

Plasma Polymerized Membranes from Organosilicon Compounds for Separation of Oxygen over Nitrogen

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SYNOPSIS

Plasma polymerized membranes were prepared from octamethyltrisiloxane for the purpose of separation of O₂ over N₂. The obtained membrane consisted of plasma prepared polymer layer on top of a porous polypropylene substrate. The membrane polymerized under the mild plasma condition (low power input and high monomer flow rate) showed the high permeation rate. Selectivity, however, was hardly affected by the plasma conditions. The selectivity and permeation rate obtained were 2.6 and 2.5×10^{-10} kmol/(m² · s · Pa) (= 7.5×10^{-4} cm³/(cm² · s · cmHg)), respectively. This high permeation rate was attributed to the use of the monomer with the long, flexible siloxane chain and the mild plasma condition. Moreover, the membranes were prepared from a series of monomers with different siloxane chain lengths (methoxytrimethylsilane, hexamethyldisiloxane, and octamethyltrisiloxane), and from those with different alkyl chain lengths (methoxytrimethylsilane, propoxytrimethylsilane, and hexyloxytrimethylsilane). As the siloxane chain lengths of the starting monomers increased and the alkyl chain lengths decreased, the permeation rates of the corresponding polymers increased. The selectivities were nearly constant regardless of the difference in the starting monomer structures. The structures of the plasma prepared polymers were analyzed by XPS and IR measurements, and discussed in relation to the membrane efficiencies. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The advantages of plasma polymerization are well-known for compounds with double bonds and also for any other organic compounds that can be polymerized on various substrates. Furthermore, the polymer films obtained by plasma polymerization are thin, uniform, and pinhole-free.¹ This polymerization method possesses the possibility of creating new, unique polymer films surpassing the properties of films prepared by conventional polymerizations. These advantages make the plasma polymerization so attractive that many studies have been performed on the applications to optical or medical materials, separation membranes, and so on.²

Concerning gas separations, Stancel and Spencer³ reported the separation of hydrogen over methane

by plasma prepared polymers from a number of monomers in 1972. Since then, much attention has been directed to the separation of oxygen over nitrogen. This is because the plasma prepared polymer which can be made into a very thin film, well-suited for the above system, which requires a high permeability rather than a high selectivity. The previous studies are summarized in Table I. Generally, the plasma prepared polymers from silicon compounds showed a high permeability, whereas those from fluorine compounds showed a high selectivity.

In this study, the plasma polymerized membranes were prepared from various organosilicon compounds, and applied to the separation of O₂/N₂. In the previous studies, the detailed effect of the plasma conditions such as power input and monomer flow rate on the selectivities and permeabilities of the membranes was only briefly examined. Moreover, no systematic studies of the effect of a series of monomers on the gas separation have been carried out except for the study using some monomers with

Table I Previous Works on Separation of O₂ over N₂ by Plasma Polymerized Membranes

Investigators	Year	Substrate (Pore Diameter)	Monomer	Permeation Rate [cm ³ /(cm ² s cmHg)]	Selectivity
Sakata et al. ⁴	1984	Cellgard (0.2 × 0.02 μm)	Hexamethyldisiloxane	1.5 × 10 ⁻⁴	2.3
Inagaki et al. ⁵	1985	Milipore VSWP (0.025 μm)	Hexamethyldisiloxane	1.7 × 10 ⁻⁵	3.1
Sakata et al. ⁶	1987	Porous glass (0.0044 μm)	Hexamethyldisiloxane	1.0 × 10 ⁻³	2.5
Kita et al. ⁷	1988	Cellgard (0.2 × 0.02 μm)	1-(Trimethylsilyl)-1-propane	1.2 × 10 ⁻⁵	2.6
Hozumi et al. ⁸	1989	Nuclepore (0.015 μm)	Tetramethylsilane	1.5 × 10 ⁻⁵	3.3
Kajiyama et al. ⁹	1985	Porous ceramics (0.78 μm)	Perfluorobenzene	2.0 × 10 ⁻⁵	4.5
Inagaki et al. ¹⁰	1986	Milipore VSWP (0.025 μm)	Hexafluoropropene/methane	1.6 × 10 ⁻⁴	2.8
Hozumi et al. ⁸	1989	Nuclepore (0.015 μm)	Tetrafluoroethylene	6.5 × 10 ⁻⁶	2.8

different oxidation numbers of Si atom.¹¹ The objectives of this study are to investigate the effect of the plasma conditions on the membrane efficiencies, and to clarify how a series of monomers with different siloxane chain lengths and those with different alkyl chain lengths influence the gas separation performances.

EXPERIMENTAL

Plasma Polymerization

The apparatus and procedures for the plasma polymerization are the same as reported previously.¹² The apparatus (Samco International Institute Co., Ltd., BP-1) consisted of a bell-jar type reaction chamber (bottom diameter: 31.5 cm; height: 35.5 cm) equipped with a pair of internal parallel electrodes, 13.56-MHz radio frequency generator, matching network, and a vessel for monomer thermostated at 298 K. After the substrate was horizontally placed on the lower electrode controlled at 298 K by circulating temperature-controlled water, and the system was evacuated to less than 2.7 Pa, the monomer vapor, adjusted to a fixed flow rate, was injected into the reaction chamber without any carrier such as argon. Then, the RF power was turned on, and glow discharge polymerization was continued for a suitable duration. The RF power, the monomer flow rate, and the deposition time were operating parameters and were varied, while the pressure in the chamber was fixed at 27 Pa.

Octamethyltrisiloxane (OMTSO), hexamethyldisiloxane (HMDSO), methoxytrimethylsilane (MTMS), propoxytrimethylsilane (PTMS), and hexyloxytrimethylsilane (HTMS), supplied from Shin-Etsu Chemical Co., Ltd., were used as monomers without further purification. A porous polypropylene film (Cellgard 2400; thickness: 25 μm; pore size: 0.2 × 0.02 μm; porosity: 38%) was used as the substrate.

Analysis of Plasma Polymer

Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) were used to analyze the chemical structure of plasma prepared polymers deposited on aluminum foils. FT-IR and XPS spectra were measured with a Shimadzu FT-IR 4100 spectrophotometer by attenuated total reflection (ATR) method using a KRS-5 element of a 45-degree reflection angle, and with a Shimadzu electrospectrometer 750 employing MgK α exciting radiation, respectively.

Gas Permeation

The gas permeation experiments were carried out by using a diffusion cell consisting of two compartments for a feed and a sweep gas. The plasma polymerized membrane was sandwiched between the two compartments. The membrane area was 9.7 cm². The feed gas (mixture of O₂ and N₂, O₂ mol %: 50%, total flow rate: 300 cm³/min) and the sweep gas (He, flow rate: 23 cm³/min) were supplied to the diffusion

cell at atmospheric pressure. The sweep gas from the cell was analyzed by a gas chromatograph equipped with a thermal conductivity detector (Shimadzu, GC-8 APT, column: molecular sieve 5A). From both the flow rate of the sweep gas and its composition, the driving-force normalized permeation rate R and the selectivity α of O_2 over N_2 were obtained. R_{O_2} and α are given:

$$R_{O_2} = N_{O_2}/\Delta P \quad (1)$$

$$\alpha = R_{O_2}/R_{N_2} \quad (2)$$

where N_{O_2} is a molar flux of O_2 and ΔP is a pressure difference between the upstream and downstream side of the membrane. The thickness of the plasma deposit layer is so thin that it is difficult to measure it accurately. We evaluated the permeation rate instead of the permeability coefficient. The diffusion cell was placed in an air-bath thermostated at the desired temperature (usually 298 K).

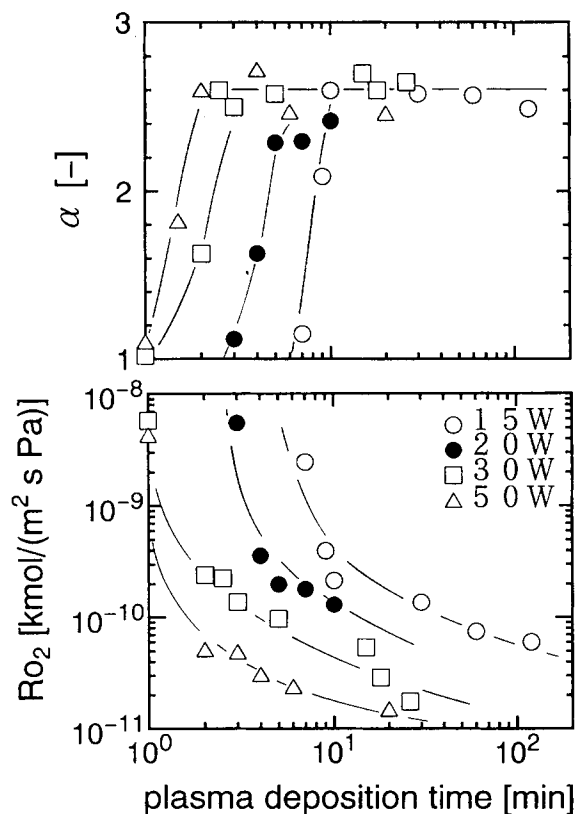


Figure 1 Effects of plasma deposition time on R_{O_2} and α at various power input conditions. $F = 1.1 \times 10^{-6}$ mol/s.

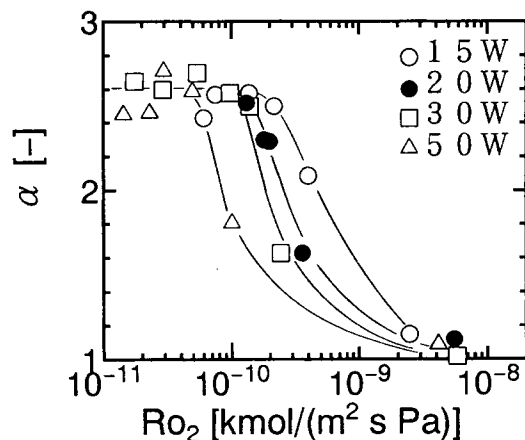


Figure 2 Relation between R_{O_2} and α at various power input conditions. $F = 1.1 \times 10^{-6}$ mol/s.

RESULTS AND DISCUSSION

Plasma Polymer from Octamethyltrisiloxane

As far as we know, the separation of O_2/N_2 by a plasma prepared polymer from OMTSO has not been reported. Figure 1 shows the effects of the plasma deposition time on R_{O_2} and α in various power input conditions. Because the thickness of the deposit layers increased with increasing deposition time, the permeation rates decreased monotonously. The selective permeations of O_2 over N_2 were not observed in the early stage of the polymerizations because all the pores of the porous substrate were not yet plugged by the plasma prepared polymer. The values of α increased drastically up to a deposition time when all the pores were probably plugged; thereafter, α remained almost constant. This indicates that the structure of the deposit layers was not changed by the deposition time, and that the constant selectivities correspond to the efficiency of the plasma prepared polymers. We previously reported that the deposition rates from OMTSO increased when increasing the power input.¹² This explains the shorter deposition time at which α became constant (T^*) at the higher power input.

The data in Figure 1 are replotted in Figure 2 in the relation of R_{O_2} vs. α . The selectivities obtained were nearly independent of the power input W , and were about 2.6, which is close to those of the plasma prepared polymers from other organosilicon compounds listed in Table I. R_{O_2} , at the deposition time when α becomes constant ($R_{O_2}^*$), increased when decreasing the power input.

Figure 3 shows the effect of the monomer flow rate F . $R_{O_2}^*$ increased with increasing F , while α was barely affected by F .

Figure 4 shows the relation between $R_{O_2}^*$ and W/FM (M : molecular weight of monomer). The parameter W/FM , which denotes a power supply per unit mass of monomer, was first presented by Yasuda and Hirotsu¹³ to describe the characteristics of the plasma polymerization. We previously showed that this parameter was useful to describe not only the deposition rates which were usually correlated with W/FM so far, but also the membrane efficiencies such as separation coefficient and permeation rate in the pervaporation.¹² Also in this case, W/FM was confirmed to be useful to describe the membrane efficiencies, because the relation between $R_{O_2}^*$ and W/FM showed a single trend, as shown in Figure 4, despite the different power inputs and monomer flow rates. At the lower W/FM condition (the milder plasma condition), $R_{O_2}^*$ became higher. The highest permeation rate obtained was 2.5×10^{-10} kmol/($m^2 \cdot s \cdot Pa$) ($= 7.5 \times 10^{-4}$ $cm^3/(cm^2 \cdot s \cdot cmHg)$). This value is fairly high, compared with the previous results using the substrates with similar pore diameters listed in Table I. Although the data of Sakata et al.⁶ are slightly higher than our result, it is not appropriate to compare the former with the latter directly because they used the substrate with so small a pore diameter (44 Å) that the thickness of the plasma layer was very thin. When cellgard was used as the substrate, they reported that the permeation rate of the plasma prepared polymer from the same monomer (hexamethyldisiloxane) was

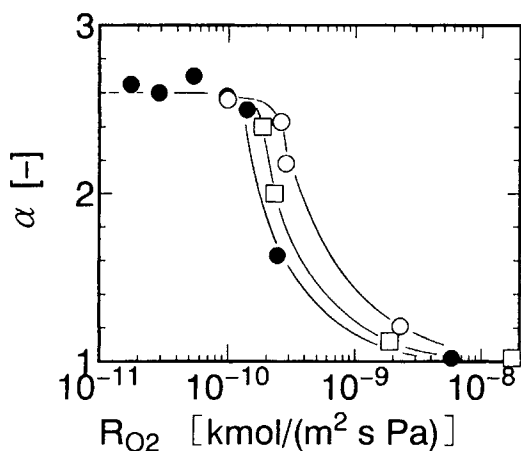


Figure 3 Effect of monomer flow rate on the relation between $R_{O_2}^*$ and α . (○) $F: 2.2 \times 10^{-6}$ mol/s; (□) $F: 1.7 \times 10^{-6}$ mol/s; (●) $F = 1.1 \times 10^{-6}$ mol/s, 30 W.

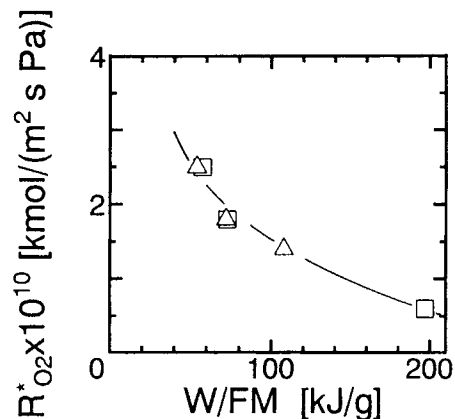


Figure 4 Relation between $R_{O_2}^*$ and W/FM . (□) Change of W , $F = 1.1 \times 10^{-6}$ mol/s; (△) Change of F , 30 W.

about 1.5×10^{-4} $cm^3/(cm^2 \cdot s \cdot cmHg)$.⁴ The achievement of the high permeation rate in this study is probably attributed to the mild plasma conditions and the use of OMTSO with the long siloxane chain, as described below.

Sakata et al. reported that the thicknesses of the plasma layers required to plug all pores of the porous substrates were always five times the pore radii regardless of the kind of substrates.⁶ Also, in this case, the thicknesses of the plasma layers are thought to be constant regardless of W/FM conditions because the weights of the plasma prepared polymers at T^* were found to be constant and independent of W/FM . Therefore, the change of $R_{O_2}^*$ with W/FM is due to the change in the chemical structures of the polymers.

Figure 5 shows the effect of W/FM on the ratio of carbon or oxygen to silicon in the plasma prepared polymer surfaces detected by XPS measurements. The C/Si ratios of the polymers were smaller than that of the monomer. This is because hydrocarbon fragments are less reactive than silicon-containing fragments.^{12,14} The C/Si ratios increased with increasing W/FM because at larger W/FM , recombination reaction of hydrocarbon fragments occurs more easily, and they become more reactive. As recognized generally, the O/Si ratios were larger than that of the monomer, and increased with increasing W/FM due to the increase of residual radicals that can react with oxygen or water vapor in the atmosphere.² The increase in both C/Si and O/Si ratios in proportion to the W/FM values indicates the decrease in the Si content of the polymers. Although the Si content of the polymer is attributed to the

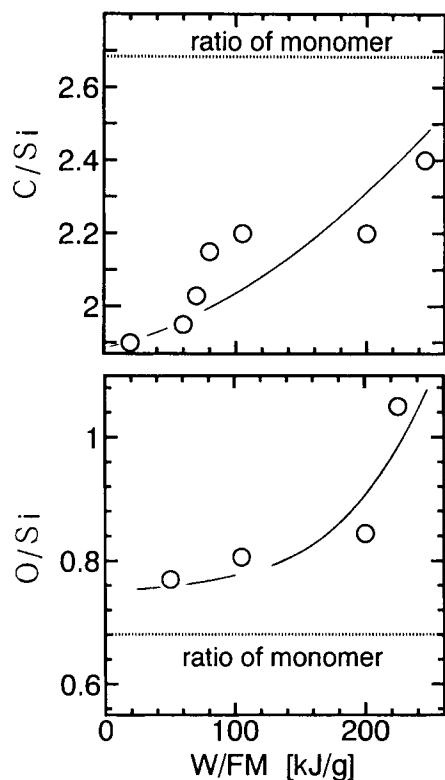


Figure 5 Effect of W/FM on C/Si and O/Si detected by XPS measurements; 15 W.

siloxane bonds and also other silicon bonds, it is possible to think that the decrease in the Si content means the decrease in the siloxane bonds. The decrease in the content of the flexible siloxane bonds may be one of the reasons for the decrease in $R_{O_2}^*$ at the larger W/FM condition, as shown in Figure 4. Previously, we reported that the IR absorptions of the plasma prepared polymers from OMTSO at $2,960\text{ cm}^{-1}$ and $1,410\text{ cm}^{-1}$ (CH_3), and $1,250\text{ cm}^{-1}$ (Si-CH_3) decreased with increasing W/FM .¹² This suggests that at the larger W/FM condition, cross-linking occurs more easily. This is probably another reason why $R_{O_2}^*$ decreased with increasing W/FM .

Although the chemical structures of the plasma prepared polymers varied with W/FM conditions as shown in Figure 5, the results in Figures 2 and 3 show that the selectivities of O_2/N_2 obtained were almost constant regardless of the W/FM conditions. It is well-known that the selectivities of O_2/N_2 are roughly in the range of 2 to 4 for various polymers,¹⁵ and that they are less influenced by the polymer structure, compared with other separation systems such as CO_2/N_2 . This lack of correlation between the structure and the selectivities may explain the constant selectivities observed in this work.

Effect of Siloxane Chain Lengths of Monomers

Figure 6 shows the effect of siloxane chain lengths of the monomers on $R_{O_2}^*$ and α . The values of α were not affected by the type of the monomers, whereas $R_{O_2}^*$ decreased with corresponding decrease in the length of siloxane chains in this series of monomers. This result indicates that OMTSO is the best monomer in terms of high permeation rate.

The relation between the deposition time when α became constant T^* and W/FM is shown in Figure 7. Because the plasma deposition rates increase with W/FM and also with the increase of the siloxane chain lengths of the monomers,¹⁶ T^* decreased with W/FM , and T^* for the monomer with the longer siloxane chain became shorter. However, the thicknesses of the polymer layers required to plug the pores of the substrate are thought to be constant regardless of the monomer used because the weights of the plasma prepared polymers at T^* were almost the same.

Figure 8 shows the results of the XPS measurements. The data of OMTSO shown in Figure 5 were also included. All the C/Si ratios were smaller than

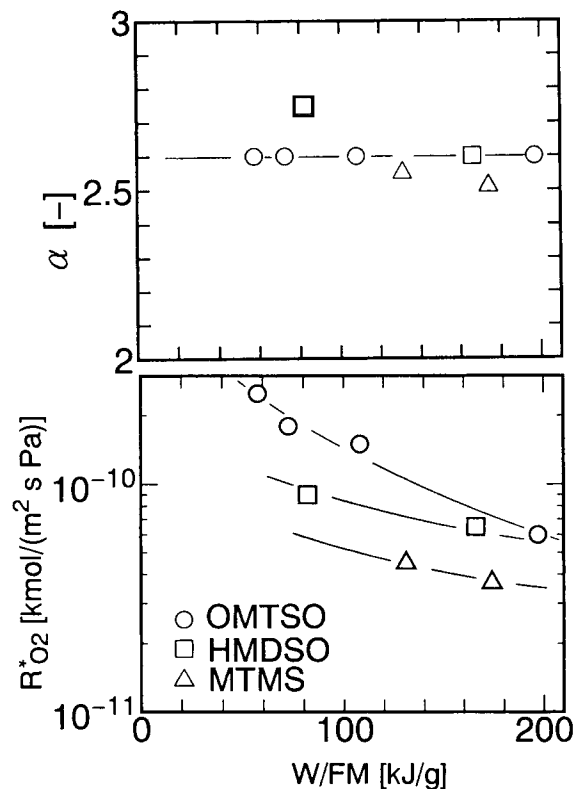


Figure 6 Effect of siloxane chain lengths of monomers on $R_{O_2}^*$ and α . $F = 1.1 \times 10^{-6}$ mol/s.

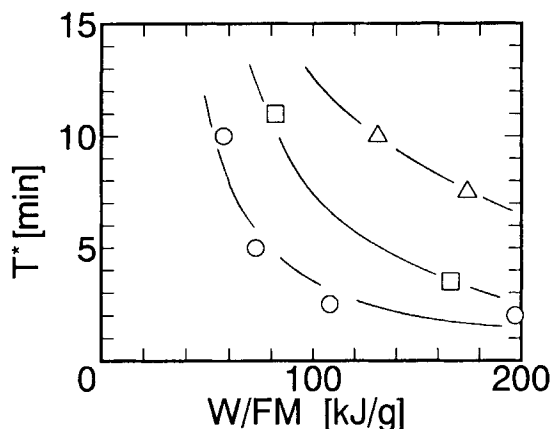


Figure 7 Relation between deposition time and W/FM when α became constant. (○) OMTSO; (□) HMDSO; (△) MTMS, $F = 1.1 \times 10^{-6}$ mol/s.

the values of the respective monomers (OMTSO: 2.67; HMDSO: 3; MTMS: 4), while all O/Si ratios were higher than those of monomers (OMTSO: 0.67; HMDSO: 0.5; MTMS: 1). These tendencies are the same as those described above. The C/Si ratio of the polymer from OMTSO was the smallest and that

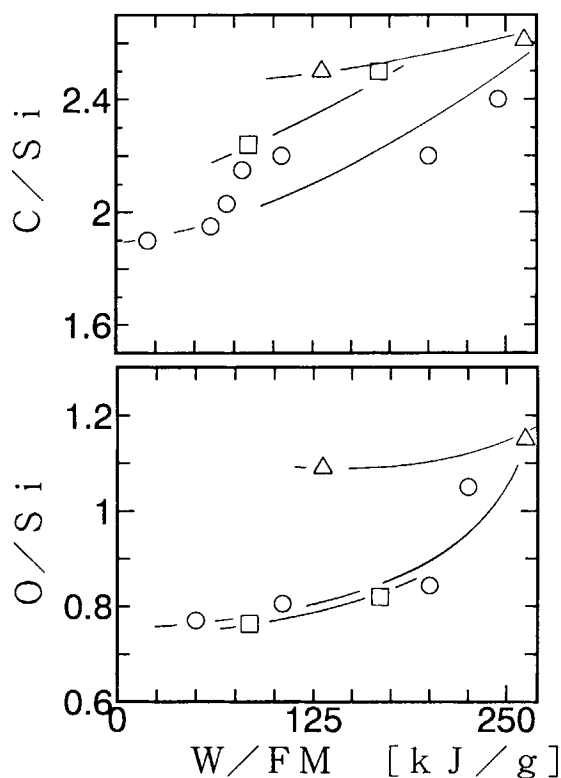


Figure 8 Effect of W/FM on C/Si and O/Si detected by XPS measurements. (○) OMTSO; (□) HMDSO; (△) MTMS.

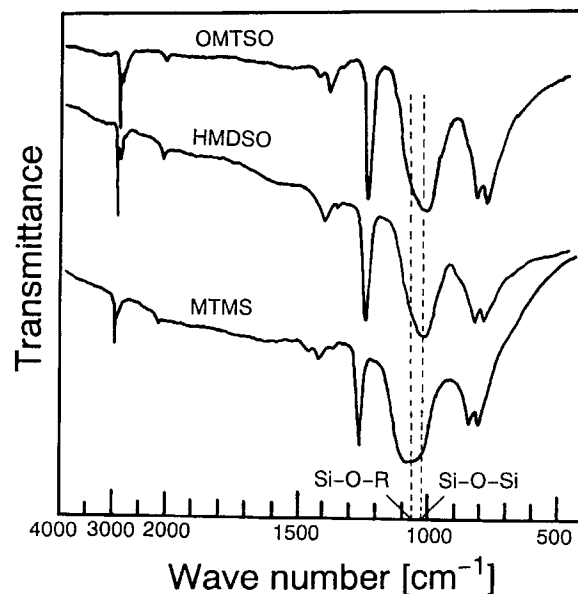


Figure 9 IR spectra of plasma prepared polymers. OMTSO: $W/FM = 98$ kJ/g; HMDSO: $W/FM = 93$ kJ/g; MTMS: $W/FM = 102$ kJ/g.

from MTMS was the largest at the same W/FM due to the influence of the chemical compositions of monomers. Although the O/Si ratio of the polymer from HMDSO was nearly equal to that from OMTSO, the polymer from MTMS showed fairly high O/Si ratio. These results indicated that the longer the siloxane chain length of the monomer was, more siloxane bonds were present in the polymer. This explains why the plasma prepared polymer from OMTSO showed the highest permeation rate.

IR spectra of the plasma prepared polymers are shown in Figure 9. There were main absorptions at $2,960\text{ cm}^{-1}$ (CH_3 stretching); $2,130\text{ cm}^{-1}$ (Si-H stretching); $1,410\text{ cm}^{-1}$ (CH_3 deformation); $1,250\text{ cm}^{-1}$ (Si- CH_3 deformation); $1,060\text{ cm}^{-1}$ (Si-O-R stretching¹⁷); $1,020\text{ cm}^{-1}$ (Si-O-Si stretching¹⁷); and $800\text{--}860\text{ cm}^{-1}$ [Si-(CH_3)₂ or Si-(CH_3)₃ stretching]. The ratio of the absorption at $1,020\text{ cm}^{-1}$ to that at $1,060\text{ cm}^{-1}$ in the spectrum of the polymer from MTMS was smaller than the ratios in the other two spectra. This suggests that the siloxane chains are linked less continuously in the polymers obtained from monomers with the shorter siloxane chains, probably due to the considerable preservation of the monomer structure. Plasma prepared polymers with flexible siloxane chains linked more continuously are expected to show a higher permeation rate. The difference in the continuity of the siloxane chains is another reason for the difference in the permeation rate, as shown in Figure 6.

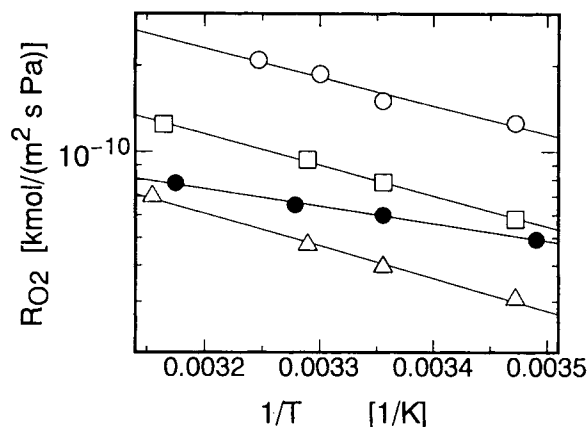


Figure 10 Effect of temperature on R_{O_2} . (○) OMTSO, $W/FM = 103$ kJ/g, deposition time = 10 min. (□) HMDSO, $W/FM = 101$ kJ/g, deposition time = 12 min. (△) MTMS, $W/FM = 110$ kJ/g, deposition time = 15 min. (●) Polydimethylsiloxane.

Figure 10 shows the effects of temperature on R_{O_2} . Assuming that the membrane thicknesses are not changed by the temperature, activation energies for permeation coefficients ($= R \cdot l$, l : membrane thickness) of O_2 were obtained from the slopes of Figure 10. The activation energies obtained are listed in Table II. The value of polydimethylsiloxane (Nitto Denko Co., NTGS-2000) is also included in this table. It is known that the magnitudes of the apparent activation energies increase as the chain rigidity of the polymer is increased.¹⁸ As the siloxane chain lengths of the monomer become short, the activation energies increase, which indicates that the polymers become more rigid. This result supports the conclusion obtained from the content and continuity of the siloxane bonds in the polymers, as described above. It was found that these plasma polymerized membranes were more suitable in the high-temperature operation than silicone membrane, which is a typical polymer showing high per-

Table II Apparent Activation Energies of Permeation Coefficients for Various Plasma Polymerized Membrane and Silicone Membrane

	Activation Energy (kJ/mol)
Plasma polymer from OMTSO	19.0
Plasma polymer from HMDSO	20.7
Plasma polymer from MTMS	21.6
Polydimethylsiloxane	11.8

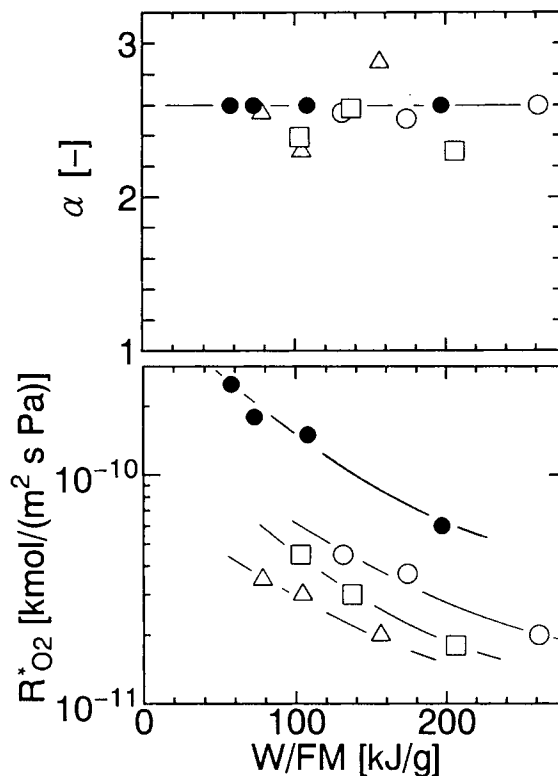


Figure 11 Effect of alkyl chain lengths of monomers on $R_{O_2}^*$ and α . (○) MTMS; (□) PTMS; (△) HTMS; (●) OMTSO.

meation rate, because the activation energies for plasma polymers were higher than that of silicone.

Effect of Alkyl Chain Lengths of Monomers

The selectivity of O_2/N_2 is about 1.9 for silicone membrane, but about 3.2 for polyethylene or polypropylene membrane.¹⁵ The existence of alkyl groups in the siloxane structures of the plasma prepared polymers has the possibility of increasing the selectivity. Figure 11 shows the effect of monomers with various alkyl chain lengths. In this figure, the data of the plasma polymer from OMTSO are also included. Contrary to our expectation, the values of α were marginally influenced by the difference in the alkyl chain lengths of monomers. This may be due to the insensitivity of the selectivity of O_2/N_2 with the chemical structure of polymer. The plasma prepared polymer from the monomer with the longer alkyl chain length showed the lower $R_{O_2}^*$, probably due to the decrease in the content of the siloxane bond in the polymer. Furthermore, the $R_{O_2}^*$ of the polymers from all other monomers were lower than that prepared from OMTSO.

CONCLUSION

1. In the plasma polymerization of octamethyltrisiloxane, the effects of the plasma conditions were investigated. The correlation between the permeation rate and the parameter W/FM showed a single trend despite the different power input and monomer flow rate. As W/FM decreased, the permeation rates increased, while the selectivity was marginally affected. From XPS measurements, it was found that the content of the siloxane bonds in the polymers increased with a decrease in W/FM . This relationship explains the high permeation rate at low W/FM . The permeation rate obtained was fairly high, compared with previous results.
2. Plasma polymers were prepared from three kinds of monomers with different siloxane chain lengths, and the polymer structures were analyzed by IR and XPS measurements. As the siloxane chain lengths of the monomers increased, the content of the siloxane bonds in the polymers increased, and the siloxane chains were linked more continuously, which led to higher permeation rates.
3. The effect of alkyl chain lengths of the monomers was also investigated. The selectivities were nearly constant regardless of the difference in the starting monomer structures.

We thank Shin-Etsu Chemical Co., Ltd., for supplying the silicon compounds, and also thank Nitto Denko Co. for supplying the silicone membrane.

NOMENCLATURE

F	monomer flow rate (mol/s)
l	membrane thickness (m)
M	molecular weight of monomer
N_{O_2}	molar flux of O_2 [$\text{kmol}/(\text{m}^2 \cdot \text{s})$]
R_{O_2}	driving-force normalized permeation rate of O_2 [$\text{kmol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$]
R_{N_2}	driving-force normalized permeation rate of N_2 [$\text{kmol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$]
$R_{O_2}^*$	driving-force normalized permeation rate of O_2 at

the deposition time when selectivity became constant [$\text{kmol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$]

T^*	deposition time when selectivity became constant (min)
W	power input (W)
α	selectivity of O_2/N_2 ($=R_{O_2}/R_{N_2}$)
ΔP	pressure difference between the upstream and downstream sides of the membrane (Pa)

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