Gas Permeability of NH_3-Plasma-Treated Poly(methyl methacrylate) Membranes

Y. Yamamoto, M. Maegawa, H. Kumazawa

Department of Chemical and Process Engineering, Toyama University, 3190 Gofuku/Toyama 930-8555, Japan

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ABSTRACT: The effect of NH_3 plasma treatment on glassy poly(methyl methacrylate) (PMMA) membranes on the diffusion process for penetrant gases (CO_2, O_2, and N_2) was investigated from mean permeability data. The mean permeability coefficient for CO_2 definitely depended on the upstream pressure, whereas those for O_2 and N_2 remained constant regardless of the upstream pressure. For O_2 transport, the permeability increased a little with increasing treatment power, and for N_2 transport, it was not affected by the treatment power. For CO_2 transport, NH_3 plasma treatment promoted the transport of Langmuir mode, presumably through an increased Langmuir capacity constant for CO_2. NH_3 plasma treatment for PMMA membranes resulted in an increase in the separation factor of CO_2 relative to N_2 and in the permeability to CO_2. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1068–1072, 2003

Key words: gas permeation; membranes; plasma treatment

INTRODUCTION

Carbon dioxide has been recognized as one of the most influential greenhouse gases because it is exhausted in massive amounts. Fossil fuel combustion facilities are one typical emission source. To prevent atmospheric buildup of CO_2, its fixation and removal has been examined; one possible process for this purpose is membrane separation. It was expected that the surface modification of the membrane by plasma treatment would induce an increase in the permselectivity of CO_2 relative to N_2.

In our preceding work,[1] NH_3 plasma treatment was used as a way to modify the surface of the glassy polymer membrane because of an expected increase in the permselectivity for CO_2 relative to N_2. Poly(phenylene oxide) (PPO) membranes, which have high chemical and thermal stability, were employed as the base glassy polymer membranes. For O_2 transport, NH_3 plasma treatment on the PPO membrane had an influence on the diffusion process of Henry's law species, whereas for CO_2 transport, it promoted the transport of Langmuir mode, presumably through an increased Langmuir capacity constant (C_H') for CO_2. It was desirable that this speculation for CO_2 transport through an NH_3-plasma-treated glassy polymer membrane be confirmed for other glassy polymer membranes.

Correspondence to: H. Kumazawa (kumazawa@eng.toyama-u.ac.jp).

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In this work, NH_3 plasma treatment was applied to glassy poly(methyl methacrylate) (PMMA) membranes, which exhibit a high permeability to CO_2. The effects of NH_3 plasma treatment on the diffusion processes of Henry's law and Langmuir modes in PMMA membranes were estimated from the permeability measurements. The degree of improvement of permselectivity for CO_2 relative to N_2 induced by NH_3 plasma treatment is discussed from the points of view of gas diffusion and dissolution processes.

EXPERIMENTAL

Membrane preparation

Homogeneous dense PMMA membranes were prepared by the casting of a solution of 25 cm^3 of acetone in which 10.7 g of PMMA resin was dissolved on a flat glass plate.

Plasma treatment

The plasma treatment was performed in a flow-type cylindrical plasma reactor with an external electrode (Yamato, PR-510A; Tokyo, Japan), which was used in our preceding work.[1] The internal diameter and length of the reactor were 21.5 and 27.5 cm, respectively. NH_3 balanced with N_2 up to 2010 ppm was used as the treatment gas, and the flow rate was maintained at 10 cm^3 (STP)/min. The glow discharge was generated under a pressure of 0.5 Torr (mm He) at a fixed frequency of 13.56 Hz. The electric power of discharge was varied up to 80 W. The duration ranged up to 1 min.

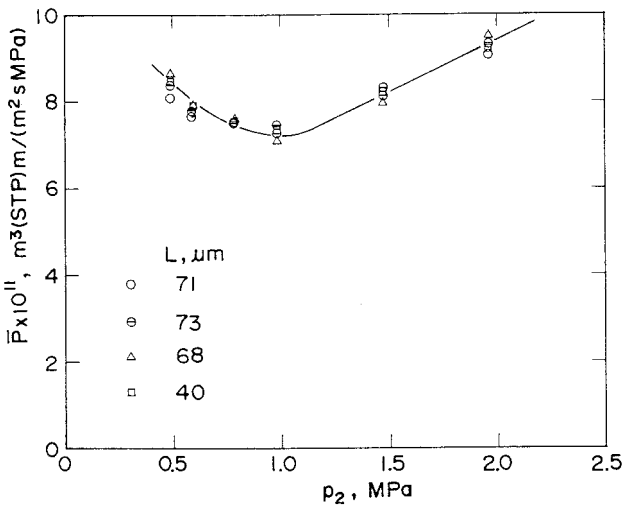

Figure 1 Pressure dependence of *P*s for CO_2 in PMMA membranes of different thicknesses at 30°C.

Measurements of steady-state permeation rates

The steady-state permeation rates for CO_2, O_2, and N_2 through dense PMMA membranes with and without NH_3 plasma treatment were measured by the variable-volume method used by Stern et al.[2] The gas to be permeated was fed into the upstream side, whereas the downstream side was filled with the same gas at 0.101 MPa. The volumetric flow rate through the membrane to the downstream side was measured by observation of the displacement of a small amount of 1-propanol in a capillary tube connected to the downstream pressure side. The mean permeability coefficient (*P*) was calculated from this steady-state permeation rate. The permeation area of the cell was 19.6 cm^2. Sorption equilibrium data for CO_2 with dense PMMA membrane samples were taken from an article by Min and Paul.[3]

RESULTS AND DISCUSSION

Figure 1 shows the pressure dependence of *P*s for CO_2 in PMMA membranes of different thicknesses. The thicknesses of membranes ranged from 40 to 73 μm. The relationship between *P* and the upstream gas pressure was almost independent of the thickness of membrane so that all of membranes prepared were believed to be dense and homogeneous. *P* decreased with increasing upstream pressure up to about 1 MPa. Such a pressure dependence of *P* may be interpreted in terms of a dual-mode mobility model. Above 1 MPa of upstream pressure, *P* increased linearly with it, and in this range, the logarithm of *P* also increased linearly with it. A linear increase in the logarithmic permeability with upstream pressure may be caused by the plasticization action of sorbed CO_2. The comparison of the observed dependence of *P* with the predictions by a dual-mode mobility model and a modified free-volume model are discussed later.

The *P*s for O_2, N_2, and CO_2 were plotted against upstream gas pressure in Figure 2. The *P*s for O_2 and N_2 substantially remained constant regardless of the upstream pressure, whereas that for CO_2 definitely depended on the upstream pressure.

As shown in Figure 3, the pressure dependencies of *P*s for CO_2 in NH_3-plasma-treated membranes at different powers of treatment were plotted under a constant duration of exposure (1 min). In the same figure, the *P*s in untreated PMMA membranes, which were averaged among the data for membranes of different thicknesses, as depicted in Figure 1, were also plotted against the upstream gas pressure. The plots for treated and untreated membranes exhibited similar curves, which shifted upward with increasing treatment power. Above 1.0 to 1.2 MPa of upstream pressure, the logarithmic permeability coefficients in treated and untreated membranes increased linearly with it. *P*s for O_2 and N_2 in PMMA membranes treated at different powers with a constant duration of exposure (1 min) are plotted against the upstream pressure in Figure 4. All of the *P*s were almost independent of upstream pressure. For O_2 transport, the permeability increased a little with increasing treatment power, whereas for N_2 transport, it was not affected by the treatment power.

In Figures 1–3, *P*s for CO_2 decreased with increasing upstream pressure up to about 0.9 MPa, presumably characteristic of glassy polymers. Thus, it was checked

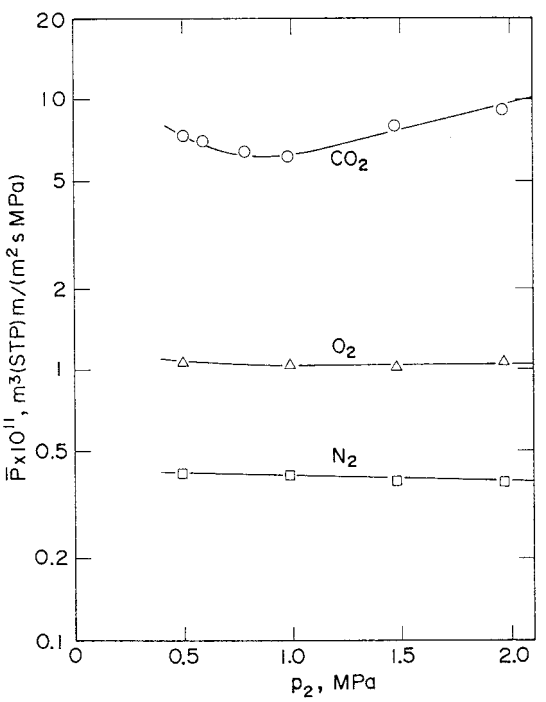

Figure 2 Relations of *P*s for CO_2, O_2, and N_2 in PMMA membrane to upstream gas pressure at 30°C.

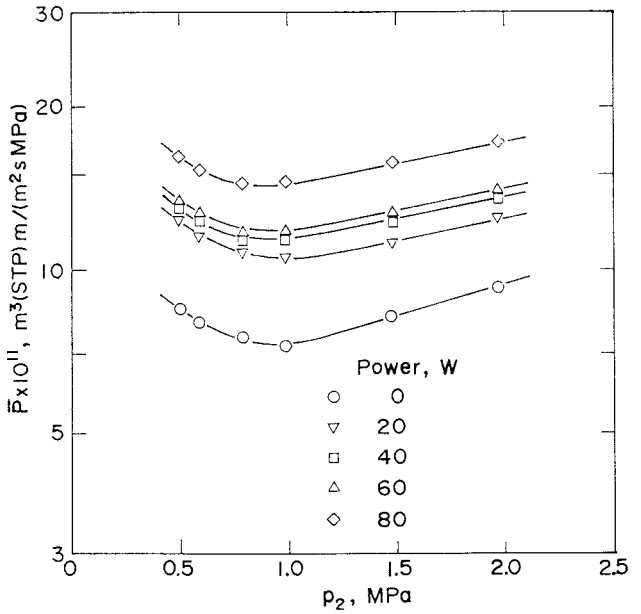

Figure 3 Pressure dependence of *P*s for CO_2 in NH_3-plasma-treated PMMA membranes at different powers of plasma treatment.

whether the dual-mode mobility model was operative or not for the pressure dependence of *P*s up to about 0.9 MPa of upstream pressure:

$$P = k_D D_D + \frac{C'_H b D_H}{(1 + bp_1)(1 + bp_2)} \quad (1)$$

for untreated membranes, where k_D is Henry's law constant, D_D is the diffusion coefficient in Henry's law mode, b is the Langmuir affinity constant, D_H is the diffusion coefficient in Langmuir law mode, p is the pressure of penetrant gas, and subscripts 1 and 2 represent the downstream and upstream surfaces, respectively, and

$$P = \bar{k}_D \bar{D}_D + \frac{\bar{C}'_H b \bar{D}_H}{(1 + bp_1)(1 + bp_2)} \quad (2)$$

for NH_3-plasma-treated membranes,[1] where b is assumed not to be affected by the plasma treatment.

P data for CO_2 in treated and untreated PMMA membranes are plotted against the term $b/(1 + bp_1)(1 + bp_2)$ on the basis of eqs. (1) and (2) in Figure 5. The dual-mode sorption parameters for CO_2 in PMMA appearing in

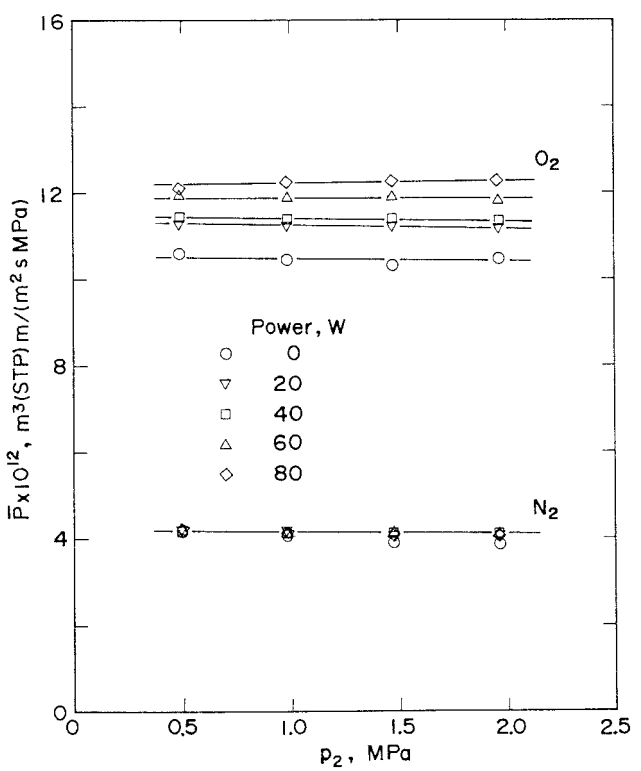

Figure 4 Pressure dependencies of *P*s for O_2 and N_2 in NH_3-plasma-treated PMMA membranes at different powers of plasma treatment.

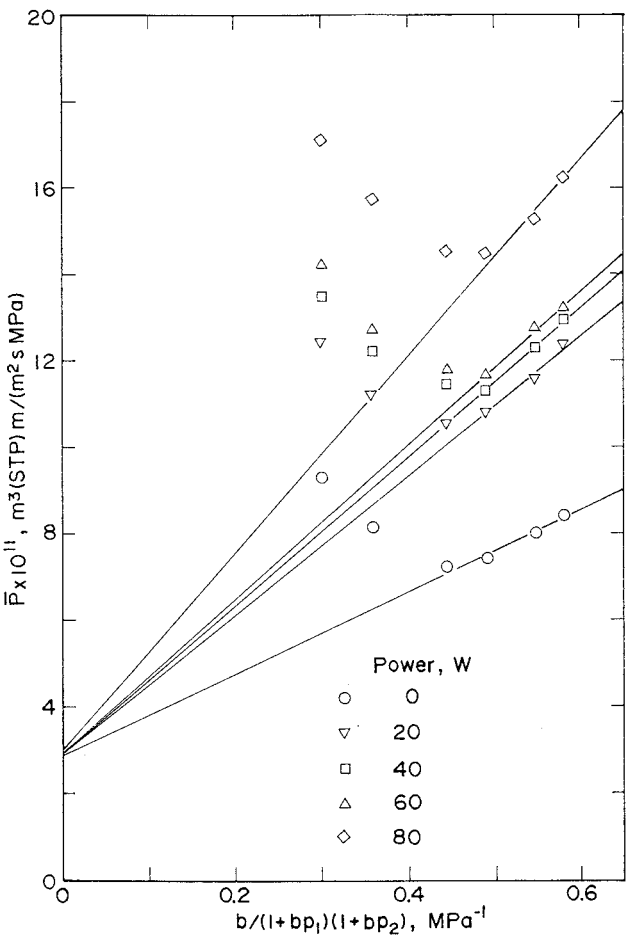

Figure 5 Test of the dual-mode mobility model for permeation of CO_2 in NH_3-plasma-treated PMMA membranes at different powers of plasma treatment.

$$C = C_D + C_H = k_D p + \frac{C'_H bp}{1 + bp} \quad (3)$$

were taken from an article by Min and Paul[3] as listed in Table I, where C is the concentration of total sorbed species, C_D is the concentration of Henry's law species, and C_H is the concentration of Langmuir species. Only the permeability data at upstream pressures below 0.9 MPa fell on straight lines. The slope of the straight line varied with the power of plasma treatment, increasing with increasing power. For CO_2 transport, NH_3 plasma treatment affected the product of C_H and D_H rather than that of k_D and D_D in eq. (2), like CO_2 transport in the NH_3-plasma-treated PPO membrane.[1] The values of $\bar{C}_H'\bar{D}_H$ and $\bar{k}_D\bar{D}_D$, evaluated from the slope and intercept, respectively, of each straight line are plotted against the power of plasma treatment in Figure 6. $\bar{k}_D\bar{D}_D$ increased a little with increasing power of treatment or rather essentially remained constant.

For O_2 transport, the permeabilities of untreated and treated PMMA membranes could be described respectively as

$$P = k_D D_D \quad (4)$$

$$P = \bar{k}_D \bar{D}_D \quad (5)$$

$k_D D_D$ and $\bar{k}_D\bar{D}_D$ data taken from Figure 4 are also plotted versus plasma-treatment power in Figure 6. The dependencies of $k_D D_D$ and $\bar{k}_D\bar{D}_D$ for O_2 on the power were similar to those for CO_2. That is, NH_3 plasma treatment had only a little bit influence on the mobility of Henry's law species.

The fact that the term $\bar{C}_H'\bar{D}_H$ for CO_2 transport increased by NH_3 plasma treatment may have resulted from an increase in $\bar{C}_H'$ and/or diffusivity of Langmuir species ($\bar{D}_H$). If $\bar{D}_H$ was not influenced by NH_3 plasma treatment, as in the case of O_2 transport in NH_3-plasma-treated PPO membranes,[1] the $\bar{C}_H'$ for CO_2 was supposed to be increased by the plasma treatment. In case of CO_2 transport in NH_3-plasma-treated PPO membranes,[1] such an increase was observed and interpreted qualitatively by the interaction of sorbed CO_2 with basic groups generated by NH_3 plasma treatment as follows.

TABLE I
Sorption Parameters for CO_2 in PMMA Membranes at 35°C

$k_D \times 10^6$ [m^3 (STP)/m^3 Pa)]	$b \times 10^6$ (Pa^{-1})	$C_{H'}$ [m^3 (STP)/m^3]	Source
1.39	0.921	25.6	Ref. [3]
9.04	2.33	12.6	Ref. [4]

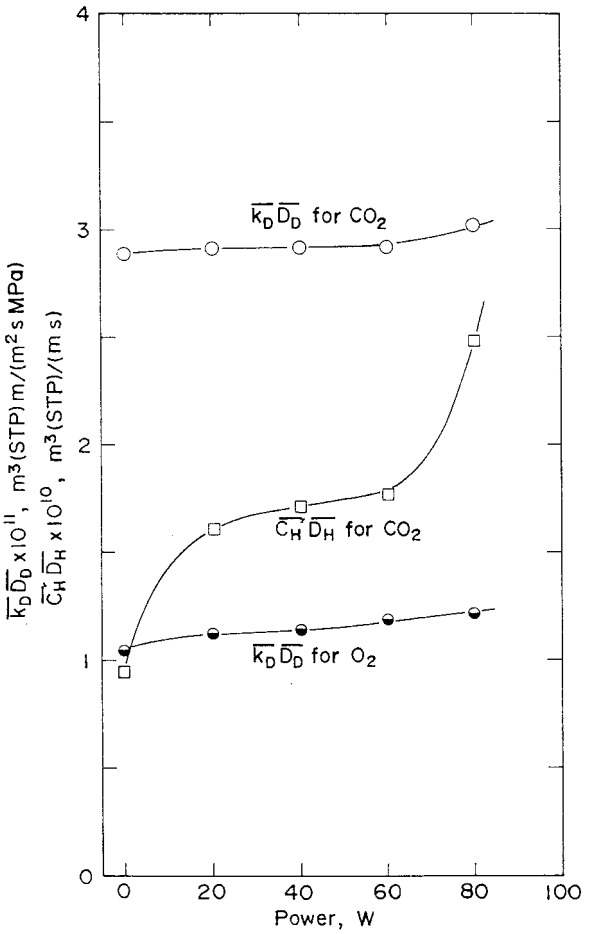

Figure 6 Variations of $\bar{k}_D\bar{D}_D$ and $\bar{C}_H'\bar{D}_H$ in a CO_2 transport in NH_3-plasma-treated PMMA membranes with power of plasma treatment.

Sorbed CO_2 (A) was assumed to react reversibly with the basic groups (B; A + B = AB), so that at equilibrium

$$K = \frac{[AB]_e}{[A]_e[B]_e} = \frac{[B]_0 - [B]_e}{[A]_e[B]_e} \quad (6)$$

where K is the equilibrium constant, the subscript e refers to the concentration at equilibrium, and the subscript 0 refers to the initial value. The total concentration of sorbed CO_2 at the equilibrium, $[A]_{tot}$ can be given as

$$[A]_{tot} = [A]_e + [AB]_e = [A]_e + \frac{K[B]_0[A]_e}{1 + K[A]_e} \quad (7)$$

The previous equation implies that the C_H' for CO_2 is augmented by NH_3 plasma treatment.

CONCLUSIONS

Ps for CO_2 in PMMA membrane decreased with increasing upstream pressure up to about 0.9 MPa, and

the pressure dependence of P in this region could be interpreted by a dual-mode mobility model. Above 1.0–1.2 MPa of upstream pressure, the logarithmic permeability coefficients in treated and untreated membranes increased linearly with upstream pressure, presumably due to plasticization action of sorbed CO_2. Ps for O_2 and N_2 remained constant, regardless of the upstream pressure. For O_2 transport, the permeability increased a little with increasing treatment power, and for N_2 transport, it was not affected by the treatment power. For CO_2 transport, NH_3 plasma treatment promoted the transport of Langmuir mode, presumably through an increased C_H' for CO_2, whereas it had only a small influence on the mobility of Henry's law species. Therefore, NH_3 plasma treatment of the PMMA membrane can increase both the permeability to CO_2 and the separation factor of CO_2 relative to N_2.

NOMENCLATURE

Symbols

b Langmuir affinity constant (Pa^{-1})
C concentration of total sorbed species [m^3 (STP)/m^3]
C_D concentration of Henry's law species [m^3 (STP)/m^3]
C_H concentration of Langmuir specie [m^3 (STP)/m^3]
C_H' Langmuir capacity constant [m^3 (STP)/m^3]
D diffusion coefficient of penetrant gas (m^2/s)
k_D Henry's law constant [m^3 (STP)/(m^3 Pa)]
L thickness of homogeneous membrane (m)
P mean permeability coefficient [m^3 (STP) m/(m^2 s Pa)]
p pressure of penetrant gas (Pa)

Subscripts

D Henry's law mode
H Langmuir mode
1 downstream surface
2 upstream surface

An overbar symbolizes an average value in the NH_3-plasma-treated membrane.

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