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The Preparation of Poly(dihydroxyphenylene) through the Electro-Oxidative Polymerization of Hydroquinone

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Hydroquinone is electro-oxidatively polymerized to poly(dihydroxyphenylene) on the Pt electrode, whose structure was confirmed by spectroscopic measurements. The polymerization proceeds via an oxidative and cationic mechanism. The poly(dihydroxyphenylene) thus formed is a Nernstian-type electro-active polymer (E°=0.7 V vs. Ag/AgCl in an acidic medium) and shows a redox reaction through two-electron transfer, accompanied by proton dissociation on the Pt electrode.

There is much interest in the thin films on electrodes by meanes of the electro-polymerization of pyrrole,$^{1)}$ thiophene,$^{2)}$ aniline,$^{3,4)}$ phenol,$^{5,6)}$ and benzene.$^{7,8)}$ These aromatic conjugated polymers exhibit significant electrical conductivity and are potentially useful materials$^{9-11)}$ because most of the polymers show electro-activity with a one-electron transfer on the electrodes. However, there remains some room for further improvement of these electric devices, such as charge storagebility and responsibility to use. To overcome these problems, a π-conjugated polymer with a multi-electron transfer redox site is expected to have advantages.

We have been studying the electro-polymerization of benzene derivatives, including hydroquinone. Hydroquinone is known to be oxidized through a two-electron transfer, accompanied by the dissociation of protons,$^{12,13)}$ and a hydroquinone polymer is expected to show a large capacity and to be applicable to electric devices. However, thus for only one paper has been reported on the electro-chemical preparation of poly(dihydroxyphenylene),$^{14)}$ except for chemically prepared poly(dihydroxyphenylene)$^{15,16)}$ and an electro active and π-conjugated polymer with a two-electron transfer redox site.

In this paper, we will report the electro-oxidative polymerization of hydroquinone to yieid poly(dihydroxyphenylene) and its two-electron transfer reaction, accompanied by a 4-proton addition-elimination on the electrode. The electro-oxidative polymerization mechanism will also be discussed.

Experimental

Materials. Hydroquinone and benzoquinone were purified by recrystallization. Solvents such as nitromethane, acetonitrile, tetrahydrofurane, and dymethyl sulfoxide were purified by two distillation before electrolysis. Tetrabutylammonium perchlorate was used as a supporting electrolyte after recrystallization from ethanol–water and was dried in vacuo for 1 d at 100 °C.

Electrolysis. A pair of platinum plate (2×5 cm) was set in a cell$^{17)}$ with 1 cm spacing as a working and an auxiliary electrode. The reference electrode was Ag/AgCl. A typical electro-polymerization was as follows. A nitromethane solution (80 cm^3) of hydroquinone (0.1 mol m^{-3}) and tetrabutylammonium perchlorate (0.2 mol m^{-3}) was kept in the cell at 20 °C under a nitrogen atmosphere. The preparative electrolysis was carried out under a controlled potential with potentiogarvanostate (NIKKO KEISOKU NPG-301) without stirring. The electricity was measured by the use of a digital coulomb meter (NIKKO KEISOKU NDCM-1). After the electrolysis, the adhered product was removed from the working electrode and dedoped by washing with methanol and aqueous ammonia. The product was washed with methanol and dried in vacuo for 1 d at 80 °C.

The current efficiency (%) was calculated by dividing the polymer yield by the theoretical value. Theoretical Yield=$(Q/2nF)\times100$ (n=molar number, F: 96484 C mol^{-1}, Q: electroricity (C)).

Electrochemical Preparation of the Thin Poly(dihydroxyphenylene) Film on Pt Disk Electrode. The thin film of poly(dihydroxyphenylene) on the Pt electrode was electrochemically prepared by means of a cyclic potential sweep between −0.5 V and 1.8 V in the same electrolytic mixture as the preparative electrolysis. The polymer-coated electrode thus prepared was used in the voltammetric measurements. The as-grown poly(dihydroxyphenylene) on the disk electrode was set in a 25 vo%l pyridine-acetonitrile solution. The electro-oxidation was carried out at an applied potential of 1.1 V. After the electrolysis, the cyclic voltammograms of the polymer on the electrode were measured in a dimethyl sulfoxide solution.

Chemical Preparation of Poly(dihydroxyphenylene). Poly(2,5-dymethoxy-1,4-phenylene) was prepared through the electro-oxidative polymerization of p-dimethyoxybenzene,$^{18)}$ whose structure was completely confirmed by means of spectroscopic measurements.$^{19)}$ A dichloromethane solution (10 cm^3) of boron tribromide (2 cm^3) was added to a dichloromethane solution (50 cm^3) containing poly(2,5-dymethoxy-1,4-phenylene) (0.39 g) at 20 °C. The heterogeneous mixture was then refluxed at 40 °C for 1 d. After the reaction, the mixture was poured into water to precipitate the polymer. The polymer was collected, washed with methanol and water, and dried in vacuo at 70 °C. The completion of the demethylation was confirmed by the disappearance of the IR absorption band at the ascribed CH_3 vibrations of 2950 and 3000 cm^{-1}.

Spectrscopic Data of the Polymer. The electrochemically prepared polymer was characterized by means of IR (JASCO IR-810) and solid ^{13}C NMR (JEOL FX-100). Poly(dihydroxyphenylene)(Dedoped sample) Found: C, 68.4; H, 3.4% Calcd for ($C_6H_4O_2$): C, 66.7; H, 3.7% IR(KBr, cm^{-1}), 3400(ν_{O-H}); 1620, 1440($\nu_{C=C}$); 1140(ν_{C-O}); 1320(δ_{O-H}); 855(δ_{C-H}). CP-Mass ^{13}C NMR(90 Mz) δ=114, 122, 131.

Cyclic Voltammetry. Cyclic voltammetry was carried out in a two-compartment cell. A platinum disk (0.126 cm^2), platinum wire, and Ag/AgCl were used as a working, an auxiliary and a reference electrode respectively. The potential was controlled with a dual potentiogarvanostate (NIKKO KEISOKU DPG-3) and a function generator (NIKKO KEISOKU NFG-3). The scanning rate of the potential was 100 mV s^{-1}.

Electrical-Conductivity Measurements. After the electrolysis, the polymer adhering to the anode was peeled off and washed with dry hexane. The d.c. conductivity of the polymer tablet was measured using a two-point probe method. The doping of the electrolyte anion was confirmed by means of IR and fluorescence X-ray spectrometry.

Results and Discussion

Electro-Polymerization of Hydroquinone. Hydroquinone (0.1 mol m^{-3}) is electro-oxidatively polymerized to form a black polymer on the electrode, with 1.5 V as the applied potential. The concentrated hydroquinone solution was used to insure that the reaction between an active species and the substrate occurred. A cyclic voltammogram of the same electrolytic mixture shows no reduction peak corresponding to the anodic peak and reveals a typical irreversible reaction (Fig. 1). The oxidation peak current is not decreased in any cycle, and the black fiim is continuously formed during a number of potential sweeps, which indicates that the conductive polymer is formed on the electrode through the oxidation of hydroquinone.

The analytical data, such as the IR and solid ^{13}C NMR of the formed polymer, were in agreement with those of poly(dihydroxyphenylene) chemically prepared through the demethylation of poly(2,5-dimethoxy-1,4-phenylene) with boron tribromide (see Experimental section). The main structure of the formed polymer contained no oxyphenyelen bond, because the strong absorption of the C-O-C bond at 1180 cm^{-1} was not detected in the IR (Fig. 2). The IR absorption of the polymer disagreed slightly with that of poly(dihydroxy-1,4-phenylene) in the region between 800—900 cm^{-1} which is ascribed to the C-H out-of-plane vibration of the benzene ring and reveals substituted position on benzene. The absorpion at 810 cm^{-1}, ascribed to 1,2,3,4-tetrasubstituted benzene,[20] suggests that the polymer contains a 1,2-conjugated or nonlinear structure. The polyer was soluble in a conc. alkaline aqueous solution. The perchlorate anion had been doped in the poly(dihydroxyphenylene) after the electrolysis, was confirmed by the IR absorption bands at 1100 and 622 cm^{-1}. The electrical conductivity of the perchlorate anion doped polymer was ca. 10^{-7} S cm^{-1}. It makes possible a continuous formation of the polymer on the electrode (<2 mm).

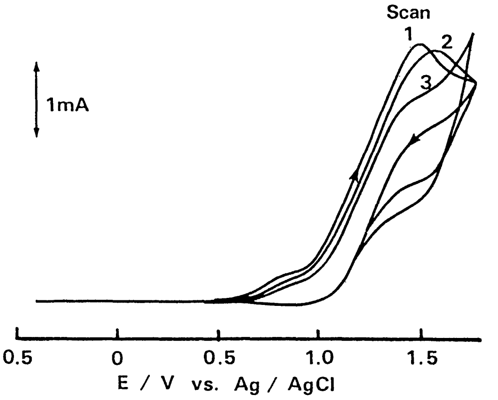


Fig. 1. Cyclic voltammograms of 0.1 mol m^{-3} of hydroquinone in nitromethane solution.

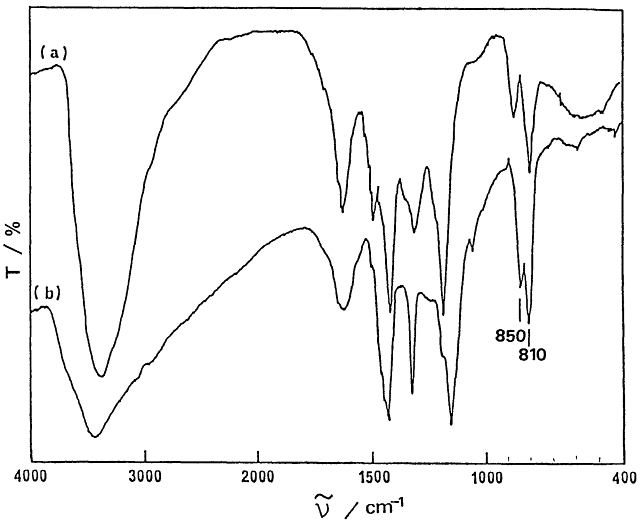


Fig. 2. IR spectra of chemically prepared poly(2,5-dihydroxy-1,4-phenylene) (a) and electrochemically prepared polymer (b).

Polymerization Mechanism. In nitromethane, hydroquinone is oxidized by means of a two-electron transfer to yield protonated benzoquinone,[21] and it is not polymerized in a dilute solution ([hydroquinone]<50 mmol m^{-3}). We found that the protonated benzoquinone cation is polymerized to yield poly(dihydroxyphenylene) when the feed concentration of

Table 1. Electro-polymerization[a] of Hydroquinone

Solvent	Solvent donor number	Current efficiency /%
CH_3NO_2	2.7	13
$C_6H_5NO_2$	4.4	22
CH_3CN	14.1	14
THF[b]	20.0	0
DMF[c]	26.6	0
DMSO[d]	19.8	0

a) Potential: 1.5 V; electricity: 0.6 F mol^{-1}. b) Tetrahydrofuran. c) *N,N*-Dimethyl formamide. d) Dimethyl sulfoxide.

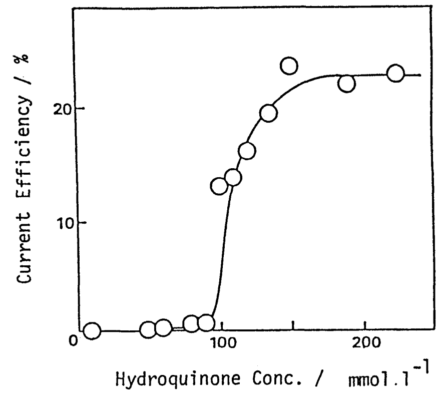


Fig. 3. Concentration of hydroquinone on the electro-polymerization in nitromethane at 1.5 V. (Electricity: 0.6 F mol^{-1}.)

hydroquinone is above 0.1 mol m^{-3} (Fig. 3). At a lower concentration, this polymerization is thought to be very slow, probably because the reaction between hydroquinone and the protonated benzoquinone does not easily occur, much as in the electro-polymerization of benzene.[8] Table 1 shows that this polymerization is suppressed by a strongly basic solvent, such as dimethylformamide and dimethyl sulfoxide. The current efficiency was not significantly influenced by oxygen bubbling through the electolytic mixture, which often deactivates a radical species. These results support the idea that this polymerization proceeds via a cationic mechanism.

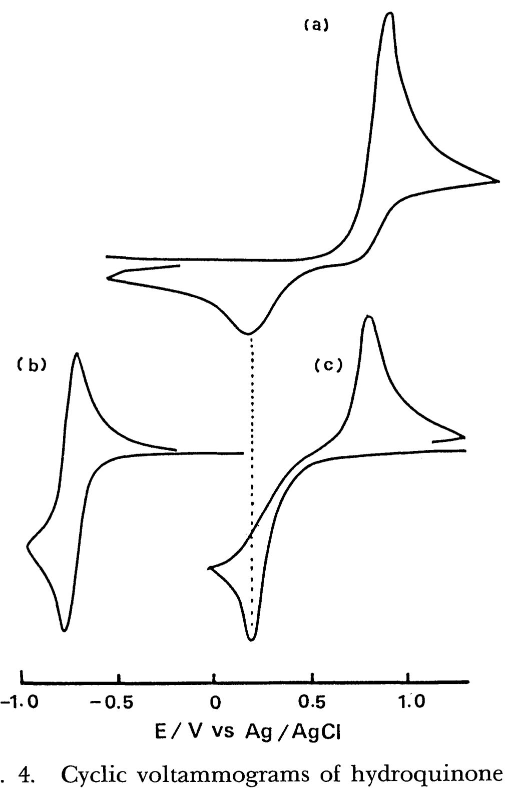


Fig. 4. Cyclic voltammograms of hydroquinone in acetonitrile (a), benzoquinone in acetonitrile (b), and benzoquinone in the presence of methanesulfonic acid (0.5 mol m^{-3}) (c).

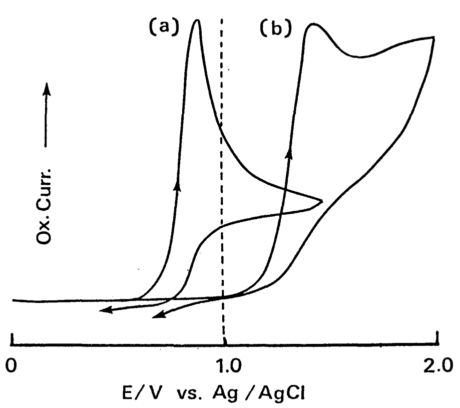
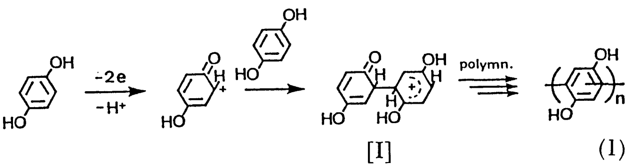


Fig. 5. Cyclic voltammograms of hydroquinone (a) and anisole (b) in nitromethane.

Hydroquinone shows an oxidation peak at 0.9 V in the acetonitrile; this peak is based on the two electron transfer (Fig. 4). The reduction peak appears at 0.1 V and is ascribed to the reduction of the protonated benzoquinone. *p*-Benzoquinone is reduced at 0.2 V in the presence of acid. This reduction peak potential agrees with that of hydroquinone. These results indicate that hydroquinone is two-electron oxidized to the protonated benzoquinone in the mixture. In a strongly basic solvent, hydroquinone is oxidized to benzoquinone, accompanied by proton elimination by the solvent, and is not polymerized. That is, it is considered that the protonated benzoquinone acts as an active species in the polymerization and electrophilically reacts with neutral hydroquinone to form the hydro dimer[I], much as in the polymerization mechanism of benzene.

The electro-polymerization of hydroquinone was carried out at 1.0 V in the co-existence of anisole in order to study the electrophilic reaction of the cation. Anisole is not electro-oxidized at this applied potential (Fig. 5). The polymer thus formed contained an anisole residue, which was confirmed by IR. That is, hydroquinone is electro-oxidized to the protonated benzoquinone. This cation acts as an active species and electrophilically reacts with the benzene ring of non-protonated hydroquinone. These processes are repeated to form poly(dihydroxyphenylene) (Eq. 1), in a manner similar to that in the electro-polymerization of benzene previously reported by the present authors.[8,22–24]



[I] (1)

Electrochemical Properties. The redox behavior of the polymer was greatly affected by the acidity of the electrolytic mixture. When the electro-oxidation of poly(dihydroxyphenylene) was carried out in a basic medium such as 25 vol% pyridine-acetonitrile, the analytical data of the polymer formed on the electrode indicates the formation of poly(benzoquinone)[25] through the complete elimination of protons. A cyclic voltammogram of this polymer in dimethyl sulfoxide gives the redox potential at −0.4 V, in the profile similar to that the benzoquinone redox couple ($BQ+e=BQ^{-*}$) (Fig. 6). In the acetonitrile, the poly(dihydroxyphenylene) film shows its oxidation peak and reduction peak at 1.0 V and 0 V respectively (Fig. 6). The later cyclic voltammogram is similar to that of hydroquinone in acetonitrile, suggesting a similar electrochemical reaction.

On the other hand, the cyclic voltammogram of the electrochemically prepared poly(dihydroxyphenylene) in an aqueous perchloric acid solution (Fig. 7) is reproducible, even after repeated scannings (10^3 times), between 0.5 and 0.9 V. Generally, the redox potential of the conductive polymer is reduced in comparison with that of the monomer. The redox potential at 0.7 V is consistent with that of hydroquinone: This means that the electron-transfer process of the polymer is of no help in estimation the redox reaction of the main chain.

The peak current is directly proportional to the scanning rate. This suggests that the polymer film is stable against the redox cycle and strongly adhers on the electrode. The i_{pa} is proportional to the sweep rate, even in very thick film (ca. 10—100 nm) (Fig. 8). This means that electron transfer occurs very rapidly, similarly to the electrochemistry of the absorption substrate on the electrode. That is, the electron-transfer process is not controlled by ion-diffusion, for the cojugated parts of poly(dihydroxyphenylene) acts as an electrode.

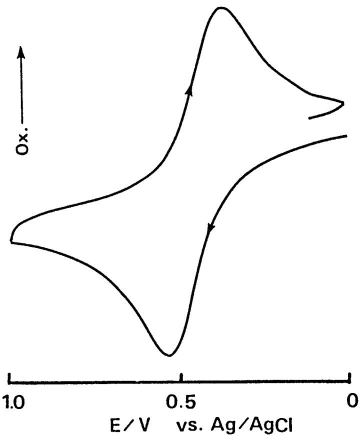


Fig. 6. Cyclic voltammogram of poly(dihydroxyphenylene) on Pt electrode in dimethyl sulfoxide after electro-oxidation in pyridine-acetonitrile solution.

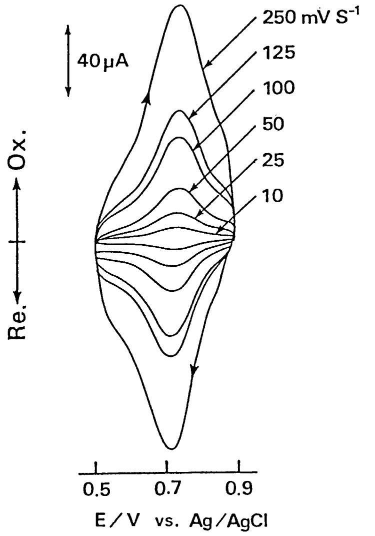


Fig. 7. Cyclic voltammograms of poly(dihydroxyphenylene) on the Pt electrode (0.126 cm^2) in 70 wt% perchloric acid-aqueous solution at various scanning rates.

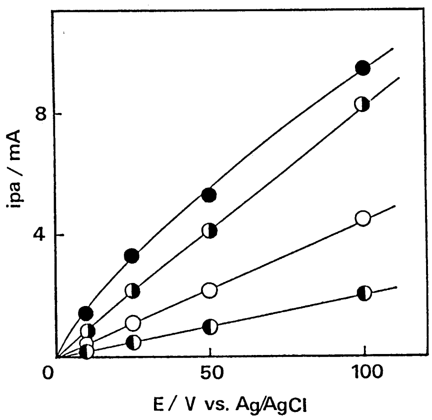


Fig. 8. Oxidation peak current on the cyclic voltammograms of poly(dihydroxyphenylene) which was electrochemically prepared by potential seep method (3 scans (◐), 4 scans (○), 5 scans (◑), and 7 scans (●), at various scan rate in perchloric acid).

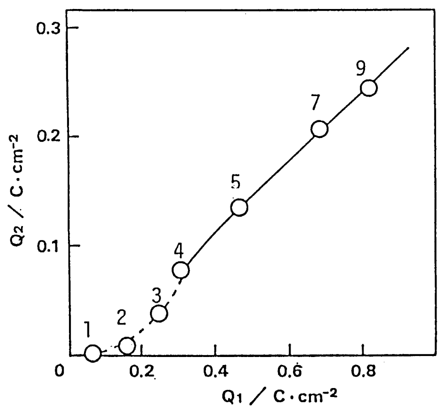


Fig. 9. The charge (Q_2) passing during redox reaction of these formed poly(dihydroxyphenylene) and the charge (Q_1) passing during the formation of poly(dihydroxyphenylene).

We comfirmed the charge storagebility of poly(dihydroxyphenylene) in comparison with the other electro-active polymers. Figure 9 shows the relationship between the charge of the polymer formation (Q_1) and the charge of the formed polymer (Q_2). Q_1 is approximately estimated to the quantity of the formed polymer. Q_2 is estimated the number of active site in poly(dihydroxyphenylene). This supports the ideas that poly(dihydroxyphenylene) is continuously deposited without the passivation and that its redox site acts efficiently, even for a thick film (ca. 10—100 μm). These characteristics of poly(dihydroxyphenylene), the efficient charge storage and rapid electron transfer, are superior to these of the conductive polymers, such as polypyrrole and polyaniline,[26] because of poly(dihydroxyphenylene) with two-electron transfer and π-conjugation.

Figure 10 shows the cyclic voltammograms of the polymer in nitromethane containing various acids. The cathodic and anodic peak potentials shift towards less anodic with an increase in the acidity of the electolytic mixture. This behavior is similar to that of hydroquinone,[21] which also supports the idea that the polymer contains a hydroquinone structure. In the acidic media, the plot of H°[27] vs the formal oxidation-reduction potential is linear, with a slope of ca. 120 mV$H^{\circ -1}$ (0.1 mol m^{-3}—2 mol^{-3} CH_3SO_3H) (Fig. 11). This indicates that protons and electrons take part in the reaction through a 2-proton/1-electron reaction, which is evaluated by the use of a Nernstian equation. Thus, it is considered that the overall electrode reaction of poly(dihydroxyphenylene) consists of two-electron transfer with a 4-proton addition-elimination reaction. The voltammogram area for the redox reaction in the acidic mixture, which corresponds to the total charge of the electrode reaction, increases with the acid concentration. From these results, it is concluded that the redox reaction of the poly(dihydroxyphenylene) in the acidic medium is schematically shown by Equation 2.[28] An acidic medium or protonation of the polymer causes the polymer to become electroactive.

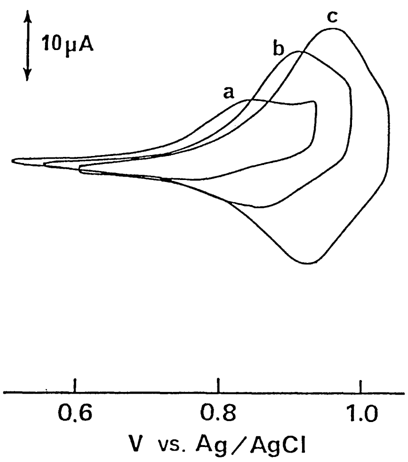


Fig. 10. Cyclic voltammograms of the polymer formed on the Pt electrode in nitromethane containing a: 0.2 mol m^{-3} Et_4NClO_4+0.15 mol m^{-3} CH_3SO_3H, b: 0.2 mol m^{-3} Et_4NClO_4+0.5 mol m^{-3} CH_3SO_3H, c: 0.2 mol m^{-3} Et_4NClO_4+1.85 mol m^{-3} CH_3SO_3H; sweep rate, 25 mV s^{-1}.

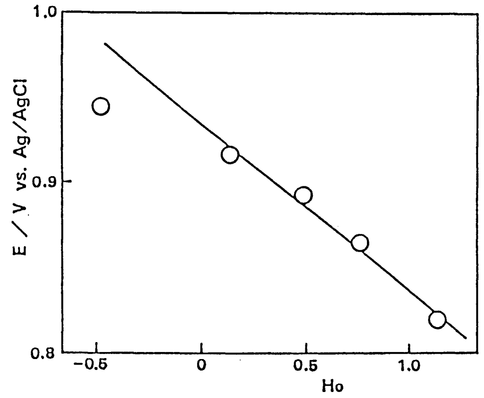
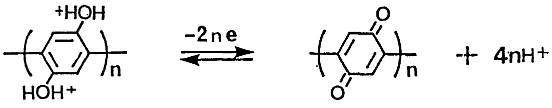


Fig. 11. Relationship between the equilibrium potential of poly(dihydroxyphenylene) film in acidic solution and the Hammet acidity function of the solution.



(2)

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25) IR(KBr, cm^{-1}): 2930($\nu_{C\text{-}H}$); 1640($\nu_{C=O}$).

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27) H° (Hammet acidity function) means, more correctly the ability of proton-donation in a concd acid solution.

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