CHEMISTRY LETTERS, pp. 65-68, 1989.

Preparation of Electroactive Poly(dihydroxyphenylene)

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Hydroquinone is electro-oxidatively polymerized to poly(dihydroxyphenylene), which is a Nernstian-type electroactive polymer (E^{o}= 0.7 V in acidic medium) and shows a redox reaction through two-electron transfer accompanied with 4 protons dissociation on Pt electrode.

Recently electrochemically prepared polymers such as polypyrrole,$^{1)}$ polythiophene,$^{2)}$ polyaniline$^{3,4)}$ and polyphenylene$^{5,6)}$ received a great attention in view of their physicochemical properties. Hydroquinone is known to be oxidized through two electron transfer accompanied with dissociation of protons, and it is expected that a hydroquinone polymer shows a large capacitance and is applicable to electric devices. But no paper has hitherto been reported on electrochemical preparation of poly(dihydroxyphenylene), except chemically prepared poly(dihydroxyphenylene),$^{7,8)}$ and an electroactive and π-conjugated polymer with a two-electron transfer redox site. In this communication, we report the electro-oxidatively polymerization of hydroquinone to yield poly(dihydroxyphenylene) and its two electron transfer reaction accompanying 4 protons addition-elimination on the electrode.

In nitromethane hydroquinone is electro-oxidized with two-electron transfer to yield protonated benzoquinone,$^{9)}$ and is not polymerized in a dilute solution (< 50 mM). We found that the protonated benzoquinone cation is electrophilically reacts with hydroquinone to yield poly(dihydroxyphenylene), when the feed concentration of hydroquinone is above 0.1 M. The electrochemical polymerization was carried out for the nitromethane solution of hydroquinone and tetraethylammonium perchlorate with controlled potential at 1.5 V (Ag/ AgCl) under oxygen-free atmosphere in one compartment cell equipped with platinum electrode. Black polymer film was formed on the electrode through the electrolysis. The analytical data of the polymer was in complete agreement with those of poly-(dihydroxyphenylene).10) The polymer was soluble in conc. alkaline aqueous solution. Electrical conductivity of the perchlorate anion-doped polymer was ca. 10^{-7} S/cm. It enables to 9 continuously formation of the polymer on the electrode (thickness < 2 mm).

Redox behavior of the polymer was greatly affected by acidity of the electrolysis solution. 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) through the complete elimination of proton.11) Cyclic voltammogram of this polymer in dimethylsulfoxide showed the redox potential at -0.4 V, in the similar profile of benzoquinone redox couple ($BQ + e = BQ^{-*}$).

On the other hand, Fig. 1a shows cyclic voltammograms of the electrochemically prepared poly(dihydroxyphenylene) in aqueous perchloric acid solution, which was reproduceable even after repeated scannings (10^3 times) between 0.5 and 0.9 V. The peak current is directly proportional to the scanning rate. This suggests

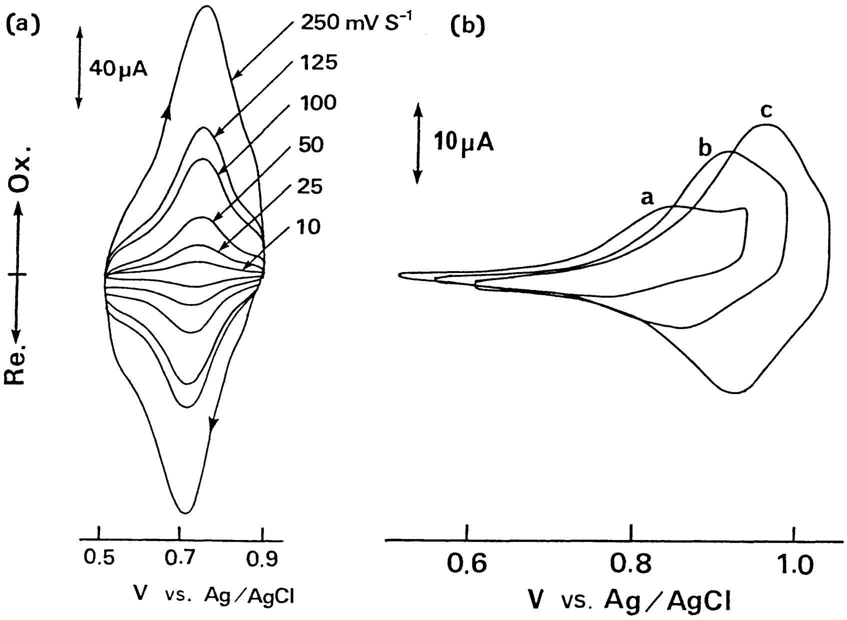
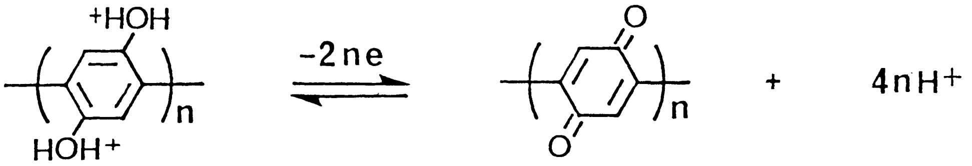


Fig. 1. (a) Cyclic voltammograms of poly(dihydroxyphenylene) on the Pt electrode ($0.126\ cm^2$) in 70 wt% perchloric acid-aqueous solution at various scanning rates. (b) Cyclic voltammograms of the polymer formed on the Pt electrode in nitromethane containing a: 0.2 M Et_4NClO_4 + 0.15 M CH_3SO_3H, b: 0.2 M Et_4NClO_4 + 0.5 M CH_3SO_3H, c: 0.2 M Et_4NClO_4 + 1.85 M CH_3SO_3H; Sweep rate, 25 mV/s.

that the polymer film is stable against the redox cycle and strongly adhered on the electrode. The redox potential at 0.7 V is consistent with that of hydroquinone: This means that electron transfer process of the polymer is not influenced by the conjugated structure of the polymer and does not involve the oxidation of the main chain.

Figure 1b shows the cyclic voltammograms of the polymer in the nitromethane containing various acids. Cathodic and anodic peak potentials shifte towards less anodic with an increase in the acidity of the electolytic mixture. This behavior is similar to that of hydroquinone,9) which also supports that the polymer contains a hydroquinone structure. In the acidic media, the plot of $\log[H^+]$ vs the formal oxidation-reduction potential was linear with the slope of ca. 120 $mV/\log[H^+]$ (0.1 M - 2 M CH_3SO_3H). This indicates that protons and electrons take part in the reaction through a 2 protons/1 electron reaction. Thus it is considered that the overall electrode reaction of poly(dihydroxyphenylene) consists of two-electron transfer with 4 protons addition-elimination reaction. The voltammogram area for 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 considered that the redox reaction of the poly(dihydroxyphenylene) in the acidic medium is schematically shown by Eq. 1.12) An acidic medium or protonation of the polymer causes the polymer electroactive.



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This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area "Macromolecular Complexes" from the Ministry of Education, Science and Culture, Japan.

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10) Poly(dihydroxyphenylene). 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}): Solid ^{13}C-NMR(90Mz, ppm) 114, 122, 151. The main structure of the formed polymer contained no oxyphenylene bond, because strong absorption of C-O-C bond at 1180 cm^{-1} was not detected in the IR. These spectroscopic data of the formed polymer also agreed with those of the poly(dihydroxyphenylene) chemically prepared through demethylation of poly(2,5-dimethoxy-1,4-phenylene) with tribromoborone.

11) IR(KBr, cm^{-1}): 2930(ν_{C-H}), 1640($\nu_{C=O}$)

12) pK of hydroquinone has been reported to be $pK[QH_3^+]/[QH_4^{2+}] = 6.9$: A. B. Hadid, P. Rimmelin, J. Sommer, and J. Devynek, J. Chem. Soc., Perkin Trans. 2, 1982, 269.

(Received September 26, 1988)