

Preparation of plasma-polymerized membranes from 1-(trimethylsilyl)-1-propyne and gas permeability through the membranes

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Summary

Plasma-polymerized membranes for gas separation were prepared from 1-(trimethylsilyl)-1-propyne. The permeation data of He, H₂, O₂, N₂, CO₂, and CH₄ through the membranes showed plasma-polymerized 1-(trimethylsilyl)-1-propyne had high permselectivity but low permeability compared with poly[1-(trimethylsilyl)-1-propyne]. This behavior is considered to be due to the crosslinking structure of the plasma-polymerized membrane. The correlation between plasma polymerization conditions and the membrane performance was studied. The optimum condition at which the deposition rate of the plasma polymer is maximized agreed with the optimum value to yield maximum separation factor of gases through the membrane.

Introduction

Membrane separation systems have recently received much attention because of their lower costs and greater flexibility. Fundamental properties required of such membranes are high permeability and high selectivity. Among existing polymeric materials, poly[1-(trimethylsilyl)-1-propyne](PTMSP) exhibits the highest gas permeability(1-3). The high permeability, however, decreases to about 1% of its original value when the membrane is left at room temperature for a few months. Thus, studies on the gas permeation through PTMSP have been the subject of much research effort (eg., polymer synthesis, permeation mechanism, and prevention of the decrease of permeability)(4-6).

In this study, we report plasma polymerization of 1-(trimethylsilyl)-1-propyne(TMSP). The permeation of gases through plasma-polymerized TMSP (PPTMSP) membranes is also reported in comparison with the conventional PTMSP membrane.

Experimental

Figure 1 shows a schematic diagram of the apparatus for plasma polymerization. A commercially available monomer was used as received. Before the monomer was introduced into the reactor, it was degassed several times via freezing and thawing cycles in vacuum. After a reactor was exposed to Argon plasma for 10 min, the reactor was then evacuated to 0.01 Torr and the monomer gas adjusted to a fixed flow rate was injected into the reactor. The plasma polymerization was carried out at pressure of 0.1-0.6 Torr and discharge power of 10-80 W for a certain period. A porous polypropylene film (Cellgard 2400) was used as the substrate of plasma-polymerized membranes.

IR spectra of plasma polymers deposited on KBr crystal were obtained with JASCO-IRA-1. ESCA spectra of plasma polymers deposited on Al foil were recorded on Shimadzu ESCA750 spectrometer.

The permeability coefficients of gases through plasma-polymerized membranes were determined at 35°C by the non-equable pressure method(7), where the low pressure side of the sample was maintained near atmospheric pressure and the transmission of the gas was measured by change in volume.

Results and Discussion

Plasma polymerization of TMSP

TMSP, like other substituted acetylene compounds(8), polymerized easily in plasma. The amount of deposition of PPTMSP was found to be linear with duration time of plasma polymerization. The effect of discharge power on the deposition rate of PPTMSP at various monomer flow rates showed a different dependency. At monomer flow rates of 2 and 7 cc(STP)/min, deposition rates increased up to a maximum and then dropped gradually with increasing discharge power. At 12 cc(STP)/min, however, deposition rate decreased with increasing discharge power.

In the plasma polymerization, it is well known that the discharge power and monomer flow rate are important factors since these two factors control the deposition rate of plasma polymerization and characteristics of the polymerized membranes(9). Yasuda has proposed the composite parameter W/FM as an empirical factor to determine the plasma polymerization process, where W is the discharge power, F is the monomer flow rate and M is the molecular weight of the monomer. The variation in the rate of polymer deposition of PPTMSP with the composite parameter W/FM is shown in Fig. 2, which also shows that the deposition rate of PPTMSP increases with increasing W/FM upto a W/FM value of 35 J/mg and

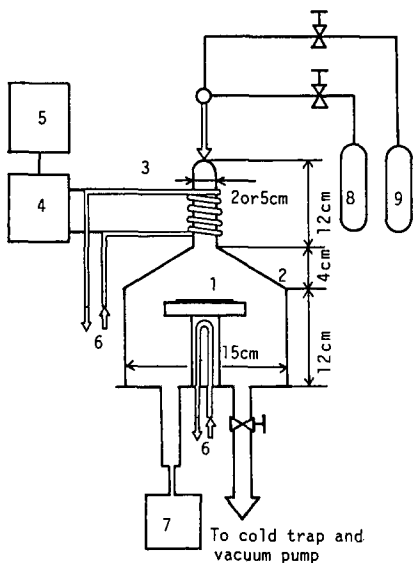


Fig. 1. A schematic diagram of the plasma polymerization system. 1, sample stage; 2, glass chamber; 3, RF coil; 4, matching unit; 5, RF generator (13.56 MHz); 6, cooling water; 7, vacuum gauge; 8, monomer; 9, Ar gas or monomer.

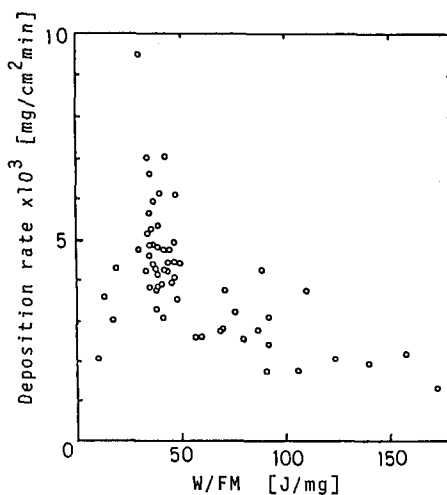


Fig. 2. Deposition rate of PPTMSP vs. the parameter W/FM .

then decreases sharply with increasing W/FM . From these results it is concluded that plasma polymerization of TMSP can be divided into two regions (energy-deficient region and monomer-deficient region) by whether the value of W/FM is more than 35 J/mg or less.

IR and ESCA Spectra of PPTMSP

IR spectra of PPTMSP, PTMSP, and TMSP are shown in Fig. 3. For all of them, a band characteristic of SiC-H deformation was observed at 1240 cm^{-1} , and those due to C-Si stretching were seen at 820 and 740 cm^{-1} . While TMSP showed a band at 2170 cm^{-1} due to C≡C stretching and PTMSP showed a band at 1540 cm^{-1} attributable to C=C stretching, both bands were absent in PPTMSP, which indicates opening of C≡C and C=C bonds. These results suggest the formation of crosslinking in the plasma polymer.

Figure 4 shows ESCA spectra of PTMSP and PPTMSP deposited on Al foils. C(1s) spectra of the two polymers showed a single peak at 285 eV and the full width at half maximum was 1.85 eV for PTMSP and PPTMSP, respectively. Si(2p) also showed a single peak at 101.4 eV and 101.6 eV and the full width at half maximum was 1.70 eV and 2.60 eV for PTMSP and PPTMSP, respectively. The relative concentration of each component was estimated from the peak area. The Si/C ratio was 0.19 and 0.21 for PTMSP and PPTMSP, respectively. Judging from the large value of the full width at half maximum of Si(2p) spectra of PPTMSP, it can be assumed that Si(2p) spectra of PPTMSP involve more than two Si(2p) species.

Gas permeation through PPTMSP membrane

Figure 5 shows the relationship between the amount of deposition of PPTMSP and the permeation rate of oxygen ($R(O_2)$) through PPTMSP membrane. The value of $R(O_2)$ decreased sharply at about 0.05 mg/cm^2 ($0.5\text{ }\mu\text{m}$ in thickness), then decreased gradually. The relationship between $R(O_2)$ and $R(O_2)/R(N_2)$ is shown in Fig. 6. Sigmoidlike relation was observed between them. $R(O_2)/R(N_2)$ gradually increased with decreasing $R(O_2)$ from 10^{-3} to $10^{-5}\text{ cc(STP)/cm}^2\text{ seccmHg}$, then it increased drastically at about 10^{-5} .

This behavior can be related to the change in thickness of plasma-polymerized membranes formed on porous substrate(10, 11). Thus, these results indicate that the pores of the porous substrate are covered with a plasma polymer and pinhole-free thin membrane of PPTMSP is formed at about $0.5\text{ }\mu\text{m}$ in thickness.

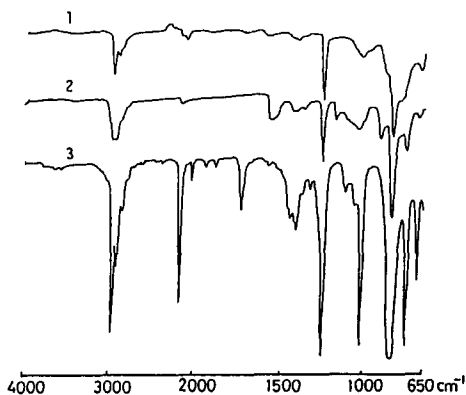


Fig. 3. IR spectra of PPTMSP(1), PTMSP(2), and TMSP(3).

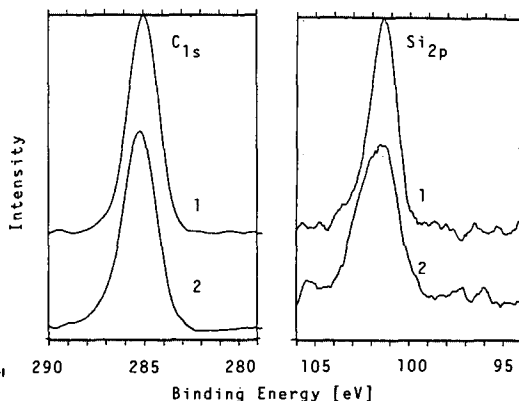


Fig. 4. ESCA spectra of PTMSP(1) and PPTMSP(2).

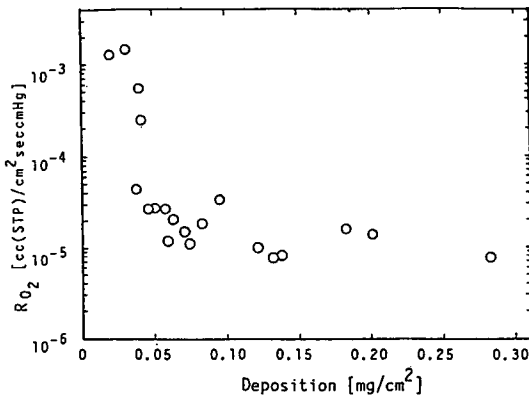


Fig. 5. Relationship between deposition of PPTMSP and permeation rate of oxygen (R_{O_2}).

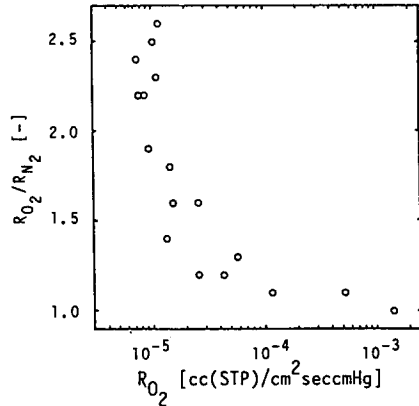


Fig. 6. Relationship between permeation rate of oxygen (R_{O_2}) and separation factor (R_{O_2}/R_{N_2}).

Table 1. Permeability coefficients^a of gases through PPTMSP

X	PPTMSP (20W 0.1Torr 15min)	PTMSP ^c
O ₂	20 x 10 ⁻¹⁰ [2.5] ^b	40 x 10 ⁻⁸ [2.0]
N ₂	8 x 10 ⁻¹⁰ [1.0]	20 x 10 ⁻⁸ [1.0]
CO ₂	64 x 10 ⁻¹⁰ [8.0]	180 x 10 ⁻⁸ [9.0]
CH ₄	15 x 10 ⁻¹⁰ [1.8]	42 x 10 ⁻⁸ [2.1]
He	119 x 10 ⁻¹⁰ [15.0]	41 x 10 ⁻⁸ [2.1]
H ₂	90 x 10 ⁻¹⁰ [11.0]	69 x 10 ⁻⁸ [3.5]

a; [cc(STP)cm/cm²sec cmHg]

b; [P_X/P_{N₂}] c; Ref. 3.

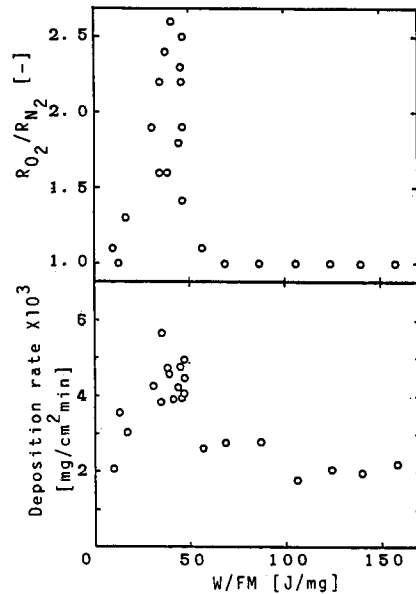


Fig. 7. Correlation between separation factor (R_{O_2}/R_{N_2}) and plasma polymerization condition.

The correlation between separation factor ($R(O_2)/R(N_2)$) and plasma polymerization condition is shown in Fig. 7, where it is easy to determine an optimum value of W/FM at which the separation factor is maximized. This value agreed with an optimum value of W/FM in the relationship between deposition rate and W/FM. Thus, it is to be noted that the optimum condition to yield maximum separation factor is in the intermediate region between the power-deficient region and the monomer-deficient region of plasma polymerization.

Permeability data of plasma-polymerized membranes are shown in Table 1 and 2. Table 1 shows the permeability coefficients of various gases

Table 2. Gas permeation rates of PPTMSP.

Monomer ^a	Plasma condition			Permeation rate ^b		R _{O₂} /R _{N₂}
	RF power [W]	Pressure [Torr]	Time [min]	R _{O₂}	R _{N₂}	
TMSP	20	0.1	15	1.16	0.45	2.6
	20	0.1	60	0.74	0.31	2.4
TMSP/HMDS	30	0.1/0.1	15	1.86	0.68	2.7
	30	0.1/0.2	15	6.52	2.47	2.6
TMSP/CF ₄	20	0.1/0.5	15	1.39	0.63	2.2
TMSP/PFH	20	0.1/0.3	15	2.36	2.09	1.1
	20	0.1/0.1	15	1.26	0.98	1.3
TMSP/TFEA	20	0.1/0.1	30	1.48	1.30	1.1

a; HMDS= hexamethyldisiloxane, PFH= perfluorohexane, TFEA= trifluoroethylacrylate.

b; $\times 10^{-5}$ [cc(STP)/cm²seccmHg].

through PPTMSP membrane together with those of PTMSP reported by Takada et al (3). It can be seen from Table 1 that the plasma polymerization of TMSP brings about a large reduction in the permeability coefficients compared with PTMSP polymerized with transition metal chlorides as catalysts. Furthermore, the permeability coefficients of PPTMSP membrane becomes more dependent on the size of the penetrant molecule. PPTMSP membrane had lower permeability to CH₄ than PTMSP membrane by about a factor of 280, whereas the permeability of He was decreased by about a factor of 40. Thus, the permselectivity is increased in the case of PPTMSP. These results are attributed to the crosslinking structure of the plasma-polymerized membrane described above. Table 2 shows the permeation rates of O₂ and N₂ through the membranes obtained by the plasma polymerization of monomer mixtures. The permeation rate and the permeation rate ratio of O₂ to N₂ were virtually unaffected by co-polymerization of TMSP with F containing monomer. On the other hand, the permeation rate was increased in the case of the membranes prepared by plasma co-polymerization of TMSP with siloxane monomer, which may be due to the presence of polysiloxane moiety which is reported to show high permeability even in the plasma-polymerized membrane(10).

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