Oxygen-Sensing Properties of 5,10,15,20-Tetraphenylporphinato Platinum(II) and Palladium(II) Covalently Bound on Poly(isobutyl-*co*-2,2,2-trifluoroethyl methacrylate)

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ABSTRACT: A novel methacrylate monomer bearing 5,10,15,20-tetraphenylporphyrinato palladium(II) (PdTPP) (monomer **1a**) was synthesized and copolymerized with isobutyl methacrylate (IBM) and 2,2,2-trifluoroethyl methacrylate (TFEM) to give poly(IBM-*co*-TFEM) bearing PdTPP (copolymer **2a**) as a dye-conjugated oxygen-permeable polymer for pressure-sensitive paint applications. The introduction of PdTPP into copolymer **2a** was confirmed by UV–vis spectroscopy and extended X-ray absorption fine structure analysis. The Stern–Volmer plots of the copolymer **2a** and a mixture of PdTPP and poly(IBM-*co*-TFEM) both showed downward curvature, unlike that of the platinum complex analogue (copolymer **2b**) previously reported. The plots were successfully fitted with a two-site model to give two distinct Stern–Volmer constants (K_{SV1} and K_{SV2}) and the partition ratio f_1. Interestingly, the f_1 values for the copolymer **2a** were almost constant at about 0.98, whereas those of the mixture of PdTPP and poly(IBM-*co*-TFEM) increased from 0.889 to 0.967 as the temperature was increased. This finding suggests that there are two distinct microheterogeneities, one temperature-dependent and the other temperature-independent, in the mixture of PdTPP and poly(IBM-*co*-TFEM). The dye-conjugation approach effectively eliminates the temperature-dependent, but not the temperature-independent microheterogeneity. The luminescence decays of copolymers **2a** and **2b** and the corresponding mixtures in the absence of oxygen indicated that the temperature-dependent microheterogeneity involves an oxygen diffusion process, whereas the temperature-independent one appears to be inherent nature in PdTPP. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 663–670, 2010

KEYWORDS: luminescence; metalloporphyrin; oxygen-sensing; photochemistry; pressure-sensitive paint; radical polymerization; sensors

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INTRODUCTION Pressure-sensitive paint (PSP) is an emerging technology to visualize an air-pressure map on the surface of a model placed in a wind tunnel.[1–5] The principle of PSP is based on luminescence quenching by oxygen molecule (O_2), whose ground state has a unique triplet character. Conventional PSP consists of a luminescent dye embedded in a film made of an oxygen-permeable polymer such as polysiloxane,[6–10] fluorinated polymethacrylate,[11,12] or poly(3-trimethylsilyl-1-propyne).[13] When the luminescent dyes are excited, the luminescence intensity or lifetime reflects the local O_2 concentration. The O_2 concentration in the film is proportional to the outer air-pressure, if Henry's law holds. Therefore, an air-pressure map on the surface can be calculated from luminescence intensity or lifetime images of a PSP-coated model. The luminescence quenching behavior is ideally described by a single Stern–Volmer equation. However, most PSPs show a downward curvature of the Stern–Volmer plots, probably because of microheterogeneity of the film. The downward deviation of the calibration curve results in serious error in the pressure measurements.

One possible reason for the microheterogeneity is segregation and aggregation of dye molecules during the vaporization process. Adopting this idea as a working hypothesis, we previously synthesized a novel methacrylate monomer having

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5,10,15,20-tetraphenylporphyrinato platinum(II) (PtTPP) and copolymerized it with isobutyl methacrylate (IBM) and 2,2,2-trifluoroethyl methacrylate (TFEM).[14] The resulting copolymer, which carries covalently bounded PtTPP dyes, showed a linear Stern–Volmer plot, whereas a the mixture of PtTPP and poly (IBM-*co*-TFEM) shows a downwardly curved plot. The conjugation of PtTPP to poly(IBM-*co*-TFEM) mainchain effectively eliminates this microheterogeneity. This is a quite attractive methodology to improve the PSP performance. However, the reason why the dye-conjugation approach reduces the microheterogeneity is not fully understood. The application and limitation of this approach should be clarified to develop novel PSP system.

On the other hand, 5,10,15,20-tetraphenylporphyrinato palladium(II) (PdTPP) is also a strong luminescence emitter, showing a longer luminescence lifetime than that of PtTPP. In addition, the longer luminescent wavelength of PdTPP allows us to use another dye for the simultaneous temperature sensing. Therefore, PdTPP is also a promising luminescent dye for PSP. In this article, we report the synthesis and characterization of poly(IBM-*co*-TFEM) bearing PdTPP and the results of an evaluation of its pressure-sensing properties to examine the availability of the dye-conjugation approach.

EXPERIMENTAL

Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded using a JEOL AL-400 instrument (400 MHz). UV–vis spectra were recorded on a JASCO V-570 spectrophotometer. IR spectra were recorded on a Shimadzu FT-IR 8700. Electron-spray ionization time-of-flight (ESI-TOF) mass spectra were recorded on a JEOL JMS-T100LC. High-resolution mass spectra were measured using α-cyclodextrin ($C_{36}H_{60}O_{30}Na$, $[M + Na]^+ = 995.30671$) as an internal standard. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O elemental analyzer. The molecular weight of the resulting polymers was measured by size exclusion chromatography (SEC) in tetrahydrofuran with two polystyrene columns (Styragel HR4 and Styragel HR3). The number-average molecular weight (M_n) was calculated on the basis of polystyrene calibration. Scanning electron microscope (SEM) images were recorded on a JEOL JSM-6060LA analytical SEM using an accelerating voltage of 15 keV.

Materials

α,α′-Azobisisobutyronitrile (AIBN) and isobutyl methacrylate (IBM) were purchased from Wako Pure Chemical Industries, Ltd. 2,2,2-Trifluoroethyl methacrylate (TFEM) was purchased from Aldrich. AIBN was recrystallized from methanol. IBM and TFEM were distilled under reduced pressure just before use. Dichloromethane was refluxed over calcium hydride and distilled just before use. *N*,*N*-Dimethylformamide (DMF) was distilled from anhydrous $CaSO_4$ just before use. Toluene was refluxed over sodium benzophenone ketyl and distilled just before use. 5,10,15,20-Tetraphenylporphinato palladium(II) (PdTPP) was prepared according to the literature.[15] 5-(4-Methoxycarbonylphenyl)-10,15,20-triphenylporphyrin was prepared as reported previously.[16]

5-(4-Methoxycarbonylphenyl)-10,15,20-triphenylporphinato Palladium(II)

5-(4-Methoxycarbonylphenyl)-10,15,20-triphenylporphyrin (690 mg, 1 mmol), $PdCl_2$ (448 mg, 2.5 mmol), sodium acetate (1.7 g), acetic acid (40 mL), and chlorobenzene (50 mL) were placed in a 300 mL flask equipped with a condenser. The flask was evacuated and backfilled with nitrogen gas five times. The mixture was heated at 135 °C for 4 days. The crude product was passed through a short plug of alumina, and the filtrate was purified by silica gel column chromatography ($CHCl_3$:hexane = 2:1) to give an orange powder (376 mg, yield 47%).

^{1}H NMR (400 MHz, $CDCl_3$, $Si(CH_3)_4 = 0$ ppm): δ (ppm) = 8.82 (d, $^3J = 4.9$ Hz, 2H, pyrrole-β*H*), 8.80 (s, 4H, pyrrole-β*H*), 8.74 (d, $^3J = 4.9$ Hz, 2H, pyrrole-β*H*), 8.41 (d, $^3J = 8.4$ Hz, 2H, 5-(3,5-Ph*H*)), 8.24 (d, $^3J = 8.4$ Hz, 2H, 5-(2,6-Ph*H*), 8.16–8.14 (m, 6H, 10-, 15-, and 20-(2,6-Ph*H*)), 7.76–7.69 (m, 9H, 10-, 15-, and 20-(3,4,5-Ph*H*), 4.09 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, *C*DCl$_3$ = 77 ppm): δ (ppm) = 167.07 (*C*=O), 146.46 (*C*), 141.55 (*C*), 141.48 (*C*), 141.39 (*C*), 140.77 (*C*), 133.98 (*C*H), 133.93 (*C*H), 131.20 (*C*H), 131.03 (*C*H), 130.97 (*C*H), 130.37 (*C*H), 129.47 (*C*), 127.80 (*C*H), 127.68 (*C*H), 126.61 (*C*H), 121.96 (*C*), 121.84 (*C*), 120.13 (*C*), 52.47 (*C*H$_3$). ESI-TOF HRMS: *m/z* for $C_{46}H_{30}O_2N_4PdNa$ ($[M + Na]^+$) calcd. 799.13175, found 799.12882 (error −2.93 mmu, −3.67 ppm). Anal. calcd. for $C_{46}H_{30}O_2N_4Pd$: C, 71.09; H, 3.89; N, 7.21. Found: C, 70.85; H, 3.82; N, 7.15. IR (KBr): ν (cm^{-1}) = 1724 ($\nu_{C=O}$), 1609 ($\nu_{C=C}$). UV–vis ($c = 3.13 \times 10^{-6}$ M, $CHCl_3$, path length = 1 cm): λ/nm ($\varepsilon/M^{-1}\ cm^{-1}$) = 418 ($3.19 \times 10^5$), 524 ($2.82 \times 10^4$), 554 ($2.94 \times 10^3$).

5-(4-Carboxyphenyl)-10,15,20-triphenylporphinato Palladium(II)

5-(4-Carboxyphenyl)-10,15,20-triphenylporphinato palladium(II) was prepared by alkaline hydrolysis of 5-(4-methoxycarbonylphenyl)-10,15,20-triphenylporphinato palladium(II) and was used without further purification.

5-[4-(2-Methacryloyloxyethoxycarbonyl)phenyl]-10,15,20-triphenylporphinato palladium(II) (1a)

5-(4-Carboxyphenyl)-10,15,20-triphenylporphinato palladium(II) (125 mg, 0.16 mmol), *N*-hydroxybenzotriazole (53 mg, 0.39 mmol), 2-hydroxyethyl methacrylate (544 mg, 4.18 mmol), and dry DMF (1.5 mL) were placed in a Schlenk tube. The tube was cooled on an ice-salt bath. To the solution was added dropwise a dry DMF solution (2 mL) of dicyclohexylcarbodiimide (74 mg, 0.36 mmol). The mixture was stirred at room temperature overnight, then washed with 1 M HCl, sat. $NaHCO_3$(aq), and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (silica gel, CH_2Cl_2) followed by recrystallization from $CHCl_3$-MeOH to give **1a** as a deep red solid (80 mg, yield 56%). TLC (silica gel, CH_2Cl_2): $R_f = 0.53$.

^{1}H NMR (400 MHz, $CDCl_3$, $Si(CH_3)_4 = 0$ ppm): δ (ppm) = 8.82 (d, $^3J = 5.0$ Hz, 2H, pyrrole-β*H*), 8.80 (s, 4H, pyrrole-β*H*), 8.74 (d, $^3J = 5.0$ Hz, 2H, pyrrole-β*H*), 8.42 (d, $^3J = 8.1$ Hz, 2H, 5-(3,5-Ph*H*)), 8.26 (d, $^3J = 8.1$ Hz, 2H, 5-(2,6-Ph*H*)), 8.15 (d, ^3J = 6.4 Hz, 6H, 10-, 15-, and 20-(2,6-Ph*H*)), 7.78–7.70 (m, 9H, 10-, 15-, and 20-(3,4,5-Ph*H*), 6.24 (s, 1H, $=CH_2$ (trans to CH_3)), 5.65 (q, ^4J = 1 Hz, 1H, $=CH_2$ (cis to CH_3)), 4.75 (dd, ^3J = 5.7 and 3.8 Hz, 2H, $—CH_2—$), 4.63 (dd, 2H, ^3J = 5.9 and 3.7 Hz, $—CH_2—$), 2.02 (s, 3H, $—CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, $CDCl_3$ = 77 ppm): δ (ppm) = 167.06 (*C*=O), 166.32 (*C*=O), 146.77 (*C*), 141.60 (*C*), 141.53 (*C*), 141.50 (*C*), 141.48 (C), 141.43 (C), 140.77 (*C*), 134.06 (*C*H), 133.95 (*C*H), 131.18 (*C*H), 131.06 (*C*H), 130.99 (*C*H), 130.35 (*C*H), 129.18 (*C*) 127.93 (*C*H), 127.71 (*C*H), 126.62 (*C*H), 126.12 ($=CH_2$), 122.01 (*C*), 121.87(*C*), 120.06(*C*), 63.04 (CH_2), 62.61 (CH_2), 18.50 (CH_3). ESI-TOF HRMS: *m/z* for $C_{51}H_{36}O_4N_4PdNa$ ([M + Na]$^+$) calcd 897.16868, found 897.16711 (error 1.57 mmu, 1.75 ppm). Anal. calcd. for $C_{51}H_{36}O_4N_4Pd$: C, 69.98; H, 4.15; N, 6.40. Found: C, 69.51; H, 3.98; N, 6.78. IR (KBr): ν (cm^{-1}) = 1720 ($\nu_{C=O}$), 1607 ($\nu_{C=C}$). UV–vis (c = 1.44 × 10^{-6} M, $CHCl_3$, path length = 1 cm): λ/nm (ε/M^{-1} cm^{-1}) = 417 (3.83 × 10^5), 523 (3.36 × 10^4), 555 (3.60 × 10^3).

Radical Copolymerization

IBM (0.925 g, 6.51 mmol), TFEM (1.127 g, 6.70 mmol), monomer **1a** (21.5 mg, 0.025 mmol), AIBN (165.8 mg, 1.01 mmol), and dry toluene (3.5 mL) were placed in a Schlenk tube. The tube was evacuated and backfilled with nitrogen gas five times, then heated at 60 °C for 24 h. The crude mixture was poured into methanol, and the precipitate was collected by filtration. The resulting powder was purified by reprecipitation with $CHCl_3$-MeOH to give an orange powder (0.9 g, 45%).

Extended X-Ray Absorption Fine Structure Measurements

Extended X-ray absorption fine structure (EXAFS) measurements were performed at beam line 10B of the Photon Factory of the High-Energy Acceleration Research Organization (KEK-PF; Tsukuba, Japan). A channel-cut Si(311) monochromator was used. The ring current was 300–450 mA, and the storage ring was operated with electron energy of 2.5 GeV. The experiments at the Pd K edge (23,348 eV) were carried out at room temperature in the transmission mode on a boron nitrate (BN) pellet containing powdered PdTPP and a cell (path length is 2 cm) filled with powdered copolymer **2a**. The $k^3\chi(k)$ values for the case of single scattering are theoretically given by eq 1:

$$k^3\chi(k) = \sum_i \left\{ \frac{k^2 N_i}{r_i^2} F_i(k) \exp(-2\sigma_i^2 k^2) \sin(2kr_i + \Phi_i(k)) \right\} \quad (1)$$

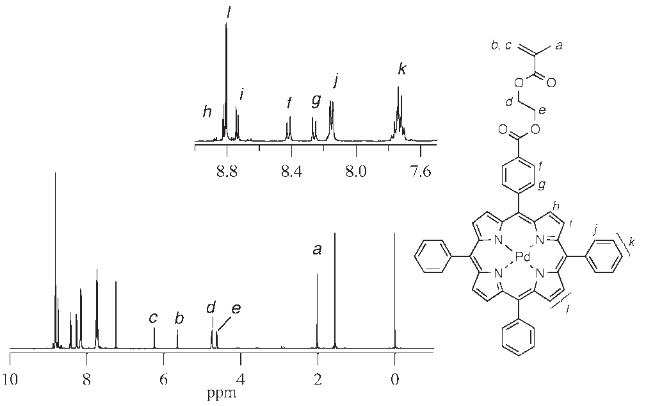


FIGURE 1 ^{1}H NMR spectrum of monomer **1a** in $CDCl_3$.

where r_i, N_i, $F_i(k)$, $\Phi_i(k)$, and σ_i represent the interatomic distance, the coordination number, the back-scattering amplitude, the phase shift, and the Debye–Waller factor of the *i*-th coordination shell, respectively. k is the photoelectron wavevector, defined as $k = [(2m/h^2)(E - E_0)]^{1/2}$ with the threshold energy E_0. The back-scattering amplitude $F_i(k)$ and the phase shift $\Phi_i(k)$ functions for the corresponding shells, such as those between Pd and N atoms and between Pd and C atoms, were derived from the EXAFS oscillation of the BN pellet of PdTPP, using N_N and N_C values fixed to 4 and 8, respectively, as well as the interatomic distances r_N and r_C fixed to 2.01 and 3.04 Å, respectively, derived from X-ray crystallography.[17] The Fourier-filtered method for each shell was applied to avoid other strong parameter correlations. All calculations were performed with REX2000 version 2.0.7 (Rigaku Co.).

Test of Pressure-Sensing Ability

Luminescence images of films made from the copolymer **2a** and from the mixture of PdTPP and poly(IBM-*co*-TFEM) were taken in the air pressure range from 5 to 100 kPa and in the temperature range from 0 to 60 °C. The copolymer **2a** or the mixture of PdTPP and poly(IBM-*co*-TFEM) was dissolved in toluene (25 g L^{-1}) and sprayed onto an aluminum plate (15 × 15 mm^2) with a conventional air-brush. The plate was then mounted in a temperature-controlled pressure chamber. Excitation was provided with a 300 W xenon lamp (C4338, Hamamatsu Photonics) equipped with a bandpass filter of 380–530 nm. The emission from the sample was detected with a cooled CCD camera (C4880-50-26W, Hamamatsu

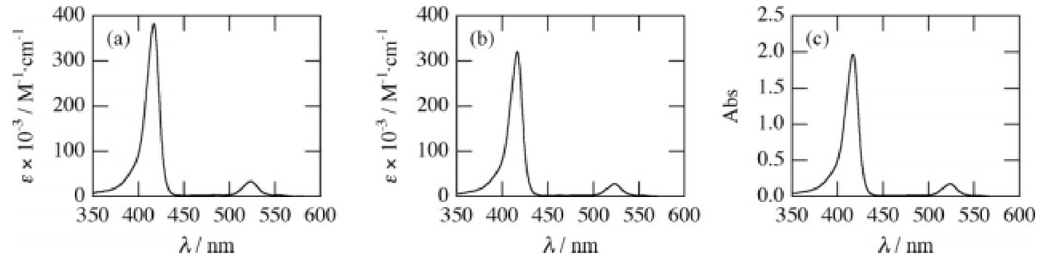
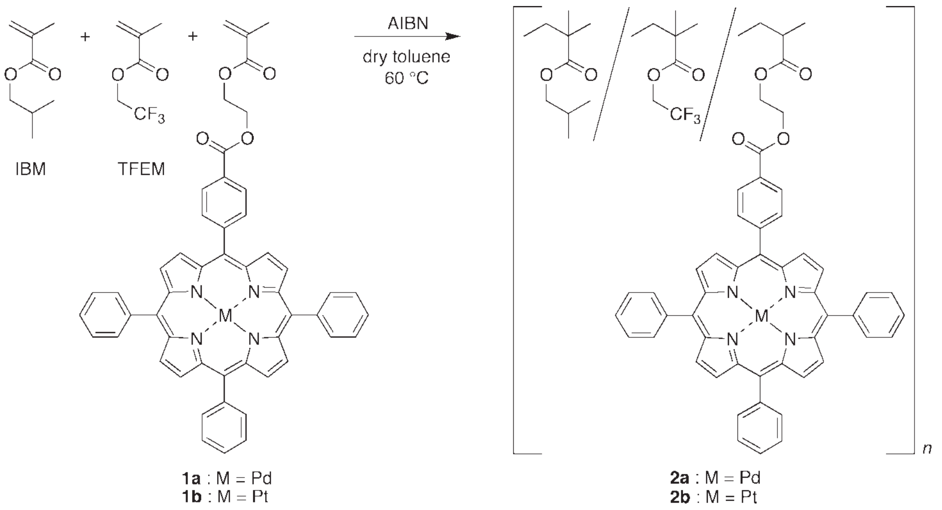


FIGURE 2 UV–vis spectra of monomer **1a** (a), PdTPP (b), and copolymer **2a** (c = 0.499 g L^{-1}) (c) in $CHCl_3$ at 25 °C.



SCHEME 1 Synthesis of PdTPP-pendant PSP.

Photonics; 1000 × 1018 pixels and 16-bit intensity resolution) with a bandpass filter of 590–710 nm.

Luminescence Lifetime Measurement

The luminescence lifetime of PSP-coated samples was determined in a temperature-controlled pressure chamber. Excitation was provided with UV-LED (ETG, ETG-5UV395-30) equipped with a bandpass filter of 400 ± 50 nm. The emission from the sample was detected with a multigate CCD camera (Hamamatsu Photonics; 1344 × 1024 pixels and 14 bit intensity resolution, 0.1 μs gate time) with a bandpass filter of 650 ± 20 nm.

RESULTS AND DISCUSSION

Synthesis of PdTPP-Bearing Copolymer 2a

5-[4-(2-Methacryloyloxyethoxycarbonyl)phenyl]-10,15,20-triphenylporphinato palladium(II) (**1a**) was prepared by a similar method to that used previously by us for 5-[4-(2-methacryloyloxyethoxycarbonyl)phenyl]-10,15,20-triphenylporphinato platinum(II) (**1b**).[14] The structure of monomer **1a** was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopies (Fig. 1), ESI-TOF high-resolution mass spectrometry, and elemental analysis. Figure 2(a,b) shows UV–vis spectra of monomer **1a** and 5,10,15,20-tetraphenylporphyrinato palladium(II) (PdTPP) in chloroform. Monomer **1a** showed a strong absorption band (Soret band) at 417 nm ($\varepsilon = 385 \times 10^3$ M^{-1} cm^{-1}) with relatively weak absorption bands (Q bands) at 523 and 555 nm ($\varepsilon = 33.6 \times 10^3$ and 3.6×10^3 M^{-1} cm^{-1}, respectively), which are identical to those of PdTPP. Hence, the 2-methacryloxyethoxycarbonyl group has no influence on the electronic structure of PdTPP dye. Radical copolymerization of isobutyl methacrylate (IBM), 2,2,2-trifluoroethyl methacrylate (TFEM), and monomer **1a** was carried out at 60 °C in toluene in the dark, using AIBN as an initiator (Scheme 1). The molar ratio of TFEM to IBM was 1 and the feed ratio of monomer **1a** was 1 wt % to the total monomer. After reprecipitation with chloroform-methanol, no unreacted monomer **1a** was found by SEC. The resulting copolymer **2a** was an orange powder soluble in common organic solvent, such as chloroform and tetrahydrofuran. The number-average molecular weight (M_n) and the polydispersity index (M_w/M_n) of the copolymer **2a** were estimated to be 2.59×10^4 and 1.46, respectively, by SEC using polystyrene standards. The ^{1}H NMR spectrum of the copolymer **2a** indicated that the molar ratio of IBM and TFEM units was 1:1. The UV–vis spectrum of the copolymer **2a** showed essentially identical absorption bands to those of monomer **1a**, namely the Soret band at 417 nm and two Q bands at 524 and 555 nm [Fig. 2(c)], indicating that there is no significant interaction between PdTPP units of the copolymer **2a** in chloroform. The amount of PdTPP dye in the copolymer **2a** was estimated to be 0.89 wt % calculated on the basis of the absorption at 417 nm (Soret band) in the UV–vis spectrum, with PdTPP ($\varepsilon = 320 \times 10^3$ M^{-1} cm^{-1}) as a standard. The steady-state luminescence spectrum of the copolymer **2a** was also almost identical to that of PdTPP in degassed chloroform at room temperature (Fig. 3). To examine

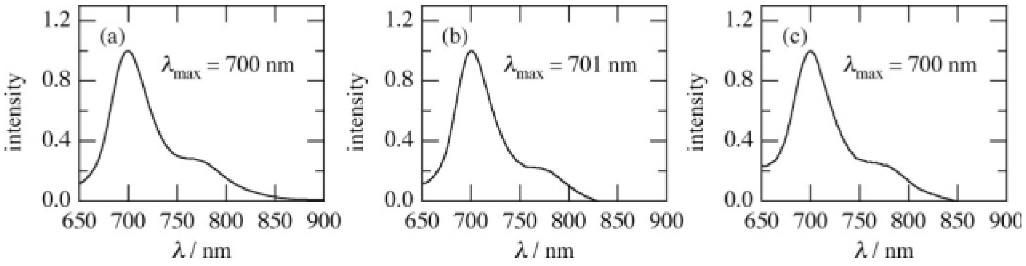


FIGURE 3 Steady-state luminescence spectra of monomer **1a** (a), PdTPP (b), and copolymer **2a** (c) in degassed CHCl$_3$ at 25 °C.

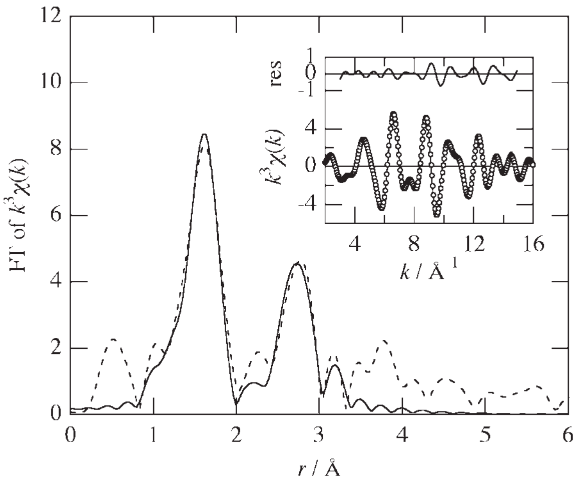
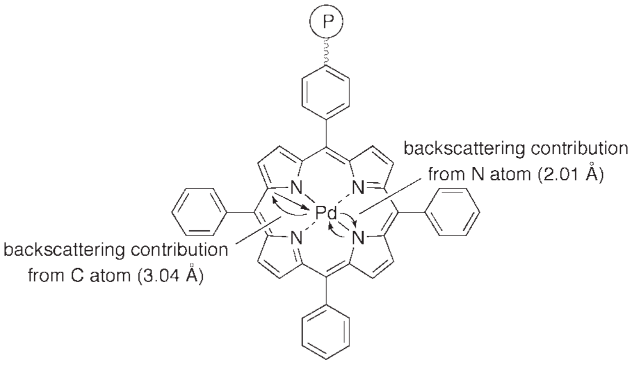


FIGURE 4 Fourier transform of EXAFS oscillation ($k^3\chi(k)$) of copolymer **2a** at the Pd K edge. The inserted plots show the observed (o) and calculated (–) $k^3\chi(k)$ for both the Pd-N and Pd-C regions.

the coordination structure at the palladium(II) atom in the copolymer **2a**, the EXAFS of **2a** was measured at the Pd K edge. Figure 4 shows the Fourier transform of the k^3-weighted EXAFS oscillation ($k^3\chi(k)$). Two peaks were found at 1.6 and 2.7 Å (before phase correction), and were assigned to the back-scattering contribution of nitrogen atoms and carbon atoms of the porphyrin ring (Scheme 2). The $k^3\chi(k)$ obtained was fitted with a sum of these contributions $k^3\chi_N(k)$ and $k^3\chi_C(k)$ using the back-scattering amplitudes $F_i(k)$ and the phase shifts $\Phi_i(k)$ derived from the $k^3\chi(k)$ and X-ray crystallographic data[17] of PdTPP. The inset of Figure 4 shows the $k^3\chi(k)$ and the best-fitted function $k^3\chi_{calc}(k)$ to confirm the reliability of the fitting. The structural parameters, i.e., the interatomic distance r_i, the coordination number N_i and the Debye–Waller factor σ_i are listed in Table 1. The r_i values are quite close to those of PdTPP determined by X-ray crystallography. This clearly indicates that the radical polymerization proceeds without significantly affecting the structure of the PdTPP dye.



SCHEME 2 Single scattering paths for EXAFS analysis.

TABLE 1 Structural Parameters Derived from EXAFS Analysis for Copolymer **2a**

Shell	N	r (Å)	dE (eV)	σ (Å)	R (%)
Pd-N	3.7	2.01	2.19	0.054	1.3
Pd-C	5.6	3.04	1.53	0.033	

N, coordination number; r, interatomic distance; dE, energy shift; σ, Debye–Waller factor; R, R-factor defined as $\Sigma[k^3\chi(k)_{obs} - k^3\chi(k)_{calc}]^2/\Sigma[k^3\chi(k)_{obs}]^2 \times 100$. The estimated errors in the N and r values are ±16% and ±0.05 Å. The back-scattering functions $F_N(k)$ and $F_C(k)$ and phase shifts $\Phi_N(k)$ and $\Phi_C(k)$ were derived from the EXAFS spectrum of a boron nitrate pellet incorporating PdTPP.

Pressure-Sensing Properties of Copolymer 2a

To examine the effect of the dye-conjugation in copolymer **2a** on the pressure-sensing properties, two types of sensing films were prepared, that is, a film consisting of a simple mixture of PdTPP and poly(IBM-*co*-TFEM) (IBM:TFEM = 1:1, $M_n = 2.20 \times 10^4$, $M_w/M_n = 1.76$) and a film of the copolymer **2a**. The polymer films were formed on an aluminum plate with a conventional air-brush filled with a toluene solution of the paint (polymer concentration was 25 g L^{-1}), as described in our previous article.[14] Figure 5 shows a representative SEM image of an aluminum plate which was painted with the copolymer **2a** on half of the surface (left side of the plate in the picture). The picture clearly shows that the thickness of the film was about 10 μm. The luminescence intensity from these films was collected in the air pressure range from 5 to 100 kPa and in the temperature range from 0 to 60 °C. Figure 6 shows the Stern–Volmer plot for the two films, made from the copolymer **2a** and the mixture of PdTPP and poly(IBM-*co*-TFEM). The Stern–Volmer plots for both films showed downward curvature, which is likely to be due to the microheterogeneity of the films. However, the plot for the film made from copolymer **2a** is quite different from that for the film made from the mixture of PdTPP and poly(IBM-*co*-TFEM). To explore the details, these plots were fitted with a two-site model,[8]

$$\frac{I_0}{I} = \frac{\dfrac{f_1}{1+K_{SV1}P_0} + \dfrac{1-f_1}{1+K_{SV2}P_0}}{\dfrac{f_1}{1+K_{SV1}P} + \dfrac{1-f_1}{1+K_{SV2}P}} \qquad (2)$$

where K_{SV1} and K_{SV2} are the Stern–Volmer constants for distinct domains 1 and 2, and f_1 is the fractional contribution of the domain 1 to the total luminescence intensity in the absence of oxygen. The best fits are shown as solid lines in Figure 6, and the parameters K_{SV1}, K_{SV2}, and f_1 are listed in Tables 2 and 3. The minor domain (domain 2) showed substantially no response ($K_{SV2} < 0.01$ kPa^{-1}) to oxygen in either the film made from the copolymer **2a** or that made from the mixture of PdTPP and poly(IBM-*co*-TFEM). The K_{SV1} values increased with increase of the temperature, and the K_{SV1} values of the copolymer **2a** are greater than those of the mixture of PdTPP and poly(IBM-*co*-TFEM). A noteworthy feature of these films is the temperature dependence of the

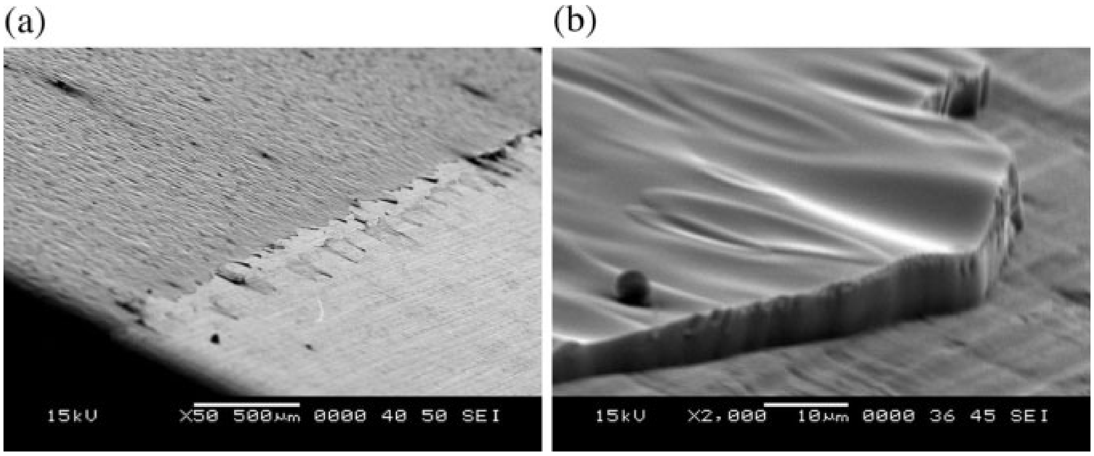


FIGURE 5 SEM image of a film made from copolymer **2a**.

f_1 values (Fig. 7). While the f_1 values of the copolymer **2a** are almost constant at ~0.98 in the range from 0 to 60 °C, the f_1 value of the mixture of PdTPP and poly(IBM-*co*-TFEM) increases from 0.889 to 0.967 with increase of temperature. This indicates that the origin of the microheterogeneity of the film made from the copolymer **2a** is different from that of the film made from the mixture of PdTPP and poly(IBM-*co*-TFEM). In addition, the f_1 values of the mixture of PdTPP and poly(IBM-*co*-TFEM) seem to be asymptotic to those of the copolymer **2a** with increase of the temperature. This suggests that there are two types of microheterogeneity, namely temperature-dependent and temperature-independent types, in the mixture of PdTPP and poly(IBM-*co*-TFEM). If this is so, the conjugation of dye with polymer main chain in copolymer **2a** effectively reduced the temperature-dependent microheterogeneity effectively, but not the temperature-independent microheterogeneity. This hypothesis is supported by the results for copolymer **2b** and the mixture of PtTPP in poly(IBM-*co*-TFEM) in our previous article.[14] While copolymer **2b** gave a linear Stern–Volmer plot, indicating $f_1 = 1$, the f_1 value of the mixture of PtTPP in poly(IBM-*co*-TFEM) increased from 0.891 to 0.954 with increase of temperature from 0 to 60 °C.

Figure 8 shows the luminescence decay curves of films consisting of a mixture of PdTPP and poly(IBM-*co*-TFEM), a mixture of PtTPP and poly(IBM-*co*-TFEM), copolymer **2a** and copolymer **2b** under vacuum at 10 and 60 °C. The luminescence decay curves for the copolymer **2a** and the mixture of PdTPP and poly(IBM-*co*-TFEM) were fitted with three exponential functions as follows:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) \quad (3)$$

The pre-exponential factors (A_i) and the lifetimes (τ_i) are listed in Table 4. The decay curves for the copolymer **2a** were different from those for the mixture of PdTPP and poly (IBM-*co*-TFEM). On the other hand, the decay curves for the copolymer **2b** were substantially identical to those for the mixture of PtTPP and poly(IBM-*co*-TFEM) at 10 and 60 °C. Hence, the photophysical properties of the copolymer **2b** and the mixture of PtTPP and poly(IBM-*co*-TFEM) are identical with each other in the absence of oxygen. These results suggest that the origin of the temperature-dependent microheterogeneity involves an oxygen-diffusion process. In addition, dye-conjugation efficiently eliminated the temperature-dependent microheterogeneity for both the PtTPP and PdTPP systems. However, the PdTPP system includes a substantial

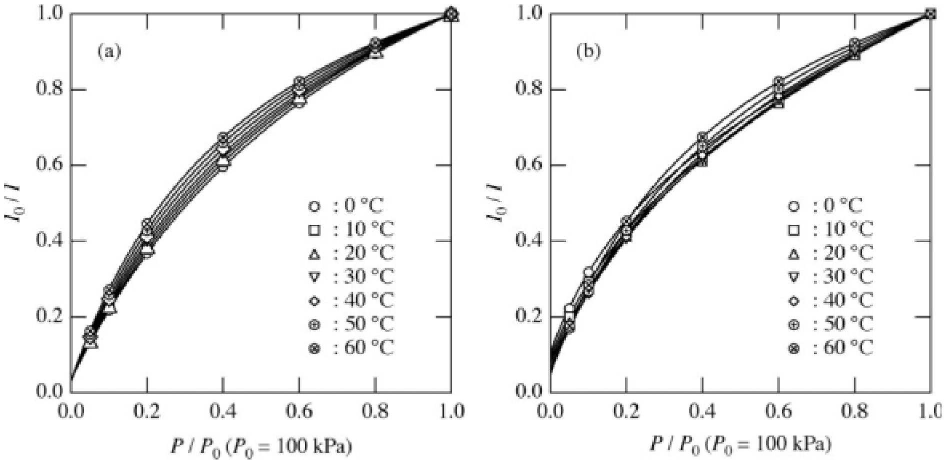


FIGURE 6 Stern–Volmer plots for copolymer **2a** (a) and a mixture of PdTPP and poly(IBM-*co*-TFEM) (b). Solid lines represent best-fit with a two-site model.

TABLE 2 Fitting Parameters for the Stern–Volmer Plot of a Film made from Copolymer **2a**

T (°C)	K_{SV1} (kPa^{-1})	K_{SV2} (kPa^{-1})	f_1
0	0.63	0.00034	0.981
10	0.66	0.00004	0.982
20	0.75	0.00016	0.982
30	0.80	0.00016	0.981
40	0.87	0.00012	0.981
50	0.93	0.00006	0.981
60	0.99	0.00012	0.980

temperature-independent microheterogeneity, resulting in a distorted Stern–Volmer plot.

CONCLUSIONS

A luminescent methacrylate monomer having 5,10,15,20-tetraphenylporphinato palladium(II) (PdTPP) moiety, that is, 5-[4-(2-methacryloyloxyethoxycarbonyl)phenyl]-10,15,20-triphenylporphinato palladium(II) (**1a**), was synthesized in moderate yield. Copolymerization of isobutyl methacrylate (IBM), 2,2,2-trifluoroethyl methacrylate (TFEM) and monomer **1a** was carried out by conventional radical polymerization to yield poly(IBM-*co*-TFEM) bearing PdTPP moieties (copolymer **2a**). The composition of copolymer **2a** was essentially identical to the feed ratio. The coordination structure around the palladium(II) atom was examined by means of EXAFS analysis, and the results indicated that the copolymerization proceeded without damage to the PdTPP dye. The oxygen-sensing properties of a simple mixture of PdTPP and poly(IBM-*co*-TFEM) and copolymer **2a** were evaluated in the air pressure range of 5–100 kPa and in the temperature range of 0–60 °C. Unlike the PtTPP-bearing poly(IBM-*co*-TFEM) (copolymer **2b**), films made from the copolymer **2a** and from a mixture of PdTPP and poly(IBM-*co*-TFEM) both showed significant deviation from a single Stern–Volmer relation. The luminescence quenching behavior was analyzed by applying a two-site model consisting of an oxygen-responsive major domain and an almost nonresponsive minor domain. The fraction of the major domain (f_1) in the film made from the copolymer **2a** was constant at 0.98 in the range from 0 to 60 °C. On the other hand, interestingly, the f_1 value for the film made from mixture of PdTPP and poly(IBM-*co*-TFEM) increased from 0.89 to 0.97 with increase of the temperature. The results suggest that there are two distinct

TABLE 3 Fitting Parameters for the Stern–Volmer Plot of a Film Consisting of a Mixture of PdTPP and Poly(IBM-*co*-TFEM)

T (°C)	K_{SV1} (kPa^{-1})	K_{SV2} (kPa^{-1})	f_1
0	0.29	0.0046	0.889
10	0.28	0.0045	0.908
20	0.29	0.0037	0.926
30	0.30	0.0020	0.945
40	0.38	0.0012	0.956
50	0.49	0.0006	0.964
60	0.61	0.0003	0.967

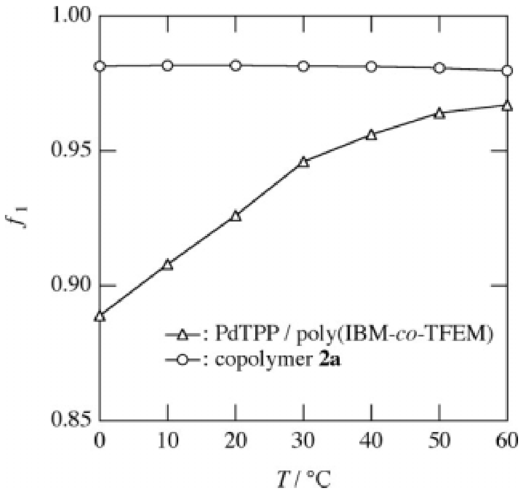


FIGURE 7 The f_1 value as a function of temperature.

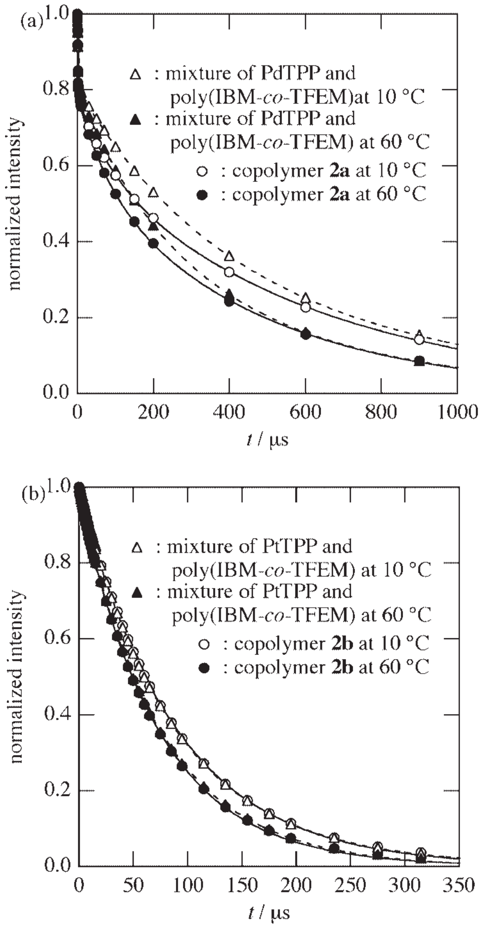


FIGURE 8 Luminescence decay curves for copolymer **2a** and the mixture of PdTPP and poly(IBM-*co*-TFEM) (a) and copolymer **2b** and the mixture of PtTPP and poly(IBM-*co*-TFEM) (b) at 10 and 60 °C under vacuum.

TABLE 4 Fitting Parameters for Luminescence Decay Curves

	T (°C)	τ_1 (μs) (A_1)	τ_2 (μs) (A_2)	τ_3 (μs) (A_3)
2a	10	602 (0.62)	84.4 (0.16)	1.7 (0.22)
	60	459 (0.58)	77.7 (0.20)	1.7 (0.22)
PdTPP in poly(IBM-*co*-TFEM)	10	834 (0.34)	359 (0.46)	1.4 (0.20)
	60	573 (0.37)	234 (0.43)	1.5 (0.20)
2b	10	87.6 (1)		
	60	70.3 (1)		
PtTPP in poly(IBM-*co*-TFEM)	10	87.1 (1)		
	60	71.7 (1)		

microheterogeneities in the sensing film using PdTPP dye, one being temperature-dependent, and the other is temperature-independent. The dye-conjugation approach efficiently reduced the temperature-dependent microheterogeneity for both PdTPP and PtTPP dyes, but was not effective to reduce the temperature-independent microheterogeneity, which appears to be inherent in PdTPP.

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