

Gas Permeabilities of Poly(trimethylsilylpropyne) Membranes Surface Modified with CF₄ Plasma

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SYNOPSIS

Surface fluorination of poly(trimethylsilylpropyne) (PTMSP) membranes by CF₄ plasma was studied. The surface fluorination of the membranes was carried out in an atmosphere of CF₄ in a capacitively coupled discharge apparatus with external electrodes. Dramatic increase in selectivity (P_{O_2}/P_{N_2}) was observed. The effect of fluorination conditions such as duration of treatment and discharge power on the permeabilities of the membranes was studied. X-ray photoelectron spectrometric data of modified PTMSP membranes showed a drastic alternation in the surface layer. The P_{O_2} and P_{O_2}/P_{N_2} of the membranes were observed to be dependent on the F/C atomic ratio. At F/C > 1, the P_{O_2}/P_{N_2} value of the membranes could be more than four. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(trimethylsilylpropyne) (PTMSP) was first synthesized in 1983 by Masuda et al.¹ and was reported to exhibit highest gas permeability among all existing polymers. The P_{O_2} value of PTMSP at 25°C reached 6000 barrer (compared with 800 barrer for silicone rubber PDMS). On the other hand, PTMSP possessed relatively poor selectivity, the oxygen/nitrogen separation factor of the polymer being 1.6–1.8, and the permeability of unmodified PTMSP decreased significantly over time. Since then, much effort has been expended to study the modification of PTMSP and to improve its selectivity as well as stability of permeation rate over time.^{2–8} Surface fluorination of PTMSP membrane by dilute gaseous fluorine in nitrogen at room temperature enhancing the selectivity P_{O_2}/P_{N_2} to 5.1 has been reported.⁵

Plasma fluorination is a potentially attractive method for obtaining poly(tetrafluoroethylene)-like surface properties. Polyethylene and polypropylene membranes were exposed to SF₆, CF₄, and C₂F₆ plasma.⁹ None of these gases polymerized in the plasma. However, all plasma treatments grafted flu-

orinated functionalities directly to the polymer surface. A fluorocarbon layer on the polymer surface was obtained without affecting the bulk properties of the material. The use of such surface functionalization by plasma, as it applies to gas permeation properties, has not been reported.¹⁰ In this article, surface fluorination of PTMSP membranes by CF₄ plasma was studied. The selectivity P_{O_2}/P_{N_2} of PTMSP membrane was obviously enhanced with retention of appropriate permeability.

EXPERIMENTAL

Tetrafluoromethane (CF₄), 99.7% in purity, was provided by the Experimental Plant of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The PTMSP was obtained from Sanyo Chemical Industries (Kyoto, Japan). Membranes of PTMSP were obtained by casting a 3% toluene solution on a glass plate. The membranes were dried for one week at room temperature to permit slow evaporation of most of the solvent. The residual solvent was completely removed *in vacuo*. The thickness of the dried membranes was about 20 μm.

Plasma treatment was carried out in a capacitively coupled reaction system with external electrodes. A schematic diagram of the reaction appa-

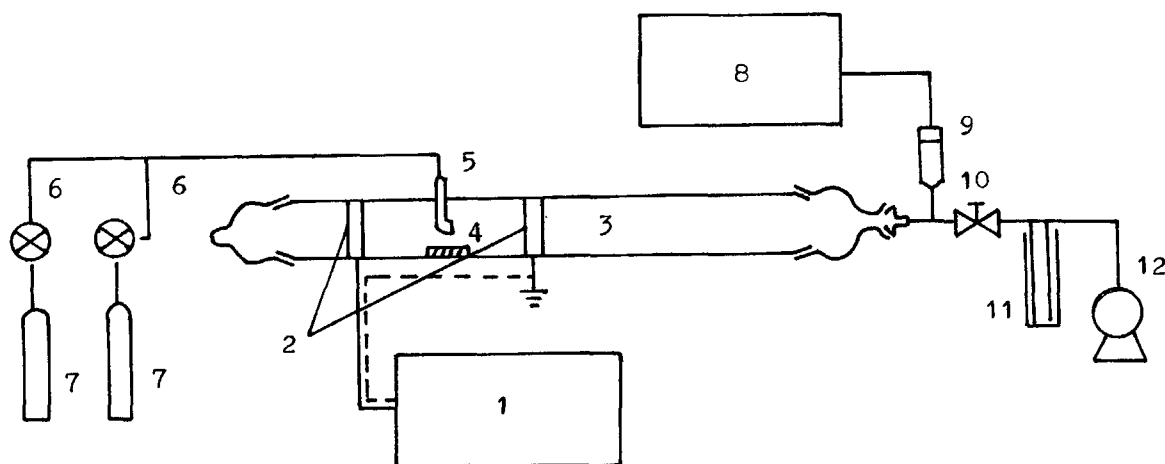


Figure 1 Schematic diagram of the plasma treatment equipment. (1) RF plasma generator; (2) electrodes; (3) reactor; (4) substrate; (5) monomer inlet; (6) needle valve; (7) monomer source; (8) vacuum gauge; (9) thermister; (10) outlet valve; (11) liquid nitrogen trap; (12) rotary pump.

ratus is shown in Figure 1. The Pyrex glass reactor (500 mm long, 45 mm i.d.) for plasma treatment was fitted with a monomer inlet, pressure gauge, vacuum system, and matching network for inductive coupling of a 13.56 MHz radiofrequency (RF) source. Two copper electrodes (15 mm wide) were wrapped around the outer wall of the reactor; one end of the RF power supply was located at 10 cm from the monomer inlet and the grounded supply

was placed at 10 cm distant. Prior to the plasma treatment, the reactor system was evacuated to 2×10^{-3} torr with a rotary pump and flushed twice with CF_4 gas. The CF_4 vapor was then introduced into the reactor until the pressure was adjusted to 0.1 torr. The plasma treatment was carried out according to given conditions.

Permeability coefficients were determined at 25°C on a K-315-N-03 gas permeability apparatus

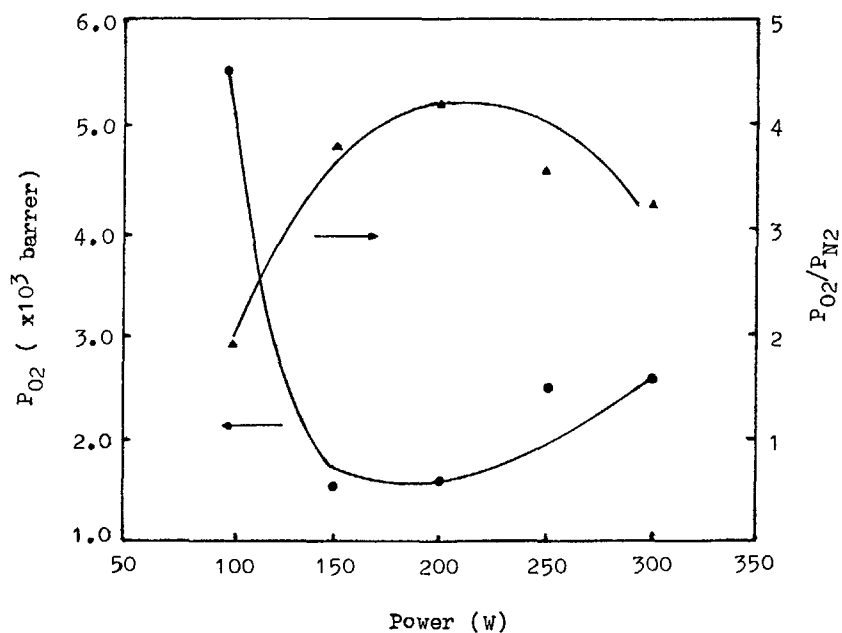


Figure 2 The effect of plasma discharge power on gas permeabilities of PTMSP membranes. Treatment time: 180 s.

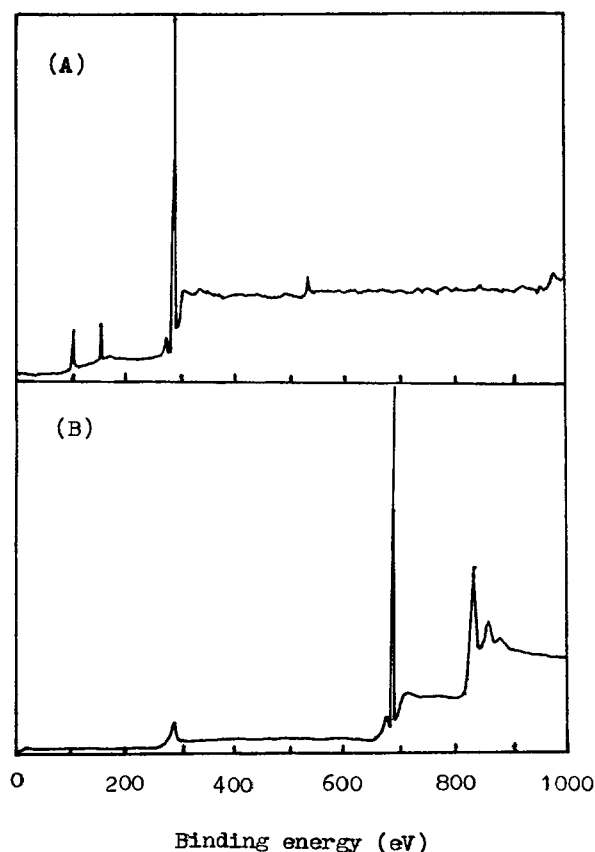


Figure 3 XPS broad scan spectra of untreated (A) and plasma treated (B) PTMSP membranes.

(Rikaseiki Co., Japan) equipped with a MKS baratron pressure transducer. Both sides of the membrane were evacuated for several hours to about 10^{-2} torr, the gas to be measured was introduced to the upstream side at 1 atm, and the increase in pressure of the downstream side with a definite volume was monitored and recorded. Permeation coefficients P were calculated from the slope of the pressure-time plot after steady state had been established. The X-ray photoelectron spectra (XPS) of the membranes were taken using a Lab-Mark II X-ray photoelectron

spectrometer operated at a pass energy of 10 kV-20 mA with a $MgK\alpha$ x-ray source. XPS experiments were performed at a collection angle of 60° .

RESULTS AND DISCUSSION

Effect of Plasma Discharge Power on Gas Permeability of PTMSP Membranes

The P_{O_2} value and the P_{O_2}/P_{N_2} ratio of the unmodified PTMSP membrane were 7740 barrer and 1.35, respectively. Figure 2 showed the effect of plasma discharge power on gas permeabilities of PTMSP membrane. The P_{O_2}/P_{N_2} ratio increased with increasing plasma discharge power, but the P_{O_2} value decreased. At a discharge power of 200 W, the P_{O_2}/P_{N_2} ratio reached a maximum of 4.17, and the P_{O_2} value decreased to 1530 barrer. It was determined that the effect of plasma ablation was gradually increased, which is unfavorable to the formation of a dense ultrathin layer. Also, too high a discharge power results in microcracking in the surface layer. Therefore, when discharge power exceeded a certain critical value, the P_{O_2} value increased while the P_{O_2}/P_{N_2} ratio decreased. Similar conclusions regarding microcracking has been obtained by other authors.^{11,12}

Figure 2 shows the P_{O_2}/P_{N_2} ratio to be drastically enhanced with retention of high permeability. This indicated that the surface structure of PTMSP membranes was significantly altered. XPS study provides important chemical information about the top most layer of the sample surface (50–100 Å) and was used to characterize the surface of fluorinated PTMSP membranes. Figure 3 showed the broad scan XPS spectra of plasma-treated and untreated membranes. After fluorination, a single peak at 690 eV corresponding to the F_{1s} electron was present, the C_{1s} signal was decreased, and the Si_{2p} and Si_{2s} signals became barely observable, indicating the elimination of trimethylsilyl groups during plasma fluorination similar to the case of gaseous fluori-

Table I XPS Elemental Analysis of PTMSP Membrane Surface^a

Power (W)	Si/C	O/C	F/C	Si, %	C, %	O, %	F, %
—	0.16	0.031	—	13.7	83.7	2.6	—
100	0.15	0.20	0.18	9.8	65.4	13.1	11.8
150	0.07	0.13	0.92	3.3	47.2	6.1	43.4
250	0.01	0.05	0.94	0.50	50.0	2.5	47.0
300	0.03	0.04	0.95	1.5	49.5	2.0	47.0

^a Monomer pressure 13.3 Pa; Duration: 180 s.

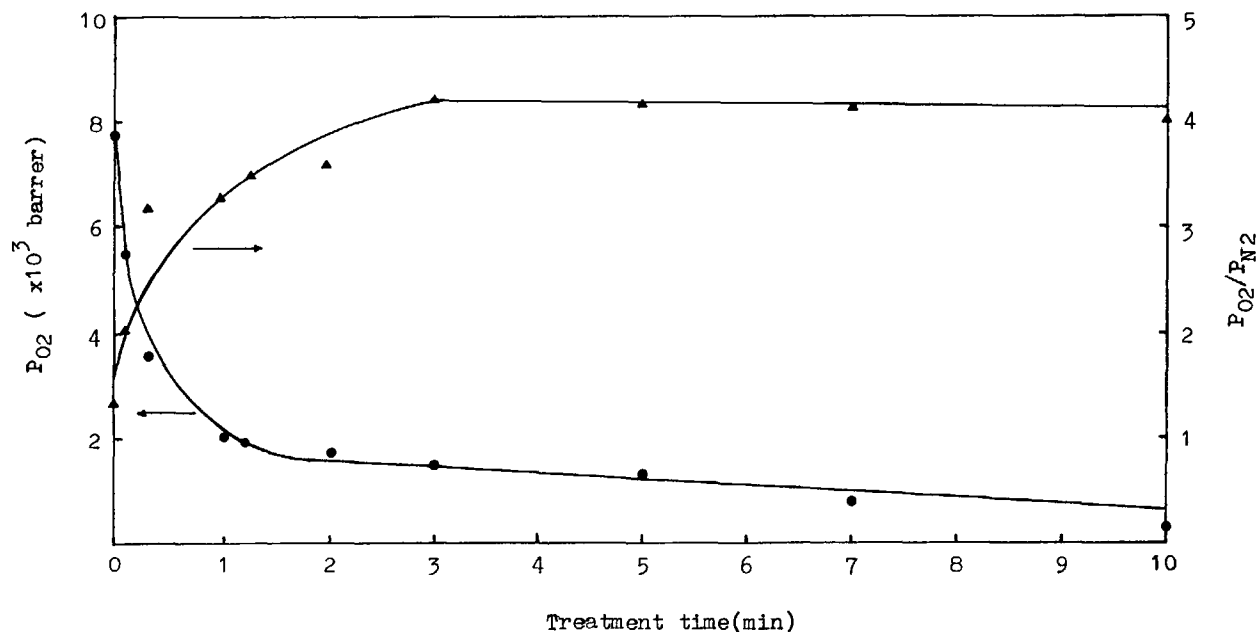


Figure 4 The effect of plasma treatment on gas permeabilities of PTMSP membranes. Discharge power: 200 W.

nation.⁵ However, on the high resolution Si_{2p} spectra, the content of Si residual on membrane surfaces can still be estimated and was shown in Table 1 as a function of discharge power. Introduction of fluorine atoms and the double bond opening resulted in a much denser structure. These structural changes caused the enhancement of oxygen/nitrogen selectivity of treated membranes.

Effect of Duration of Plasma Treatment on Gas Permeabilities of PTMSP Membranes

Effect of plasma treatment time on gas permeabilities of PTMSP membranes is shown in Figure 4. The P_{O_2} value gradually decreased with increasing duration of plasma treatment, but the $P_{\text{O}_2}/P_{\text{N}_2}$ ratio obviously increased. The $P_{\text{O}_2}/P_{\text{N}_2}$ ratio reached a maximum value at 180 seconds of treatment, but

changed very little with longer treatment time; however, the P_{O_2} value continued to decrease. This can be explained by the following: The surface structure and the physical morphology were changed gradually during plasma treatment. A continuous fluorinated surface layer was formed at certain durations of plasma treatment, giving high selectivity with lower permeability. Further fluorination, exceeding the critical value, increased only the thickness of the surface fluorinated layer, resulting in a continuous decrease of the P_{O_2} value; however, the $P_{\text{O}_2}/P_{\text{N}_2}$ ratio remained unchanged after reaching the maximum value.

XPS data showed that the $P_{\text{O}_2}/P_{\text{N}_2}$ ratio of the membranes was strongly dependent on the F/C atomic ratio of the surface layer (cf. Table II), which was increased gradually with the increase of duration of plasma treatment. For $P_{\text{O}_2}/P_{\text{N}_2}$ ratio exceeding

Table II XPS Elemental Analysis of PTMSP Membrane Surface^a

Duration (s)	Si/C	O/C	F/C	Si, %	C, %	O, %	F, %
7	0.01	0.05	1.01	0.48	48.3	2.4	48.8
20	0.08	0.17	0.50	4.6	57.1	9.7	28.6
80	0.05	0.17	0.67	2.6	52.9	9.0	35.4
120	0.02	0.04	1.00	0.97	48.5	1.9	48.5
300	0.01	0.05	1.05	0.47	47.4	2.4	49.8
600	0.02	0.06	1.06	0.93	46.7	2.8	49.5

^a Discharge power: 200 W; Monomer pressure: 13.3 Pa.

Table III Permeance of Fluorinated Surface Layer of PTMSP Membrane^a

Duration (s)	Surface J_{O_2}	Permeance J_{N_2}	J_{O_2}/J_{N_2} ^b
7	117	31.7	3.69
20	36.4	7.77	4.68
60	15.2	4.08	3.73
80	15.9	3.76	4.23
120	14.1	3.21	4.39
180	12.9	2.65	4.87
300	10.0	2.11	4.74
600	2.01	0.49	4.10

^a Discharge power: 200 W; Monomer Pressure: 13.3 Pa.

^b J in $\text{cc(STP)/cm}^2 \text{ s cmHg} \times 10^{-5}$.

4, the F/C atomic ratio was over 1, and the fluorine content in the surface layer reached 50%.

Surface Permeance of the Fluorinated Layer of PTMSP Membranes

PTMSP membranes were fluorinated by CF_4 plasma and a fluorocarbon layer on polymer surface was

obtained without affecting the bulk properties of PTMSP. Thus, the treated membrane can be considered as being composed of two distinct layers, and by using a series resistance model,^{13,14} the surface permeance of the fluorinated layer $[P/l]_s$ can be calculated as:

$$1/[P/l]_s = 1/[P/l]_o - 1/[P/l]_b$$

where P and l denote the permeability coefficient and the thickness, respectively, and the subscripts: o , b , and s referred to the overall composite membrane, the bulk and the fluorinated surface layer, respectively. Since l_s is much smaller than l_b , it may be a fairly good approximation to assume that l_o was nearly equal to l_b . Then, the surface permeance of the fluorinated layer could be calculated for each gas penetrant using the series resistance model above. The results was shown in Table III. Compared with the original membrane, the fluorinated layer had high P_{O_2}/P_{N_2} ratio, and the selectivity of composite membrane depended mainly on the selectivity of the fluorinated layer.

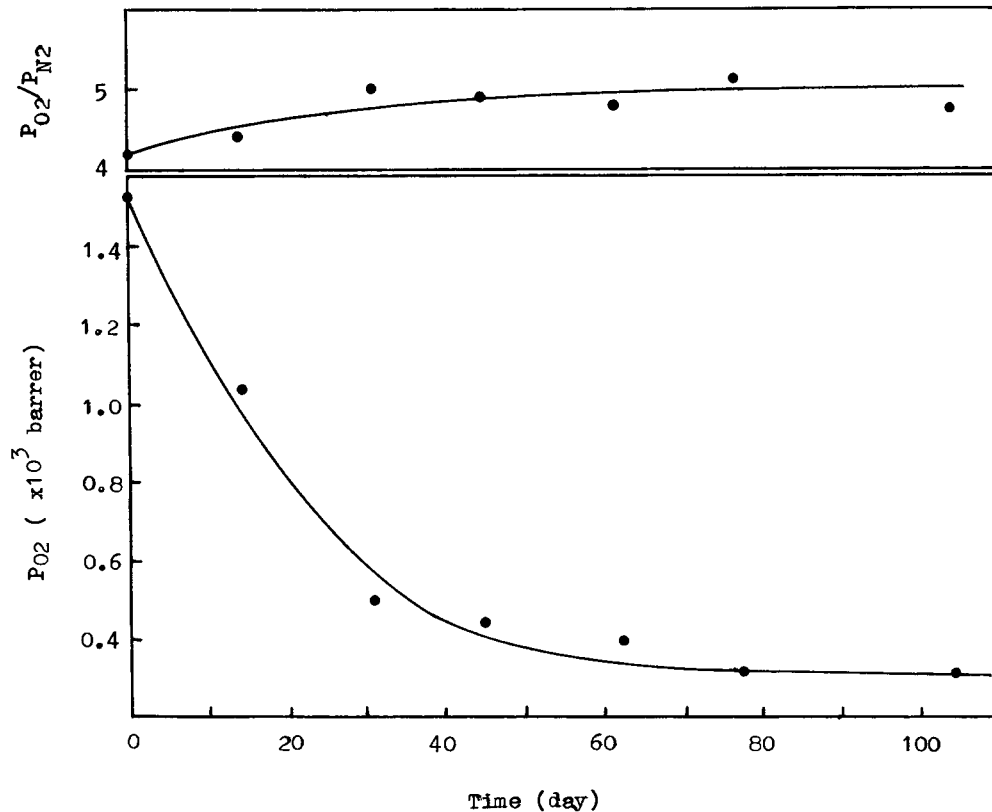


Figure 5 Time dependence of oxygen permeability coefficient of modified PTMSP membrane.

Stability of Gas Permeability Coefficient of Modified PTMSP Membranes in Time

Some decrease in oxygen permeability coefficient of plasma modified membrane kept at room temperature in air was also observed (Fig. 5). The P_{O_2} value decreased fastly in the initial period, and the P_{O_2}/P_{N_2} ratio increased at the same time. After 50 days, the P_{O_2} reached a stable value. After 104 days, the P_{O_2} value was 307 barrer and the P_{O_2}/P_{N_2} was 4.70. The oxygen permeability coefficient of modified PTMSP was at the same level as PDMS, but the P_{O_2}/P_{N_2} was much higher.

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REFERENCES

1. T. Masuda, E. Isobe, and T. Higashimura, *J. Am. Chem. Soc.*, **105**, 7473 (1983).
2. JP 86-268745.
3. JP 89-67210.
4. JP 86-35824.
5. M. Langsam, M. Anad, and E. J. Karwacki, *Gas Separ. Purif.*, **2**, 162 (1988).
6. T. Nakagawa, T. Saito, S. Asakawa, and Y. Saito, *Gas Separ. Purif.*, **2**, 3 (1988).
7. Yu. Nagase, T. Ueda, K. Matsui, and M. Uchikura, *J. Polym. Sci., Polym. Phys.*, **29**, 171 (1991).
8. T. Aoki and E. Oikawa, *J. Membrane Sci.*, **57**, 207 (1991).
9. M. Strobel, S. Corn, C. S. Lyone, and G. A. Korba, *J. Polym. Sci., Polym. Chem.*, **25**, 1295 (1987).
10. P. W. Kramer, Y. S. Yeh, and H. Yasuda, *J. Membrane Sci.*, **46**, 1 (1989).
11. H. Nomura, P. W. Kramer, and H. Yasuda, *Thin Solid Film*, **118**, 187 (1984).
12. C. P. Ho and H. Yasuda, *J. Appl. Polym. Sci.*, **8**, 1541 (1990).
13. R. M. Barrer, in *Diffusion in Polymers*, J. Crank and G. S. Park Eds., Academic Press, New York, 1975.
14. J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1975.

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