Gas Permeabilities of Poly(trimethylsilylpropyne) Membranes Surface Modified with CCl_4 Plasma

INTRODUCTION

Gas separation by membrane methods is an interesting subject from the energy saving point of view. The oxygen enrichment of air has attracted special attention. Gas separation membranes for oxygen enrichment require a high oxygen permeability coefficient. Generally available membrane materials do not meet the fundamental properties for oxygen enrichment: if a membrane material has a high oxygen permeability coefficient, it usually gives too low a separation factor, and vice versa.[1,2]

Gas separation properties are dependent on the structure of the polymer that composes the membrane. Many efforts have been directed at the development of new polymer materials with high permeabilities and permselectivities.[3,4] Recently special attention has also been paid to surface modification of existing polymers for improving the gas separation properties of membranes,[5-7] especially surface fluorination.[8-14] For example, surface fluorination of poly(trimethylsilylpropyne) (PTMSP) membrane by dilute gaseous fluorination in nitrogen at room temperature enhancing the selectivity P_{O_2}/P_{N_2} from 1.5 to 5 has been reported.[8] Mohr et al. also reported that the permselectivities of poly(4-methyl-1-pentene) and polysulfone membranes are significantly improved by a gas fluorination process.[12-14] Up to now, the effect of surface photochlorine on permeability of polymer membranes has been reported by Nakagawa and Yamada,[15] although the substantial chlorination of polyethylene and polypropylene has been studied widely under a variety of conditions in the presence or absence of light for the main purpose of improving impact strength, adhesion, and hydrophilicity.[16-18]

In our previous article we reported that the surface fluorination of PTMSP membranes by CF_4 plasma improves its selectivity.[19] The present work deals with the effect of CCl_4 plasma treatment on the permeability of PTMSP membranes.

EXPERIMENTAL

Carbon tetrachloride (analytical grade) was provided by Tianjing Chemical Plant and used without further purification. 1-Trimethylsilyl-1-propyne was prepared from organomagnesium compounds of propyne (using the Grignard reaction) and trimethylchlorosilane. The monomer was polymerized in toluene solution over $TaCl_5$ as catalyst.[20] Membranes of PTMSP were obtained by casting a 3% toluene solution on a glass plate. The membranes were dried at room temperature for a week to evaporate most of the solvent slowly, and the residual solvent was completely removed *in vacuo*. The thickness of the dried membranes was about 30 μm.

Plasma treatment was carried out in a capacitively coupled reaction system with external electrodes. A schematic diagram of the reaction apparatus was the same as reported elsewhere.[19] Radiofrequency (RF) power at a fixed frequency of 13.56 MHz was supplied to the plasma reactor by a Model GP 300-1 generator. The level of RF power (up to 300 W) could be changed continuously, and was kept constant at a selected value for a given time. Two copper electrodes were wrapped around the outer wall of the reactor; the one connecting the RF power supply, located 10 cm from the first, was grounded. Prior to plasma treatment, the reaction system was evacuated to 2×10^{-3} torr with a rotary pump and flushed twice with argon gas. The monomer gas was then introduced into the reactor until the pressure reached a selected value. 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 (Rikaseiki Co., Japan) equipped with an 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 and 20 mA with a MgK X-ray source. XPS experiments were performed at a collection angle of 60°.

RESULTS AND DISCUSSION

Elemental Composition of CCl_4 Plasma Treated Membranes

It is well known that plasma treatment only modifies the surface structure and properties of polymeric materials.[21]

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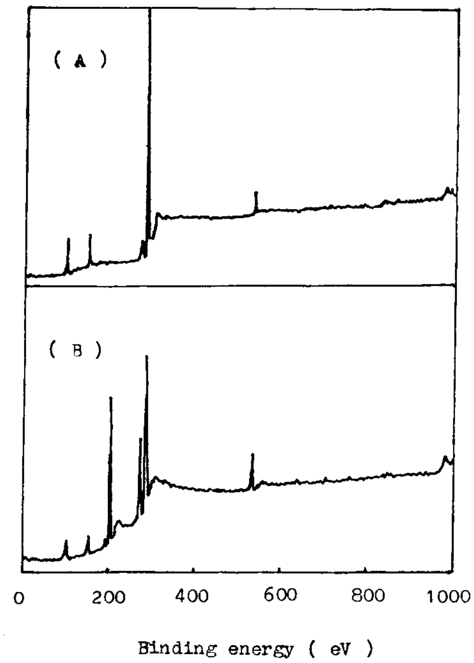

Figure 1 XPS broad scan spectra of (A) untreated and (B) plasma treated PTMSP membranes.

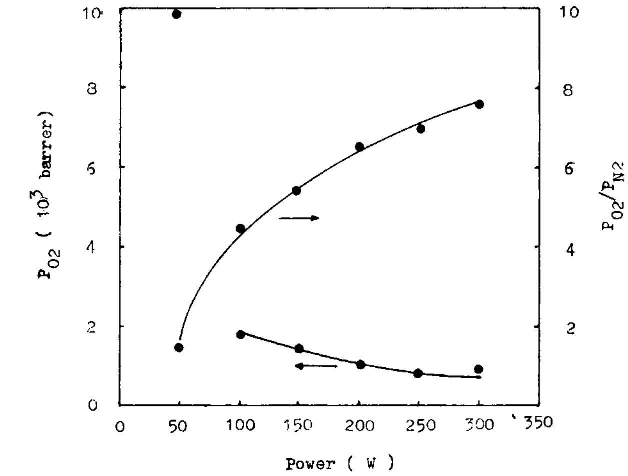

Figure 2 The effect of plasma discharge power on gas permeabilities of PTMSP membrane. Treatment time 180 s.

The surface sensitivity of XPS makes it particularly suited to characterize this surface structural change. Figure 1 shows the typical broad scan XPS spectra of plasma treated and untreated membranes. After CCl_4 plasma treatment, two single peaks at 206 and 277 eV corresponding to the Cl_{2P} and Cl_{2S} were present, the C_{1S} signal was decreased. Compared with the CF_4 plasma treatment,[19] the stronger Si_{2P} and Si_{2S} signals were also observed, which indicated that less elimination of trimethysily groups during the CCl_4 plasma treatment. The elemental compositions of the membranes determined from the signal intensities of XPS spectra are shown in Table I. From Table I, the Cl/C atomic ratio for CCl_4 plasma treated PTMSP membranes are influenced by either plasma discharge power or plasma treatment duration.

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 membranes were 9922 barrer and 1.4, respectively. Figure 2 shows the effect of plasma discharge power on gas permeabilities of PTMSP membranes. 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 300 W, the P_{O_2}/P_{N_2} ratio reached 7.53, and the P_{O_2} value decreased to 922 barrer. However, in the case of CF_4 plasma treatment, the P_{O_2}/P_{N_2} ratio of CF_4 plasma treated PTMSP membrane reached a maximum of 4.17 at a discharge power of 200 W, and then the P_{O_2}/P_{N_2} ratio decreased with increasing discharge power.[19] We considered

Table I XPS Elemental Analysis of PTMSP Membrane Surface

Plasma Treatment						Gas Permeability (barrer)	
Time (min)	Pressure (torr)	Power (W)	Cl/C	Si/C	O/C	P_{O_2}/P_{M_2}	P_{O_2}
—	—	—	—	0.16	0.03	1.40	9922
3	0.1	50	0.14	0.15	0.16	1.44	9920
1	0.1	100	0.07	0.16	0.10	1.96	8830
3	0.1	100	0.35	0.10	0.22	4.37	1670
5	0.1	100	0.70	0.05	0.17	6.26	1010
7	0.1	100	0.63	0.07	0.14	6.80	521
3	0.1	150	0.45	0.06	0.25	5.37	1360
3	0.1	200	0.43	0.08	0.17	6.49	1013
3	0.1	250	0.48	0.10	0.16	6.93	698
3	0.1	300	0.39	0.09	0.29	7.53	922

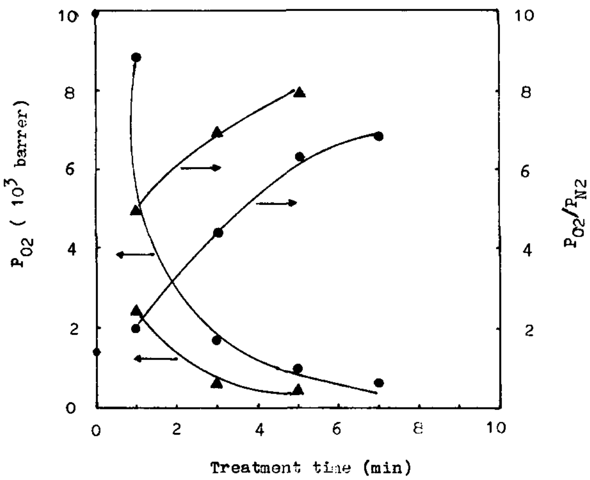

Figure 3 The effect of plasma treatment time on gas permeabilities of PTMSP membrane. Discharge power (●) 100 W and (▲) 250 W.

that this phenomena resulted from the different effect of plasma ablation. As mentioned above, the stronger Si_{2P} and Si_{2S} signals of CCl_4 plasma treated membrane were observed compared with the CF_4 plasma treatment. This result indicated that surface ablation with CCl_4 plasma is less than that with CF_4 plasma. In the case of CF_4 plasma treatment, the stronger plasma ablation, especially the high discharge power, was unfavorable to the formation of a dense ultrathin layer, which resulted in a decrease of P_{O_2}/P_{N_2} ratio.

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 3. The P_{O_2}/P_{N_2} ratio increased rapidly in the first few minutes of plasma treatment. As expected, the general tread of an increasing gas selectivity associated with a decreasing permeability coefficient was observed in this system similar to the other value reported.[22] The Cl/C atomic ratio of PTMSP membranes treated by CCl_4 plasma at plasma discharge power of 100 W also increased with increasing duration of plasma treatment (cf. Table I). This indicated that the P_{O_2}/P_{N_2} ratio of the membranes was related to the Cl/C atomic ratio of the surface layer. In addition, the P_{O_2}/P_{N_2} ratio of the membranes was also related to plasma discharge power. At plasma discharge power of 300 W and plasma treatment time of 3 min, the P_{O_2}/P_{N_2} ratio of the membrane was 7.53 with the Cl/C atomic ratio of 0.41. Surface crosslinking of a membrane exposed to a chemical reaction plasma takes place in addition to functionalization of the polymer surface.[22] The increasing crosslinking of the membrane surface with increasing discharge power caused an increase of the gas permselectivity. Introduction of chlorination atoms and surface crosslinking resulted in a much denser structure. These structural changes caused the enhancement of oxygen/nitrogen selectivity of treated membranes.

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