

Plasma Polymerization of Organosilicon Compounds

N. INAGAKI, S. KONDO, M. HIRATA, and H. URUSHIBATA,
Laboratory of Polymer Chemistry, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432 Japan

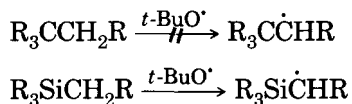
Synopsis

Plasma polymerizations in five silicon compounds having chemical formula of $(\text{CH}_3)_3\text{Si}-\text{X}-\text{Si}(\text{CH}_3)_3$, X = none, CH_2 , NH, O, and S atoms, were investigated by elemental analysis, infrared spectroscopy, and ESCA. The chemical composition of polymers plasma-polymerized was influenced by the X groups in $(\text{CH}_3)_3\text{Si}-\text{X}-\text{Si}(\text{CH}_3)_3$. Polymers, when X was S atoms, possessed no sulfur; and X was CH_2 groups polymers rich in carbon and hydrogen atoms were formed. Details in chemical composition were discussed by IR and ESCA. Such differences in chemical composition reflected on gas permeability of the plasma films.

INTRODUCTION

Plasma polymerization is a process of thin-film formation in which monomers are subjected to fragmentation and recombination stepwise to form polymers. This concept, named atomic polymerization, has been proposed by Yasuda.¹ Therefore, we believe that chemical composition of the formed plasma polymers could depend strongly on the fragmentation process of the monomers in plasma. Smolinsky and Vasile^{2,3} have reported that species present in plasma polymerization of trimethylvinylsilane were $\text{C}_2\text{H}_5\text{Si}(\text{CH}_3)_2$, $\text{Si}(\text{CH}_3)_3$, and $\text{HSi}(\text{CH}_3)_2$, which were the same as those produced by low-energy electron impact. This evidence shows that the fragmentation process of the monomers occurring in plasma may be similar to that occurring by electron impact in mass spectroscopy, although bimolecular reactions are negligible in mass spectroscopy.

The Si element is positioned just under the carbon element, and Si compounds are analogous to corresponding carbon compounds in chemistry. However, there are some differences in chemistry because the Si element having vacant d-orbital there frequently occurs $p_\pi-d_\pi$ conjugation which contributes in chemical reactions.⁴ For example, secondary hydrogen is not abstracted with *t*-butoxy radicals but corresponding hydrogen of silicon compounds is abstracted⁵:



In this study we investigate plasma polymerization of silicon compounds having $(\text{CH}_3)_3\text{Si}-\text{X}-\text{Si}(\text{CH}_3)_3$ formula, where X is none, CH_2 , NH, O, and S, to evaluate plasma chemistry of silicon compounds.

EXPERIMENTAL

Plasma Polymerization

Two reaction chambers made of Pyrex glass and coupled inductively with rf power were used in this study for plasma polymerization. The two chambers were similar in the shape but different in the dimension. The chamber A was 35 mm inner diameter and 400 mm long, and used to prepare polymer samples for analysis such as elemental analysis, IR, and ESCA spectra. The chamber B was 100 mm inner diameter and 400 mm long, and used to prepare membranes for gas permeability measurement. These reaction chambers have been detailed in a previous paper.⁶ The experimental procedures performed for plasma polymerization in this study, when either of the chambers was used, were essentially the same. Prior to the plasma polymerization the reaction chamber was evacuated to 0.13 Pa with the combination of a diffusion and a rotary pump, then the polymerization was initiated at a pressure of 1.3 Pa at a constant rf power (13.56 MHz), and continued for a given duration. The monomer gas stored in a reservoir was injected into the reaction chamber at a flow rate adjusted by a metering valve. The flow rate of the monomer gas was determined from pressure increases according to the ideal gas equation when the outlet valve of the reaction chamber was closed. In operation using chamber A the flow rate of the monomers was 2 cm³ (STP)/min, and rf power was 50 W. In operation using chamber B the flow rate of the monomers was 4 cm³ (STP)/min, and the rf power was 50–150 W.

Hexamethyldisilane (HMDS), bis(trimethylsilyl) methane (BTMSM), hexamethyldisilazane (HMDSZ), hexamethyldisiloxane (HMDSO), and hexamethyldisilthiane (HMDST) were purchased from Petrarch System Inc. and used as monomers without further purification.

Elemental Analysis

Polymers deposited on the glass plates and scraped off with a knife were provided for C, H, N, S, and Si analysis. The C, H, and N content of the polymers were determined with a Yanagimoto CHN corder MT-2. The S content was determined according to Wagner method.⁷ The Si content was determined from weight of residual products (SiO₂) when heated in oxygen atmosphere at 850°C until the residue reached a constant weight.

Infrared and ESCA Spectra

Infrared spectra of the polymers as KBr disks were recorded with a Nihon Bunko spectrometer A-3. Polymer films (approximately 0.1 μm thick determined by interferometry) deposited on silicon wafers were provided for measurement of ESCA spectra. ESCA spectra were recorded with a Shimadzu electronspectrometer ESCA 750 employing Mg K_α exciting radiation at 8 kV and 30 mA. The Au core level at 84.0 eV was temporarily used for calibration of the energy scale. The complex spectra were subjected to curve-fitting procedure using a Shimadzu ESCAPAC 760. Gaussian distribution was assumed and three parameters—the position and the height of the

peak, and the full width at half-maximum (FWHM)—were varied to correspond roughly to the observed spectra.

Gas Permeability

On membrane filter (MF Milipore VSWP 04700, pore size 0.025 μm) films polymerized by the plasma polymerization deposited. In the polymerization chamber B was used, and to get uniform polymer deposition the filters as substrates mounted on the brass plate in the chamber were rotated at 30–40 rpm by an electric motor drive during the polymerization. These films deposited on the membrane filters were served for the measurement of gas permeability. The permeation rate of gases across the membrane was measured according to ASTM D1434V. The pressure difference between the inlet and outlet side was 0.6–2.0 $\times 10^5$ Pa. Oxygen (99.99%) and nitrogen gas (99.99%) were injected after further purification with a line filter (Fuji Kinzoku Kohsaku Co. Ltd., FUFL 915) and a dry column (Nika Seiko Co. Ltd., DC-A4). The thickness of the plasma films deposited on the Milipore filters was directly determined from SEM pictures of the cross section of their films crushed in liquid nitrogen.

RESULTS AND DISCUSSION

Polymer Deposition Rate

Plasma polymerizations in the five monomer systems yielded colorless and polymeric films. In plasma polymerization in the HMDST system stink ing gas like mercaptans evolved from the exhaust pipe of the reaction chamber. Figure 1 shows the polymer deposition rate as a function of monomer flow rate in the plasma polymerization in the five monomer systems. The transversal axis in the figure is graduated (mg/min) to correct different molecular weight among the monomer used.

The polymer deposition rate increased gradually with increasing the monomer flow rate. It has been generally observed that the polymer deposition rate decreases with increasing substrate temperature by some investigators.^{8–11} In this experiment substrate temperature was not controlled and monitored during the polymerization. However, the substrate temperature, when the plasma polymerization was just finished, was in the range of 50–60°C using a thermocouple. There were remarkable changes in the substrate temperature in plasma polymerization of the five monomers. Accordingly, the polymer deposition rate in Figure 1 may be allowed semi-quantitative comparison. Figure 1 shows less influence of X groups in the monomers having $(\text{CH}_3)_3\text{Si}-\text{X}-\text{Si}(\text{CH}_3)_3$ formula on the polymer deposition rate.

Chemical Composition of the Formed Polymers

Chemical composition of plasma polymers, even if the same monomer was used, generally alters, depending on operating conditions such as the rf power, the monomer flow rate, the pressure in the reactor, the substrate temperature, etc.¹ Such dependence is result from how the monomer has

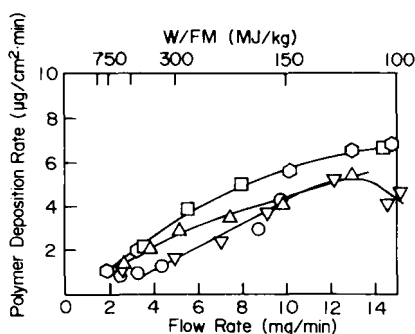


Fig. 1. Polymer deposition rate in plasma polymerization of HMDS (Δ), BTMSM (∇), HMDSZ (\square), HMDSO (\circ), and HMDST (\circ).

been fragmented in a plasma. In order to summarize such dependence Yasuda¹ has proposed a concept of the W/FM parameter which means apparent rf input energy per mass of the monomer, where W , F , and M are the rf power, the flow rate, and the molecular weight of the monomer, respectively. This concept indicates that the monomer may be subjected to vigorous fragmentation as increasing the W/FM value to yield plasma polymers rich in crosslinkage and poor in organic residues.

Table I shows the elemental composition of polymers prepared from the five monomers at two levels of W/FM values (ca. 100–200 and 600–700 MJ/kg). All the polymers consisted of carbon, hydrogen, silicon, and oxygen element with a small amount of nitrogen element. The polymers prepared from HMDST did not possess sulfur element but oxygen in a large amount, which indicates replacement of sulfur with oxygen atoms during the polymerization. A source of incorporated oxygen element which the monomers used never contained may be due to either residual air and/or water ad-

TABLE I
Elemental Composition of Polymers Prepared from
(CH_3)₃Si—X—Si(CH_3)₃ by Plasma Polymerization

Monomer	X	W/FM (MJ/kg)	Empirical formula of polymers
HMDS ($\text{C}_6\text{H}_{18}\text{Si}_2$)	None	120	$\text{C}_{4.5}\text{H}_{11.5}\text{O}_{2.8}\text{Si}$
BTMSM ($\text{C}_7\text{H}_{20}\text{Si}_2$)	CH_2	720	$\text{C}_{4.7}\text{H}_{12.4}\text{N}_{0.1}\text{O}_{1.0}\text{Si}$
		120	$\text{C}_{8.8}\text{H}_{25.8}\text{O}_{6.1}\text{Si}$
HMDSZ ($\text{C}_6\text{H}_{19}\text{NSi}_2$)	NH	620	$\text{C}_{4.7}\text{H}_{15.6}\text{N}_{1.0}\text{O}_{1.8}\text{Si}$
		100	$\text{C}_{4.7}\text{H}_{15.6}\text{N}_{1.0}\text{O}_{1.8}\text{Si}$
HMDSO ($\text{C}_6\text{H}_{18}\text{OSi}_2$)	O	420	$\text{C}_{2.1}\text{H}_{5.6}\text{N}_{0.4}\text{O}_{0.1}\text{Si}$
		120	$\text{C}_{3.1}\text{H}_{9.8}\text{O}_{2.3}\text{Si}$
HMDST ($\text{C}_6\text{H}_{18}\text{SSi}_2$)	S	830	$\text{C}_{2.6}\text{H}_{5.9}\text{O}_{1.3}\text{Si}$
		200	$\text{C}_{4.1}\text{H}_{11.7}\text{N}_{0.3}\text{O}_{4.5}\text{Si}$
		690	$\text{C}_{2.0}\text{H}_{5.2}\text{N}_{0.6}\text{O}_{2.3}\text{Si}$

sorbed on the reaction chamber walls or interactions of radicals generated in the plasma polymers with air after the polymerization. Table I shows many features of the five plasma polymers in comparison in elemental ratio between the plasma polymers and the starting monomers. All the plasma polymers are different in elemental composition from the starting monomers, which indicates fragmentation of the monomers in polymer-forming process. The differences depend strongly on the monomers as well as the W/FM value. In plasma polymerization at low W/FM values of 100–200 MJ/kg, plasma polymers rich in carbon and hydrogen contents (C/Si and H/Si ratio) are formed, and, at high W/FM values of 600–700 MJ/kg, polymers poor in carbon and hydrogen contents are formed. The five polymers formed at low W/FM value are higher in C/Si and H/Si ratios than the respective monomers. Especially, the plasma polymers from BTMSM possess the highest C/Si and H/Si ratios, and those from HMDSO possess the lowest C/Si and H/Si ratios. The plasma polymers from HMDST involving sulfur contain no sulfur. In plasma polymerization at high W/FM values the polymers formed from HMDSZ, HMDSO, and HMDST possess lower C/Si and H/Si ratios than the respective monomers, while plasma polymers from HMDS and BTMSM possess still higher C/Si and H/Si ratios than the respective monomers. Difference in C/Si and H/Si ratios between the plasma polymers at low and high W/FM values is small in the plasma polymerization of HMDSO. Such alterations of these plasma polymers in elemental composition with the monomers and the W/FM value may be results from fragmentation of the monomers occurring during polymer-forming process. Successively, the chemical composition of these plasma polymers were examined by ir spectroscopy and ESCA.

Figures 2–5 show IR spectra for the polymers prepared from HMDS, BTMSM, HMDSZ, and HMDSO as a function of W/FM value. IR spectra for the polymers from HMDST were not dealt with here because sulfur-silicon bonds were completely split off to form polymers free from sulfur atom. All the polymers prepared from the four monomers showed similar infrared spectra, although there were additional absorptions due to nitrogen residues for the polymers from HMDSZ. For the polymers prepared from HMDSZ strong absorptions appeared at 3430 (OH), 2960 (CH_3), 2900 (CH_2), 1700 (C=O), 1405 (CH_3), 1260 (Si— CH_3), 1050 (Si—O—Si, Si—O—C), 840 (CH), 800 (Si— CH_3 , Si— CH_2), and 690 cm^{-1} (unknown) (Fig. 2). No absorption due to Si—Si groups, which is expected at 404 cm^{-1} , could be detected, which indicates complete bond scission of Si—Si groups. The polymers prepared from BTMSM, as seen in Figure 3, showed similar absorptions to the formers. Compared with the polymers from HMDS, these absorptions due to CH_3 and CH_2 groups were somewhat intense. The polymers from HMDSZ showed strong absorptions due to C—N (at 1180 cm^{-1}) and Si—NH—Si groups (at 940–830 cm^{-1}) as well as CH_3 , CH_2 , Si— CH_3 , Si—O—Si, and Si—O—C groups (Fig. 4). These absorptions at 1180 and 940–830 cm^{-1} characterize the polymers from HMDSZ. The polymers prepared from HMDSZ were similar to those from HMDS and BTMSM in infrared spectra (Fig. 5). Strong absorptions appeared at 2960, 2900, 1410, 1260, 1040, 840, 800, and 690 cm^{-1} . These comparisons in infrared spectra could not completely distinguish among the polymers formed from HMDS, BTMSM, HMDSZ, and HMDSO in chemical composition.

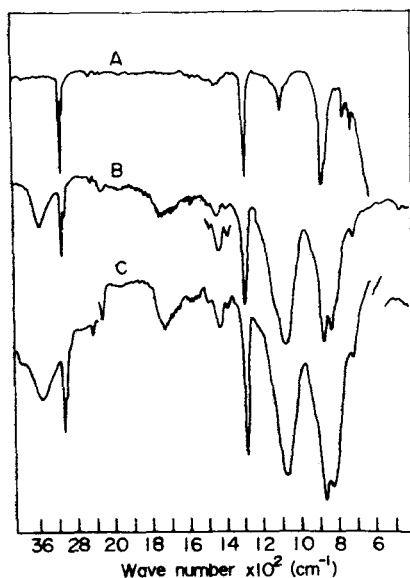


Fig. 2. IR spectra of polymers prepared from HMDS (A) and HMDS polymerized at a W/FM value of 120 MJ/kg (B) and at 720 MJ/kg (C).

ESCA (C_{1s} and Si_{2p}) spectra were recorded to distinguish the four plasma polymers in chemical composition. All the C_{1s} spectra were single peak in the range from 282 to 292 eV, and their FWHM values were more than 2 eV. The necessity for at least two curves is obvious to deconvolute these spectra.

The third curve was determined from the difference between the observed curve and the sum of the first and the second component. According to this

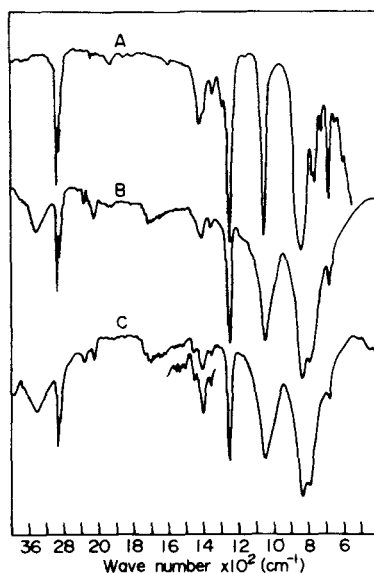


Fig. 3. IR spectra of polymers prepared from BTMSM (A) and BTMSM polymerized at a W/FM value of 120 MJ/kg (B) and at 620 MJ/kg (C).

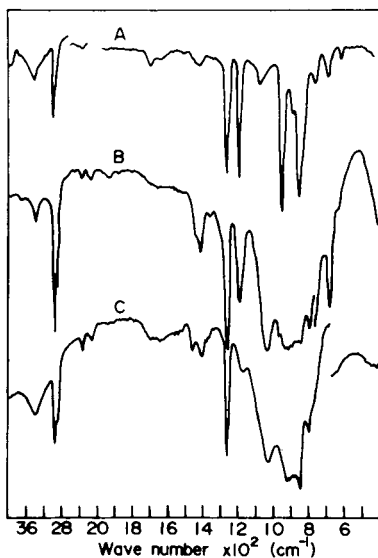


Fig. 4. IR spectra of polymers prepared from HMDSZ (A) and HMDSZ polymerized at a *W/FM* value of 100 MJ/kg (B) and at 400 MJ/kg (C).

curve-fitting procedure each of the C_{1s} spectra could be fitted by two or three Gaussian curves. The peak position and the relative peak area for each component are listed in Table II. The C_{1s} spectra for the plasma polymers prepared from HMDS were divided into two components of which peak position was at 285.0 (aliphatic carbon) and 286.5 or 287.0 eV (C—O groups). The C_{1s} spectra for the plasma polymers from BTMSM consisted of three components due to aliphatic carbon (at 285.0 eV), C—O (286.5 eV),

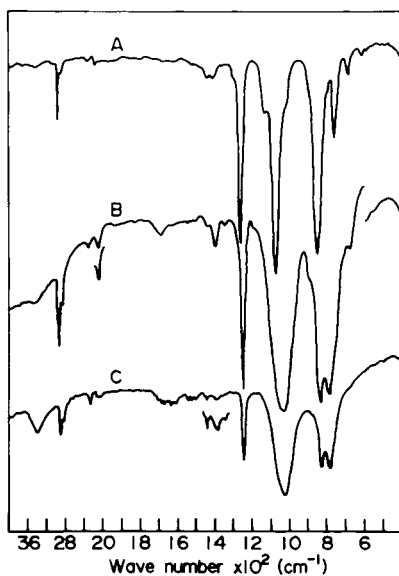


Fig. 5. IR spectra of polymers prepared from HMDSO (A) and HMDSO polymerized at a *W/FM* value of 140 MJ/kg (B) and at 830 MJ/kg (C).

TABLE II
ESCA Spectra of Polymers Prepared from
(CH₃)₃Si—X—Si(CH₃)₃ by Plasma Polymerization^a

Monomer		W/FM (MJ/kg)	Core level	Peak position (eV) ^b , peak area (%) ^c			
X	Peak #1			Peak #2	Peak #3	Peak #4	
HMDS	None	120	C _{1s}	285.0 ^b (88) ^c	287.0 (12)		
		720		285.0 (81)	286.5 (19)		
BTMSM	CH ₂	120		285.0 (69)	286.5 (21)	288.1 (10)	
		620		285.0 (6)	286.5 (74)	288.0 (20)	
HMDSZ	NH	104		285.0 (87)	286.3 (13)		
		415		285.0 (82)	286.7 (18)		
HMDSO	O	120		285.0 (82)	287.0 (13)	289.0 (5)	
		830		285.0 (87)	287.3 (10)	289.3 (3)	
HMDS	None	120	Si _{2p}		101.5 (64)		103.0 (36)
		720			101.3 (42)	102.3 (38)	103.5 (20)
BTMSM	CH ₂	120					103.0 (100)
		620					103.3 (100)
HMDSZ	NH	104			101.4 (59)	102.4 (34)	104.1 (7)
		415			101.4 (53)	102.5 (47)	
HMDSO	O	120			101.6 (100)		
		830		100.3	101.1		103.4

^a C_{1s}: peak #1: aliphatic carbon; peak #2: C—O; peak #3: C=O.

^b Si_{2p}: peak #1: Si—C; peak #2: Si—O; peak #3: Si—(O—C)_{2 or 3} and/or Si—(O—Si)_{2 or 3}; peak #4: SiO₂.

and C=O groups (288.0–288.1 eV). The plasma polymers from HMDSZ showed C_{1s} spectra composed of two components due to aliphatic carbon and C—O groups. Those from HMDSO showed C_{1s} spectra composed of three components due to aliphatic carbon, C—O, and C=O groups. Although these four plasma polymers show similar C_{1s} features, there are significant differences in their relative intensity of the C_{1s} features among the plasma polymers. The plasma polymers except those prepared from BTMSM possess aliphatic carbon component of 80–87 mol % and C—O component of 10–20 mol %, and these concentrations are scarcely dependent on W/FM value. However, in plasma polymerization of BTMSM-oxidized carbon components of C—O and C=O groups became main and increased by increasing W/FM value. At a W/FM value of 620 MJ/kg, C—O and C=O component

reached 74 and 20 mol %, respectively. This indicates easy fragmentation and oxidation of BTMSM.

The Si_{2p} spectra for the four plasma polymers also could be resolved into two or three components by the curve-fitting procedure. The peak position and the relative peak area are listed in Table II. The Si_{2p} spectra having three main peaks for the polymers plasma-polymerized from HMDSO at 830 MJ/kg were too complex to be resolved. These Si_{2p} spectra show significant differences in Si_{2p} feature among the four plasma polymers as the C_{1s} spectra did. The Si_{2p} spectra for the polymers plasma-polymerized from HMDS consisted of Si—O—C and/or Si—O—Si , and SiO_2 components. By increasing W/FM value, a new component of $\text{Si—(O—C)}_{2 \text{ or } 3}$ and $\text{Si—(O—Si)}_{2 \text{ or } 3}$ appeared. The plasma polymers from BRMSM showed simple Si_{2p} spectra due to only SiO_2 components, of which the FWHM value was ca. 2.0 eV. The Si_{2p} spectra for the plasma polymers from HMDSZ consisted of two or three components at 101.4, 102.4–102.5, and 104.1 eV. The first component at 101.4 eV could be assigned an Si—N feature because of strong absorption due to Si—NH groups at 940–830 cm^{-1} on infrared spectra and due to the N—Si feature at 398.0 eV on the N_{1s} spectra. The assignment of the Si—O feature, however, is not excluded. The second and the third component at 102.4–102.5 eV and 104.1 eV could be assigned $\text{Si—(O—C)}_{2 \text{ or } 3}$ or $\text{Si—(O—Si)}_{2 \text{ or } 3}$, and SiO_2 features, respectively. The polymers plasma-polymerized from HMDSO at 120 MJ/kg showed simple Si_{2p} spectra at 101.6 eV due to Si—O feature with a FWHM of ca. 1.9 eV. The comparison of these Si_{2p} spectra indicates that (1) all the Si atoms in plasma polymers are oxidized to form Si—O—C and/or Si—O—Si sequences, (2) the oxidation of Si atoms depends strongly on the used silicon compounds, and (3) the easy oxidation of Si atoms is in the order of $\text{BTMSM} > \text{HMDS} > \text{HMDSZ} > \text{HMDSO}$.

Gas Permeation

To evaluate physical properties of the plasma polymers from HMDS, BTMSM, HMDSZ, and HMDSO, these plasma polymers were deposited on the surfaces of Milipore filters, and the composite films were used for the permeation experiments. The thickness-uniform and pinhol-free polymer deposition is required for the permeation measurement. To accomplish uniform deposition Milipore substrates were rotated at 30–40 rpm during plasma polymerization. The deviation in thickness of films deposited on Milipore filters was within 5% in the radius direction from observation of SEM picture of the cross section of the composites. SEM pictures of the cross section of the composites, although these pictures are not represented here for the sake of brevity, showed smooth deposition of plasma polymers, and an irregular part like a pinhole could not be observed at a magnification of 4×10^4 . The permeability coefficient for the composites decreased rapidly as increasing the deposited film thickness, and then leveled off at film thickness above 0.5 μm . This indicates that porous parts of Milipore filter were filled up with plasma films more than 0.5 μm thick. Accordingly, composites deposited with plasma films more than 1 μm thick were served for permeation experiments.

TABLE III
Oxygen and Nitrogen Permeabilities of Polymers Prepared from $(\text{CH}_3)_3\text{Si}-\text{X}-\text{Si}(\text{CH}_3)_3$ by Plasma Polymerization

Monomer	W/FM (MJ/kg)	Thickness (μm)	Permeability coefficient		
			P_{O_2}	P_{N_2}	$P_{\text{O}_2}/P_{\text{N}_2}$
HMDS	120	1.2	3.5×10^{-9}	2.9×10^{-9}	1.2
		1.6	2.4	2.2	1.1
	720	0.9	6.7	7.1	0.94
		1.3	8.8	9.4	0.94
BTMSM	120	1.8	2.8	2.3	1.2
	620	1.2	1.1	1.1	1.0
HMDSZ	110	2.4	0.85	0.40	2.1
	420	2.6	2.4	2.0	1.2
HMDSO	120	1.7	5.1	2.1	2.4
		2.6	4.3	1.4	3.1
	820	1.1	2.3	2.4	0.96
		1.4	3.9	4.6	0.85

Table III shows their permeability coefficient of nitrogen and oxygen gas. All the films had the permeability coefficient of nitrogen (P_{N_2}) and oxygen gas (P_{O_2}) in the range of 10^{-9} cm^3 (STP) cm/cm^2 s cm Hg, which indicates that these films are somewhat easy in gas permeation. Some influences of the monomers used on the ratio between the permeability coefficient of oxygen gas and that of nitrogen gas could be observed. For the films plasma-polymerized from HMDS and BTMSM independently of W/FM value the ratio of $P_{\text{O}_2}/P_{\text{N}_2}$ was about unity. On the contrary, for the films from HMDSZ and HMDSO the ratio was above 2; especially, the ratio for the films from HMDSO reached 3.1. Plasma polymerizations at low W/FM values are favorable for formation of plasma films having high $P_{\text{O}_2}/P_{\text{N}_2}$ ratios. Such difference in the $P_{\text{O}_2}/P_{\text{N}_2}$ ratio may be related to chemical composition of plasma films, especially surrounding of Si atoms. Easy formation of SiO_2 groups in plasma polymerizations is unfavorable for accomplishing high $P_{\text{O}_2}/P_{\text{N}_2}$ ratios, and formation of $\text{Si}-\text{O}-\text{C}$ or $\text{Si}-\text{O}-\text{Si}$ groups is favorable in accomplishing high $P_{\text{O}_2}/P_{\text{N}_2}$ ratios. Figure 6 shows the $P_{\text{O}_2}/P_{\text{N}_2}$ ratio as

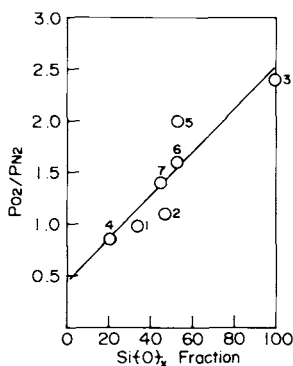


Fig. 6. Permeation coefficient ratio between oxygen and nitrogen gas as a function of $\text{Si}-\text{(O}-\text{C)}_x$ and $\text{Si}-\text{(O}-\text{Si)}_x$ fraction in plasma films prepared from HMDSZ at 110 MJ/kg (1), 420 MJ/kg (2), HMDSO at 140 MJ/kg (3) and 820 MJ/kg (4), TMDSO at 140 MJ/kg (5), TMS/ O_2 mixture at 200 MJ/kg (6), and TMS at 240 MJ/kg (7).

a function of relative concentration of $\text{Si}-(\text{O}-\text{C})_x$ and $\text{Si}-(\text{O}-\text{Si})_x$, $x = 1-3$. In the figure, plasma films which have been reported in a previous paper,¹² i.e., films prepared from tetramethyldisiloxane (TMDSO), a mixture of tetramethylsilane and oxygen gas (TMS/O_2), and TMS, are involved. The $P_{\text{O}_2}/P_{\text{N}_2}$ ratio, as shown in Figure 6, increased with increasing the $\text{Si}-(\text{O}-\text{C})_x$ and $\text{Si}-(\text{O}-\text{Si})_x$ concentration, which indicates the importance of surrounding of Si atoms of plasma films.

References

1. H. Yasuda, *J. Polym. Sci. Macromol. Rev.*, **16**, 199 (1981).
2. G. Smolinsky and M. J. Vasile, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 147 (1973); *Org. Mass Spectrom.*, **7**, 1069 (1973).
3. M. J. Vasile and G. Smolinsky, *Int. J. Mass Spectrom. Ion Phys.*, **13**, 381 (1974).
4. E. W. Colvin, *Silicon in Organic Synthesis*, Butterworths, London, 1981.
5. Y. Yamamoto and Y. Narita, *Uki Kinzoku Kagaku*, in Japanese, Maruzen, Tokyo, 1983.
6. N. Inagaki and H. Kawai, *Sen-i Gakkaishi*, **40**, T337 (1984).
7. K. Ueno, *Kagaku no Ryoiki*, **12**, 942 (1956).
8. R. Secrist and J. D. MacKenzie, *J. Electrochem. Soc.*, **113**, 914 (1966).
9. A. R. Westwood, *Eur. Polym. J.*, **7**, 363 (1971).
10. S. P. Mukherjee and P. E. Evans, *Thin Solid Films*, **14**, 105 (1972).
11. A. M. Wrobel, J. E. Klemberg, M. R. Wertheimer, and H. P. Schreiber, *J. Macromol. Sci. Chem.*, **A15**, 197 (1981).
12. N. Inagaki, S. Kondo, and T. Murakami, *J. Appl. Polym. Sci.*, **29**, 3595 (1984).

Received November 13, 1984

Accepted January 14, 1985