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Electrochemical Characteristics of an Insulating Polymer-Modified Electrode Prepared by Electrochemical Polymerization

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The electrochemical polymerization of 1,4-bis(2-methylstyryl)benzene and the electrochemical behavior of the resulting polymer-modified electrode have been studied. The rapidly decreasing polymerization current of the 1,4-bis(2-methylstyryl)benzene can be attributed to the passivation effect of the resulting polymer coating. The polymer-modified electrode showed an electrochemical response in an aqueous electrolyte solution corresponding to solute electroactive ions. The electrochemical behavior was dependent on the polymerization charge and the size of the electroactive ions. The polymer-modified electrode is applicable as the selective electrode for electroactive ions and molecules in an electrolyte solution containing electroactive bacterial cells.

Electrochemical polymerization of various aromatic compounds has been studied for the preparation of conducting polymers.[1] The electrochemical polymerization method is usually suitable for obtaining the polymer films with high electrical conductivity. However, the morphology and properties of the films obtained are strongly dependent on the polymerization conditions.[2] In some cases, the polymerization is thought to be initiated by nucleation upon the electrode surface followed by growth of islands, resulting in a relatively rough surface morphology of the film.[3] Even fractal pattern formation has been reported in electrochemical polymerizations of some aromatic heterocyclic molecules.[4]

On the other hand, we have recently reported the electrochemical polymerization of 1,4-bis(2-methylstyryl)benzene(MSB), shown in Fig. 1, resulting in the formation of a thin insulating polymer film, PMSB film, with a smooth surface.[5] Although the chemical structure of the polymer film has not yet been characterized because of its maximum thickness of ca. 100 nm, PMSB may have a structure similar to poly (1,4-phenylene) and/or poly (1,4-phenylene vinylene) in its main chain as judged from the monomer structure. The relative dielectric constant of 2.7 also suggests that PMSB film is composed of an aromatic moiety. However, the conjugation length of its main chain should be restricted by a twisted structure as judged from electrical conductivity as low as 7×10^{-14} S cm^{-1}. Its structure seems to be a crosslinked and network structure rather than linear and non-crosslinked since PMSB showed good mechanical stability and common solvent resistivity.

Although the complete film of 100 nm thickness is pinhole-free, it seems to be possible to control the density and size of pinholes by controlling the polymerization conditions and thickness. These characteristics of PMSB film as an insulating coating may be applicable for some functional applications such as an passivation and insulating films and also as a functional membrane.

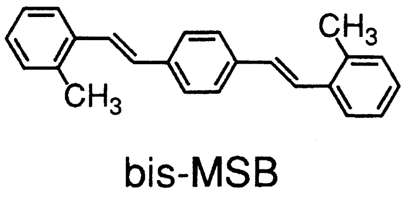

Fig. 1. Chemical structure of MSB.

In the present paper, the electrochemical characteristics of PMSB-coated electrodes in an aqueous electrolyte solution containing an electroacitve substrate are reported. The permeabilities of some electroactive substrates including ions, metal complexes, and even bacterial cells have been investigated by cyclic voltammetry as a function of the preparation conditions of the PMSB layer. Among various bacterial cells, *Streptococcus mutans* is one of the most interested ones, since it lives in the mouth of mammals and decays teeth in the human mouth. In this study, GS-5 was studied as a typical example of various *Streptococcus mutans.*

Experimental

Commercially available MSB was used as received while acetonitrile (AN), tetrabutylammonium tetrafluoroborate (TBAFB), and water, which were used to prepare the electrolyte solutions, were purified by the usual methods. The electrochemical polymerization of MSB was performed by applying a potential of 2.0 V vs. Ag to an ITO (In-Sn-Oxide)-coated electrode immersed in 0.1 M TBAFB+0.01 M MSB/AN solution, utilizing an Ag reference electrode and a Pt wire counter electrode ($1\,\mathrm{M}=1\,\mathrm{mol\,dm^{-3}}$). The electrochemical polymerization charge was determined by using a bipolarcoulomb meter (Hokuto Denko HC-203D). The PMSB-coated electrode was treated with purified AN and dried under purified Ar gas flux followed by washing with methanol and re-drying under vacuum.

The electrochemical characteristics of the PMSB-coated electrodes were studied in aqueous electrolyte solutions containing 0.1 M Na_2SO_4 as a supporting salt and 2 mM electroactive salts, $K_4[Fe(CN)_6]$, $[Ru(bpy)_3]Cl_2$, or tetraethylammonium iodide (TEAI). These solutions show electrochemical waves corresponding to the redox couples of $Fe^{2+/3+}$, $Ru^{2+/3+}$ and $I^{-/0}$. GS-5 was grown in the usual manner at 37 °C in Trypticases soy broth.[6] After 48 h, the cultured medium, which was in the logarithmic phase, was diluted and centrifuged. The precipitated bacteria were washed with a small amount of phosphate buffer solution and recentrifuged. The obtained bacteria were dispersed in a neutral aqueous phosphate solution. This solution was used for the electrolyte solution. The concentration of GS-5 in the electrolyte solution was 1×10^4 cells/ml.

Results and Discussion

Electrochemical polymerization of PMSB was performed by the constant potential method at 2.0 V vs. Ag. As shown in Fig. 2, the oxidation current decreased rapidly immediately after potential application. Usually, the Faradic current in constant potential electrolysis follows the Cottrell equation (1),

$$i = nFAD^{1/2}C\pi^{-1/2}t^{-1/2}, \qquad (1)$$

where n, F, A, D, and C are the number of electrons, Faraday constant, electrode area, diffusion coefficient of the electroactive substrate, and concentration of the electroactive substrate, respectively.[7] As observed in the inset of Fig. 2, however, the oxidation current of MSB did not follow the Cottrell equation. That is, the oxidation current of MSB decreased faster than predicted by the Cottrell equation resulting in the super linear increase in the oxidation current with an increase in the $t^{-1/2}$ as shown in the inset of Fig. 2. On the other hand, the oxidation current of ferrocene at the same concentration in the same measurement cell increased linearly against $t^{-1/2}$ in the same time range. Therefore, the rapidly decreasing oxidation current of MSB shown in Fig. 2 is thought to originate not in the diffusion-limitation of the monomer within the solution phase, but in the passivation effect of the insulating PMSB layer on the ITO-coated electrode. Since the PMSB layer has quite low electrical conductivity, 7×10^{-14} S cm^{-1}, electrochemical reactions on the PMSB film surface should be quite slow.[5] Actually, the polymerization current could not be observed after the polymerization of 200 mC even when the polymerization bath was stirred. When the polymerization charge was restricted to some appropriate amount, the PMSB layer may possibly have had specific characteristics as a size selective membrane since there still existed some defects on the PMSB surface.

The electrochemical characteristics of the PMSB-coated electrode were studied in aqueous electrolyte solutions containing $[\mathrm{Ru(bpy)_3}]^{2+}$, $[\mathrm{Fe(CN)_6}]^{4-}$, or iodide ions. Figs. 3 and 4 show cyclic voltammograms of PMSB-coated and noncoated electrodes in the $[\mathrm{Fe(CN)_6}]^{4-}$ and $[\mathrm{Ru(bpy)_3}]^{2+}$ containing solutions. In the case of the noncoated electrode, these electroactive ions showed well-defined reversible redox current waves. However, the electrochemical current waves were suppressed by the PMSB layer. When the electrode was coated with a PMSB layer with a polymerization charge larger than 200 mC, any electrochemical cur-

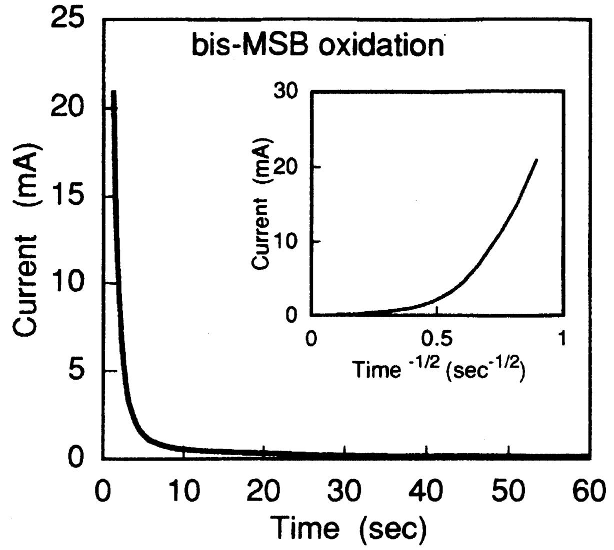

Fig. 2. Oxidation current of MSB/acetonitrile solution at 2.0 V vs. Ag (inset; Cottrell plot of the oxidation current).

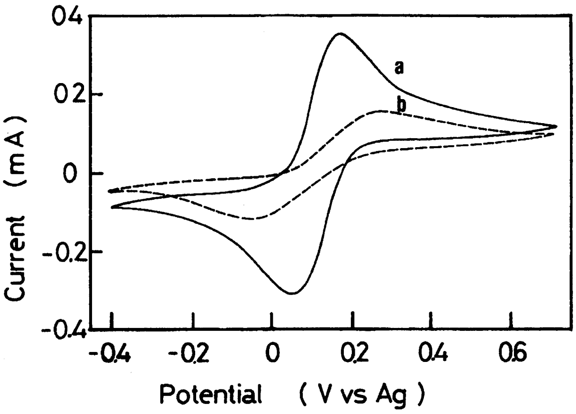

Fig. 3. Cyclic voltammograms of (a) noncoated and (b) PMSB-coated (100 mC) electrodes in 2 mM $\mathrm{K_4[Fe(CN)_6]}$ solution.

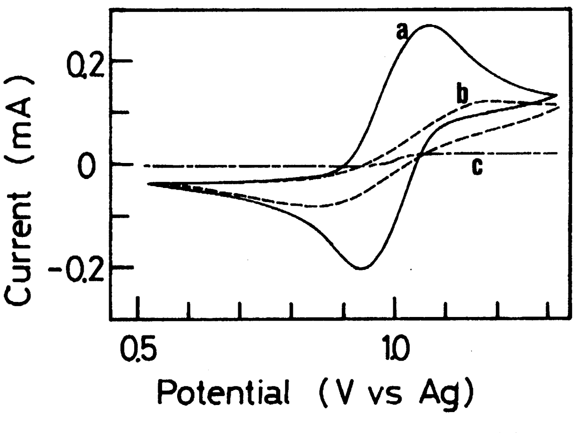

Fig. 4. Cyclic voltammograms of noncoated (a) and PMSB-coated (b; 130 mC), (c; 160 mC) electrodes in 2 mM $\mathrm{[Ru(bpy)_3]Cl_2}$ aqueous solution.

rent larger than 1 μA was not observed. That is, the PMSB layer acts as a passivation layer for the electrochemical reactions and swelling of the polymer film in the aqueous electrolyte solution can be neglected. The polymer layer is thought to be hydrophobic as in the monomer. However, the decreased electrochemical current peaks shown in Figs. 3 and 4 can not be attributed not only to the passivation effect of the PMSB layer, since the voltammetric waves obtained with the PMSB-coated electrodes were very broad. If the PMSB layer acts as a simple passivation layer, only the effect of the decreased effective electrode surface area should be observed in the cyclic voltammogram of the PMSB-coated electrode, resulting only in suppressed electrochemical current but not in the diffused current peaks and the large peak-to-peak potential.

The diffused current peaks and small hysteresis in current waves upon the anode and cathode scans shown in Fig. 4c can not be explained in terms of simple passivation and apparent resistance effects of the PMSB coating. The current waves in Fig. 4c resemble "thin-layer voltammetry" or voltammograms of the microdisk array electrode in an electrolyte solution containing dissolved electroactive molecules.[8] This typical voltammetric bahavior can be explained as follows.

The PMSB film contains a considerable amount of microholes through which the Ru complex can pass to the ITO electrode surface. In such a case, the coated electrode should show behavior similar to that of an assembly of microdisk electrodes which have a diameter smaller than 1 μm and give no current peak in cyclic voltammetry. Though the detailed interpretation of these voltammetric characteristics will be described elsewhere, the maximum current of the oxidation current of these cyclic voltammograms are thought to be determined mainly by the effective diffusion coefficient of the electroactive ions in the PMSB layer.

Figure 5 shows the dependencies of the anodic peak currents of the cyclic voltammograms of $[Fe(CN)_6]^{4-}$, $[Ru(bpy)_3]^{2+}$, and iodide with the PMSB-coated electrodes on the polymerization charge for the PMSB coating. The peak current was normalized with that of the noncoated electrode. The peak current decreased with an increase in the polymerization charge of PMSB. The increases in the polymerization charge and in the polymerization time are thought to result in the dense coating and in the small permeation of the electroactive ions through the dense coating. Furthermore, for the intermediate polymerization charge of PMSB (30—100 mC), the normalized oxidation peak currents of $[Fe(CN)_6]^{4-}$ and $[Ru(bpy)_3]^{2+}$ ions were smaller than that of iodide ion. In the case of a polymerization charge of 90 mC, only 12% of the oxidation peak current of iodide ion was suppressed while the oxidation peak currents of the metal complexes were suppressed to one half of that of the noncoated electrode. Therefore, the diffusion coefficient of iodide ion in the PMSB layer is larger than that of the metal complexes. The difference in these diffusion coefficients in the PMSB layer should be larger than that in the solution phase. These differences might be caused by the difference in the sizes of the electroactive ions. The PMSB layer should contain a large amount of microholes having a diameter less than ca. 20 Å even with a large polymerization charge. Therefore, The iodide ion having a diameter of about 3 Å can permeate the PMSB layer easier than the metal complexes which have a diameter larger than 5 Å.

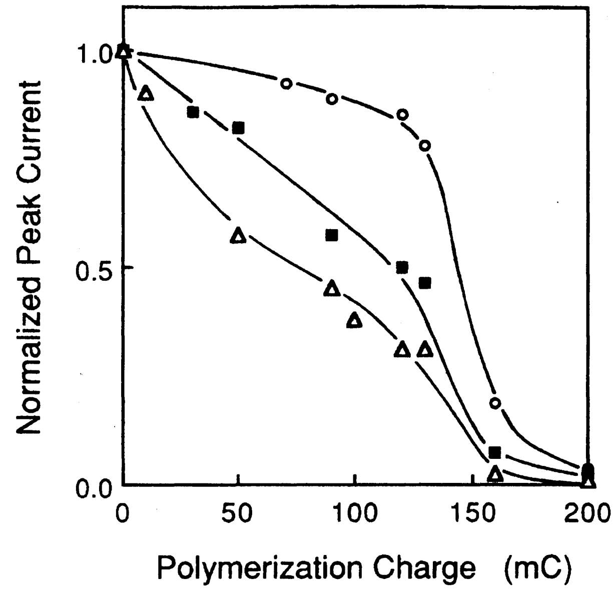

Fig. 5. Plots of oxidation peak currents of cyclic voltammograms of PMSB coated electrodes in (△) $K_4[Fe(CN)_6]$ solution (■) $[Ru(bpy)_3]Cl_2$ solution and (○) TEAI solution as functions of the polymerization charge of PMSB.

Clear size selectivity in the permeation current is expected in the case of an electroactive substance having a diameter much larger than that of MSB monomer (ca. 19 Å in length). For example, the electrochemical behavior of the PMSB-coated electrode in the electrolyte solution containing bacterial cells has been investigated. Figure 6 shows the cyclic voltammograms of PMSB-coated (with a polymerization charge of 20 mC) and noncoated electrodes in GS-5 and $[Ru(bpy)_3]^{2+}$ containing electrolyte solutions. The non-coated electrode showed both electrochemical current waves corresponding to GS-5 (marked with an arrow) and the Ru complex.

As reported in our previous paper, the current waves of GS-5 could not be observed when the solution was treated with a membrane filter having a pore size smaller than the size of the cell body.[6] Therefore, the oxidation current wave of GS-5 should originate from CoA on the cell body surface. The current wave of GS-5 could not be observed when the PMSB-coated electrode was used. However, the redox current waves of the Ru

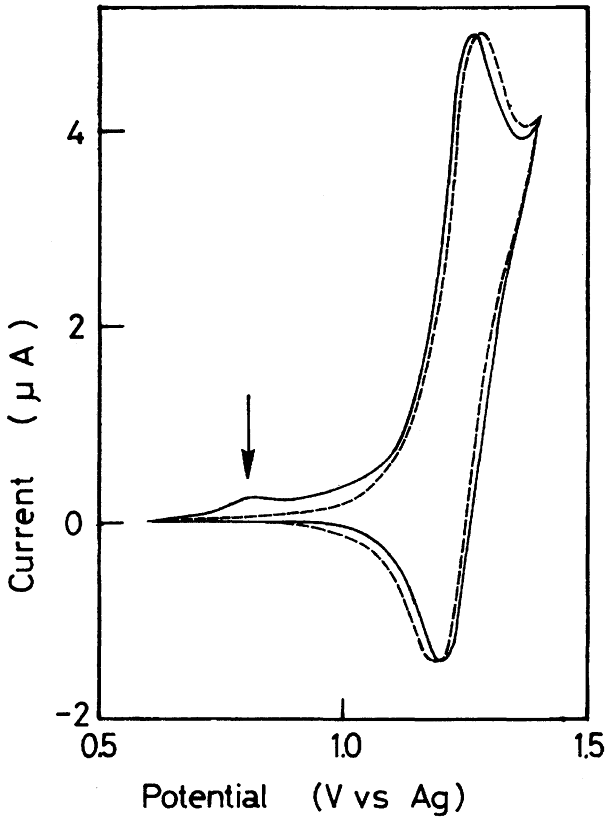

Fig. 6. Cyclic voltammograms of noncoated (solid line) and PMSB-coated (broken line) electrodes in aqueous electrolyte solutions containing [Ru(bpy)$_3$]-Cl$_2$ (20 μM) and GS-5. (The capacitive current was collected by using data obtained in the blank solutions.)

complex showed no marked suppression. It should also be noted that the peak-to-peak potential of the redox waves of the Ru complex increased when the electrode was coated with the PMSB layer, indicating a very thin coating on the ITO surface. These results indicate that the GS-5 cells which have a large diameter of 2—5 μm, can not reach the ITO surface, but the much smaller Ru complex can permeate through the PMSB layet to the ITO surface and give clear redox waves. The cyclic voltammogram illustrated in Fig. 6 by the broken line is similar to that of a solution after removing the GS-5 cell body by filtration. Therefore, the PBSM-coated electrode may be applicable for a functional electrode which can detect ions and molecules dissolved in the test solution containing bacterial cells without inhibition from the bacterial cells.

In conclusion, the electrochemical behavior of the PMSB-coated electrode, which can be prepared by the electrochemical polymerization of MSB, has been studied in aqueous electrolyte solutions. The voltammetric response of the PMSB-coated electrode was suppressed with increasing polymerization charge through the formed PMSB film. Small electroactive ions permeate easily. The selectivity of the PMSB-coated electrode seems to be based on the surface morphology and porosity of the coating layer which changes with the polymerization charge. The PMSB-coated electrode may apply as the selective electrode in electrolyte solutions containing various bacterial cells.

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