

Gas Transport in Polymer Membrane at Temperatures Above and Below Glass Transition Point

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SYNOPSIS

The processes of gas sorption and permeation in a polymer membrane at temperatures above and below the glass-transition point were examined using poly-4-methylpentene-1 (glass-transition temperature reported to be 40°C) as a membrane material. The permeabilities to O₂ and N₂ were independent of applied gas pressure at every temperature; the mean permeability coefficient to CO₂ increased with increasing gas pressure. The logarithm of the mean permeability coefficient to CO₂ increased linearly with gas pressure due to the plasticization effect induced by sorbed CO₂. From the sorption isotherms for CO₂ at 20 and 30°C it was judged that the glass transition was brought about by sorbed CO₂ at temperatures below the glass-transition point of the pure polymer. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The dual-mode sorption and mobility model has been widely used to describe sorption and diffusion behavior of a gas in glassy polymer membranes. In the original dual-mode sorption model, sorption parameters are assumed to be independent of sorbed gas concentration. Recently, Kamiya et al.¹ extended the dual-mode sorption model to polymer-gas systems in which sorbed gas molecules plasticized the polymer matrix. In their extended model, both Henry's law and Langmuir capacity constants are influenced by sorbed gas species of the plasticizing ability to the polymer. They observed the plasticization of polymer by sorbed gas clearly in sorption equilibria for CO₂-glassy polymers, for example, decreasing the excess free volume in the glassy state and depressing the glass-transition temperature.¹⁻³ Concerning the dual-mode mobility model, some deviation has been reported. Zhou and Stern proposed a modified dual-mode mobility model⁴ wherein the diffusivities of Henry's law dissolution and Langmuir adsorption species depend on the concentration of the respective species, and the dual-mode sorption

parameters are independent of the concentration of each species. The observed pressure dependences for CO₂ in homogeneous membranes of cellulose triacetate and methylmethacrylate-butyl acrylate copolymer were simulated well by this modified model.⁵

Thus far, the plasticization effects by sorbed gas molecules were examined separately from the standpoints of sorption and diffusion. There are no experimental results available on the plasticization action of sorbed gas exerting on both sorption and diffusion processes simultaneously. But when the temperatures for sorption and permeation runs are not so high as the glass-transition temperature of the pure polymer, the plasticization effect possibly comes out in both the processes simultaneously in a moderate pressure range. By considering these, we used poly-4-methylpentene-1 as a membrane material (nominal glass-transition temperature 40°C) and attempted to investigate the permeation and sorption mechanism at temperatures above and below the glass-transition point.

THEORETICAL BACKGROUND: DEVIATION FROM DUAL-MODE MODEL

The sorption isotherm for gases and vapors in glassy polymers has been found to be described well by a

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so-called dual-mode sorption model,⁶ which postulates that sorbed molecules are retained in the polymer via Henry's law dissolution in the polymer matrix and Langmuir-type adsorption in the unrelaxed microvoids, namely

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

It has been reported that Henry's law constant (k_D) and Langmuir capacity constant (C'_H) are not constant, but are affected by plasticization action of sorbed gas. Kamiya et al.¹ extended the dual-mode sorption model to polymer-gas systems in which the gas molecules plasticized the polymer matrix. Quantitatively, the sorption equilibrium based on their extended dual-mode sorption model is given as

$$C = [k_D \exp(\sigma C^*)] p + \frac{C'_{H0} b p (1 - C^*/C_g)}{1 + b p} \quad (2)$$

where σ is the parameter characterizing the concentration dependence of C_D/p introduced by Suwandi and Stern,⁷ C'_{H0} the Langmuir capacity constant in the limit of $p \rightarrow 0$, and C_g the glass-transition concentration. C^* refers to the effective concentration for plasticization by sorbed gas, which is defined as

$$C^* = C_D + f C_H \quad (3)$$

where f is the ratio of the plasticizing ability of Langmuir species to that of Henry's law species. In the limit of $C^* \rightarrow C_g$, the concentration of Langmuir species becomes equal to zero, that is, the glass transition is brought out.

The two sorbed species (Henry's law and Langmuir species) can execute diffusive movements with different mobilities at local equilibrium with each other. This approach has been termed the dual-mode mobility model. According to a dual-mode mobility model driven by gradients of concentration, the mean permeability coefficient defined by

$$\bar{P} = J_s \delta / (p_2 - p_1) \quad (4)$$

can be derived as follows:

$$\bar{P} = k_D D_D + \frac{C'_H b D_H}{(1 + b p_1)(1 + b p_2)}. \quad (5)$$

Here it should be noted that all of the sorption and diffusion parameters are assumed to be independent

of sorbed gas concentration. Recently, concentration-dependent diffusivities have been reported.^{5,8,9}

Zhou and Stern proposed a modified dual-mode mobility model,⁴ in which all of the sorption parameters are assumed to be constant, but the diffusivities of Henry's law dissolution and Langmuir adsorption species depend on the concentration of the respective species:

$$D_D = D_{D0} \exp(\beta_D C_D) \quad (6)$$

$$D_H = D_{H0} \exp(\beta_H C_H). \quad (7)$$

The mean permeability coefficient can analytically be derived as follows⁸:

$$\begin{aligned} \bar{P} = & \frac{D_{D0}}{\beta_D (p_2 - p_1)} [\exp(\beta_D C_{D2}) - \exp(\beta_D C_{D1})] \\ & + \frac{D_{H0}}{\beta_H (p_2 - p_1)} [\exp(\beta_H C_{H2}) - \exp(\beta_H C_{H1})]. \quad (8) \end{aligned}$$

The increase of the mean permeability coefficient in glassy polymer membranes with increasing gas pressure has been reported and attributed to membrane plasticization induced by sorbed CO₂. Such a pressure dependence has been interpreted by the total immobilization model wherein the diffusivity of Henry's law species depends on gas pressure via a modified free-volume model.^{10,11}

EXPERIMENTAL

Sorption equilibria and permeabilities for a gas in a polymeric membrane were measured at different temperatures encompassing the nominal glass-transition temperature (T_g) of the pure polymer. Carbon dioxide, oxygen, and nitrogen were used as a penetrant gas or sorbate, and a homogeneous film of poly-4-methylpentene-1 (PMP) was used as a membrane. All PMP film samples were kindly provided by Mitsui Petrochemical Industries, Ltd., Japan. The T_g has been reported to be 40°C by that company.

Sorption isotherms for a gas were determined by the pressure decay method. The sorption cell is similar to one designed by Koros et al.¹² The pressure in the sorption chamber was determined using a pressure transducer. The apparatus for gas permeability measurements is similar to the variable volume method employed by Stern et al.¹³ The procedure for the permeation experiment has been described in detail elsewhere.¹⁴ The low-pressure side

of the permeation cell was filled with the same penetrant gas at 0.101 MPa.

RESULTS AND DISCUSSION

The experimental results on the mean permeability coefficients for pure O₂, N₂, and CO₂ at various temperatures encompassing the T_g of PMP were indicated as a function of upstream gas pressure in Figures 1 and 2. Figure 1 shows the pressure dependences of the mean permeability coefficients to O₂ and N₂ at various temperatures between 20 and 45°C. Figure 2 shows the pressure dependence of the mean permeability coefficient to CO₂ at the same temperatures. For O₂ and N₂, the mean permeability coefficients are shown to be independent of upstream pressure at every temperature. On the other hand, the mean permeability coefficients to CO₂ are found to increase with upstream pressure. At temperatures above 30°C, the logarithm of the mean permeability coefficient increases linearly with upstream pressure. At 20°C, the mean permeability coefficient in the low pressure range remains constant or slightly decreases with increasing upstream pressure. And at 25°C, the logarithm of the mean permeability coefficient slightly deviates upward from a straight line in the low pressure region. The linear relationship

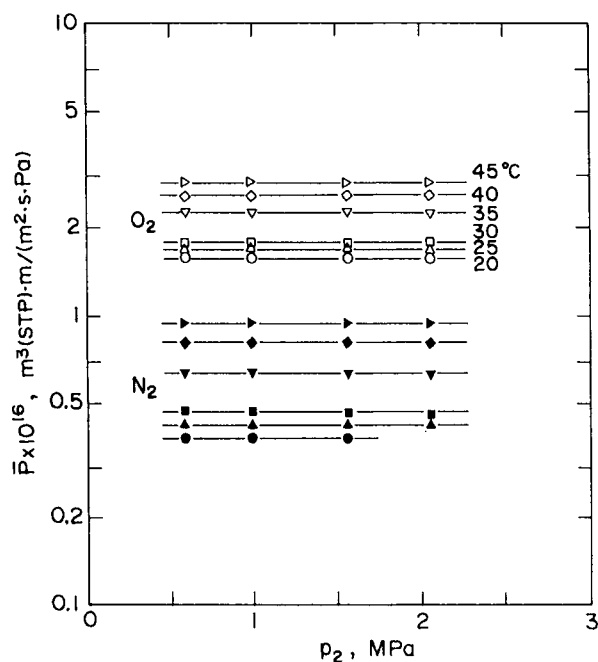


Figure 1 Mean permeability coefficients for O₂ and N₂ in PMP membrane as a function of upstream pressure at various temperatures.

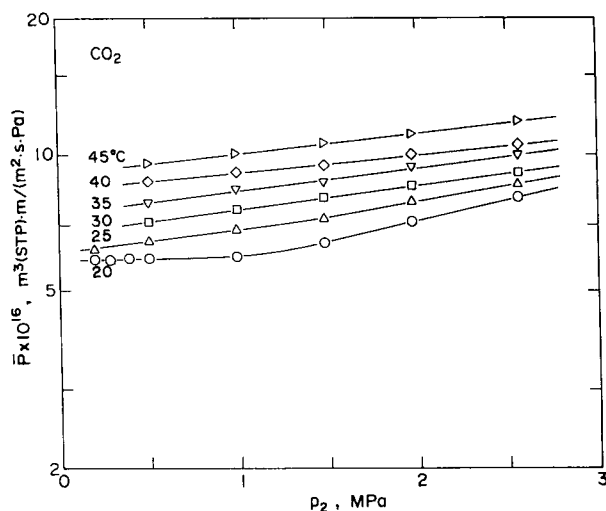


Figure 2 Mean permeability coefficients for CO₂ in PMP membrane as a function of upstream pressure at various temperatures.

between the logarithm of the mean permeability coefficient to CO₂ and the upstream gas pressure reminds us of a plasticization effect of sorbed CO₂. Such a pressure dependence of the permeability can be interpreted in terms of a free-volume model in rubbery polymer membranes described later.

For O₂ and N₂ the mean permeability coefficients, which are constant irrespective of upstream pressure, were examined regarding their temperature dependence. Figure 3 shows the Arrhenius plots of them. For both gases (especially for N₂), the Arrhenius plots can be approximated by two straight lines and at around 34°C, the slopes of the lines become different. Sorbed O₂ and N₂ do not apparently exert plasticization action because the permeabilities are independent of upstream pressure. That is, the amount of O₂ and N₂ sorbed is too little to depress the T_g . The T_g of PMP in the absence of plasticization effect here is judged to be about 34°C, though nominal T_g of pure PMP has been reported to be 40°C. Above this T_g (34°C), PMP membrane is in its rubbery state.

The experimental evidence that the logarithm of the mean permeability coefficient to CO₂ at temperatures of 35–45°C increases linearly with upstream pressure, can be explained by the plasticization action of sorbed CO₂ in a rubbery polymer membrane. At 30°C, a linear increase of the logarithm of the mean permeability coefficient has also been observed, and hence the membrane seems to be in a rubbery state during the permeation of CO₂. At 25°C, the relation of the logarithm of the mean permeability coefficient to gas pressure in the low

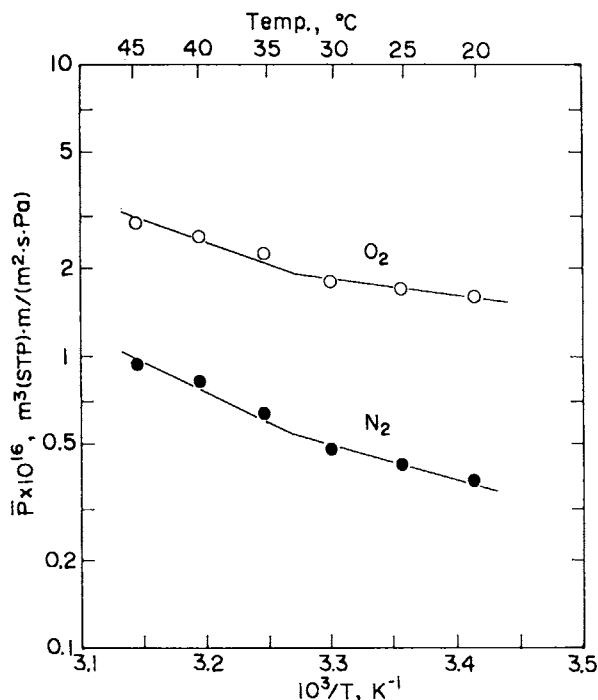


Figure 3 Temperature dependence of mean permeability coefficients to O₂ and N₂ in PMP membrane.

pressure region is found to slightly deviate upward from a straight line. At 20°C, the coefficient in the low pressure region is almost independent of pressure or rather slightly decreases with increasing pressure. But at 20 and 25°C, the logarithm of the coefficient in the high pressure region is shown to increase linearly with pressure, and at these temperatures the membrane may change to a rubbery state in the high CO₂ pressure region. Such experimental evidence is supported by observed sorption isotherms of CO₂ described below.

A modified free-volume model was applied in order to interpret a linear relation of the logarithm of the mean permeability coefficient to CO₂ to upstream pressure. According to a modified Fujita free-volume model,¹¹ the thermodynamic diffusion coefficient (D_T) of penetrant gas in a polymer can be written as

$$D_D = D_T = RTA_d \exp(-B_d/\phi_a v_f) \quad (9)$$

where v_f refers to the fractional free-volume, which is the functions of temperature, pressure, and volume fraction of a sorbed gas. Also, the polymer is in its rubbery state, and hence D_T is set equal to D_D . When the reference state for the free-volume is taken as pure polymer at some reference temperature T_s and pressure p_s , the free-volume near this reference state can be described as

$$v_f = v_{fs}(T_s, p_s, 0) + \alpha(T - T_s) - \beta(p - p_s) + \gamma v \quad (10)$$

where α [$=(\partial v_f/\partial T)_s$] is the thermal expansion coefficient, β [$=-(\partial v_f/\partial p)_s$] the compressibility, and γ [$=(\partial v_f/\partial v)_s$] the concentration coefficient that defines the plasticization action of the penetrant. Then, on the basis of the above model, the mean permeability coefficient can be derived as follows:

$$\bar{P} = \frac{RTA_d}{p_2 - p_1} \int_{v_1}^{v_2} \exp\left(\frac{-B_d/\phi_a}{v_f^0 + \gamma v}\right) dv \quad (11)$$

where

$$\begin{aligned} v_f^0 &= v_{fs}(T_s, p_s, 0) + \alpha(T - T_s) - \beta(p - p_s) \quad (12) \\ &= v_{fs}(T_s, p_s, 0) + \alpha(T - T_s) - \beta(p_2 - p_s). \quad (13) \end{aligned}$$

[Note to eq. (13): when the membrane is rigidly supported, hydrostatic pressure p is equal to applied penetrant gas pressure p_2 .] Expanding the term $(v_f^0 + \gamma v)^{-1}$ in the integrand of eq. (11) into series, retaining the series up to the first-order term as an approximation, and integrating the resultant equation with respect to v , one gets¹⁵

$$\begin{aligned} \ln \bar{P} &\cong \ln(RTA_d \bar{S}) - \frac{B_d}{\phi_a v_f^*} \\ &+ \frac{B_d}{2\phi_a (v_f^*)^2} (\gamma \bar{S} - 2\beta) p_2 + \frac{B_d \gamma \bar{S}}{2\phi_a (v_f^*)^2} p_1 \quad (14) \end{aligned}$$

where v_f^* refers to the fractional free-volume of the pure polymer at $p = 0$, namely

$$v_f^* = v_{fs}(T_s, p_s, 0) + \alpha(T - T_s) + \beta p_s. \quad (15)$$

Equation (14) represents that the logarithm of the mean permeability coefficient should be linear to upstream gas pressure, therefore consistent with experimental results at temperatures above 30°C depicted in Figure 2.

Figure 4 shows the sorption isotherms of CO₂ at 20, 30, and 40°C. The isotherm at 40°C is shown to be linear. Such experimental evidence is valid, because the polymer is in its rubbery state. So the sorption equilibrium in a rubbery state can be written as

$$C = C_D = k_D p. \quad (16)$$

At 20 and 30°C, the isotherms have the form of a dual-mode sorption model at low gas pressures, but

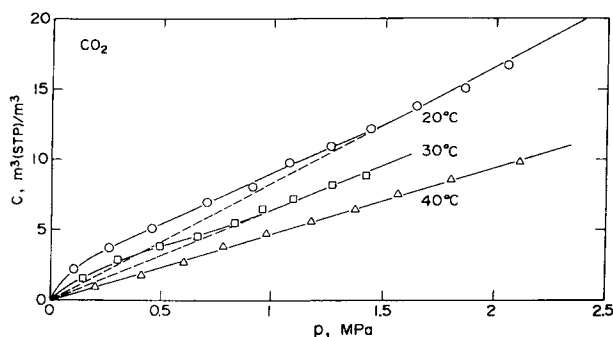


Figure 4 Sorption isotherms of CO₂ in PMP membrane at different temperatures.

become linear like the isotherm at 40°C, at pressures above 1.5 and 0.8 MPa, respectively. The T_g in the absence of sorbed CO₂ is about 34°C, but sorption of CO₂ results in a decrease of T_g continuously as the amount of sorbed CO₂ increases. Figure 4 implies that when equilibrated with about 1.5 or 0.8 MPa of CO₂, the T_g for the polymer-CO₂ mixture approaches the sorption temperature, 20 or 30°C. The isotherms at pressures above 1.5 and 0.8 MPa become linear and extrapolate to the origin since the polymer is in its rubbery state. At 20 and 30°C the concentration of Henry's law species is given by eq. (1). The values of Henry's law constant (k_D) for CO₂ at these temperatures are listed in Table I. Above and below the T_g (34°C), k_D is shown to continuously decrease with rising temperature on the van't Hoff plot.

In the present system, the plasticization of polymer by sorbed CO₂ might result in a decrease in the unrelaxed microvoid in the glassy polymer and in a decrease in T_g . That is, the glass transition is brought out by the sorbed CO₂ at temperatures below T_g of the pure polymer. According to an extended dual-mode sorption model proposed by Kamiya et al.¹ the Langmuir capacity constant (C'_H) has been written as

$$C'_H = C'_{H0}(1 - C^*/C_g). \quad (17)$$

When C^* approaches C_g , the concentration of Langmuir species becomes absent, consistent with the experimental observation.

Figure 5 presents the sorption isotherms for O₂ and N₂ at 30°C. They can approximately be described by straight lines passing through the origin, that is, eq. (16). The apparent values of Henry's law constant for both gases are also listed in Table I.

In order to reveal the effect of the plasticization action of sorbed CO₂ on both processes of sorption and permeation for CO₂, the sorption isotherm and

Table I Henry's Law Constants for CO₂, O₂, and N₂ in PMP Membrane

Gas	Temp. (°C)	$k_D \times 10^6$ [m ³ (STP)/(m ³ Pa)]
CO ₂	20	8.26
CO ₂	30	6.35
CO ₂	40	4.69
O ₂	30	1.28
N ₂	30	0.90

the pressure dependence of the mean permeability coefficient for CO₂ at 20°C depicted in Figures 4 and 2, respectively, will be examined.

The inflection in the isotherm at 20°C occurs at 1.5 MPa of CO₂ pressure when the T_g for the polymer-CO₂ mixture equates the sorption temperature (20°C). At pressures above 1.5 MPa, the isotherm becomes linear, characteristic of rubbery polymers. In the corresponding high pressure region, where the polymer is in its rubbery state, the logarithm of the mean permeability coefficient to CO₂ increases linearly with upstream pressure. Such a linear increase is ascribed to the plasticization action of sorbed CO₂ to the rubbery polymer. The plasticization action to the rubbery polymer comes out in the diffusion process rather than the sorption process within gas pressures covered here (below 2 MPa).

CONCLUSIONS

The sorption isotherms and the pressure dependences of mean permeability coefficients for CO₂, O₂, and N₂ in a homogeneous membrane of poly-4-methylpentene-1 whose nominal T_g is 40°C, were measured at temperatures encompassing the glass-transition point. The permeabilities to O₂ and N₂ were independent of applied gas pressure at every temperature, whereas the permeabilities to CO₂ in-

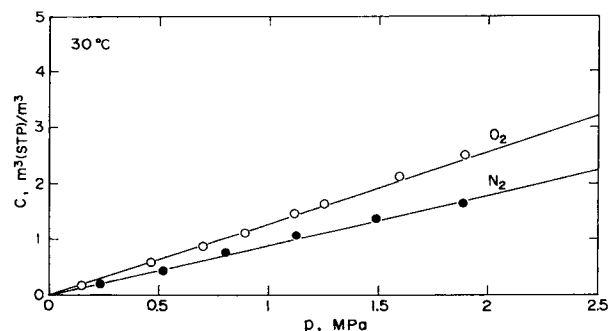


Figure 5 Sorption isotherms of O₂ and N₂ in PMP membrane at 30°C.

creased with increasing gas pressure. At temperatures above 30°C, the logarithm of the permeability increased linearly with applied gas pressure. At temperatures of 20 and 25°C, the permeabilities remained constant and deviated upward from a linear relation, respectively, in the low pressure region; and in the high pressure region, the logarithms of permeabilities increased linearly with applied gas pressure. The linear increase in the logarithm of the permeability might be ascribed to the plasticization action of sorbed CO₂. From the sorption isotherms for CO₂ at 20 and 30°C, it was found that the glass transition was brought out by sorbed CO₂ at temperatures below the glass-transition point of the pure polymer, consistent with a linear increase in the logarithm of the mean permeability coefficient with gas pressure.

NOMENCLATURE

- A_d characteristic parameter in eq. (9) (mol s/kg)
 B_d characteristic parameter in eq. (9)
 b Langmuir affinity constant (Pa⁻¹)
 C total sorbed concentration [m³ (STP)/m³]
 C_D concentration of Henry's law dissolution species [m³ (STP)/m³]
 C_g glass-transition concentration appearing in eq. (2) [m³ (STP)/m³]
 C_H concentration of Langmuir adsorption species [m³ (STP)/m³]
 C'_H Langmuir capacity constant [m³ (STP)/m³]
 C^* effective concentration for plasticization by sorbed gas [m³ (STP)/m³]
 D diffusion coefficient in membrane (m²/s)
 f ratio of the plasticizing ability of Langmuir species to that of Henry's law species appearing in eq. (3)
 J_s steady-state permeation rate [m³ (STP)/(m² s)]
 k_D Henry's law constant [m³ (STP)/(m³ Pa)]
 \bar{P} mean permeability coefficient or permeability [m³ (STP) m/(m² s Pa)]
 p pressure of penetrant gas or hydrostatic pressure (Pa)
 R gas constant [J/(mol K)]
 \bar{S} mean solubility coefficient [m³ (STP)/(m³ Pa)]
 T temperature (K)
 T_g glass-transition temperature (°C)
 v volume fraction concentration of penetrant gas in membrane [m³ (STP)/m³]
 v_f volume fraction of free-volume

Greek Letters

- α thermal expansion coefficient of free-volume defined by $(\partial v_f/\partial T)_s$ (K⁻¹)

- β compressibility of free-volume defined by $-(\partial v_f/\partial p)_s$ (Pa⁻¹)
 β_D concentration-dependence parameter appearing in eq. (6) [m³/m³ (STP)]
 β_H concentration-dependence parameter appearing in eq. (7) [m³/m³ (STP)]
 γ concentration coefficient of free-volume defined by $(\partial v_f/\partial v)_s$
 δ thickness of membrane (m)
 σ parameter characterizing the concentration dependence of Henry's law constant appearing in eq. (2) [m³/m³ (STP)]
 ϕ_a amorphous fraction of membrane

Subscripts

- D Henry's law mode
 H Langmuir mode
 s reference state
 0 zero concentration state
 1 downstream surface
 2 upstream surface

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