPP, and related compounds[a]

	E_p^a of monomer (V *vs.* SSCE)	$E^{\circ\prime}$ of polymer (V *vs.* SSCE)
DMPP	0.48[b]	0.10[b,e]
PP	0.54[b,c]	−0.10[b,c]
N-Methylpyrrole	1.12[d]	0.45[d]
Pyrrole	1.2[d]	−0.20[d]

[a] E_p^a and $E^{\circ\prime}$ are the anodic peak potential and formal redox potential, respectively, estimated from the cyclic voltammograms (obtained at 50 mV s^{-1}) of the corresponding monomer and polymer films. [b] Supporting electrolyte 0.1M-NaClO$_4$ in acetonitrile. [c] Taken from ref. 1. [d] Taken from ref. 5. [e] The $E^{\circ\prime}$ values seem to vary slightly with the thickness (φ) of the poly-DMPP film, as seen from Figure 5. This value was obtained for poly-DMPP film with φ = 0.8 μm.

Results and Discussion

Electro-oxidative Polymerization of DMPP.—Typical cyclic voltammograms of DMPP at a BPG electrode in 0.1M-NaClO$_4$ and 10mM-DMPP in acetonitrile are shown in Figure 1(A); the electrode potential was swept at 50 mV s^{-1} continuously between −0.8 and 0.6 V *vs.* SSCE. DMPP is electro-oxidized irreversibly and the oxidation of the monomer appears as the peak at 0.48 V *vs.* SSCE. After the first reverse scan, the cathodic and anodic currents were observed in the potential region between *ca.* −0.3 and 0.3 V *vs.* SSCE, and increased continuously with successive potential scans, indicating the build-up of the electroactive polymeric product (poly-DMPP) on the electrode surface. As the potential scan was continued, the electrode became covered with a thin black film. Similar cyclic voltammograms were obtained with Pt,Au and ITO electrodes.

The reversible redox response corresponding to oxidation–reduction of the poly-DMPP film produced on the BPG electrode surface was observed at *ca.* 0.1 V *vs.* SSCE, when after the electrolysis the electrode was washed with acetonitrile and then transferred into an acetonitrile solution containing only 0.1M-NaClO$_4$ [Figure 1(B)]. The amounts of charge involved in oxidation and reduction processes were almost equal. The redox response was relatively stable under successive potential scans below about 1.0 V *vs.* SSCE. On extending the positive limit to 1.9 V, however, it became clear that the film exhibited an oxidation–reduction peak at *ca.* 1.7 V and that the current on the reverse scan decreased markedly; very little oxidation current was seen on the second scan [see Figure 1(C)]. This suggests that the poly-DMPP film undergoes degradation *via* electrochemical oxidation, as observed for polypyrrole,[3] polyaniline,[4] and poly-(1,4-dihydropyrrolo[3,2-*b*]pyrrole) (PPP).[1]

The anodic peak potentials (E_p^a) of the monomers DMPP and 1,4-dihydropyrrolo[3,2-*b*]pyrrole (PP) are almost the same (Table 1). Thus the oxidation is not influenced by the methyl substituent. This result is not unexpected since such alkyl groups have little effect on the oxidation potentials of aromatic compounds such as *N*-alkyl-pyrrole and -carbazole derivatives.[5,6] The E_p^a values of the monomers differ from the formal redox potentials ($E^{\circ\prime}$) of the corresponding polymer films: the $E^{\circ\prime}$ values of PPP and poly-DMPP are −0.10 and 0.10 V *vs.* SSCE, respectively. Similar results have been observed[5] with polypyrrole and poly-(*N*-methylpyrrole) films ($E^{\circ\prime}$ −0.2 and 0.45 V *vs.* SSCE, respectively). Diaz *et al.*[5] have also reported that the $E^{\circ\prime}$ values for poly-(*N*-alkylpyrrole)s (alkyl groups: methyl, ethyl, n-propyl, n-butyl, and isobutyl) are in the potential region 0.45—0.64 V *vs.* SSCE. They have explained the uniquely low $E^{\circ\prime}$ value of polypyrrole in terms of hydrogen bonding with the counter ion or the neighbouring polymer segment, which would provide additional stabilization for the π-cation in the oxidized polymer and give rise to an $E^{\circ\prime}$ value much less positive than for the substituted pyrroles. If this idea also applies to the present systems, the different $E^{\circ\prime}$ values of PPP and poly-DMPP should be ascribable to hydrogen-bonding interactions in the PPP film. The presence of the N–H bond may promote stable chain–chain interactions through hydrogen bonding and provide less disturbance to the ring–ring coplanarity of the extended π-electron systems than does the more bulky methyl group.

Morphology and Thickness Control of Poly-DMPP Film.—The vertical sectional profile of the poly-DMPP film shows that it is continuous and has a fairly smooth surface [Figure 2(A)]. Further, from the scanning electron micrograph [Figure 2(B)], we can see that the film displays a granular appearance like the PPP film prepared from an acetonitrile solution containing tetrabutylammonium perchlorate (0.1M)[1] and the conventional pyrrole films.[7] The relation between the thickness (φ) and the amount (*Q*) of charge passed during the polymerization was examined. The poly-DMPP films were prepared on ITO electrodes by constant-potential electrolysis at 0.9 V *vs.* SSCE.

The results (Figure 3) showed that φ was proportional to Q in the examined range of Q (20—1 000 mC cm^{-2}), and the slope of the φ *vs.* Q plot was *ca.* 4 µm C^{-1} cm^{2}. This value is almost the same as that obtained for the PPP film.[1]

Chemical analysis of the films obtained in this way gave the composition of $C_{7.9}H_{8.4}N_2(ClO_4)_{0.73}$. The poly-DMPP films are polymer–anion composites. This was confirmed by their i.r. spectral measurements (see later). The perchlorate content suggests that there are approximately three perchlorate anions for every four DMPP units. The electropolymerization efficiency, estimated on the basis of the chemical analysis results from the weight of the poly-DMPP film prepared by passing a known amount of charge, was about 90—100%. The poly-DMPP films were insoluble in the commonly used organic solvents and acids irrespective of the film thickness. This fact limited the techniques available for characterization of the film, *e.g.* n.m.r. studies were not possible.

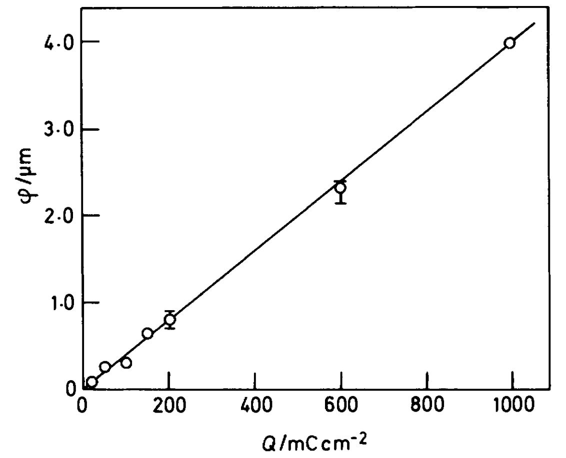

Figure 3. Correlation between film thickness (φ) and amount (Q) of the charge passed during electropolymerization. The poly-DMPP films were prepared on ITO electrodes as for Figure 2. Widths of error bars indicate uncertainties in thickness measurements

Infrared Transmission Spectra of poly-DMPP Film.—Figure 4 shows typical i.r. transmission spectra of poly-DMPP films (KBr pellets). The spectra of the DMPP monomer and $NaClO_4$ are also shown for comparison. At first sight, it is obvious that the spectra of the poly-DMPP films are broader than that of DMPP monomer. This is considered to be a result of the poor crystallinity of the polymer films, as often observed for the films produced by electropolymerization.[1,8—10] Thus, the assignment of the peaks is not easy. However, some characteristic peaks may be assigned as follows. The relatively strong peaks in the region 1 095—1 150 cm^{-1} are due to the poly-DMPP film itself and the presence of the ClO_4^- ions used as electrolyte anions during the electropolymerization.[11] The presence of ClO_4^- ions in the oxidized poly-DMPP film is supported by the observation of a clear peak at 620 cm^{-1} (ref. 11) and the fact that this peak has disappeared almost completely in the NH_3-treated film. The peak observed at 2 960 cm^{-1} for both DMPP monomer and poly-DMPP films is ascribable to C–H stretching in the *N*-methyl groups.[11] The broad band near 3 500 cm^{-1} in spectrum (B) is considered to correspond to O–H stretching of OH^- ions[11c] incorporated into the film in place of ClO_4^-

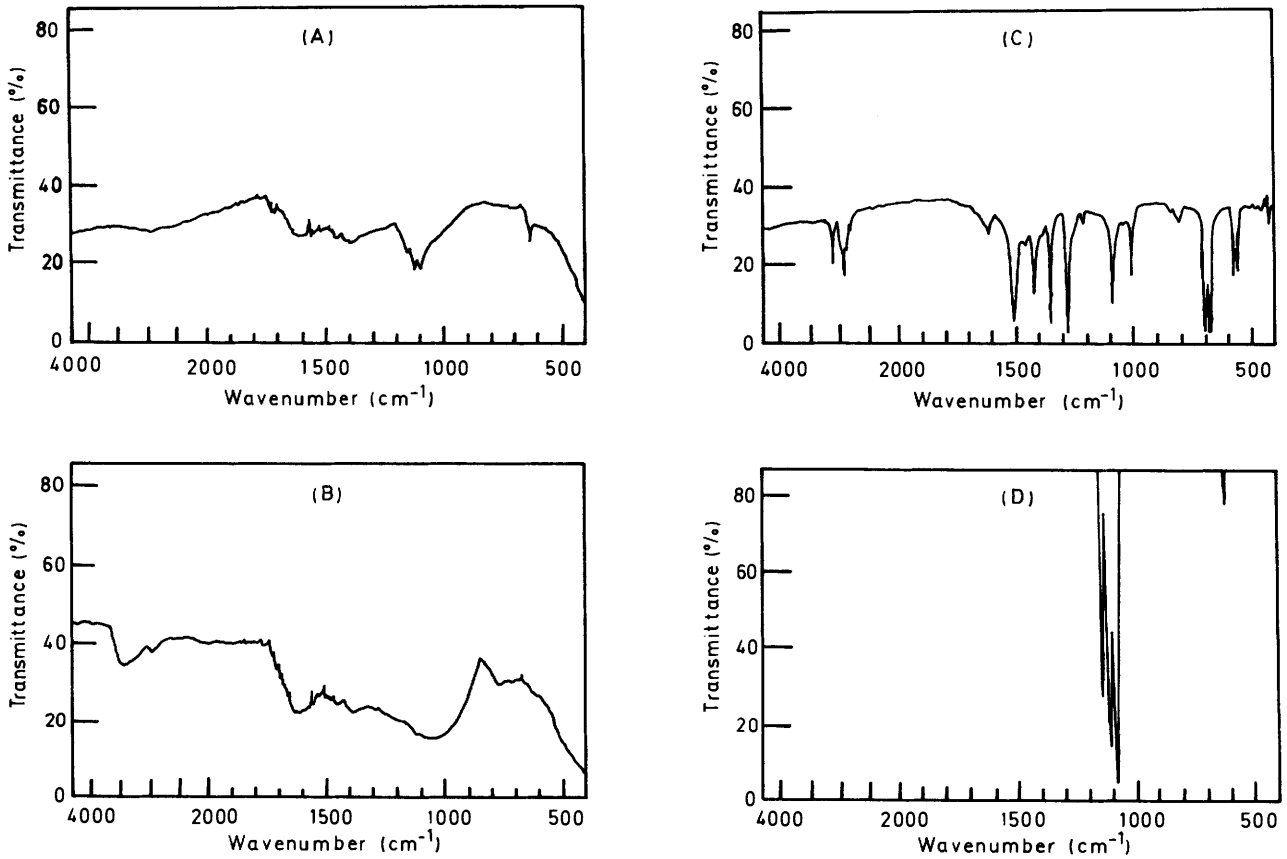

Figure 4. I.r. transmission spectra of (A) ClO_4^--doped poly-DMPP film, (B) NH_3-treated poly-DMPP film, (C) DMPP monomer, and (D) $NaClO_4$. The ClO_4^--doped poly-DMPP film was prepared as for Figure 2. The NH_3-treated poly-DMPP film was prepared by soaking the ClO_4^--doped film in aqueous ammonia overnight, washing it with distilled water, and drying it under reduced pressure

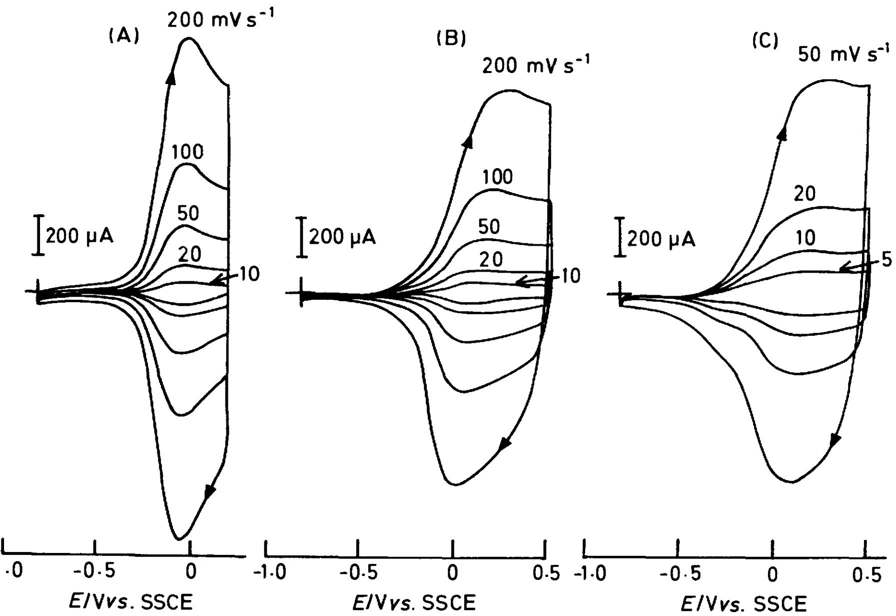

Figure 5. Cyclic voltammograms of poly-DMPP film deposited on BPG electrodes in 0.1M-NaClO$_4$ in acetonitrile at various potential scan rates. The poly-DMPP films were prepared on BPG electrodes by constant-potential electrolysis at 0.9 V *vs.* SSCE in the same solution as used for Figure 1(A). Film thicknesses: (A) 0.08, (B) 0.8, (C) 4.0 μm

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Table 2. Conductivities of ClO$_4^-$-doped poly-DMPP films at 298 K

	σ/S cm^{-1}	
Time (min)[a]	Poly-DMPP film[b]	PPP film[c]
0	$(1.1 \pm 0.4) \times 10^{-5}$	$(5.0 \pm 1.0) \times 10^{-5}$
3	$(2.6 \pm 1.0) \times 10^{-6}$	
60	$(2.7 \pm 1.0) \times 10^{-6}$	$(5.0 \pm 1.0) \times 10^{-6}$
120	$(2.6 \pm 1.0) \times 10^{-6}$	
720		$(3.0 \pm 1.0) \times 10^{-6}$
2 880	$(3.2 \pm 0.6) \times 10^{-6}$	

[a] The period during which the poly-DMPP film was exposed to air. [b] The poly-DMPP film was prepared on an ITO electrode by constant-potential electrolysis at 0.9 V *vs.* SSCE in an acetonitrile solution containing 10mM-DMPP and 0.1M-NaClO$_4$. The thickness was 2.4 μm. The conductivities were measured by a two-point probe technique. [c] Taken from ref. 1.

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ions during treatment with NH$_3$; the oxidized form of the poly-DMPP film is positively charged and thus for charge neutrality the negatively charged counterions (in this case OH$^-$ ions in aqueous ammonia) must be trapped.

Conductivities of Poly-DMPP Films.—The electrical conductivities (σ) of the ClO$_4^-$-doped poly-DMPP films are summarized in Table 2. The σ value (1.1×10^{-5} S cm^{-1}) is 3—4 times smaller than that of PPP film. Further, exposure of the film to air caused lowering of the conductivity: the σ value decreased by *ca.* one third on exposure for 3 min and remained unchanged on further exposure. Similar results were obtained with the PPP film.[1] The detailed interpretation of this air-sensitivity of poly-DMPP and PPP films, which probably arises from their less positive $E^{\circ\prime}$ values, is not yet clear. The σ values of poly-DMPP films are *ca.* 100 times smaller than those (*ca.* 10^{-3} S cm^{-1}) of poly-(*N*-methylpyrrole) films.[5]

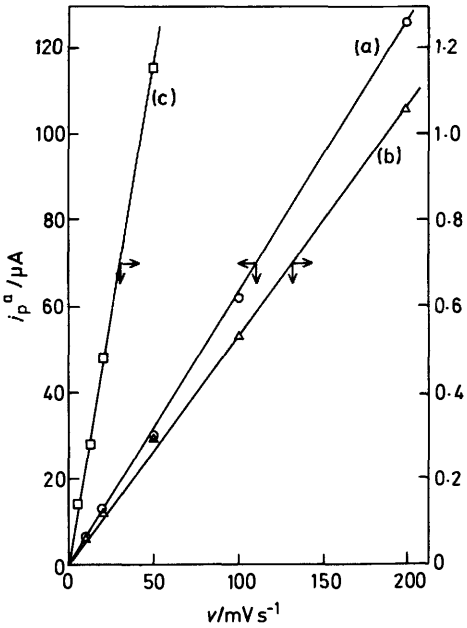

Figure 6. Anodic peak currents, i_p^a, for the oxidation of poly-DMPP films deposited on BPG electrodes as a function of potential scan rate (v). Supporting electrolyte 0.1M-NaClO$_4$ in acetonitrile. The films were the same as those used for Figure 5; thicknesses: (a) 0.08, (b) 0.8, (c) 4.0 μm

Electrochemical Properties of Poly-DMPP Films.—The cyclic voltammograms of poly-DMPP films on BPG electrodes in acetonitrile solution (0.1M-NaClO$_4$) at various potential scan rates are shown in Figure 5; the films with different thicknesses (φ) were employed. The reversible cyclic voltammetric response was observed for all thicknesses studied. For $\varphi = 0.08$ μm, symmetrical cyclic voltammograms were obtained: the anodic and cathodic peak currents (i_p^a and i_p^c) were almost the same, and the potential difference (ΔE_p) between anodic and cathodic peak potentials was nearly zero, as expected for the electrode reaction of a surface-confined redox species where diffusion phenomena do not occur.[12,13] Essentially similar features are

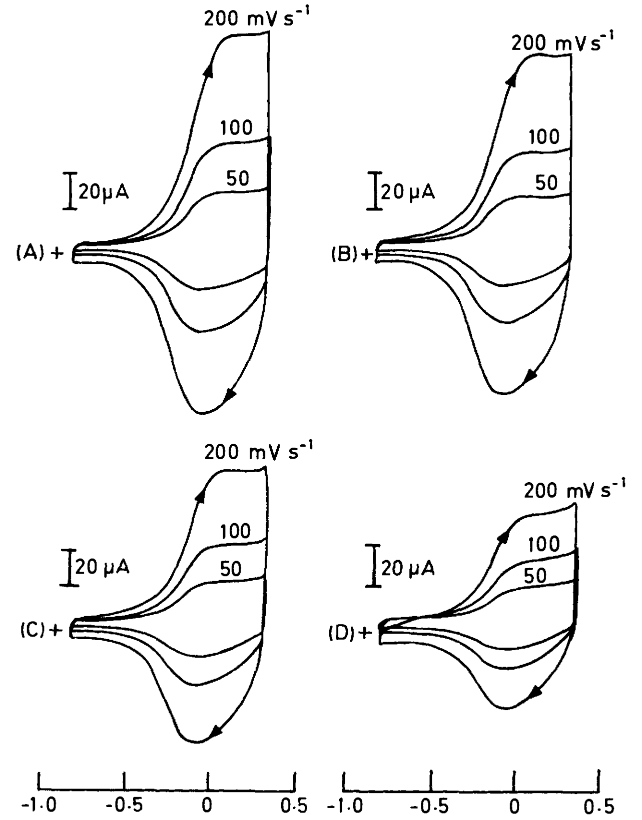

Figure 7. Typical cyclic voltammograms of poly-DMPP film deposited on a BPG electrode in buffered aqueous solutions containing 0.2M-$NaClO_4$ at pH (A) 3.0, (B) 5.0, (C) 7.0, or (D) 10.0. The poly-DMPP film (thickness 0.08 µm) was prepared on a BPG electrode as for Figure 5. The numbers on each voltammogram indicate potential scan rates (in mV s^{-1})

shown by thicker films (φ = 0.8 and 4.0 µm), except that peak separation can be observed at high scan rates such as 100 and 200 mV s^{-1} (*i.e.* $\Delta E_p \neq 0$). This peak separation may be ascribed to 'film resistance'.[13] For the films used in Figure 5, the relation between the anodic peak current ($i_p{}^a$) and scan rate (v) was found to be linear in the range of v from 10 to 200 mV s^{-1} (see Figure 6). This fact, together with the data in Figure 5, indicates that the electrode reaction of the poly-DMPP film is phenomenologically equivalent to that of a surface-attached redox species.[12,13] Cyclic voltammetric behaviour essentially similar to that shown in Figure 5, where $NaClO_4$ was used as supporting electrolyte, was also observed in acetonitrile solutions containing tetrabutylammonium perchlorate or tetrabutylammonium tetrafluoroborate.

The electrochemical behaviour of poly-DMPP film deposited on BPG electrodes was also examined in aqueous solutions of various pH values. A typical example of such experiments is shown in Figure 7. A reversible cyclic voltammetric response was obtained in all the electrolyte solutions irrespective of potential scan rate (v). At given v, the anodic and cathodic peak potentials ($E_p{}^a$ and $E_p{}^c$) were independent of pH, and the peak currents ($i_p{}^a$ and $i_p{}^c$) decreased with increasing pH. The fact that the formal redox potentials ($E^{o\prime}$), estimated as averages of $E_p{}^a$ and $E_p{}^c$ values, are independent of pH indicates that protons are not involved in the electrode reaction itself. This case is apparently different from that of the electrode reactions for PPP film[1] and other electroactive films formed by electropolymerization [*e.g.* polyaniline (PA),[14] poly(pyrene-1-amine) (PPA),[9a] poly-(*o*-phenylenediamine) (PPD),[15] and poly-(*N*-alkylaniline)

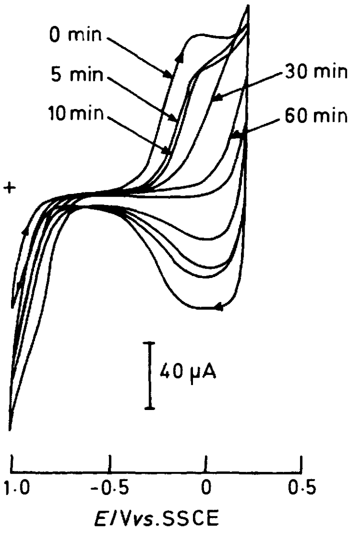

Figure 8. The stability of poly-DMPP film in air-saturated acetonitrile solution containing $NaClO_4$ (0.1M); scan rate 200 mV s^{-1}. The poly-DMPP film (thickness 0.8 µm) was prepared as for Figure 5. The cyclic voltammograms were taken after 0, 5, 10, 30, and 60 min from immersion of the poly-DMPP-film-coated electrode in air-saturated acetonitrile solution (0.1M-$NaClO_4$)

(PAA)[16] films], where linear $E^{o\prime}$ *vs.* pH plots with the slopes of about −60 mV per pH unit are obtained; thus protons and electrons take part in the electrode reactions in 1:1 ratio. Further, the pH dependences of $i_p{}^a$ and $i_p{}^c$ observed for the poly-DMPP film are essentially different from those observed for PPP, PA, PPA, PPD, and PAA films.[1,9a,14–16] In the case of these latter films, protons participate in the electrode reactions and thus the peak currents reflect the kinetics of the reactions, the rates of which depend on concentration of protons in the film. For these films, as expected, $i_p{}^a$ and $i_p{}^c$ were found to decrease with increasing pH. On the other hand, in the case of the poly-DMPP film, protons are not involved in the electrode reaction, as can be seen from the aforementioned fact that $E^{o\prime}$ is independent of pH. If protons did take part in the electrode reaction, then the $E^{o\prime}$ values should change with pH. The effective protonation constants of poly-DMPP film might be expected to be in the pK_a region of about 3—10, since the pK_a value of 3,6-di-t-butyl-1,4-dihydropyrrolo[3,2-*b*]pyrrole[2d] is 3.6, and it is known that the effective pK_a of polymers varies with the degree of protonation. Thus, as a result of protonation, the change of pH is considered to cause variation in swelling of poly-DMPP film in the pH range examined (3—10). The rate for the overall charge-transport process* within the solvent-swollen poly-DMPP film consequently changes with pH, and thus pH dependence of the peak currents is observed.

Figure 8 shows the results of the examination of the sensitivity of the poly-DMPP films to oxygen by cyclic voltammetry. In this case, the cyclic voltammetric measurements were carried out in an air-saturated acetonitrile solution. When the voltammograms were not taken, the potentiostat was kept off and the solution remained air-saturated. The cathodic and anodic peak currents decreased gradually with time after the immersion of the poly-DMPP film-coated ITO electrodes into the electrolyte solution. From comparison of Figure 1(B) with

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* The overall charge-transport process is thought to involve electron-hopping between redox-active sites, the charge-compensating counter-ion motion which is necessarily coupled to electron transfer, the motion of solvent, and/or the segmental motion of the polymer chain, as in the case of other redox polymer films.[13,17]

Figure 8, we consider that the decrease in electroactivity is due to degradation (or decomposition) of the film by oxygen. Although the mechanism of this oxidative degradation is not clear, it is probable that oxygen atoms or OH radicals, formed as the primary intermediates, chemically rupture a part of the polymer spine and/or the DMPP rings. This idea is qualitatively supported by the fact that the cathodic currents (observed below *ca.* -0.8 V *vs.* SSCE in Figure 8) corresponding to the reduction of O_2 molecules, which reach the electrode surface through the poly-DMPP film, increase gradually with a decrease in the electroactivity of the film itself; partial decomposition of the film is expected to make penetration of oxygen into it easy. This air-sensitivity would be a serious problem in practical applications of the poly-DMPP films and film-coated electrodes, *e.g.* as active materials for rechargeable polymer batteries.

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