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Optical oxygen sensing based on the luminescence change of metalloporphyrins immobilized in styrene–pentafluorostyrene copolymer film

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A series of new fluoropolymers, poly(styrene-co-pentafluorostyrene) (poly-Sty$_n$-co-PFS$_m$) with different ratios of Sty and PFS units, were synthesized and applied as an optical oxygen sensing matrix using phosphorescence quenching of metalloporphyrins, platinum and palladium octaethylporphyrin (PtOEP and PdOEP), by oxygen. The phosphorescence intensity of PtOEP of PdOEP in poly-Sty$_n$-co-PFS$_m$ films decreased with increase in oxygen concentration. The ratio I_0/I_{100} was used to express the sensitivity of the sensing film, where I_0 and I_{100} represent the detected phosphorescence intensities from a film exposed to 100% argon and 100% oxygen, respectively. For PtOEP in poly-Sty$_n$-co-PFS$_m$ films, the I_0/I_{100} values were >24.0 and large Stern–Volmer constants of $>0.23\%^{-1}$ were obtained compared with PtOEP in PS films. For PdOEP in poly-Sty$_n$-co-PFS$_m$ films, on the other hand, large I_0/I_{100} values of >92.0 are obtained. However, the Stern–Volmer plots of PdOEP in poly-Sty$_n$-co-PFS$_m$ films exhibit considerable linearity at lower oxygen concentrations between 0 and 20%. These results indicates that PtOEP and PdOEP films are useful optical oxygen sensors for oxygen concentrations between 0 and 100% and between 0 and 20%, respectively. No effect of the ratio of Sty to PFS units in poly-Sty$_n$-co-PFS$_m$ and on the oxygen sensing properties of PtOEP and PdOEP were observed. The response times of PtOEP and PdOEP immobilized in poly-Sty$_1$-co-PFS$_{0.21}$ films were 5.6 and 3.0 s on going from argon to oxygen and 30.0 and 90.1 s on going from oxygen to argon, respectively. This result indicates that PtOEP and PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ films represent a highly sensitive device for oxygen.

Oxygen sensing techniques are applied in various fields, such as chemical, clinical analysis and environmental monitoring.[1–3] The sensing system is classified into the following categories: titration,[4] amperometry,[5] chemiluminescence[6] and thermoluminescence.[7] Among these systems, the most popular method is the amperometric method using an oxygen electrode,[5] in which the rate of diffusion of oxygen to the cathode is measured. This system is limited, however, because of the stability of the electrode surface. Recently, a variety of devices and sensors based on photoluminescent quenching of organic dyes were developed to measure oxygen concentrations on the solid surface. Many optical oxygen sensors are composed of organic dyes, such as polycyclic aromatic hydrocarbons (pyrene and its derivatives, quinoline and phenanthrene),[8–14] transition metal complexes (ruthenium,[15–20] osmium[21] or rhenium–polypyridine complexes[22]) and metalloporphyrins,[23–25] immobilized in an oxygen permeable polymer (silicon polymer, polystyrene, *etc.*). Among these dyes, platinum and palladium porphyrins show no more than weak prompt fluorescence and phosphorescence yields Φ_P variable over the entire range from 10^{-4} to 1 at room temperature. Phosphorescence lifetimes are long, typically <3.0 ms.[26] Especially platinum and palladium octaethylporphyrin (PtOEP and PdOEP) display strong room-temperature phosphorescence with a high quantum yield ($\Phi_P < 0.5$) and a long lifetime (*ca.* 100 μs for PtOEP and *ca.* 770 μs for PdOEP).[26] Some optical oxygen sensors based on phosphorescence quenching of PtOEP–polymer by oxygen have been developed.[27,28] As organic dyes interact with polymer molecules, the optical sensing films depend strongly on the properties of polymer matrices. Oxygen permeable polymers with a low diffusion barrier for oxygen are desired. In general, fluoropolymer film has a high permeability to oxygen.[29] As the oxygen affinity is induced by the high electronegativity of fluorine, the oxygen permeability of the fluoropolymer is high.[29–32] Thus, fluoropolymer is suitable for the above requirements.

We have reported previously the development of a highly oxygen sensitive optical sensor based on the phosphorescence intensity change of PtOEP immobilized in fluoropolymer, poly(styrene–pentafluorostyrene) copolymer (poly-styrene-co-PFS) film.[33] However, the effects of the composition ratio of styrene to PFS units in poly-styrene-co-PFS on the oxygen sensing properties have not yet been clarified.

In this work a series of fluoropolymers, poly(styrene-co-pentafluorostyrene) (poly-Sty$_n$-co-PFS$_m$), with different ratios of styrene to PFS units, as shown in Fig. 1, were synthesized and applied as an optical oxygen sensing matrix using phosphorescence quenching of PtOEP and PdOEP.

Experimental

Materials

PtOEP was obtained from Porphyrin Products (Logan, UT, USA). Polystyrene (PS, average molecular weight 280 000, GPC grade) was purchased from Aldrich (Milwaukee, WI,

USA). Styrene (Sty) was purchased from Wako Chemical (Osaka, Japan). Octaethylporphyrin (OEP), pentafluorostyrene (PFS) and azobis(isobutyronitrile) (AIBN) were obtained from Tokyo Chemical Industry (Tokyo, Japan). PFS was distilled under reduced pressure prior to use in order to remove the inhibitor. AIBN was recrystallized from ethanol.

Synthesis of palladium octaethylporphyrin (PdOEP)

Palladium octaethylporphyrin (PdOEP) was synthesized by refluxing OEP and excess palladium chloride in dimethylformamide solution at 150 °C for 3 h. The reaction was monitored using UV–vis spectroscopy. During the synthesis of PdOEP, the initial absorption bands at 400 (Soret band), 498, 530, 568 and 622 nm (Q band) were shifted and disappeared and new bands appeared at 393 (Soret band), 512 and 546 nm (Q band). After the mixture had cooled to room temperature, PdOEP was precipitated in water. PdOEP was collected by filtration and washed with water. Purification was performed by column chromatography on silica gel (eluent: chloroform), followed by recrystallization.

Synthesis of poly(styrene-co-pentafluorostyrene) (poly-Sty$_n$-co-PFS$_m$)

Sty, PFS and AIBN were dissolved in toluene and the reaction mixture was heated at 80 °C for 5 h under a nitrogen atmosphere. After the mixture had 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. To obtain samples with different molar ratios of Sty and PFS, the initial concentrations of Sty and PFS were changed. The ratio of Sty to PFS units was determined by measuring the molar absorption coefficient of PS at 280 nm. The molecular weight was determined using gel permeation chromatography (column, Plegel 5 μm Mixed-D, Polymer Laboratories, Amherst, MA, USA; detector, Shimadzu (Tokyo, Japan) RID-10A; eluent, tetrahydrofuran). The system was calibrated using polystyrene standards: poly-Sty$_1$-co-PFS$_{0.089}$, M_n = 6532, M_w = 10451 and M_w/M_n = 1.60; poly-Sty$_1$-co-PFS$_{0.21}$, M_n = 7718, M_w = 13 458 and M_w/M_n = 1.74; poly-Sty$_1$-co-PFS$_{1.11}$, M_n = 7859, M_w = 11 621 and M_w/M_n = 1.48; poly-Sty$_1$-co-PFS$_{1.33}$, M_n = 6378, M_w = 10 971 and M_w/M_n = 1.72; poly-Sty$_1$-co-PFS$_{1.60}$:, M_n = 4078, M_w = 6952 and M_w/M_n = 1.70.

Preparation of PtOEP or PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ film

PtOEP or PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ film was formed by casting a mixture of 10 wt.% poly-Sty$_n$-co-PFS$_m$ film and PtOEP or PdOEP in toluene on to 1.4 × 5.0 cm non-luminescent glass slides. The PtOEP or PdOEP concentration in the film was approximately 2.9 × 10^{-5} mol dm^{-3}. As a reference, PtOEP or PdOEP immobilized in PS film was prepared. The films were dried at room temperature and stored in the dark prior to use. The thickness of the films was determined by use of a micron-sensitive caliper. The thickness of the prepared film was between 50 and 80 μm.

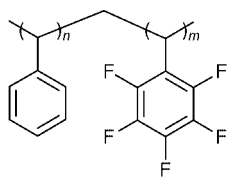


Fig. 1 Structure of poly(styrene-co-pentafluorostyrene) (poly-Sty$_n$-co-PFS$_m$).

Spectroscopic measurements

The absorption spectrum of PtOEP or PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ film was recorded using a Shimadzu U-2400PC spectrometer. Steady state phosphorescence spectra and excitation spectra of the PtOEP or PdOEP in films were measured using a Shimadzu F-5300PC spectrofluorimeter with a 150 W xenon lamp as a visible excitation light source. The excitation and emission bandpasses were 5.0 nm.

Oxygen sensing properties of PtOEP or PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ film

Oxygen sensing was carried out using a spectrofluoroimeter with a 150 W xenon lamp as a visible excitation light source. The sample films were mounted at a 45° angle in the quartz cell to minimize light scattering from the sample and substrate. Different oxygen standards (in the range 0–100%) in 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 (1 Torr = 133.322 Pa).[27,28] All the experiments were carried out at room temperature. The oxygen sensing properties of PtOEP or PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ film were characterized by the Stern–Volmer quenching constant, K_{SV}, obtained from the following equation:

$$I_0/I = 1 + K_{SV}[O_2]$$

where I_0, I and $[O_2]$ are the phosphorescence intensities in the absence and presence of oxygen, and the oxygen concentration, respectively. K_{SV} was obtained from a linear plot of $(I_0/I) - 1$ *versus* $[O_2]$.

Results and discussion

Spectroscopic properties of PtOEP or PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ film

The absorption spectra of PtOEP and PdOEP in poly-Sty$_1$-co-PFS$_{0.21}$ film were almost the same as those in toluene solution (absorption maxima = 534, 501 and 378 nm for PtOEP and 546, 512 and 394 for PdOEP in poly-Sty$_1$-co-PFS$_{0.21}$; 535, 500 and 377 nm for PtOEP and 546, 512 and 393 for PdOEP in toluene solution), as shown in Fig. 2. In the case of other poly-Sty$_n$-co-PFS$_m$ films, the spectra also were almost the same as in toluene solution and no peak shift was observed. These results indicate no electronic interaction between PtOEP or PdOEP and poly-Sty$_n$-co-PFS$_m$ in the ground state.

Phosphorescence spectrum change of PtOEP or PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ film by oxygen

PtOEP and PdOEP immobilized in poly-Sty$_1$-co-PFS$_{0.21}$ film showed phosphorescence at 645.4 and 663.8 nm, respectively, when excited at the wavelength attributed to the Q-band (535.0 nm for PtOEP and 546 nm for PdOEP), as shown in Fig. 3. The phosphorescence intensity of the film depended on the oxygen concentration. The intensity decreased with increasing oxygen concentration, as shown in the inset in Fig. 3. In the case of other poly-Sty$_n$-co-PFS$_m$ films, the intensity decreased with increasing oxygen concentration. These results indicate that the phosphorescence of PtOEP and PdOEP in poly-Sty$_n$-co-PFS$_m$ film was quenched by oxygen. They also show that

PtOEP or PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ film can be used as an optical oxygen sensing device based on phosphorescence quenching by oxygen. The ratio I_0/I_{100} is used to express the sensitivity of the sensing film, where I_0 and I_{100} represent the detected phosphorescence intensities from a film exposed to 100% argon and 100% oxygen, respectively. In general, a sensor having $I_0/I_{100} > 3.0$ is a suitable oxygen sensing device.[34] For PtOEP films, the I_0/I_{100} values of PtOEP immobilized in PS film, as reference, and in poly-Sty$_1$-co-PFS$_{0.21}$ film were estimated to be 4.5 and 24.9, respectively. The I_0/I_{100} values of the other poly-Sty$_n$-co-PFS$_m$ films are given in Table 1. For all the poly-Sty$_n$-co-PFS$_m$ films, the I_0/I_{100} values were > 24.0. For PdOEP, on the other hand, the I_0/I_{100} of PS film and poly-Sty$_1$-co-PFS$_{0.21}$ film were estimated to be 46.0 and 93.6, respectively. The I_0/I_{100} values of the other poly-Sty$_n$-co-PFS$_m$ films are also listed in Table 1. For all the poly-Sty$_n$-co-PFS$_m$ films, the I_0/I_{100} values were > 92.0. For PtOEP and PdOEP, the sensitivity for oxygen was increased by using poly-Sty$_n$-co-PFS$_m$ film. However, the sensitivity was not affected by the ratio of Sty and PFS unit in poly-Sty$_n$-co-PFS$_m$. These results indicate that PtOEP and PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ film are highly sensitive devices for oxygen.

Stern–Volmer relationship for PtOEP or PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ film

Fig. 4 shows the Stern–Volmer plots for PtOEP and PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ films. For PtOEP, the plots of PtOEP immobilized in poly-Sty$_n$-co-PFS$_m$ films exhibit considerable linearity at oxygen concentrations in the range 0–100%. K_{SV} values for PtOEP immobilized in poly-Sty$_n$-co-PFS$_m$ and PS films are given in Table 2. For all the poly-Sty$_n$-co-PFS$_m$ films, large K_{SV} values of $> 0.23\%^{-1}$ were obtained compared with PS film ($K_{SV} = 0.035\%^{-1}$). These results indicate that PtOEP immobilized in poly-Sty$_n$-co-PFS$_m$ films are useful optical oxygen sensors at oxygen concentrations in the range between 0–100%. For PdOEP, on the other hand, the plots of PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ films exhibit considerable linearity at lower oxygen concentrations in the range 0–20%, but the curvature increases at higher oxygen concentrations. This result indicated that the phosphorescence of PdOEP was fully quenched by oxygen at a concentration of about 20%. K_{SV} values for PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ films and in PS film at oxygen concentrations in the range 0–20% are also given in Table 2. For all the poly-Sty$_n$-co-PFS$_m$ films, large K_{SV} values of $> 1.80\%^{-1}$ were obtained compared with PS films ($K_{SV} = 0.85\%^{-1}$). These results indicate that PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ films are useful optical oxygen sensors at lower oxygen concentrations in the range 0–20%. In both M-OEP, however, K_{SV} was not affected by the ratio of Sty and PFS units in poly-Sty$_n$-co-

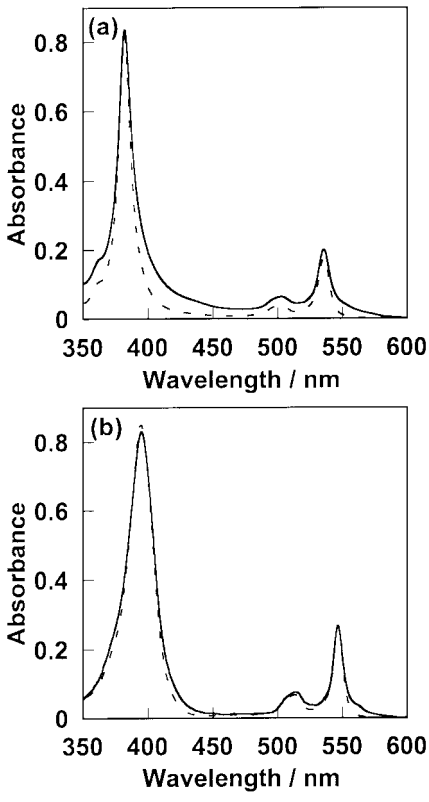


Fig. 2 Absorption spectra of (a) PtOEP and (b) PdOEP immobilized in poly-Sty$_1$-co-PFS$_{0.21}$ film. The dashed lines indicate the spectra of PtOEP and PdOEP in toluene solution.

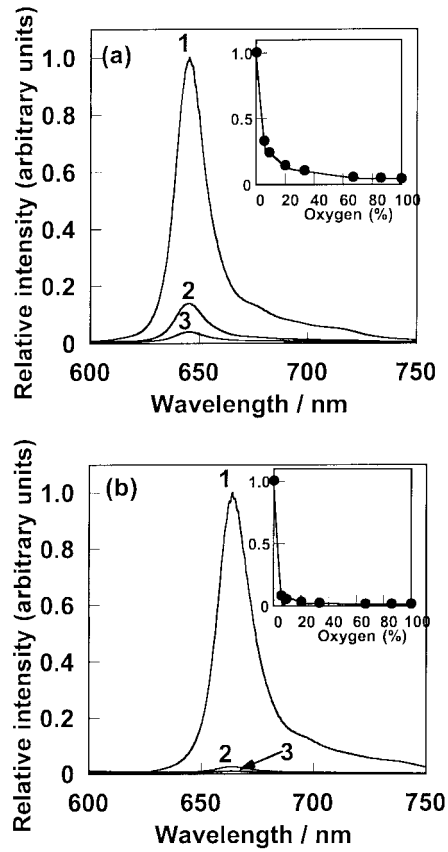


Fig. 3 Phosphorescence spectra of (a) PtOEP and (b) PdOEP immobilized in poly-Sty$_1$-co-PFS$_{0.21}$ film: (1) 100% argon; (2) 20% oxygen; and (3) 100% oxygen. The excitation wavelengths for PtOEP and PdOEP were 535.0 and 546.0 nm, respectively. The insets shows the relative phosphorescence intensity changes of PtOEP and PdOEP in poly-Sty$_1$-co-PFS$_{0.21}$ film at various oxygen concentrations. The emission wavelengths for PtOEP and PdOEP were 645.4 and 663.8 nm, respectively.

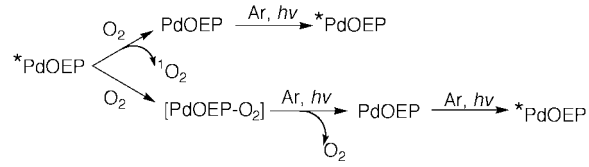
Table 1 I_0/I_{100} values for PtOEP and PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ films

Sensing film	I_0/I_{100}
PtOEP–PS	4.5
PtOEP–poly-Sty$_1$-co-PFS$_{0.089}$	24.5
PtOEP–poly-Sty$_1$-co-PFS$_{0.21}$	24.9
PtOEP–poly-Sty$_1$-co-PFS$_{1.11}$	24.6
PtOEP–poly-Sty$_1$-co-PFS$_{1.33}$	27.2
PtOEP–poly-Sty$_1$-co-PFS$_{1.67}$	25.6
PdOEP–PS	46.0
PdOEP–poly-Sty$_1$-co-PFS$_{0.089}$	92.7
PdOEP–poly-Sty$_1$-co-PFS$_{0.21}$	93.6
PdOEP–poly-Sty$_1$-co-PFS$_{1.11}$	92.6
PdOEP–poly-Sty$_1$-co-PFS$_{1.33}$	92.6
PdOEP–poly-Sty$_1$-co-PFS$_{1.67}$	92.5

PFS_m. These results show that a highly sensitive optical sensor is developed using the fluoropolymer poly-Sty_n-co-PFS_m as a polymer matrix.

Operational stability and response time of PtOEP or PdOEP immobilized in poly-Sty_n-co-PFS_m film

Fig. 5 shows an operational stability test conducted by reading the intensity signals from PtOEP and PdOEP immobilized in poly-Sty_1-co-$PFS_{0.21}$ film when oxygenated and deoxygenated gases were switched for 300 s. For PtOEP, the response times of the film were 5.6 s on going from argon to oxygen and 30.0 s on going from oxygen to argon (35.0 s on going from argon to oxygen and 100 s on going from oxygen to argon for PtOEP immobilized in PS). By using poly-Sty_1-co-$PFS_{0.21}$ as the polymer matrix, a fast response time was obtained. For PdOEP, on the other hand, the response times of the film were 3.0 s on going from argon to oxygen and 90.1 s on going from oxygen to argon (10.6 s on going from argon to oxygen and 158.8 s on going from oxygen to argon for PdOEP immobilized in PS). From Fig. 5(a) and (b), the response time of oxygen to argon was faster than that of PtOEP. On the other hand, the response curve of argon to oxygen consisted of two processes, a faster process (1) and a slower process (2). For PdOEP immobilized in PS film, the same phenomenon was observed. One possible process is shown in following scheme:



where *PdOEP and [PdOEP–O_2] are the photoexcited state of PdOEP and the PdOEP complex with an oxygen molecule, respectively.

The phosphorescence quenching of PdOEP by oxygen is classified into two different processes. One is the energy transfer from the photoexcited PdOEP to an oxygen molecule and the other is complex formation between PdOEP and an oxygen molecule. Hence process (1) is only the phosphorescence change of PdOEP which does not form a complex with an oxygen molecule induced by a change from oxygen saturated to argon saturated conditions. On the other hand, the phosphorescence change of PdOEP in process (2) is as follows. In the first stage, dissociation of an oxygen molecule occurred from the adsorption or complex formation between PdOEP and the oxygen molecule. Then the phosphorescence change induced by a change to argon saturated conditions occurred.

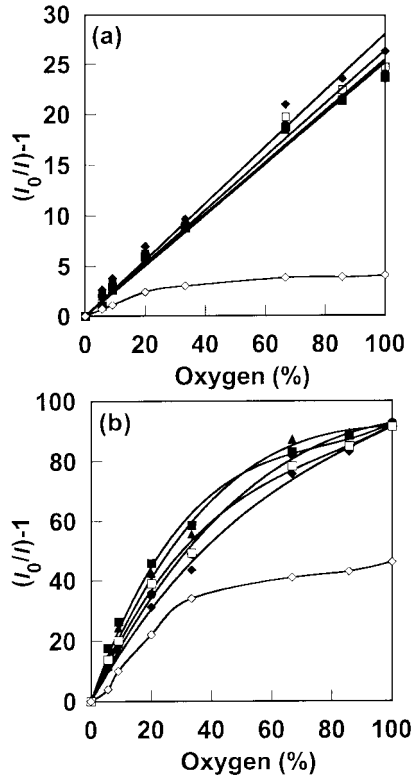


Fig. 4 Stern–Volmer plots for (a) PtOEP and (b) PdOEP immobilized in poly-Sty_n-co-PFS_m film. m = ■, 0.089; ●, 0.21; ▲, 1.11; ◆, 1.33; and □, 1.67; ◇, PS film. The excitation wavelengths for PtOEP and PdOEP were 535 and 546 nm, respectively, and the emission wavelengths were 645.4 and 663.8 nm, respectively.

Table 2 Stern–Volmer constants K_{SV} of PtOEP and PdOEP immobilized in poly-Sty_n-co-PFS_m films

Sensing film	K_{SV} ($\%^{-1}$)
PtOEP–PS	0.035
PtOEP–poly-Sty_1-co-$PFS_{0.089}$	0.235
PtOEP–poly-Sty_1-co-$PFS_{0.21}$	0.249
PtOEP–poly-Sty_1-co-$PFS_{1.11}$	0.236
PtOEP–poly-Sty_1-co-$PFS_{1.33}$	0.262
PtOEP–poly-Sty_1-co-$PFS_{1.67}$	0.256
PdOEP–PS	0.85[a]
PdOEP–poly-Sty_1-co-$PFS_{0.089}$	2.24[a]
PdOEP–poly-Sty_1-co-$PFS_{0.21}$	1.94[a]
PdOEP–poly-Sty_1-co-$PFS_{1.11}$	2.22[a]
PdOEP–poly-Sty_1-co-$PFS_{1.33}$	1.83[a]
PdOEP–poly-Sty_1-co-$PFS_{1.67}$	2.03[a]

[a] Oxygen concentration in the range 0–20%.

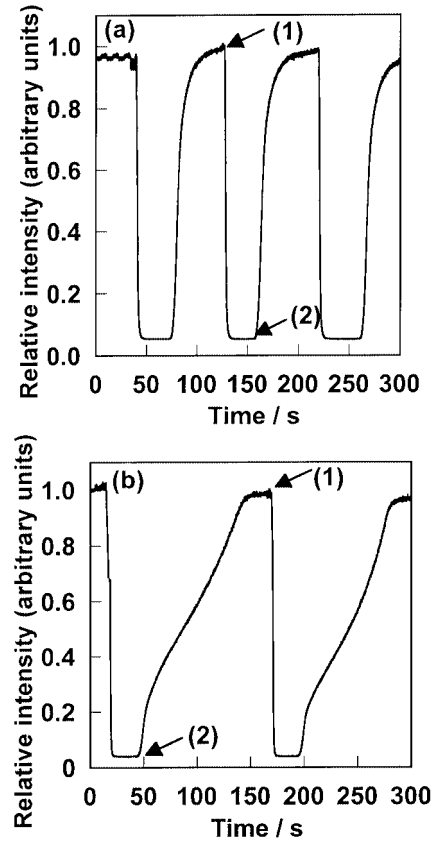


Fig. 5 Response times and relative intensity changes for (a) PtOEP and (b) PdOEP immobilized in poly-Sty_1-co-$PFS_{0.21}$ film on switching between 100% argon (1) and 100% oxygen (2) for 300 s. The excitation wavelengths for PtOEP and PdOEP were 535 and 546 nm, respectively, and the emission wavelengths were 645.4 and 663.8 nm, respectively.

The dynamic response of PtOEP and PdOEP immobilized in poly-Sty$_1$-co-PFS$_{0.21}$ film at various oxygen concentrations is shown in Fig. 6. When different decreasing oxygen concentrations are supplied, the signal become lower and finally reaches the lowest level at 0% oxygen. When increasing oxygen concentrations are fed, in turn, the signal increases and reaches the initial signal level of 0% oxygen again. This test was repeated and the signal changes were monitored when increasing and decreasing oxygen concentrations were changed randomly. For both M-OEP, the signal changes were fully reversible and measurement hysteresis was not observed. PtOEP and PdOEP immobilized in poly-Sty$_n$-co-PFS$_m$ films are photostable films induced by the fluoro group in the polymer matrix that exhibits minimal deterioration (PtOEP *ca*. 2.0% and PdOEP *ca*. 3.0%) of the initial intensity after continuous irradiation for 24 h.

Conclusions

A series of new fluoropolymers, poly(styrene-co-pentafluorostyrene) (poly-Sty$_n$-co-PFS$_m$), were synthesized and applied as an optical oxygen sensing matrix using phosphorescence quenching of PtOEP and PdOEP by oxygen. The phosphorescence intensity of PtOEP of PdOEP in poly-Sty$_n$-co-PFS$_m$ films decreased with increase in oxygen concentration. For PtOEP in poly-Sty$_n$-co-PFS$_m$ films, the I_0/I_{100} values were >24.0 and large Stern–Volmer constants of $>0.23\%^{-1}$ were obtained compared with PtOEP in PS film. For PdOEP in poly-Sty$_n$-co-PFS$_m$ films, on the other hand, large I_0/I_{100} values of >92.0 were obtained. However, the Stern–Volmer plots for PdOEP in poly-Sty$_n$-co-PFS$_m$ films exhibited considerable linearity at lower oxygen concentrations in the range 0–20%. These results indicate that PtOEP and PdOEP films are useful optical oxygen sensors at oxygen concentrations in the ranges 0–100% and 0–20%, respectively. No effect of the ratio of Sty to PFS units in poly-Sty$_n$-co-PFS$_m$ on the oxygen sensing properties of PtOEP and PdOEP were observed.

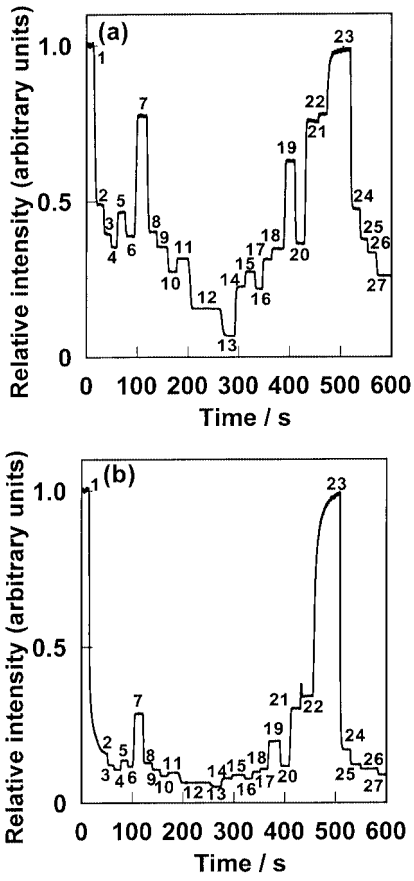


Fig. 6 Dynamic responses of (a) PtOEP and (b) PdOEP immobilized in poly-Sty$_1$-co-PFS$_{0.21}$ film when the oxygen concentrations were changed randomly. (1) 0; (2) 5.30; (3) 7.40; (4) 9.09; (5) 5.66; (6) 7.40; (7) 1.57; (8) 6.72; (9) 9.09; (10) 14.2; (11) 11.1; (12) 33.3; (13) 100; (14) 16.7; (15) 14.3; (16) 20.0; (17) 11.1; (18) 9.09; (19) 2.91; (20) 7.41; (21) 1.57; (22) 0.10; (23) 0; (24) 0; (25) 3.85; (26) 9.09; and (27) 14.3% oxygen. The excitation wavelengths for PtOEP and PdOEP were 535 and 546 nm, respectively, and the emission wavelengths were 645.4 and 663.8 nm, respectively.

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