Preparation of Polycarbonate/Metal Salt Gas Separation Membranes

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SYNOPSIS

Polycarbonate (PC) membranes possess high O_2/N_2 selectivity and mechanical strength, but have low gas permeability. In order to improve the pure PC membrane's gas permeability and selectivity of O_2/N_2, in this study we attempt to combine transition metal salts into the membrane to form a complex membrane. Tensile strength and elongation at break of the membrane are not significantly changed. The effect of casting solution composition and solvent evaporation time on morphology, gas permeability, and selectivity of O_2/N_2 of PC membranes are studied. The gas permeabilities of PC/DMF/Metals membranes are significantly improved, as compared to those of pure PC membrane. For example, an oxygen permeability of 137 cm^3 (STP)-cm/cm^2-sec-cmHg and separation ratio of oxygen to nitrogen of 4.0 for PC/DMF/$CuCl_2$ membrane with [PC/CH_2Cl_2]/[$CuCl_2$/DMF] = 17/3 mL/mL, and $CuCl_2$/DMF = 0.1 g/mL, can be obtained. The FT-IR spectra and elementary analysis suggest that there is interaction among metal, DMF, and PC.

INTRODUCTION

The use of membranes for gas separation has recently received much attention due to its inherent energy efficiency. Silicone rubber membranes were found to be more permeable to most of the gases than other polymer membranes. However, silicone rubber has a P_{O_2}/P_{N_2} permeability ratio of 2. Therefore, silicone rubber membranes cannot be used to enrich the oxygen more than 30%.

Matsushita Denta Co. has been awarded a patent[1] for a polyvinyl-pyridine membrane with a high O_2/N_2 selectivity ratio of 12.2 and moderate oxygen permeability of 2.7×10^{-9} cm^3 (STP) cm/cm^2–sec–cmHg. Polycarbonate (PC) membranes possess a higher O_2/N_2 selectivity ratio and excellent mechanical strength, but have low gas permeability.

Unfortunately, the abovementioned membranes cannot meet all the operating requirements. Though many polymer membranes have been reported in the literature, they still cannot meet all these requirements. Plate et al.[2] modified the polymer substrate and developed composite membranes by a physical or chemical method. The synthesized poly(silicons olefines) had high oxygen permeability and O_2/N_2 selectivity ratio, but low mechanical strength.

Sakai et al.[3] prepared Nafion–silver microcomposite membranes by permeating hydrogen through silver ion-exchanged Nafion at 110–130°C. The Nafion–Ag membrane had significantly improved O_2/N_2 selectivity ratio, due to the affinity between oxygen and silver.

To modify the membrane's oxygen transport properties, much research[4-8] has been done with specific metal ions and chelating ligands with various polymers. The chelates of certain metal ions can improve the polymer's affinity for oxygen.

In our research, a polycarbonate (PC) membrane is used as a substrate, which has excellent mechanical strength and higher P_{O_2}/P_{N_2} selectivity. To improve the permeability of the PC membrane, transition metal salts were added to the substrate to form a porous-like membrane.

The factors that affect the structure and performance of the membrane are: concentration of the

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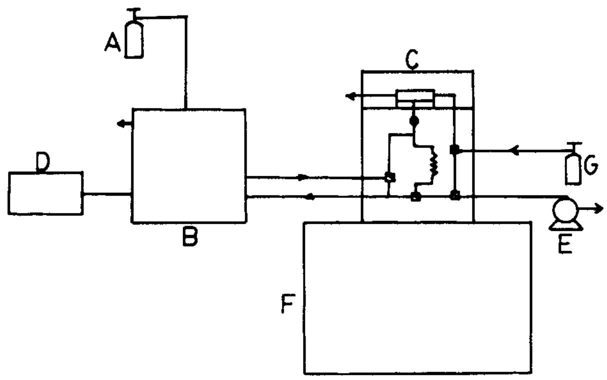

Figure 1 Schematic diagram of permeation apparatus (A) Carrier gas, (B) G.C., (C) Gas permeability analyzer, (D) Integrator, (E) Pump, (F) Refrigerator, and (G) Test gas.

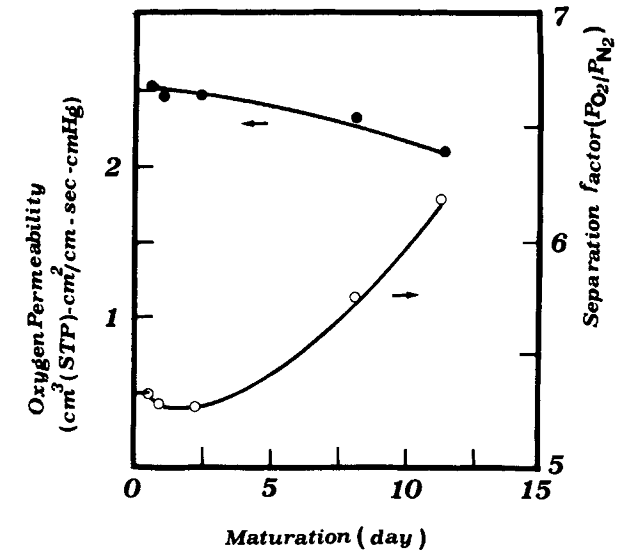

Figure 3 Effect of maturation time on oxygen permeability and separation factor of PC membrane. Operation temperature: 35°C, operation pressure: 1 Kg/cm^2, (●) O_2, (○) P_{O_2}/P_{N_2}.

salt in the DMF solvent, salt content in casting solution, solvent evaporation time, maturation time, and operation temperature.

EXPERIMENTAL

Polycarbonate (Uplion S-2000) was supplied by Mitsubishi Gas Chemical Co. Dichloromethane and N,N-dimethylformamide, supplied by Merck Co., were used as casting solvents. Cobalt (II) chloride, Copper (II) chloride, Iron (III) chloride, and Zinc (II) chloride were used as complex transition metal salts. All the above chemicals were of reagent grade. Oxygen, Nitrogen, and air of 99.9% purity were used.

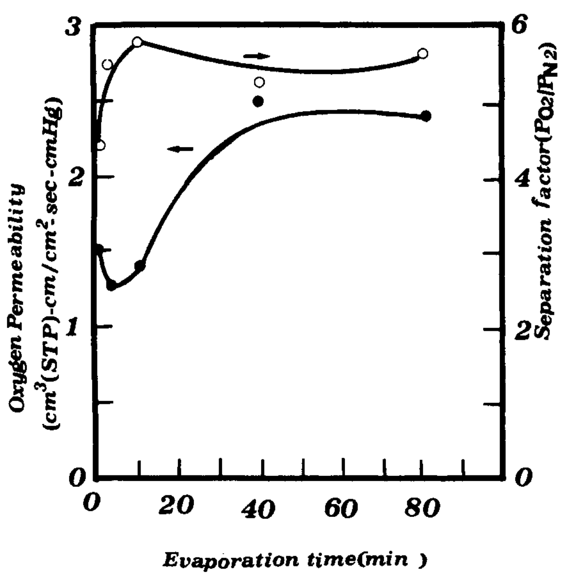

Figure 2 Effect of solvent evaporation time on oxygen permeability and separation factor of PC membrane. Operation temperature: 35°C, operation pressure: 1 Kg/cm^2, (●) O_2, and (○) P_{O_2}/P_{N_2}.

MEMBRANE PREPARATION

The PC membrane was prepared from a casting solution of polycarbonate in dichloromethane (CH_2Cl_2). The PC/metal salt membranes were prepared from solutions of varying compositions of PC/CH_2Cl_2 mixed with metal salts/DMF. The membrane was formed by casting the solution onto a glass plate to a predetermined thickness using a Gardner knife. The solution on the glass plate was evaporated for 0.5 to 80 min at room temperature and was gelled in a refrigerator at −10°C for 40 min. Then, the membrane was peeled off and dried in vacuum for 24 h. The average membrane thickness was about 40 μm.

GAS PERMEABILITY MEASUREMENTS

The apparatus for measuring the permeability of gas through the membrane is shown in Figure 1. Gas separation properties of polymeric films were studied in the experimental apparatus shown in Figure 1. The synthetic air to be separated was fed continuously from a cylinder (G) to the feed chamber of gas permeability analyzer (C). The system (C) must have approached the pressure of about 0.05 torr by pump (E) in order to remove the residual air for accurate measurement. The penetrated gas through the membrane could be fed into the chromatograph (B) by carrier gas (A) to analyze quantity and record by integrator (D). The gas permeability was determined by the following equation:

$$P = \frac{l}{(P_1 - P_2)}\left(\frac{q/t}{A}\right)$$

where P is the gas permeability [cm^3(STP)-cm/cm^2-sec-cmHg], q/t is the volumetric flow rate of gas permeate [cm^3(STP)/sec], l is the membrane thickness (cm), P_1 and P_2 are the pressures (cmHg) on the high pressure side and low pressure side of the membrane, respectively, and A is the effective membrane area (cm^2).

MEASUREMENTS OF MECHANICAL PROPERTIES

The tensile strength measurement of blended membranes was carried out using the Toyo Baldwin type Tensilon/UTM-III-100 instrument. The membranes were tested by the ASTM method[9] for their tensile strengths and elongation in the dry state.

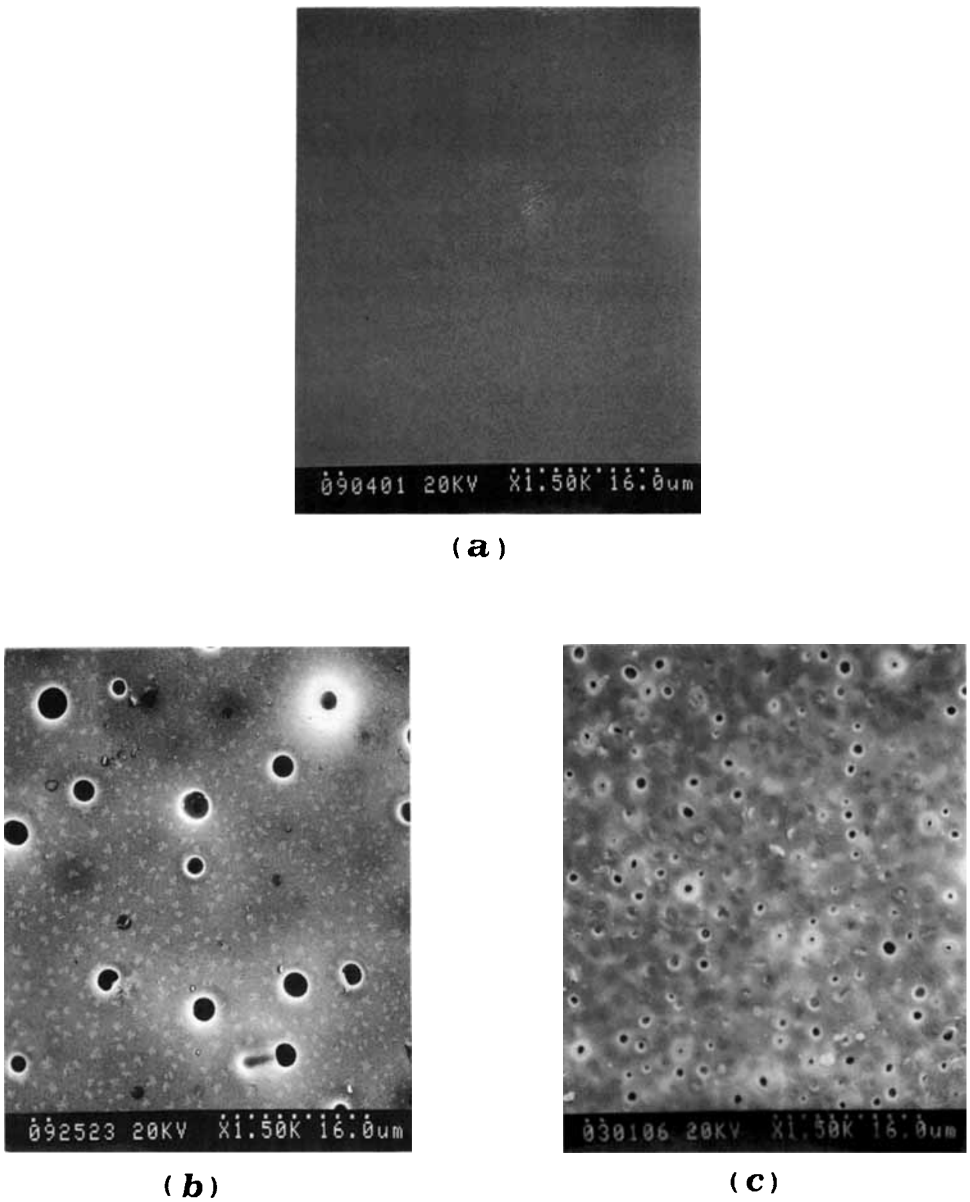

Figure 4 S.E.M. of membrane surface. (a) pure PC/CH_2Cl_2, (b) PC/CH_2Cl_2/DMF, and (c) [PC/CH_2Cl_2]/[$CuCl_2$/DMF].

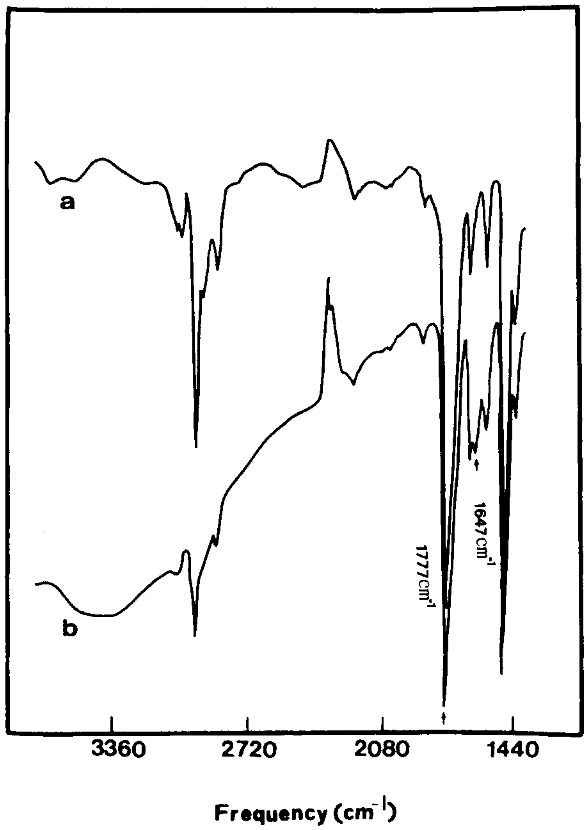

Figure 5 Infrared adsorption spectra. (a) PC membrane, (b) PC/DMF/$CuCl_2$ ($CuCl_2$/PC = 0.15) membrane.

FT-IR AND ELEMENTARY ANALYSIS

FT-IR spectra were obtained at 1 cm^{-1} resolution using a Bomem DA 3.002 FT-IR and a Perkin-Elmer 2400 Elementary Analyzer.

SEM STRUCTURAL ANALYSIS

The structures of the prepared membranes were examined by a Hitachi Model S570 scanning electron microscope (SEM). The samples were coated with gold to a thickness of about 150 Å.

VISCOMETRIC MEASUREMENTS

Viscometric measurements were carried out with an Ubbelhode Viscometer. The PC polymer was dissolved in a dichloromethane/DMF casting solvent. The viscosities of the solvent and of the casting solutions with different concentrations were measured at 25 ± 0.1°C.

RESULTS AND DISCUSSION

Effect of Solvent Evaporation Time on Membrane Performance

Kesting[10] studied the kinetics of acetone evaporation from the casting solution of cellulose acetate-acetone-water-inorganic salt. It was established that modification with different evaporation time occurs at the film surface, giving rise to a layer with a different structure than the bulk.

Since the PC membrane was prepared by evaporation and refrigeration steps, the residual solvent in the membrane increased with decreasing evaporation time. A dense membrane structure was formed because the residual solvent evaporated slowly under refrigeration.

Figure 2 shows the effect of solvent evaporation time at room temperature on PC membrane performance in terms of oxygen permeability [cm^3(STP)-cm/cm^2-sec-cmHg] and a separation factor with this symbolism should improved P_{O_2}/P_{N_2}. As can be seen, the oxygen permeability increases with increasing the solvent evaporation time and levels off at about 40 min.

The same effect on the separation factor was observed. Forty min of evaporation time was hence

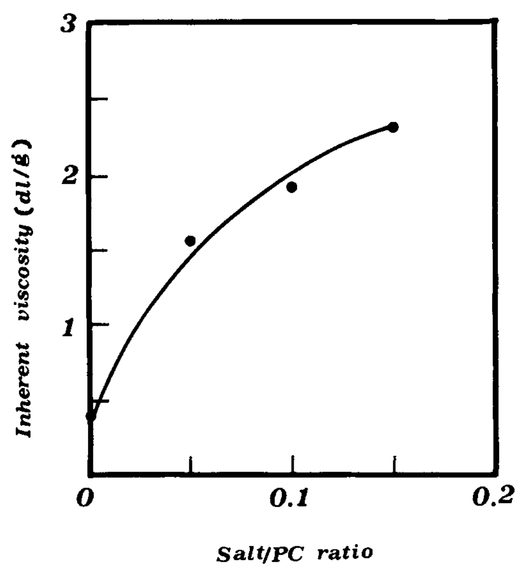

Figure 6 Effect of an additional amount of $CuCl_2$ in the casting solution of [PC/CH_2Cl_2]/[$CuCl_2$/DMF] = 17/3 on inherent viscosity measured temperature: 25°C.

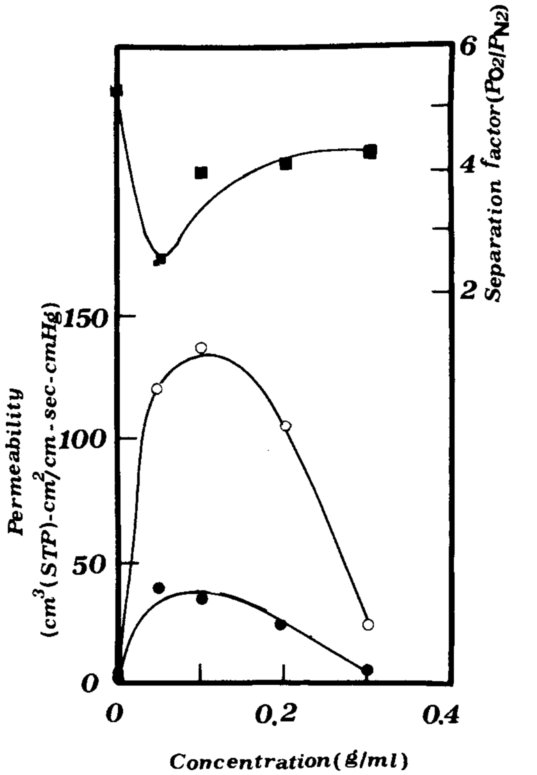

Figure 7 Effect of $CuCl_2$ concentration in DMF solution on gas permeability and separation factor of PC/DMF/$CuCl_2$ membrane. [PC/CH_2Cl_2]/[$CuCl_2$/DMF] = 17/3. Operation temperature: 35°C, operation pressure: 1 Kg/cm^2, (○) O_2, (●) N_2, (■) P_{O_2}/P_{N_2}.

found to be the best operating condition in this study. The stable oxygen permeability and separation factor obtained for a PC membrane is about 2.5 Barrer and 5.4, respectively.

Effect of Maturation Time on Oxygen Permeability and Separation Factor with P_{O_2}/P_{N_2}

In the previous articles,[11,12] we reported that the maturation time, from the polymer solution preparing to casting, plays an important role on the reverse osmosis and hemodialysis process. The solute permeability decreases with increasing maturation time. Nevertheless, it is interesting to note whether the gas permeability has the same trend or not. Thus, the effect of maturation time on oxygen selectivity and permeability is shown in Figure 3. The oxygen permeability decreases and oxygen selectivity increases with increasing maturation time. These phenomena might be due to the fact that the PC molecular chains in dichloromethane solution can be extended thoroughly if the maturation time is sufficient, resulting in the increase of structure homogeneity of the PC membrane and an increase in the oxygen selectivity. A similar trend is found in this study for [PC/CH_2Cl_2]/[DMF/$CuCl_2$] solution.

This suggests that the proper maturation time for the casting solution is about 2 days for optimum permeability of the PC and the PC/DMF/$CuCl_2$ membranes.

Membrane Morphology

Membrane formation through the phase inversion casting procedure involves complicated phenomena. During the coagulation step, the nonsolvent penetrates into the coating polymer, while solvent diffuses out into the nonsolvent and begins to form a porous membrane.[13] A porous PC membrane was obtained by adding DMF to the PC/CH_2Cl_2 solution through the phase inversion effect. Morphologies of membranes, casting with different compositions, are shown in Figure 4(a–c). The pure PC membrane exhibits a smooth surface. However, from the [PC/

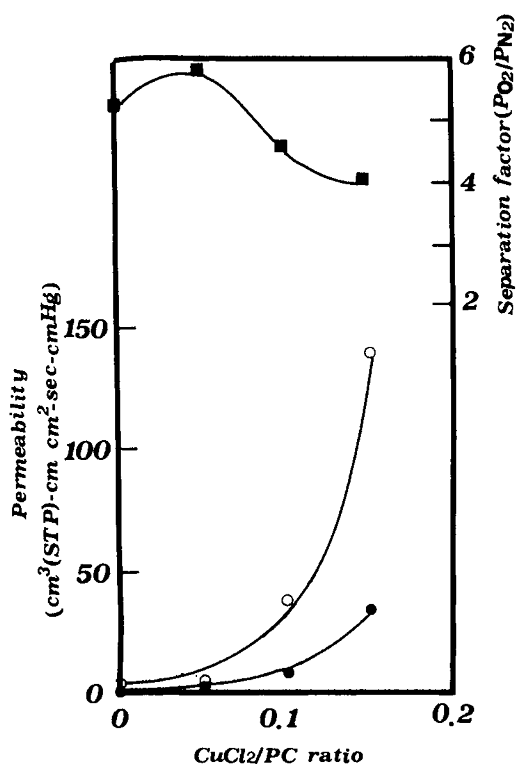

Figure 8 Effect of the ratio of $CuCl_2$/PC in PC/DMF/$CuCl_2$ membrane on gas permeability and separation factor. Operation temperature: 35°C, operation pressure: 1 Kg/cm^2, (○) O_2, (●) N_2, and (■) P_{O_2}/P_{N_2}.

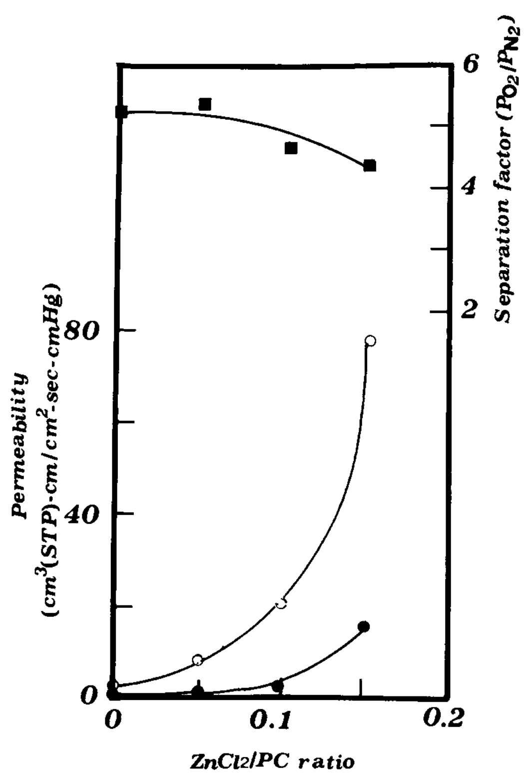

Figure 9 Effect of the ratio of $ZnCl_2$/PC in PC/DMF/$ZnCl_2$ membrane on gas permeability and separation factor. Operation temperature: 35°C, operation pressure: 1 Kg/cm^2, (○) O_2, (●) N_2, and (■) P_{O_2}/P_{N_2}.

CH_2Cl_2]/[DMF/$CuCl_2$] casting solution, membranes with the different sizes of cavity depend on the amount of additive DMF/$CuCl_2$. The PC/DMF/$CuCl_2$ membrane exhibits less porosity than the porous PC membrane, which formed by adding DMF as a nonsolvent because of the salt effect.

FT-IR Spectra

The FTIR Spectra of PC and PC/DMF/$CuCl_2$ membrane is shown in Figure 5. From Figure 5(b), a new absorption peak was shown at 1647 cm^{-1} and the C=O stretching band of the ester group for pure PC polymer at 1777 cm^{-1} shifted to shorter frequency upon addition of DMF/$CuCl_2$. The above might be due to the fact that the complex formed between the Cu^{++} ion and amide group of DMF, resulting in the C=O stretching band of DMF, shifted from 1685 cm^{-1} to 1647 cm^{-1}. These phenomena were also observed by Balasubramanian and Shaikh[14] and Yen et al.[15] Then, the C=O stretching band of the pure PC polymer shifted to a shortened frequency, resulting from the interaction between PC polymer and the complex of $CuCl_2$/DMF. Elementary analysis of the PC/DMF/$CuCl_2$ membrane shows a significant amount of nitrogen in the membrane (C : H : N = 64.83 : 5.00 : 1.35).

The above results suggest the existence of complexes derived from PC/DMF/Salts. Membranes containing PC/DMF/$FeCl_3$, PC/DMF/$CoCl_2$, and PC/DMF/$ZnCl_2$ are also similar to those of the PC/DMF/$CuCl_2$ membrane.

Effect of the Additional Amount of $CuCl_2$ in Casting Solution on Viscosity

Figure 6 presents the effect of the additional amount of $CuCl_2$ on the viscosity of [PC/CH_2Cl_2]/[$CuCl_2$/DMF] solutions. As can be seen, the viscosity is sensitive to the amount of $CuCl_2$ added, following a nonlinear relationship. The increase in viscosity arises from strong $CuCl_2$–DMF–PC interaction and probably also from those of Cu cation, DMF, and electron donor group of PC, which favor the for-

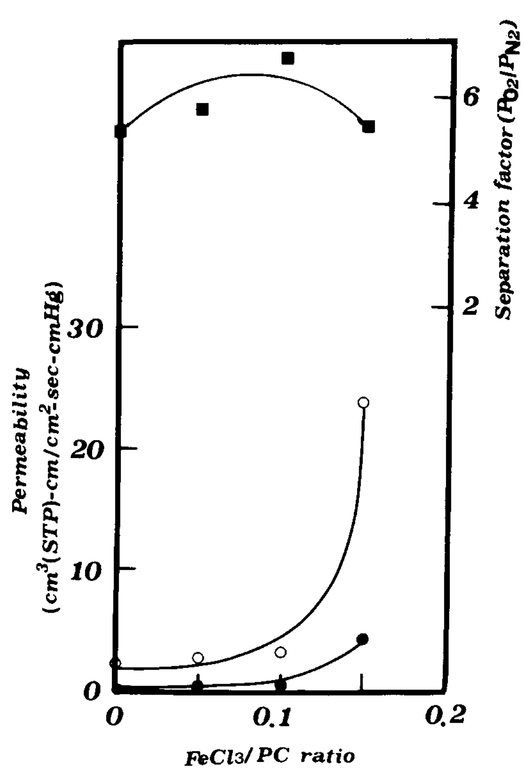

Figure 10 Effect of the ratio of $FeCl_3$/PC in PC/DMF/$FeCl_3$ membrane on gas permeability and separation factor. Operation temperature: 35°C, operation pressure: 1 Kg/cm^2, (○) O_2, (●) N_2, and (■) P_{O_2}/P_{N_2}.

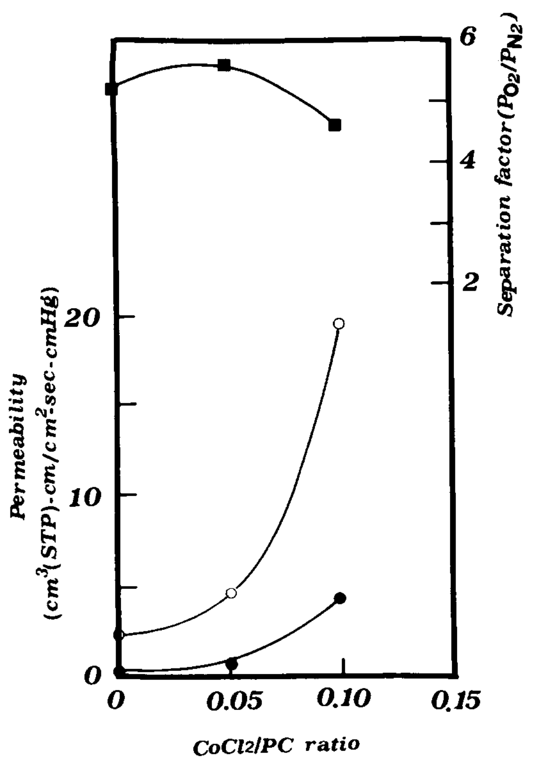

Figure 11 Effect of the ratio of $CoCl_2$/PC in PC/DMF/$CoCl_2$ membrane on gas permeability and separation factor. Operation temperature: 35°C, operation pressure: 1 Kg/cm^2, (○) O_2, (●) N_2, and (■) P_{O_2}/P_{N_2}.

mation of macromolecular fluctuating networks.[16] This interpretation is supported by the fact that the viscosity of a casting solution tends to increase with an increase in the amount of $CuCl_2$/DMF additive in the solution.

Effect of Salt/DMF Concentration on Membrane Performance

The concentration of inorganic salt $CuCl_2$ in the DMF solution of casting solution at [PC/CH_2Cl_2]/[$CuCl_2$/DMF] = 17/3 by volume ratio affects the permeability of oxygen, as shown in Figure 7. With an increasing concentration of salt in DMF, at the concentration of $CuCl_2$/DMF = 0.1 g/mL, the membrane had a maximum oxygen permeability of 137 cm^3 (STP)-cm/cm^2-sec-cmHg and a separation factor of P_{O_2}/P_{N_2} = 4. Then, with increasing concentration of $CuCl_2$ salt in the DMF, the oxygen permeability would become lower because the complex formation of PC/DMF/$CuCl_2$ could affect the porous structure in the membrane. These results could be explained as follows: the pores of the PC membrane are due to the volatilization of the uncomplexed DMF during the membrane formation that would shrink after adding $CuCl_2$ to form the complex structure (PC/CH_2Cl_2/DMF). Comparing these data to those of the Figure 4, the shrinkage phenomena could be confirmed. Accordingly, when the concentration of $CuCl_2$ exceeded a certain limit, the pores were filled with the free $CuCl_2$ (uncomplexed), resulting in a maximum oxygen permeability at which the concentration of $CuCl_2$/DMF was 0.1 g/mL.

The result indicates the possibility of high selectivity for the PC/DMF/$CuCl_2$ membrane at the concentration $CuCl_2$/DMF = 0.1 g/mL in the casting solution.

Effect of the Ratio of Metal Salts/PC in PC/DMF/Salts Membrane on Gas Permeability and Selectivity

The effect of added metal salt/DMF into the PC/CH_2Cl_2 solution on membrane performance is optimum at a concentration of 0.1 g/mL, from Figure 7. The membrane structure is affected by the complex formation and nonsolvent effect. It also affects the gas permeability and separation factor for the PC/DMF/$CuCl_2$ membrane. For $CuCl_2$/PC = 0.05, the oxygen permeability increases to 3.65 cm^3–cm/

Table I Effect of Various Transition Metal Salts on Membrane Gas Permeability and Separation Factor

Salt	Salt/PC Ratio	Oxygen Permeability (cm^3 (STP)–cm/cm^2–sec–cmHg) × 10^{10}	Separation Factor (P_{O_2}/P_{N_2})
$CuCl_2$	0.15	137	4.0
$ZnCl_2$	0.15	80	4.4
$FeCl_3$	0.15	24	5.4
$CoCl_2$	0.15	—[a]	—[a]

[a] Gas flux was too high and permeability was unmeasured.

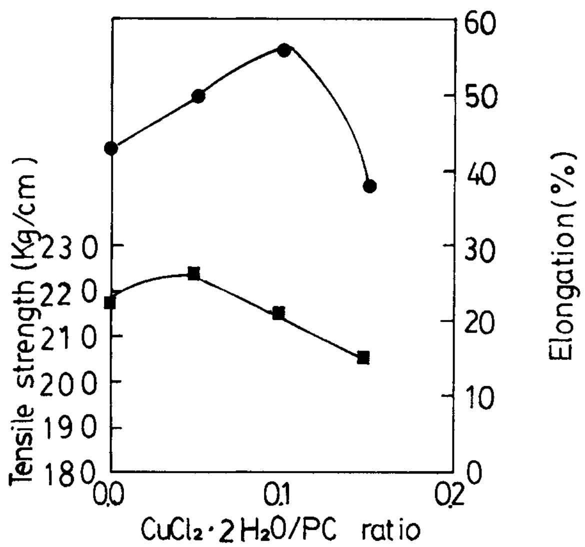

Figure 12 Effect of the ratio of $CuCl_2$/PC membrane on tensile strength and elongation at break.

cm^2–sec–cmHg and the separation factor of P_{O_2}/P_{N_2} reaches 5.82, as shown in Figure 8. With increasing the ratio of $CuCl_2$/PC for the PC/DMF/ $CuCl_2$ membrane, the oxygen permeability is markedly increased and the separation factor of P_{O_2}/P_{N_2} slightly decreased. The maximum permeability was obtained at $CuCl_2$/PC = 0.15. A similar result could be obtained with various other salts: $ZnCl_2$, $FeCl_3$, and $CoCl_2$, as shown in Figures 9, 10, and 11, respectively.

While the ratio of $CuCl_2$/PC, $ZnCl_2$/PC, or $FeCl_3$/PC reached 0.2, the gas flux was too high because of poor membrane formation during preparation. The same result also occurred in the ratio of $CoCl_2$/PC = 0.15 (Table I).

Effect of the Ratio of $CuCl_2$/PC Membrane on Mechanical Properties

The effects of $CuCl_2$ salt amount in PC membrane matrix on tensile strength and elongation at break are shown in Figure 12. With increasing the ratio of $CuCl_2$/PC to 0.05, the tensile strength reaches a maximum. While the elongation at break reaches a maximum, the ratio for the $CuCl_2$/PC membrane is 0.1. Then, with increasing salt amount in PC membrane, the tensile strength and elongation at break would be lower. The increase in tensile strength and elongation, with increasing the ratio of $CuCl_2$/PC, might be attributed to the interpolymer complex. However, the decrease trend is difficult to explain while the $CuCl_2$/PC exceed the abovementioned values. But, a similar result was reported by Yen et al.[15] Nevertheless, the tensile strength and elongation at break for the ratio $CuCl_2$/PC of 0.15 are about 204 kg/cm^2 and 37% elongation, close to the tensile strength and elongation of the pure PC membrane, about 218 kg/cm^2 and 41% elongation, respectively.

Effect of Temperature on Gas Transport Properties of Membranes

Figure 13 shows that the permeability of PC/DMF/ $CuCl_2$ membrane increases with increasing temperature in the range of −5°C–45°C, considered here. Comparing the oxygen permeability of the PC/ DMF/$CuCl_2$ membrane to the PC membrane, the permeability of the PC/DMF/$CuCl_2$ membrane is greater and both membranes decrease with decreas-

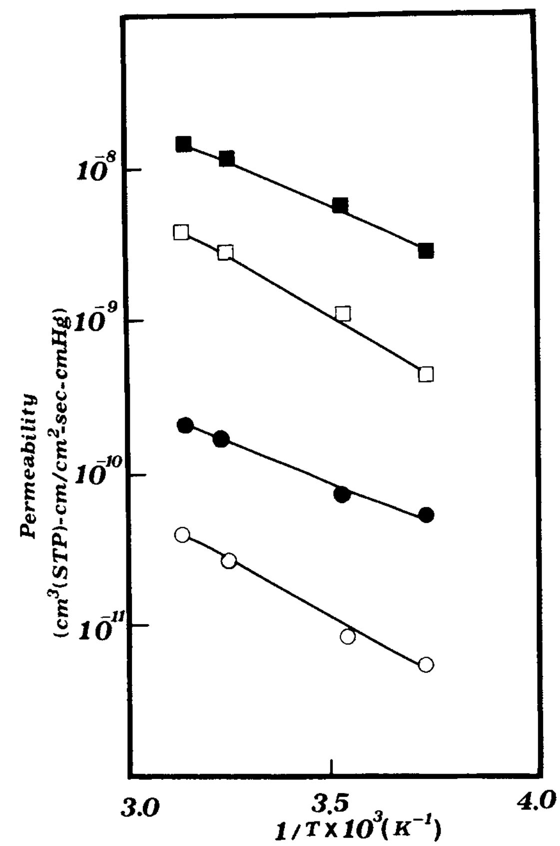

Figure 13 Effect of operation temperature on gases' permeabilities. Operation pressure: 1 Kg/cm^2, PC/DMF/ $CuCl_2$ ($CuCl_2$/PC = 0.15) membrane: (■) O_2, (□) N_2; PC membrane: (●) O_2, (○) N_2.

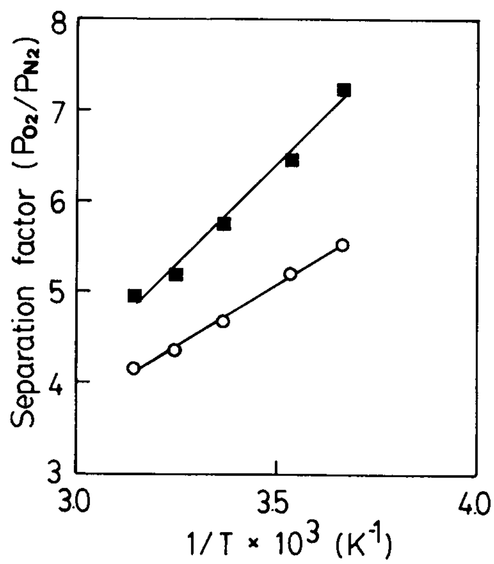

Figure 14 Effect of operation temperature on gas separation factor. Operation pressure: 1 Kg/cm^2, (○) PC/DMF/$CuCl_2$($CuCl_2$/PC = 0.15) membrane, (■) PC membrane.

ing temperature. The oxygen permeabilities of the PC/DMF/$CuCl_2$ and PC membranes were 26 and 0.5 cm^3 (STP)-cm/cm^2-sec-cmHg, respectively, at −5°C. Then, the oxygen permeability is increased to 140 and 2.0 cm^3 (STP)-cm/cm^2-sec-cmHg for PC/$CuCl_2$ and PC membranes, respectively, where the operation temperature is increased to 45°C. In the same way, the effect of the operation temperature on the separation factor of PC/$CuCl_2$ and the PC membrane is shown in Figure 14.

COMPARISON TO THE RESULT OF PREVIOUS WORKS

Table II shows a comparison of the data obtained so far by other authors with those of this study. Paul wrote many reports on PC membranes in which gas transport properties had been discussed in detail.[17-20] Muruganadam and Paul[20] prepared PC membranes in which the oxygen permeability was 1.484 cm^3 (STP)-cm/cm^2-sec-cm Hg, having a separation factor of P_{O_2}/P_{N_2} that was 5.14. The oxygen permeability of the silicon/PC (60/40) membrane was about 200 Barrer, having a separation factor of P_{O_2}/P_{N_2} that was 2.1.[21] Comparing this data to that of the PC/DMF/$CuCl_2$ membrane, the PC/DMF/$CuCl_2$ membrane was of higher permselectivity. The oxygen permeability of PC/DMF/$CuCl_2$ membrane was twice that of PVTMS membrane.[2] The PC/$CuCl_2$ membrane showed a good gas permeability, selectivity, and membrane formation.

CONCLUSIONS

The gas permeabilities of PC/DMF/metals membranes are significantly improved as compared to those of pure PC membranes. For example, an oxygen permeability of 137 cm^3 (STP)-cm/cm^2-sec-cmHg and separation ratio of oxygen to nitrogen of 4.0 for the PC/DMF/$CuCl_2$ membrane with [PC/CH_2Cl_2]/[$CuCl_2$/DMF] = 17/3 mL/mL and $CuCl_2$/DMF = 0.1 g/mL, can be obtained. The FT-IR spectra and elementary analysis suggest that there is interaction among metal, DMF, and PC.

Table II Comparison of Literature with this Study

Membrane	$P_{O_2} \times 10^{10}$	P_{O_2}/P_{N_2}	Ref.
PC	1.4	5.1	20
poly(dimethyl siloxane)			
PDMS	600	2.1	2
Silicone/PC (60/40)	200	2.3	21
Nafion - Ag	0.7	11.0	3
poly(vinyl trimethylsilane)			
PVTMS	44	4.0	2
poly(trimethyl silypropyne)			
PTMSP	4000	2.0	22
PC	2.5	5.1	This Study
PC/DMF/$CuCl_2$(Cu/PC = 0.15)	137	4.0	This Study

Unit of permeability: cm^3 (STP)-cm/cm^2-sec-cmHg.

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