Electroless Formation of Pressure Sensitive Thin Films of Platinum Porphyrin Using Surfactants with an Azobenzene Group

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Pressure sensitive thin films of platinum porphyrin with a polymer binder are prepared by the micelle disruption method using redox-active surfactants with an azobenzene group. Much thinner films can be prepared by this method than conventional methods, which provide a quick time response to pressure changes. Furthermore, the thin films prepared by this method show a good linearity in the Stern–Volmer plot and a high sensitivity to pressure.

In the aerodynamic field, pressure sensitive paint is the focus of interest in order to provide a continuous pressure mapping on a model surface.[1–3] Oxygen quenching reduces the phosphorescence intensity of pressure sensing molecules, so that we can obtain pressure mapping in airflows containing oxygen through the phosphorescence intensity.[1] Coatings of pressure sensitive paint onto the model have been mainly produced by conventional methods, e.g., spraying, brushing or dipping.[2] However, these methods have disadvantages in uniformity and thickness of these films, which lead to a slow response to pressure changes and difficulty in application to a micro model. Anodized aluminum can be directly adsorbed pressure sensing molecules without polymer binder because of porous structure.[4] This method has a quick response to pressure changes; however, the substrate is limited to the anodized aluminum. Previously, we demonstrated that micelles formed from redox-active surfactants with an azobenzene group (AZPEG, Figure 1) dissociate into monomers owing to the formation of hydrophilic aniline derivatives by electrochemical reduction, and this phenomenon was applied to the electrochemical formation of organic thin films (micelle disruption (MD) method).[5–7] Organic particles dispersed with AZPEG release by electrochemical reduction of AZPEG, and then released particles are deposited on the substrate. The MD method enables the facile formation of organic thin films on various base metal substrates, which have the negative standard potentials than that of AZPEG (approximately -0.1 V vs SCE at pH 1[5]), by simple immersion[5] and noble metal substrates by contact plating.[6,7] Furthermore, the MD method forms uniform and thinner films since reduction of AZPEG and deposition of particles homogeneously occur over the substrate. In this paper, we report the preparation of pressure sensitive thin films of platinum octaethylporphyrin (PtOEP) and poly(styrene-co-methyl methacrylate) (P(St/MMA)) on various substrates by the MD method using AZPEG, which shows a quick time response to pressure changes and is applicable to a micro model.

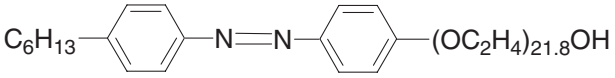

Figure 1. Molecular structure of a surfactant with an azobenzene group (AZPEG).

The preparation of AZPEG has been described in a previous paper.[5] P(St/MMA) was selected as polymer binder since size-controlled P(St/MMA) fine particles are easily available and excellent thin film is obtained by the MD method. Aqueous dispersions containing 0.1 g L^{-1} PtOEP (Porphyrin Products Inc.), 10 g L^{-1} P(St/MMA) particles (particle size: 0.4 μm, Soken Chemical & Engineering Co., Ltd.), 0.25 mM AZPEG and 0.1 M HCl with 10% acetone were prepared by sonicating for 20 min and stirring for 1 day. PtOEP–P(St/MMA) films were formed on an indium tin oxide (ITO) and a stainless steel plate by contact plating, and on a Ni plate by simple immersion of the Ni plate for 24 h. These PtOEP–P(St/MMA) films were heat-treated at 120 °C for 60 min. The surface structure of the thin films was observed using a scanning electron microscope (SEM, JSM-T220, JEOL Ltd.). The intensity of the luminescence was measured in a temperature and pressure-controlled chamber composed of a 300-W xenon lamp (L2480-06, Hamamatsu Photonics K. K.) as the excitation light source, a short wave pass filter which the excitation light from 310 to 410 nm pass through, a band pass filter which the luminescence from 630 to 670 nm pass through, and a CCD camera (C4880, Hamamatsu Photonics K. K.) as the luminescence detector. The time response to pressure change of the PtOEP–P(St/MMA) film was determined by the luminescence intensity profile accompanied by the step change from air (oxygen pressure P_{O_2}: 21 kPa) to oxygen (P_{O_2}: 100 kPa) using a spectrofluorophotometer with a 150–W xenon lamp (FluoroMax-2, Horiba, Ltd.) as the excitation light source.

A pink thin film was formed on an ITO plate by immersing

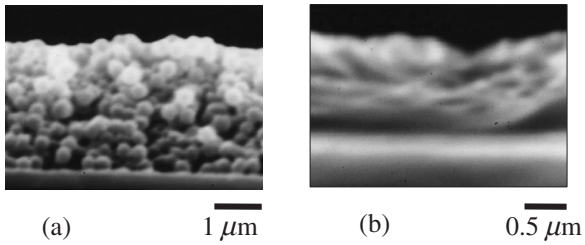

Figure 2. SEM photographs of PtOEP–P(St/MMA) film on an ITO plate prepared by the contact plating method using a dispersion containing 0.1 g L^{-1} PtOEP, 10 g L^{-1} P(St/MMA) particles, 0.25 mM AZPEG and 0.1 M HCl with 10% acetone. Plating time: 24 h. (a) Before the heat treatment, (b) after the heat treatment with 120 °C for 60 min.

both the ITO and aluminum plates in the aqueous dispersion containing $0.1\,g\,L^{-1}$ PtOEP, $10\,g\,L^{-1}$ P(St/MMA) particles and 0.25 mM AZPEG, in which the two plates were short-circuited with a metal clip. Similar PtOEP–P(St/MMA) thin films were also prepared on stainless steel and Ni plates using the MD method. Figure 2 shows SEM photographs of the PtOEP–P(St/MMA) film on the ITO plate prepared by the contact plating method. Before the heat treatment, the PtOEP–P(St/MMA) film is mainly composed of multilayers of P(St/MMA) particles, PtOEP molecules adsorbed on the surface of the P(St/MMA) particles, and a few weight percentage of the AZPEG.[8] Under this condition, the thickness of the PtOEP–P(St/MMA) film is about 2 μm. After the heat treatment, the thickness of the PtOEP–P(St/MMA) film decreased to about 1 μm because of softening and packing of space of P(st/MMA) particles by heat treatment over the glass transition temperature.[9] Furthermore, the thickness of the PtOEP–P(St/MMA) film decreased to submicron by control of the dipping time.[6] The thickness of this film prepared by the MD method is less than that of the film prepared by the conventional spray method.[4,10]

Figure 3 shows the time response of the phosphorescence intensity to a pressure change of the PtOEP–P(St/MMA) film prepared by the MD method and conventional cast method (thickness: 5–8 μm). Assuming that the time response to pressure change follows a first-order response, the relative intensity $(I - I_{min})/(I_{max} - I_{min})$ is represented as $\exp(-t/\tau)$, where I_{min} and I_{max} are the minimum and maximum luminescence intensities, and τ is the response time, respectively.[10] Usually, it is known that the τ is proportional to the square of the thickness of the film.[2,4] τ's of PtOEP in the PtOEP–P(St/MMA) films prepared by the MD method and cast method with increase of oxygen pressure were 0.088 and 0.69 s, respectively. The inverse pressure step test also was examined, which showed the similar tendency (MD method: 0.26 s and cast method: 1.8 s). These results indicate that the thinner PtOEP–P(St/MMA) films prepared by the MD method improve the time response compared with that of the conventional method, and support the above theory.

Figure 4 shows a plot of the relative intensity of the luminescence of the PtOEP–P(St/MMA) film versus relative pressure (Stern–Volmer plot). The Stern–Volmer equation is usually applicable during the luminescence intensity profile by oxygen quenching:[1] $I_0/I = 1 + K_{SV}P_{O2}$, where I_0 and I are the luminescence intensities of PtOEP–P(St/MMA) films in the absence and presence of oxygen, and K_{SV} is the Stern–Volmer quenching constant, respectively. The Stern–Volmer equation is converted into the following reference equation: $I_{ref}/I = A + B(P/P_{ref})$, where A and B are constants derived from the Stern–Volmer quenching constant, and the subscript 'ref' is the reference condition, $P_{ref} = 100\,kPa$ and $T_{ref} = 293\,K$. The pressure sensitivities B of the Stern–Volmer plot of the PtOEP–P(St/MMA) films prepared by the MD method are 0.768, 0.783, and 0.780 on ITO, stainless steel, and Ni plates, respectively. These values are close to the value of B of 0.81 for a PtOEP–polystyrene film prepared by the spray method.[1] Furthermore, the coefficients of determination (R^2) of the Stern–Volmer linear fit of these thin films are 0.9988, 0.9988, and 0.9989 on the ITO, stainless steel, and Ni plates, respectively. These results indicate that PtOEP–P(St/MMA) films prepared by the MD method have a good sensitivity to pressure, which show the absence of self-quenching and a sufficient oxygen permeability by the matrix.

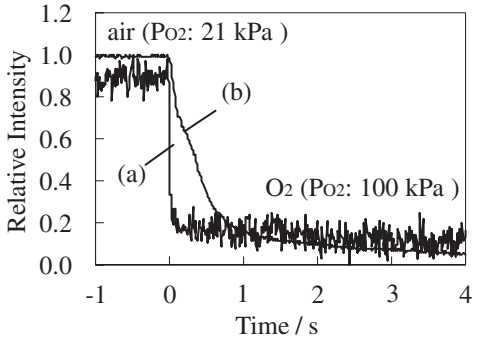

Figure 3. Time response of phosphorescence intensity vs pressure change of PtOEP–P(St/MMA) film prepared by (a) MD method, and (b) cast method. Excitation wavelength: 382 nm, emission wavelength: 646 nm, excitation and emission bandpass: 5.0 nm.

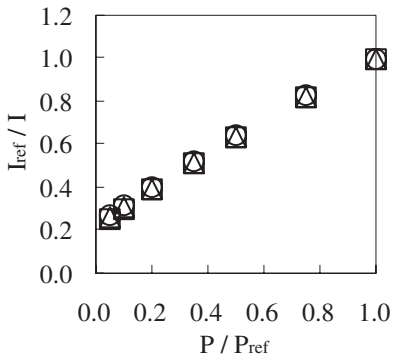

Figure 4. A plot of relative phosphorescence intensity versus relative pressure (Stern–Volmer plot) for PtOEP–P(St/MMA) films. P_{ref}: 100 kPa, T_{ref}: 293 K. Substrate: ITO (○), stainless steel (□), and Ni (△) plate.

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