Registry No. KSCN, 333-20-0; H_2SO_4, 7664-93-9; KIO_3, 7758-05-6; Ba, 7440-39-3; Ca, 7440-70-2; Ag, 7440-22-4; Pb, 7439-92-1.

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Oxygen Binding and Transport in the Membrane of Poly[[tetrakis(methacrylamidophenyl)porphinato]cobalt-*co*-hexyl methacrylate]

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Received December 23, 1987

ABSTRACT: The copolymer of [α,α′,α″,α‴-*meso*-tetrakis(*o*-methacrylamidophenyl)porphinato]cobalt with hexyl methacrylate (**1**) gives a transparent and flexible membrane. The covalently introduced (porphinato)cobalt reversibly forms its oxygen adduct in the membrane state. Oxygen-binding equilibrium and kinetic constants of the (porphinato)cobalt are much larger than those of the corresponding [α,α′,α″,α‴-*meso*-tetrakis(*o*-pivalamidophenyl)porphinato]cobalt (**2**) dispersed in the membrane of poly(butyl methacrylate). Oxygen-permeation behavior through the membrane is in accordance with a dual-mode transport model. Ratio of D_C to D_D (D_C and D_D are diffusion coefficients of oxygen via the fixed (porphinato)cobalt and through polymer matrix) is 10 times larger for the copolymer membrane **1** in comparison with that for the dispersed membrane **2**, which indicates effective facilitation in the oxygen transport.

Introduction

A polymer membrane containing a metal complex that interacts specifically and reversibly with molecular oxygen is of great interest as a facilitated transport membrane of oxygen. The authors have recently reported[1-6] that oxygen transport through a poly(alkyl methacrylate) membrane was augmented by the addition of a [α,α′,α″,α‴-*meso*-tetrakis(*o*-pivalamidophenyl)porphinato]cobalt (CoPP, **2**) complex or a (*N*,*N*′-bis(salicylidene)ethylenediamine)cobalt complex, which forms oxygen adducts rapidly and reversibly even in the solid state. The authors discussed the oxygen permeation profile based on a dual-mode transport model (eq 1).[1-3,7] Here, P is permeability coefficient of

$$P = k_D D_D[1 + FR/(1 + Kp_2)] \qquad (1)$$

$$F = D_C/D_D \qquad R = C'_C K/k_D$$

oxygen, k_D is solubility coefficient of oxygen dissolved in a polymer matrix according to Henry's law, D_C and D_D are diffusion coefficients of oxygen via the complex and through a polymer matrix, C_C' is saturated amount of oxygen reversibly bound to the complex, K is oxygen-binding equilibrium constant, and p_2 is upstream oxygen pressure. The first term of eq 1 represents the permeation for a rubbery polymer membrane, and P is enhanced by the additional second term representing the contribution of the complex.

Four requisites are considered from eq 1 to increase the second term or P: a decrease in p_2, an increase in C_C', large K, and large D_C. In fact, P_{O_2} increases with a decrease in p_2[1-6] and higher concentration of the complex in a membrane brought about higher oxygen permselectivity.[2,3] From the study using the CoPP and

$$M + O_2 \underset{k_{off}}{\overset{k_{on}}{\rightleftharpoons}} M{-}O_2 \qquad (2)$$

$$K = k_{on}/k_{off}$$

M = metal ion of the porphinato complex

the FePP complex with various axial, nitrogenous lig-

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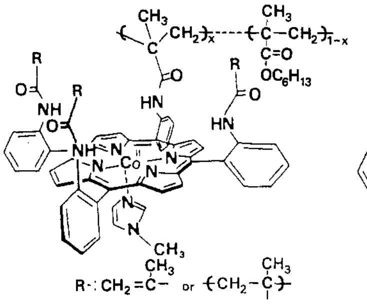
ands,[5,6] the authors concluded that the complex is to have both a strong oxygen-binding affinity (large K) and a large oxygen-dissociation kinetic parameter ($k_{\rm off}$ or D_C) in order to enhance the facilitated oxygen transport in the membrane. For example, if one assumes a complex with both a strong oxygen affinity of $K = 1$ cmHg^{-1} and a large kinetic parameter of $D_C/D_D = 0.2$, an outstanding oxygen permeation coefficient of $P_{O_2} = 1.3 \times 10^{-7}$ cm^3(STP) cm^{-2} s^{-1} cmHg^{-1} is estimated with eq 1 for $p_2 = 15$ cmHg (air), $D_D = 1 \times 10^{-6}$ cm^2 s^{-1}, $k_D = 1 \times 10^{-3}$ cm^3(STP) cm^{-3} cmHg^{-1}, and $C_C' = 10$ cm^3(STP) cm^{-3}. But there still remain a couple of unsolved problems along this assumption. First, it is difficult to prepare the membrane containing the complex homogeneously in higher concentration by dispersing it in polymer. Second, the variation in the complex often increases its oxygen-binding affinity but is accompanied with a decrease in the kinetic parameter.

The authors have synthesized novel metalloporphyrin derivatives with oxygen-binding ability in homogeneous solutions,[8] and in this study selected one of them: [*α*,*α*′,*α*″,*α*‴-*meso*-tetrakis(*o*-methacrylamidophenyl)porphinato]cobalt (CoMP).[9] The CoMP complex is expected due to its methacrylamido residues in the porphyrin structure to show both a strong oxygen-binding affinity and a large oxygen binding/dissociation kinetic parameter and to be covalently introduced in a polymer chain. This paper describes the preparation of copolymer of CoMP and hexyl methacrylate (1), excellent oxygen-binding capability of the covalently fixed CoMP complex in solid state, and efficiently facilitated transport of oxygen in the membrane.



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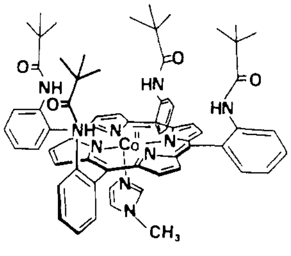

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Experimental Section

Materials. *α*,*α*′,*α*″,*α*‴-*meso*-Tetrakis(*o*-methacrylamidophenyl)porphine (MP) was synthesized by reacting *α*,*α*′,*α*″,*α*‴-*meso*-tetrakis(*o*-aminophenyl)porphine with an excess of methacrylic acid chloride as in the previous paper[9] and was purified by chromatography on silica gel.

Copolymerization. MP (84 mg, 0.09 mmol) was dissolved in 30 mL of benzene, and 74 g (440 mmol) of hexyl methacrylate and 360 mg (2.2 mmol) of azobis(isobutyronitrile) were added. This was degassed, sealed, and then heated with stirring at 60 °C for 4 h. The reaction mixture was added dropwise in a large amount of methanol. The precipitate was dissolved in benzene and purified by several reprecipitations. Yield: 55.6 g. The MP residue content in the copolymer was determined spectroscopically by using the assumption that the molar extinction coefficient of the porphine residue of the copolymer is the same as that of MP. The MP content in the copolymer was 0.15 wt % (27 mmol %). Molecular weight of the copolymer was determined to be 9.1×10^4 by gel-permeation chromatography (with THF as the solvent and polystyrene as the standard).

The incorporation of cobaltous ion was carried out by heating the copolymer with cobaltous acetate in chloroform/methanol. The CoMP copolymer was purified by chromatography on silica gel. The complete incorporation of cobaltous ion was confirmed by disappearance of fluorescence based on the metal-free MP residue and complete change of UV spectrum.

Preparation of Membrane. The CoMP copolymer was complexed with 1-methylimidazole (Im) ([Im]/[CoMP residue] = 10) in toluene under nitrogen atmosphere. The toluene solution was carefully cast on a Teflon plate under an oxygen-free atmosphere, followed by drying in vacuo, to yield a transparent, wine-red color membrane containing 0.17 wt % CoMP residue and with a thickness of 55 μm.

Spectroscopic and Permeation Measurements. Oxygen binding to the CoMP complex of the copolymer in a solid membrane state was observed by a spectral change in visible absorption using high-sensitivity spectrophotometer (Shimazu Model UV 2000). Oxygen and nitrogen permeation coefficients for various upstream gas pressure were measured with a low-vacuum permeation apparatus (Rika Seiki Inc. Model K-315 N-01), as reported in previous paper.[2]

Table I
Visible Absorption Maxima of the CoMP Copolymer and Lifetime of Its Oxygen Adduct at 25 °C

	abs max, nm		lifetime	
complex[a]	deoxy	oxy	in solid membrane	in toluene
CoMP copolymer	528	545	>1 month	ca. 1 day
CoMP	528	(545)	<5 min[b]	0
CoPP	528	545	>1 month[b]	ca. 1 week

[a] Complexed with 1-methylimidazole (Im) ([Im]/[Co] = 10). [b] Dispersed in the PBMA membrane.

Results and Discussion

Oxygen Binding in the CoMP Copolymer Membrane. The MP porphyrin was covalently introduced in poly(hexyl methacrylate) by radical copolymerization. The content of MP residue in the copolymer was restricted to less than 5 wt % in the present paper because copolymers with higher content gave a brittle powder and could not be made into a membrane. The MP copolymer was completely derived to the CoMP copolymer by the incorporation reaction of cobaltous ion (see Experimental Section). The copolymer containing 0.17 wt % CoMP gives a transparent, wine-red color, and flexible membrane.

The UV-visible adsorption spectrum of the deoxy CoMP membrane was changed to the spectrum assigned to the oxy CoMP complex (Co/O_2 = 1:1 adduct, $\lambda_{\max}$, see Table I). The Co(II) complex slowly oxidized during the oxygen binding to the Co(III) complex that cannot bind oxygen any longer. The lifetime (half-life period) of the oxygen adduct is also given in Table I. It is known that the oxygen adduct of the Co(II) complex forms with another Co(II) complex a μ-dioxo adduct (Co/O_2 = 2:1) which is

$$\mathrm{Co{-}O_2 + Co(II) \rightleftharpoons Co{-}O_2{-}Co \rightarrow Co(III){-}O^{2-}{-}Co(III)} \tag{3}$$

converted irreversibly to a μ-oxo Co(III) complex (eq 3).[8] The *α*,*α*′,*α*″,*α*‴-tetrakis substituents on the porphyrin plane sterically inhibit this μ-dioxo adduct formation and enable the (porphinato)cobalt(II) complex to bind oxygen reversibly.[10] Actually the tetrakis(pivalamido) groups of CoPP (2) prolong the lifetime of the CoPP–oxygen adduct in toluene[10] and also in the solid membrane state. On the other hand, the CoMP complex is irreversibly oxidized on exposure to oxygen in toluene and forms its oxygen adduct for only a few minutes in the solid membrane state. It is considered that the tetrakis(methacrylamido) groups of CoMP are not large enough to sterically inhibit the irreversible μ-dioxo adduct formation.

In contrast to the monomeric CoMP complex, the CoMP copolymer (1) forms its oxygen adduct reversibly. The CoMP complex is covalently fixed in the polymer chain in dilute concentration, which strikingly suppress the irreversible μ-dioxo adduct formation of CoMP and prolongs the lifetime of the reversible oxygen adduct. Especially

Table II
Equilibrium Constant[a] and Thermodynamic Parameters for Oxygen Binding of the CoMP Copolymer in Solid Membrane State

complex	K, cmHg^{-1}	ΔH, kcal mol^{-1}	ΔS, eu
CoMP copolymer	3.7	−14	−37
CoPP[c]	0.056	−14	−44

[a] Data at 25 °C. [b] Data from Figure 2. [c] Dispersed in the PBMA membrane.

Table III
Kinetic Parameters[a] and Activation Energy (E_a) for Oxygen Binding of the CoMP Copolymer

complex	10^2k_{on}, mmHg^{-1} s^{-1}	$10k_{off}$, s^{-1}	E_a(on), kcal mol^{-1}	E_a(off), kcal mol^{-1}
CoMP copolymer	4.5	1.4	9.5	25
CoPP[b]	0.016	0.28	8.7	22

[a] Apparent rate constants (thickness of the membranes; 55 μm) at 25 °C. [b] Dispersed in the PBMA membrane.

in the membrane state, the CoMP copolymer maintains its oxygen-binding ability for over a month even under air atmosphere.

Oxygen-binding equilibrium constants (K) were determined by conducting the Langmuir-type oxygen-binding equilibrium measurement as in the previous papers[2,3] and are given in Table II. Thermodynamic parameters for the oxygen binding were determined from the temperature dependence of K (20–40 °C) and also are given in Table II. The K value of the CoMP copolymer is extremely larger than that of the corresponding CoPP complex dispersed in the PBMA membrane. Table II indicates that the larger ΔS value of the CoMP copolymer in comparison with the one of CoPP contributes to the extraordinarily strong oxygen-binding affinity of the CoMP copolymer. It has been reported that the amido groups of CoPP interact with the cobalt-bound oxygen molecule through an intramolecular hydrogen bond and suppresses a rotational motion of the bound oxygen molecule along the cobalt–oxygen coordination bond.[11] It has been also reported that an increase in freedom of the rotational motion of cobalt-bound oxygen molecule reduces the negative entropy change for the oxygen binding and results in a very large K value.[12] It is considered that the methacrylamido groups combined with the polymer matrix produces a distortion between the methacrylamido fence and the porphyrin plane, induces a decrease of the intramolecular hydrogen bond between the amido group and cobalt-bound oxygen molecule, and brings about the strong oxygen-binding affinity.

Apparent k_{on} and k_{off} were estimated by analyzing time courses of the oxygen adsorption to the CoMP copolymer membrane according to pseudo-first-order kinetics and listed in Table III. Both the k_{on} and k_{off} values of the CoMP copolymer are much larger than those for the CoPP dispersed in the PBMA membrane at the measuring temperature. These large kinetic parameters for the oxygen binding are also probably explained by the distorted structure of CoMP combined with the polymer matrix mentioned above. Effect of the oxygen-binding capability of the fixed CoMP complex with both of extraordinarily large K and k_{off} upon oxygen transport in the membrane is discussed below.

Oxygen Permeability in the CoMP Copolymer Membrane. Oxygen sorption and desorption to and from the CoMP complex fixed in the copolymer membrane were very rapid and according to the Langmuir isotherm. It is expected that oxygen is not immobilized to the CoMP complex during the passage through the membrane and that oxygen transport is facilitated by the additional Langmuir mode transport, as has been reported[1-4] by the authors for the membranes containing a cobalt porphyrin complex as a fixed carrier.

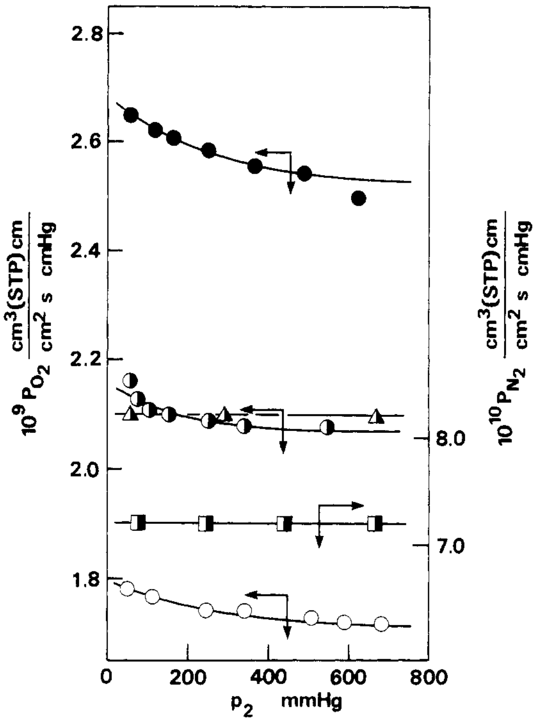

Figure 1. Effect of upstream gas pressure on permeation coefficient for the CoMP copolymer membrane (oxygen at (○) 20 °C, (◑) 25 °C, and (●) 30 °C; nitrogen at (◨) 25 °C). A control oxygen permeation coefficient for poly(hexyl methacrylate) at 25 °C (▲).

Figure 1 shows the effect of upstream oxygen pressure ($p_2(O_2)$) on the oxygen permeability coefficient (P_{O_2}) in the copolymer membrane covalently containing 0.17 wt % CoMP residue. The glass transition temperature is −17 °C for the copolymer membranes with and without imidazole, and the membranes were in a rubbery state at the temperatures for the permeability measurement. This denies a physical effect of p_2 on P which often has been reported for glassy polymers. A control P_{O_2} value for poly(hexyl methacrylate) is plotted also in Figure 1, which is independent of $p_2(O_2)$. Another control experiment was carried out for nitrogen permeability coefficient (P_{N_2}) in the copolymer membrane. P_{N_2} in Figure 1 is independent of $p_2(N_2)$ because the CoMP complex does not interact with nitrogen. On the other hand, P_{O_2} for the copolymer membrane obviously increases with a decrease in $p_2(O_2)$ in Figure 1, which indicates that oxygen transport occurs by the dual mode.

As has been shown in Table II, the oxygen-binding equilibrium constant (K) of the CoMP copolymer decreases with temperature (negative enthalpy change). Therefore, it is assumed that contribution of the Langmuir population based on the CoMP complex decreases with temperature. However the $p_2(O_2)$ dependency of P_{O_2} is rather enhanced at higher temperature as is seen in Figure 1. The oxygen desorption rate from the CoMP complex is much reduced with a decrease in temperature (see Table III), so that this kinetic property of the CoMP complex in the oxygen binding influences the oxygen-transport phenomenon more than the property of CoMP in the oxygen-binding equilibrium does.

The effect of $p_2(O_2)$ on P_{O_2} could be analyzed by using eq 1, which means that the oxygen permeability in the

Table IV
Dual-Mode Transport Parameters for the CoMP Copolymer

complex	T, °C	D_D, cm^2/s	D_C, cm^2/s	$F(D_C/D_D)$	k_D, cm^3(STP)/cm^3 cmHg	C'_C, cm^3(STP)/cm^3
CoMP copolymer[a]	20	1.2×10^{-6}	8.7×10^{-8}	0.07	1.3×10^{-3}	0.03
	25	1.4×10^{-6}	2.2×10^{-7}	0.16	1.5×10^{-3}	0.03
	30	1.7×10^{-6}	5.0×10^{-7}	0.29	1.5×10^{-3}	0.03
CoPP[b]	25	7.0×10^{-7}	1.4×10^{-8}	0.02	1.0×10^{-3}	0.2
CoPP[c]	25	1.2×10^{-6}	1.1×10^{-8}	0.01	1.1×10^{-3}	0.3

[a] CoMP content = 0.17 wt %. [b] Dispersed in PBMA membrane; CoPP content = 2.5 wt %. [c] Complexed with poly(octyl methacrylate-*co*-1-vinylimidazole); CoPP content = 1.3 wt %.

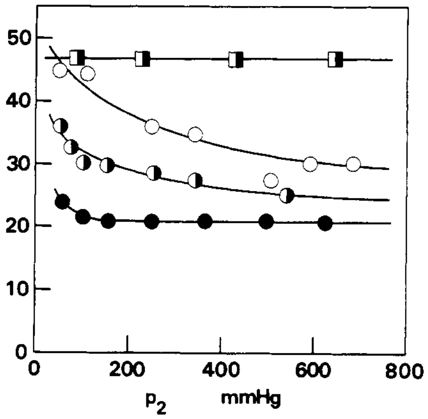

Figure 2. Effect of upstream gas pressure on induction period for the CoMP copolymer membrane (oxygen at (○) 20 °C, (◑) 25 °C, and (●) 30 °C; nitrogen at (◧) 25 °C).

CoMP copolymer membrane can be explained in terms of the dual-mode theory.

The time lag (θ) for oxygen permeation also depends on $p_2(O_2)$, as shown in Figure 2, in the same manner as the permeation coefficient. This behavior indicates that oxygen clearly interacts with the CoMP complex in the membrane. This is further supported by the result that θ_{N_2} is independent of the upstream gas pressures for nitrogen permeation in the copolymer membrane. In Figure 2 one also notices that θ_{O_2} and the $p_2(O_2)$ dependency of θ_{O_2} decrease with temperature. θ_{O_2} and the $p_2(O_2)$ dependency of θ_{O_2} are based on the oxygen binding to the fixed CoMP complex and are enhanced at lower temperature because the oxygen-binding equilibrium constant (K) of CoMP increases and the desorption kinetic parameter (k_{off}) of oxygen from CoMP decreases with a decrease in temperature (see Tables II and III).

The effect of $p_2(O_2)$ on the time lag could be analyzed by using the theoretical equation for the dual-mode transport.[2] This also supports the dual-mode transport of oxygen in the copolymer membrane and a pathway of oxygen permeation via the fixed CoMP complex.

The oxygen permeation parameters calculated are given in Table IV. Attention should be paid to the $F(D_C/D_D)$ values which indicate the mobility of the adsorbed oxygen to the complex. The F value in the CoMP copolymer membrane is much larger than those for the PBMA membrane containing the CoPP complex and the poly(octyl methacrylate-*co*-1-vinylimidazole)–CoPP complex membrane. This is corresponding to the larger k_{off} of the CoMP copolymer in comparison with the referenced complex fixed in the membrane (see Table III). The F increases with temperature, which suggests that an increase of the k_{off} with temperature (also see Table III) enhances the F value and which contributes to the facilitated transport of oxygen at higher temperature as has shown in Figure 1.

In the CoMP copolymer membrane, the facilitation of oxygen transport is clearly observed although the membrane contains a small amount of the complex ([CoMP] = 0.17 wt %). This is based on the oxygen-binding capability of the fixed CoMP complex with both of extraordinarily large K and k_{off}.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area "Macromolecular Complexes" from the Ministry of Education, Science and Culture, Japan.

Registry No. O_2, 7782-44-7.

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