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Synthesis of Poly(ethynylplatinumporphyrin) and its Application as an Oxygen Pressure-Sensitive Paint

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Summary: 5-(4-Trimethylsilyethynylphenyl)-10,15,20-triphenylplatinumporphyrin was synthesized and copolymerized with trimethylsilylpropyne to give a new high-molecular-weight porphyrin polymer. The polymer formed a smooth and tough coating on many types of surfaces. The coating showed a strong blue luminescence from the platinumporphyrin residue which was quenched in the presence of oxygen. The relationship of the luminescence intensity vs oxygen pressure displayed a remarkably high pressure sensitivity in the low oxygen pressure area, which was ascribed to the high oxygen permeability of the polymer.

Keywords: luminescence quenching; metalloporphyrin; poly(trimethylsilylpropyne); trace analysis for oxygen

Introduction

The measurement of the oxygen concentration or oxygen partial pressure is important in various fields of engineering and clinical analysis and environmental monitoring.[1-3] The sensing methods for oxygen pressure are classified into conductivity measurements with ceramics or metal oxides to detect adsorbed oxygen from the gas phases, electrochemical methods to measure the reduction current of oxygen in aqueous solutions, luminescence quenching of organic dyes with oxygen, and colorimetry based on the reactions of dye molecules with oxygen.[1-6] A variety of optical oxygen sensors based on the luminescence quenching of organic dyes were recently developed in order to analyze oxygen pressures: They used organic aromatic dyes such as pyrene and quinoline,[7,8] transition metal complexes such as ruthenium and osmium-polypyridne complexes,[9,10] and metalloporphyrins,[11,12] which were dispersed in the coatings or membranes of polymers. Among these organic dyes, platinumporphyrins show a strong phosphorescence at room temperature with high quantum

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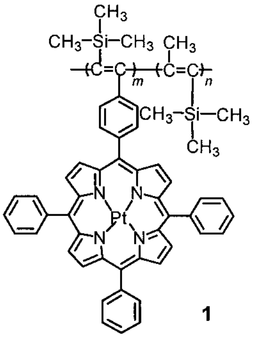
yield.[13] Some optical oxygen sensors based on the phosphorescence quenching of platinumporphyrins have been studied by dispersing them in polymer matrices such as silicone and polystyrene.[14] As the organic dye is surrounded with the polymer molecule, the optical sensing performance strongly depends on the properties of polymer matrix. An oxygen permeable polymer with a low diffusion barrier of oxygen is desired for a highly sensitive and responding oxygen sensor. Poly(dimethylsiloxane)s are rubbery with a high gas permeability and have been conventionally used as the polymer matrix.[15] However, they lack the mechanical strength in thin membranes, and become glassy at low temperature (below glass transition temperature T_g) and lose their high gas permeability.

It has recently been reported that the gas permeability of poly(1-trimethylsilyl-1-propyne) [poly(TMSP)] is about 10-50 times greater than those rubbery polymers such as poly(dimethylsiloxane).[16,17] Poly(TMSP) is a glassy (T_g>200 °C) and amorphous polymer, and its extraordinarily high gas permeability is ascribed to the significantly large frozen free volume. The activation energy for the gas permeability is very small (-0.2 kcal/mol) in comparism with those of other polymers (2-16 kcal/mol). We have successfully applied poly(TMSP) as a polymer matrix of an optical oxygen sensor based on the luminescence change in the platinumporphyrin.[18,19] The poly(TMSP)-embedded platinumporphyrin displayed a very high quenching constant or oxygen pressure sensitivity, especially in a low-pressure region, maintained its sensitivity even at low temperature and exhibited a fast response time. The poly(TMSP)-based platinumporphyrin is now being developed as a novel pressure-sensitive paint suitable for use in cryogentic and unsteady wind-tunnel testing.[20]



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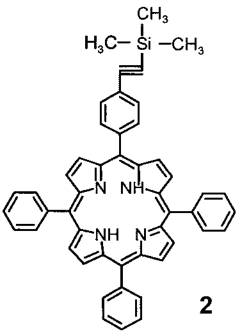
The oxygen pressure-sensitive paint comprised of platinumporphyrin and poly(TMSP) was improved in this study by synthesizing a high molecular weight copolymer **1** of the ethynyl derivative of platinumporphyrin and 1-trimethylsilyl-1-propyne. The copolymer could realize a simple painting process from a one-component solution. It was also expected that the photo-responsible metalloporphyrin residue is molecularly dispersed or a dye aggregation is suppressed in the new copolymer.

Synthesis of Ethynylplatinumporphyrin and its Polymerization

5-(4-Trimethylsilyethynylphenyl)-10-15-20-triphenylplatinumporphyrin **3** was synthesized to be copolymerized with 1-trimethylsilyl-1-propyne. 4-Bromobenzaldehyde was coupled with trimethylsily acetylene to give 4-[(trimethylsily)ethynyl]benzaldehyde. 4-Bromobenzaldehyde (8.5 g, 46 mmol) and triphenylphosphine (0.35 g, 1.3 mmol) were dissolved in 100 mL of anhydrous triethylamine, and 9.8 mL (80 mmol) of 1-trimethylsilylacetylene and then 0.3g (0.3 mmol) of palladium(II) acetate was sucessively added under nitrogen. The mixture was heated at 85 °C for 2.5 h. After cooling, the solvent was removed under reduced pressure. The residue was purified by column chromatography using silica gel with hexane and dichloromethane (1/1) as the eluent. A yellow powder of 4-[(trimethylsily)ethynyl]benzaldehyde was obtained: yield 97%. IR (KBr pellet, cm^{-1}) 2957($\gamma_{Si\text{-}C\text{-}H}$), 2156($\gamma_{C\equiv C}$); ^{1}H-NMR (δ, $CDCl_3$, ppm) 9.99 (s, 1H, CHO), 7.61 (q, 4H, J=4Hz, C_6H_5), 0.25(s, 9H, $Si(CH_3)_3$); MS(m/e) 202(18, M^+), 187(100, M^+, $-CH_3$).

The trimethylsilyl derivative of tetraphenylporphyrin **2** was synthsized by the ring formation reaction of 4-(trimethylsily)ethynylbenzaldehyde with benzaldehyde and pyrrole. 4-[(Trimethyl sily)ethynyl]benzaldehyde (4 g, 19.6 mmol), benzaldehyde (3.2 mL, 30 mmol), and pyrrole (2 mL, 9.8 mmol) were dissolved in 400 mL of chloroform. 1mL of the borontrifluoride diethylether complex was added to the solution, and the mixture was stirred for 1 h at room temperature. It became black, then 5 g of tetrachloro-1,4-benzoquinone dissolved in 100 mL of tetrahydrofuran was added and the mixture was stirred for 24 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography by using silica gel with hexane and dichloromethane (1/1) as the eluent. Freeze-drying produced a purple powder of **2**: yield 15%. UV-vis (in toluene, nm) 419, 515, 555, 591, 648; ^{1}H-NMR (δ, $CDCl_3$, ppm) 8.83 (s, 8H, pyrrole), 8.10-7.80 (m, 19H, C_6H_5), 0.25 (s, 9H, $Si(CH_3)_3$), -2.83 (s, 2H, NH); FAB-MS(m/e) 711 (MH^+).



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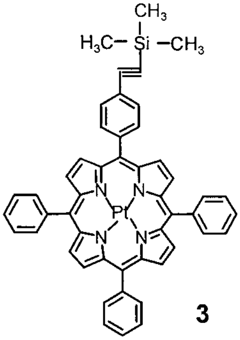

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2 was then converted to the corresponding platinumporphyrin **3**. **2** (80 mg, 0.1 mmol) was dissolved in 8 mL of benzonitrile under nitrogen. Platinum chloride (160 mg, 0.6 mmol) was added, and the mixture was heated at 170 °C for 3 h. After cooling, the solvent was evaporated. The residue was purified by column chromatography using aluminium oxide with dichloromethane as the eluent. A brownish powder of **3** was obtained: yield 23%. UV-vis(in toluene, nm) 408, 512, 539; ^{1}H-NMR (δ, $CDCl_3$, ppm) 8.73 (s, 8H, pyrrole) 8.14 (m, 8H, C_6H_5) 7.75 (m, 12H, C_6H_5) 0.18 (s, 9H, $Si(CH_3)_3$); FAB-MS(m/e) 904 (M^+).

It has been reported that trimethylsilyl-substituted acetylenes are polymerized in the presence of a rhodium complex or tantalum (δ) chloride.[21] The homopolymerization of the ethynylporphyrin **3** and the copolymerization of **3** with trimethylsilylpropyne were examined using the rhodium norbornadiene chloride complex or tantalum chloride as the catalyst. Neither trimethylsilypropyne itself nor it with **3** were polymerized in the presence of the rhodium norbornadiene chloride complex, while **3** with the Rh complex gave an oligomeric product of **3**; a deeply reddish powder at a yield of 60%. Although trimethylsilypropyne was easily polymerized with $TaCl_5$, **3** was not. However, we found that the copolymer of **3** with trimethylsilypropyne was produced by adding **3** to the trimethylsilylpropyne solution with $TaCl_5$ just after the start of the polymerization.

3 was copolymerized with trimethylsilylpropyne using a $TaCl_5$ catalyst, as follows. Tantalum chloride (30 mg, 83 mmol) was added to 30 mL of the toluene solution of trimethylsilylpropyne (8 mL, 93 mmol) and the mixture was heated at 90°C under nitrogen. After 5 min, the mixture turned from brown to black. Then, 30 mg (0.7 mmol) of **3** was then added and the mixture was heated at 90°C for 24 h. After cooling, the reaction mixture was filtered, and the filtrate was poured into methanol. The precipitated brownish powder was collected by filtration and washed with methanol. The powder was redissolved in a minimum amount of toluene and was reprecipitated in methanol again. The precipitate was dried under reduced pressure to give a brownish powder: yield 8.2%. IR (KBr pellet, cm^{-1}) 1560($\gamma_{C=C}$), 1245($\gamma_{Si\text{-}C}$) 821($\gamma_{Si\text{-}C\text{-}H}$); ^{1}H-NMR ($CDCl_3$, 500MHz, δ, ppm): 0.14-0.18 (s, 9H, $Si(CH_3)_3$), 1.53 (s, 3H, CH_3); UV-vis(in toluene, nm) 403, 510, 538; GPC: weight-average molecular weight (M_w) = 3.0×10^4; weight-average molecular weight / number-average molecular weight (M_w/M_n) = 1.4

The copolymerization results are summarized in Table 1.

Table 1. Copolymerization of the ethynylporphyrin with trimethylsilylpropyne (TMSP).

Run	[TMSP]/[**3**] Feed molar ratio	Yield (%)	M_w 10^4	M_w/M_n	**3** residue content in **1** (mol%)	[**3** residue] / [One polymer chain]
0	1/0	87	85	5.5	0	0
1	1/1	1.5	30	1.4	1.0	8.0
2	2/1	8.0	15	1.5	1.2	5.0
3	10/1	1.6	25	1.3	1.8	16

[$TaCl_5$] = 83 mmol, solvent = toluene, reaction temperature = 90 °C, reaction time = 24 h.

Oxygen Permeability through the Polymer Membrane

The copolymer **1** was soluble in the common solvents such as toluene, chloroform, and tetrahydrofuran. It was easy to make a mechanically tough and smooth thin coating on any type of surface including stainless steel and ceramics. No glass transition was observed up to 200°C (T_g>200°C) by differential scanning calorimetry, and **1** was completely glassy over this temperature range. The toluene solution of **1** was cast on a porous supporting membrane (Celgard 2500, Hoechst Celanese Co; polypropyne; pore dimension 0.05 × 0.19 μm; porosity 0.43; thickness 25 μm) to form a dense membrane of **1** with a membrane thickness of 40 μm. Oxygen permeation was measured using a low-vacuum permeation apparatus in the chamber with a stable thermostat (Rika Seiki K315N-03). The oxygen pressure on the upstream and the downstream sides were detected using a Baratron absolute pressure gauge (MKS Instrument). The oxygen permeation coefficients (P) and the induction period (time lag, θ) before the steady-state permeation were calculated from the slope of the steady-state straight-line sections of the permeation curves and the intercept of the straight-line, respectively. The solubility coefficient of oxygen (S) and diffusion constant of oxygen (D) in the polymer, respectively, were estimated by the equations $D = \ell^2/6\,\theta$ and $S = P/D$, where ℓ is the membrane thickness. A poly(dimethylsilioxane) control membrane was also prepared using a commercially available silicone polymer GP197[22] and platinumporphyrin. The oxygen permeation data were listed in Table 2.

The oxygen permeability of the poly(TMSP)-based copolymer **1** was 10 times greater than that of the conventional poly(dimethylsiloxane) rubber membrane in which platinumporphyrin was dispersed. The diffusivity and the solubility of oxygen in the copolymer was twice and 5 times lagrer than those in the rubber membrane, respectively; both the higher oxygen diffusivity and solubility contribute to the high oxygen permeability in the copolymer membrane. One can also note in Table 2 that the activation energy for oxygen permeation in the copolymer membrane was very small or almost zero and that the high oxygen permeability was maintained over a wide temperature range.

Table 2. Oxygen permeability coefficient (P_{O2}), activation energy for oxygen permeation (ΔE_a), diffusion coefficient of oxygen (D_{O2}), and solubility coefficient of oxygen (S_{O2}) at 25°C.

Polymer matrix	$10^7 P_{O2}$ cm^3(STP)cm/cm^2s cmHg	ΔE_a kcal/mol	$10^5 D_{O2}$ cm^2/s	$10^2 S_{O2}$ cm^3(STP)cm/cm^2s cmHg
1/poly(TMSP)	1.45	-0.031	1.3	1.1
GP193	0.184	3.8	0.86	0.24

GP193=poly(dimethylsiloxane)-based rubber.
ΔE_a was determined from the Arrhenius plots of P_{O2} in the temperature range of 5-45°C.

Luminescence Quenching and Oxygen Pressure Analysis

A toluene solution (5 mg/ml) of the ethnylplatinumporphyrin copolymer **1** was sprayed on an aluminum plate. The platinumporphyrin copolymer coating displayed a strong blue luminescence under UV irradiation. The copolymer-coated plate was set in a calibration chamber in which the pressure and the temperature were controlled. Excitation light was provided by a light guide connected to a pulsed Xenon light source with a bandpass filter (400±50 nm) for excitation light. The intensity measurements required low noise instrumentation. This was achieved with a cooled numerical CCD camera. This camera can be used for image or discrete spectral measurements.

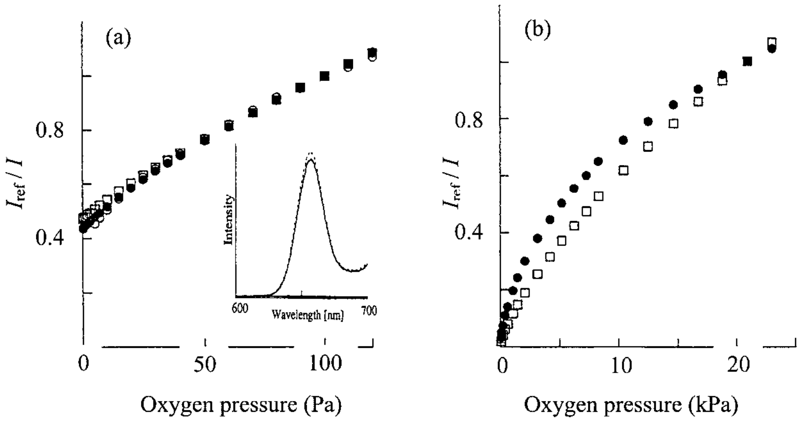

Fig. 1. Stern-Volmer plots for the platinumporphyrin copolymer **1** (●), the mixture of the platinumporphyrin **3** monomer and poly(TMSP) (○), and the mixture of platinumtetrakis (pentafluorophenyl)porphyrin and poly(TMSP) (□). (a) Normalized at 100 Pa oxygen. (b) in the oxygen dilute region (normalized at air pressure). Inset in (a): phosphorescence spectrum of the platinumporphyrin copolymer **1** (—) coated on an aluminum plate; (---) the mixture of the platinumporphyrin and poly(TMSP); excitation = 460 nm.

An example of the luminescence spectrum was given in the inset of Figure 1 (a). The copolymer **1** displayed a strong phosphorescence at 660 nm, which almost agreed with that of the mixture of the platinumporphyrin monomer **3** and poly(TMSP). The luminescence intensity was measured in the oxygen pressure range of 0-25 kPa. The luminescence intensity decreased with the oxygen pressure: This indicates that the luminescence of the platinumporphyrin residue in the copolymer **1** was effectively quenched by oxygen.

Figure 1 shows the luminescence intensity variation with oxygen pressure or the Stern-Volmer plots for the platinumporphyrin copolymer **1** and for the mixture of platinumporphyrin and poly(TMSP). The plots showed a considerable linearity in Figure 1 (a), which exhibited a good oxygen pressure-sensitivity of the platinumporphyrin coating. Especially, in the dilute oxygen region (Figure 1) (b), the Stern-Volmer plots for the copolymer **1** yielded a steep slope in comparison with that for the mixture coating. That is, the platinumporphyrin copolymer **1** coating displays a very high quenching efficiency (oxygen pressure-sensitivity) for a low oxygen pressure measurement.

Figure 2 shows a spacial noise distribution of the luminescence change or the oxygen sensitivity for the platinum copolymer **1** coating. The ratio of the luminescence intensities at the oxygen pressure of 10 and 100 Pa was normalized by the average ratio value and monitored at each "pixel". The abscissa of Figure 2 is the cutting plane of the coated plate. The standard deviation or the spacial noise was 3.2×10^{-3} and 2.3×10^{-3} for the platinumporphyrin copolymer **1** and the mixture of the platinumporphyrin monomer and poly(TMSP), respectively. It is concluded that the platinumporphyrin copolymer efficiently suppressed the aggregation of the porphyrin residue and significantly reduced the spacial noise in comparison with those of the simple mixture of the platinumporphyrin and the poly(TMSP) homopolymer.

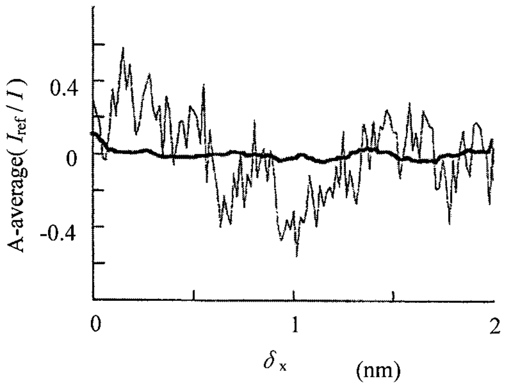

Fig. 2. Noise distribution in the intensity ratio images: (—): the platinumporphyrin copolymer **1**, (---): the mixture of the platinumporphyrin and poly(TMSP).

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