Cobalt Porphyrin-Mediated Oxygen Transport in a Polymer Membrane: Effect of the Cobalt Porphyrin Structure on the Oxygen-Binding Reaction, Oxygen-Diffusion Constants, and Oxygen-Transport Efficiency

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New derivatives of $(meso-\alpha,\alpha,\alpha,\alpha$ -tetrakis(o-pivalamidophenyl)porphinato)cobalt (CoPs) were characterized by oxygen-binding equilibrium and rate constants of the cobalt centered in the porphyrins. They depended on the structure of the porphyrin; for example, the rate constants of oxygen binding and dissociation $(k_{on} \text{ and } k_{off})$ for $\alpha^{3}\beta$ -CoP₄P (Chart 1) were 3 and 20 times as large as those for α^{4} -CoB₄P, respectively. Oxygen transport through the polymer membranes containing CoPs as the fixed oxygen carriers was facilitated and was affected by the oxygen-binding character or the structure of CoPs. The logarithmically linear correlation of the oxygendissociation rate constant of CoPs $(k_{off} = (3-66) \times 10^3 \text{ s}^{-1})$ with the diffusion constant of oxygen via CoPs fixed in the membranes $(D_{cc} = (3-140) \times 10^{-9} \text{ cm}^2 \text{ s}^{-1})$ was given for those six CoP derivatives.

Introduction

Carrier-mediated transport or facilitated transport is defined as a process in which a chemically distinct entity (carrier molecule) forms a complex with a specific component, thereby increasing the transport rate of this component relative to other components in the feed stream.¹ Such a process of selective transport across the membranes had been first studied for air separation (oxygen/ nitrogen separation) with microporous membranes in which the solution of a cobalt chelate is retained as a specifically oxygenbinding mobile carrier.^{2,3} The liquid membranes holding cobalt chelates for facilitated oxygen transport could provide an elegant method for oxygen/nitrogen separation with the advantages of both improved selectivity and increased flux. But there remained the following unresolved issues for air separation, such as evaporation loss of the liquid medium, membrane thickness, and lower mobility of the bulky carrier molecule than that of permeant small gaseous molecules. Solid or solvent-free polymer membranes containing fixed carrier molecules for the facilitated transport are expected to be candidates to overcome the problems of liquid/mobile carrier membranes.

Recently, we have demonstrated metalloporphyrin-mediated oxygen transport in solid polymer membranes:4-10 The metalloporphyrin bonded to a solid polymer acted as a fixed carrier of oxygen and facilitated the transport of oxygen relative to components such as nitrogen in a feed stream. The fixed metalloporphyrin enormously enhanced sorption of oxygen in the membrane due to chemically specific oxygen binding to the metalloporphyrin. This specific and reversible oxygen-binding reaction established a gradient in the concentration of oxygen across the membrane from the upstream side to the downstream side and yielded the facilitated oxygen transport. However, low diffusivity of the permeant oxygen via the fixed carrier molecule (metalloporphyrin) interfered with the augmented permeability of oxygen. Analysis of the oxygen diffusion via the fixed metalloporphyrin in the membrane will elaborate the mechanism of the carrier-mediated or facilitated transport, and in the previous communication paper¹¹ we have preliminarily reported the analysis on the oxygen diffusion.

This paper describes effects of the cobalt porphyrin (CoP) structure on the oxygen-binding reaction and, moreover, on oxygen diffusion and oxygen transport in a solid polymer membrane, by usage of poly(octyl methacryalte-co-vinylimidazole) membranes containing five new CoP derivatives (Chart 1) of the well-known

 $(meso-\alpha, \alpha, \alpha, \alpha, \alpha$ -tetrakis(o-pivalamidophenyl)porphinato)cobalt-(II) (CoB₄P): (meso- α -(o-methacrylamidophenyl)- α , α , α -tris-(o-pivalamidophenyl)porphinato)cobalt(II) (CoP₁B₃P), (meso- α -(o-acrylamidophenyl)- α , α , α -tris(o-pivalamidophenyl)porphinato)cobalt(II) (CoE₁B₃P), (meso- α -(o-acetoamidophenyl)- α, α, α -tris(o-pivalamidophenyl)porphinato)cobalt(II) (CoM₁B₃P), (meso- α, α -bis(o-methacrylamidophenyl)- α, α -bis-(o-pivalamidophenyl)porphinato)cobalt(II) (CoP₂B₂P), and (meso- α, α, α -tris(o-methacrylamidophenyl)- β -(o-methacrylamidophenyl)porphinato)cobalt(II) ($\alpha^{3}\beta$ -CoP₄P). We measured both the oxygen-binding reaction spectroscopically and the oxygen and nitrogen permeation, to provide the oxygen-binding rate and equilibrium constant of the CoPs fixed in the solid poly(octyl methacrylate-co-vinylimidazole) membrane and the oxygensolubility coefficient and oxygen-diffusion constants in the membrane and to discuss the question of whether the oxygenbinding reactivity of CoP correlates to the oxygen diffusivity via the fixed CoP and to the oxygen permeability in the membrane.

Experimental Section

Materials. meso- $(\alpha, \alpha, \alpha, \alpha, \alpha$ -Tetrakis(o-aminophenyl)porphyrin¹² was reacted with the prescribed amount of pivaloyl chloride and methacryloyl chloride in water-free acetone-diethylether (1/1)v/v) at 0-5 °C, to adjust the introduction number of the alkyl groups and to avoid α,β -isomerization of the ortho substituents. The product was purified by chromatography on a silica gel column using cyclohexane-ethyl acetate (3/2v/v) as a developing solvent. R_f values of three isomers, (o-methacrylamidophenyl)_n(pivalamidophenyl)_mporphyrin (n + m = 4): H₂B₄P (n = 0, m = 4), 0.42; $H_2P_1B_3P$ (n = 1, m = 3), 0.34; $H_2P_2B_2P$ (n = 2, m = 2), 0.30. ¹H-NMR (CDCl₃) δ (ppm) for H₂M₁P₃P: -2.61 (2H, inner-H), 0-0.20 (27H, (CH₃)₃), 0.79-0.90 (3H, CH₃), 7.13-7.85 (16H, phenyl-H), 8.54-8.68 (4H), 8.75 (8H). UV/vis λ_{max} : 643, 586, 544, 511, 417 nm in toluene. ¹H-NMR (CDCl₃) δ (ppm) for H₂P₂B₂P: -2.61 (2H), 0.01-0.12 (18H), 0.90-0.97 (6H), 4.29-4.33 (4H), 7.20-7.90 (16H), 8.63-8.76 (4H), 8.79 (8H). UV/vis λ_{max} : 644, 588, 546, 513, 419 nm in toluene. Cobalt ion was inserted into the porphyrin plane by reacting $H_2P_1B_3P$ with cobalt acetate, and the CoP was purified with a silica gel column using chloroform-diethyl ether (4/1 v/v). UV/ vis λ_{max} : 524, 407 nm in toluene for CoP₁B₃P and 525, 411 nm for CoP_2B_2P .

meso- $(\alpha, \alpha, \alpha$ -Tris(o-methacrylamidophenyl)- β -(o-methacrylamidophenyl)porphyrin $(\alpha^{3}\beta$ -H₂P₄P) was synthesized by reacting meso- α, α, α -tris(o-aminophenyl)- β -(o-aminophenyl)porphyrin¹³ with an excess of methacryloyl chloride. ¹H-NMR

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CHART 1: Cobalt Porphyrin Derivatives





 $(CDCl_3): \delta(ppm) -2.68 (2H), 1.00-1.15 (12H), 4.35-4.45 (8H), 7.40-7.98 (16H), 8.76 (4H), 8.88 (8H). UV/vis <math>\lambda_{max}$: 643, 586, 545, 513, 419 nm in toluene. UV/vis λ_{max} (after the cobalt insertion): 525, 411 nm in toluene.

meso- α -(o-Acetoamidophenyl)- α , α , α -tris(o-pivalamidophenyl)porphyrin (H₂M₁B₃P) was synthesized as follows. Pivaloyl chloride and acetyl chloride in that order were added to the chloroform-acetone (1/1 v/v) solution of meso- α , α , α , α -tetrakis-(o-aminophenyl)porphyrin at 0-5 °C. The product was purified by chromatography on a silica gel column using cyclohexaneethyl acetate (1/2 v/v) as solvent (R_f value = 0.54). ¹H-NMR (CDCl₃): δ (ppm)-2.61 (2H, inner-H), 0.16, 0.21 (27H, (CH₃)₃), 1.39 (3H, CH₃), 7.12-7.65 (16H, phenyl-H), 8.53 (4H, amido-H), 8.75 (8H, pyrrole-H). UV/vis λ_{max} : 643, 586, 544, 511, 417 nm in toluene. UV/vis λ_{max} (after the cobalt insertion): 524, 407 nm in toluene.

meso-α-(α-Acrylamidophenyl)-α,α,α-tris(α-pivalamidophenyl)porphyrin (H₂E₁B₃P) was synthesized as follows. Pivaloyl chloride and acryl chloride in that order were added to the chloroformacetone (1/1 v/v) solution of meso-α,α,α,α-tetrakis(α-aminophenyl)porphyrin at 0–5 °C. The product was purified by chromatography on a silica gel column using cyclohexane-ethyl acetate (2/1 v/v) as solvent (R_f value = 0.45). ¹H-NMR (CDCl₃): δ (ppm) -2.75 (2H, inner-H), 0.06, 0.11 (27H, (CH₃)₃), 4.96, 5.68 (2H, CH₂=CH), 5.87 (H, CH₂=CH), 7.16-7.76 (16H, phenyl-H), 8.60 (4H, amino-H), 8.70 (8H, pyrrole-H). UV/vis λ_{max} (after the cobalt insertion): 524, 407 nm in toluene.

Poly(octyl methacrylate-co-vinylimidazole) was prepared by the radical copolymerization of octyl methacrylate and 1-vinylimidazole initiated by azobis(isobutyronitrile). Molecular weight and vinylimidazole residue content of the copolymer were determined to be 1.7×10^6 and 3.3 mol %, by gel permeation chromatography (with tetrahydrofuran as the solvent and polystyrene as the standard) and elemental analysis, respectively. The chloroform solutions of the copolymer and CoP were mixed to combine the vinylimidazole residue of the copolymer with the fifth coordination site of CoP. The solution was carefully cast on a Teflon plate under an oxygen-free atmosphere, followed by drying in vacuo, to yield a transparent, red-colored membrane with a thickness of 60 μ m and containing 1.3 wt % CoP. The fixed and active CoP concentration in the membrane was estimated from an uptaken amount of oxygen to the membrane measured with a sorption apparatus.

Spectroscopic and Permeation Measurements. Oxygen binding to the CoP fixed in the solid membrane was measured by a spectral

change in visible absorption using a spectrophotometer (Shimadzu Model UV-2100). ESR spectroscopy on CoP was measured with a JEOL RE-2X ESR spectrometer operating at the X-band at 110 and 210 K, setting the membrane piece in a glass tube with a vessel for deaeration. The magnetic fields were corrected with the splitting of Mn(II) in MnO ($\Delta H = 86.9$ G).

A pulse and laser flash was applied perpendicularly to the light path of the spectrophotometer (Unisoku FR-2000), and the membrane was placed at the crossing of the laser flash and the light path, 45° to both. Changing the monitored wavelength from 410 to 430 nm allowed a differential spectrum before and after the flash irradiation, and 411 and 428 nm were selected as the monitoring wavelengths. These wavelengths agreed with the maxima of the oxy- and deoxy-CoP in the Soret band region, respectively. A rapid absorbance change for the recombination reaction of photodissociated oxygen to CoP was recorded with a contact-type photomultiplier. Oxygen-binding and oxygendissociation rate constants were calculated by pseudo-first-order kinetic analysis in the absorbance time courses. The concentration of oxygen in the membrane was calculated using the oxygensolubility coefficient determined by the permeation measurement.

Permeation Measurement. Oxygen and nitrogen permeation coefficients for various upstream gas pressures were measured with a low-vacuum permeation apparatus in the chamber with a stable thermostat (Rika Seiki K-315N-03). The pressures on the upstream and the downstream sides were detected by using a Baratron absolute pressure gauge (MKS Instruments). The permeation coefficients were calculated from the slopes of the steady-state straight-line sections of the permeation curves.

Results and Discussion

Oxygen-Binding Reaction to the Cobalt Porphyrins Fixed in the Polymer Membrane. Many recent works on chemical modification of porphyrins have been successful in reversible oxygen binding to their porphinatometals.¹⁴ A typical example is Collman's "picket-fence" metalloporphyrin;¹⁵ (α , α , α , α -tetrakis-(σ -pivalamidophenyl)porphinato)metal, which has steric bulkiness constructed with pivalamido groups on one side of the porphyrin plane and leaves the other side unencumbered. An imidazole ligand is allowed to coordinate to the unhindered side of the metalloporphyrin, with the other side remaining as a pocket for oxygen binding. A cavity structure around the oxygen-binding site in the porphyrin is important to form the reversible oxygen adduct and to control the oxygen-binding reactivity. In this paper, we synthesized new derivatives of the "picket fence" cobalt



Figure 1. ESR spectra of CoB_4P fixed in the polymer membrane (a) in an oxygen-free atmosphere and (b) in air at 77 K.

TABLE 1: Oxygen-Binding Equilibrium Constant (K), Enthalpy and Entropy Change (ΔH , ΔS), and Rate Constants (k_{on} , k_{off}) for the CoPs Fixed in the Polymer Membranes at 20 °C

CoP	10-3 K (M ⁻¹)	ΔH (kcal mol ⁻¹)	ΔS (eu)	$10^{-7} k_{on}$ (M ⁻¹ s ⁻¹)	$\frac{10^{-3} k_{\text{off}}}{(\text{s}^{-1})}$
CoB₄P	3.0	-13	37	0.98	3.2
CoP ₁ B ₃ P	4.3	-13	-38	1.4	3.2
CoE_1B_3P	5.3	-14	38	1.5	2.8
CoM_1B_3P	6.8	-14	38	1.7	2.5
CoP ₂ B ₂ P	4.0	-13	-38	2.3	5.7
$\alpha^{3}\beta$ -CoP ₄ P	0.51	-11	-36	3.4	66

porphyrin (CoB₄P): CoP₁B₃P, CoE₁B₃P, CoM₁B₃P, CoP₂B₂P, and $\alpha^{3}\beta$ -CoP₄P. These cobalt porphyrins (CoPs) have a less crowded cavity structure in comparison with that of CoB₄P, as can be seen in Chart 1.

The coordination of CoP to a polymeric nitrogenous ligand such as the vinylimidazole copolymer yielded both an active and homogeneous dispersed CoP for oxygen binding in the solid state and a flexible and mechanically tough membrane.^{4,6}

Reversible oxygen binding and 1/1 oxygen/CoP adduct formation for the CoP fixed in the solid polymer membrane were first recognized by ESR spectroscopy. Figure 1 showed the example of ESR spectra of the polymer membrane containing CoB₄P. In an oxygen-free atmosphere (Figure 1a), $g_{\parallel} = 2.03$, $g_{\perp} = 2.31$, and the super-hyperfine splitting pattern attributed to the nitrogen on the CoP's fifth site indicated that the imidazole residue of the copolymer coordinated to the fifth coordination site of CoB₄P and that its sixth coordination site was vacant for oxygen binding even in the solid state. After introducing air to the polymer membrane (Figure 1b), g-values shifted to $g_{\parallel} = 2.08$ and $g_{\perp} = 2.00$ and the eight-line hyperfine splitting pattern was observed. This spectrum revealed formation of an oxygen adduct (O₂/Co = 1/1).

The visible absorption spectrum of the deoxy CoP ($\lambda_{max} = 528$ nm) fixed in the transparent membrane was changed to the spectrum with $\lambda_{max} = 545$ nm assigned to the oxygen adduct (oxy) of CoP immediately after the exposure of the membrane to oxygen. The oxy-deoxy spectral change was rapid and reversible in response to partial oxygen pressure of the atmosphere, with isosbestic points at 480, 538, and 667 nm.

The oxygen-binding affinity or equilibrium constant (K) of the CoPs was determined from this spectral measurement of the membranes at an oxygen partial pressure of 0–760 mmHg. The obtained K (mmHg⁻¹) was converted to K (M⁻¹) by substituting the physical solubility coefficient of oxygen, k_D , in the membrane (cm³ (STP) cm⁻³ cmHg⁻¹ or M⁻¹ cmHg⁻¹, given in Table 2) determined by the oxygen permeation measurement mentioned later and given in Table 2. The K values for CoPs are in the order CoM₁B₃P > CoE₁B₃P > CoP₁B₃P > CoP₂B₂P > CoB₄P > $\alpha^3\beta$ -CoP₄P.

Enthalpy and entropy change (ΔH and ΔS) for the oxygen binding were determined from the temperature dependence of K

and are also given in Table 1. ΔH or enthalpy gain through the oxygen binding was the smallest for $\alpha^3\beta$ -CoTP₄P, of which oxygenbinding affinity was the lowest among the present CoP derivatives.

Photodissociation and recombination of bound oxygen from and to the CoPs fixed in the membrane were observed by laser flash photolysis. For example, the reaction for the $\alpha^3\beta$ -CoP₄P membrane was completed within 100 μ s, and it was very rapid despite a reaction in the solid state. Oxygen-binding and oxygendissociation rate constants (k_{on} and k_{off}) were estimated by pseudofirst-order kinetics on the spectral time courses in the oxygen recombination and are given in Table 1. The k_{on} value increases with reduction of bulkiness in the substituent group on the porphyrin plane or in the oxygen-binding cavity, in the order $\alpha^3\beta$ -CoP₄P > CoP₂B₂P > CoM₁B₃P > CoE₁B₃P > CoP₁B₃P > CoB₄P. The k_{off} value increases in almost the same order, $\alpha^3\beta$ -CoP₄P \gg CoP₂B₂P > CoM₁B₃P \sim CoE₁B₃P \sim CoP₁B₃P \sim CoB₄P.

It has been found that a weak and hydrogen-bond-like interaction between the metal-bound dioxygen and the protons of amidophenyl groups on the porphyrin plane contributes to the oxygen binding.¹⁶⁻²⁰ For example, Momenteau et al. reported that the oxygen-binding affinity was much enhanced for the CoPs substituted with amido groups in comparison with those substituted with alkyl and ether groups and described that the oxygendissociation rate was suppressed by the interaction. In the oxygen binding also for our CoPs, k_{on} relates with the steric hindrance of the substituted groups or of the oxygen-binding cavity on the porphyrin plane, and k_{off} is affected both by the steric hindrance in the oxygen-binding cavity and by the interaction between the bound oxygen and the amido protons of the substituent group. The oxygen-binding affinity $K = k_{on}/k_{off}$ is also yielded by these effects of the substituents on the porphyrin plane. As a result of these effects, the largest k_{on} and k_{off} or the kinetically highest activity was observed for $\alpha^{3}\beta$ -CoP₄P, of which steric hindrance on the porphyrin plane or on the oxygen-binding and oxygendissociation pathway is significantly reduced, and the largest Kwas for CoM_1B_3P , in which the bound oxygen is expected to interact with the amido protons more effectively due to its less bulky acetyl groups.

Anyway, the CoPs fixed in the polymer membrane bind oxygen reversibly with different affinity and kinetic character and will act as the oxygen carrier for oxygen permeation in the membranes.

Analysis of Facilitated Oxygen Transport in the Membranes. The permeation time courses for the membranes containing CoPs reached steady-state straights lines, of which slopes gave permeation coefficients P. Before the steady state, there was an induction period. The time lag (θ) was estimated from the crossing point of the steady-state straight line and the abscissa on the permeation curve. The θ values for the oxygen and nitrogen permeation (θ_{O2} and θ_{N2}) are shown in Figure 2 vs upstream oxygen and nitrogen pressure $(p_2(O_2) \text{ and } p_2(N_2))$. While θ_{N_2} is short and independent of $p_2(N_2)$, θ_{O2} is longer than θ_{N2} and increases with the decrease in $p_2(O_2)$. θ_{O2} is also short and independent of $p_2(O_2)$ for the control membranes which contain inactive Co(III)P for oxygen binding. These results are explained as follows: the fixed CoP in the membrane interacts specifically with oxygen and retards the diffusion of oxygen through the membrane.

Figure 3 shows the permeation coefficients of oxygen and nitrogen (P_{O2} and P_{N2}) for the CoP membranes. P_{N2} is smaller than P_{O2} and independent of $p_2(N_2)$, because the fixed CoP does not bind with nitrogen. In contrast, P_{O2} is larger than P_{N2} and increases with the decrease in $p_2(O_2)$, which indicates that the fixed CoP carrier in the solid membrane clearly interacts with oxygen and facilitates oxygen transport in the membrane. P_{O2} for the control and inactive Co(III)P membrane is not enhanced at the low $p_2(O_2)$, where P_{O2} for the active membranes significantly increases.



Figure 2. Effect of upstream gas pressure on the time lag of the permeation for the CoP polymer membranes at 45 °C. Oxygen: (O) CoB₄P, (O) CoP₁B₃P, (O) CoP₂B₂P, (O) $\alpha^{3}\beta$ -CoP₄P, (Δ) inactive (control) $\alpha^{3}\beta$ -Co^{III}P₄P, (Δ) inactive Co^{III}B₄P. Nitrogen: (\Box) $\alpha^{3}\beta$ -CoP₄P, (\blacksquare) CoB₄P.



Figure 3. Effect of upstream gas pressure on the permeability coefficient for the CoP polymer membranes at 45 °C. Oxygen: (O) CoB₄P, (O) CoP₁B₃P, (O) CoP₂B₂P, (\odot) $\alpha^{3}\beta$ -CoP₄P, (Δ) inactive (control) $\alpha^{3}\beta$ -Co^{III}P₄P. Nitrogen: (\Box) $\alpha^{3}\beta$ -CoP₄P.

One notices in comparing the P_{O2} values for a series of CoP that P_{O2} for the membrane containing $\alpha^3\beta$ -CoP₄P increases more than other membranes at low $p_2(O_2)$ in Figure 3, to yield permselectivity of oxygen to nitrogen (P_{O2}/P_{N2}) to be ca. 6.1.

We have analyzed this facilitated transport in the membranes containing CoPs, by a modified dual-mode transport model,^{21,22} as represented by the following equation.

$$P_{O2} = k_{\rm D} D_{\rm DD} + \frac{C_{\rm C}' K D_{\rm CC}}{l + K p_2} + \left[\frac{C_{\rm C}' K D_{\rm CD} - k_{\rm D} D_{\rm DC}}{1 + K p_2} + \frac{2k_{\rm D} D_{\rm DC}}{K p_2} \ln(1 + K p_2) \right] (1)$$

TABLE 2: Diffusion Constants of Oxygen in the CoP Polymer Membranes at $45 \, {}^{\circ}C^{a}$

	diffusion constants (cm ² /s)						
CoP	$10^6 D_{\rm DD}$	$10^7 D_{\rm DC}$	$10^8 D_{\rm CD}$	10 ⁹ D _{CC}			
CoB₄P	2.2	0.97	0.87	3.1			
CoP_1B_3P	2.2	2.2	1.5	7.3			
CoE_1B_3P	2.4	2.8	0.55	2.3			
CoM ₁ B ₃ P	2.4	3.0	0.32	1.8			
CoP ₂ B ₂ P	2.3	2.6	2.0	9.0			
$\alpha^{3}\beta$ -CoP ₄ P	2.2	3.2	22	144			

^{*a*} $10^{4}k_{D}$ (cm³ (STP) cm⁻³ cmHg⁻¹) = 7.2; C_{C}' (cm³ (STP) cm⁻³) = 0.2; the CoP concentration in the membranes, 1.3 wt %.



Figure 4. Contribution of each term in the modified dual-mode model to permeation coefficients for the $\alpha^3\beta$ -CoP₄P polymer membrane at 45 °C: (bottom shaded area) the first term in eq 1, (middle shaded area) the second term in eq 1, (top shaded area) the exchange term.

Here, k_D is the physical solubility coefficient of oxygen in a polymer matrix. $C_{C'}$ is the fixed and active CoP concentration in the membrane, and those values of each membrane were measured to be 0.2 cm³ cm⁻³ from oxygen-sorption experiments. P_{O2} is the sum of the first term, representing the physical oxygen permeation through a polymer matrix, the second term, representing the carrier-mediated mode, *i.e.*, a specific permeation of oxygen *via* the fixed CoP, and the third term, representing the exchanging mode between the first and the second terms. D_{DD} , D_{DC} , D_{CD} , and D_{CC} are the diffusion constants of oxygen, in order, for the physical diffusion in the polymer membrane, for the diffusion from the polymer matrix to the fixed CoP, for the diffusion from the fixed CoP to the polymer matrix, and for the hopping diffusion through CoP, respectively.

The experimental data in Figure 3 were analyzed by eq 1, and the parameters for oxygen transport through the membranes given by the modified dual-mode transport model are listed in Table 2. D_{DD} was calculated to be 10^{-6} cm² s⁻¹, which agreed with the previously reported diffusion constants of oxygen in rubbery polymers⁸ (glass transition temperature of the membranes of this experiment ca. 0 °C) and is almost one-tenth of those in liquids (*e.g.*, 10^{-5} cm² s⁻¹ for oxygen in water at 25 °C^{23,24}). That suggests that segmental mobility of the polymer matrix does not significantly retard oxygen diffusivity in the membrane. Furthermore, D_{DD} is not influenced by CoP species or the porphyrin structure.

On the other hand, D_{DC} , D_{CD} , and D_{CC} involving the oxygen diffusion via the fixed CoP carrier are smaller than D_{DD} and



Figure 5. Oxygen permeability coefficient and permselectivity of oxygen to nitrogen for the CoP polymer membranes at 45 °C. Oxygen: (O) CoB₄P, (O) CoP₁B₃P, (O) CoP₂B₂P, (O) CoE₁B₃P, (O) CoM₁B₃P, (O) $\alpha^{3}\beta$ -CoP₄P.

depend on the CoP species or the oxygen-binding properties of CoP. One notices in Table 2 especially that D_{CD} and D_{CC} are enormously large for $\alpha^3\beta$ -CoP₄P. Comparison of the diffusion constants in Table 2 with the data in Table 1 elucidates a logarithmically linear correlation of the rate constants of oxygen binding and dissociation of CoPs with the diffusion constant *via* CoPs. That is, k_{on} corresponds to D_{DC} , and k_{off} to D_{CD} . D_{CC} relates to both k_{on} and k_{off} ; especially k_{off} clearly reflects on D_{CC} . The polymer membrane containing CoP with a large rate constant of oxygen binding and dissociation of CoP leads to a large diffusion constant to yield oxygen permaselectivity or facilitated oxygen transport.

Noble^{25,26} analyzed the facilitated transport by using our previously reported data⁴ on the α^4 -CoB₄P membranes. He described two distinct features of the facilitated transport of oxygen in the CoP membranes: (i) "terrain" dependency of the effective diffusion constant for the permeant-carrier adduct and (ii) no percolation limit. His descriptions are not in conflict with the results in this paper about the decrease of the permeability coefficient of oxygen in the membrane with higher CoP concentration and the effect of $D_{\rm DC}$ and $D_{\rm CD}$ on the facilitated oxygen transport.

Figure 4 shows the contribution of each transport mode in eq 1 to the permeation coefficient, by using the example of the membrane of $\alpha^3\beta$ -CoP₄P. The most important among these factors in the oxygen transport is the diffusion constants of oxygen via CoP. The diffusion constant D_{DC} for the exchange third term in eq 1 augments P_{O2} or the facilitated transport of oxygen at a wide range of $p_2(O_2)$. On the other hand, the binding affinity K enhances P_{O2} at low $p_2(O_2)$ because the specific oxygen uptake into the membrane is effective at its dilute feed condition.

Correlation between permeation coefficients (P_{02}) and oxygen permselectivity (P_{02}/P_{N2}) is given in Figure 5: (P_{02}/P_{N2}) increases with the increase in P_{O2} . We first succeeded by utilizing the carrier-mediated or facilitated transport in enhancing both permeability and permselectivity; their relationship had remained a reverse one for presently available polymers.³ P_{O2}/P_{N2} is more than 6 for the membrane containing $\alpha^3\beta$ -CoP₄P at an upstream pressure of 5 mmHg, in spite of its low concentration (1.3 wt %) in the membrane. Oxygen permselectivity for the membrane containing a large amount of $\alpha^3\beta$ -CoP₄P (5 wt %) is calculated to be 11, according to eq 1. Although the reduction in steric bulkiness of the substituent on the porphyrin plane causes the decrease in oxygen-binding affinity for the $\alpha^3\beta$ -CoP₄P, its much larger D_{DC} , D_{CD} , and D_{CC} efficiently facilitate the oxygen transport. The high diffusivity of oxygen via CoP contributes strongly to the transport, besides the oxygen-binding affinity.

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