Highly Oxygen Permselective Membrane of Cobalt-Complexed Polyazomethine Containing Tridentate Ligand and Oligosiloxane in the Repeating Pairs of the Main Chain

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ABSTRACT: Four new polyazomethines containing a tridentate ligand and different length of oligosiloxane in the repeating pairs were synthesized and cobalt(II) salt was added to the polymer to yield a cobalt(II)-complexed membrane. Oxygen permselectivities of the cobalt(II)-complexed membranes at one atm pressure difference were excellent: oxygen permeability coefficient (P_{O_2}) = $1.1\text{--}2.9 \times 10^{-8} \text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$, oxygen separation factor ($\alpha = P_{O_2}/P_{N_2}$) = $3.4\text{--}4.0$, which were very close to those on the upper boundary line reported in the literature [L. M. Robeson, *J. Membrane Sci.*, **62**, 165 (1991)]. Since P_{O_2} increased with decrease in the upstream pressure and P_{N_2} was independent, a cobalt(II)-complex in the membrane is shown to function as a fixed oxygen carrier.

KEY WORDS Oxygen Permselective Membrane / Polyazomethine / Cobalt Complex / Tridentate Macromolecular Ligand / Fixed Oxygen Carrier / Oligosiloxane / Pyridine /

So far, many attempts have been made to design polymeric membrane materials for oxygen separation. For oxygen permselective membrane, high oxygen permeability coefficient (P_{O_2} : $\text{cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$) and a high oxygen separation factor ($\alpha = P_{O_2}/P_{N_2}$) are required. However, a trade-off relationship between P_{O_2} and α values and upper boundary line reported by Robeson (1991)¹ are present in the α - P_{O_2} plots of reported polymeric membranes. One of our purposes at present for the development of oxygen permselective membranes is to produce a high performance polymer which approaches and exceeds this boundary line.

Only 3 pure polymers which have well-defined structure have been reported to exhibit high P_{O_2} of more than 1.0×10^{-8} in the literature, *i.e.*, poly(1-trimethylsilylpropyne),² poly(dimethylsiloxane),³ polyphosphazene,⁴ and their derivatives and copolymers. However, α of these highly permeable polymer membranes shows a low value of about 2.0.

To obtain a highly oxygen permeable membrane with higher α , we synthesized several novel polymers such as poly[*o*-,*p*-bis(trimethylsilyl)phenylacetylene] ($P_{O_2} = 4.7 \times 10^{-8}$, $\alpha = 2.7$),⁵ poly(*p*-1*H*,1*H*,2*H*,2*H*-perfluorohexyloxydimethylsilylphenylacetylene) ($P_{O_2} = 3.5 \times 10^{-8}$, $\alpha = 3.0$),⁶ and poly[*o*-,*p*-bis(trifluoromethyl)phenylacetylene] ($P_{O_2} = 1.6 \times 10^{-8}$, $\alpha = 2.7$).⁷ Although these novel polymers showed high P_{O_2} of more than 10^{-8} and α ($= 2.5\text{--}3.0$) were relatively high, α did not exceed the boundary line ($\alpha = 3.0\text{--}4.0$).

On the other hand, as a highly oxygen permselective membrane, many membranes containing cobalt complexes such as cobaltporphyrin and cobalt-salen which function as oxygen carriers have been reported.⁸⁻¹⁶ These membranes showed a very high α , for example, $\alpha = 12$ for CoP/Im-PBMA membrane (See Appendix for the code) at low pressure difference such as 5.0 mmHg ($P_{O_2} = 2.3 \times 10^{-9}$).⁸ However, α values were reported to

be not high at high pressure difference such as 760 mmHg and P_{O_2} values were less than 10^{-8} , *e.g.*, $P_{O_2} = 8.8 \times 10^{-10}$, $\alpha = 4.19$ for CoP/Im-PBMA membrane,⁹ $P_{O_2} = 1.0 \times 10^{-9}$, $\alpha = 2.86$ for CoMPP/PBIm membrane.¹⁰ Decrease in α and low P_{O_2} values were accounted for by the saturation of the carrier with oxygen and low permeability of the polymer itself, respectively.

In this study, to produce an oxygen permselective membrane having both high P_{O_2} and α , *i.e.*, $P_{O_2} > 10^{-8}$ and $\alpha > 3.0$, which are close to those of the upper boundary line, we designed a series of novel polyazomethines containing pyridine ring and oligosiloxane (Scheme 1). The polymers are expected to show high P_{O_2} of more than 10^{-8} owing to the oligosiloxane moieties and expected to function as macromolecular tridentate ligands consisting of pyridine rings and azomethine moieties (Scheme 2). Since the short length of an oligosiloxane unit and ligand unit of the polymer alternated along the main chain, permeating oxygen molecules are expected to be affected by both units, and as a result, good performance may be attained.

This paper reports very good oxygen permselectivity of cobalt-complexed polyazomethine membranes at one atm pressure difference and discusses the oxygen transport mechanism and chemical structure of a polymer suitable for the high performance.

EXPERIMENTAL

Materials

1,7-Bis(3-aminopropyl)octamethyltetrasiloxane was prepared by hydrosilation of 1,1,3,3,5,5,7,7-octamethyltetrasiloxane to allyl amine.¹⁷ 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and α,ω -bis(3-aminopropyl)oligosiloxane ($n = 16$) were purchased from Toray Dow Corning Silicone Co. 2,6-Pyridinedicarbaldehyde was synthesized from 2,6-pyridinedicarboxylic acid *via* the methyl ester¹⁸ and purified by sublimation (70°C/20 mmHg) just before use.

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Polyazomethine	n	-Ar-
I	2	
II	3	
III	4	
IV	16	
V	2	 molar ratio = 61/39

Scheme 1. Polyazomethines containing oligosiloxane and pyridine.

Scheme 2. Cobalt-complexed polyazomethine. L, Ligand.

Polycondensation

Polyazomethines I, II, III, and IV were synthesized according to our previous paper (Scheme 1).^{19,20} A typical procedure is as follows, II: 2.30 g of 1,5-bis(3-aminopropyl)hexamethyltrisiloxane (7.14 mmol) in 25 ml of toluene were added dropwise into 0.964 g 2,6-pyridinedicarbaldehyde (7.14 mmol) in 25 ml of toluene, and the mixture was stirred for 18 h at 90 or 110°C. Evaporation of the toluene and freeze-drying of the resulting polymer gave a brownish red polymer (3.01 g). ¹H NMR (CDCl₃): δ (ppm) 0.07 (s, 6H, O-Si(CH₃)₂-O), 0.12 (s, 12H, O-Si(CH₃)₂-CH₂-), 0.62 (m, 4H, Si-CH₂-), 1.03 (s, 0.8H, NH₂), 1.80 (tt, 4H, Si-CH₂-CH₂-), 3.70 (t, 4H, N-CH₂-), 7.67–8.13 (m, 3H, pyridine ring), 8.40 (s, 2H, -CH=N-), 10.13 (s, 0.12H, -CH=O), IR (NaCl) cm⁻¹: 2964 (C-H), 1650 (C=N), 1261 (Si-C), 1044 (SiOSi).

Polyazomethines I–IV were very soluble in all organic solvents such as methanol, diethyl ether, *n*-hexane, and methylene chloride, and no poor solvents were found. We previously reported synthetic routes to polyazomethine V and poly(azomethine-amide) VI (Schemes 1 and 3).^{19,20} Other characterizations are presented in Table I.

Poly(azomethine-amide), VI

Scheme 3. Synthetic route to poly(azomethine-amide) containing disiloxane and pyridine.

Table I. Properties of pyridine and oligosiloxane-containing polyazomethines and poly(azomethines-amide)

Polymer ^a	Si% ^b	Polymn. temp	$\bar{M}_w^c$	$\bar{M}_w/\bar{M}_n^c$
		°C	× 10 ³	
I	38.1	90	8.41	1.84
II-a	49.0	90	8.37	3.29
-b	49.0	110	2.61	1.92
III-a	56.6	90	1.77	2.11
-b	56.6	110	1.13	3.82
IV	84.4	90	21.9	1.56
V	38.2	110	16.1	1.46
VI	36.5	60	0.708 ^d	—

^a See Schemes 1 and 3. ^b Weight % of [Si(CH₃)₂O]_n in the polymer determined by ¹H NMR. ^c By GPC correlated to standard polystyrene.

^d Since bimodal peaks were observed, $\bar{M}_n$ of the peak with a higher molecular weight are listed.

Scheme 4. Ligands of low molecular weight.

Preparation of Ligands of Low Molecular Weight (Scheme 4)

N,N'-disalicylidene-1,2-ethylenediamine (La): 1.04 g of ethylenediamine (34.6 mmol) in 15 ml of toluene were added dropwise into 4.23 g salicylaldehyde (Lc) (34.6 mmol) in 15 ml of toluene, and the mixture was stirred for 18 h at 100°C. Evaporation of the toluene and recrystallization of the resulting residue from *n*-hexane gave a yellow solid (4.14 g, 89.2%, mp 103.5°C). ¹H NMR [dimethyl sulfoxide (DMSO)-*d*₆/tetramethylsilane (TMS)] δ (ppm): 3.41 (s, 2H, -OH), 3.93 (s, 4H, N-CH₂-), 6.88, 7.33, and 7.42 (m, 8H, aromatic ring), 8.60 (s, 2H, -CH=N-), IR (KBr) cm⁻¹: 2904 (C-H), 1638 (C=N).

N,N'-Disalicylidene-1,2-phenylenediamine (Lb) was prepared similarly using *o*-phenylenediamine instead of ethylenediamine (96.9%, mp 149.0°C).

Preparation of Cobalt-Complexed Polyazomethine Membranes

(a) The addition of CoCl₂ or Co(acac)₂ and ligands (La, Lb, or Lc)

Method A III_{Co10-La,b} or III_{Coac10} (run no. 14 in

Table II or run no. 26 in Table III): 21.7 mg of CoCl_2 (0.167 mmol) or 42.9 mg of $\text{Co}(\text{acac})_2$ (0.167 mmol) in 2 ml of ethanol/tetrahydrofuran (THF) (= 1/1, v/v) were added to 0.828 g polyazomethine III (1.67 mmol) in chloroform (10 wt%). To the solution were added 44.8 mg La (0.167 mmol) and 52.8 mg Lb (0.167 mmol) in 2 ml of THF. The solution was cast on a polytetrafluoroethylene sheet and the solvents were evaporated for 12 h at room temperature (r.t.) and 3 h at 70°C.

Method B As an alternative method, a mixture of CoCl_2 in ethanol/THF and La and Lb in THF was added to polyazomethine II (10 wt%) in chloroform. A membrane was obtained by casting the resulting solution and evaporating similarly to Method A.

(b) *Addition of CoCl_2 or $\text{Co}(\text{acac})_2$ Alone*

III_{Co10} (run no. 12 in Table II, Method A): 18.7 mg of CoCl_2 (0.144 mmol) in 2 ml of ethanol/THF (= 1/1, v/v) were added to 0.609 g of polyazomethine III (1.44 mmol, for monomeric unit) in chloroform (10 wt%). Similar treatment of casting and evaporation gave a membrane.

Characterization

NMR spectra were recorded on a Varian Gemini 200H spectrometer. IR spectra were obtained by a Hitachi 270-30 type spectrometer. Measurement of average molecular weights (M_w , M_n) and distributions (M_w/M_n) was performed by a Hitachi liquid chromatograph 655A-11 instrument in THF using a GL-A100 column correlated to the polystyrene standard.

Measurement of Oxygen Permeability

Oxygen permeabilities of disc-type samples of 30 mm diameter and 20–50 μm thickness were measured by supplying air to the upstream side at one atm pressure difference at 25°C with a Yanaco GTR-10 (gas chromatographic method). Permeability coefficients (P_{O_2} , P_{N_2} ; $\text{cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$) and separation factors ($\alpha = P_{\text{O}_2}/P_{\text{N}_2}$) were calculated from the slopes in a time-volume curve at a steady state. Diffusion coefficients (D_{O_2} , D_{N_2} ; $\text{cm}^2 \cdot \text{s}^{-1}$) were determined by the time-lag method with the same apparatus and solubility coefficients (S_{O_2} , S_{N_2} ; $\text{cm}^3(\text{STP}) \cdot \text{cm}^{-3} \cdot \text{cmHg}^{-1}$) were calculated using $S = P/D$.

RESULTS AND DISCUSSION

Properties and Oxygen Permselectivity of Polyazomethines

Five polyazomethines (I, II, III, IV, and V in Scheme 1) and one poly(azomethine-amide) (VI in Scheme 3) had self membrane-forming ability. M_w of II and III did not affect P_{O_2} or α values (No. 4 and 5, and 10 and 11 in Table II and Figure 1). The polyazomethines I, II, and III showed relatively good performance as oxygen permselective membranes, but P_{O_2} and α of $P_{\text{O}_2} > 1.5 \times 10^{-9} \text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$ and $\alpha > 2.45$ (No. 1, 4, 5, 10, and 11 in Table II and Figure 1) were not close to those on the upper boundary line reported by Robeson.¹

Effects of Cobalt Salt on Oxygen Permselectivity

α of II and III increased but P_{O_2} decreased by the addition of CoCl_2 (No. 4, 5→6 and 10, 11→12 in Figure

Figure 1. Oxygen selective permeation behavior of cobalt-complexed polyazomethine membranes prepared by adding CoCl_2 and a ligand of low molecular weight. Numbers in the figure correspond to those in Table II. a, from ref 1, b, from ref 13. See Appendix. ○, polyazomethine I series; ●, polyazomethine II series; □, polyazomethine III series; ▲, polyazomethine IV series.

1). Decrease in P_{O_2} was attributed to decrease in D_{O_2} , as shown in Table II, which may be caused by ionic crosslinking bonds between the macromolecular ligands *via* cobalt ions. Since S_{O_2} and $S_{\text{O}_2}/S_{\text{N}_2}$ were enhanced by CoCl_2 , assuming that decrease in D_{O_2} is suppressed as much as possible by avoiding ionic cross-linking, a membrane having high P_{O_2} and α could be obtained. To avoid the ionic cross-linking, ligands of a low molecular weight such as La, Lb, and/or Lc were added. The extent of decrease in D_{O_2} became lower by adding the ligands in addition to CoCl_2 to polyazomethines I, II, and III. P_{O_2} and α were close to those of the upper boundary line reported by Robeson¹ (No. 3, $P_{\text{O}_2} = 6.56 \times 10^{-9}$, $\alpha = 4.31$; No. 9', $P_{\text{O}_2} = 2.91 \times 10^{-8}$, $\alpha = 3.40$ in Table II and Figure 1). At one atm pressure difference, these values are maximal in cobalt complex-containing polymer membranes previously reported in the literature.^{8–16}

When a comparison was made between Methods B and A in which the order of the addition of the cobalt salt and ligand of low molecular weight was changed (see EXPERIMENTAL part), Method B brought about higher P_{O_2} than Method A by the complexation of CoCl_2 . The enhancement was attributed to increase in S_{O_2} (No. 8 and 8', and 9 and 9' in Table II and Figure 1). In the case of $\text{II}_{\text{Co10-Lac}}$ with the addition of CoCl_2 , La, and Lc, increment of P_{O_2} by Method B (No. 9') was 3.03 times higher than that by Method A (No. 9). The authors think that the formation of the ionic crosslinking bonds between macromolecules *via* cobalt ions was effectively suppressed because the empty coordination sites of cobalt ions were partly used for the ligand of low molecular weight instead of the macromolecular ligand.

The addition of CoCl_2 and ligands was not effective for IV having longer siloxane chains ($n = 16$) (No. 16→17, 18 in Table II and Figure 1). This may be because oxygen molecules permeated mainly the oligosiloxane domain which was microphase-separated from the domain of the complexes as oxygen carriers and, therefore, the oxygen carrier did not work in the permeation.

S_{O_2} and $S_{\text{O}_2}/S_{\text{N}_2}$ of the cobalt-complexed polyazomethine membranes were enhanced simultaneously as

Table II. Oxygen permeation behavior of cobalt-complexed polyazomethine membranes using CoCl_2

Run no.	Poly-azomethine ^a	Code	CoCl ₂	Ligand ^b (mol%)	Complex content		P_{O_2} ^c	α	D_{O_2} ^d	D_{O_2}	S_{O_2} ^e	S_{O_2}
			mol%		mol%	wt%	$\times 10^{-8}$		$\times 10^{-6}$	D_{N_2}	$\times 10^{-3}$	S_{N_2}
1	I	I	0	None	0	0	0.153	3.56	1.27	1.61	1.20	1.88
2		I _{Co5-La,b}	5	La (5) & Lb (5)	4.76	9.32	0.447	4.15	0.892	1.79	5.01	2.32
3		I _{Co7-La,b}	7	La (7) & Lb (7)	6.54	12.6	0.656	4.31	0.990	1.54	6.63	2.80
4	II	II-1	0	None	0	0	0.593	2.94	4.85	2.24	1.22	1.31
5		II-2	0	None	0	0	0.600	2.93	4.81	2.25	1.25	1.30
6		II _{Co5}	5	None	4.76	1.52	0.492	3.02	1.54	1.30	3.19	2.32
7		II _{Co5-La}	5	La (5)	4.76	4.51	0.562	3.41	2.33	1.26	2.41	2.71
8		II _{Co7-La,c}	7	La (7) & Lc (7)	6.54	7.95	0.918	3.51	3.10	1.39	2.96	2.53
8' ^f		II _{Co7-La,c}	7	La (7) & Lc (7)	6.54	7.95	2.24	3.34	3.63	1.08	6.17	3.10
9		II _{Co10-La,c}	10	La (10) & Lc (10)	9.09	11.0	0.958	3.54	3.21	1.35	2.98	2.62
9' ^f		II _{Co10-La,c}	10	La (10) & Lc (10)	9.09	11.0	2.91	3.40	3.70	1.10	7.86	3.09
10	III	III-1	0	None	0	0	2.02	2.45	5.15	1.26	3.92	1.94
11		III-2	0	None	0	0	2.01	2.45	5.17	1.24	3.88	1.98
12		III _{Co10}	10	None	9.09	2.55	1.29	2.55	1.63	1.21	7.91	2.11
13		III _{Co5-La}	5	La (10)	4.76	3.86	2.29	2.62	3.40	1.14	6.73	2.29
14		III _{Co10-La,b}	10	La (10) & Lb (10)	9.09	12.6	3.24	2.70	3.85	1.27	8.42	2.13
15		III _{Co13-La,b}	13	La (13) & Lb (13)	11.5	15.8	4.19	2.84	3.99	1.26	9.52	2.25
16	IV	IV	0	None	0	0	4.22	1.99	8.80	1.24	4.80	1.61
17		IV _{Co13-La,b}	13	La (13) & Lb (13)	11.5	6.28	3.90	2.03	5.14	1.31	7.59	1.55
18		IV _{Co15-La,b}	15	La (15) & Lb (15)	13.0	7.18	3.89	2.04	5.11	1.30	7.61	1.57
19	V	V	0	None	0	0	0.203	3.32	1.17	1.67	1.74	1.99
20		V _{Co5-La,b}	5	La (5) & Lb (5)	4.76	9.32	0.390	3.74	0.945	1.68	4.13	2.23
21	VI	VI	0	None	0	0	0.0531	4.39	0.121	1.08	4.39	4.06
22		VI _{Co5-La,b}	5	La (5) & Lb (5)	4.76	9.32	0.0606	4.41	0.0907	1.11	6.68	3.97

^a See Schemes 1 and 3. ^b See Scheme 4. ^c In $\text{cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$. ^d In $\text{cm}^2 \cdot \text{s}^{-1}$. ^e In $\text{cm}(\text{STP}) \cdot \text{cm}^{-3} \cdot \text{cmHg}^{-1}$. ^f Using Method B (see EXPERIMENTAL part).

shown in Figure 2. Therefore, increase in P_{O_2} and α was attributed mainly to the increase in S_{O_2} and $S_{\text{O}_2}/S_{\text{N}_2}$. This suggests that the cobalt complexes which formed in the membrane function as oxygen carriers. Increments of S_{O_2} and $S_{\text{O}_2}/S_{\text{N}_2}$ of cobalt-complexed II membranes (●) were larger than those of cobalt-complexed III membranes (○) as shown in Figure 2; that is, the effect of an oxygen carrier in the membrane was strengthened with increasing content of pyridine moieties having coordination ability. This shows that the complex behaves as an oxygen carrier.

Effects of the Macromolecular Ligand in Polyazomethine

When adding $\text{Co}(\text{acac})_2$ instead of CoCl_2 without the ligand of low molecular weight, lower decrease in D_{O_2} and simultaneous enhancement of P_{O_2} and α were observed (No. 4→25—27 in Table III and Figure 3). Since the bulkier ligand of $\text{Co}(\text{acac})_2$ suppressed ionic cross-linking between the macromolecular ligands *via* cobalt ions compared with CoCl_2 , lower decrease in D_{O_2} was observed. The ratio ($\Delta\alpha/\alpha_0$) of increment $\Delta\alpha$ ($=\alpha-\alpha_0$) to initial α ($=\alpha_0$) in adding $\text{Co}(\text{acac})_2$ was larger than that in adding CoCl_2 (No. 4→6 and No. 10→12 in Figure 1 and Table II, $\Delta\alpha/\alpha_0=0.027$ and 0.041, respectively, and No. 4→25 and No. 10→32 in Figure 3 and Table III, $\Delta\alpha/\alpha_0=0.16$ and 0.098, respectively). Increase in the content of $\text{Co}(\text{acac})_2$ (6.54→11.5 mmol%) was accompanied by enhancement of $\Delta\alpha/\alpha_0$ (No. 25→27 in Figure 3, $\Delta\alpha/\alpha_0=0.16\rightarrow0.20$ based on No. 4). We found a similar tendency for increment of P_{O_2} . Enhancement of P_{O_2} and α was attributed to that of S_{O_2} and $S_{\text{O}_2}/S_{\text{N}_2}$ (Figure 4). These findings suggest that the polyazomethine itself acts as a macromolecular ligand of a cobalt complex. In addition, by adding the ligand of low molecular weight to the $\text{Co}(\text{acac})_2$ -containing

Figure 2. Oxygen selective solution behavior of cobalt-complexed polyazomethine membranes prepared by adding CoCl_2 and ligands of low molecular weight. Numbers in the figure correspond to those in Table II. ●, polyazomethine II series; ○, polyazomethine III series.

polyazomethine, both P_{O_2} and α became much higher and close to those of the upper boundary line as shown in Figure 3 (No. 28, 29, and 31, $P_{\text{O}_2} > 10^{-8}$, $\alpha > 3.8$).

Mechanism of the Highly Oxygen Selective Permeation

P_{O_2} of the cobalt-complexed polyazomethine membranes was enhanced as the content of $\text{Co}(\text{acac})_2$ and ligand of low molecular weight increased, with P_{N_2} almost constant (Figure 5). This suggests a complex working as an oxygen carrier. Figure 6 shows P_{O_2} was dependent on the upstream pressure. P_{O_2} was also enhanced with decrease in the upstream pressure and P_{N_2} was independent of the pressure. By the complex, only P_{O_2} was enhanced. Since T_g of the pure polymeric membrane is lower (-18.8°C for No. 4) than the temperature of

Table III. Oxygen permeation behavior of cobalt complex-containing polyazomethine membranes using Co(acac)₂

Run no.	Poly-azomethine ^a	Code	Co(acac) ₂	Ligand ^b (mol%)	Complex content		P_{O_2} ^c	α	D_{O_2} ^d	D_{O_2}	S_{O_2} ^e	S_{O_2}
			mol%		mol%	wt%	$\times 10^{-8}$		$\times 10^{-6}$	D_{N_2}	$\times 10^{-3}$	S_{N_2}
1	I	I	0	None	0	0	0.153	3.56	1.27	1.61	1.20	1.88
23		I _{Coac7-La}	7	La (7)	6.54	9.57	0.420	4.32	0.981	1.69	4.28	2.56
24		I _{Coac7-Lb}	7	Lb (7)	6.54	10.4	0.439	4.30	0.915	1.60	4.80	2.69
4		II	0	None	0	0	0.593	2.94	4.85	2.24	1.22	1.31
25	II	II _{Coac7}	7	None	6.54	4.09	0.751	3.40	2.89	1.18	2.59	2.88
26		II _{Coac10}	10	None	9.09	5.75	0.849	3.48	2.93	1.19	2.90	2.92
27		II _{Coac13}	13	None	11.5	7.34	0.902	3.52	2.93	1.18	3.08	2.98
28		II _{Coac7-La}	7	La (7)	6.54	8.02	1.34	3.89	3.62	1.40	3.70	2.78
29		II _{Coac7-Lb}	7	Lb (7)	6.54	8.69	1.08	3.95	3.55	1.28	3.04	3.09
30		II _{Coac7-Lc}	7	Lc (7)	6.54	5.92	1.21	3.64	3.59	1.30	3.37	2.80
31		II _{Coac7-Et₃N}	7	Et ₃ N (7)	6.54	5.61	1.28	3.80	3.18	1.22	4.03	3.11
10		III	0	None	0	0	2.02	2.45	5.15	1.26	3.92	1.94
32		III _{Coac10}	10	None	9.09	4.93	2.09	2.69	3.07	1.21	6.81	2.22
33		III _{Coac13}	13	None	11.5	6.32	2.63	2.73	3.65	1.25	7.21	2.18

^a See Scheme 1. ^b See Scheme 4. ^c In cm³(STP)·cm·cm⁻²·s⁻¹·cmHg⁻¹. ^d In cm²·s⁻¹. ^e In cm³(STP)·cm⁻³·cmHg⁻¹.

Figure 3. Oxygen selective permeation behavior of cobalt-complexed polyazomethine membranes prepared by adding Co(acac)₂ and ligands of low molecular weight. Numbers in the figure correspond to those in Table III. ○, polyazomethine I series; ●, polyazomethine II series; □, polyazomethine III series.

Figure 4. Oxygen selective solution behavior of cobalt-complexed polyazomethine membranes prepared by adding Co(acac)₂ and ligands of low molecular weight. Numbers in the figure correspond to those in Table III. ●, polyazomethine II series; ○, polyazomethine III series.

oxygen permeability measurement (25°C), there is no specific binding site for permeant in the pure polymeric membrane. Therefore, specific binding sites are formed by adding CoCl₂ or Co(acac)₂. This also suggests that

Figure 5. Plots of P_{O_2} and P_{N_2} versus content of Co(acac)₂ and ligands of low molecular weight. Numbers in the figure correspond to those in Table III. ○, P_{O_2} ; ●, P_{N_2} .

Figure 6. Effects of upstream pressure on P_{O_2} and P_{N_2} through II_{Co5-La,c} and II_{Co7-La,c} membranes. Molar percentages in this figure show the ratio of the cobalt complex of low molecular weight to repeating unit of the polymer.

the complex function as a fixed oxygen carrier and oxygen transport is thus facilitated.^{21,22}

Stability of High Oxygen Permselectivity

Since cobalt complexes can be oxidized in air, it is possible that the function of the complex as an oxygen carrier is gradually reduced. To investigate how this undesirable decline occurs, aging effects of P_{O_2} and α were examined in air and under nitrogen. As shown in Figure 7, P_{O_2} and α gradually decreased in air (□, ■), while under nitrogen only slight decrease in P_{O_2} and α

Figure 7. Aging effects on P_{O_2} and α for the $II_{Co10-LA,c}$ membrane. An identical membrane was used for each oxygen permeability measurement under nitrogen (●, ○) and in air (■, □), respectively.

Figure 8. Comparison of $\Delta\alpha/\alpha_0$ for polyazomethine membranes by the addition of 5 mol% cobalt salt and ligand of low molecular weight (Co5-La, b). $\Delta\alpha = \alpha - \alpha_0$; α , α of cobalt-complexed membrane; α_0 , α of pure polymeric membrane; a, from ref 13.

was observed (○, ●). P_{O_2} and α did not recover their initial values by degassing. Therefore, reduction of the function of the complex may be due to irreversible oxidation. However, at more than 45–50 days, P_{O_2} and α became constant and were still better than those of pure polyazomethine II. The reason for the slight decrease in P_{O_2} and α under nitrogen is exposure to oxygen during permeation measurement.

Suitable Chemical Structure of Polymer for Cobalt-Complex-Containing Membrane

The enhancement of α of the five polyazomethines and one poly(azomethine-amide) at one atm pressure difference by the addition of 5 mol% La, Lb, and $CoCl_2$ (Co5-La, b) to the polymers is shown in Figure 8. $\Delta\alpha/\alpha_0$ of polyazomethine I containing the pyridine ring and disiloxane was the highest of all the polymers in this study. The ratio decreased as siloxane length increased (I to IV). Therefore, the shorter the siloxane length, the greater is the increment in α . This may be because, in the membrane with shorter siloxane chains, permeating oxygen molecules are separated from nitrogen molecules by the cobalt-complexes. The polyazomethine V containing disiloxane and benzene ring in addition to pyridine ring and the poly(azomethine-amide) VI containing disiloxane and amide bonds in addition to azomethine bonds showed a $\Delta\alpha/\alpha_0$ lower than the polyazomethine I containing disiloxane and the pyridine ring. Therefore,

Figure 9. Oxygen permselectivities of cobalt complex-containing membranes in the literature and this study at one atm pressure difference. a, for a membrane containing inert cobalt (III) complex; b, for a poly[bis(*n*-butoxy)phosphazene] membrane from ref 23. ●, complex-containing membrane; ○, pure membrane.

Table IV. Maximal cobalt concentrations of complex-containing polymer membranes

Membrane	Maximal concn
	$\mu\text{mol g}^{-1}$
$I_{Co7-LA,b}$	176
$II_{Co10-LA,c}$	211
$III_{Co13-LA,b}$	221
$IV_{Co15-LA,b}$	100
CoP/Im-PBMA ⁹	22
CoMPP/PBIm ¹⁰	12
CoP/POMA-co-Im ¹¹	13
CoMP-co-PHMA ¹²	1.7
CoS/POM-co-VP ¹⁴	37

the pyridine and azomethine moieties in the polymers are effective for enhancing α by the addition of the cobalt salt. This also suggests the polyazomethines to function as macromolecular ligands.

Figure 9 shows plots of P_{O_2} and α of cobalt-complex containing membranes in the literature^{9–14} and this study. At one atm pressure difference, P_{O_2} and α in this study were maximal in all cobalt-complex containing polymer membranes. The maximal concentrations of cobalt-complexes in the membrane at which the polymer have self membrane-forming ability are listed in Table IV. In addition of the most excellent oxygen permselectivity, the maximal concentrations of the membrane were also the highest in those of all the reported membranes. Since the polyazomethines contain a great number of ligands in their main chain and have self membrane-forming ability, the polymer membranes are able to contain cobalt-complexes in high concentration.

The polymer structure containing a short siloxane and ligand in the repeating pairs was found very suitable for preparing high performance oxygen permselective membrane. The siloxane moieties were useful for obtaining high P_{O_2} , and ligand moieties in the backbone could contain large amounts of cobalt-complexes as oxygen carriers. The alternating alignment of siloxane and ligand moieties in the polyazomethines was effective for enhancing both P_{O_2} and α .

CONCLUSIONS

The oxygen permselectivities of cobalt(II)-complexed polyazomethine membranes at one atm pressure difference were the best in cobalt complex-containing polymer membranes whose $P_{O_2} = 1.1\text{--}2.9 \times 10^{-8} \text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$, $\alpha = 3.4\text{--}4.0$ were very close to those on the upper boundary line reported by Robeson¹. The complex functioned as a fixed oxygen carrier. The polyazomethine worked as a macromolecular ligand of the cobalt complex. Low molecular weight ligands were effective for avoiding ionic cross-linking between macromolecular ligands *via* cobalt ions and enhancing D_{O_2} . The ligands in the main chain could contain large amounts of cobalt-complexes, and the short siloxane moieties were useful for enhancing P_{O_2} . Moreover, the alternating alignment led to greater P_{O_2} and α .

APPENDIX

- CoP/Im-PBMA, [$\alpha, \alpha', \alpha'', \alpha'''$ -*meso*-tetrakis(*o*-pivalamidophenyl)porphinato]cobalt(II)/[1-methylimidazole]-poly(butyl methacrylate)⁹
- CoMPP/PBIm, [α -mono(*o*-methacrylamidophenyl)- α, α -tris(*o*-pivalamidophenyl)porphinato]cobalt/poly(butyl methacrylate-*co*-1-vinylimidazole)¹⁰
- CoP/POMA-*co*-Im, *meso*-tris(α, α, α -*o*-methacrylamidophenyl)mono(β -*o*-methacrylamidophenyl)porphinatocobalt/poly(octyl methacrylate-*co*-vinylimidazole)¹¹
- CoMP-*co*-PHMA, poly[$\{\alpha, \alpha', \alpha'', \alpha'''$ -*meso*-tetrakis(*o*-methacrylamidophenyl)porphinato}cobalt-*co*-hexyl methacrylate]¹²
- CoP/PBtP, cobaltporphyrin/poly[bis(*n*-butoxy)phosphazene]¹³
- CoS/POM-*co*-VP, *N, N'*-bis(salicylidene)ethylenediamine cobalt(II)/poly(octyl methacrylate-*co*-4-vinylpyridine)¹⁴

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