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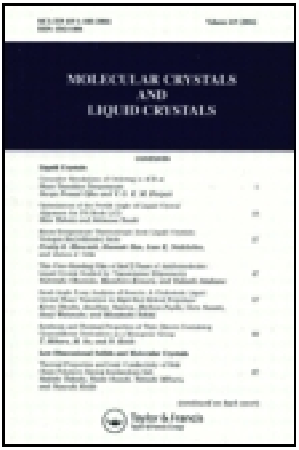

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Gas Selective Plasma Polymerization Membrane

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Gas Selective Plasma Polymerization Membrane

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Two silicon- and six fluorine-containing compounds were chosen as monomers and plasma-polymerized for preparation of permselective membranes. The oxygen and nitrogen permeability coefficients and separation factor (P_{O2}/P_{N2}) of the plasma films deposited on Millipore membranes were discussed. Plasma polymers deposited from silicon-containing compounds, hexamethyldisiloxane and hexamethyldisilane, and from aliphatic fluorine-containing compounds, tetrafluoroethylene, and perfluoromethylcyclohexane, are not adequate materials for oxygen-selective membrane. Plasma polymers deposited from aromatic fluorine-containing compounds, perfluoro-benzene, pentafluorobenzene, trifluoro-benzene, and ditrifluoromethyl-benzene, however, are adequate materials for oxygen-selective membranes. The CF_4 addition into the aromatic fluorine-containing compounds leads to the formation of plasma polymers with improved separation factor (P_{O2}/P_{N2}). The CF_4 addition brought about changes in fluorinated carbon distribution, and contributed to the formation of crosslinkings in polymeric chains. The crosslinkings might restrict the thermal motion of polymeric chains and might improve the separation factor.

Keywords: permselective membranes, plasma polymerization, oxygen/nitrogen, separation factor, silicon-containing compounds

INTRODUCTION

Plasma polymerization is a combination process of a polymer-forming and thin-film-forming process and does not refer to the mechanism of the polymerization. When starting molecules, monomers, are introduced into a plasma zone the molecules are activated by the collision of activated species, electrons, ions, and radicals, in the plasma zone, and fragmented into activated fragments. Two activated fragments are recombined to form a larger molecule. A successive repetition of the fragmentation and recombination continues until polymer is formed, and then, the polymer deposits on the surface of substrates.[1] Therefore the formed polymer is not able to be described in the term of repeating unit. The chemical composition and chemical structure of the formed polymer, if the same monomer was used, show a strong dependence of the plasma polymerization conditions, how the monomer molecules were fragmented in the plasma zone before the polymer deposition on substrate surfaces. In this sense plasma polymerization is a particular polymer-

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forming process. It is emphasized that what monomer is served for plasma polymerization and what level of operating conditions, the monomer flow rate, the electric power for maintenance of a glow discharge, the pressure of reaction chamber, etc., are used for plasma polymerization are important factors to obtain thin films with desired properties.

From the viewpoint of thin film fabrication plasma polymerization is an advantage process. Thin films from a few hundreds to a few microns thick deposit directly on the surface of all substrates in the plasma polymerization reactor without any fabrication. The film thickness is able to be controlled by the duration of the deposition. Therefore the ultrathin-film deposition on the surface of porous membranes is easily accomplished by plasma polymerization process.

This study focussed on the preparation of membranes for oxygen/nitrogen separation by plasma polymerization. Silicon- and fluorine-containing compounds were used as starting materials for the plasma polymerization. The chemical composition and permeability properties of the plasma-polymerized films were discussed.

BACKGROUND OF GAS SEPARATION PROCESS

When small molecules permeate through a polymer membrane the rate of permeation is expressed by the term of permeability.[2] The flux of the permeate (J) is written by Equation 1

$$J = P\frac{A\Delta pt}{l} \tag{1}$$

where A, Δp, t, and l are the membrane area, pressure drop between the upper- and down-stream side, time, and film thickness, respectively. The term of P is called as permeation coefficient which is the rate of permeation per unit film thickness, unit membrane area, unit time, and unit pressure drop between the upper- and down-stream sides.

$$P = \frac{\text{(amount of permeant)(film thickness)}}{\begin{array}{l}\text{(membrane area)(time)(pressure drop}\\ \text{between the upper- and down-stream sides)}\end{array}}$$

The permeation coefficient, P, has the dimension of cm^3(STP)-cm/cm^2-s-cmHg and $P = J$ for a 1 cm thick membrane with a surface area of 1 cm^2 at a partial pressure of 1 cmHg.

The permeation coefficient, P, is a function of membrane properties, the nature of the permeant species, and the interaction between the polymer membrane and permeant species. When permeants such as nitrogen and oxygen do not interact with the polymer membrane, the permeability coefficient is characteristic for the permeant-polymer system. In the case of permeation without interaction between the polymer membrane and permeants, gas transport phenomenon through polymer membranes is interpreted by the solution-diffusion model. When gas molecules

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such as oxygen and nitrogen touch at the surface of the membrane the gas molecules are adsorbed and dissolved near the surface layer of the membrane (Henry's law), and then are diffused in the direction of the other side of the membrane surface by the gradient of the gas concentration (Fick's law). Therefore, the permeation coefficient, P, is written by Equation 2

$$P = DS \tag{2}$$

where D and S are the diffusion coefficient in the polymer membrane and solubility coefficient of the permeant into the polymer membrane, respectively. The selectivity or separation factor, α, of gas 1 relative to gas 2 is equal to the ratio of their permeability coefficients at an equal ΔP. When gas mixtures of gases 1 and 2 permeate through the polymeric membrane the total flux, F, of the gases 1 and 2 is the sum of each flux, F_1 and F_2, of gases 1 and 2.

$$F = F_1 + F_2 \tag{3}$$

$$F_1 = P_1 \frac{\text{(film thickness)}}{\begin{array}{l}\text{(membrane area)(time)(pressure drop}\\ \text{between the upper- and down-stream sides)}\end{array}}$$

$$F_2 = P_2 \frac{\text{(film thickness)}}{\begin{array}{l}\text{(membrane area)(time)(pressure drop}\\ \text{between the upper- and down-stream sides)}\end{array}}$$

Therefore, the selectivity, α, is written by Equation 4.

$$\alpha = \frac{F_1}{F_2} = \frac{P_1}{P_2} = \frac{D_1S_1}{D_2S_2} \tag{4}$$

From the above conception of the gas permeation process, polymers membranes for gas separation process are requested to possess gas permeation properties with large differences in solubility or diffusion coefficient between two gases.

Tables I–III show typical polymers with high oxygen diffusion coefficient, high oxygen solubility coefficient, and high separation factor of oxygen.[3] These tables suggest polymer materials suitable for permselective separation membranes. Poly(dimethylsiloxane) is a polymeric material with the excellent permeation properties, the oxygen diffusion coefficient is 12×10^{-6} cm^2/s and the oxygen solubility coefficient 4.1×10^{-3} cm^3(STP)/cm^3-cmHg. The oxygen permeation coefficient is 488×10^{-10} cm^3(STP)-cm/cm^3-s-cmHg. Meanwhile, poly(tetrafluoroethylene) is a polymeric material having high solubility but low diffusibility. The oxygen diffusion coefficient is 0.15×10^{-6} cm^2/s, the oxygen solubility coefficient is 2.8×10^{-3} cm^3(STP)/cm^3-cmHg, and the permeation coefficient, as result, is 4.26×10^{-10} cm^3(STP)-cm/cm^3-s-cmHg. Poly(vinylfluoride) is a polymeric material with a high separation factor of 11.6 but a low oxygen permeation coefficient of 0.025×10^{-10} cm^3(STP)-cm/cm^3-s-cmHg. From these comparisons we conclude that

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TABLE I

Effects of chemical structure on oxygen solubility

Polymers	Oxygen Permeation			P_{O2}/P_{N2}
	$S \times 10^3$	$D \times 10^6$	$P \times 10^{10}$	
Poly(dimethylsiloxane)	4.07	12.0	488	2.16
Poly(methyl-1-pentenylene)	3.19	1.01	32.2	4.12
Poly(tetrafluoroethylene)	2.79	0.152	4.26	3.20
Poly(tetrafluoroethylene-co-hexafluoropropene)	2.69	0.184	4.89	3.09
Ethyl cellulose	2.30	0.639	14.6	3.31

S : in cm^3(STP)/cm^2-cmHg, D : in cm^2/s, P : in cm^3(STP)-cm/cm^2-s-cmHg.

TABLE II

Effects of chemical structure on oxygen solubility

Polymers	Oxygen Permeation			P_{O2}/P_{N2}
	$D \times 10^6$	$S \times 10^3$	$P \times 10^{10}$	
Poly(butadiene-co-acrylonitrile) (61/39)	13.6	0.709	0.959	4.07
Poly(dimethylsiloxane)	12.0	4.07	488	2.16
cis-1,4-Poly(butadiene)	1.50	1.27	19.0	2.95
Poly(methyl-1-pentenylene)	1.01	3.19	32.2	4.12
Ethyl cellulose	0.639	2.30	14.6	3.31

D : in cm^2/s, S : in cm^3(STP)/cm^2-cmHg, P : in cm^3(STP)-cm/cm^2-s-cmHg.

silicon- or fluorine-containing compounds are suitable materials as monomers for plasma polymerization to obtain permselective plasma polymerization membranes.

EXPERIMENTAL

Materials

Two silicon-containing compounds, hexamethyldisiloxane (HMDSO) and hexamethyldisilane (HMDS), which were purchased from Tokyo Kasei Kogyo Co. Ltd.,

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TABLE III

Effects of chemical structure on oxygen solubility

Polymers	P_{O2}/P_{N2}	Oxygen Permeation		
		$P \times 10^{10}$	$S \times 10^{3}$	$D \times 10^{6}$
Cellulose nitrate	16.8	1.94	1.30	0.15
Poly(vinyl fluoride)	11.6	0.018	-	-
Poly(trifluorochloro-ethylene)	8.36	0.025	-	-
Poly(vinyl benzoate)	5.77	0.951	1.21	0.079
Poly(vinylidene chloride)	5.42	0.005	-	-

P : in cm^3(STP)-cm/cm^2-s-cmHg, D : in cm^2/s, S : in cm^3(STP)/cm^2-cmHg.

Japan, and six fluorine-containing compounds, hexafluoropropene (HFP), perfluorocyclohexane (PFCMH), perfluorobenzene (PFB), pentafluorobenzene (PnFB), trifluorobenzene (TFB), and ditrifluoromethylbenzene (DTFMB), which were purchased from PCR Research Chemicals Inc., U.S.A., were used as starting materials for plasma polymerization without further purification. The purity of all compounds are more than 98%. The chemical structure of these compounds is shown in Table IV.

Millipore filters (VSWP 04700, pore size 0.025 μm) were used as porous substrate for deposition of plasma polymers and served for gas permeability measurement.

Plasma Polymerization

Plasma polymerizations were carried out using two reactors with inductively or capacitively coupled system. For plasma polymerization of the silicon-containing compounds an inductively coupled system at 13.56 MHz was used. It was consisted of a tubular Pyrex glass chamber (100 mm diameter, 400 mm long), a monomer inlet, a pressure gauge, a vacuum system, a substrate stage (90 mm diameter) for plasma polymer deposition, and a coil with a matching network for inductive coupling with a 13.56 MHz generator. The substrate stage was rotated at 20 rpm by an electric motor drive to obtain homogeneous plasma polymer deposition on the substrate surface during the plasma polymerization. Figure 1 shows a schematic of the tubular reactor. For plasma polymerization of the fluorine-containing compounds a capacitively coupled system at 20 kHz was used. It was consisted of a bell-jar chamber (400 mm diameter, 470 mm high), a monomer inlet, a pressure gauge, a thickness monitor, a vacuum system, a stage for plasma polymer deposition, and a pair of parallel aluminum electrodes (150 × 150 mm) separated by a distance of 100 mm. The stage (340 mm diameter) for plasma polymer deposition was centered between the electrodes and rotated during plasma polymerization at

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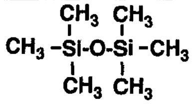
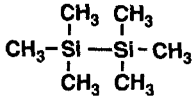
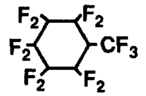
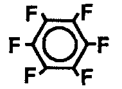
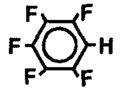
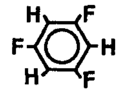
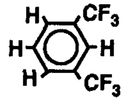
TABLE IV

Chemical structure of silicon- and fluorine-containing compounds used for plasma polymerization

Hexamethyldisiloxane (HMDSO)	 $\begin{array}{c} \quad CH_3\;\; CH_3 \\ CH_3\text{-}Si\text{-}O\text{-}Si\text{-}CH_3 \\ \quad CH_3\;\; CH_3 \end{array}$
Hexamethyldisilane (HMDS)	 $\begin{array}{c} \quad CH_3\;\; CH_3 \\ CH_3\text{-}Si\text{—}Si\text{-}CH_3 \\ \quad CH_3\;\; CH_3 \end{array}$
Hexafluoropropene (HFP)	$CF_3CF{=}CF_2$
Perfluorocyclomethylhexane (PFMCH)	
Perfluorobenzene (PFB)	
Pentafluorobenzene (PnFB)	
Trifluorobenzene (TFB)	
Ditrifluoromethylbenzene (DTFMB)	

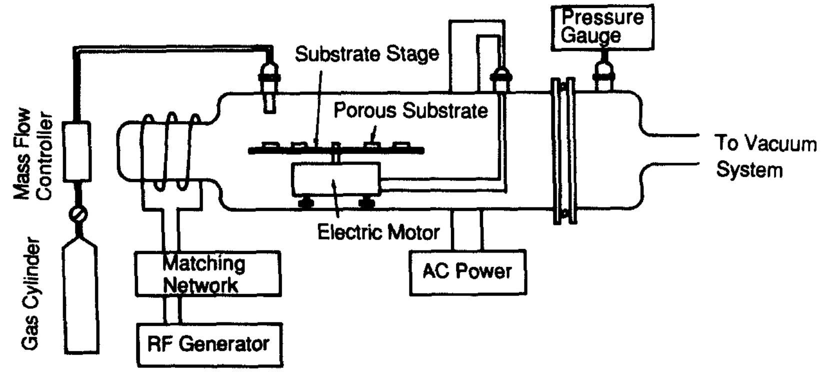


FIGURE 1 Schematic of tubular reactor for plasma polymerization.

60 rpm by an electric motor drive. Figure 2 shows a schematic of the bell-jar chamber.

The experimental procedure for plasma polymerization, when either of the reaction chambers was used, was essentially same. The reaction chamber was evacuated to 0.013 Pa, and the substrate surface was exposed to argon plasma for 20

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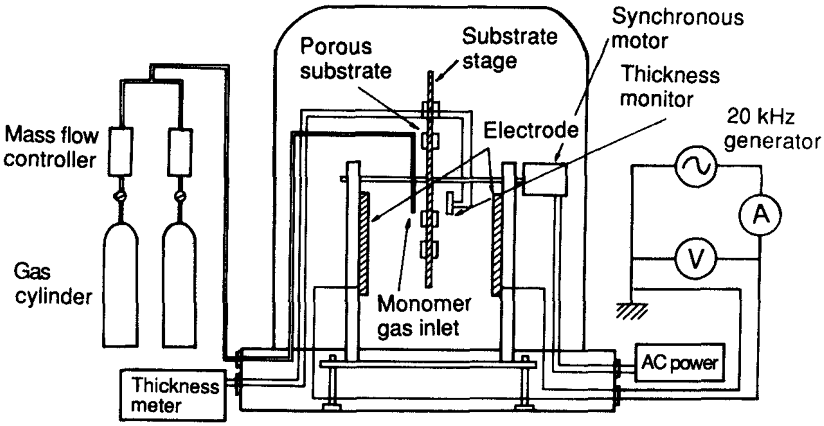

FIGURE 2 Schematic of bell-jar reactor for plasma polymerization.

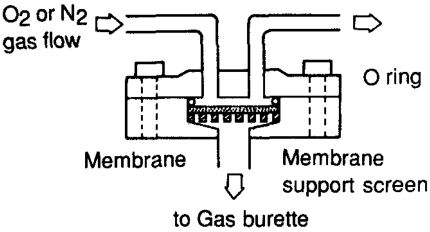

FIGURE 3 Schematic of gas permeation cell.

min to eliminate water adsorbed on it. The system was again evacuated to 0.013 Pa, then the monomer gas, adjusted at a given flow rate at 16 Pa, was introduced into the reaction chamber, and then the electric power was turned on to initiate a glow discharge.

Permeability Measurement

Plasma polymers (about 1 μm thick) deposited on the surface of Millipore membranes (VSWP, the pore size 0.025 μm) were served to permeability measurement. The oxygen and nitrogen permeation rates for the composite membranes were measured according to ASTM D143V. Figure 3 shows a schematic of the gas permeation cell for the permeation rate measurement used in this study. The composite membrane was placed on the support screen in the gas permeation cell, oxygen or nitrogen gas at 7.8–19.6 × 10^4 Pa (0.8–2.0 kg/cm^2) was fed from the feed side of the membrane, and effluent from the membrane was measured with a gas burette. The oxygen and nitrogen permeability coefficients (P_{O2}, P_{N2}) were calculated from the data of the permeation rate and the plasma polymer thickness which was determined from SEM pictures of the cross section of the composite membranes. The performance of the composite membranes was evaluated from the P_{O2} value and separation factor (P_{O2}/P_{N2} ratio).

Chemical Composition of the Plasma Polymers

The chemical composition of the deposited plasma polymers was analyzed with a FT IR spectrometer (Nihon Bunko fourier transform infrared spectrometer FT/IR-3) and XPS (Shimadzu photoelectron spectrometer 750). The C_{1s} core level spectra were decomposed with a Shimadzu data system ESCAPAC 760 computer.

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RESULTS AND DISCUSSION

Permeability of Silicone Plasma Polymers

HMDSO and HMDS were plasma-polymerized to deposit colorless or light-yellow films. Table V shows the permeation properties of the plasma polymer films prepared form HMDSO and HMDS. The oxygen permeability coefficients (P_{O2}) for the films plasma-polymerized from HMDSO and HMDS, as shown in Table V, are in the order of 10^{-9} cm^3(STP)-cm/cm^2-s-cmHg, 5.1×10^{-9} and 3.5×10^{-9}, respectively, and are lower by about ten times than that of poly(dimethylsiloxane) (4.88×10^{-8}). The separation factors (P_{O2}/P_{N2}) of them are almost same as that of poly(dimethylsiloxane).

We expected in the previous section that silicon-containing plasma polymers would possess oxygen permeability coefficients as high as poly(dimethylsiloxane) because of flexibility of siloxane chains but they do not. From this comparison we conclude that the plasma films from HMDSO and HMDS are not adequate materials for oxygen-selective membrane.

Permeability of Fluoro Plasma Polymers

Plasma polymerizations of HFP, PFCMH, PFB, PnFB, TFB, and DTFMB deposited good films on Millipore membrane. Permeation properties for these fluoro

TABLE V

Oxygen and nitrogen permeation coefficient and separation factor for the plasma polymers prepared from HMDSO and HMDS

Membranes	P_{O2}	P_{N2}	Separation Factor
HMDSO-plasma-polymerized film	51×10^{-10}	21×10^{-10}	2.4
HMDS-plasma-polymerized film	35	29	1.2
Polydimethylsiloxane	488	226	2.2

*: in cm^3(STP)-cm/cm^2-s-cmHg.

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plasma polymers are shown in Table VI. The polymer films plasma-polymerized from aromatic fluorine-containing compounds such as PFB, PnFB, TFB, and DTFMB showed higher oxygen permeability coefficients than those from aliphatic fluorine-containing compounds such as HFP and PFMCH. For example, the plasma polymers from PFB, as shown in Table VI, possess an oxygen permeation coefficient of 1.39×10^{-8} cm^3(STP)-cm/cm^2-s-cmHg and those from PFMCH do 2.4×10^{-9} cm^3(STP)-cm/cm^2-s-cmHg. The plasma polymers from PFB have higher permeability coefficient than poly(tetrafluoroethylene, TFE) (4.26×10^{-10} cm^3(STP)-cm/cm^2-s-cmHg). In addition to high oxygen permeability coefficient, the plasma polymers from aromatic compounds show higher separation factor (P_{O2}/P_{N2}) than those from aliphatic fluorine-containing compounds. The separation factor is 3.3 for the plasma polymers from PFB and 1.1 for the plasma polymers from PFMCH.

This comparison indicates that the polymer films plasma-polymerized from aromatic fluorine-containing compounds may be suitable materials for oxygen-selective membranes, but are not yet sufficient materials for oxygen-selective membranes. The separation factor should be improved for practical use of membrane separation.

Plasma Polymers from Mixture of Aromatic Fluorine-containing Compounds and Tetrafluoro Methane

To obtain plasma polymer membranes with high separation factors, plasma polymerization conditions were examined. Plasma polymerizations under high discharge powers deposited plasma polymer films with higher separation factor but with lower oxygen permeation coefficient. For example, when the plasma discharge current in the plasma polymerization of PFB increased from 75 to 120 mA the separation factor for the deposited plasma polymer film increased from 3.3 to 4.1 but the P_{O2} value decreased from 139 to 24×10^{-10} cm^3(STP)-cm/cm^2-s-cmHg. The decrease

TABLE VI

Oxygen and nitrogen permeation coefficient and separation factor for the plasma polymers prepared from HFP, PFMCH, and PFB

Membranes	P_{O2}	P_{N2}	Separation Factor
HFP-plasma-polymerized film	10 x 10^{-10}	6.2 x 10^{-10}	1.6
PFMCH-plasma-polymerized film	24	22	1.1
PFB-plasma-polymerized film	139	43	3.3

*: in cm^3(STP)-cm/cm^2-s-cmHg.

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in oxygen permeation coefficient may be due to decrease in solubility of oxygen by defluorination from the plasma polymer films. This result indicates that the permeation properties of the plasma polymers are influenced by operating conditions in the plasma polymerization, especially a discharge current.

To improve the separation factor plasma polymerizations of PFB, PnFb, TFB, and DTFMB in the presence of tetrafluoromethane, CF_4, were carried out. Figure 4 shows a typical effect of the presence of CF_4 and the discharge current on the separation factor of polymer films plasma-polymerized from PFB. The separation factor, as shown in 3, increases from 3.3 to 7.15 at a CF_4 concentration of 50 mol% in the plasma polymerization at a discharge current of 75 mA and from 4.1 to 5.04 at a CF_4 concentration of 25 mol% in the plasma polymerization at a discharge current of 120 mA. For the other plasma polymers the separation factor is listed in Table VII. Similar improvements in the separation factor by the addition of CF_4 could be observed in the other plasma polymerizations of PnFB, TFB, and DTFMB (Table VII). The separation factor (P_{O2}/P_{N2}) increases from 2.0 to 5.5 in the plasma polymerization of PnFB/CF_4 mixtures, and from 1.8 to 5.0 in the plasma polymerization of DTFMB/CF_4 mixtures. The CF_4 addition, however, makes the oxygen permeability coefficient (P_{O2}) low. The oxygen permeability coefficient (P_{O2}) decreases from 1.39×10^{-8} to 1.2×10^{-9} cm^3(STP)-cm/cm^2-s-cmHg in the plasma polymerization of PFB/CF_4 mixtures, and from 6.1×10^{-9} to 3.5×10^{-10} cm^3(STP)-cm/cm^2-s-cmHg in the plasma polymerization of DTFMB/CF_4 mixtures. These decreases in oxygen permeability coefficient may be due to the formation of cross-linkings by CF_4.

From these results we could conclude that the CF_4 addition in plasma polymerization of aromatic fluorine-containing compounds improves separation factor. The plasma polymers deposited from plasma polymerization of PFB/CF_4 and PnFB/CF_4 mixtures give membranes with both high oxygen permeability coefficient and high separation factor.

Chemical Structure of Plasma Polymers

To explain why the separation factor (P_{O2}/P_{N2}) of the plasma polymers plasma-polymerized from PFB/CF_4 and PnFB/CF_4 mixtures was improved their chemical structure was investigated from IR and XPS spectra. The elemental composition determined from XPS spectra for the plasma polymers deposited from the plasma

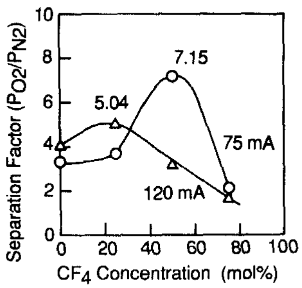

FIGURE 4 Separation factor (P_{O2}/P_{N2}) for plasma polymers prepared from PFB/CF_4 mixtures as function of CF_4 concentration and discharge current.

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TABLE VII

Oxygen and nitrogen permeation coefficient and separation factor for the plasma polymer films prepared from PFB/CF_4, PnFB/CF_4, TFB/CF_4, and DTFMB/CF_4 mixtures

Monomer Mix. System	CF4 Conc. (mol%)	P_{O2}*1	P_{N2}*1	Separation Factor
PFB/CF4	0	139	43	3.3
	50	12	1.8	7.2
PnFB/CF4	0	2.6	1.3	2.0
	25	18	3.3	5.5
TFB/CF4	25	1.8	0.54	3.4
DTFMB/CF4	0	61	34	1.8
	75*2	17	5.5	3.0
	75*3	3.5	0.7	5.0

*1: in cm^3(STP)-cm/cm^2-s-cmHg.

*2: discharge current of 100 mA, *3: discharge current of 150 mA.

polymerization of PFB/CF_4 and PnFB/CF_4 mixtures depended strongly on the CF_4 concentration. In the plasma polymerization of PFB/CF_4 mixtures at a discharge current of 75 mA the F/C atomic ratio increased from 0.34 at no CF_4 concentration to 0.97 at a CF_4 concentration of 50 mol%, and 1.24 at a CF concentration of 75 mol%. In the plasma polymerization of PnFB/CF_4 mixtures at a discharge current of 120 mA, likewise, the F/C atomic ratio changed from 0.58 to 0.87 and 1.24 at CF_4 concentrations of 25 and 75 mol%, respectively. These results indicate obviously that the CF_4 addition leads to fluorination of the plasma polymers but there is no relationship between the improved selectivity and the fluorine concentration. Therefore, we conclude that fluorination by the CF_4 addition occurring in the plasma polymerization of PFB/CF_4 and PnFB/CF_4 mixtures scarcely contributes the improvement of the separation factor (P_{O2}/P_{N2}).

Infrared spectra of the plasma polymers deposited from the plasma polymerization of PFB/CF_4 and PnFB/CF_4 mixtures showed characteristic absorption peaks at 1845, 1733–1690, 1225, and 670 cm^{-1}; which were assigned to C(O)—F, CF═F, and C—F groups,[4] respectively, but did not provide information enough to characterize details of the plasma polymers. XPS (C_{1s}) spectra of the plasma polymers were helpful in characterization of the plasma polymers. Figure 5 shows typical C_{1s} spectra of the plasma polymers deposited from PFB/CF_4 mixtures as a function of the CF_4 concentration. The C_{1s} spectra are decomposed into 3–6 components, which are assigned to —C—, C—(CF), CF, CF—(CF), CF_2, and CF_3 features in the order of binding energy.[5] We could observe effects of the CF_4 addition on these spectra, especially fluorinated carbon distribution. The plasma polymers from PFB

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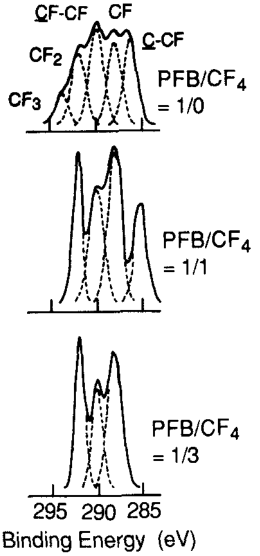

FIGURE 5 XPS (C_{1s}) spectra for plasma polymers prepared from PFB/CF_4 mixtures as a function of CF_4 concentration.

are composed of C—(CF), CF, CF—(CF), and CF_2 features at almost equivalent concentration (19–27 mol%) and of a small amount of CF_3 features (8 mol%). The plasma polymers from PFB/CF_4 mixtures containing a CF_4 concentration of 50 mol%, which showed the highest separation factor (7.15) of the plasma polymers prepared from the PFB/CF_4 mixtures, possess —C— (tertiary carbons) (20 mol%), CF (32), CF—(CF) (26), and CF_2 features (22). Apparently the CF_4 addition brings about differences in composition of polymeric carbon chains. Likewise the plasma polymers deposited from the PnFB/CF_4 mixtures showed similar changes in C_{1s} spectra, which are not presented here for the sake of brevity. The concentration of C—(CF), CF, CF—(CF), CF_2, and CF_3 features for the plasma polymers from PnFB was 37, 26, 21, 12, and 3 mol%, respectively, and the plasma polymers deposited from the PnFB/CF_4 mixtures containing CF_4 concentration of 25 mol%, which showed the highest separation factor (5.04) of the plasma polymers from the PnFB/CF_4 mixtures, possess —C— (tertiary carbon) (13 mol%), C—(CF) (9), CF (32), CF—(CF) (29), and CF_2 (17) features without CF_3 features. A comparison of these spectra indicates that the CF_4 addition leads to rearrangement of fluorine atoms to form tertiary carbon and to inhibit the formation of CF_3 side groups in the plasma polymer chains. We speculate that tertiary carbon in the plasma polymer chains might contribute to the formation of crosslinkings. The crosslinkings restricts thermal motions of polymeric chains and as result, contributes to increase in separation factor (P_{O2}/P_{N2}).

CONCLUSION

Plasma polymerizations of two silicon- and six fluorine-containing compounds were investigated for preparation of permselective membranes. The oxygen and nitrogen

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permeability coefficients and separation factor (P_{O2}/P_{N2}) were examined for the evaluation of the membranes, and chemical composition of the plasma polymers was analyzed with FT IR spectroscopy and XPS. The results are summarized as follows.

(1) Plasma polymers deposited from silicon-containing compounds, hexamethyldisiloxane and hexamethyldisilane, are not adequate materials for oxygen-selective membrane.

(2) Plasma polymers deposited from aromatic fluorine-containing compounds, perfluorobenzene (PFB), pentafluorobenzene (PnFB), trifluorobenzene (TFB), and ditrifluoromethylbenzene (DTFMB), are adequate materials for oxygen-selective membranes, but those deposited from aliphatic fluorine-containing compounds are not.

(3) The CF_4 addition into the aromatic fluorine-containing compounds leads to the formation of plasma polymers with improved separation factor (P_{O2}/P_{N2}). In the plasma polymerization of PFB/CF_4 mixtures the separation factor was increased from 3.3 to 7.15 by the CF_4 addition of 50 mol%, and also in the plasma polymerization of PnFB/CF_4 mixtures, the separation factor was increased from 4.1 to 5.04 by the CF_4 addition of 25 mol%.

(4) The CF_4 addition brought about changes in fluorinated carbon distribution, and contributed to the formation of crosslinkings in polymeric chains. The crosslinkings might restrict the thermal motion of polymeric chains and might improve the separation factor.

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