NOTES

Plasma-Polymerized Membranes and Gas Permeability. IV

Since Goodman[1] reported the glow discharge polymerization in vapor phase, this plasma polymerization method has been studied by many authors.[2-5] The principal features of plasma polymerization are: Most organic compounds can be polymerized; plasma polymers are highly crosslinked; uniform, pinhole-free, and thin polymeric films can be formed on various substrates; these films adhere well to the substrates. Several studies have been made on applications of plasma polymerization methods having above features to membranes for gas separation.[6-12]

We reported previously that composite membranes composed of porous substrates and pinhole-free thin films formed thereon by plasma polymerization were recognized to have fairly high oxygen permeation rates and oxygen to nitrogen permeability ratios, and organosilicic compounds were suitable as monomers for the preparation of highly permeable oxygen separation membranes.[8]

As mentioned above, highly crosslinked polymers can be formed in the plasma state; therefore, plasma films possessing highly crosslinked structures seem to be suitable to separate hydrogen from other gases depending on the difference in molecular size. However, in order to prepare permselective composite membranes composed of porous substrates and plasma films, thicker plasma films are required; according to our previous study, the thickness required was five times as large as the pore radius of the porous substrate.[11] It is expected that the permeation rate becomes too small because of the thickness of the plasma film. Furthermore, it is known that microcracks are apt to form in the highly crosslinked plasma film when the film is thicker.[12] Therefore, it is necessary to make permselective plasma film as thin as possible in order to break through these difficulties.

Stancel reported that hydrogen permselectivity of a homogeneous silicone film could be improved by the formation of thin plasma films on it.[6] In this present work, a double layered structure membrane, which was composed of a porous substrate, a highly permeable plasma film, and a highly permselective plasma film, was prepared to make the permselective layer thinner, and its gas permeability, especially hydrogen permeability, was investigated.[3]

EXPERIMENTAL

Materials

The porous substrate used was a porous polypropylene membrane (Cellgard) with a thickness of 20 μm and rectangular pores of 2000 $\times$ 400 Å in their maximum size.

Organic compounds used for plasma polymerization were hexamethyldisiloxane (M_2, Nakarai Chemical Co. Ltd), octamethylcyclotetrasiloxane (D_4, Tokyou Kasei Co. Ltd), 1-hexene, cyclohexene, toluene, styrene, divinylbenzene, 1-heptyne, acrylic acid, ethyl acrylate, 1,3-pentadiene, 1,3-cyclohexadiene, acetylenecarboxylic acid, benzonitrile, furan, allylamine (Nakarai Chemical Co. Ltd), and acetylene (Nippon Sanso Co. Ltd). They were used without further purification.

Plasma System

The apparatus for plasma polymerization was the same as those reported previously in detail.[8] The system was constructed with a Pyrex glass chamber of bell jar type, a monomer inlet, a rotary vacuum pump, a Pirani gauge, and a radio frequency (RF) electronic power supply of 13.56 MHz with a matching network.

Preparation of the First Layer

The porous substrates with a length of 38 cm and a width of 15.5 cm were wound around an inside and an outside of a copper pipe. The copper pipe was placed on a sample stage in the chamber, as shown in Figure 1(A). The system was evacuated to 0.01 torr by the rotary vacuum
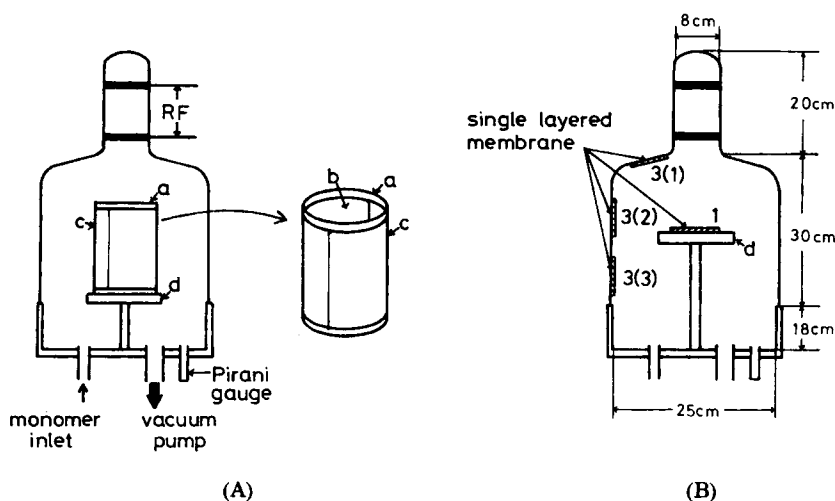
Fig. 1.   Schematic diagrams of the apparatus of the plasma polymerization for the first layer formation (A) and the second layer formation (B): (a) a copper pipe with a diameter of 12 cm and a height of 18 cm; (b) the porous substrate on the inside of the pipe; (c) the porous substrate on the outside of the pipe; (d) a metallic sample stage; 1,3(1), 3(2), and 3(3) are sample positions.

pump. Vapor of M_2 or D_4 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 these conditions the radio frequency electric power of 50 W was supplied to continue plasma polymerization for 10 or 15 min with the pressure being kept at 0.2 torr. After the electric power supply was stopped and the system isolated from the pump, air was introduced, and the vacuum was released. Subsequently, the copper pipe was placed upside down on the sample stage. The chamber was evacuated, and the plasma polymerization was performed again for the same period of time as mentioned above. Thus, the single-layered composite membrane composed of the porous substrate and the homogeneous plasma film in thickness was prepared.

Preparation of the Second Layer

The single-layered composite membranes with a size of 7.5 × 7.5 cm were placed on the sample stage (1) and the wall of the chamber [3(1), 3(2), 3(3)] as shown in Figure 1(B). Vapor of an organic compound was introduced into the chamber and the pressure was controlled at 0.2 torr. Under these conditions, the radio frequency electric power of 50 W was supplied, and the plasma polymerization was continued for a certain length of time with the pressure being kept at 0.2 torr. Thus the double layered composite membranes were prepared.

SEM Observation

The microstructure of a double layered structure membrane was observed under a Hitachi S-450 scanning electron microscope. The sample was coated with evaporated gold using a Eico IB-3 ion coater to a thickness of about 200 Å.

Measurement of Gas Permeability

Gas permeability of the composite membranes was measured at 25°C on a Yanako GTR 10S constructed with a test cell, a rotary vacuum pump, valves, and a measuring tube with an internal volume of 2 mL, in which the gas permeating through the membrane was collected. The test cell, containing a membrane and a measuring tube, were evacuated to a pressure of 0.01 torr with the vacuum pump before each run. After the system was isolated from the vacuum pump by a valve, each gas with atmospheric pressure was introduced to one side of the membrane and the gas permeating through the membrane was collected in the measuring tube for certain periods of

time. Subsequently, a carried gas (Ar) stream was made to pass through the measuring tube, and the collected gas was carried to a gas chromatographic (GC) analyzer. GC analysis was carried out on a Yanako G180 instrument with columns of molecular sieve 5 Å and thermal conductivity detectors for determination of the volume of permeating gas. The gases tested were air, hydrogen helium and methane. The permeation rate of X gas (R_X) can be expressed by the expression of $R_X = v/s \cdot t \cdot \Delta P_X$, where v is the volume of the permeating gas, s is the area of the membrane, t is the collecting time, and ΔP_X is the partial pressure of the gas between the membrane.

RESULTS AND DISCUSSION

Gas Permeability of the Single Layered Composite Membranes

In order to prepare the double layered composite membranes, it is necessary to make the single-layered composite membrane with a large area be homogeneous in gas permeability. The deposition rates of plasma-polymerized films varied with the positions where the films were deposited, especially with the distance from the electrode.[11] In this study the electrodes were wound around the top of the chamber as shown in Figure 1. Therefore, the thickness of the plasma films varied widely in the direction of top and bottom. In order to prepare homogeneous membranes in gas permeability, the single-layered membranes were prepared as shown in the experimental section. The plasma polymerized M_2 or D_4 prepared by this method was recognized to be almost uniform in thickness by observing the interference colors of the films, irrespective of the position. Figure 2 shows relationship between gas permeability of the singe-layered composite membrane prepared on the inside of the copper pipe and the sample position in the vertical direction. The gas permeability of the membranes was almost constant, independent of the sample position. From these results, it was found that homogeneous composite membranes could be prepared by this method.

Gas permeation rates of the single layered composite membranes prepared from M_2, D_4, and furan by plasma polymerization (hereafter denoted by M_2/PP, D_4/PP, and furan/PP respectively) are presented in Table I. The ratio of the permeation rates of hydrogen to nitrogen (R_{H_2}/R_{N_2}) of M_2/PP and D_4/PP were 9.2 and 5.8, respectively. These values are larger than the value of polydimethylsiloxane membrane, which is 2.1. These larger values of R_{H_2}/R_{N_2} are attributed to the crosslinked structure of plasma polymer. However, the values of R_{H_2}/R_{N_2} are not sufficient for the hydrogen separation membrane, because most conventional polymers have
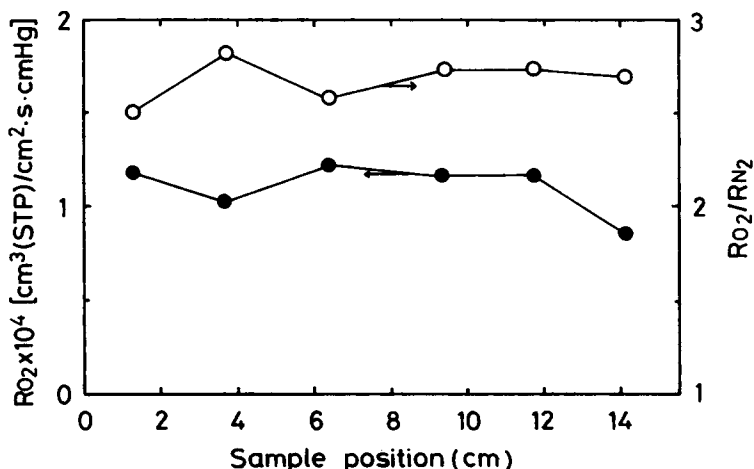

Fig. 2. Variation of gas permeability of the single layered composite membranes, prepared from M_2 on the inside of the copper pipe, with the sample position in the vertical direction (polymerization time was 10 + 10 min): (●) oxygen permeation rates (R_{O_2}); (○) ratio of oxygen to nitrogen permeation rates (R_{O_2}/R_{N_2}); the sample position is the distance from the upper end of the membrane to the sample tested.

TABLE I
Gas Permeability of Plasma Polymerized Membranes
(Single Layered Membranes)

Test gas X	Monomer gas		
	$M_2{}^a$	$D_4{}^b$	Furan^c
	$R_X{}^d$ (cm^3 (STP)/cm^2 s cm Hg) $[R_X/R_{N_2}{}^e]$		
O_2	7.1×10^{-5} [2.8]	1.2×10^{-4} [2.1]	1.3×10^{-5} [1.3]
N_2	2.5×10^{-5} [1.0]	5.7×10^{-5} [1.0]	9.8×10^{-6} [1.0]
H_2	2.3×10^{-4} [9.2]	3.3×10^{-4} [5.8]	9.0×10^{-5} [9.2]
He	1.7×10^{-4} [6.8]	2.3×10^{-4} [4.0]	7.5×10^{-5} [7.7]
CH_4	5.7×10^{-5} [2.3]	1.2×10^{-4} [2.1]	1.2×10^{-5} [1.3]

^{a} Polymerization time was 15 + 15 min.
^{b} Polymerization time was 10 + 10 min.
^{c} The membrane was prepared according to the procedure for the preparation of the second layer except for the use of the porous substrate instead of the use of single layered membrane, polymerization time was 20 min, and the sample position was 3(1) in Figure 1(B).
^{d} Gas permeation rates.
^{e} Ratios of X gas to nitrogen permeation rates.

higher values of R_{H_2}/R_{N_2} than do the plasma polymerized M_2 and D_4. In the case of furan/PP, the plasma polymer of furan is expected to have a highly crosslinked structure because of unsaturated bonds of furan, and the value of R_{H_2}/R_{N_2} is expected to be larger than that of M_2/PP. However, it shows only 9.2 and the value of R_{O_2}/R_{N_2} is also low, 1.3.

From these results, it is considered that microcracks formed in the plasma-polymerized film of furan and the cracks reduced permselectivity of the composite membrane. Therefore, it is difficult to obtain highly permselective hydrogen separation membranes from highly crosslinked plasma polymers because of the problem of formation of micro cracks. Nomura said that crack formation depended on thickness of plasma films; the number of cracks in plasma films increased with the thickness, and permselectivity of the films decreased.[12] It is necessary to make permselective layer as thin as possible, in order to solve the problem of the microcracks. As previously reported, minimum thickness of plasma polymer required to plug all pores on porous substrates and to show permselectivity was about five times larger than pore radii of the porous substrates used, irrespective of the kinds of monomers.[9,11] Therefore, it can be said that the double-layered structure is necessary to make permselective plasma films thinner and permeability of the membrane larger.

Gas Permeability of Double Layered Composite Membrane

The double layered structure composite membrane, which was composed of a porous substrate, the first layer of plasma-polymerized M_2, and the second layer of plasma-polymerized furan (hereafter denoted by furan/M_2/PP), were prepared with changing the polymerization time for the second layer, 5, 10, and 20 min. The gas permeability characteristics were measured. Effects of the polymerization time on gas permeability of the membranes were shown in Figure 3. The R_{H_2}/R_{N_2} increased drastically to over 30 by formation of the second layer for only 5 min, and increased gradually with increasing the polymerization time for furan, whereas R_{H_2} decreased slightly. It was found that hydrogen permselectivity of the composite membranes could be improved by the formation of the second layer. This appearance of high permselectivity for hydrogen in the furan/M_2/PP is attributed to high permselectivity of the second layer without the micro cracks.

Figure 4 shows a typical electron micrograph of the double-layered structure composite membrane of furan/M_2/PP (polymerization time for the second layer was 5 min). This double-layered structure can be observed from the SEM photograph. The hydrogen permselectivity (R_{H_2}/R_{N_2}) was improved from 9 to 37 by the formation of the second layer, which was thin, about 1000 Å in thickness. From these results, it is found that the double-layered structure can make the permselective layer thinner.
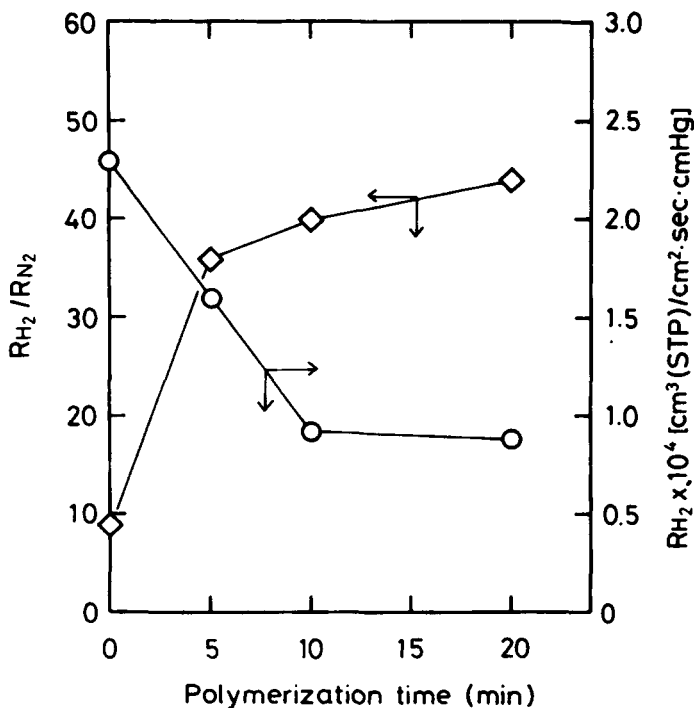
Fig. 3. Hydrogen permeation rate R_{H_2} and ratio of hydrogen to nitrogen permeation rates R_{H_2}/R_{N_2} vs. polymerization time for the second layer formation from furan: Plasma polymerized M_2 was deposited as the first layer on the porous substrate, and plasma-polymerized furan was deposited as the second layer at the position 1 in Figure 1(B).

TABLE II
Gas Permeability of Double Layered Composite Membranes

| Monomer | $R_X \times 10^{-6}$ (cm³ (STP)/cm² s cm Hg) $[R_X/R_{N_2}]$ | | | | |
	O_2	N_2	H_2	He	CH_4
1-Hexene	13 [4.2]	3.1	94 [30]	81 [26]	3.7 [1.2]
Cyclohexene	11 [3.4]	3.2	137 [43]	—	—
Toluene	6.5 [3.3]	2.0	77 [39]	—	—
Styrene	2.9 [3.9]	0.75	32 [43]	32 [43]	1.3 [1.7]
Divinylbenzene	21 [4.4]	4.8	164 [34]	139 [29]	5.6 [1.2]
1,3-Pentadiene	20 [4.2]	4.8	134 [28]	108 [23]	6.8 [1.4]
1,3-Cyclohexadiene	4.0 [3.3]	1.2	43 [36]	39 [33]	1.4 [1.2]
Acetylene	4.4 [2.4]	1.8	95 [53]	93 [52]	1.7 [0.9]
1-Heptyne	15 [3.4]	4.4	95 [22]	78 [18]	6.8 [1.5]
Acrylic acid	30 [3.3]	9.2	179 [20]	142 [15]	1.2 [1.3]
Ethyl acrylate	9.5 [4.1]	2.3	104 [45]	—	—
Acetylenecarboxylic acid	4.9 [1.5]	3.3	58 [18]	59 [18]	3.7 [1.1]
Furan	6.0 [3.8]	1.6	77 [48]	75 [47]	1.5 [0.9]
Benzonitrile	21 [4.0]	5.2	170 [33]	142 [27]	6.4 [1.2]
Allylamine	3.4 [1.1]	3.0	40 [13]	—	—
M_2	71 [2.8]	25	230 [9.2]	170 [6.8]	57 [2.3]
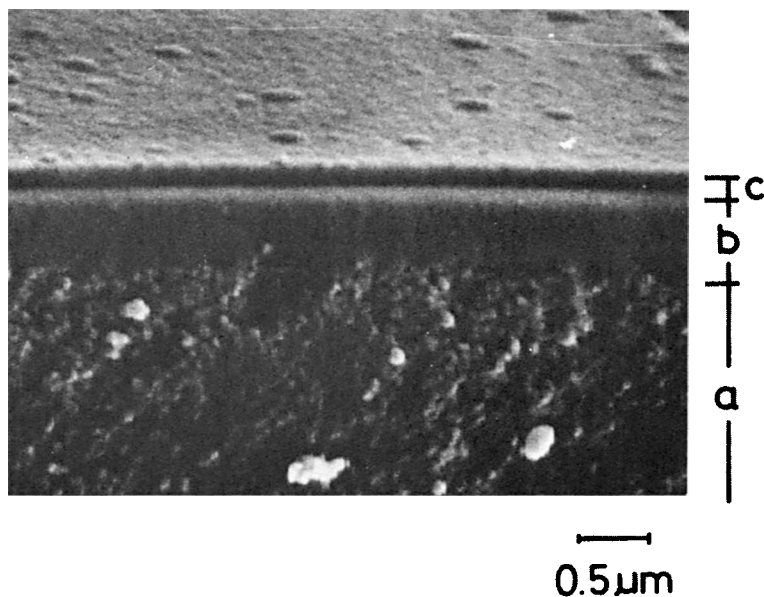
Fig. 4. SEM photograph of a cross section of the double layered structure composite membrane: (a) the porous substrate which was a porous glass hollow fiber[11]; (b) the first layer prepared from M_2 under the polymerization conditions that monomer pressure was 0.2 torr, RF power was 50 W, and polymerization time was 15 min; (c) the second layer prepared from furan under the conditions that pressure was 0.2 torr, RF power was 50 W, and polymerization time was 5 min.

Monomers for the second layer and polymerization time were changed, and the double layered structure composite membranes were prepared. The gas permeability properties of the membranes were shown in Table II. The values in Table II were those of the membranes which showed the highest value of R_{H_2}/R_{N_2}. It was found that almost all of the monomers improved the hydrogen permselectivity, especially cyclohexene, acetylene, ethyl acrylate, and furan. On the other hand, the membranes prepared from the carboxylic acids and allylamine showed small values of R_{H_2}/R_{N_2}, and those prepared from the open chain compounds had relatively small values. The reason why hydrogen permselectivity depends on the monomer is not clear; however, it seems that hydrogen permselectivity is affected by the degree of crosslinkage and the number of cracks.

CONCLUSION

The double-layered structure could make the second layer thinner than the first layer, which had to be thick enough to plug the pores on the porous substrates. Organosilicic compound M_2 was employed as the monomer for the first layer showing high permeability, and organic compounds, such as furan, acetylene, cyclohexene, and so on, were employed as the monomers for the second layer showing high permselectivity. In these systems, composite membranes with high separation characteristics and high flux could be prepared, for example, they showed R_{H_2} of over 10^{-4} cm^3 (STP)/cm^2 s cm Hg and R_{H_2}/R_{N_2} of over 40.

References

1. J. Goodman, *J. Polym. Sci.*, **44**, 551 (1960).
2. H. Yasuda, *J. Polym. Sci., Macromol. Rev.*, **16**, 199 (1981).
3. M. Shen, Ed., *Plasma Chemistry of Polymers*, Dekker, New York, 1976, p. 1.
4. Y. Segui and Bui Ai, *J. Appl. Polym. Sci.*, **20**, 1611 (1976).

5. M. J. Vasile and G. Smolinsky, *J. Electrochem. Soc.*, **119**, 451 (1972).
6. A. F. Stancel and A. T. Spencer, *J. Appl. Polym. Sci.*, **16**, 1505 (1972).
7. A. S. Chawla, *Artificial Organs*, **3**, 92 (1979).
8. M. Yamamoto, J. Sakata, and M. Hirai, *J Appl. Polym. Sci.*, **29**, 2981 (1984).
9. J Sakata, M. Yamamoto, and M. Hirai, *J. Appl. Polym. Sci.*, **31**, 1999 (1986).
10. J. Sakata, M. Yamamoto, and I. Tajima, *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 1721 (1988).
11. J. Sakata, M. Hirai, and M. Yamamoto, *J. Appl. Polym. Sci.*, **34**, 2701 (1987).
12. H. Nomura, P. W. Krammer, and H. Yasuda, *Thin Solid Films*, **118**, 187 (1984).
13. M. Yamamoto, M. Hirai, and J. Sakata, U.S. Pat. 4,410,338 (1983).

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