Novel Optical Oxygen Pressure Sensing Materials: Platinum Porphyrin-Styrene-Trifluoroethylmethacrylate Copolymer Film

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Poly(styrene-co-trifluoroethylmethacrylate), (poly-styrene -co-TFEM), is synthesized and applied to the matrix of optical oxygen sensing using phosphorescence quenching of PtOEP by oxygen. Stern-Volmer constant of poly-styrene-co-TFEM film is estimated to be 0.39 $Torr^{-1}$ (1 Torr =133.322 Pa) indicating that PtOEP-poly-styrene-co-TFEM film is higher sensitive device for oxygen.

Determination of oxygen concentration is important in various fields of chemical, clinical analysis and environmental monitoring.[1-3] Recently, much attention has been paid to optical sensors based on the luminescence quenching of the indicator such as polycyclic aromatic hydrocarbons,[4-9] platinum or palladium porphyrins[10,11] and transition metal complexes,[12-14] by oxygen, because of their highly sensitivity and specificity. Many optical oxygen sensors are composed of indicator compounds immobilized in oxygen permeable polymer. We showed the optical oxygen sensing using phosphorescence quenching of platinum octaethylporphyrin (PtOEP) immobilized various oxygen permeable polymer films.[10] As indicator compounds interacted with polymer molecules, however,, the sensing properties strongly depend on the polymer matrices. One of the most important properties of polymer matrix is oxygen permeability. Thus, the polymer with highly oxygen permeability is desired for matrix of optical oxygen sensing system. In general, fluoro-polymer film has large permeability for oxygen.[15] As an oxygen affinity is induced by large electronegativity of fluorine, the oxygen permeability of the fluoro-polymers will be large.[16-20] Thus, fluoro-polymers are suitable for above requirements properties. In this work poly(styrene-co-trifluoroethyl-methacrylate) (poly-styrene-co-TFEM) as shown in Figure 1, is synthesized and applied to the matrix of optical oxygen sensing using PtOEP.

Poly-styrene-co-TFEM is synthesized as the following method. Styrene (0.16 mol), TFEM (0.15 mol) and azobis-(isobutyronitrile) (25 mmol) are dissolved in 80 ml of toluene. The reaction mixture was heated at 80 °C for 5 h under nitrogen atmosphere. After the mixture was cooled to room temperature, the polymer was precipitated in methanol. The solid was collected by filtration, washed with methanol to remove unreacted monomer, and finally dried in vacuum. The composition ratio of styrene and TFEM unit was determined using the molar absorption coefficient styrene and TFEM at 270 nm. The molecular weight was determined using gel permeation chromatography (TSK HLC-802A TOYO SODA). Styrene /TFEM= 1.0; GPC: M_n=93280, M_w=148800, and M_w/M_n=1.59.

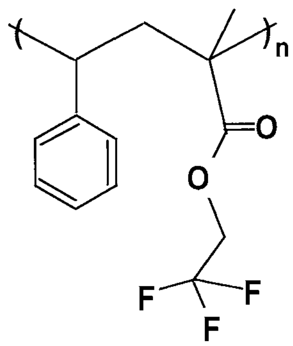

Figure 1. Chemical structure of poly(styrene-co-trifluoroethyl-methacrylate) (poly-styrene-co-TFEM).

PtOEP-poly-styrene-co-TFEM film was formed by casting the mixture of 30-wt% polymer and PtOEP in toluene onto non-luminescent glass slides. PtOEP concentration in the film was approximately to be 2.9 × 10^{-5} mol dm^{-3}. The films were dried at room temperature and stored in dark prior to use. Thickness of the films was determined by use of a micron-sensitive caliper.

Steady state phosphorescence spectra and excitation spectra of the films were measured using a Shimadzu F-5300PC spectrofluorometer with a 150 W Xenon lamp as a visible excitation light source. Excitation and emission bandpasses were 5.0 nm. The sample films were mounted at 45° angle in the quartz cell to minimize light scatter from the sample and substrate. Different oxygen standards (in the range 0-100%) in

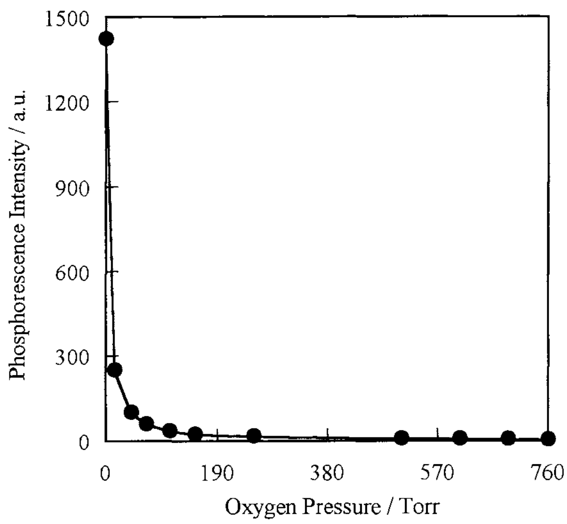

Figure 2. Relative phosphorescence intensity change of PtOEP-poly-styrene-co-TFEM film under various oxygen pressures. Excitation and emission wavelength was 535 and 646 nm, respectively.

a gas stream were produced by controlling the flow rates of oxygen and argon gases entering a mixing chamber. The total pressure was maintained at 760 Torr. All the experiments were carried out at room temperature.

PtOEP-poly-styrene-co-TFEM film showed strong phosphorescence at 646 nm when excited at wavelength attributed to the Q-band (535 nm). The phosphorescence intensity of the film depended on the oxygen pressure. The intensity decreased with increase of oxygen pressure as shown in Figure 2. This result indicates that the phosphorescence of PtOEP in poly-styrene-co-TFEM was quenched by oxygen. Especially, the emission peak at 646 nm disappeared at oxygenated conditions, showing that this film can be used as an optical oxygen sensing device based on phosphorescence quenching by oxygen. The ratio I_0/I_{100} is important factor of oxygen sensing, where I_0 and I_{100} represent the detected phosphorescence intensities from a film exposed to 100% argon and 100% oxygen, respectively. The I_0/I_{100} of polystyrene and poly-styrene-co-TFEM film is estimated to be 4.5 and 297, respectively. This result indicates that PtOEP-poly-styrene-co-TFEM film is higher sensitive device for oxygen.

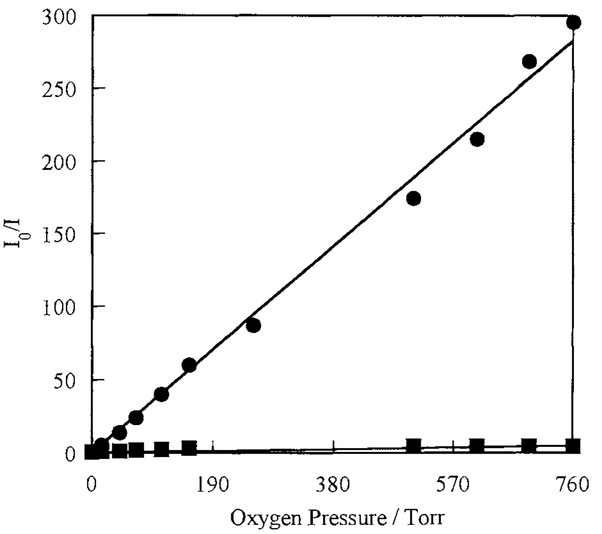

Figure 3. Stern-Volmer plot for PtOEP in poly-styrene-co-TFEM (●) and in polystyrene (■). Excitation and emission wavelength was 535 and 646 nm, respectively.

Figure 3 shows a plot of the phosphorescence intensities of PtOEP film as a function of oxygen pressure (Stern-Volmer Plot, $I_0 / I = 1 + K_{SV}\,pO_2$; where I_0 and I are phosphorescence intensities in the absence and in the presence of oxygen, respectively; K_{SV} is the Stern-Volmer quenching constant; pO_2 is the oxygen pressure). K_{SV} is used as an oxygen sensitivity of the sensing film. In both polymers, the plot exhibits considerable linearity. K_{SV} of polystyrene and poly-styrene-co-TFEM is estimated to be 5.9×10^{-3} and 0.39 $Torr^{-1}$, respectively. Thus, the oxygen sensitivity of PtOEP-poly-styrene-co-TFEM film is about 66 times as high as that of polystyrene film. There are some differences between these polymers e.g., the size and rigidity of the side functional groups and efficiencies of collision with oxygen molecules. In the case of poly-styrene-co-TFEM, interfacial intermolecular force between gaseous phase and surface on polymer film is lower than that of polystyrene, and oxygen affinity is induced by large electronegativity of fluorine.[16-20] Thus, large oxygen permeability of poly-styrene-co-TFEM is induced by lower surface free energy and larger electronegativity of fluorine. Higher sensitive optical sensor is developed using poly-styrene-co-TFEM.

Next let us focus on the sensing properties of PtOEP-poly-styrene-co-TFEM film for oxygen. The response of the oxygen sensing when switching between fully oxygenated and fully deoxygenated atmospheres. The response times of the sensing are 15 s on going from argon to oxygen and 30 s on going from oxygen to argon. The signal changes were fully reversible and measurement hysteresis was not observed. In general, the oxygen sensing systems using dye-polymer film are strongly affected by the thickness of film. A thinner film allows less time for the oxygen migration inside the film to reach equilibrium with the environmental oxygen pressure. In this system, however, K_{SV} seems to be little affected by differences in the film thickness (60~ 80 μm). The photostability of sensing film is important factor to apply for optical oxygen sensing system. To characterize the photostability of PtOEP-poly-styrene-co-TFEM film, the absorption spectrum of the film was measured after continuous irradiation for 12 h. No spectrum change was observed, indicating that the PtOEP-poly-styrene-co-TFEM film has a good photostability under irradiation.

The studies on diffusion processes for oxygen in poly-styrene-co-TFEM and the effects of the composition ratio of styrene to TFEM units and the degree of polymerization on the oxygen sensing properties are now in progress.

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