Plasma Polymerized Membranes and Gas Permeability. II

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Synopsis

Thin films were deposited onto porous substrates by plasma polymerization using three kinds of organosilicic compounds, tetramethylsilane (TMS), hexamethyldisiloxane (M_2), and octamethylcyclotetrasiloxane (D_4). Those composite membranes showed different characteristics of gas permeability. When D_4 was plasma-deposited onto a porous substrate, the composite membrane showed the highest oxygen permeability and the lowest oxygen-to-nitrogen permeability ratio. The composite membrane prepared from TMS showed the permeability characteristics opposite to the membrane obtained from D_4. Infrared spectrum of the polymer from D_4 resembles that of dimethylpolysiloxane. The plasma polymers from TMS and M_2 showed different profiles in Si—O absorption bands in the range 1100–1000 cm^{-1} or in absorption bands of SiCH$_3$ groups in the range 850–750 cm^{-1} from respective monomers. X-ray photoelectron spectroscopic observation indicated that all the plasma polymers contained more than two species of Si atom with different oxidation states. The greater part of Si atoms in plasma polymers took the same oxidation states in corresponding monomer. The gas permeability characteristics were closely related to the oxidation states of Si atom in the plasma polymers.

INTRODUCTION

Polymeric materials can be formed in electric discharge from organic vapors. Since Goodman reported the glow discharge polymerization in vapor phase, this plasma polymerization has been studied by many authors.[1-6] The principal features of plasma polymerization are said that most of organic compounds can be polymerized, and uniform, pinhole-free and thin polymeric films can be formed on various substrates and the films adhere well to the substrates. Studies have been made on applications of plasma polymerization technique to reverse osmosis membranes, films for electric condensers, resist films, surface modification of polymers, and membranes for gas separation.[7-12]

Fundamental properties required of membranes for gas separation are high permeability and high selectivity.[13] These properties are considerably different for membrane materials. For example, the film of dimethylpolysiloxane has high oxygen permeability coefficient and low oxygen-to-nitrogen permeability ratio, while the film of polycarbonate has low oxygen permeability and high oxygen-to-nitrogen permeability ratio.[14]

It is well known that permeability and selectivity of membranes depend on chemical structures, thickness, and homogeneity of polymeric films. We reported previously that the composite membranes comprising a porous substrate and a pinhole-free thin film formed thereon by plasma polymer-

ization were recognized to have fairly high oxygen permeability and oxygen-to-nitrogen permeability ratio, and organosilicic compounds were suitable as monomers for this purpose.[12]

In the present work, the relationship between gas permeability and chemical structure of such polymeric films was studied by using three organosilicic compounds for plasma deposition.

EXPERIMENTAL

Materials

A porous polypropylene film (Cellgard) with 20 μm thickness and rectangular pores of 2000 × 200 Å in their maximum size was used as the porous substrate of composite membranes.

Organosilicic compounds used for plasma polymerization were tetramethylsilane (TMS, Tokyo Kasei Co., Ltd.), hexamethyldisiloxane (M_2, Nakarai Chemical Co., Ltd.), and octamethylcyclotetrasiloxane (D_4, Tokyo Kasei Co., Ltd.), and they were used without further purification.

Plasma Polymerization

The apparatus and experimental procedures for plasma polymerization were same as those reported previously in detail.[12] The system is constructed of a pyrex glass chamber of bell jar type, a monomer inlet, a vacuum pump, a Pirani gage, and an rf power supply of 13.56 MHz with a matching network. Porous substrates were placed at several positions in the chamber, and the system was evacuated to 0.01 torr by the rotary vacuum pump. Vapor of an organosilicic compound was introduced into the chamber, and the pressure was controlled at 0.2 torr by appropriate opening of a needle valve in accordance with the evacuating speed of the pump. Under this condition the radio frequency electric power of 50 W was supplied to continue plasma polymerization for a certain period.

Measurement of Gas Permeability

The permeability measurements were performed at 25°C by partition method on a Yanako GTR 10s. A test cell containing a membrane and a measuring tube for collecting the gas permeated through the membrane were evacuated to a pressure of 0.01 torr before each run. Atmospheric air was introduced to one side of the membrane, and the gas permeated through the membrane was collected in the measuring tube for a few minutes. The collected gas was carried to a gas chromatographic (GC) analyzer, and the volumes of oxygen and nitrogen gases were determined. GC analysis was carried out on a Yanako G180. Permeation rate P_x was calculated from the expression $P_x = v/s \cdot t \cdot (\triangle)P_x$, where v is the volume of permeated gas, s the area of membrane, t the collecting time, and $(\triangle)P_x$ the partial pressure difference of gases between membrane.

Measurement of Thickness

A plasma-polymerized film was deposited on a slide glass and thickness of the film was determined by the multibeam interferometry method.

Chemical Characterization

Chemical characterization of the plasma-polymerized film was made by infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS).

IR spectra of plasma polymers deposited on porous polypropylene films were obtained with Jasco DS-701G Infrared Spectrophotometer by the ATR method. IR spectra of monomers and dimethylpolysiloxane were measured by conventional methods.

XPS spectra of plasma polymers deposited on porous polypropylene films were recorded on DuPont-Shimadzu ESCA 650B Spectrometer. As standard samples of different oxidation states of Si atoms, Si_{2p} spectra of various organosilicic compounds were measured, and the binding energy are shown in Table I. Here, the oxidation number denotes the numbers of Si—O bonds. The Si_{2p} spectra of plasma polymers were resolved into several peaks by three parameters; that is, the average binding energy in Table I and the height of peaks and the full width at half-maximum which was about 1.8 eV. The contents of Si atoms with different oxidation states were determined from the areas of individual peaks.

RESULTS AND DISCUSSION

Gas Permeability

In the plasma polymerization, the polymerization times and the positions of porous substrates in a glass chamber were changed in order to vary thickness of plasma polymerized films. Measurement was made of oxygen permeation rate (P_{O_2}) expressed in terms of cm^3 (STP)/cm^2 sec cm Hg and

TABLE I
Binding Energy of Si_{2p} of Various Organosilicic Compounds

Materials	Oxidation number of Si atom	Binding energy of Si_{2p} (eV)	Average binding energy (eV)
Tetraphenylsilane	0	100.5	100.5_5
Polytrimethylvinylsilane	0	100.6	
Triphenylsilanol	1	101.4	101.4
Dimethyltetraphenyldisiloxane	1	101.3	
Octadecyloxytrimethylsilane	1	101.5	
Octaphenylcyclotetrasiloxane	2	101.9	102.0
Hexamethylcyclotrisiloxane	2	102.1	
Methylsilsesquioxane	3	102.8	102.8
Tetraphenoxysilane	4	103.3	103.4_5
Silicon dioxide	4	103.6	

oxygen-to-nitrogen permeability ratios (P_{O_2}/P_{N_2}) of these composite membranes.

Figure 1 shows the relationship between P_{O_2} and P_{O_2}/P_{N_2} of composite membrane prepared under various conditions. Sigmoidlike relation was observed between these two parameters for gas permeability, irrespective of monomers. This relation can be divided into three parts characterized as follows: in the first part (denoted by A) P_{O_2}/P_{N_2} keeps a constant value of about 1.0 with decreasing P_{O_2} from 10^{-2} to 10^{-4}, in the second part (denoted by B) P_{O_2}/P_{N_2} increases rapidly with decreasing P_{O_2}, and in the third part (denoted by C) C_{O_2}/P_{N_2} slightly increases with decreasing P_{O_2}. These behaviors may be related to the change in thickness of plasma-polymerized films formed on porous substrates rather than the change in chemical structures of plasma polymers. In the course of the deposition process, reduction of pore size, gradual clogging of pores and formation of homogeneous pinhole-free film on a porous substrate would take place successively in each part of curves shown in Figure 1.

Parts B and C are found at different regions of gas permeabilities, for different monomers. This may relate to the change in chemical structures of plasma polymers. The pair of values (P_{O_2} and P_{O_2}/P_{N_2}) at a point of intersection of lines B and C (denoted by D) were adopted as an indication to estimate gas permeability performance of each plasma polymer, since all the pores in a porous substrate are clogged with the minimum thickness of the plasma polymer film at this point.

Thickness of plasma-polymerized films were measured for those polymerized from M_2 and D_4. Film deposition was made on a slide glass and a porous substrate under the same conditions of plasma polymerization. Thickness was determined with the former sample and gas permeability
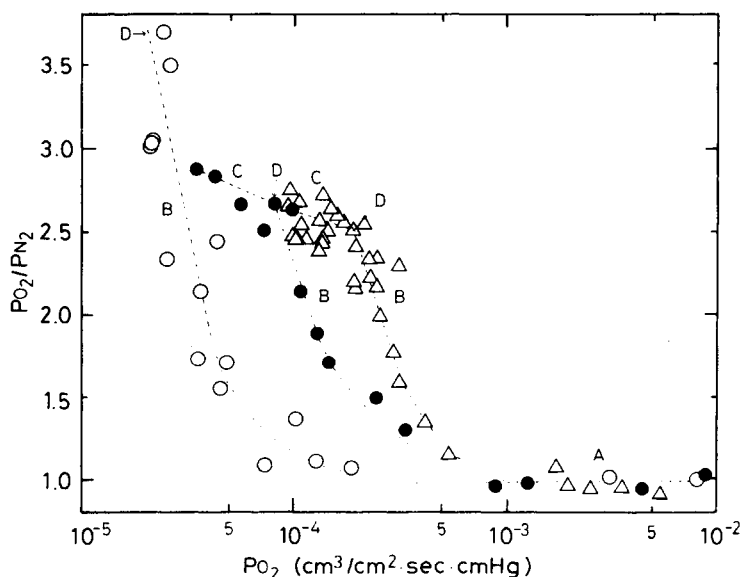

Fig. 1. Gas permeability of composite membranes: (○) plasma-polymerized TMS (PTMS): (●) plasma-polymerized M_2 (PM$_2$); (△) plasma-polymerized D_4 (PD$_4$).
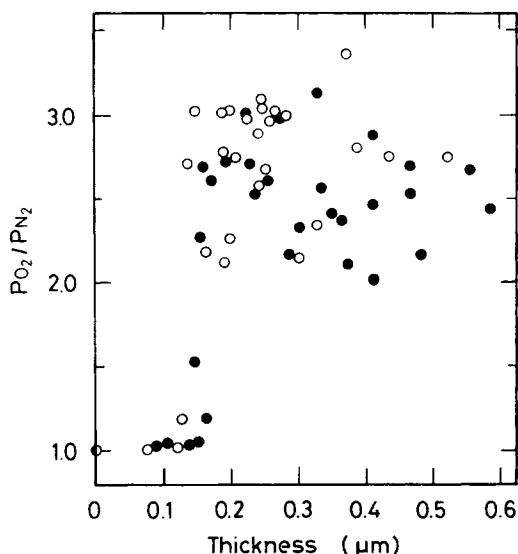
Fig. 2.   Relationship between thicknesses of plasma-polymerized films and P_{O_2}/P_{N_2} (○) PM$_2$; (●)PD$_4$.

was determined with the latter sample. Figure 2 shows the relationship between thickness of plasma polymerized films and P_{O_2}/P_{N_2} of composite membranes. The values of P_{O_2}/P_{N_2} increased drastically at about 1600 Å of thickness for both monomers. This result indicates that thickness of polymer films required to clog all pores of a porous substrate is about 1600 Å irrespective of the kind of monomers, and the value of p_{O_2} of each plasma polymer at point D is proportional to oxygen permeability coefficient of each polymer. Figure 3 shows P_{O_2} and P_{O_2}/P_{N_2} values at the point D of the polymers with respect to the oxidation numbers of Si atoms in their monomers. It is found that P_{O_2} increases and P_{O_2}/P_{N_2} decreases with increasing oxidation numbers of Si atoms. In other words, the polymer of D$_4$ shows
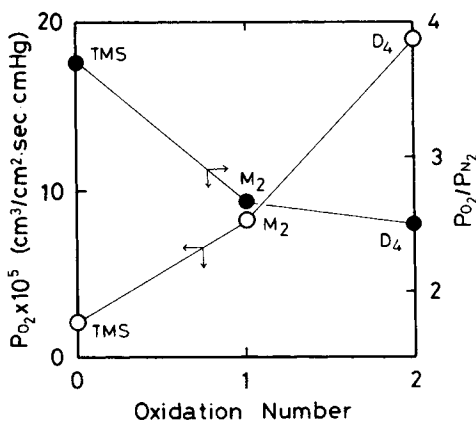

Fig. 3.   Relation of P_{O_2}/P_{N_2} of composite membranes to the oxidation numbers of Si atoms in monomers.
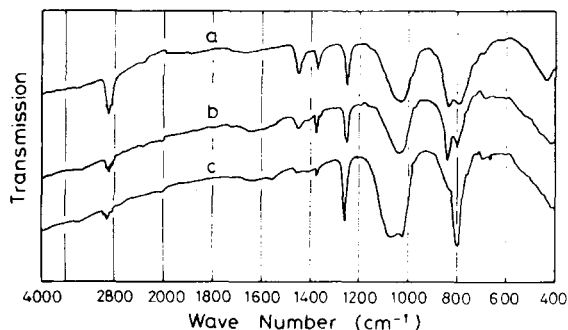
Fig. 4. IR spectra of plasma-polymerized films formed on porous polypropylene: (a) PTMS; (b) PM_2; (c) PD_4.

the highest P_{O_2} and the lowest P_{O_2}/P_{N_2}, while that of TMS shows the opposite performance.

Chemical Characterization of Plasma Polymer

Infrared (IR) spectra of plasma polymers of TMS, M_2, and D_4 deposited on porous polypropylene films are shown in Figure 4, and IR spectra of individual monomers and polydimethylsiloxane (PDS) are shown in Figure 5. The positions of the major spectra features and their assignments to specific groups are shown in Table II.[15] In the spectra shown in Figures 4 and 5, there are many common absorption bands, but some differences are found in the positions and the patterns of the Si—O absorption bands in the range 1100—1000 cm^{-1}. The Si—O absorption bands of plasma polymer of TMS were observed in spite of the absence of Si—O band in the monomer. This reason is considered as follows: The silicon atoms of TMS are oxidized
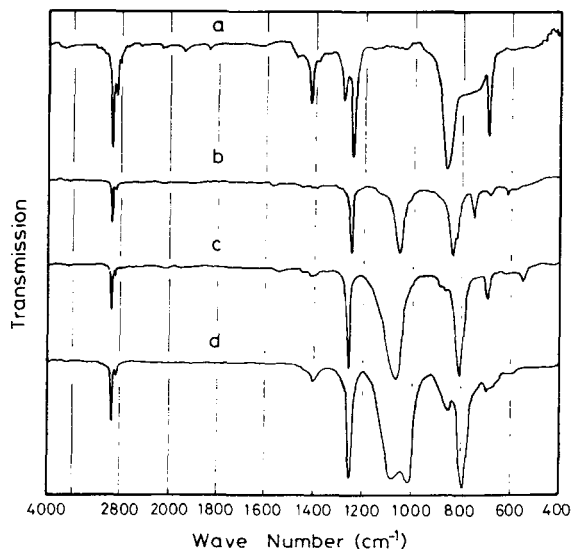

Fig. 5. IR spectra of monomers and polydimethylsiloxane (PDS): (a) TMS (CCl_4); (b) M_2 (neat); (c) D_4 (neat); (d) PDS (neat).

TABLE II
Infrared Frequencies and Band Assignments

Frequency (cm^{-1})	Band assignments[a]
3000–2850	νCH
1260–1250	δ_sCH$_3$ in SiCH$_3$
1100–1000	ν_{as}SiOSi or SiOC
860–830	ρCH$_3$ in —OSi (CH$_3$)$_3$ (M type) or νSiC in —CH$_2$Si (CH$_3$)$_3$ (A type)
810–790	ρCH$_3$ in —OSi (CH$_3$)$_2$O— (D type) or νSiC in =SiCH$_3$— (T type)

[a] See Ref. 15.

by trace amount of oxygen in the plasma reactor during polymerization, or Si free radicals produced in the plasma polymerization process react with oxygen or humidity upon exposure to the atmosphere. The Si—O absorption band of plasma polymer of M$_2$ (PM$_2$) is similar to that of monomer. In spite of single absorption band of Si—O at 1073 cm^{-1} for monomer D$_4$, two strong absorption bands at 1021 and 1072 cm^{-1} are observed in the spectrum of plasma polymer of D$_4$ (PD$_4$), which resembles that of polydimethylsiloxane (PDS). This fact suggests that open chain and/or large ring siloxanes are formed by the ring-opening reaction of D$_4$ in the plasma polymerization process, and the polymer has mainly dimethylsiloxane structure. There are also some differences in the absorption bands of SiCh$_3$ groups observed at range 850–750 cm^{-1}. In the spectra of D$_4$, PD$_4$, and PDS, the single band at 800–810 cm^{-1} is identified as —Si(Ch$_3$)$_2$ group (D type) or =Si (Ch$_3$) group (T type). On the other hand, there are two bands observed at 840–830 and 800–790 cm^{-1} in both PTMS and PM$_2$: The former which would be seen in their monomers was identified as —Si(CH$_3$)$_3$ group (M type) or —Ch$_2$Si(CH$_3$)$_3$ (A type); the latter which could not be seen in the monomers indicates the presence of D type. From these results the existence of two different species of Si in the polymers of TMS and M$_2$ is estimated.

The polymers prepared from TMS, M$_2$, and D$_4$ were examined by XPS analysis. The Si$_{2p}$ spectra of individual polymers could be resolved into more than two peaks which are corresponding to different oxidation states of Si atoms, and the results of analysis are shown in Table III. Here, the oxidation number denotes the numbers of Si—O bond. It was found that

TABLE III
Oxidation States of Si Atoms in Plasma Polymers

Plasma polymer (oxidation number of Si in monomer)	Oxidation number of Si in plasma polymer (content, %)
PTMS (0)	0 (86)
	≥ 1 (14)
PM$_2$Q (1)	1 (73)
	≥ 2 (27)
PD$_4$Q (2)	2 (97)
	≥ 3 (3)

any plasma polymer contained more than two species of Si atom: One of them was same as that in corresponding monomer, and others were further oxidized species. The former species in polymers of TMS, M_2, and D_4 accounted for 86, 73, and 97% of all the species, respectively. These results suggest that the chemical structure of the plasma polymers retain considerably those of individual monomers.

Chemical Structure and Gas Permeabilities

P_{O_2} of the composite membranes becomes larger in the order, PTMS, PM_2, PD_4, but P_{O_2}/P_{N_2} becomes smaller in the same order.

From spectroscopic studies of IR and XPS, it was recognized that plasma polymers retain considerably the chemical structure of individual monomers. Oxidation states of Si atom in plasma polymers increased in the order PTMS, PM_2, PD_4. Oxidation states of Si atom in plasma polymers seem to influence gas permeability characteristics.

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